

01006977q

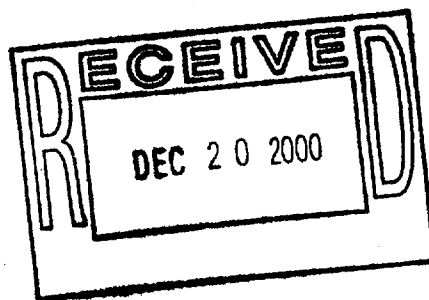
Enantioselective Syntheses of ^{13}C -Labeled 2*R*- and 2*S*-Phytochromobilin Dimethyl Ester

Peter A. Jacobi* and Douglas Pippin

*Burke Chemical Laboratory, Dartmouth College,
Hanover, New Hampshire 03755*

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. ¹H NMR spectra were recorded at 500 MHz and are expressed as ppm downfield from tetramethylsilane as an internal standard.

Z3-[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 NH₃. 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 NH₃. The remaining solution was concentrated to dryness under an argon stream and without purification was dissolved in 20 mL of CHCl₃, 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 CH₂Cl₂ and ice cold NaH₂PO₄/Na₂HPO₄ buffer (pH 7) and the aqueous layer was extracted with 3 x 5 mL of CH₂Cl₂. The combined organic extracts were dried (Na₂SO₄), 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; [α]_D²⁸ - 6.47° (*c* = 27.1, CHCl₃); 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 ¹H NMR (CDCl₃) 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 (CDCl₃) 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 C₁₈H₂₂N₂O₄: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.33; H, 6.65; N, 8.39.

Pyrrromethenone ¹³C₁₀-10. This material was prepared in 95% yield in identical fashion as for pyrrromethenone **10** above, employing 76 mg (0.17 mmol, 1.0 eq) of lactone ¹³C₁₀-**14**, and 3 mL of condensed NH₃ 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 CHCl₃ for 24 hr. Chromatography afforded 54 mg (95%) of ¹³C₁₀-**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 ¹H NMR (CDCl₃) 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 ¹³C NMR (CDCl₃) 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.

Pyrrromethenone *ent*-10. This material was prepared in 93% yield in identical fashion as for pyrrromethenone **10** above, employing 244 mg (0.555 mmol, 1.00 eq) of lactone *ent*-**14** and 5 mL of condensed NH₃ 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; [α]_D²⁸ + 6.49° (*c* = 17.9, CHCl₃). IR and ¹H NMR are identical to those of pyrrromethenone **10**.

Pyrrromethenone *ent*-¹³C₁₀-10. 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*-¹³C₁₀ **14** and 3 mL condensed NH₃ 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*-¹³C₁₀-**10** as yellow green solid, mp 184-85 °C; having IR and ¹H NMR that are identical to those of pyrromethenone ¹³C₁₀-**10**.

3-[4-Methyl-5-(3-methyl-5-oxo-4-vinyl-1,5-dihydro-pyrrol-2-ylidenemethyl)-1H-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 CH₂Cl₂ and treated with K₂HPO₄/KOH buffer pH 12. The frozen mixture was slowly warmed to 0 °C and stirred for additional 2 hr, then partitioned between CH₂Cl₂ and ice cold pH 12 K₂HPO₄/KOH buffer. The organic layer was washed with H₂O, dried (Na₂SO₄), filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (silica 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 ¹H NMR (CDCl₃) 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 C₁₇H₂₀N₂O₃: 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-1H-pyrrol-3-yl)-propionic acid methylester (¹³C-13).¹ A solution of 266 mg (1.05 mmol, 1.00 eq) of 5-¹³C-Formyl-4-(2-methoxycarbonyl-ethyl)-3-methyl-1H-pyrrole-2-carboxylic acid² in 20 mL of MeOH was treated with a solution of 605 mg (7.20 mmol, 6.5 eq) of NaHCO₃ in 20 mL of H₂O, stirred at rt for 20 min to which was added dropwise a solution of 267 mg (1.05 mmol, 1.00 eq) of I₂ 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 Na₂S₂O₃ and partitioned between CH₂Cl₂ and ice cold NaHCO₃. The aqueous phase was extracted with 2 x 25 mL CH₂Cl₂ and the combined organic extracts were dried (Na₂SO₄), filtered, concentrated under reduced pressure and chromatographed (silica gel, 10-30 % EtOAc/ pet ether) to afford 314 mg (89%) of ¹³C- labeled iodopyrrole ¹³C-**13**,¹ mp 92 °C; R_f 0.45 (30% EtOAc/pet ether); 500 MHz ¹H NMR (CDCl₃) 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 ¹³C NMR (CDCl₃) δ 11.83, 19.75, 35.36, 52.10, 126.41, 132.69, 133.43, 133.93, 172.83, 176.63.

3R-[5-[3S-(1-Benzoyloxy-ethyl)-4R-methyl-5-oxo-dihydro-furan-2-ylidenemethyl]-2-formyl-4-methyl-1H-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(PPh₃)₄, and 319 mg (1.40 mmol, 1.00 eq) of BnNEt₃Cl in 11.0 mL of dry CH₃CN and 1.95 mL (14.0 mmol, 10.0 eq) of Et₃N 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 CH₂Cl₂ and H₂O, and the aqueous phase extracted with CH₂Cl₂. The combined organic extracts were washed with brine, dried (Na₂SO₄), 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 ¹H NMR (CDCl₃) 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* = 7.5 Hz, 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 ¹³C NMR (CDCl₃) 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 (C₂₅H₂₉NO₆ + H)([M + H]⁺): 440.2073; found 439.2073.

Enelactone $^{13}\text{C}_{10}$ -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 $\text{Pd}(\text{PPh}_3)_4$, 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 $^{13}\text{C}_{10}$ -**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 ^1H 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 $\text{Pd}(\text{PPh}_3)_4$, 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 ^1H 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 $\text{Pd}(\text{PPh}_3)_4$, 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 $^{13}\text{C}_{10}$ -**14**. 500 MHz ^1H 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 $^{13}\text{C}_{10}$ -**14**.

Pyrroloaldehyde ^{13}C -17.⁴ 0.300 mL (290 mg, 3.88 mmol, 2.00 eq) of $\text{Me}_2\text{N}^{13}\text{CHO}$ 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 ester⁴ 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 $\text{NaOH}/\text{H}_2\text{O}$ solution, stirred at rt for 2 hr, then partitioned between $\text{NaHCO}_3/\text{H}_2\text{O}$ 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 ^1H 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 (607 μL , 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 adducts ^{13}C -19a-d. This material was prepared in 97% overall 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 adduct 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 ^1H 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 $\text{C}_{39}\text{H}_{57}\text{ClN}_2\text{O}_8\text{SeSi}$: C, 56.82; H, 6.97; N, 3.39. Found: C, 57.07; H, 6.84; N 3.40; relative stereochemistry not assigned.

Aldol adduct $^{13}\text{C}_{15}$ -19a. Recrystallization from EtOAc/pet ether afforded $^{13}\text{C}_{15}$ -**19a** as a white solid, mp 106-7 °C; R_f 0.90 (silica gel, 30% EtOAc/pet ether); 500 MHz ^1H 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 $\text{C}_{38}^{13}\text{CH}_{57}\text{ClN}_2\text{O}_8\text{SeSi}$: C, 56.87; H, 6.96; N, 3.39. Found: C, 57.11; H, 6.89; N, 3.28; relative stereochemistry not assigned.

Aldol adduct 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 ^1H 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 $\text{C}_{39}\text{H}_{57}\text{ClN}_2\text{O}_8\text{SeSi}$: C, 56.82; H, 6.97; N, 3.39. Found: C, 57.08; H, 6.82; N, 3.28; relative stereochemistry not assigned.

Aldol adduct 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 ^1H 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 adduct $^{13}C_{15}$ -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 1H 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 adduct 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 1H 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, 55.67, 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-ylidene-methyl}-4-methyl-1H-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 1H 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 (0.281 mmol, 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 1H 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-Chlorophenylselanyl-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 $^\circ\text{C}$, 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 ^1H 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 $\text{C}_{41}\text{H}_{45}\text{ClN}_4\text{O}_6\text{Se}$: C, 61.23; H, 5.64, N, 6.97. Found: C, 61.39; H, 5.70; N, 6.91.

Tetrapyrrole $^{13}\text{C}_{15}$ -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 $^{13}\text{C}_{15}$ -**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 $^{13}\text{C}_{15}$ -**22** as a cobalt blue powder, mp 192-92.5 $^\circ\text{C}$, 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 ^1H 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 $^{13}\text{C}_{10}$ -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 $^{13}\text{C}_{10}$ -**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 tetrapyrrole $^{13}\text{C}_{10}$ -**22** as cobalt blue powder, mp 191.5-92 $^\circ$, 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 ^1H 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-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 (*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 μ L (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 $^{13}\text{C}_{15}$ -*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 $^{13}\text{C}_{15}$ -*ent*-**20**, 20 mg (0.061 mmol, 1.0 eq) of formylpyrrole **10**, and 92 μ L (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 $^{13}\text{C}_{15}$ -**22** as a cobalt blue powder, mp 192-92.5°C, having IR and ^1H NMR identical those of tetrapyrrole $^{13}\text{C}_{15}$ -**22**.

Tetrapyrrole $^{13}\text{C}_{10}$ -*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 $^{13}\text{C}_{10}$ -*ent*-**10**, and 68 μ L (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 $^{13}\text{C}_{10}$ -**22** as cobalt blue powder, mp 191.5-192°C, having IR and ^1H NMR identical to those of tetrapyrrole $^{13}\text{C}_{10}$ -**22**.

4*R*-Phytochromobilin dimethylester (4). A solution of 37 mg (0.046 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 $\text{K}_2\text{HPO}_4/\text{KOH}$ 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 $\text{K}_2\text{HPO}_4/\text{KOH}$ 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 $\text{C}_{35}\text{H}_{40}\text{N}_4\text{O}_6$: C, 68.61, H, 6.58, N, 9.14. Found: C, 68.73; H, 6.62; N, 9.02.

$^{13}\text{C}_{15}$ -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 $^{13}\text{C}_{15}$ -**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 $^{13}\text{C}_{15}$ -**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 $^{13}\text{C}_{15}$).³

$^{13}\text{C}_{10}$ -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 $^{13}\text{C}_{10}$ -**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 $^{13}\text{C}_{15}$ -**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 $^{13}\text{C}_{10}$).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 $^{13}\text{C}_{15}$ -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 $^{13}\text{C}_{15}$ -*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 $^{13}\text{C}_{15}$ -*ent*-**5** as a cobalt colored powder, mp 179-80°C; having IR and ^1H NMR identical to those of tetrapyrrole $^{13}\text{C}_{15}$ -**5**.

References

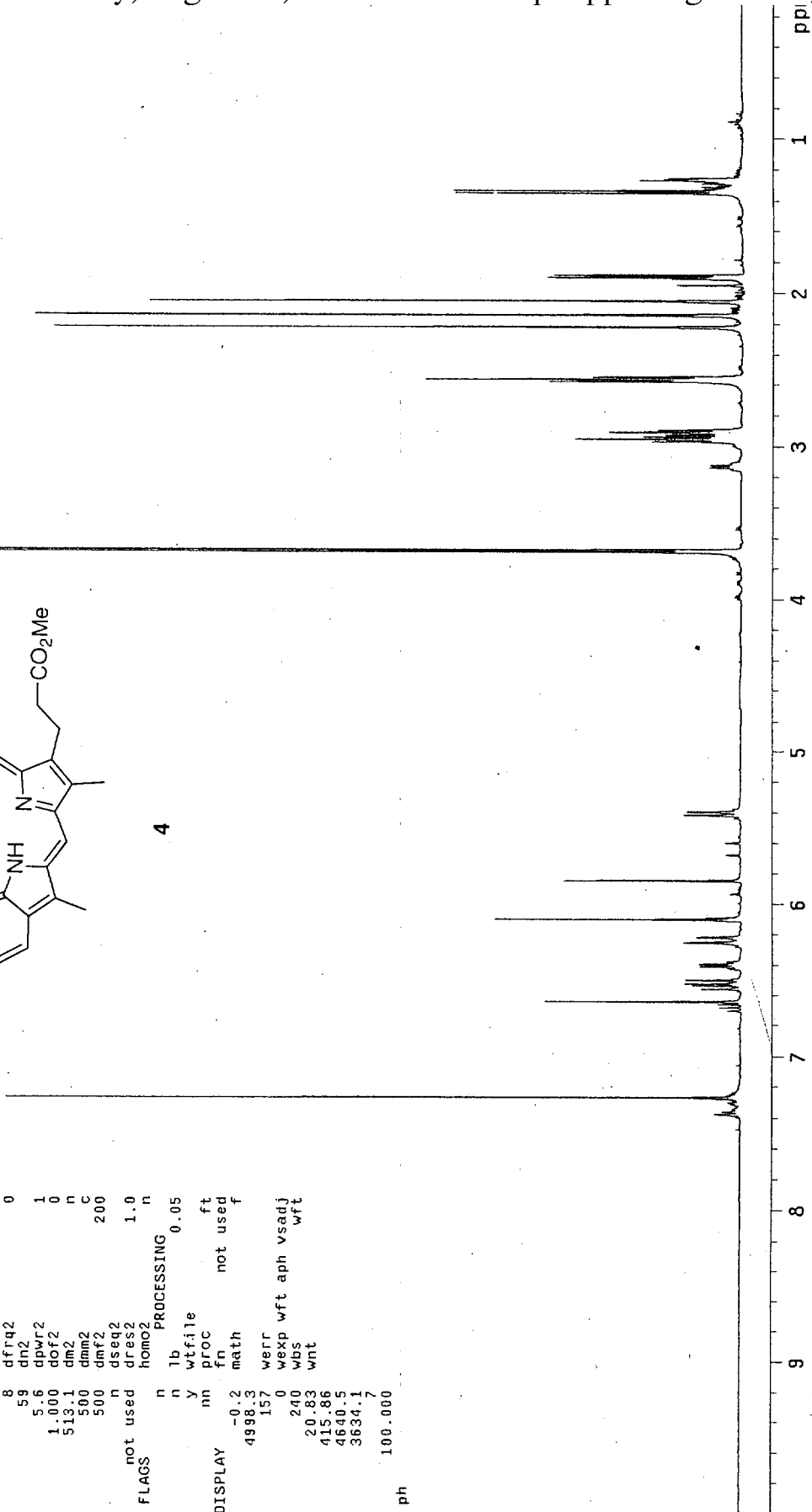
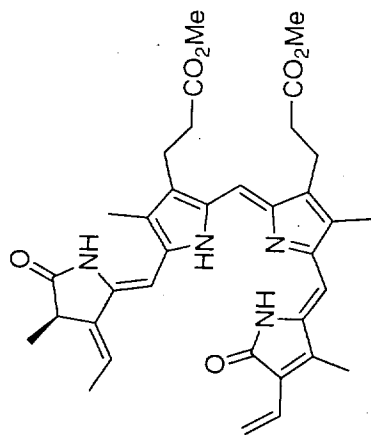
- Engel, J.; Gossauer, A. *Liebigs Ann. Chem.* **1976**, 1637.
- Jackson, A. H.; Kenner, G. W.; Sach, G. S. *J. Chem. Soc. C.* **1967**, 2045.
- Weller, J.; Gossauer, A. *Chem. Ber.* **1980**, 1603. {Note: first assignment of the C_{15} and C_{10} chemical shifts in PΦB DME.}
- Gossauer, A.; Miehe, D. *Liebigs Ann. Chem.* **1974**, 3, 352
- Jacobi, P.A.; DeSimone, R.W.; Ghosh, I.; Guo, J.; Leung, S.H.; Pippin, D. *J. Org. Chem.* **2000**, 65, in press (ASAP 11/10/00).
- Jacobi, P.A.; Liu, H. *J. Org. Chem.* **1999**, 64, 1778.

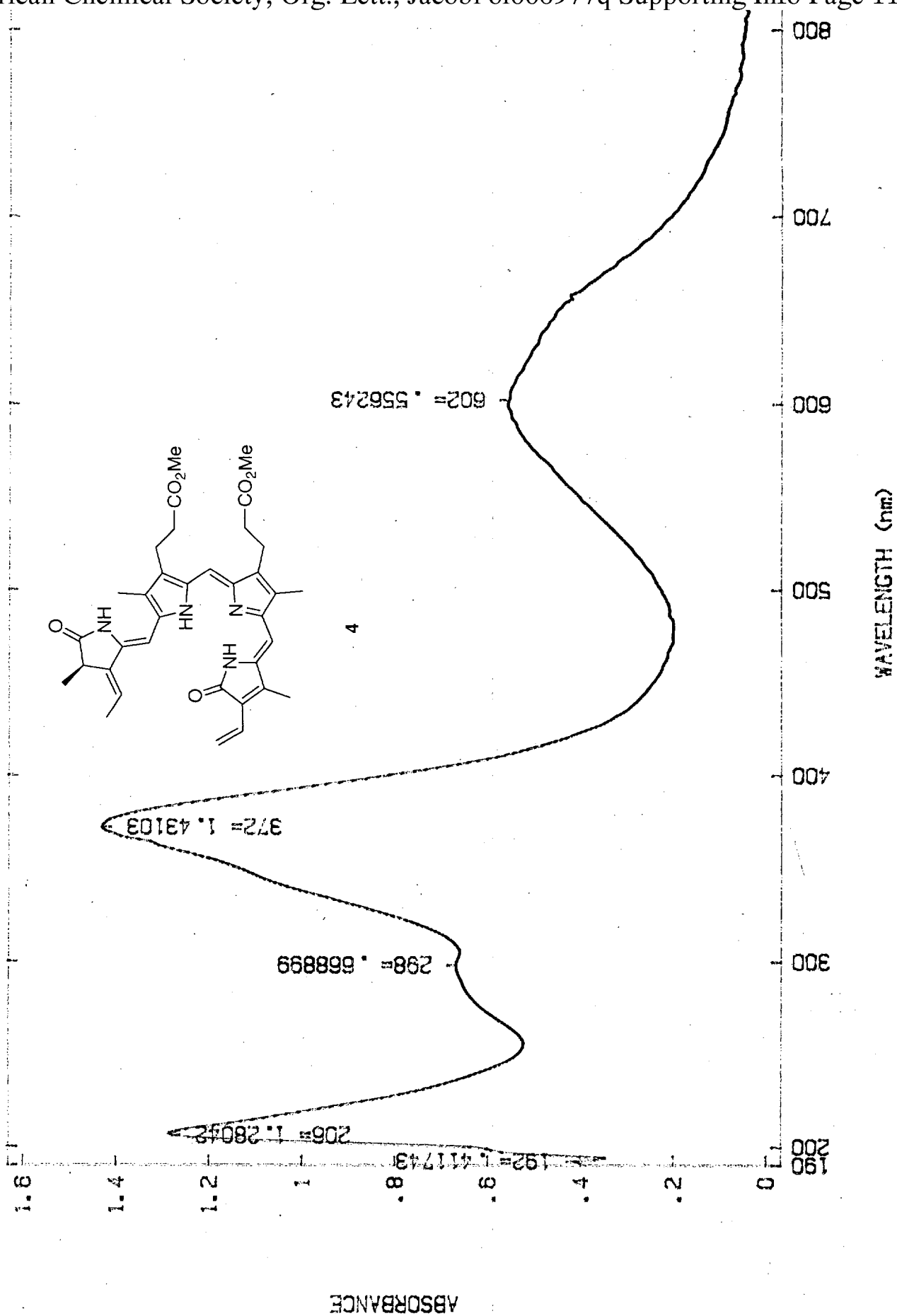
DP-II-236 phytychromobilin dimethylester

exp1 s2pul

```

SAMPLE          DEC. & VT
date            1.00 dfrq 499.875
solvent         CDC13  dn   H1
file            /data1/guest/~dpwr
DP500/DP-II-236.ph~ dof   38
                                     nnn
ACQUISITION    111111
sfrq           499.875  dmm   C
tn             H1      dmf   111111
at            1.500    dseq  1.0
np            24000    dres  n
sw            7998.4   temp  23.0
fb            4400    DECE2
bs            8       dfrq2  0
tpwr          59     dn2    1
pw            5.6    dpwr2  0
d1            1.000  dof2   0
tof           513.1  dm2    n
nt            500    dmm2   C
ct            500    dmf2   200
alock         not used
gain          not used
dres2         1.0
homo2         n
PROCESSING    0.05
il            n     lb
in            y     wtfile
dp            nm    fn
hs            not used
DISPLAY      -0.2  math
sp           4998.3 werr
vs           157    wexp
sc            0     wft
wc           240    wph
hzm          20.83 vsadj
is           415.86 wbs
rf1          4640.5 wnt
rff          3634.7
th            100.000
ins
nm            ph
    
```

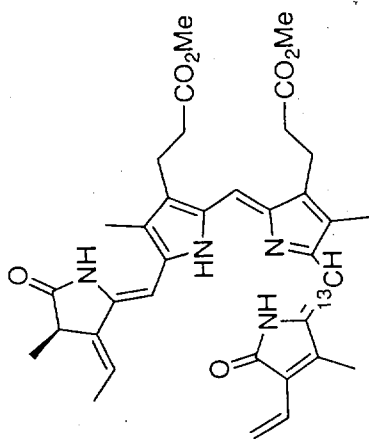




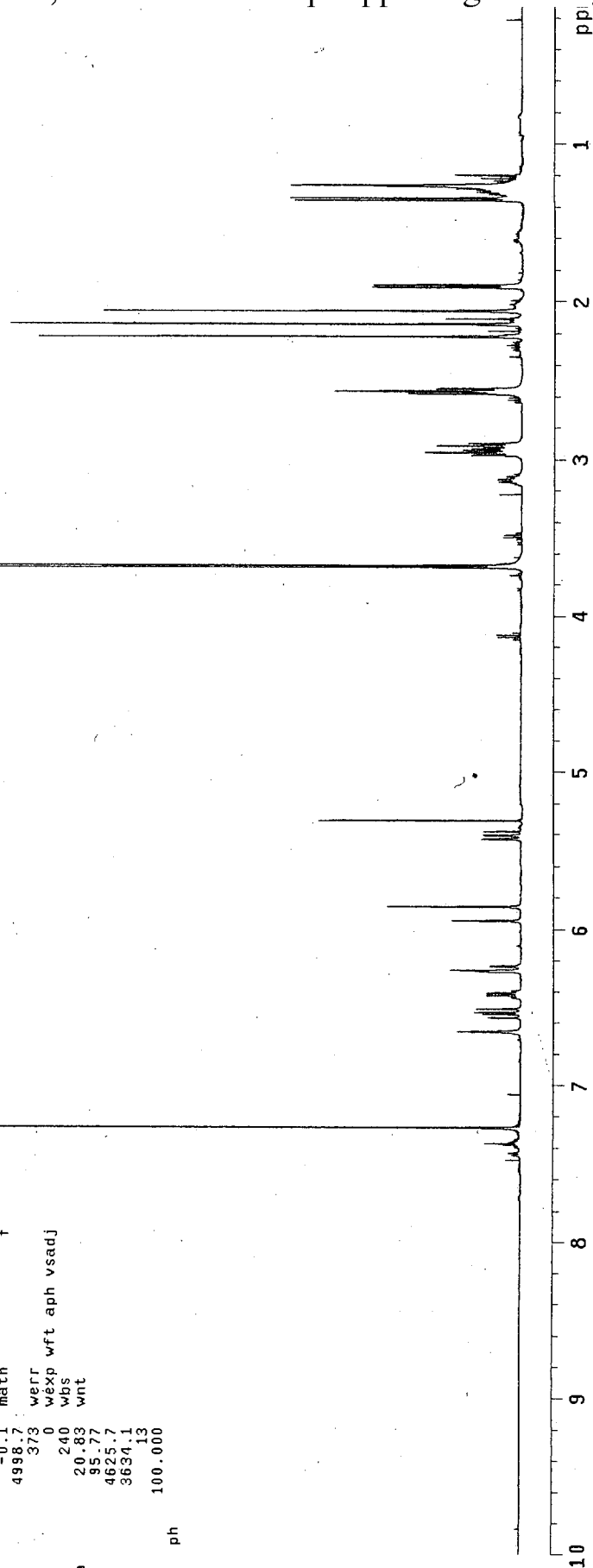
DP-III-72 1H 13C/C15 4R phyto-DME

exp3 s2pul

date	Oct 18 00	dfrq	DEC. & VT	499.875
solvent	CDCl3	dn	H1	38
file	/data1/gust/~	dpwr		0
DP500/DP-III-72-1H	~	dof	nmn	
.13C.C15:2R-phyto	dm	dmm	c	
ACQUISITION	499.875	dmf	11111	
tn	H1	dseq	1.0	
at	2.997	dres	21.0	
np	47936	homo		
sw	7998.4	temp	DEC2	
fb	4400			
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	lb	PROCESSING	
in	n	wtfile	0.05	
dp	y	fn	ft	
hs	nm	proc	not used	
sp	DISPLAY	math	f	
wp	-0.1	werr		
vs	4998.7	wexp		
sc	373	wbs	aph vsadj	
wc	0	wnt		
hzmm	240			
is	20.83			
rfl	95.77			
rff	4625.7			
th	3634.1			
tns	13			
nm	100.000			



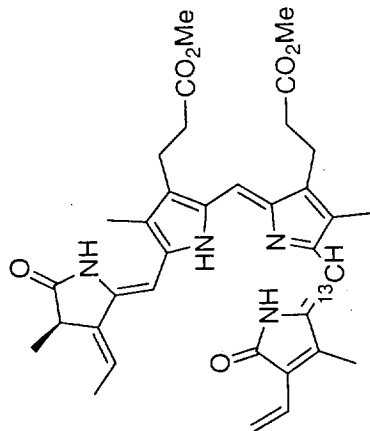
¹³C₁₅-5



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

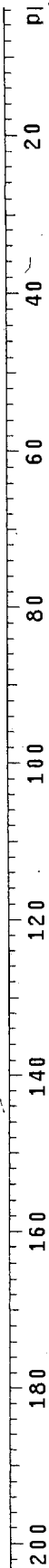
exp5 s2pul

date	Oct 16 00	dfrq	DEC. & VI	499.875
solvent	CDC13	dn	H1	
file	/data1/guest/~	dpwr	41	
DP500/DP-III-67-13~		dof	0	
C.13C-C15.4RphytoD~		dm	nvj	
	ME	dmm	w	
		dmf	14815	
ACQUISITION				
sfrq	125.706	dseq		
tn	1.0	dres	1.0	
at	1.500	homo	n	
np	79232	temp	21.0	
sw	26402.6	DEC2		
fb	14600	dfrq2	0	
bs	16	dn2	0	
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	
ct	1664	homo2	n	
alock	n			
gain	not used	lb	PROCESSING	0.50
il		wtfile		
in	n	proc	ft	
dp	y	fn	not used	
hs	mn	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			

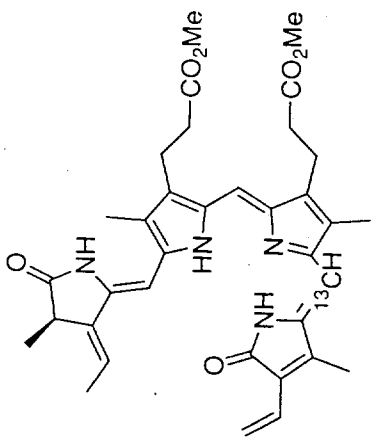


¹³C₁₅-5

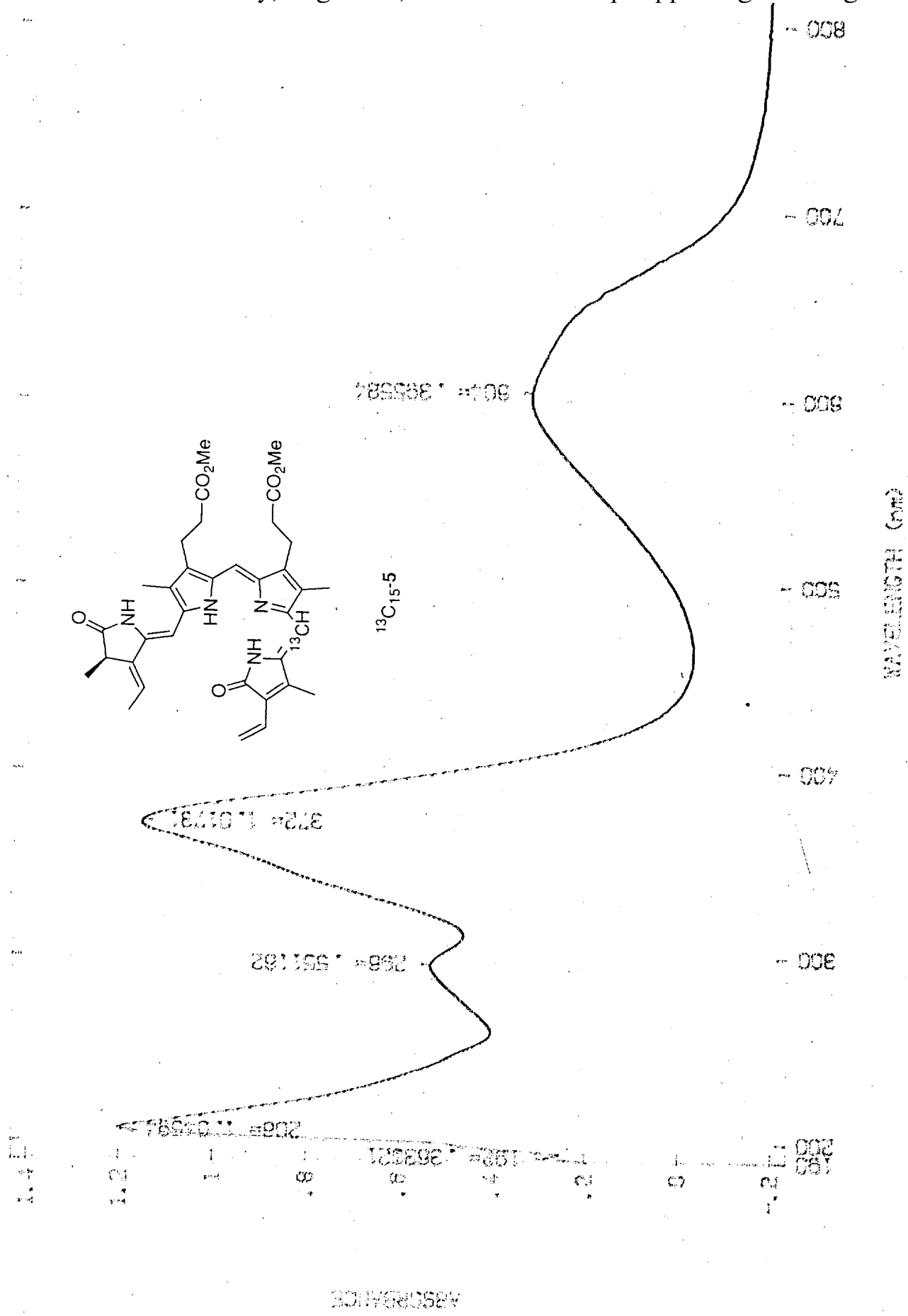
97.444



$^{13}\text{C}_{15}$
phytyl



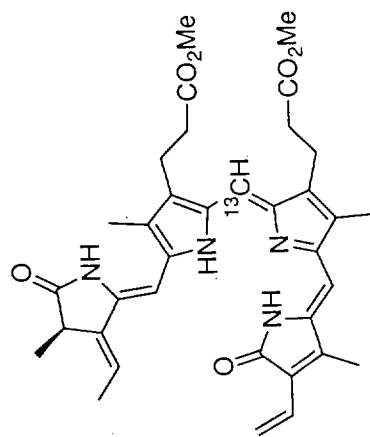
$^{13}\text{C}_{15-5}$



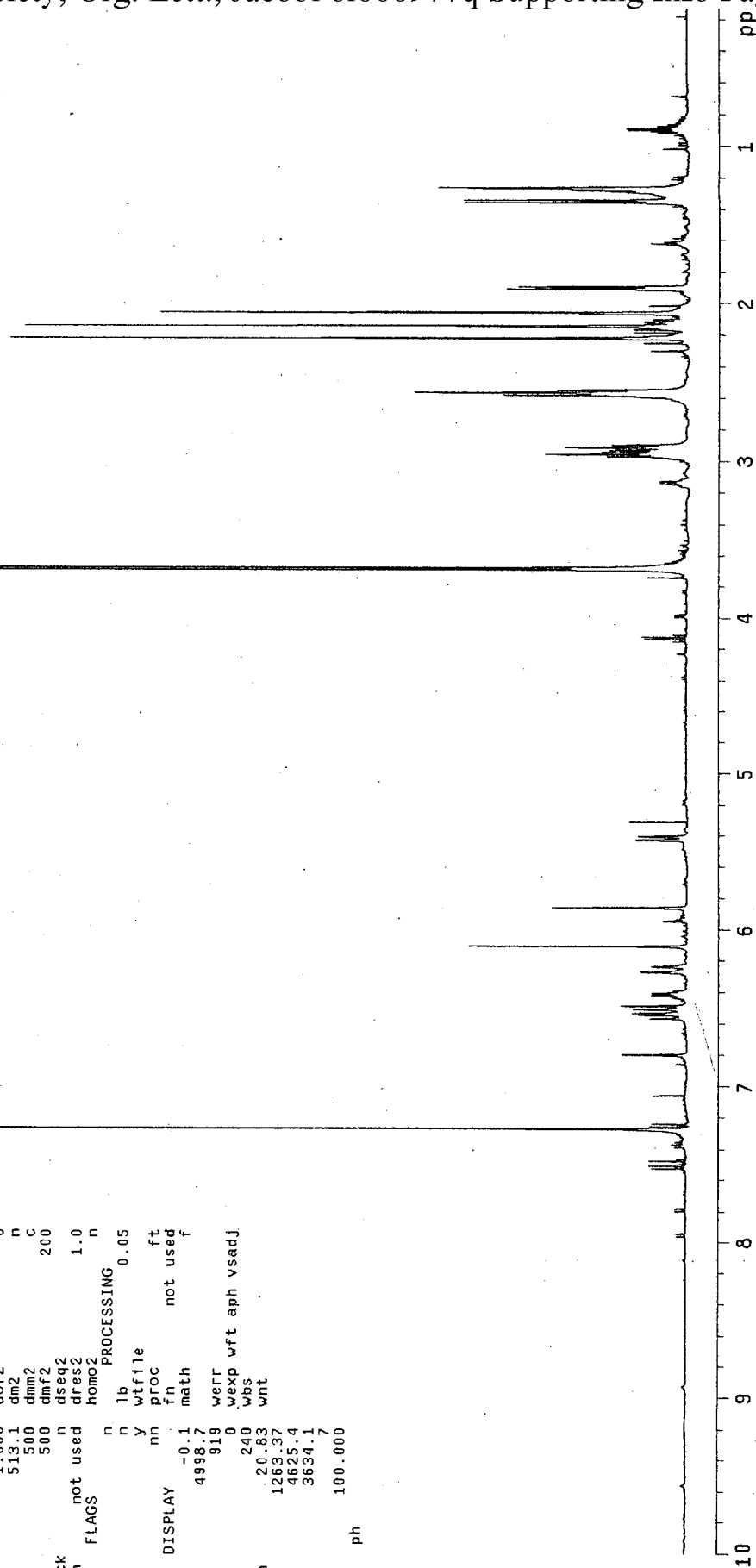
DP-III-121 4S ¹³C/¹⁰ labeled phytochrom
 obilin DME

exp2 szpu1

date	Dec 11 00	DEC. & VT	dfrq	499.875
solvent	CDCl3		dn	H1
file	/data/guest/~		dpwr	38
DP500/DP-III-121.1~			dof	0
H.13C.C10.4S.phyto			dm	nmn
ACQUISITION			dmm	C
sfrq	499.875		dmf	11111
tn	H1		dseq	
at	2.997		dres	1.0
np	47836		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	500		dmf2	200
alock	n		dseq2	
gain	not used		dres2	1.0
FLAGS			homo2	n
fl	n	PROCESSING	lb	n
in	n		wtfile	0.05
dp	y		proc	ft
hs	nn		fn	not used
sp	-0.1		math	f
wp	4998.7		werr	
vs	919		wexp	wft aph vsadj
sc	0		wbs	
wc	240		wnt	
hzmm	20.83			
ls	1263.37			
rfl	4625.4			
rfp	3634.1			
th				
ins				
nm	100.000			
				ph



¹³C-10-6

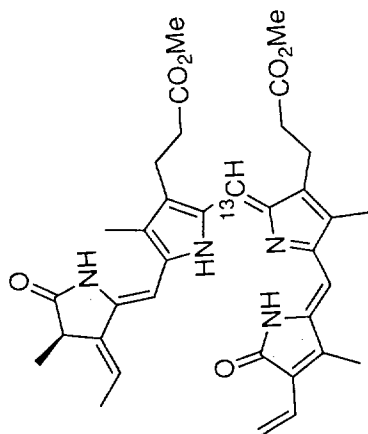


DP-III-121 13C-C10 labeled 4S-phyto DME

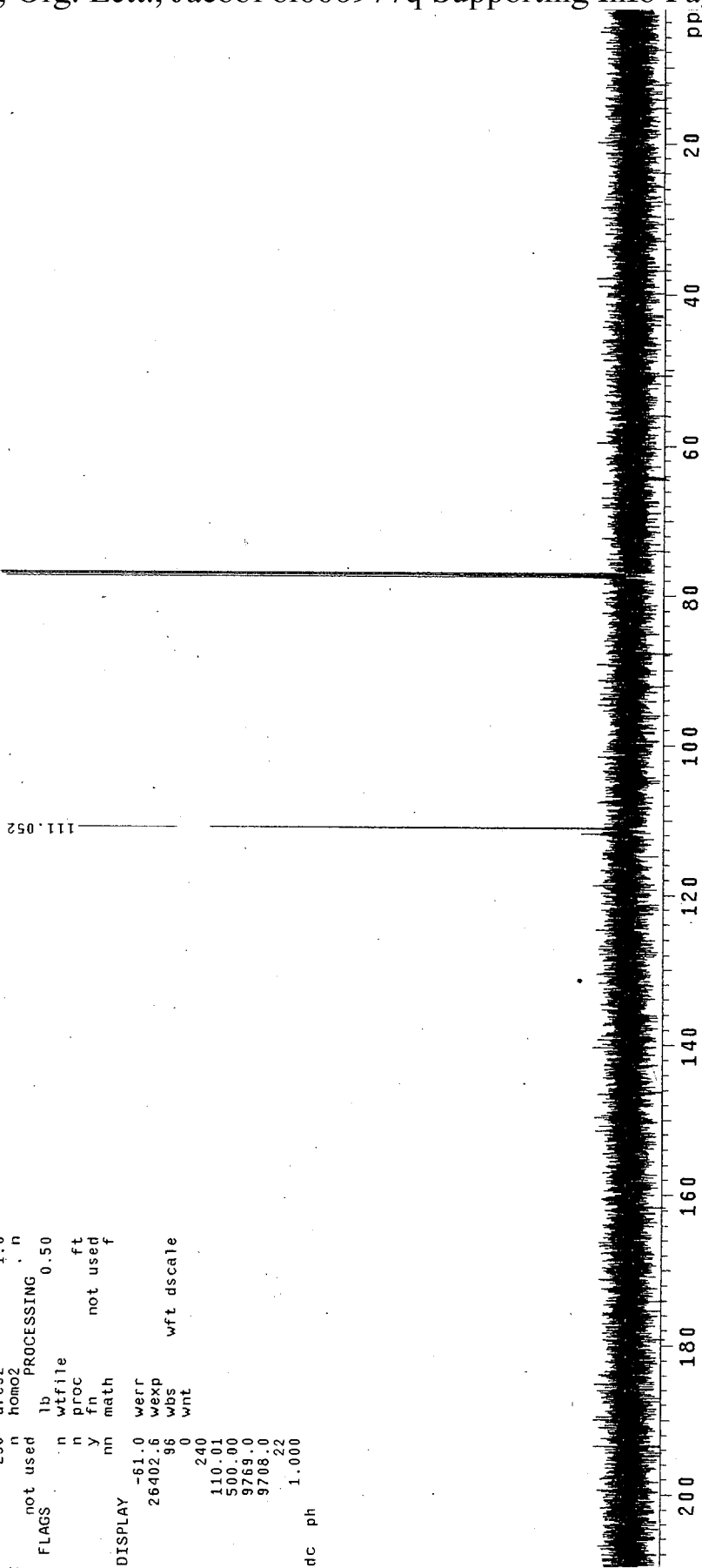
exp6 s2pul

```

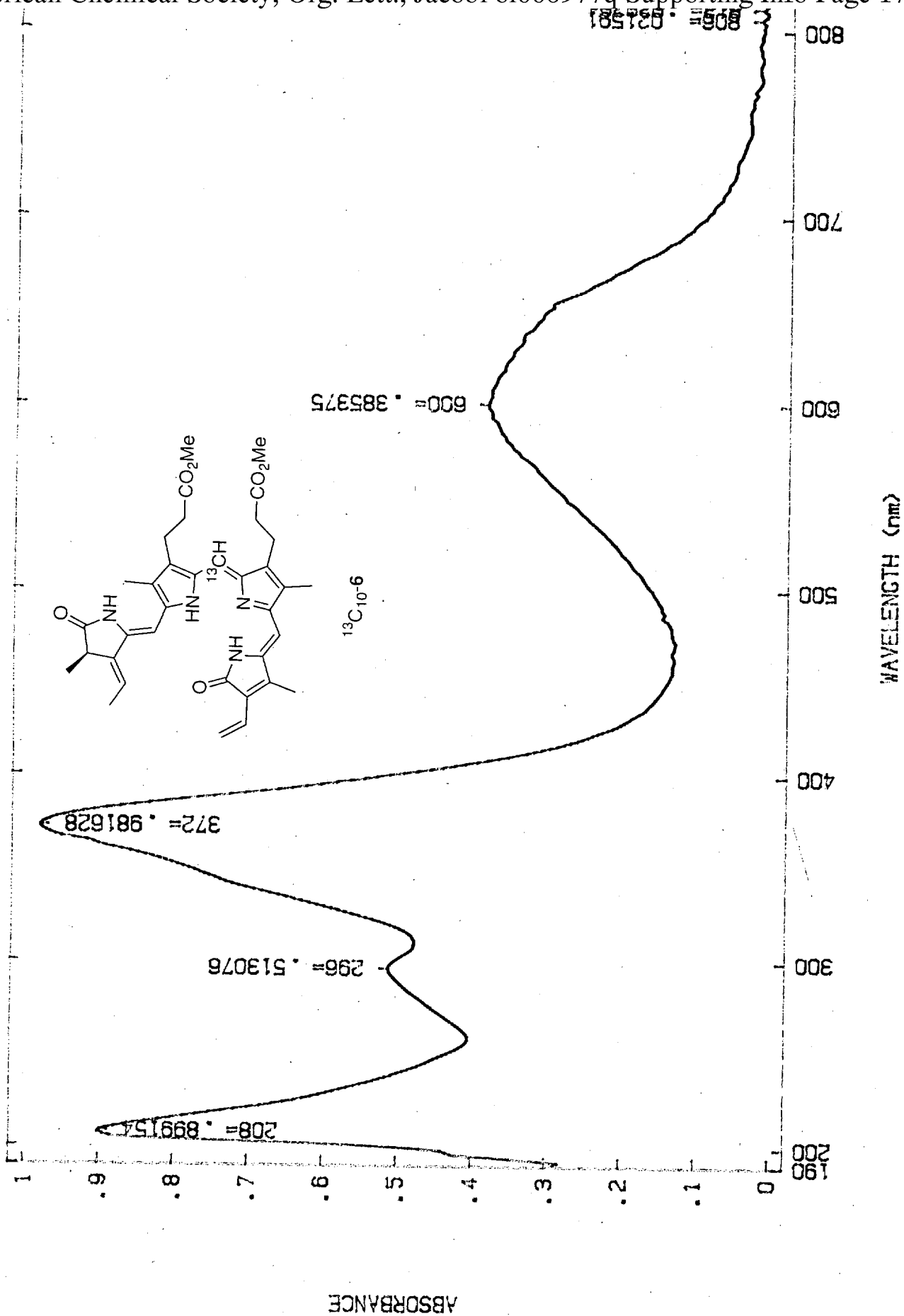
SAMPLE          DEC. & VT
date            11 00 dfrq          499.875
solvent         CDC13 dn           41
file            /data1/guest/~dpr
DP500/DP-III-121.1~ dof          0
3C.13C-C10.lbid.4S~ dm           nyy
phyto           dmm              w
ACQUISITION    dmf             14815
sfrq           125.706 dseq
tn             C13 dres          1.0
at            1.500 homo         n
np            79232 temp         21.0
sw            26402.6 dfrq2      0
fb            14600 dh2         32
bs            60 dpwr2          1
tpwr          10.2 dof2         0
pw            0.800 dm2         n
d1            0.300 dmm2        C
d2            1202.3 dmf2        10000
tof           1024 dseq2
ct            256 dres2         1.0
alock         n homo2          n
gain          not used lb       0.50
FLAGS         n wtfile
il            n proc          ft
in            y fn            not used
dp            nn math
hs            DISPLAY
sp            -61.0 werr
wp            26402.6 wexp
vs            96 wbs
sc            0 wnt
wc            240
hzmm         110.01
ls            500.00
rfl          9769.0
rff          9708.0
th           22
ins          1.000
nm           cdc ph
    
```



¹³C₁₀-6



6 ^{13}C photo

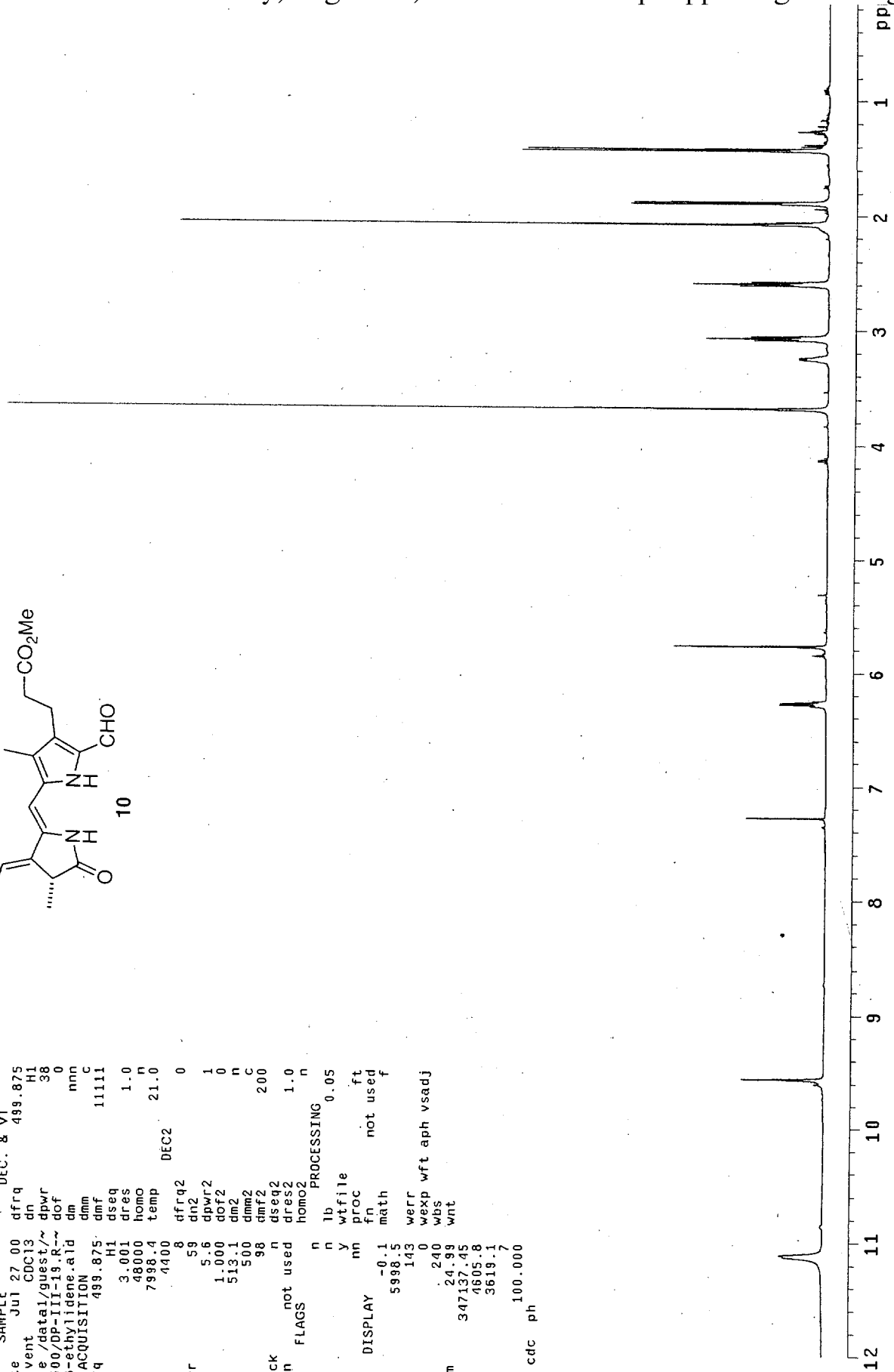
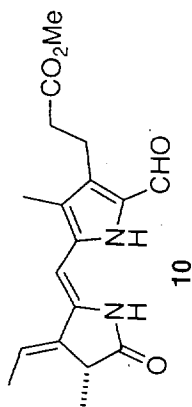


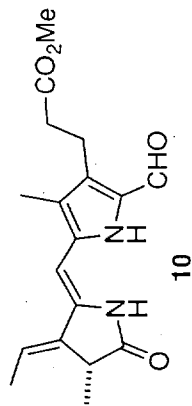
DP-III-19 4R AB ethyllidene pyrromethenon

exp3 s2pu1

```

SAMPLE      DEC. & VT
date        Jul 27 00   dfrq      499.875
solvent     CDC13   dn          H1
file        /data1/quest/~ dpwr     38
DP500/DP-III-19.R~ dof         0
AB-ethylidene.a.id dm          nnn
ACQUISITION dmm          111111
sfrq       499.875   dmf          C
tn          H1      dseg         1.0
at          3.001   dres         n
np          48000   homo         n
sw          7998.4 temp        21.0
fb          4400   DEC2
bs          8      dfrq2      0
tpwr       59      dn2        1
pw         5.6    dpwr2      1
dl         1.000  dof2       0
tof        513.1  dm2        n
nt         500    dmm2       C
ct         98     dmf2       200
alock      n      dscq2      1.0
gain       not used dres2
flags      homo2  n
          n      lb          n
          n      y          wtfile  0.05
          nn     proc         ft
          -0.1   fn          not used
          5998.5 math         f
          143    werr
          0      wexp wft aph vsadj
          .240   wbs
          24.99  wnt
          347137.45 is
          4605.8  rfl
          3619.7  rfp
          100.000 ins
          nm   cdc   ph
    
```

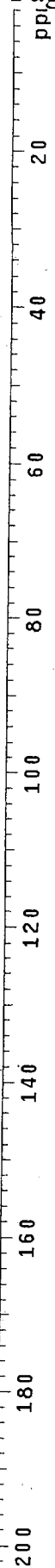




STANDARD CARBON PARAMETERS

```

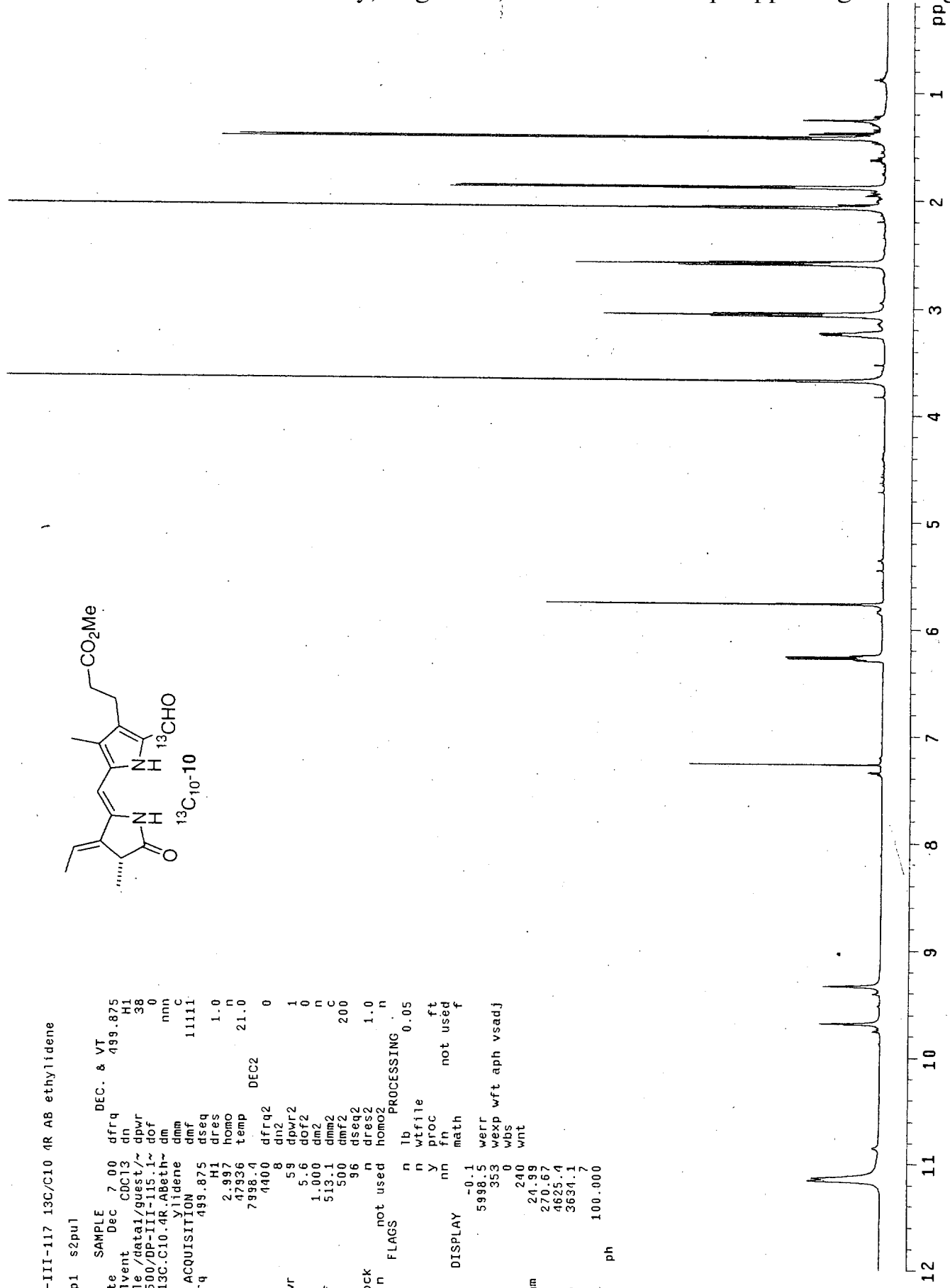
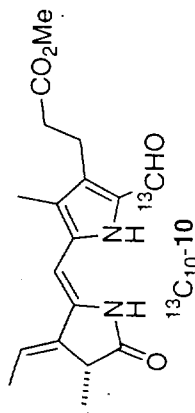
exp1 s2pul
SAMPLE      date      Oct 11 00      dfrq      DEC. & VT
            solvent   CDC13         dn         499.875
            file      /data1/guest/~ dpwr      H1
            DP500/DP-III-60.13~ dof      41
            C.R-ABethylidine.a~ dm         nyy
            ACQUISITION id      dmm         14815
            sfrq      125.706      dseq
            tn        Cl3         dres      1.0
            at        1.500         homo      n
            np        79232         temp      21.0
            sw        26402.6       DECD2
            fb        14600         dfrq2     0
            bs        8             dn2
            tpwr     60             dpwr2     1
            pw       10.2          dof2      0
            d1       0.800         dm2       n
            d2       0.300         dhmm2    c
            tof      1202.3        dmf2     10000
            nt       100000        dseq2
            ct       31408         dres2    1.0
            alock   not used      n homo2
            gain    not used      lb        PROCESSING
            FLAGS   not used      lb        0.50
            l1      n             wtfile
            l2      n             n proc   ft
            dp      y             y fn     not used
            hs      nn          math      f
            DISPLAY -63.4         werr
            wp      26402.6       wexp
            vs      116          wbs
            sc      250          wnt
            wc      105.61
            hzmm    500.00
            is      9771.4
            rfl     9708.0
            rfp
            th      1.000
            ins     1.000
            nm      cdc          ph
    
```



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

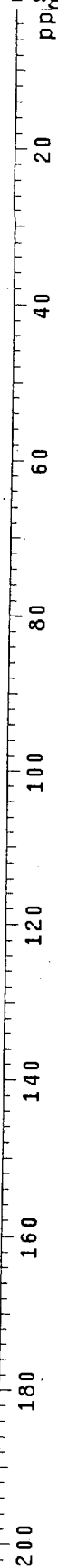
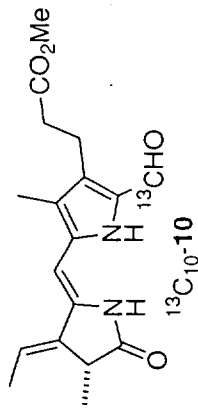
expl s2pul

date	Dec	7 00	dfreq	DEC. & VT	499.875
solvent	CDCl3	dn	H1		
file	/data1/guest/~dpwr		38		
DP500/DP-III-115	1~	dof	0		
H.13C.C10.4R.ABeth~	dm	nnh			
Ylidene	dmm		111111		
ACQUISITION	dmf				
sfrq	499.875	dseq			
tn	H1	dres	1.0		
at	2.997	homo			
np	47936	temp	21.0		
sw	7998.4				
fb	4400	dfreq2	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	wfile			
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					
IS	24.99				
RF1	270.67				
RF2	4625.4				
TH	3634.1				
INS					
RM	100.000				



DP-III-117 13C/13C/C10 4S AB ethylidene
exp2 s2pu1

date	SAMPLE	DEC. & VT
solvent	Dec	499.875
file	CDCl3	H1
	exp	41
	dof	0
	nyy	w
	dm	14815
	dmm	
	dmf	
	dseq	
	dres	1.0
	homo	n
	temp	21.0
	tpwr	DEC2
	pw	60
	d1	10.2
	d2	2.000
	dpwr2	0.500
	dof2	1
	dm2	0
	dmm2	n
	dmf2	c
	dseq2	10000
	dres2	
	homo2	1.0
	lb	n
	wtfile	PROCESSING
	proc	0.50
	fn	ft
	math	not used
	werr	f
	wexp	
	wbs	wfts
	wnt	dscale
	hzm	110.01
	rfl	6196.36
	rff	9771.8
	rth	9708.0
	th	68
	ins	100.000
	nm	cdc
	ph	



DP-III-18 CD unsubstituted alkene

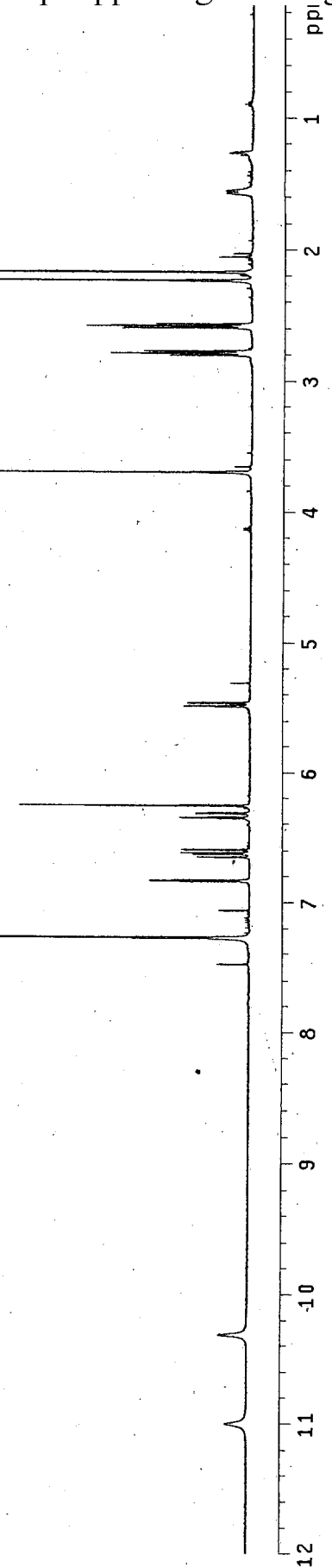
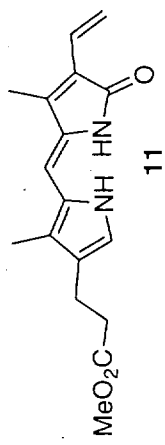
exp1 s2pul

SAMPLE date Jul 27 00 dfrq DEC. & VT 499.875
 solvent CDC13 dn H1 38
 file /data1/guest/~ dpwr 0
 DP500/DP-III-18.CD~ dof nnn
 .unsub.vinylquantity~ dm 11111 C

ACQUISITION ld dnm
 sfrq 499.875 dseq 11111
 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 1
 tpwr 59 dpwr2 1
 pw 5.6 dof2 0
 dl 1.000 dm2 n
 tof 513.1 dmm2 C
 nt 10000 dmf2 200
 ct 504 dseq2 n
 alock n dres2 1.0
 gain not used homo2 n

PROCESSING 0.05
 lb n
 in n wtfile ft
 dp y proc not used f
 hs nn fn math

DISPLAY -0.1
 sp 5998.5 verr
 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 3634.5
 ins 100.000
 nm ph

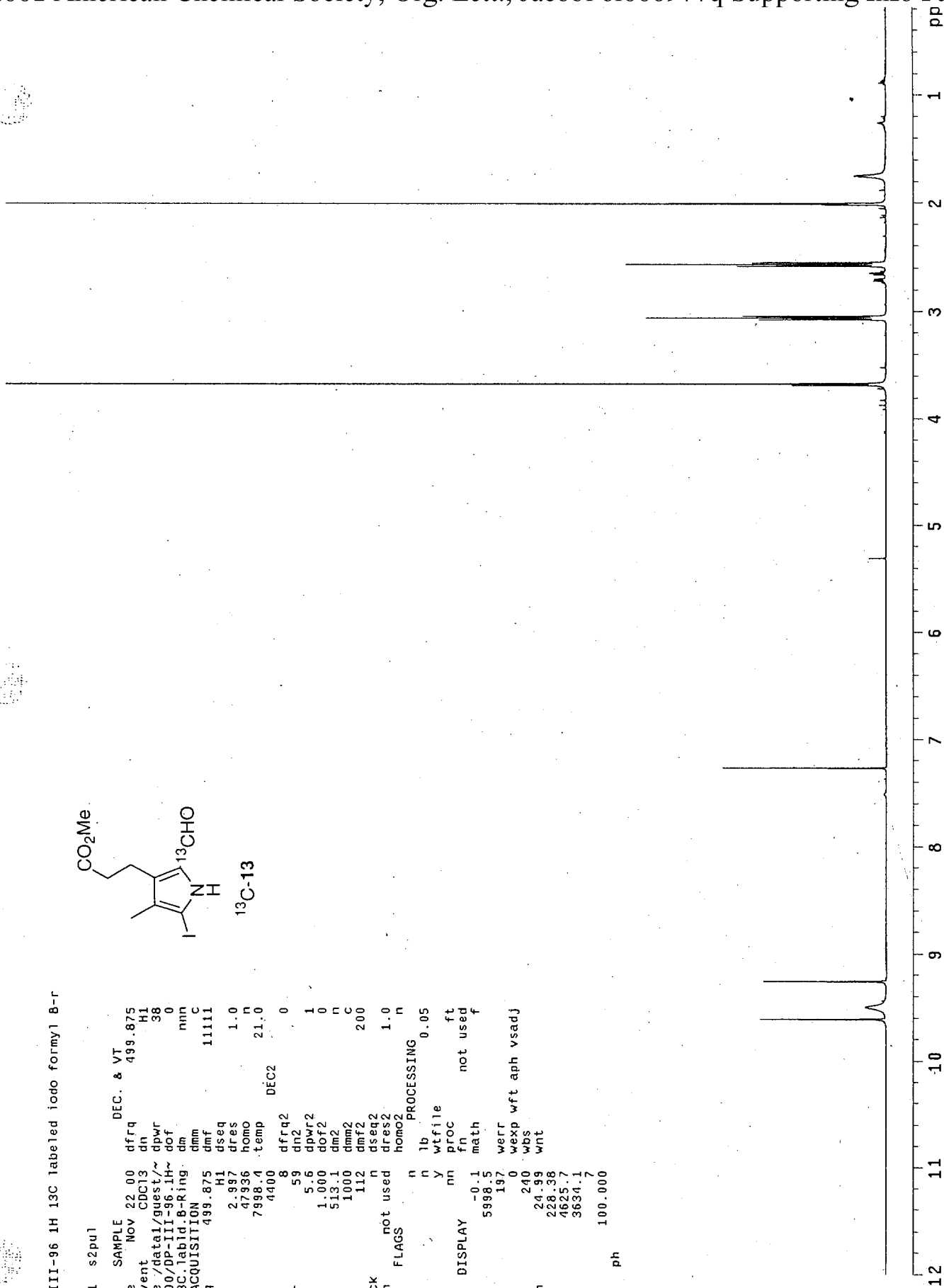
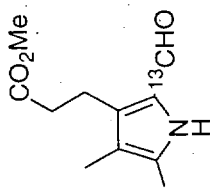


DP-III-96 1H 13C labeled iodo formyl B-r
ing

exp1 s2pul

```

SAMPLE Nov 22 00 dfrq DEC. & VT 499.875
solvent Nov CDC13 dn H1 499.875
file /data/guest/~ dpwr 38
DP500/DP-III-96.1H~ dof 0
.13C.labld.B-Ring dm nnn
ACQUISITION dnm 11111 C
sfrq 499.875 dmf 11111
tn H1 dseq 1.0
at 2.997 dres n
np 47936 homo n
sw 7998.4 temp 21.0
fb 4400 DEC2
bs 8 dfrq2 0
tpwr 59 dn2 1
pw 5.6 apwr2 1
dl 1.000 dof2 0
tof 513.1 dm2 n
nt 1000 dnm2 C
ct 112 dmf2 200
alock n dseq2
gain not used dres2 1.0
homo2 n
ll n PROCESSING 0.05
in n lb
dp n y wtfile
hs nn fn proc ft
DISPLAY -0.1 math not used f
sp 5998.5 werr
vs 197 wexp wft aph vsadj
wc 240 wbs
hzmm 24.99 wnt
is 228.38
rfl 4625.7
rfp 3634.1
th
ins 100.000
nm ph
    
```

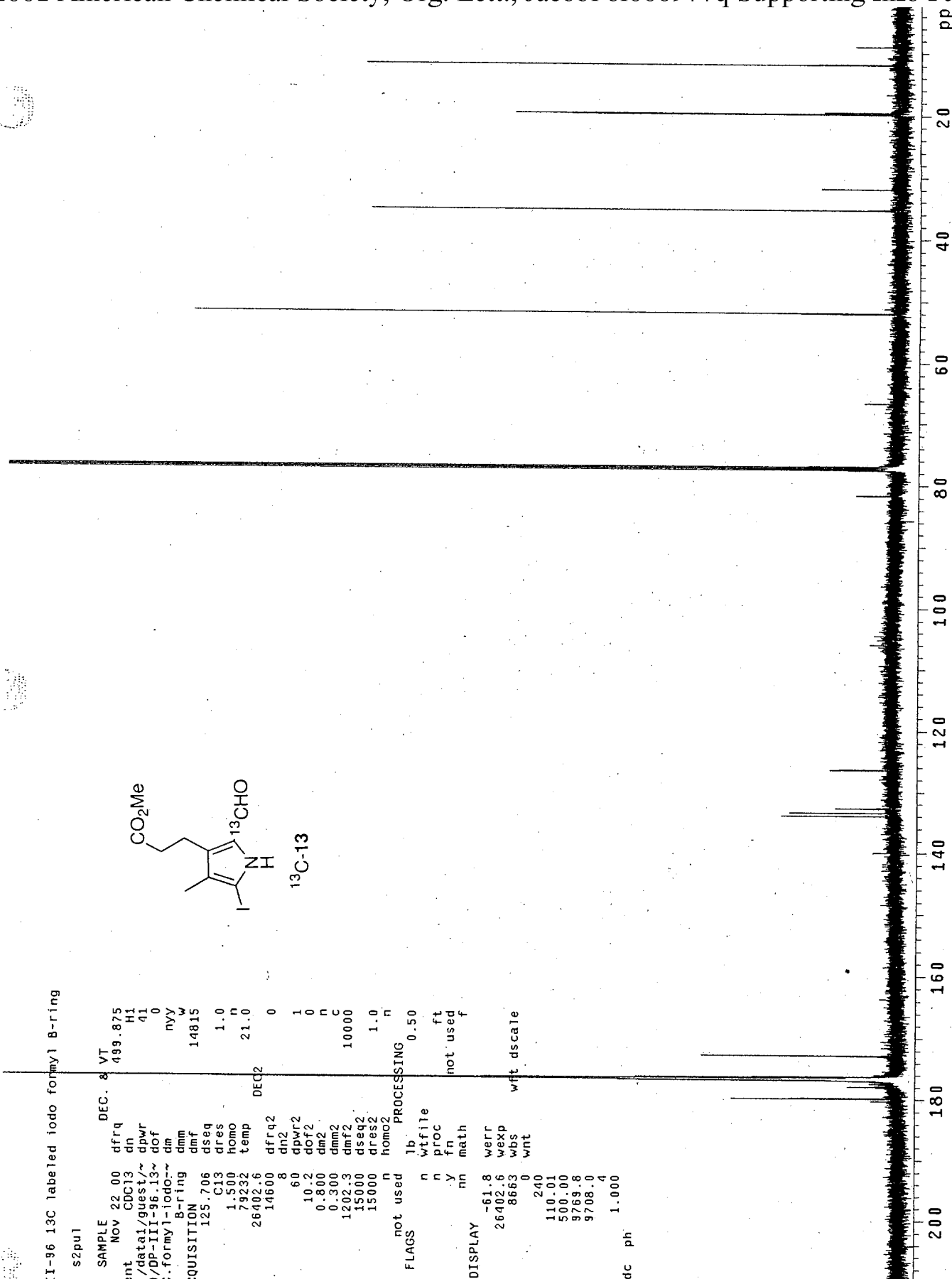
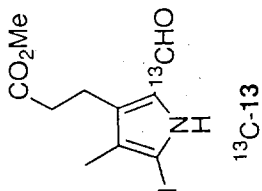


DP-III-96 13C labeled iodo formyl B-ring

exp1 s2pul

```

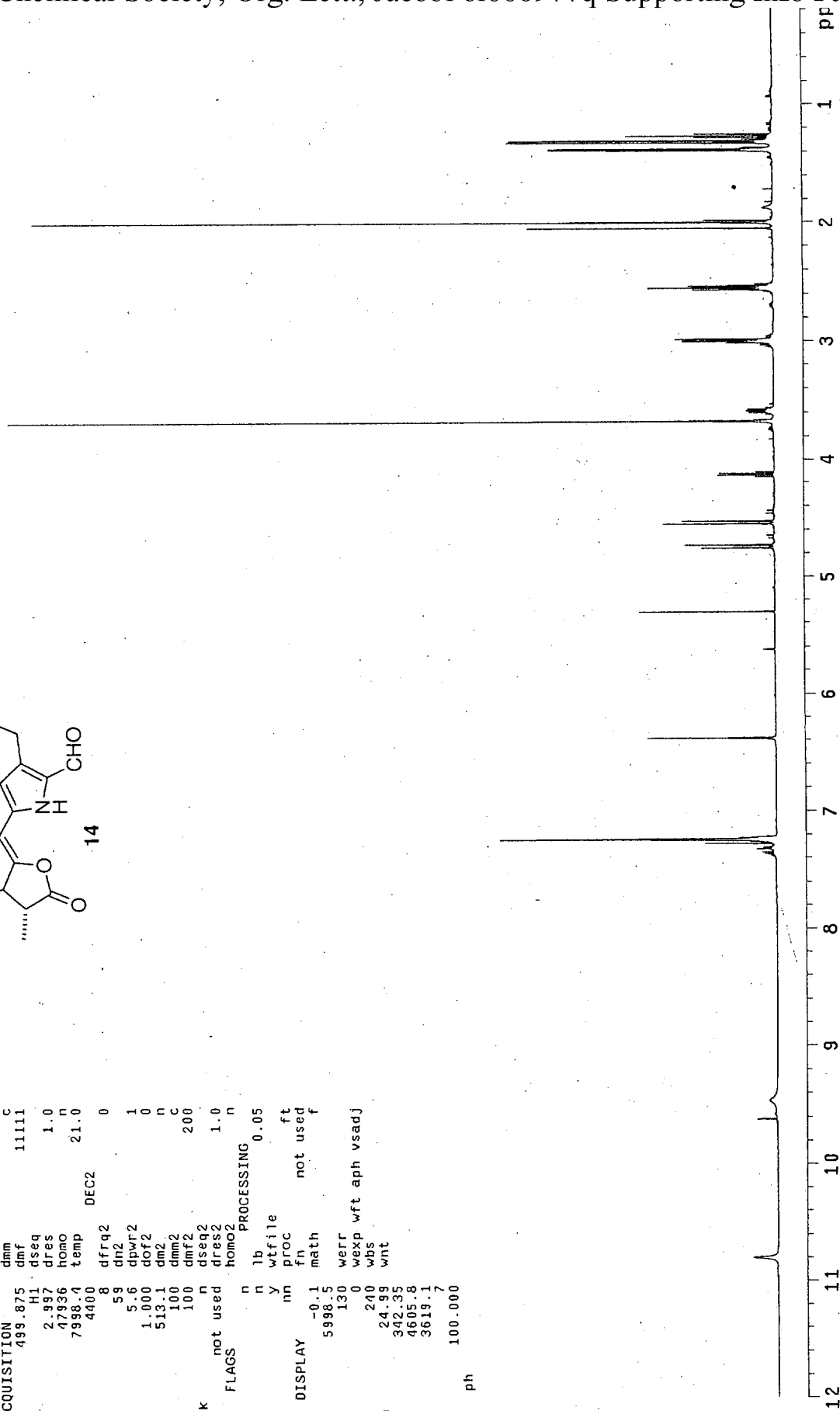
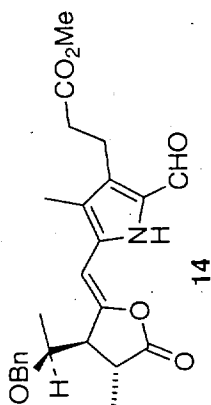
SAMPLE      DEC. & VT
date        Nov 22 00   dfrq      499.875
solvent     Nov CDC13   dn          1
file        /data1/guest/~ dpwr     41
DP500/DP-III-96.13~ dof          0
C.13C.formyl-Iodo-~ dm           nvy
B-ring      dmf         14815   w
ACQUISITION
sfrq       125.706   dseq
tn          C13     dres
at          1.500   homo
np          78232   temp
sw          26402.6 DEC2
fb          14600   dfrq2
bs          8       dn2
tpwr        60     dpwr2
pw          10.2   dof2
d1          0.800  dm2
d2          0.300  dnm2
tof         1282.3 dmf2
nt          15000  dseq2
ct          15000  dres2
alock      not used homo2
gain       not used lb
          FLAGS    lb      0.50
          in       n      wfile
          dp       n      proc
          hs       y      rn
          ns       nn     math
          DISPLAY  -61.8  werr
          wp       26402.6 wexp
          vs       8663   wbs
          sc       0      wnt
          wc       240
          hzmm     110.01
          ls       500.00
          rfl      9769.8
          rfp      9708.0
          th       4
          ins      1.000
nm          cdc   ph
    
```



DP-III-69

expl s2pul

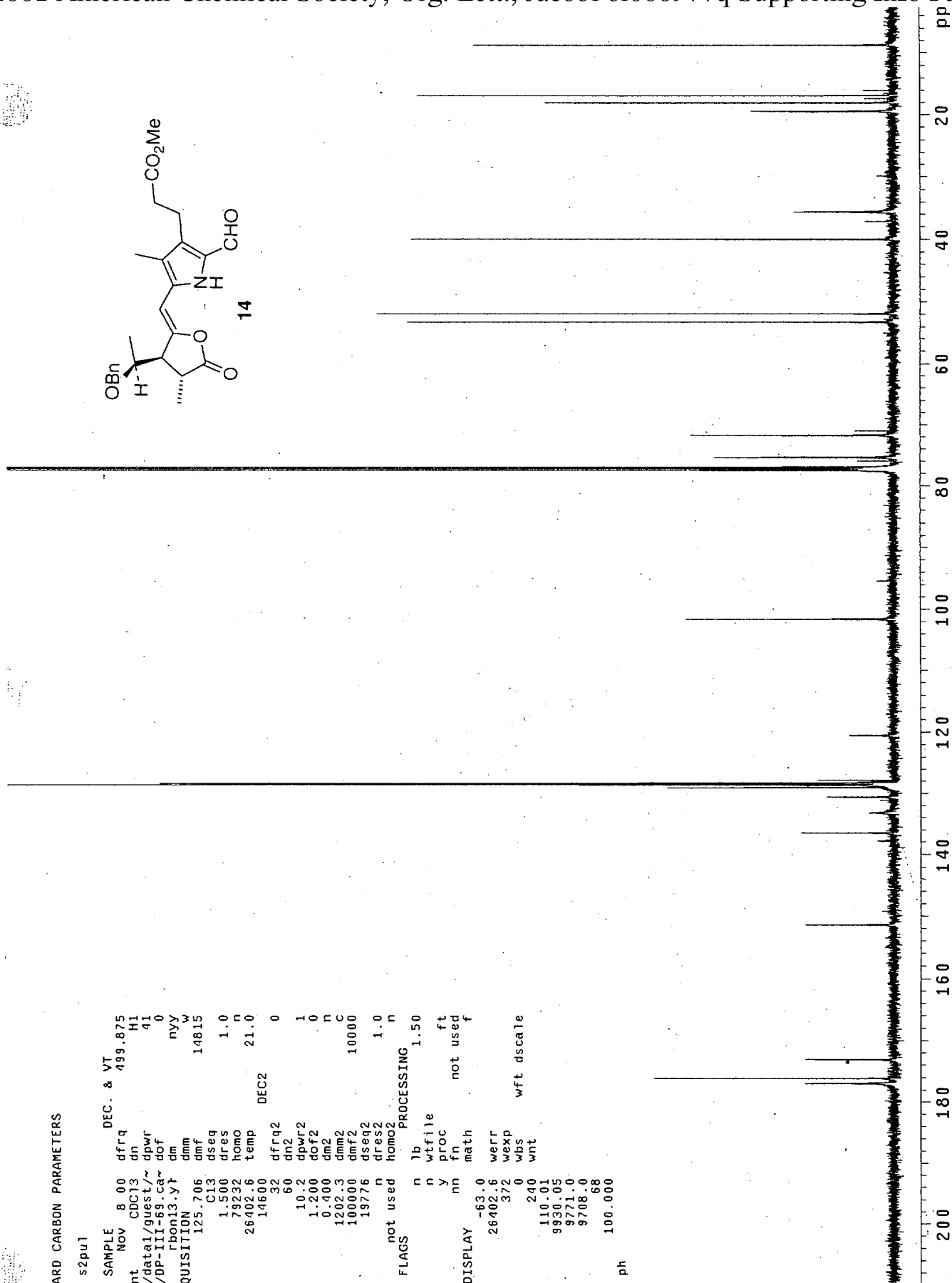
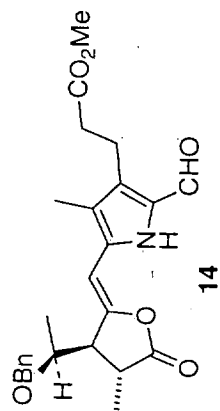
date	SAMPLE	DEC. & VT
Nov	1 00	499.875
solvent	CDCl3	H1
file	/data1/quest/~	38
DP500/DP-III-69-2P~	dpr	0
-A-Benzoyloxy-B-ald	dof	0
ACQUISITION	dmm	C
499.875	dmf	11111
at	H1	dseq
2.997	dres	1.0
47936	homo	n
7998.4	temp	21.0
4400	DEC2	
bs	dfrq2	0
tpwr	dn2	59
pw	dpwr2	1
d1	dof2	0
tof	dm2	513.1
nt	dmm2	n
ct	dmf2	C
atlock	ct	100
gain	dseq2	200
not used	dres2	1.0
FLAGS	homo2	n
in	lb	PROCESSING
in	Y	0.05
dp	wtfile	
hs	proc	ft
not used	fn	not used
math		f
sp	-0.1	
werr	5998.5	
vs	130	wexp wft aph vsadj
sc	0	wbs
wc	240	wnt
hzm	24.99	
is	342.35	
rfl	4605.8	
rff	3619.7	
th		
ins	100.000	
nm	ph	



STANDARD CARBON PARAMETERS

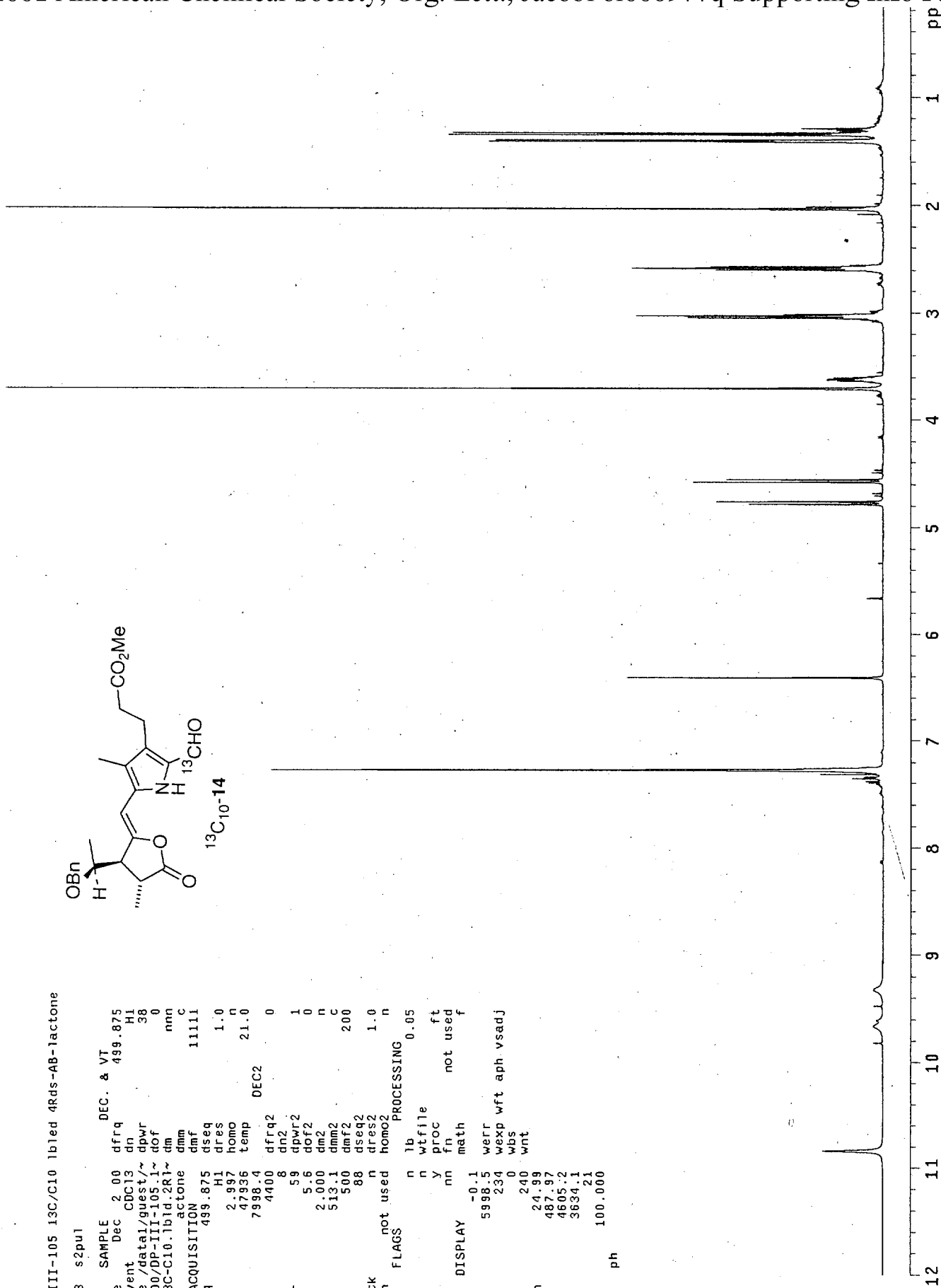
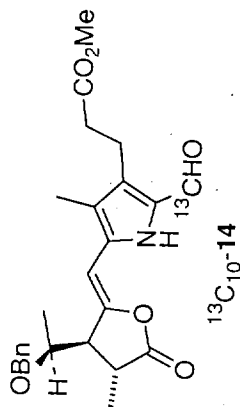
```

exp1 s2pul
date NOV 8 00 dfrq DEC. & VT 499.875
solvent CDC13 dn H1
file /data1/guest/~ dpwr 41
DP500/DP-III-69.ca~ dof 0
rbon13.yt dm nyv
ACQUISITION dmm 14815
sfrq 125.706 dmf
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 1
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
PROCESSING
it n lb 1.50
in n wtfile ft
dp y proc not used
hs nn math
DISPLAY -63.0 werr wft dscale
vs 26402.6 wexp
sc 372 wbs
wc 240 wnt
hzm 110.01
is 9930.05
rfl 9771.0
rfp 9708.0
th 68
ins 100.000
nm ph
    
```

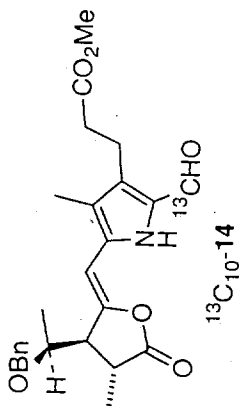


DP-III-105 13C/C10 lbled 4R4s-AB-lactone
exp3 s2pu1

date	Dec 2 00	DEC. & VT	dfrq	499.875
solvent	CDCl3	dn	HI	38
file	/data/guest/~dpwr	dof	0	0
DP500/DP-III-105.1~		dm	nnn	
H.13C-C10.1blld.2R1~		dmm	C	
actone		dmf	11111	
ACQUISITION		dseq		
sfrq	499.875	dres	1.0	
tn	HI	homo	n	
at	2.997	temp	21.0	
np	47936			
sw	7998.4	DEC2		
fb	4400	dfrq2	0	
bs	8	dn2		
tpwr	59	dpwr2	1	
pw	5.8	dof2	0	
d1	2.000	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	
		math	f	
sp	-0.1	werr		
wp	5998.5	wexp	wft	
vs	234	wbs	aph	
sc	0	wnt	vsadj	
wc	240			
hzmm	24.99			
is	487.97			
rfl	4605.2			
rffp	3634.1			
th	21			
ins	100.000			
nm	ph			



DP-III-97 13C 13C labeled 2R AB lactone



200 180 160 140 120 100 80 60 40 20 ppi

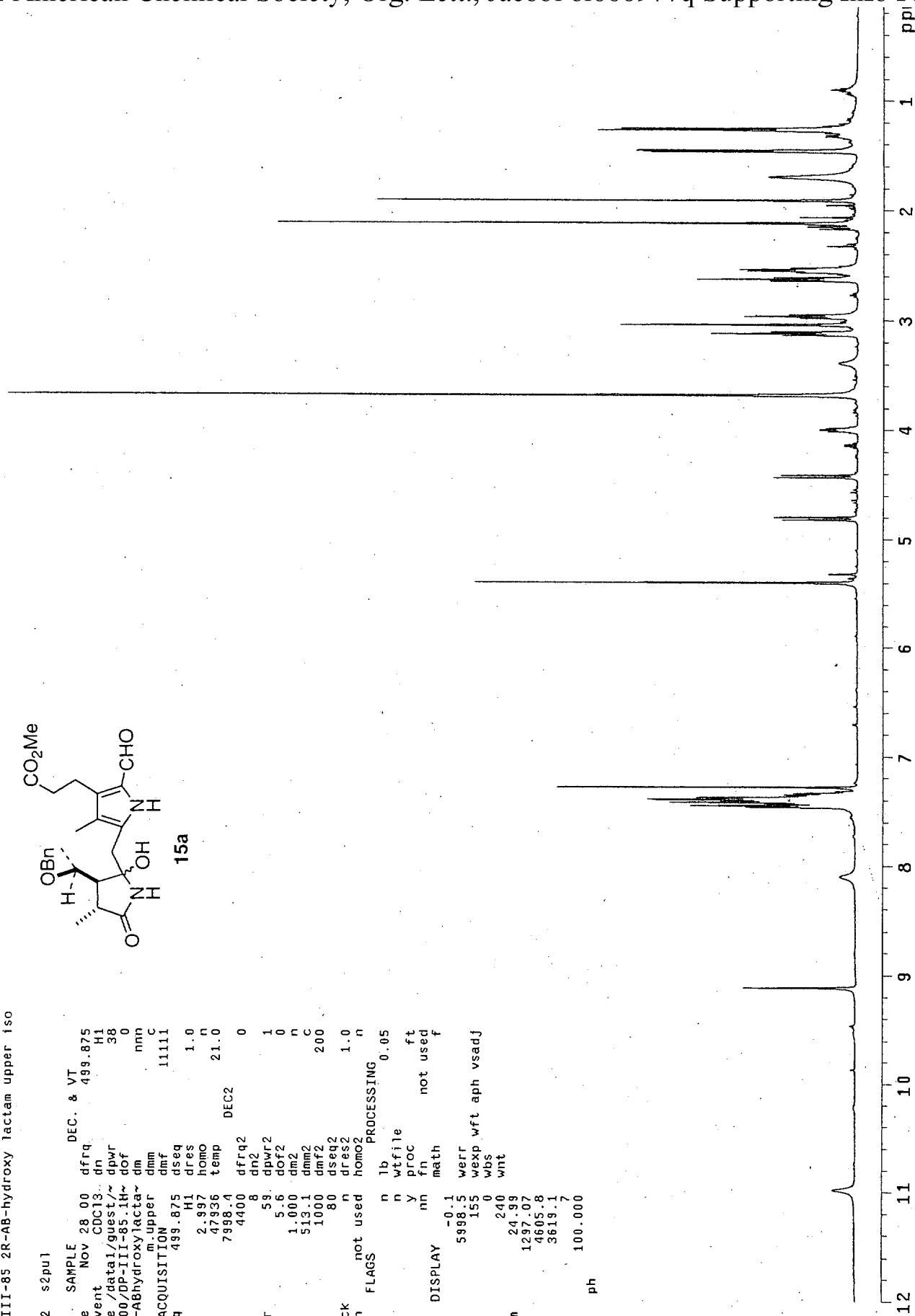
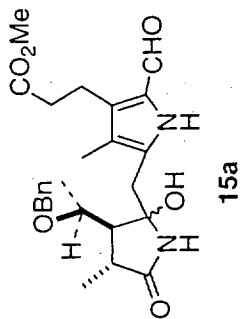


DP-III-85 2R-AB-hydroxy lactam upper iso
mer

exp2 s2pu1

```

SAMPLE          DEC. & VT
date Nov 28 00  dfrq 499.875
solvent CDC13.  dn    H1
file /data1/guest/~dpwr 38
DP500/DP-III-85.1H~ dof 0
.2R-ABhydroxy/lacta- dmm nnn
m.upper          C
ACQUISITION    11111
sfrq 499.875  dseq
tn 2.897      H1
at 47336     dres 1.0
np 7398.4   homo  n
sw 4400     temp 21.0
fb 8        dfrq2 0
bs 59.      dn2
tpwr 59.    dpwr2 1
pw 5.6      dof2 0
dl 1.000    dm2  n
tof 513.1   dmm2  C
nt 1000     dmf2 200
ct 80      dseq2
alock n     dres2 1.0
gain not used homo2 n
FLAGS          PROCESSING 0.05
il n         lb
in n         wfile
dp y         proc
hs nn        fn
          math
DISPLAY -0.1
sp 5998.5    werr
vs 155      wexp wft aph vsadj
sc 0        wbs
wc 240      wnt
hzmnm 24.89
ls 1237.07
rfl 4605.8
rfp 3619.1
th 7
ins 100.000
nm ph
    
```

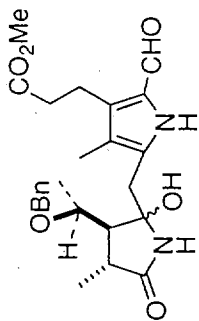


DP-III-85 2R-AB-hydroxylactam lower isom
er

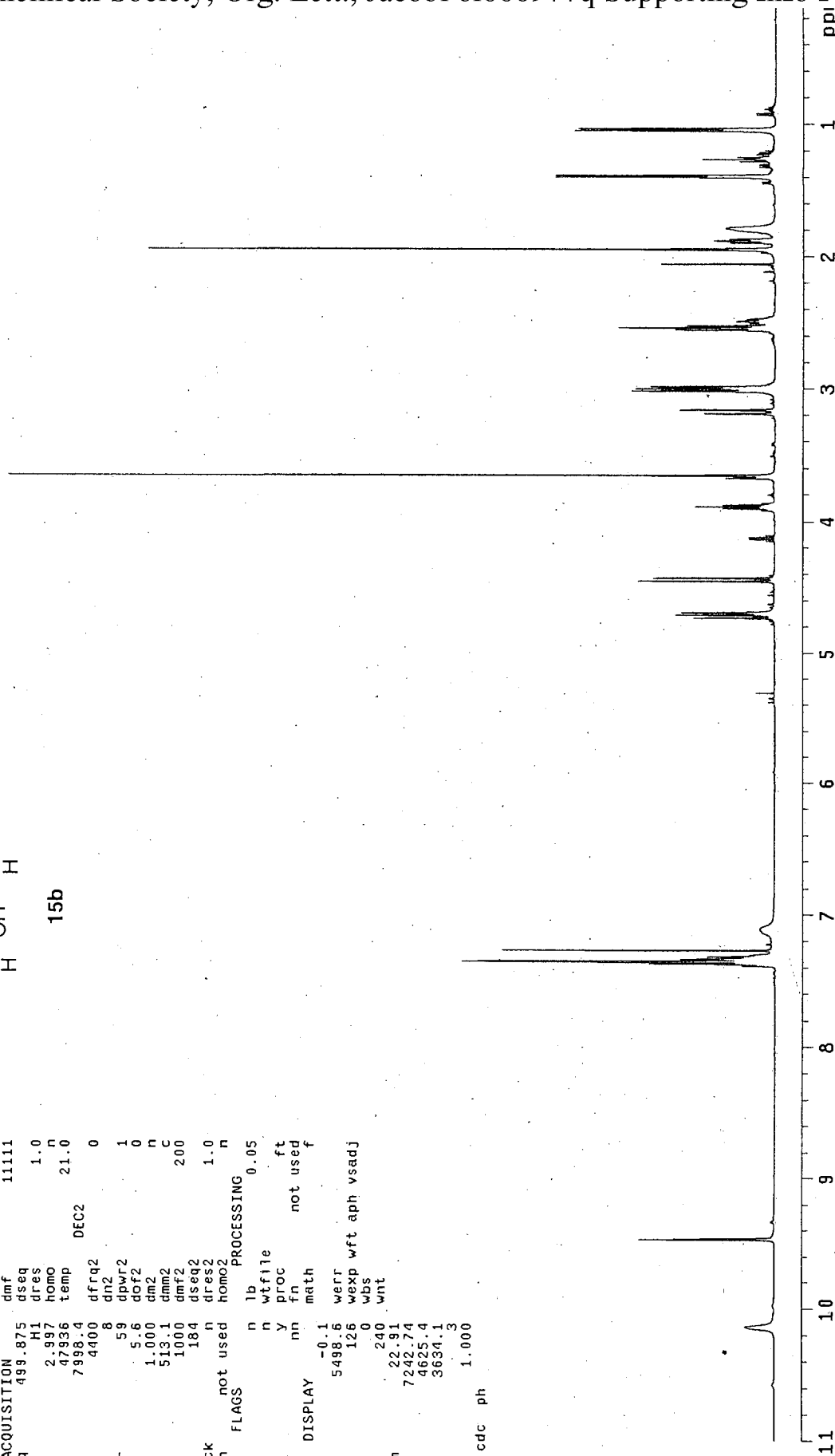
exp2 s2pu1

```

SAMPLE          DEC. & VT
date Nov 28 00  dfrq 499.875
solvent CDC13   dn H1
file /data1/guest/~ dpwr 38
DPS00/DP-III-85.1H~ dof 0
.2R-ABhydroxylacta~ dmm nnn
m.lower         c
ACQUISITION    11111
sfrq 499.875   dseq
tn H1         dres 1.0
at 2.997      homo
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 1000      dmrf2 200
ct 184       dseq2
alock n      dres2 1.0
gain not used homo2 n
PROCESSING
il n lb      0.05
in n wf1le
dp y proc   ft
hs nn fn    not used f
DISPLAY
sp -0.1
wp 5498.6   werr
vs 126      wexp wft aph vsadj
sc 0        wbs
wc 240      wnt
hzmm 22.91
ls 7242.74
rfl 4625.4
rff 3634.1
th 3
ins 1.000
nm cdc ph
    
```



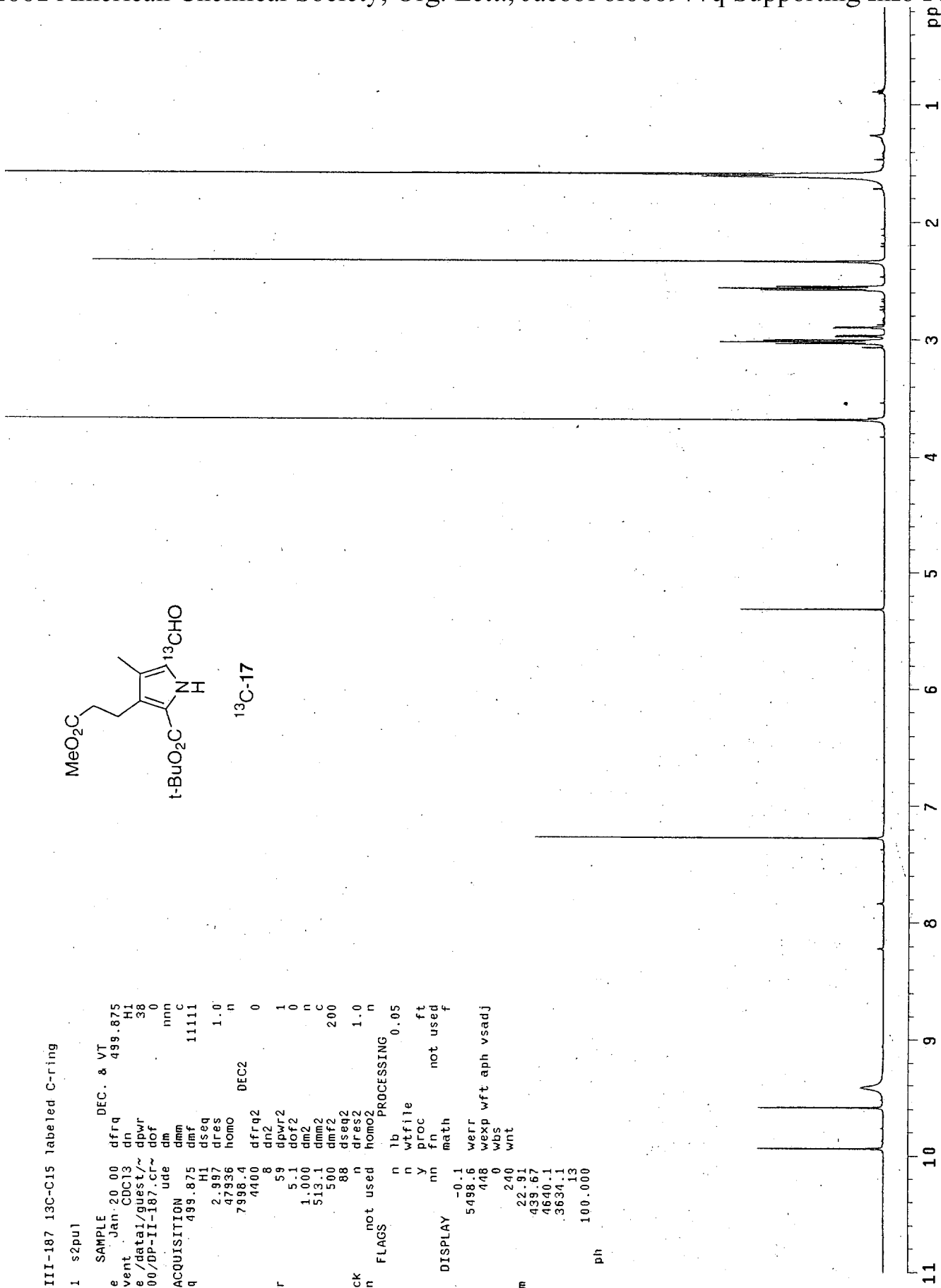
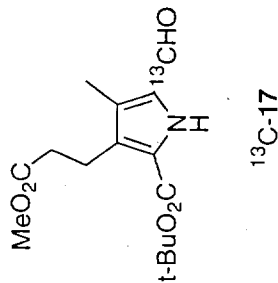
15b



OP-III-187 13C-C15 labeled C-ring

exp1 s2pul

SAMPLE	DEC. & VT
date Jan-20 00	dfrq 499.875
solvent CDC13	dn H1
file /data1/quest/~	dpwr 38
DP500/DP-II-187.cr~	dof 0
	dm nnn
	ude 111111
ACQUISITION	dmn c
sfrq 499.875	dfrq2 0
tn H1	dn2 8
at 2.997	dseq 1
np 47936	dres 0
sw 7998.4	homo n
	DEC2
bs 4400	dfrq2 0
tpwr 8	dn2 8
pw 59	dpwr2 1
d1 1.000	dof2 0
tof 513.1	dm2 n
nt 500	dmm2 c
ct 88	dmf2 200
alock n	dseq2 1.0
gain not used	dres2 n
	homo2 n
FLAGS	PROCESSING
ll n	lb 0.05
in n	wtfile
dp y	proc ft
hs nn	fn not used
	math f
DISPLAY	
sp -0.1	werr
wp 5498.6	wexp wft aph vsadj
vs 448	wbs
sc 0	wnt
wc 240	
hzmm 22.91	
is 439.67	
rfl 4640.1	
rff 3634.1	
th 100.000	
ins 13	
nm ph	

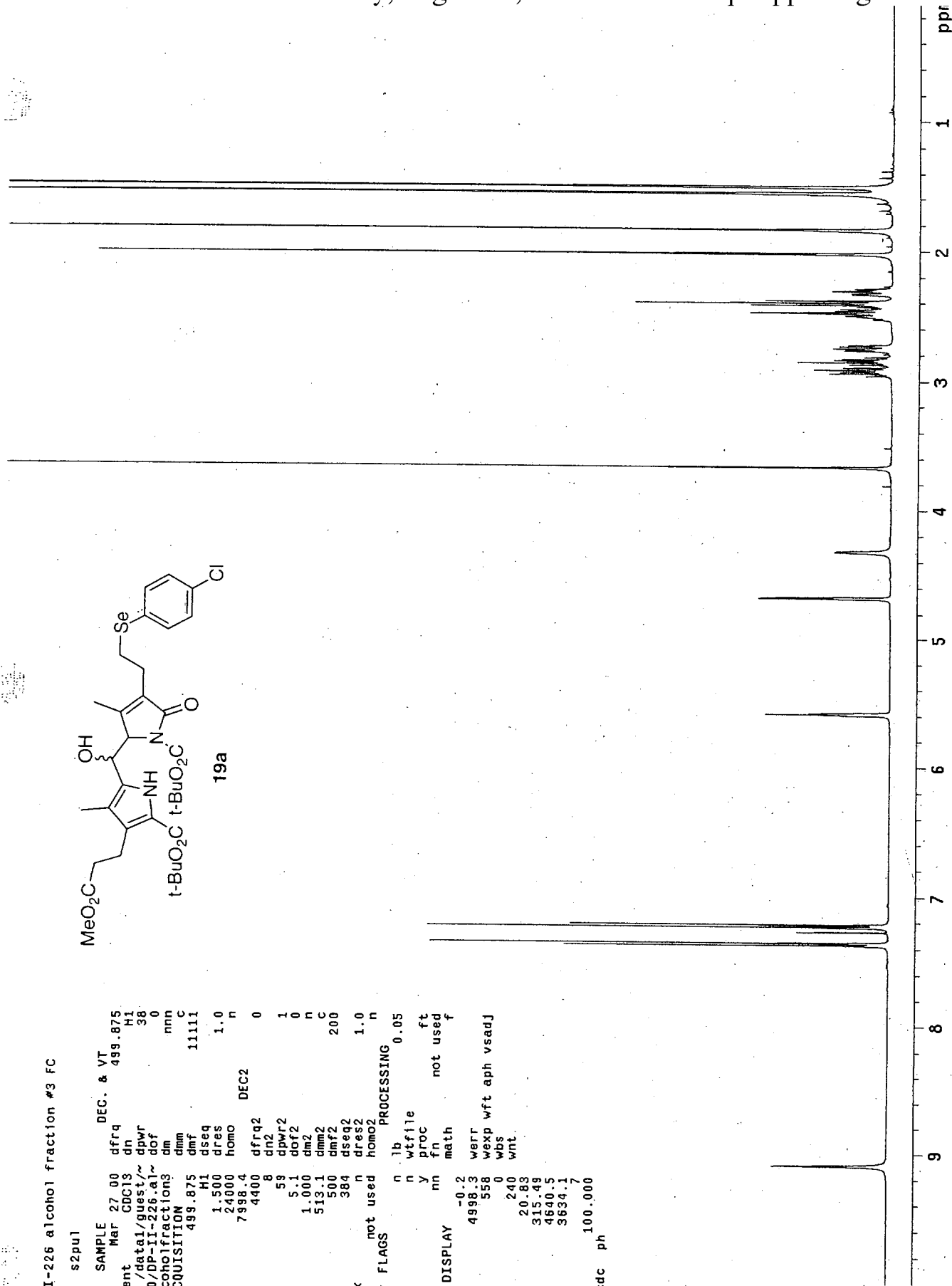
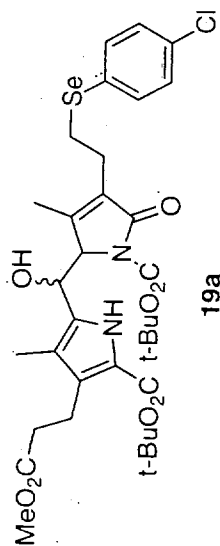


DP-II-226 alcohol fraction #3 FC

exp1 s2pu1

```

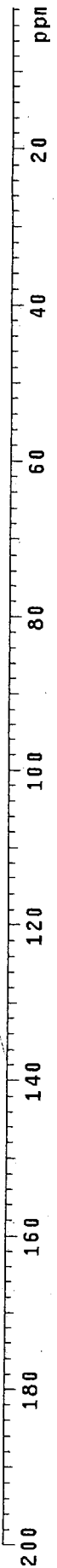
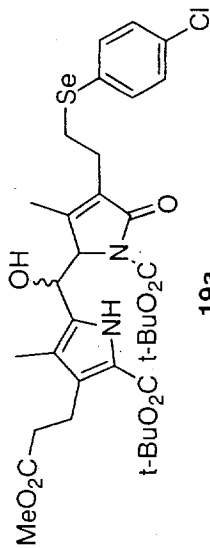
SAMPLE Mar 27 00 dfrq DEC. & VT 499.875
solvent Mar CDC13 dn H1 38
file /data1/guest/~dpwr DP500/DP-II-226.al~ dof 0
coho1fraction3 dm mnn C
ACQUISITION dmm 11111
sfrq 499.875 dmf 0
tn H1 dseq 1
at 1.500 dres n 1.0
np 24000 homo DEC2 0
sw 7998.4 dfrq2 0
fb 4400 dn2 1
bs 8 dpwr2 1
tpwr 59 dpwr2 0
pw 5.1 dor2 0
di 1.000 dmm2 n
tof 513.1 dmm2 C
nt 500 dmf2 200
ct 384 dseq2 1.0
alock n homo2 n
gain not used PROCESSING 0.05
FLAG n lb n wtfile ft
in n y proc fn not used f
hs nn math
DISPLAY -0.2 warr
sp 4998.3 wexp wft aph vsadj
vs 558 wbs
sc 0 wnt
wc 240
hzmm 20.88
ls 315.49
rfl 4640.5
rff 3634.1
th ins
nm cdc ph 100.000
    
```



DP-II-226 C13 alcohol fraction #3

exp1 s2pu1

date	SAMPLE	Mar 27 00	DEC. & VT	499.875
solvent	file	CDCl3	dn	H1
DP50/DP-II-226.C1~	3	alcoholfraction3	dof	504.0
ACQUISITION	dmm	11111	nyy	w
sfrq	125.708	dmf	11111	w
tn	C13	dseq		
at	1.500	dres	1.0	n
np	79232	homo		
sw	26402.6	DEC2		
fb	14600	dfrq2	0	
bs	32	dn2		
tpwr	60	dpwr2	1	
pw	10.2	dof2	0	
d1	1.500	dm2	n	
d2	0.300	dmm2	c	
tof	1202.3	dmf2	10000	
nt	10000	dseq2		
ct	5024	dres2	1.0	n
alock	not used	homo2	n	
gain	not used	lb	PROCESSING	
ll	FLAGS	lb	0.50	
in	n	wtfile		
dp	n	proc	ft	
hs	y	fn	not used	
	nn	math	f	
SD	DISPLAY	-0.1	werr	
wp	25140.4	wexp	wft	
vs	1292	wbs		
sc	0	wnt		
wc	240			
hzm	104.75			
ls	5526.43			
rf1	9775.4			
rff	9708.0			
th	14			
ins	1.000			
at	ph			

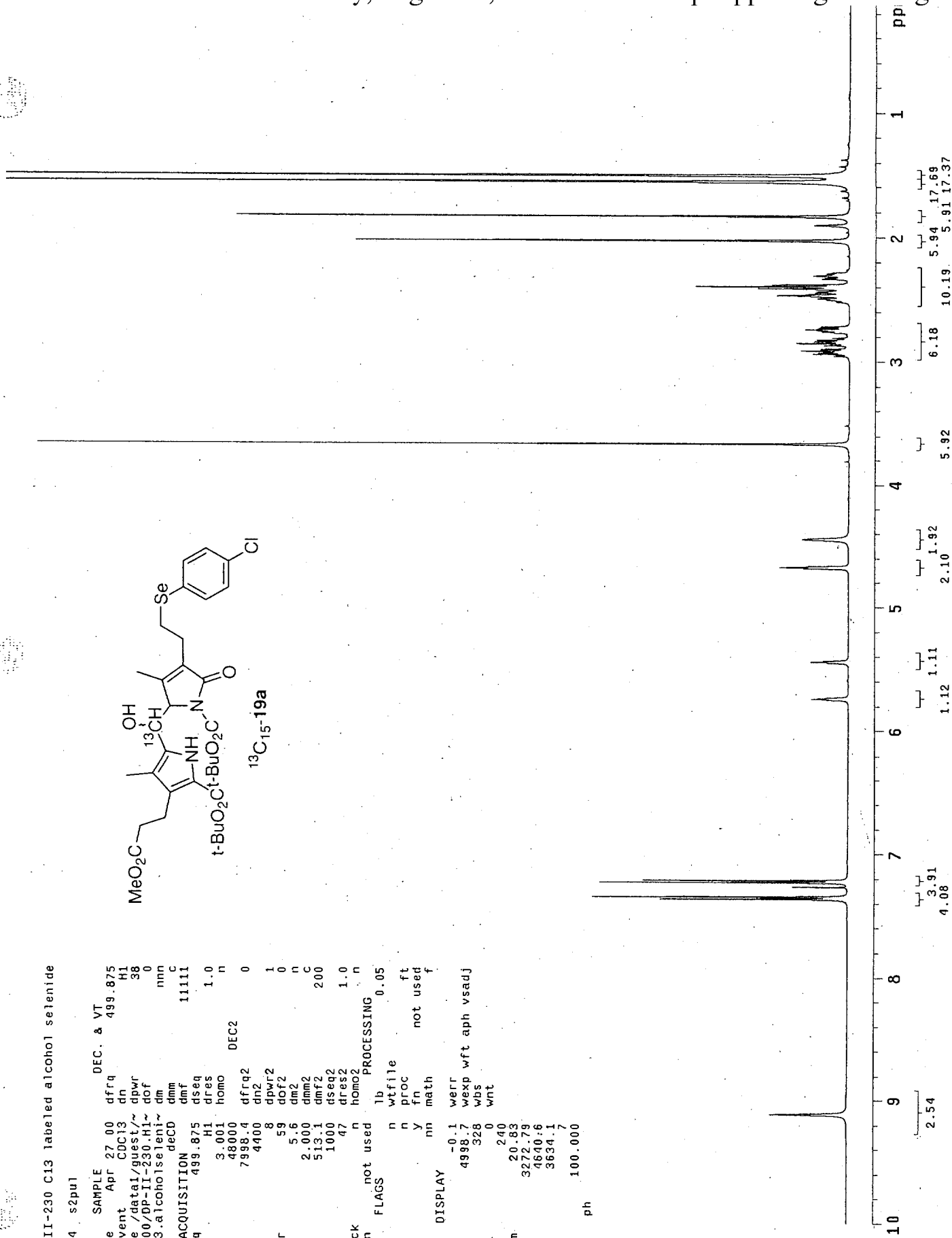
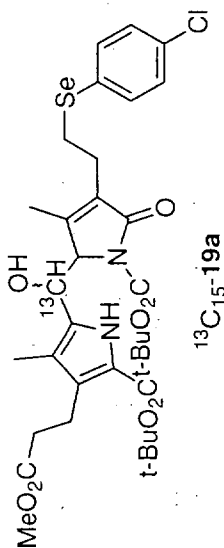


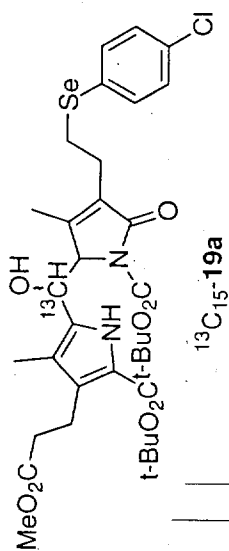
DP-II-230 C13 labeled alcohol selenide

exp4 s2pul

```

SAMPLE      DEC. & VT
date        Apr 27 00 dfrq 499.875
solvent     CDCl3 dn H1
file        /data1/guest/~ dpwr 38
DP500/DP-II-230.H1~ dof 0
.C13-alcohol selenide~ dm nnn
deCD        deCD 111111 C
ACQUISITION
sfrq        499.875 dseq
tn          3.001 H1 dres 1.0
at          48000 homo n
np          7998.4 dfrq2 0
sw          4400 dn2
bs          8 dpwr2 1
tpwr        59 dof2 0
pw          5.6 dm2 n
d1          2.000 dnm2 C
tof         513.1 dmf2 200
nt          1000 dseq2
ct          47 dres2 1.0
alock       n homo2 n
gain        not used lb PROCESSING 0.05
            FLAGS
il          n wfile
in          n proc ft
dp          y fn not used
hs          nm math f
DISPLAY    -0.1 werr
wp          4998.7 wexp wft aph vsadj
vs          328 wbs
sc          0 wnt
wc          240
h2mm       20.83
ls         3272.78
rf1        4640.6
rfp        3634.1
th         100.000
fns
nm
    
```

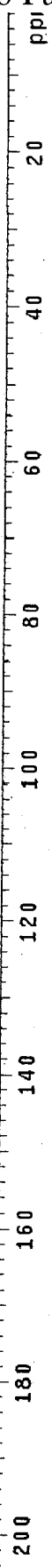




DP-II-230 C13 labeled CD alcohol selenid

```

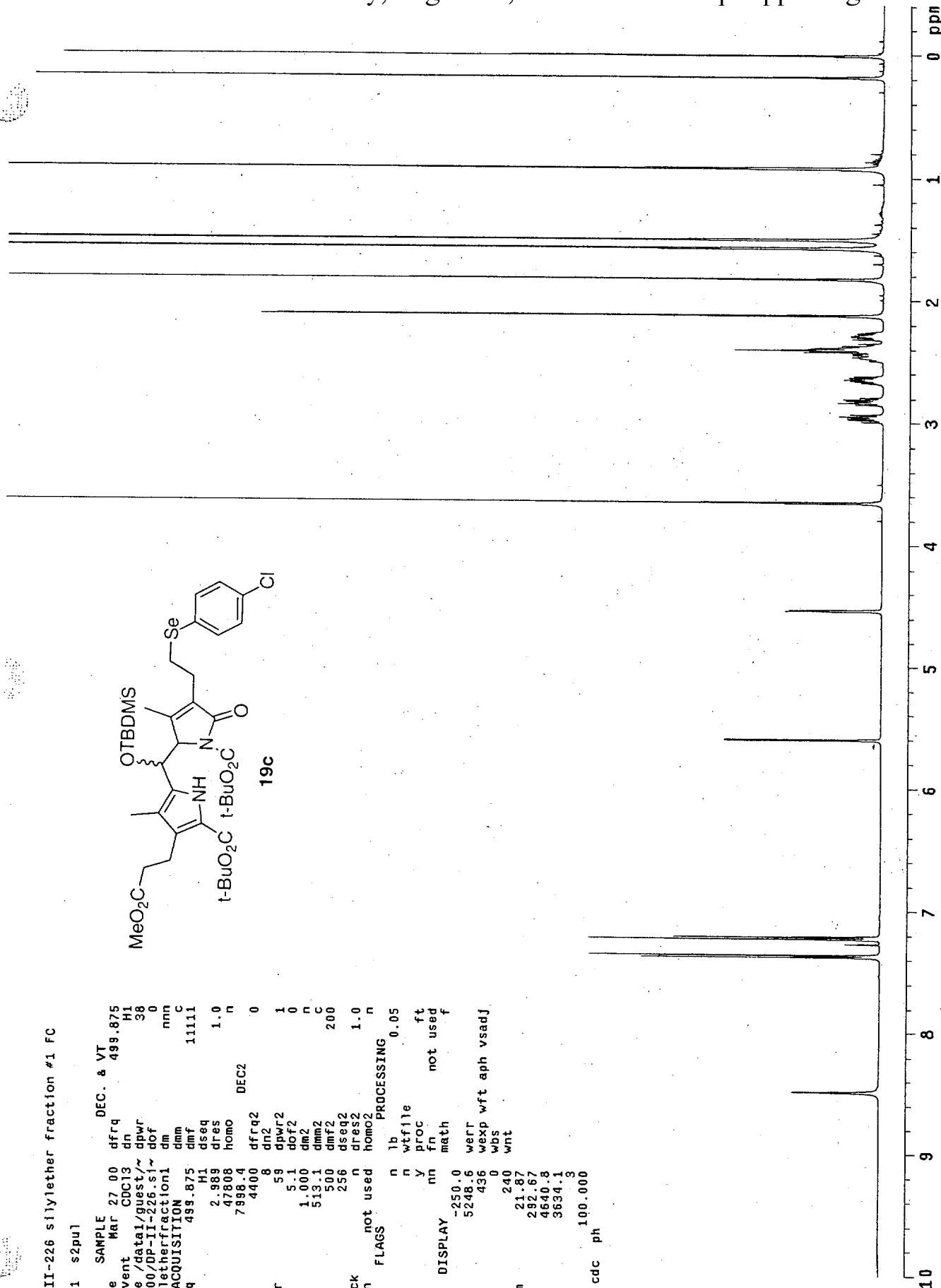
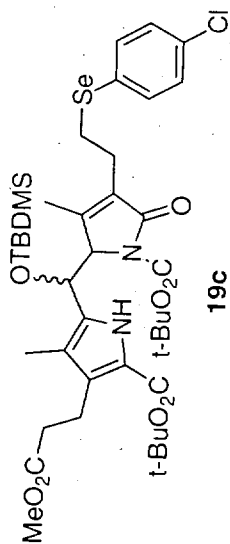
exp1 $2ru1
SAMPLE 27.00 dfrq DEC. & VT
date Apr CDC13 dn 499.875
solvent H1
file exp 41
ACQUISITION dof 0
sfrq 125.706 dm rvy w
tr C13 dmm 14815
at 2.424 dmf dseq
np 128000 dres 1.0 n
sw 26402.6 homo
fb 14600
bs 8
tpwr 60 dfrq2 0
pw 10.2 dn2
d1 1.500 dpwr2 1
d2 0.300 dot2 0
cof 1202.3 dm2 n
nt 100000 dmm2 C
ct 9152 dmf2 10000
alock n dseq2
gain not used dres2 1.0
FLAGS n
ii n lb n
in n y wfile
dp n y wfile
hs nn proc ft
DISPLAY -67.8 math not used f
sp 26402.6 werr
vs 2606 wexp
sc 0 wps
vc 240 wnt
hzmm 110.01 wft dscale
ls 500.00
rfl 9775.8
rff 9708.0
th 4
ins 1.000
nm sdc ph
    
```



DP-II-226 silylether fraction #1 FC

exp1 s2pu1

date	Mar 27 00	dfrq	DEC. & VT	499.875
solvent	CDC13	dn	H1	38
file	/data1/guest/~dpwr	dpwr		0
DP500/DP-II-226.s1~	dof	dm	nmn	11111
lyletherfraction1	dm	dmm	C	
ACQUISITION	sfrq	dmf		
tn	499.875	dseq		
at	2.989	dres	1.0	n
np	47808	homo	DEC2	
sw	7998.4	dfrq2	0	
fb	4400	dn2		
bs	8	dpwr2	1	
tpwr	59	dof2	0	n
pw	5.1	dm2		C
di	1.000	dmm2		200
df	513.1	dmf2		
nt	500	dseq2		1.0
ct	256	dres2		n
alock	not used	homo2		
gain	not used	PROCESSING		
ll	11	lb	n	0.05
in	n	wtfile	n	
dp	y	proc	ft	
hs	nm	fn	not used	f
	math			
sp	-250.0	werr		
wp	5248.6	wexp	wft	aph vsadj
vs	436	wbs	0	
sc	0	wnt		
wc	240			
hzm	21.87			
is	292.67			
rfl	4640.8			
rff	3634.1			
th	3634.3			
ins	100.000			
nm	cdc	ph		

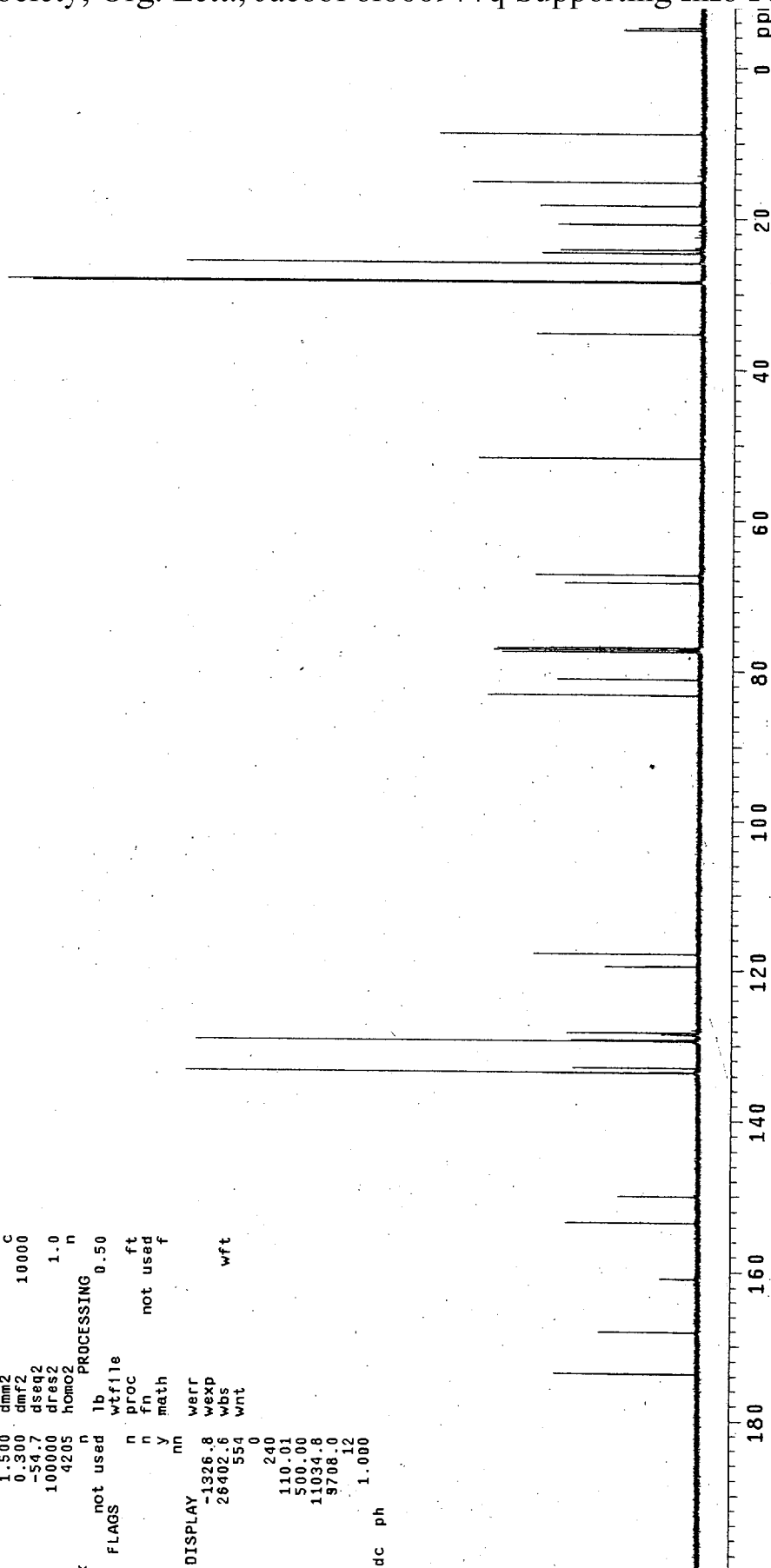
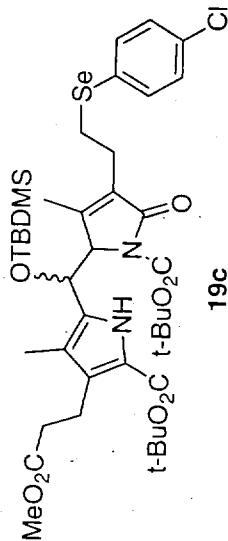


DP-II-226 C13 silylether frac #1

exp1 s2pul

```

SAMPLE      DEC. & VT
date Mar 27 00 dfrq
solvent CDC13 dn
file /data1/guest/~ dpwr
DP500/DP-II-226.C1~ dof
3.silyletherfracj~ dm
On1 dmm dmf dnm w
111111
ACQUISITION
sfrq 125.705 dseq
tn C13 dres 1.0
at 1.500 homo DEC2
sw 26402.6 dfrq2 0
bs 14600 dn2
tpwr 16 dpwr2 1
pw 60 dof2 0
d1 10.2 dnm2 n
d2 1.500 dmf2 C
tof 0.300 dmf2 10000
nt -54.7 dseq2
ct 100000 dres2 1.0
a lock n
gain not used lb wtfile 0.50
fl proc n ft
in n n not used
dp n n
hs y math f
nn nn werr
DISPLAY -1326.8 wexp
wp 26402.6 wbs wft
vs 554 wnt
sc 0
wc 240
hzmm 110.01
fs 500.00
rfl 11034.6
rff 9708.0
th 12
fns 1.000
a1 cdc ph
    
```

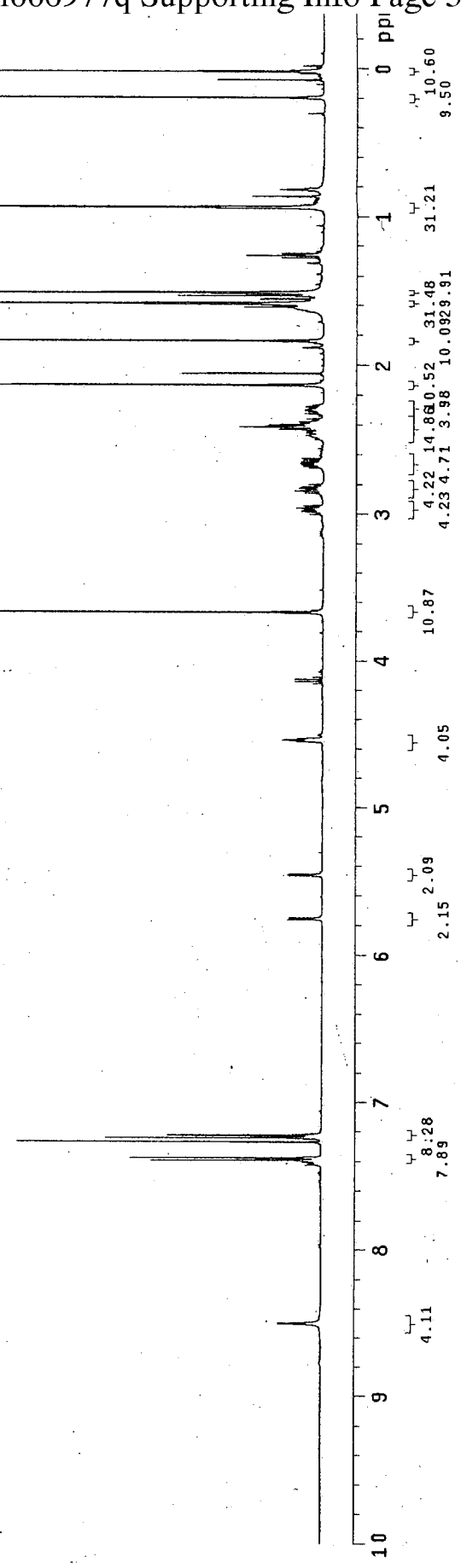
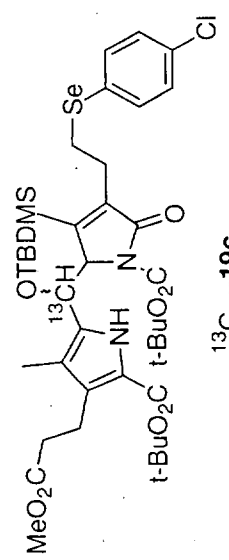


DP-II-230 C13 labeled silyl ether

exp1 szpu1

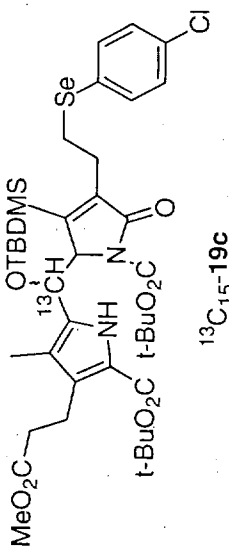
```

SAMPLE          DEC. & VT
date            499.875
solvent         May CDC13
file            /data1/guest/~pbwr
DP500/DP-II-230.HI~ dof
.C13.silyletherfrq~ dm
                  dmm
ACQUISITION    11111
sfrq           499.875
tn             499.875
at             2.987
np             47396
sw             7398.4
fb             4400
bs             8
tpwr          59
pw            5.6
d1            1.000
tof           513.1
nt            500
ct            116
alock         not used
gain          not used
PROCESSING    0.05
il            n
in            n
dp            y
hs            nn
sp            -250.0
wp            5248.6
vs            292
sc            0
wc            240
hzmm         21.87
is            2832.06
rfl          4640.6
rfp          9634.1
th           3634.1
ins          100.000
nm           ph
    
```



Chemical Shift (ppm)
9.50
10.60
31.21
31.48
10.0929.91
3.98
14.86
4.22
4.23
4.71
3.98
10.87
4.05
2.09
2.15
7.89
8.28
4.11

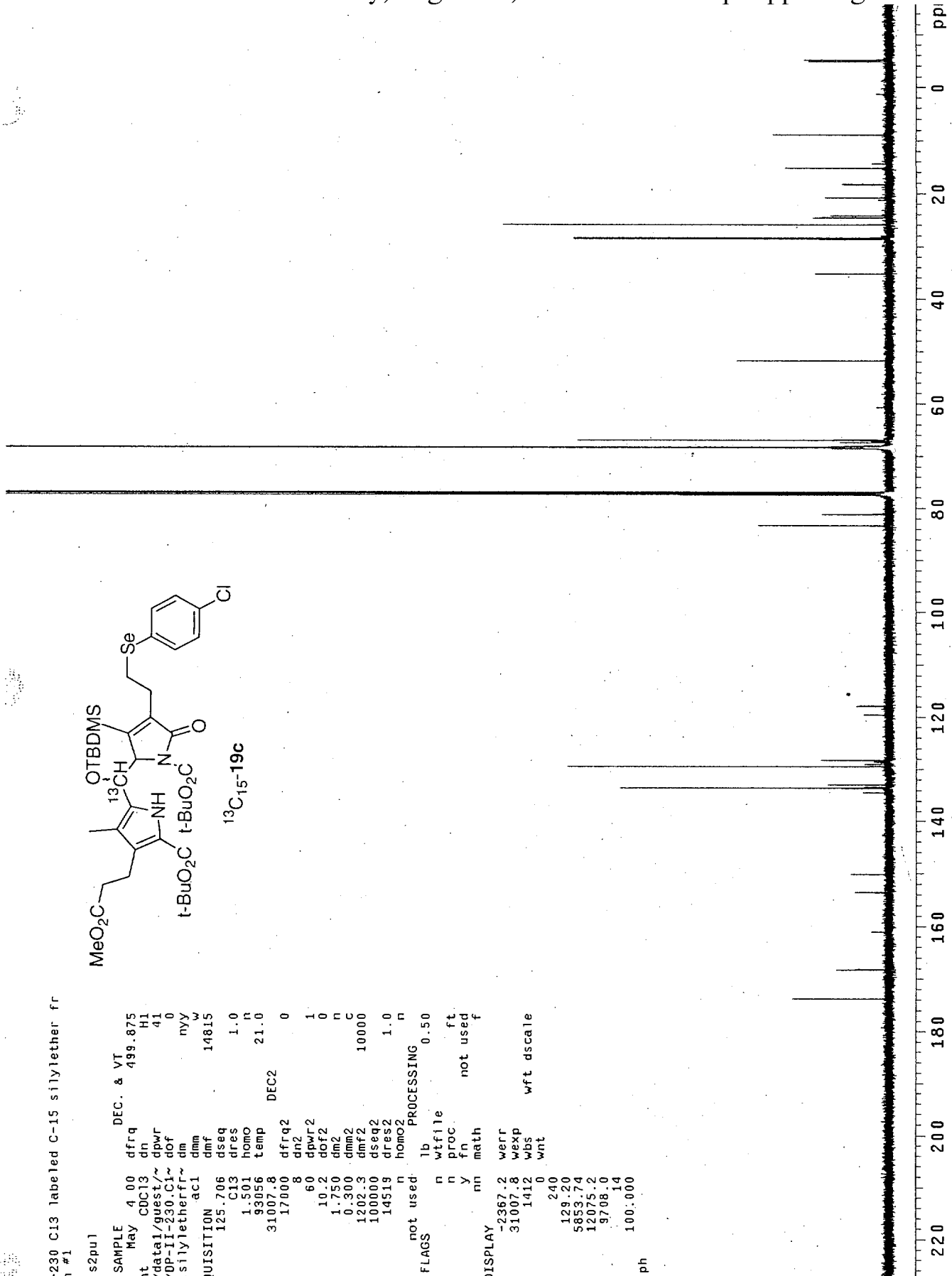
DP-II-230 C13 labeled C-15 silylether fr
action #1



```

exp4 s2pul
SAMPLE May 4 00 dfrq DEC. & VT 499.875
solvent CDC13 dn H1
file /data1/guest/~ dpwr 41
DP500/DP-II-230.C1~ dof 0
3.C13.silyletherfr~ dm nvy
          ac1 w
ACQUISITION dmf 14815
sfrq 125.706 dseq
tn C13 dres 1.0
at 1.501 homo n
np 93056 temp 21.0
sw 31007.8 DEC2
fb 17000 dfrq 0
bs 8 dn2
tpwr 60 dpwr2 1
pw 10.2 dof2 0
d1 1.750 dm2 n
d2 0.300 dmm2 c
tof 1202.3 dmf2 10000
nt 100000 dseq2
ct 14519 dres2 1.0
alock n homo2 n
gain not used PROCESSING 0.50
ll lb wtfile n
in in n
dp dp y n proc. ft.
hs nn math not used f

DISPLAY -2367.2 werr
          31007.8 wexp
          1412 wbs wft dscale
          0 wnt
          240
          hzmm
          129.20
          5853.74
          rfl
          12075.2
          rfp 9708.0
          th 14
          ins 100.000
          nm ph
    
```



DP-II-227 unsubstituted CD selenide

exp1 s2pu1

```

SAMPLE      DEC. & VT
date        Jul 11 00 dfrq 499.875
solvent     CDCl3 dn H1
file        /data1/guest/~ dpuwr 38
DPS00/DP-II-227.a dof 0
ACQUISITION dms nnn
sfrq        499.875 dmm 11111
tn          H1 dmf
at          2.997 dseq 1.0
np          47936 dres
sw          7998.4 homo 21.0
fb          4400 temp
bs          DEC2
tpwr        59 dfrq2 0
pw          5.1 dn2
dl          1.000 dpwr2 1
tof         513.1 dof2 0
nt          500 dm2 n
ct          280 dmm2 c
alock       not used dmf2 200
gain        not used dseq2 1.0
FLAGS      n homo2 n
           n lb wtfile 0.05
           nn proc ft
           n fn not used f
           nn math
           n werr
           n wexp wft aph vsadj
           240 wbs
           560.06 wnt
           4625.4
           3634.7
           100.000
           ph
    
```

