

## Palladium Catalyzed Synthesis of *N*-Vinyl Pyrroles and Indoles

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**General Procedures.** All reactions were performed in oven-dried or flame-dried round bottomed flasks or modified Schlenk (Kjeldahl shape) flasks. The flasks were fitted with rubber septa and reactions were conducted under a positive pressure of argon. Stainless steel syringes or cannulae were used to transfer air- and moisture-sensitive liquids. Flash column chromatography was performed as described by Still et al. using silica gel (60-Å pore size, 32–63 μm, standard grade) or non-activated alumina gel (80–325 mesh, chromatographic grade).<sup>1</sup> Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel or neutral alumina gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light and/or by exposure to an ethanolic phosphomolybdic acid (PMA), an acidic solution of *p*-anisaldehyde (anis), an aqueous solution of ceric ammonium molybdate (CAM), an aqueous solution of potassium permanganate (KMnO<sub>4</sub>) or an ethanolic solution of ninhydrin followed by heating (<1 min) on a hot plate (~250 °C). Organic solutions were concentrated on a rotary evaporators at ~20 Torr (house vacuum) at 25–35 °C, then at ~1 Torr (vacuum pump) unless otherwise indicated.

**Materials.** Commercial reagents and solvents were used as received with the following exceptions: Dichloromethane, diethyl ether, tetrahydrofuran, acetonitrile, and toluene were purified by the method of Grubbs et al. under positive argon pressure,<sup>2</sup> 1,4-dioxane was distilled from sodium hydride. Potassium phosphate was dried at 180 °C under vacuum (~1 torr) for 24 h then stored in a

<sup>1</sup> Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925.

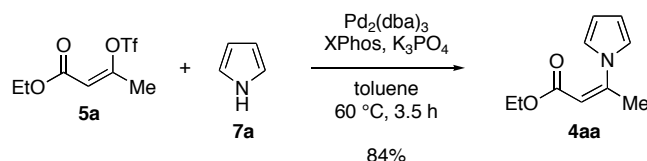
<sup>2</sup> Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.

glove box. Sodium hydride was purchased as a 60% dispersion in oil and then washed four times with hexanes and stored dry in a glove box. The molarity of *n*-butyllithium solutions was determined by titration using diphenylacetic acid as an indicator (average of three determinations).<sup>3</sup> Vinyl triflates used in this study were prepared according to literature procedures as noted below. Pyrrole was distilled from calcium hydride and stored at  $-10\text{ }^{\circ}\text{C}$  in the dark. Commercially available azaheterocycles and XPhos were purchased and used as received.

**Instrumentation.** Proton nuclear magnetic resonance ( $^1\text{H}$  NMR) spectra were recorded on a 500 MHz spectrometer. Chemical shifts are recorded in parts per million from internal tetramethylsilane on the  $\delta$  scale and are referenced from the residual protium in the NMR solvent ( $\text{CHCl}_3$ :  $\delta$  7.27,  $\text{C}_6\text{H}_6$ :  $\delta$  7.16). Data is reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant(s) in Hertz, integration, assignment]. Carbon-13 nuclear magnetic resonance spectra were recorded on a 500 MHz spectrometer and are recorded in parts per million from internal tetramethylsilane on the  $\delta$  scale and are referenced from the carbon resonances of the solvent ( $\text{CDCl}_3$ :  $\delta$  77.2, benzene- $d_6$ :  $\delta$  128.0). Data is reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant(s) in Hertz, assignment]. Infrared data were on a FT-IR and are reported as follows: [frequency of absorption ( $\text{cm}^{-1}$ ), intensity of absorption (s = strong, m = medium, w = weak, br = broad), assignment]. Gas chromatography was performed on a HP-5 5% Phenyl Methyl Siloxane column.

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<sup>3</sup> Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 1879–1880.



**Z-3-Pyrrol-1-yl-but-2-enoic acid ethyl ester (4aa, Table 1, entry 1):**

Toluene (1.90 mL) was added to an argon-purged sample of Pd<sub>2</sub>(dba)<sub>3</sub> (17.5 mg, 19.1 μmol, 0.05 equiv), XPhos (18.2 mg, 38.1 μmol, 0.10 equiv), and rigorously anhydrous K<sub>3</sub>PO<sub>4</sub> (113 mg, 534 μmol, 1.40 equiv) in a flame-dried flask. Pyrrole (**7a**, 40.0 μL, 572 μmol, 1.50 equiv) was then added and the deep red mixture was heated to 60 °C. After 30 min, triflate **5a**<sup>4</sup> (100 mg, 381 μmol, 1 equiv) was added via syringe, producing a color change to forest green within approximately 10 min then to brown within an additional 1h. After 3.5h TLC analysis indicated that the reaction was complete, whereupon the mixture was allowed to cool to 23 °C, was diluted with EtOAc (10 mL), and was vacuum filtered through a plug of celite (diam. 2.5 cm, ht. 2.5 cm). The celite-plug and flask were rinsed with an additional 15-mL portion of EtOAc, and the combined organic filtrates were washed with water (7.5 mL) and brine (7.5 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure to give a deep brown residue. Purification of the crude material by flash column chromatography (silica gel: diam. 3.0 cm, ht. 22 cm; 60% EtOAc–hexanes) afforded the vinyl pyrrole **4aa**<sup>5</sup> (57.1 mg, 84%) as a yellow oil.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 20 °C): 6.90 (app t, *J* = 2.2 Hz, 2H), 6.23 (app-t, *J* = 2.2 Hz, 2H), 5.52 (q, *J* = 1.2 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.26 (d, *J* = 1.3 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H).

<sup>13</sup>C NMR (125.7 MHz, CDCl<sub>3</sub>, 20 °C): 165.2, 147.7, 121.4, 110.1, 107.6, 60.5, 24.5, 14.4.

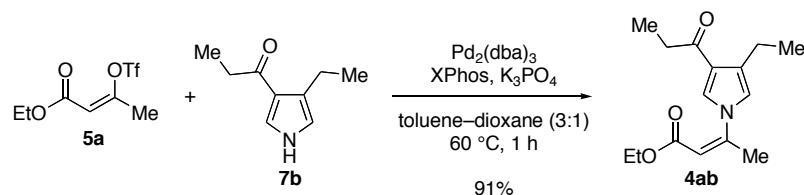
FTIR (neat): 2982 (w, C–H), 1718 (s, C=O), 1641 (s, C=C), 1481, 1182, 1051.

HRMS–ESI (*m/z*): calcd for C<sub>10</sub>H<sub>13</sub>NO<sub>2</sub>Na [M + Na]<sup>+</sup>: 202.0838, found: 202.0839

TLC (7.5% EtOAc–hexanes), *R*<sub>f</sub>: 0.15 (UV, anis)

<sup>4</sup> For the general procedure used to prepare the vinyl triflate **5a**, see: Kim, H.-O.; Ogbu, C. O.; Nelson, S.; Kahn, M. *Synlett* **1998**, 1059–1060.

<sup>5</sup> For an alternate synthesis of **4aa**, see: Rainka, M. P.; Aye, Y.; Buchwald, S. L. *Proc. Nat. Acad. Sci., USA* **2004**, *101*, 5821–5823.



**Z-3-(3-Ethyl-4-propionyl-pyrrol-1-yl)-but-2-enoic acid ethyl ester (4ab, Table 1, entry 3):**

A mixture of toluene–dioxane (3:1, 1.90 mL) was added to an argon–purged sample of acyl pyrrole **7b**<sup>6</sup> (86.5 mg, 572  $\mu\text{mol}$ , 1.50 equiv),  $\text{Pd}_2(\text{dba})_3$  (17.5 mg, 19.1  $\mu\text{mol}$ , 0.05 equiv), XPhos (18.2 mg, 38.1  $\mu\text{mol}$ , 0.10 equiv), and rigorously anhydrous  $\text{K}_3\text{PO}_4$  (113 mg, 534  $\mu\text{mol}$ , 1.40 equiv) in a flame-dried flask and the resulting deep red mixture was heated to 60 °C. After 30 min, triflate **5a** (100 mg, 381  $\mu\text{mol}$ , 1 equiv) was added via syringe, producing a color change to brown within approximately 1 min. After 1h, GC analysis indicated that the reaction was complete, whereupon the mixture was allowed to cool to 23 °C, was diluted with EtOAc (10 mL), and was vacuum filtered through a plug of celite (diam. 2.5 cm, ht. 2.5 cm). The celite-plug and flask were rinsed with a 15-mL portion of EtOAc, and the combined organic filtrates were washed with water (7.5 mL) and brine (7.5 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure to yield a deep brown residue. Purification of the crude material by flash column chromatography (silica gel: diam. 3.0 cm, ht. 18 cm, 20% EtOAc–hexanes) gave the vinyl pyrrole **4ab** (91.2 mg, 91%) as a yellow oil.

<sup>1</sup>H NMR (500 MHz,  $\text{CDCl}_3$ , 20 °C): 7.53 (d,  $J = 2.3$  Hz, 1H), 6.60 (dt,  $J = 2.3, 1.2$  Hz, 1H), 5.64 (q,  $J = 1.2$  Hz, 1H), 4.13 (q,  $J = 7.1$  Hz, 2H), 2.78 (qd,  $J = 7.3, 1.2$  Hz, 2H), 2.75 (q,  $J = 7.3$ , 2H), 2.29 (d,  $J = 1.2$  Hz, 3H), 1.22 (t,  $J = 7.1$  Hz, 3H), 1.19 (t,  $J = 7.3$  Hz, 3H), 1.17 (t,  $J = 7.3$  Hz, 3H).

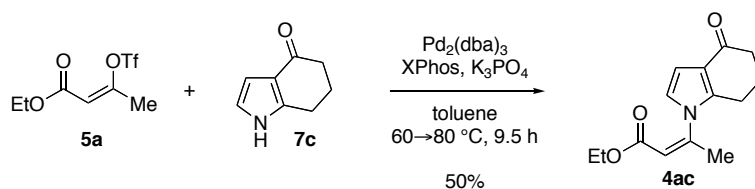
<sup>13</sup>C NMR (125.7 MHz,  $\text{CDCl}_3$ , 20 °C): 197.3, 164.7, 146.9, 129.3, 128.0, 123.8, 119.4, 109.8, 60.7, 33.2, 24.3, 20.2, 14.4, 14.3, 8.8.

FTIR (neat): 2971 (m, C–H), 1705 (m, C=O), 1662 (s, C=O), 1518, 1189, 1047.

HRMS–ESI ( $m/z$ ): calcd for  $\text{C}_{15}\text{H}_{21}\text{NO}_3\text{Na}$  [ $\text{M} + \text{Na}$ ]<sup>+</sup>: 286.1414, found: 286.1417

TLC (40% EtOAc–hexanes), *R<sub>f</sub>*: 0.42 (UV, anis)

<sup>6</sup> For the synthesis of pyrroles using tosylmethylisocyanide, see: (a) van Leusen, A. M.; Siderius, H.; Hoogenboom, B. E.; van Leusen, D. *Tetrahedron Lett.* **1972**, 52, 5337–5340 and (b) Chamberlin, K. S.; LeGoff, E. *Heterocycles* **1979**, 12, 1567–1570.



**Z-3-(4-Oxo-4,5,6,7-tetrahydro-indol-1-yl)-but-2-enoic acid ethyl ester (4ac, Table 1, entry 7):**

A mixture of toluene–dioxane (3:1, 1.90 mL) was added to an argon–purged sample of 1,5,6,7-tetrahydro-4*H*-indol-4-one (**7c**, 77.3 mg, 572  $\mu\text{mol}$ , 1.50 equiv),  $\text{Pd}_2(\text{dba})_3$  (17.5 mg, 19.1  $\mu\text{mol}$ , 0.05 equiv), XPhos (18.2 mg, 38.1  $\mu\text{mol}$ , 0.10 equiv), and rigorously anhydrous  $\text{K}_3\text{PO}_4$  (113 mg, 534  $\mu\text{mol}$ , 1.40 equiv) in a flame-dried flask and the resulting deep red mixture was heated to 60  $^\circ\text{C}$ . After 30 min, triflate **5a** (100 mg, 381  $\mu\text{mol}$ , 1 equiv) was added via syringe, producing a color change to forest green within approximately 1 min. After 2.5 h, the temperature was increased to 80  $^\circ\text{C}$  and the green–brown mixture stirred for 7h, at which point GC analysis indicated that the reaction was complete. The mixture was then allowed to cool to 23  $^\circ\text{C}$ , was diluted with EtOAc (10 mL), and was vacuum filtered through a plug of celite (diam. 2.5 cm, ht. 2.5 cm). The celite-plug and flask were rinsed with an additional 15-mL portion of EtOAc, and the combined organic filtrates were washed with water (7.5 mL) and brine (7.5 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure to give a deep brown residue. Purification of the crude material by flash column chromatography (silica gel: diam. 3.0 cm, ht. 22 cm; 60% EtOAc–hexanes) afforded the vinyl indolone **4ac** (47.3 mg, 50%) as a white solid.

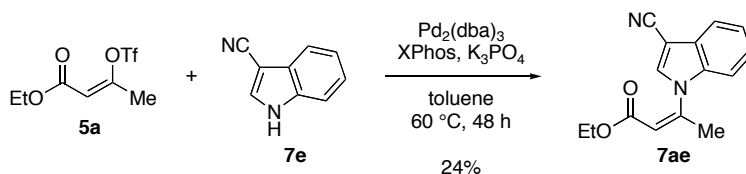
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 20 $^\circ\text{C}$ ): 6.65 (d,  $J = 1.2$  Hz, 1H), 6.55 (d,  $J = 1.2$  Hz, 1H), 6.01 (q,  $J = 1.2$  Hz, 1H), 4.04 (q,  $J = 7.1$  Hz, 2H), 2.63 (t,  $J = 6.2$  Hz, 2H), 2.48 (app t,  $J = 6.2$  Hz, 2H), 2.21 (d,  $J = 1.3$  Hz, 3H), 2.12 (pentet,  $J = 6.2$  Hz, 2H), 1.12 (t,  $J = 7.1$  Hz, 3H).

$^{13}\text{C}$  NMR (125.7 MHz,  $\text{CDCl}_3$ , 20 $^\circ\text{C}$ ): 194.7, 163.7, 147.0, 143.9, 121.6, 121.2, 118.1, 106.9, 60.9, 38.1, 24.9, 24.1, 22.4, 14.2.

FTIR (neat): 2944 (m, C–H), 1722 (s, C=O), 1659 (s, C=O), 1464, 1048.

HRMS–ESI ( $m/z$ ): calcd for  $\text{C}_{14}\text{H}_{17}\text{NO}_3\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$ : 270.1101, found: 270.1102

TLC (60% EtOAc–hexanes),  $R_f$ : 0.29 (UV, anis)



**Z-3-(3-Cyano-indol-1-yl)-but-2-enoic acid ethyl ester (7ae, Table 1, entry 8):**

Toluene (1.90 mL) was added to an argon-purged sample of 3-cyanoindole (**7e**, 81.3 mg, 572  $\mu\text{mol}$ , 1.50 equiv),  $\text{Pd}_2(\text{dba})_3$  (17.5 mg, 19.1  $\mu\text{mol}$ , 0.05 equiv), XPhos (18.2 mg, 38.1  $\mu\text{mol}$ , 0.10 equiv), and rigorously anhydrous  $\text{K}_3\text{PO}_4$  (113 mg, 534  $\mu\text{mol}$ , 1.40 equiv) in a flame-dried flask and the resulting deep red mixture was heated to  $60\text{ }^\circ\text{C}$ . After 30 min, triflate **5a** (100 mg, 381  $\mu\text{mol}$ , 1 equiv) was added via syringe, producing a color change to olive green within approximately 3 min. After 48 h, GC analysis indicated that the reaction was no longer proceeding at an appreciable rate. The mixture was then allowed to cool to  $23\text{ }^\circ\text{C}$ , was diluted with EtOAc (10 mL), and was vacuum filtered through a plug of celite (diam. 2.5 cm, ht. 2.5 cm). The celite-plug and flask were rinsed with an additional 15-mL portion of EtOAc and the combined organic filtrates were washed with water (7.5 mL) and brine (7.5 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure to an orange residue. Analysis of the crude product mixture by  $^1\text{H}$  NMR revealed the presence of unreacted starting triflate **5a**, product **7ae**, and ethyl but-2-ynoate (**5a:7ae:9a** = 30:17:5). Purification of the crude material by flash column chromatography (silica gel: diam. 3.0 cm, ht. 22 cm; 20% EtOAc–hexanes) provided the vinyl indole **7ae** (23.0 mg, 24%) as an off-white solid.

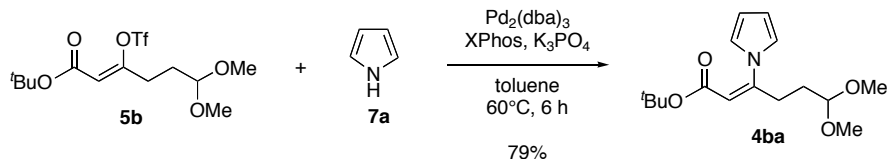
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ,  $20\text{ }^\circ\text{C}$ ): 7.78 (dd,  $J = 6.6, 1.5\text{ Hz}$ , 1H), 7.63 (s, 1H), 7.29–7.36 (m, 3H), 6.15 (q,  $J = 1.2\text{ Hz}$ , 1H), 3.90 (q,  $J = 7.1\text{ Hz}$ , 2H), 2.36 (d,  $J = 1.2\text{ Hz}$ , 3H), 0.90 (t,  $J = 7.1\text{ Hz}$ , 3H).

$^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ ,  $20\text{ }^\circ\text{C}$ ): 163.9, 146.1, 135.6, 134.6, 129.0, 128.1, 125.2, 123.4, 120.7, 118.8, 116.0, 112.1, 61.4, 24.5, 14.4.

FTIR (neat): 2983 (w, C–H), 2222 (s, C $\equiv$ N), 1720 (s, C=O), 1660, 1535, 1217.

HRMS–ESI ( $m/z$ ): calcd for  $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_2\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$ : 277.0947, found: 277.0950

TLC (35% EtOAc–hexanes),  $R_f$ : 0.33 (UV, CAM)



**Z-3-(3-Ethyl-4-propionyl-pyrrol-1-yl)-but-2-enoic acid ethyl ester (4ba, equation 2):**

Toluene (1.90 mL) was added to an argon-purged sample of Pd<sub>2</sub>(dba)<sub>3</sub> (17.5 mg, 19.1 μmol, 0.05 equiv), XPhos (18.2 mg, 38.1 μmol, 0.05 equiv), and rigorously anhydrous K<sub>3</sub>PO<sub>4</sub> (113 mg, 534 μmol, 1.40 equiv) in a flame-dried flask. Pyrrole (**7a**, 40.0 μL, 572 μmol, 1.50 equiv) was then added via syringe and the deep red mixture was heated to 60 °C. After 30 min, triflate **5b**<sup>7</sup> (100 mg, 381 μmol, 1 equiv) was added via syringe, producing a color change to brown within approximately 10 min. After 6h, GC analysis indicated that the reaction was complete, whereupon the mixture was allowed to cool to 23 °C, was diluted with EtOAc (10 mL), and was vacuum filtered through a plug of celite (diam. 2.5 cm, ht. 2.5 cm). The celite-plug and flask were rinsed with a 15-mL portion of EtOAc, and the combined organic filtrates were washed with water (7.5 mL) and brine (7.5 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure to yield a deep brown residue. Purification of the crude material by flash column chromatography (silica gel: diam. 2.0 cm, ht. 17 cm, 5% EtOAc-CH<sub>2</sub>Cl<sub>2</sub>) gave the vinyl pyrrole **4ba** (89.1 mg, 79%) as a yellow oil.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 20 °C): 6.73 (app t, *J* = 2.2 Hz, 2H), 6.22 (app t, *J* = 2.2 Hz, 2H), 5.55 (s, 1H), 4.28 (t, *J* = 5.5 Hz, 1H), 3.27 (s, 6H), 2.53 (t, *J* = 7.8 Hz, 2H), 1.64 (dt, *J* = 7.8, 5.5 Hz, 2H), 1.37 (s, 9H).

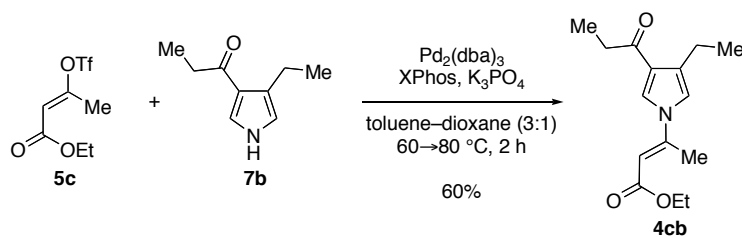
<sup>13</sup>C NMR (125.7 MHz, CDCl<sub>3</sub>, 20 °C): 164.6, 150.1, 121.1, 112.0, 109.9, 103.6, 81.0, 53.3, 32.5, 30.1, 28.1.

FTIR (neat): 2978 (m, C-H), 1704 (m, C=O), 1645 (m, C=C), 1482, 1367, 1154.

HRMS-ESI (*m/z*): calcd for C<sub>16</sub>H<sub>25</sub>NO<sub>4</sub>Na [M + Na]<sup>+</sup>: 318.1676, found: 318.1674

TLC (20% EtOAc-hexanes), *R<sub>f</sub>*: 0.34 (UV, anis)

<sup>7</sup> For general procedures used to prepare the vinyl triflate **5b**, see: Comins, D. L.; Dehghani, A. *Tetrahedron Lett.* **1992**, 33, 6299–6302 and Kim, H.-O.; Ogbu, C. O.; Nelson, S.; Kahn, M. *Synlett* **1998**, 1059–1060.



**E-3-(3-Ethyl-4-propionyl-pyrrol-1-yl)-but-2-enoic acid ethyl ester (4cb, Table 1, entry 12):**

A mixture of toluene–dioxane (3:1, 1.90 mL) was added to an argon–purged sample of acyl pyrrole **7b** (86.5 mg, 572  $\mu\text{mol}$ , 1.50 equiv),  $\text{Pd}_2(\text{dba})_3$  (17.5 mg, 19.1  $\mu\text{mol}$ , 0.05 equiv),  $\text{XPhos}$  (18.2 mg, 38.1  $\mu\text{mol}$ , 0.10 equiv), and rigorously anhydrous  $\text{K}_3\text{PO}_4$  (113 mg, 534  $\mu\text{mol}$ , 1.40 equiv) in a flame-dried flask and the resulting deep red mixture was heated to 60 °C. After 30 min, triflate **5c**<sup>8</sup> (100 mg, 381  $\mu\text{mol}$ , 1 equiv) was added via syringe, producing a color change to brown within approximately 5 min. After 30 min, the temperature was increased to 80 °C and the brown mixture stirred for 1.5 h, at which point GC analysis indicated that the reaction was complete. The mixture was then allowed to cool to 23 °C, was diluted with EtOAc (10 mL), and was vacuum filtered through a plug of celite (diam. 2.5 cm, ht. 2.5 cm). The celite-plug and flask were rinsed with a 15-mL portion of EtOAc, and the combined organic filtrates were washed with water (7.5 mL) and brine (7.5 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure to give a deep brown residue. Purification of the crude material by flash column chromatography (silica gel: diam. 3.0 cm, ht. 24 cm; 20% EtOAc–hexanes) afforded the vinyl pyrrole **4cb** (59.8 mg, 60%) as a yellow oil.

<sup>1</sup>H NMR (500 MHz,  $\text{CDCl}_3$ , 20 °C): 7.56 (d,  $J = 2.3$  Hz, 1H), 6.84 (dt,  $J = 2.3, 1.3$  Hz, 1H), 5.97 (q,  $J = 0.9$  Hz, 1H), 4.22 (q,  $J = 7.1$  Hz, 2H), 2.78 (qd,  $J = 7.4, 1.3$  Hz, 2H), 2.78 (q,  $J = 7.3$ , 2H), 2.70 (d,  $J = 0.9$  Hz, 3H), 1.32 (t,  $J = 7.1$  Hz, 3H), 1.20 (t,  $J = 7.4$  Hz, 3H), 1.18 (t,  $J = 7.3$  Hz, 3H).

<sup>13</sup>C NMR (125.8 MHz,  $\text{CDCl}_3$ , 20 °C): 197.9, 167.2, 150.7, 131.4, 125.8, 124.7, 117.8, 105.9, 60.9, 33.7, 20.7, 16.7, 15.0, 14.7, 9.2.

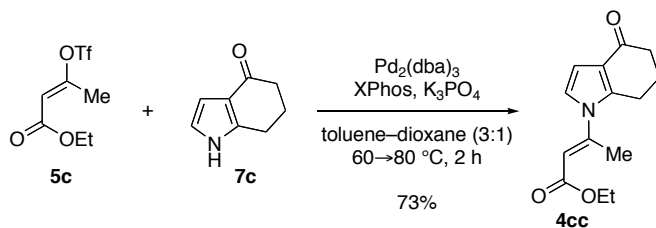
FTIR (neat): 2976 (m, C–H), 1713 (s, C=O), 1640 (s, C=O), 1516, 1409, 1154.

HRMS–EI ( $m/z$ ): calcd for  $\text{C}_{15}\text{H}_{21}\text{NO}_3\text{Na}$  [ $\text{M} + \text{Na}$ ]<sup>+</sup>: 286.1414, found: 286.1419

TLC (25% EtOAc–hexanes),  $R_f$ : 0.39 (UV, anis)

<sup>8</sup> For the synthesis of *Z*-vinyl triflate **5c**, see: Ohba, M.; Kawase, N.; Fujii, T. *J. Am. Chem. Soc.* **1996**, *118*, 8250–8257.





**E-3-(4-Oxo-4,5,6,7-tetrahydro-indol-1-yl)-but-2-enoic acid ethyl ester (4cc, Table 1, entry 14):**

A mixture of toluene–dioxane (3:1, 1.90 mL) was added to an argon–purged sample of 1,5,6,7-tetrahydro-4*H*-indol-4-one (**7c**, 77.3 mg, 572  $\mu\text{mol}$ , 1.50 equiv),  $\text{Pd}_2(\text{dba})_3$  (17.5 mg, 19.1  $\mu\text{mol}$ , 0.05 equiv),  $\text{XPhos}$  (18.2 mg, 38.1  $\mu\text{mol}$ , 0.10 equiv), and rigorously anhydrous  $\text{K}_3\text{PO}_4$  (113 mg, 534  $\mu\text{mol}$ , 1.40 equiv) in a flame-dried flask and the resulting deep red mixture was heated to 60 °C. After 30 min, triflate **5c** (100 mg, 381  $\mu\text{mol}$ , 1 equiv) was added via syringe, producing a color change to forest green within approximately 5 min. After 30 min, the temperature was increased to 80 °C and the brown mixture stirred for 1.5 h, at which point GC analysis indicated that the reaction was complete. The mixture was then allowed to cool to 23 °C, was diluted with EtOAc (10 mL), and was vacuum filtered through a plug of celite (diam. 2.5 cm, ht. 2.5 cm). The celite-plug and flask were rinsed with a 15-mL portion of EtOAc, and the combined organic filtrates were washed with water (7.5 mL) and brine (7.5 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated to a deep brown residue. Purification of the crude material by flash column chromatography (silica gel: diam. 3.0 cm, ht. 25 cm; 60% EtOAc–hexanes) gave the vinyl indolone **4cc** (68.7 mg, 73%) as a yellow oil.

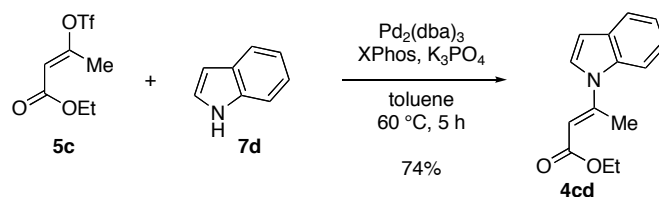
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 20 °C): 6.76 (d,  $J = 3.3$  Hz, 1H), 6.64 (d,  $J = 3.3$  Hz, 1H), 5.81 (q,  $J = 1.1$  Hz, 1H), 4.32 (q,  $J = 7.2$  Hz, 2H), 2.87 (t,  $J = 6.2$  Hz, 2H), 2.62 (d,  $J = 1.1$  Hz, 3H), 2.51 (app t,  $J = 6.2$  Hz, 2H), 2.15 (pentet,  $J = 6.2$  Hz, 2H), 1.32 (t,  $J = 7.2$  Hz, 3H).

$^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ , 20 °C): 195.3, 166.5, 151.1, 143.4, 129.0, 123.6, 122.0, 114.8, 107.9, 61.2, 38.4, 24.8, 19.7, 15.0.

FTIR (neat): 2943 (w, C–H), 1712 (s, C=O), 1659 (s, C=O), 1461, 1158.

HRMS–ESI ( $m/z$ ): calcd for  $\text{C}_{14}\text{H}_{17}\text{NO}_3\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$ : 270.1101, found: 270.1106

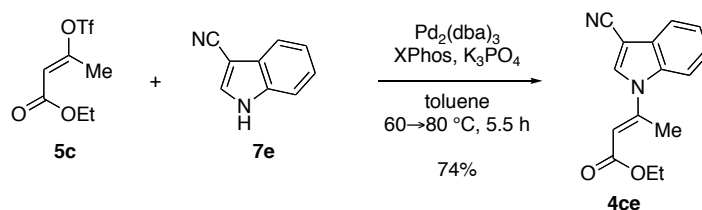
TLC (65% EtOAc–hexanes),  $R_f$ : 0.38 (UV, anis)



**E-3-Indol-1-yl-but-2-enoic acid ethyl ester (4cd, Table 1, entry 15):**

Toluene (1.90 mL) was added to an argon-purged sample of indole (**7d**, 67.0 mg, 572  $\mu\text{mol}$ , 1.50 equiv),  $\text{Pd}_2(\text{dba})_3$  (17.5 mg, 19.1  $\mu\text{mol}$ , 0.05 equiv), XPhos (18.2 mg, 38.1  $\mu\text{mol}$ , 0.10 equiv), and rigorously anhydrous  $\text{K}_3\text{PO}_4$  (113 mg, 534  $\mu\text{mol}$ , 1.40 equiv) in a flame-dried flask and the resulting deep red mixture was heated to  $60^\circ\text{C}$ . After 30 min, triflate **5c** (100 mg, 381  $\mu\text{mol}$ , 1 equiv) was added via syringe, producing a color change to brown within approximately 5 min. After 5 h at  $60^\circ\text{C}$  GC analysis indicated that the reaction was complete, whereupon the mixture was allowed to cool to  $23^\circ\text{C}$ , was diluted with EtOAc (10 mL), and was vacuum filtered through a plug of celite (diam. 2.5 cm, ht. 2.5 cm). The celite-plug and flask were rinsed with a 15-mL portion of EtOAc, and the combined organic filtrates were washed with water (7.5 mL) and brine (7.5 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure to give a deep brown residue. Purification of the crude material by flash column chromatography (silica gel: diam. 2.0 cm, ht. 24 cm; 3.5 $\rightarrow$ 7.5% EtOAc-hexanes) afforded the vinyl indole **4cd** (65.3 mg, 74%) as a colorless oil.

$^1\text{H}$ NMR (500 MHz, $\text{CDCl}_3$ , $20^\circ\text{C}$ ):	7.70 (dq, $J = 8.4, 0.8$ Hz, 1H), 7.62 (dt, $J = 7.6, 0.8$ Hz, 1H), 7.29 (d, $J = 3.4$ , 1H), 7.27 (ddd, $J = 8.4, 7.1, 0.8$ Hz, 1H), 7.18 (ddd, $J = 7.6, 7.1, 0.8$ Hz, 1H), 6.64 (dd, $J = 3.4, 0.8$ Hz, 1H), 6.12 (q, $J = 0.8$ Hz, 1H), 4.23 (q, $J = 7.1$ Hz, 2H), 2.78 (d, $J = 0.8$ Hz, 3H), 1.32 (t, $J = 7.1$ Hz, 3H).
$^{13}\text{C}$ NMR (125.7 MHz, $\text{CDCl}_3$ , $20^\circ\text{C}$ ):	167.3, 151.7, 135.4, 130.6, 126.2, 123.4, 121.7, 121.7, 112.9, 109.1, 105.9, 60.3, 19.0, 14.6.
FTIR (neat):	2980 (s, C-H), 1710 (s, C=O), 1633 (s, C=C), 1454, 1151.
HRMS-EI ( $m/z$ ):	calcd for $\text{C}_{14}\text{H}_{15}\text{NO}_2\text{Na}$ [ $\text{M} + \text{Na}$ ] $^+$ : 252.0995, found: 252.1003
TLC (7.5% EtOAc-hexanes), $R_f$ :	0.29 (UV, anis)



**E-3-(3-Cyano-indol-1-yl)-but-2-enoic acid ethyl ester (4ce, Table 1, entry 16):**

A mixture of toluene–dioxane (3:1, 1.90 mL) was added to an argon–purged sample of 3-cyanoindole (**7e**, 81.3 mg, 572  $\mu\text{mol}$ , 1.50 equiv),  $\text{Pd}_2(\text{dba})_3$  (17.5 mg, 19.1  $\mu\text{mol}$ , 0.05 equiv), XPhos (18.2 mg, 38.1  $\mu\text{mol}$ , 0.10 equiv), and rigorously anhydrous  $\text{K}_3\text{PO}_4$  (113 mg, 534  $\mu\text{mol}$ , 1.40 equiv) in a flame-dried flask and the resulting deep red mixture was heated to 60  $^\circ\text{C}$ . After 30 min, triflate **5c** (100 mg, 381  $\mu\text{mol}$ , 1 equiv) was added via syringe, producing a color change to forest green within approximately 5 min. After 2.5 h, the temperature was increased to 80  $^\circ\text{C}$  and the brown mixture stirred for an additional 3 h, at which point GC analysis indicated that the reaction was complete. The mixture was then allowed to cool to 23  $^\circ\text{C}$ , was diluted with EtOAc (10 mL), and was vacuum filtered through a plug of celite (diam. 2.5 cm, ht. 2.5 cm). The celite-plug and flask were rinsed with a 15mL portion of EtOAc, and the combined organic filtrates were washed with water (7.5 mL) and brine (7.5 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure to provide an orange residue. Purification of the crude material by flash column chromatography (silica gel: diam. 3.0 cm, ht. 24 cm; 20% EtOAc–hexanes) gave the vinyl indole **4ce** (71.9 mg, 74%) as an off–white solid.

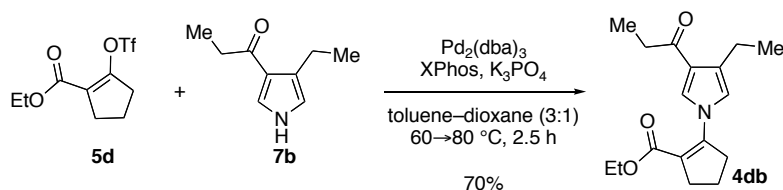
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 20 $^\circ\text{C}$ ): 7.79 (dd,  $J = 8.2, 1.1$  Hz, 1H), 7.78 (s, 1H), 7.67 (dd,  $J = 8.4, 0.9$  Hz, 1H), 7.41 (ddd,  $J = 8.4, 7.1, 1.1$  Hz, 1H), 7.37 (ddd,  $J = 8.2, 7.1, 0.9$  Hz, 1H), 6.19 (q,  $J = 0.9$  Hz, 1H), 4.28 (q,  $J = 7.2$  Hz, 2H), 2.77 (d,  $J = 0.9$  Hz, 3H), 1.35 (t,  $J = 7.2$  Hz, 3H).

$^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ , 20 $^\circ\text{C}$ ): 166.5, 150.1, 135.2, 133.5, 129.0, 125.8, 124.2, 121.0, 115.5, 114.6, 113.5, 90.6, 61.4, 19.5, 15.0.

FTIR (neat): 2983 (w, C–H), 2225 (s, C $\equiv$ N), 1717 (s, C=O), 1644, 1551, 1182.

HRMS–ESI ( $m/z$ ): calcd for  $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_2\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$ : 277.0947, found: 277.0951

TLC (25% EtOAc–hexanes),  $R_f$ : 0.37 (UV, CAM)



**2-(3-Ethyl-4-propionyl-pyrrol-1-yl)-cyclopent-1-enecarboxylic acid ethyl ester (4db, Table 1, entry 18):**

A mixture of toluene–dioxane (3:1, 1.90 mL) was added to an argon–purged sample of acyl pyrrole **7b** (86.5 mg, 572  $\mu\text{mol}$ , 1.50 equiv),  $\text{Pd}_2(\text{dba})_3$  (17.5 mg, 19.1  $\mu\text{mol}$ , 0.05 equiv), XPhos (18.2 mg, 38.1  $\mu\text{mol}$ , 0.10 equiv), and rigorously anhydrous  $\text{K}_3\text{PO}_4$  (113 mg, 534  $\mu\text{mol}$ , 1.40 equiv) in a flame-dried flask and the resulting deep red mixture was heated to 60  $^\circ\text{C}$ . After 30 min, triflate **5d**<sup>9</sup> (110 mg, 381  $\mu\text{mol}$ , 1 equiv) was added via syringe, producing a color change to brown within approximately 5 min. After 30 min, the temperature was increased to 80  $^\circ\text{C}$  and the brown mixture stirred for 2 h, at which point GC analysis indicated that the reaction was complete. The mixture was then allowed to cool to 23  $^\circ\text{C}$ , was diluted with EtOAc (10 mL), and was vacuum filtered through a plug of celite (diam. 2.5 cm, ht. 2.5 cm). The celite–plug and flask were rinsed with an additional 15-mL portion of EtOAc, then the combined organic filtrates were washed with water (7.5 mL) and brine (7.5 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure to give a deep brown residue. Purification of the crude material by flash column chromatography (silica gel: diam. 3.0 cm, ht. 24 cm; 17.5 $\rightarrow$ 20% EtOAc–hexanes) provided the vinyl pyrrole **4db** (77.3 mg, 70%) as a yellow oil.

<sup>1</sup>H NMR (500 MHz,  $\text{CDCl}_3$ , 20 $^\circ\text{C}$ ): 7.84 (d,  $J = 2.3$  Hz, 1H), 6.77 (dt,  $J = 2.3, 1.1$  Hz, 1H), 4.21 (q,  $J = 7.2$  Hz, 2H), 2.93 (app tt,  $J = 7.6, 2.1$  Hz, 2H), 2.84 (app tt,  $J = 7.6, 2.1$  Hz, 2H), 2.78 (qd,  $J = 7.4, 1.1$  Hz, 2H), 2.77 (q,  $J = 7.3, 2\text{H}$ ), 1.99 (pentet,  $J = 7.6$  Hz, 2H), 1.27 (t,  $J = 7.2$  Hz, 3H), 1.19 (t,  $J = 7.3$  Hz, 3H), 1.17 (t,  $J = 7.4$  Hz, 3H).

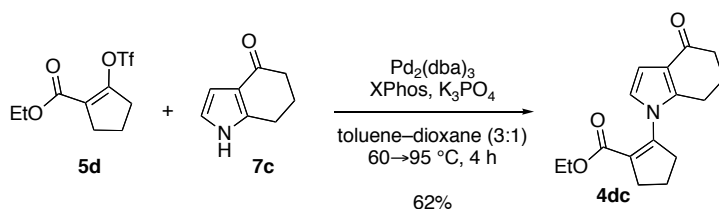
<sup>13</sup>C NMR (125.8 MHz,  $\text{CDCl}_3$ , 20 $^\circ\text{C}$ ): 197.9, 165.5, 146.7, 129.5, 129.0, 124.3, 120.7, 118.1, 61.2, 37.6, 34.4, 33.6, 20.8, 20.6, 14.9, 14.8, 9.3.

FTIR (neat): 2969 (s, C–H), 1708 (s, C=O), 1666 (s, C=O), 1518, 1199, 1063.

HRMS–ESI ( $m/z$ ): calcd for  $\text{C}_{17}\text{H}_{23}\text{NO}_3\text{Na}$  [ $\text{M} + \text{Na}$ ]<sup>+</sup>: 312.1570, found: 312.1566

TLC (25% EtOAc–hexanes), *R*<sub>f</sub>: 0.44 (UV, anis)

<sup>9</sup> For the synthesis of vinyl triflate **5d**, see: Jasperse, C. P.; Curran, D. P. *J. Am. Chem. Soc.* **1990**, *112*, 5601–5609.



**2-(4-Oxo-4,5,6,7-tetrahydro-indol-1-yl)-cyclopent-1-enecarboxylic acid ethyl ester (4dc, Table 1, entry 20):**

A mixture of toluene–dioxane (3:1, 1.90 mL) was added to an argon–purged sample of 1,5,6,7-tetrahydro-4*H*-indol-4-one (**7c**, 77.3 mg, 572  $\mu\text{mol}$ , 1.50 equiv),  $\text{Pd}_2(\text{dba})_3$  (17.5 mg, 19.1  $\mu\text{mol}$ , 0.05 equiv), XPhos (18.2 mg, 38.1  $\mu\text{mol}$ , 0.10 equiv), and rigorously anhydrous  $\text{K}_3\text{PO}_4$  (113 mg, 534  $\mu\text{mol}$ , 1.40 equiv) in a flame-dried flask and the resulting deep red mixture was heated to 60 °C. After 30 min, triflate **5d** (110 mg, 381  $\mu\text{mol}$ , 1 equiv) was added via syringe, producing a color change to olive green within approximately 10 min. After 30 min, the temperature was increased to 95 °C and the green–brown mixture stirred for 3.5 h, at which point GC analysis indicated that the reaction was complete. The mixture was then allowed to cool to 23 °C, was diluted with EtOAc (10 mL), and was vacuum filtered through a plug of celite (diam. 2.5 cm, ht. 2.5 cm). The celite–plug and flask were rinsed with an additional 15-mL portion of EtOAc, and the combined organic filtrates were washed with water (7.5 mL) and brine (7.5 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure to provide a deep brown residue. Purification of the crude material by flash column chromatography (silica gel: diam. 3.0 cm, ht. 22 cm, 60% EtOAc–hexanes) gave the vinyl indolone **4dc** (63.7 mg, 62%) as an off–white solid.

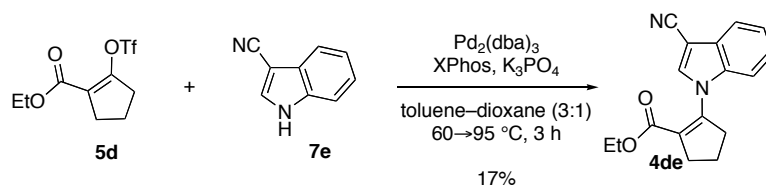
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 20°C): 6.62 (d,  $J = 3.4$  Hz, 1H), 6.58 (d,  $J = 3.4$  Hz, 1H), 4.08 (q,  $J = 7.1$  Hz, 2H), 2.84 (app tt,  $J = 7.6, 2.5$  Hz, 2H), 2.80 (app tt,  $J = 7.6, 2.5$  Hz, 2H), 2.64 (t,  $J = 6.3$  Hz, 2H), 2.48 (app t,  $J = 6.3$  Hz, 2H), 2.11 (pentet,  $J = 6.3$  Hz, 2H), 2.07 (pentet,  $J = 7.6$  Hz, 2H), 1.11 (t,  $J = 7.1$  Hz, 3H).

$^{13}\text{C}$  NMR (125.7 MHz,  $\text{CDCl}_3$ , 20°C): 194.7, 163.9, 146.7, 144.3, 128.4, 122.1, 121.6, 106.5, 60.9, 38.1, 37.7, 32.4, 24.1, 22.7, 20.5, 14.2.

FTIR (neat): 2948 (m, C–H), 1710 (s, C=O), 1660 (s, C=O), 1499, 1464, 1237.

HRMS–EI ( $m/z$ ): calcd for  $\text{C}_{16}\text{H}_{19}\text{NO}_3\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$ : 296.1257, found: 296.1248

TLC (65% EtOAc–hexanes),  $R_f$ : 0.22 (UV, anis)



**2-(3-Cyano-indol-1-yl)-cyclopent-1-enecarboxylic acid ethyl ester (4de, Table 1, entry 22):**

A mixture of toluene–dioxane (3:1, 1.90 mL) was added to an argon–purged sample of 3-cyanoindole (**7e**, 81.3 mg, 572  $\mu\text{mol}$ , 1.50 equiv),  $\text{Pd}_2(\text{dba})_3$  (17.5 mg, 19.1  $\mu\text{mol}$ , 0.05 equiv), XPhos (18.2 mg, 38.1  $\mu\text{mol}$ , 0.10 equiv), and rigorously anhydrous  $\text{K}_3\text{PO}_4$  (113 mg, 534  $\mu\text{mol}$ , 1.40 equiv) in a flame-dried flask and the resulting deep red mixture was heated to 60  $^\circ\text{C}$ . After 30 min, triflate **5d** (110 mg, 381  $\mu\text{mol}$ , 1 equiv) was added via syringe, producing a color change to olive green within approximately 10 min. After 30 min, the temperature was increased to 95  $^\circ\text{C}$  and the green–brown mixture stirred for 2.5 h, at which point GC analysis indicated that the reaction was complete. The mixture was then allowed to cool to 23  $^\circ\text{C}$ , was diluted by the addition of EtOAc (10 mL), and was vacuum filtered through a plug of celite (diam. 2.5 cm, ht. 2.5 cm). The celite–plug and flask were rinsed with an additional 15-mL portion of EtOAc, and the combined organic filtrates were washed with water (7.5 mL) and brine (7.5 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated to yield a deep brown residue. Purification of the crude material by flash column chromatography (silica gel: diam. 3.0 cm, ht. 22 cm, 25% EtOAc–hexanes) gave the vinyl indole **4de** (18.9 mg, 17%) as an off–white solid.

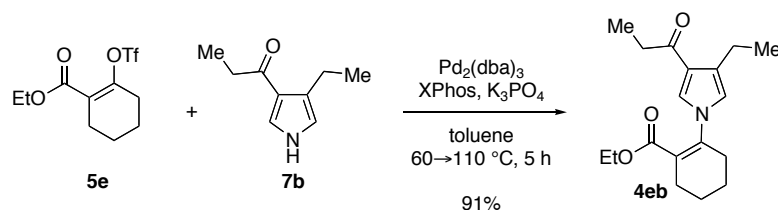
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 20 $^\circ\text{C}$ ): 7.77 (m, 1H), 7.69 (s, 1H), 7.27–7.37 (m, 3H), 3.97 (q,  $J = 7.2$  Hz, 2H), 2.98 (app tt,  $J = 7.6, 2.5$  Hz, 2H), 2.93 (app tt,  $J = 7.6, 2.5$  Hz, 2H), 2.16 (pentet,  $J = 7.6$  Hz, 2H), 0.89 (t,  $J = 7.2$  Hz, 3H).

$^{13}\text{C}$  NMR (125.7 MHz,  $\text{CDCl}_3$ , 20 $^\circ\text{C}$ ): 163.7, 145.4, 135.5, 135.1, 128.1, 127.7, 124.6, 123.0, 120.2, 115.5, 112.3, 88.4, 61.0, 36.9, 32.5, 20.7, 13.9.

FTIR (neat): 2978 (w, C–H), 2221 (s, C $\equiv$ N), 1710 (s, C=O), 1536, 1461, 1213.

HRMS–ESI ( $m/z$ ): calcd for  $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$ : 303.1104, found: 303.1095

TLC (25% EtOAc–hexanes),  $R_f$ : 0.23 (UV, anis)



**2-(3-Ethyl-4-propionyl-pyrrol-1-yl)-cyclohex-1-enecarboxylic acid ethyl ester (4eb, Table 1, entry 24):**

Toluene (1.90 mL) was added to an argon-purged mixture of acyl pyrrole **7b** (86.5 mg, 572  $\mu\text{mol}$ , 1.50 equiv),  $\text{Pd}_2(\text{dba})_3$  (17.5 mg, 19.1  $\mu\text{mol}$ , 0.05 equiv), XPhos (18.2 mg, 38.1  $\mu\text{mol}$ , 0.10 equiv), and rigorously anhydrous  $\text{K}_3\text{PO}_4$  (113 mg, 534  $\mu\text{mol}$ , 1.40 equiv) in a flame-dried flask and the resulting deep red mixture was heated to 60  $^\circ\text{C}$ . After 30 min, vinyl triflate **5e**<sup>10</sup> (110 mg, 381  $\mu\text{mol}$ , 1 equiv) was added via syringe, producing a color change to burgundy within approximately 15 min. After an additional 2.5 h, the reaction temperature was raised to 110  $^\circ\text{C}$  and the deep brown mixture stirred for 2 h, at which point GC analysis indicated that the reaction was complete. The mixture was then allowed to cool to 23 $^\circ\text{C}$ , was diluted with EtOAc (10 mL), and was vacuum filtered through a plug of celite (diam. 2.5 cm, ht. 2.5 cm). The celite-plug and flask were rinsed with an additional 15-mL portion of EtOAc, and the combined organic filtrates were washed sequentially with water (7.5 mL) and brine (7.5 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure to give a deep brown residue. Purification of the crude material by flash column chromatography (silica gel: diam. 3.0 cm, ht. 24 cm, 20% EtOAc-hexanes) gave vinyl pyrrole **4eb** (105 mg, 91%) as a yellow oil.

<sup>1</sup>H NMR (500 MHz,  $\text{CDCl}_3$ , 20 $^\circ\text{C}$ ): 7.22 (d,  $J = 2.3$  Hz, 1H), 6.77 (dt,  $J = 2.3, 1.1$  Hz, 1H), 3.99 (q,  $J = 7.1$  Hz, 2H), 2.77 (qd,  $J = 7.5, 1.1$  Hz, 2H), 2.71 (q,  $J = 7.4$ , 2H), 2.46 (m, 4H), 1.82 (dtd,  $J = 8.8, 6.0, 2.7$  Hz, 2H), 1.73 (dtd,  $J = 8.8, 6.0, 2.7$  Hz, 2H), 1.17 (t,  $J = 7.5$  Hz, 3H), 1.16 (t,  $J = 7.4$  Hz, 3H), 1.01 (t,  $J = 7.1$  Hz, 3H).

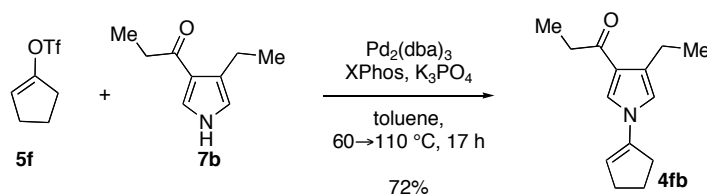
<sup>13</sup>C NMR (125.8 MHz,  $\text{CDCl}_3$ , 20 $^\circ\text{C}$ ): 197.7, 169.2, 141.0, 129.4, 127.1, 126.1, 123.9, 120.1, 61.7, 33.6, 31.2, 27.1, 22.9, 22.1, 20.6, 14.9, 14.6, 9.5.

FTIR (neat): 2937 (m, C-H), 1710 (s, C=O), 1659 (s, C=O), 1516, 1282.

HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{18}\text{H}_{25}\text{NO}_3\text{Na}$  [ $\text{M} + \text{Na}$ ]<sup>+</sup>: 326.1727, found: 326.1731

TLC (35% EtOAc-hexanes), *R<sub>f</sub>*: 0.38 (UV, anis)

<sup>10</sup> For the synthesis of vinyl triflate **5e**, see: Li, S.-J.; Dieter, R. K. *J. Org. Chem.* **2003**, *68*, 969–973.



**1-(3-Ethyl-4-propionyl-pyrrol-1-yl)-cyclopentene (4fb, Table 1, entry 26):**

Toluene (1.90 mL) was added to an argon-purged sample of acyl pyrrole **7b** (86.5 mg, 572  $\mu\text{mol}$ , 1.50 equiv),  $\text{Pd}_2(\text{dba})_3$  (17.5 mg, 19.1  $\mu\text{mol}$ , 0.05 equiv), XPhos (18.2 mg, 38.1  $\mu\text{mol}$ , 0.10 equiv), and rigorously anhydrous  $\text{K}_3\text{PO}_4$  (113 mg, 534  $\mu\text{mol}$ , 1.40 equiv) in a flame-dried flask and the resulting deep red mixture was heated to 60  $^\circ\text{C}$ . After 30 min, triflate **5f**<sup>11</sup> (82.4 mg, 381  $\mu\text{mol}$ , 1 equiv) was added via syringe, producing a color change to green within approximately 10 min. After 1 h, the temperature was increased to 110  $^\circ\text{C}$  and the brown mixture stirred for 16 h, at which point GC analysis indicated that the reaction was complete. The mixture was then allowed to cool to 23  $^\circ\text{C}$ , was diluted with EtOAc (10 mL), and was vacuum filtered through a plug of celite (diam. 2.5 cm, ht. 2.5 cm). The celite-plug and flask were rinsed with an additional 15-mL portion of EtOAc, then the combined organic filtrates were washed with water (7.5 mL) and brine (7.5 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure to give a deep brown residue. Purification of the crude material by flash column chromatography (silica gel: diam. 2.0 cm, ht. 23 cm; 7.5% EtOAc–hexanes) provided the vinyl pyrrole **4fb** (60.4 mg, 72%) as a white solid.

<sup>1</sup>H NMR (500 MHz,  $\text{CDCl}_3$ , 20 $^\circ\text{C}$ ): 7.35 (d,  $J = 2.1$  Hz, 1H), 6.71 (dt,  $J = 2.1, 1.0$  Hz, 1H), 5.58 (app pentet,  $J = 2.2$  Hz, 1H), 2.77 (qd,  $J = 7.4, 1.0$  Hz, 2H), 2.74 (m, 2H), 2.74 (q,  $J = 7.4$  Hz, 2H), 2.50 (app tq,  $J = 7.3, 2.2$  Hz, 2H), 2.07 (app pentet,  $J = 7.4$ , Hz, 2H), 1.18 (t,  $J = 7.4$  Hz, 3H), 1.16 (t,  $J = 7.4$  Hz, 3H).

<sup>13</sup>C NMR (125.7 MHz,  $\text{CDCl}_3$ , 20 $^\circ\text{C}$ ): 197.3, 139.6, 129.6, 124.6, 123.4, 117.9, 111.9, 33.1, 31.8, 30.9, 22.3, 20.2, 14.5, 9.0.

FTIR (neat): 2967 (m, C–H), 1648 (s, C=O), 1519 (s, C=C), 1206.

HRMS–ESI ( $m/z$ ): calcd for  $\text{C}_{14}\text{H}_{19}\text{NONa}$   $[\text{M} + \text{Na}]^+$ : 240.1359, found: 240.1367

TLC (10% EtOAc–hexanes),  $R_f$ : 0.22 (UV, anis)

<sup>11</sup> For the synthesis of vinyl triflate **5f**, see: (a) Pfeifer, W. D.; Bahn, C. A.; Schleyer, P. v. R.; Bocher, S.; Harding, C. E.; Hummel, K.; Hanack, M.; Stang, P. J. *J. Am. Chem. Soc.* **1971**, 93, 1513–1516 and (b) Stang, P. J.; Treptow, W. *Synthesis* **1980**, 283–284.

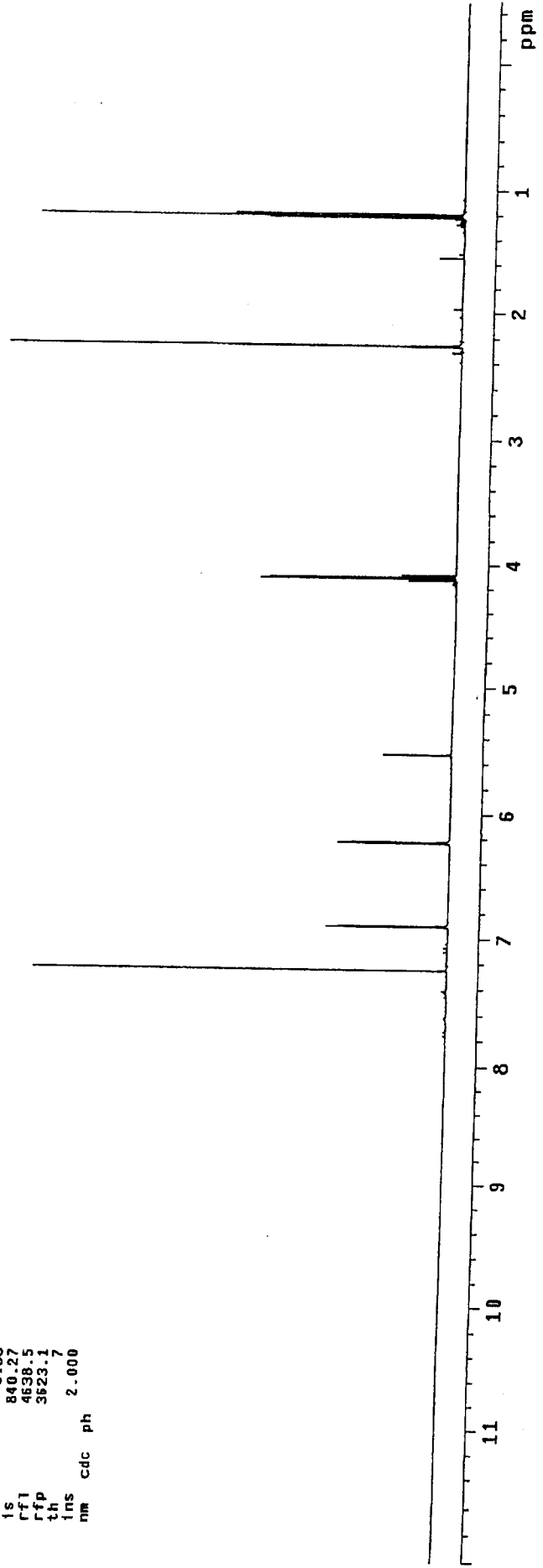
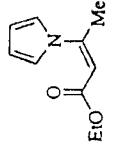


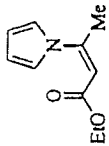
exp1 s2pul

```

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solvent CDC13
file /data/export/~dpwr 34
home /movassag/Mao/~dpwr 1498.1
bulwinkle/Mao_042-
505_A011161_1H.fid
ACQUISITION
sfrq 499.749
in H1
at 3.277
np 65556
sw 9998.8
fb not used
bs 4
tpwr 56
pw 8.2
d1 2.000
tof 1498.1
nt 18
ct 18
alock gain not used
gain not used
flags
l1 n
in n
dp n
hs y
DISPLAY
sp -250.1
wp 6246.5
vs 71
sc 0
wc 250
hzman 6.88
fs 840.27
rfi 4638.5
rfp 3523.1
th
fms
nm cdc ph 2.000
    
```

DEC. & VT

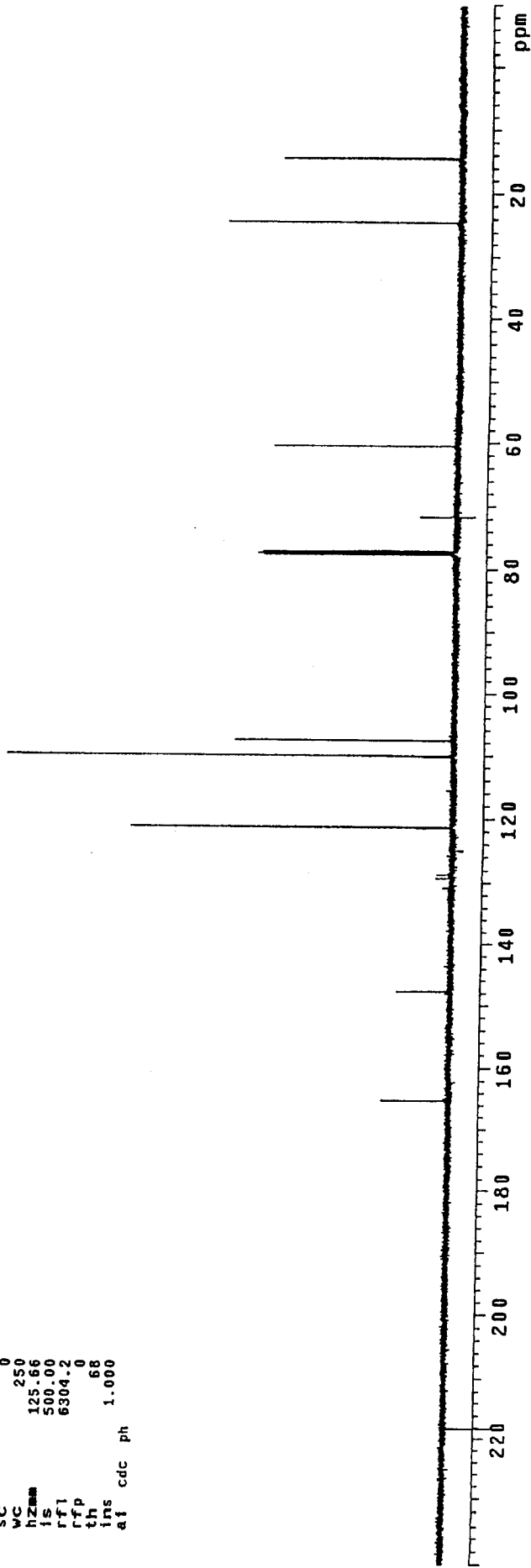




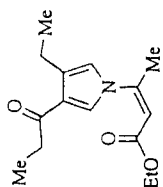
4aa

```

exp2 s2pul
SAMPLE DEC. & VT
date Apr 30 2005 dfrq 499.747
solvent CDC13 dn H1
file /data/export/~ dpwr 34
home/movassag/Mao/~ dcf 0
bulwinkle/Mao_043- da yyy
005_AQ11161_13C.f1- dam w
                                d 10000
ACQUISITION
sfrq 125.673 dseq
tn 125.673 dres 1.0
at 0.869 C13 homo n
np 65536 lb PROCESSING
sw 37718.1 wtfile 1.00
fb not used proc ft
bs lb fn 131072 f
ss i math
tpwr 58
pw 7.5 werr
d1 3.000 wexp
tof 615.5 wbs
nt 10000 wnt
ct 336
alock n
gain not used
flags
it n
in n
dp y
hs nn
DISPLAY
sp -1256.8
wp 31414.8
vs 295
sc 0
wc 250
hZmax 125.66
fs 500.00
rfl 6304.2
rff 0
th 68
ins 1.000
af cdc ph
  
```



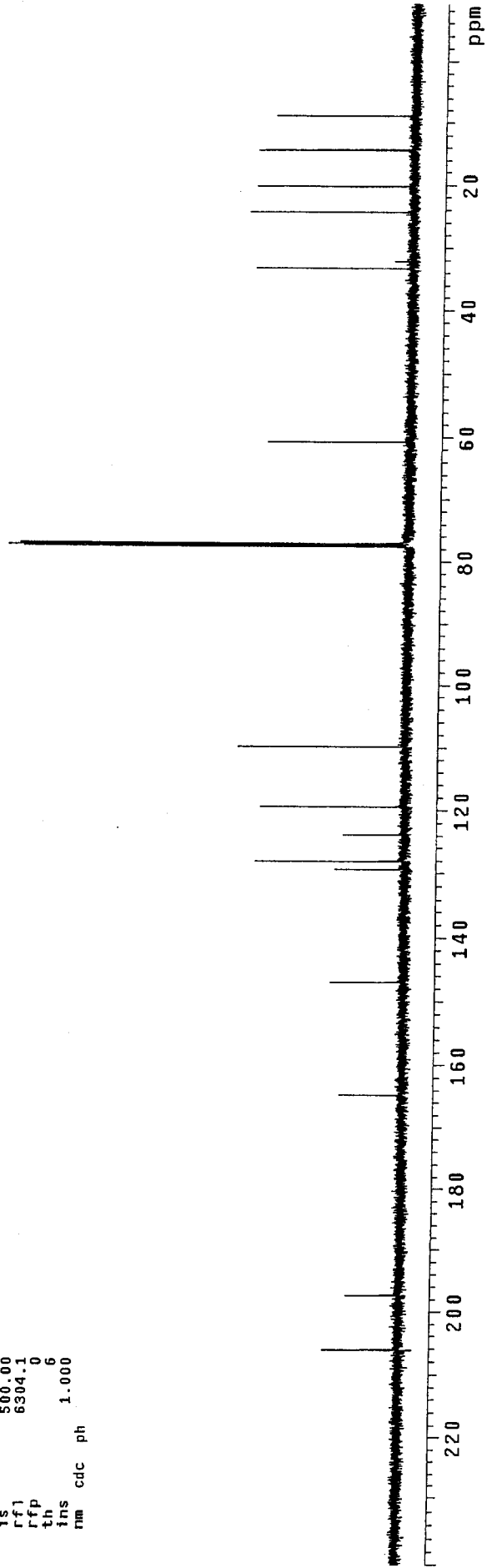


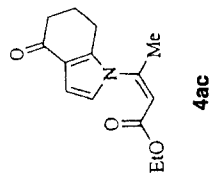


4ab

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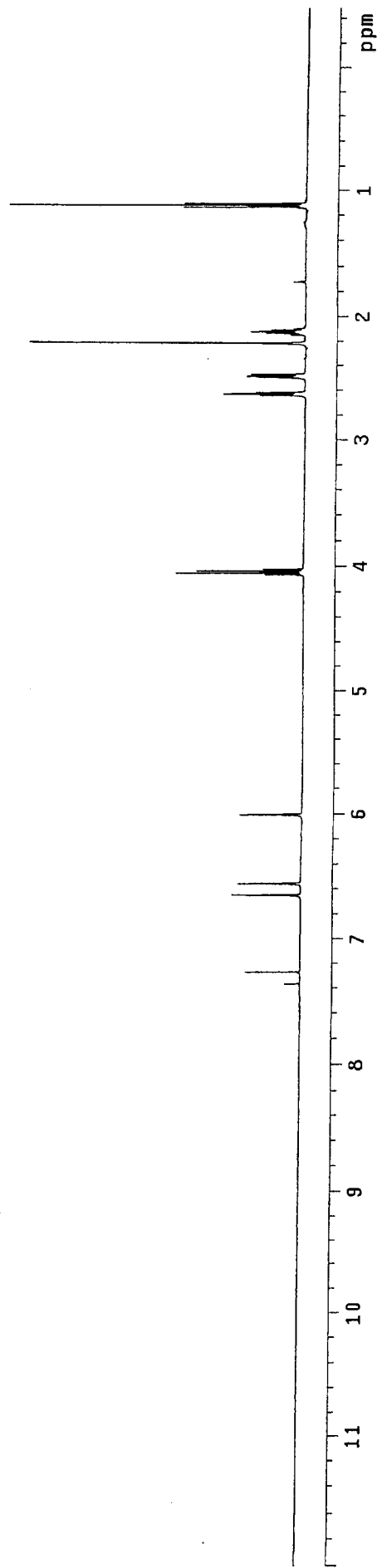
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SAMPLE
date Feb 12 2005 dfrq DEC. & VT 499.756
solvent CDCl3 dn hi
file /data/export/~ dpwr 34
home/movassag/Mao/~ dof 0
bulwinkle/Mao_021~ dm yvy
205_A011074_13C.f1~ dmh
dmf 10000
w
ACQUISITION
sfrq 125.676 dseq
fn C13 dres 1.0
at 0.869 homo n
np 65536 lb PROCESSING
sw 37718.1 wtfile 1.00
fb not used proc ft
ss 16 fn 131072
tpwr 1 math f
pw 58
dl 7.5 werr
di 3.000 wexp
tof 615.5 wbs
nt 1000000 wnt
ct 576
alock n
gain not used
flags
f1 n
in n
dp y
hs nn
DISPLAY
sp -1256.7
wp 31415.4
vs 63
sc 0
wc 250
hzmm 125.66
ls 500.00
rf1 6304.1
rfp 0
th 6
ins 1.000
nm cdc ph
  
```





```

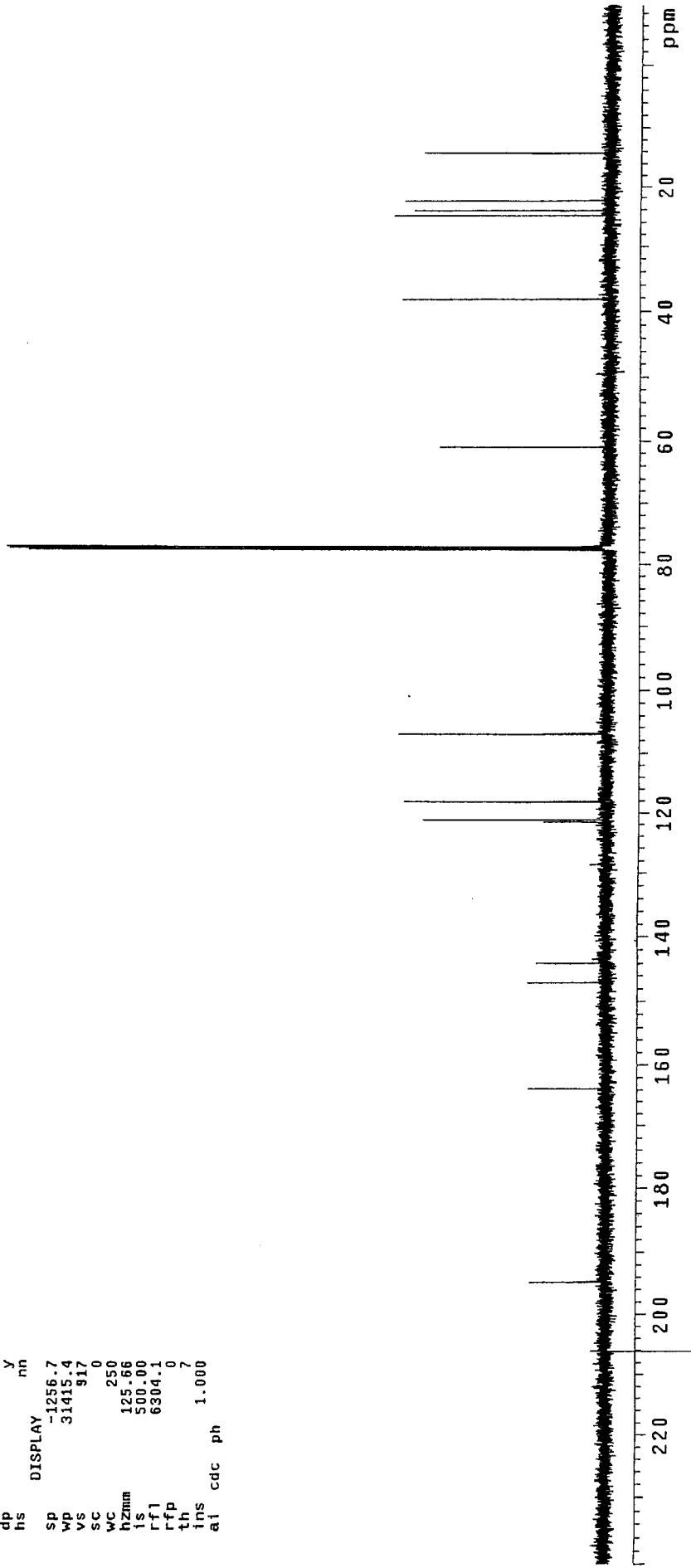
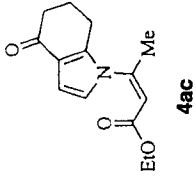
exp1 s2pu1
SAMPLE DEC. & VT
date Feb 15 2005 dfrq 125.677
solvent CDC13 dn C13
file /data/export/~ dpwr 34
home/movassag/Mao/~ dof 1498.1
bulkinke/Mao_021~ dm nnn
5-5_AOI1051_IH.fid dmm w
ACQUISITION dmf 10000
sfrq 499.758 dseq
tn H1 dres 1.0
at 3.277 homo PROCESSING n
nb 65536
sw 9998.8 wtfile ft
fb not used 4 fn 65536
bs tpwr 56 math f
pw dl 8.2
d1 2.000 werr
tof 1498.1 wexp
nt 20 wbs
ct 20 wnt
aLock gain not used n
gain FLAGS
  l) n
  in n
  dp n
  hs y
  sp DISPLAY -250.1
  wp 6246.8
  vs 11
  sc 0
  wc 250
  hzmm 40.00
  ls 33.57
  rfl 1002.5
  rfp 0
  th 7
  ins 2.000
  ai cdc ph
  
```

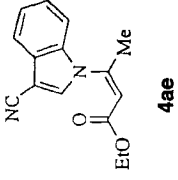


```

exp1 s2pu1
SAMPLE DEC. & VT
date Feb 15 2005 dfr4 499.756
solvent CDC13 dn H1
file /data/export/~ dpwr 34
home/movassag/Mao/~ dof 0
bulwinkle/Mao_021~ dm yyv
505_AOII051_13C.f1~ dnm 10000
ACQUISITION
sfrq 125.676 dseq
tn 125.676 dres 1.0
at 0.869 C13 homo n
np 65536 lb PROCESSING
sw 37718.1 wfile 1.00
fb not used proc ft
bs 16 fn 131072
ss i math
tpwr 58 i
pw 7.5 werr
dl 3.000 wexp
tof 615.5 wbs
nt 10000 wnt
ct 672
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1256.7
wp 31415.4
vs 917
sc 0
wc 250
hzmh 125.66
ls 500.00
rfl 6304.1
rff 0
th 7
ins 1.000
al cdc ph

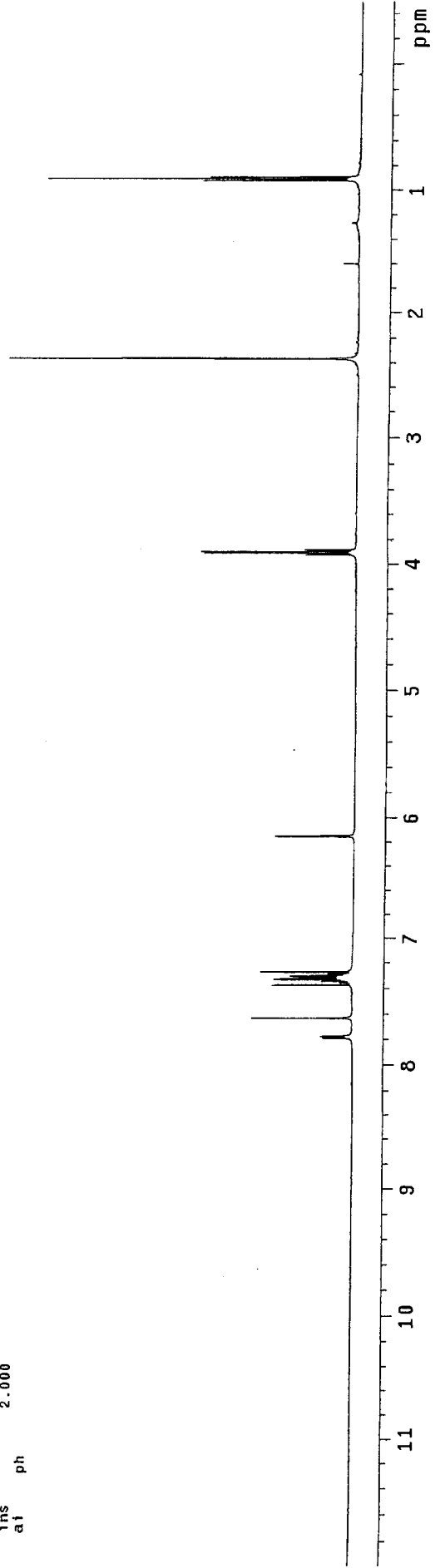
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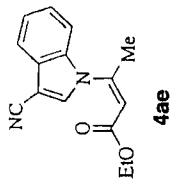




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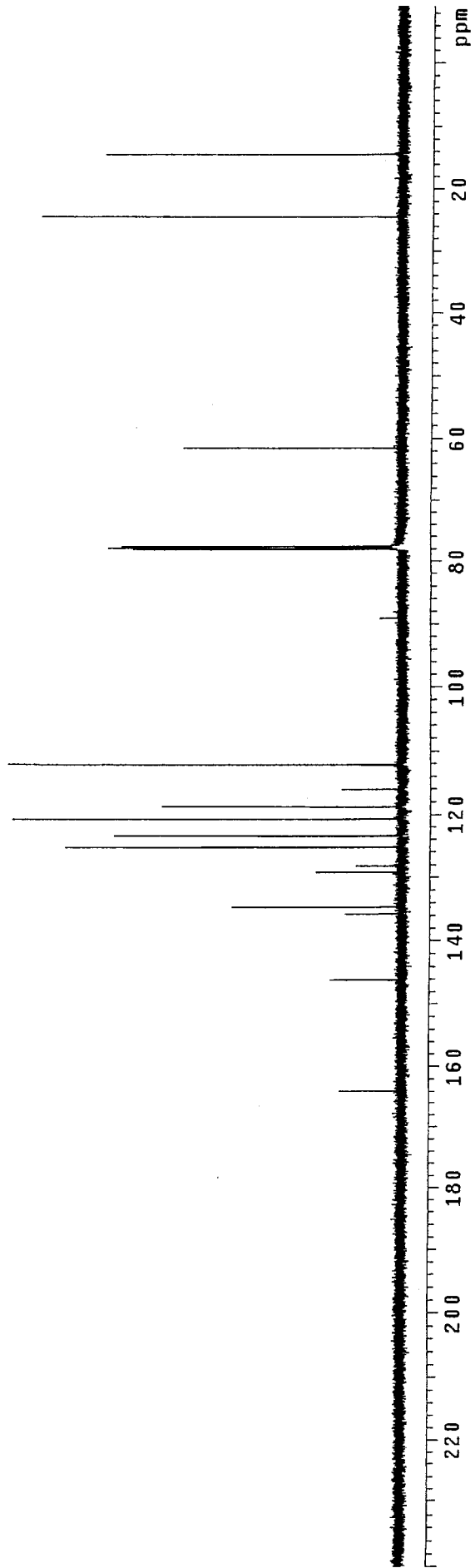
exp1  s2pul
SAMPLE
date      Feb 15 2005
solvent   CDC13
file      /data/export/~dpwr
home      /movassag/Mao/~dof
rocky/Mao.021505.A~dm
O1105283.1H.f1d dmm
ACQUISITION dmf 10000
sfrq      500.235
tn        H1
at        3.200
np        64000
sw        10000.0
fb        not used
bs        4
ss        1
tpwr      59
pw        9.8
d1        2.000
tof       1488.2
nt        20
ct        20
alock     not used
gain      not used
          FLAGS
il        n
in        n
dp        y
hs        nn
          DISPLAY
sp        -250.1
wp        6246.6
vs        45
sc        0
wc        250
hzmhmm    40.00
ls        100.00
rfl       4632.9
rff       3636.7
th        2.000
ins       ph
ai
  
```



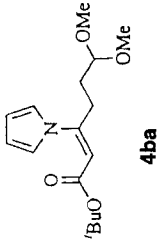


```

exp1 s2pu1
SAMPLE DEC. & VI
date Feb 15 2005 dfrq 500.233
solvent CDCl3 dn HI
file /data/export/~ dpwr 37
home/movassag/Mao/~ dof -500.0
rocky/Mao_021505_A~ dm
011052083_13C.fid dmm w
ACQUISITION dmf 10000
sfrq 125.796 dseg
tn C13 dres 1.0
at 1.736 homo n
np 131010 PROCESSING
sw 37735.8 lb wfile 0.30
bs not used 8 proc ft
ss 1 fn 131072
tpwr 53 math f
pw 6.9
dl 0.763 werr
tof 631.4 wexp
nt 10000 wbs
ct 968 wnt
alock n
gain not used
flags
il n
in n
dp y
hs nn
DISPLAY
sp -1258.3
wp 31448.1
vs 4325
sc 0
wc 250
hzmm 125.79
is 500.00
rf1 15911.8
rfp 9686.0
th 4
lms 1.000
al ph
  
```

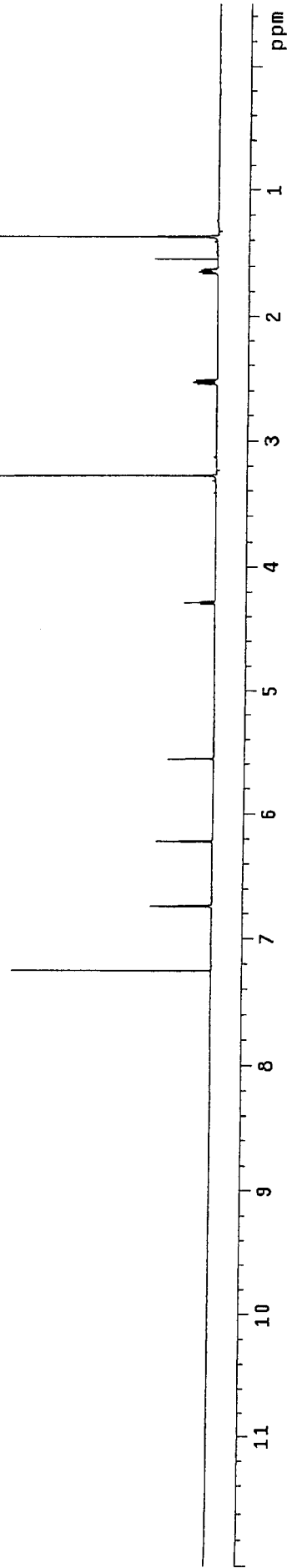






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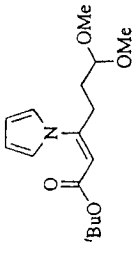
exp1 s2pu1
SAMPLE DEC. & VI
date May 6 2005 dfrq 125.674
solvent CDC13 dn C13
file /data/export/~ dpwr 34
home/movassag/Mac/~ dof 1498.1
bulwinkie/Mac_050~ dm nmh
605_A011178_1H.fid dmm w
ACQUISITION dmf 10000
sfrq 499.749 dseq
tn H1 dres 1.0
at 3.277 homo
np 65536
sw 9998.8 wfile
fb not used proc ft
bs 4 fn 65536
tpwr 56 math f
pw 8.2
d1 2.000 werr
tof 1498.1 wexp
nt 20 wbs
ct 20 wnt
alock n
gain not used
flags
il n
in n
dp n
hs y
DISPLAY nn
sp -250.1
wp 6246.5
vs 101
sc 0
wc 250
hzmm 40.00
fs 33.57
f1 4638.2
rfp 3623.1
th
ins cdc
nm ph 1.000
    
```



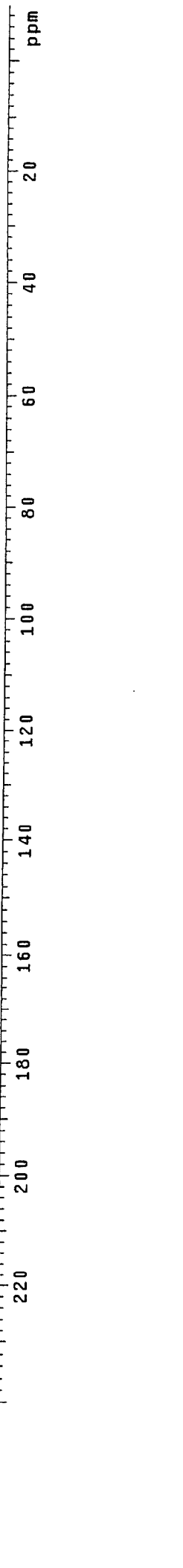
exp2 s2pu1

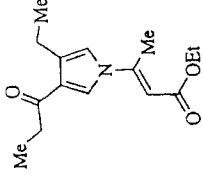
```

SAMPLE          DEC. & VI
date    May 6 2005    dfrq    499.747
solvent  May CDC13    dn      H1
file    /data/export/~ dpwr    34
home/movassag/Mao/~ dof      0
bulwinkle/Mao_050~ dm       yy
605_A011178_13C.f1~ dnmf    10000
                        dmf     10000
ACQUISITION
sfrq    125.673    dseq    1.0
fn      0.869     dres    n
at      65536     homo    n
rp      37718.1   lb      PROCESSING
sw      not used  wf      1.00
fb      16        fn      ft
ss      1         fn      131072
tpwr    1         math    f
pw      58
pwr     7.5      werr
dl      3.000    wexp
tof     615.5   wbs
nt      10000   wnt
ct      752
alock   not used
gain    not used
flags   n
fl      n
fn      n
dp      y
hs      nn
DISPLAY
sp      -1256.8
wp      31414.3
vs      423
sc      0
wc      250
hzmm    125.66
ts       500.00
rfl     6304.2
rff      0
th      68
ins     1.000
ai      cdc    ph
    
```



4ba

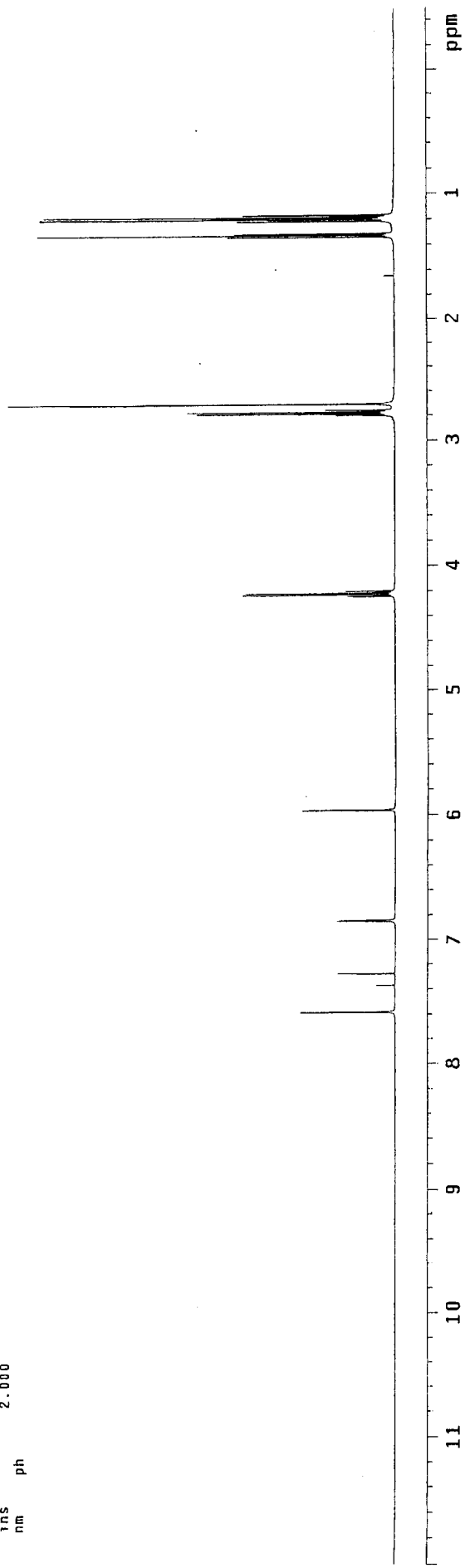


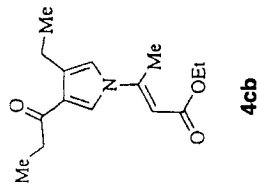


4cb

```

exp1 s2pu1
SAMPLE DEC. & VI
date Feb 15 2005 dfrq 125.795
solvent CDCl3 C13
file CDC13 37
ACQUISITION exp 0
sfrq 500.235 nnn
in H1 dmm c
at 3.200 dmf 10000
np 64000 dseq
sw 10000.0 dres 1.0
fb not used homo n
bs 4 PROCESSING
ss 1 wfile
tpwr 59 proc ft
pw 9.8 fn 131072
d1 2.000 math f
tof 1498.2
nt 20 werr
ct 20 wexp
alock n wbs
gain not used wnt
FLAGS
f1 n
f2 n
f3 n
f4 y
f5 nn
DISPLAY
sp -250.2
wp 6252.8
ve 62
sc 0
wc 250
hzmm 40.00
fs 119.21
rf1 4632.8
rfp 3636.7
th 23
ins nm
nm 2.000 ph
  
```



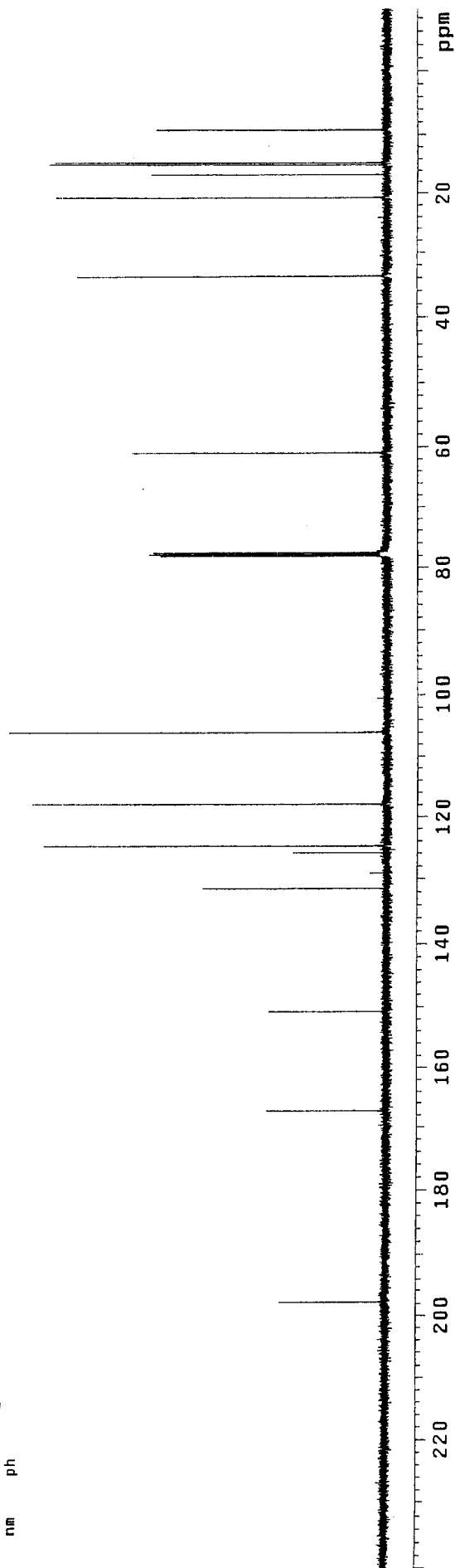


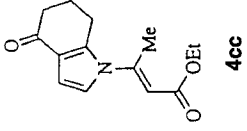
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exp5 s2pu1
SAMPLE
date Feb 15 2005
solvent CDCl3
file ACQUISITION exp
sfrq 125.796
in C13
at 1.736
np 131010
sw 37735
fb not used
bs 8
ss 1
tpwr 53
pw 6.9
d1 0.763
tof 631.4
nt 10000
ct 904
alock not used
gain not used
flags
il n
in n
dp y
hs nn
DISPLAY
sp -1258.3
wp 31448.0
vs 60
sc 0
wc 250
hzmm 125.73
ls 500.00
rf1 15911.8
rfp 9686.0
th 5
ins 1.000
nm ph
    
```

```

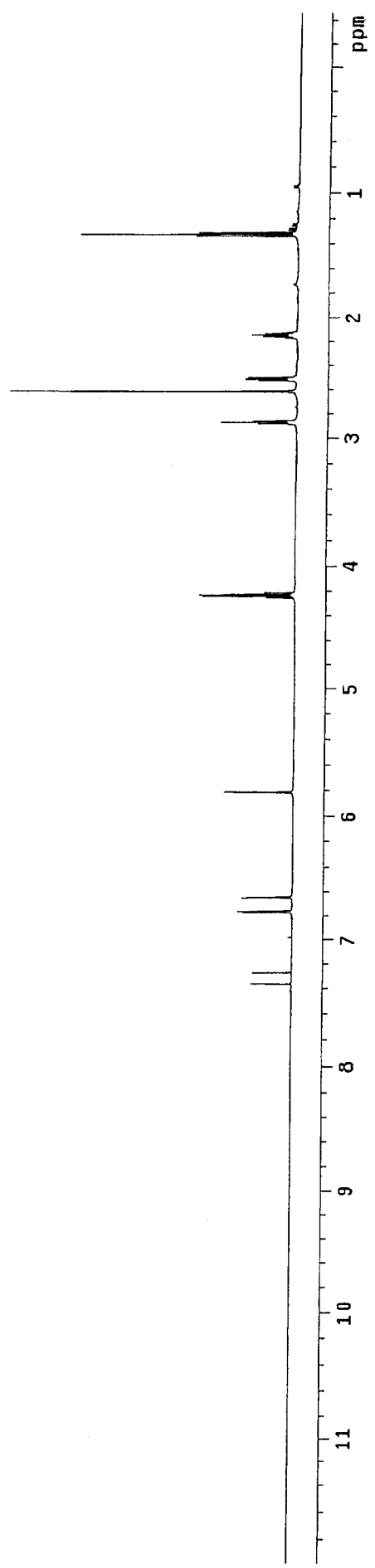
DEC. & VT
dfrq 500.233
dn H1
dpwr 37
dof -500.0
dm y
dmm w
dmf 10000
dseq 1.0
dres n
homo n
PROCESSING
i 1
lb 0.30
vtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
    
```





```

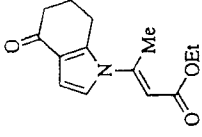
exp1 s2pu1
SAMPLE DEC. & VT
date Feb 15 2005 dfrq 125.295
solvent CDC13 dn C13
file /data/export/~ dpwr 37
home/movassag/Mao/~ dof 0
rocky/Mao_021505-A~ dmn nnn
011079_1H.fid dm c
ACQUISITION dmf 10000
sfrq 500.235 dseg
tn H1 dres 1.0
at 3.200 homo PROCESSING n
np 64000
SW 10000.0 wfile
fb not used proc ft
bs 4 fn 131072 f
ss 1 math
tpwr 59
pw 9.8 werr
d1 2.000 wexp
tof 1498.2 wbs
ct 20 wnt
allok n
gain not used
flags n
ii n
in n
dp y
hs mn
DISPLAY
sp -250.4
wp 6246.3
vs 46
sc 0
wc 250
hzmm 2.00
fs 100.00
rfl 4632.9
rfp 3636.7
th 7
ins 2.000
nm ph
  
```



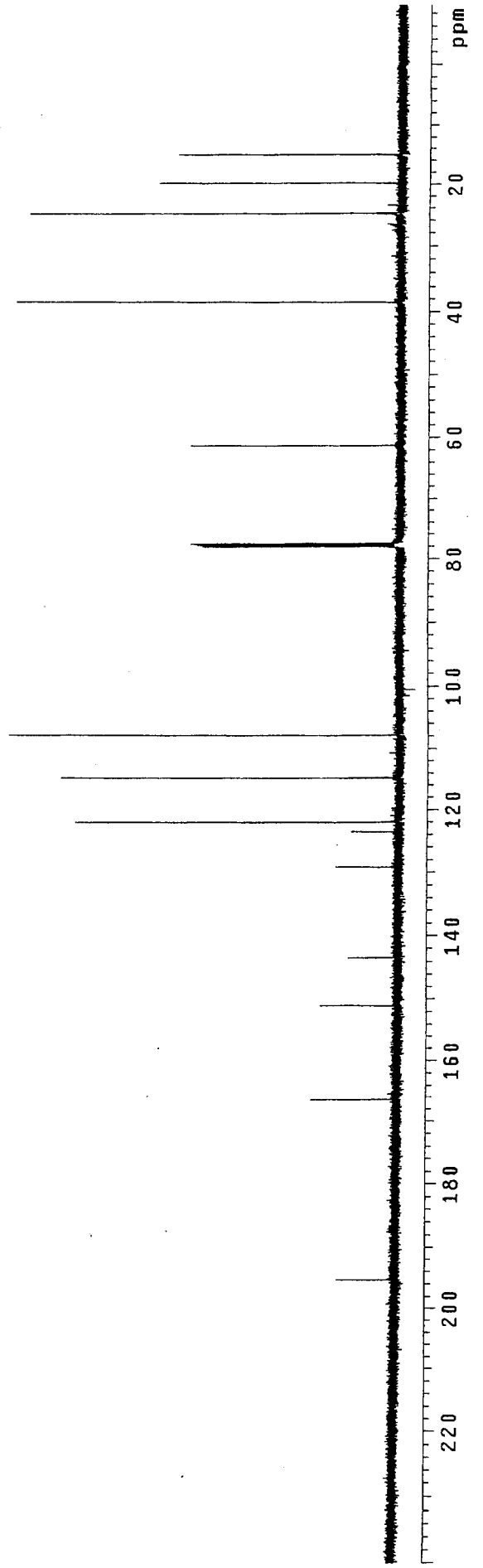
exp1 s2pu1

```

SAMPLE      DEC. & VT
date    Feb 15 2005    dfrq    500.233
solvent  CDC13         dn      HI
file    /data/export/~ dpwr    37
home/movassag/Mao/~ dof    -500.0
rocky/Mao_021505_A~ dm
011079_13C.fid  dmm
ACQUISITION dmf      10000
sfrq    125.796    dseg
tn      1.736    dres    1.0
at      131010    homo    n
np      37735.8    lb      PROCESSING
sw      not used  wfile   0.30
bs      8         proc    ft
ss      1         fn      131072
tpwr    53        math
pw      6.9
dl      0.763    werr
tof     631.4    wexp
nt      1e+06    wbs
ct      616     wnt
alock   n
gain    not used
flags   not used
il      n
in      n
dp      y
hs      nn
DISPLAY
sp      -1258.3
wp      31448.1
vs      3026
sc      0
wc      250
hzmms  125.79
ls      500.00
rf1     15811.8
rfp     9686.0
th      4
lms     1.000
al      ph
    
```

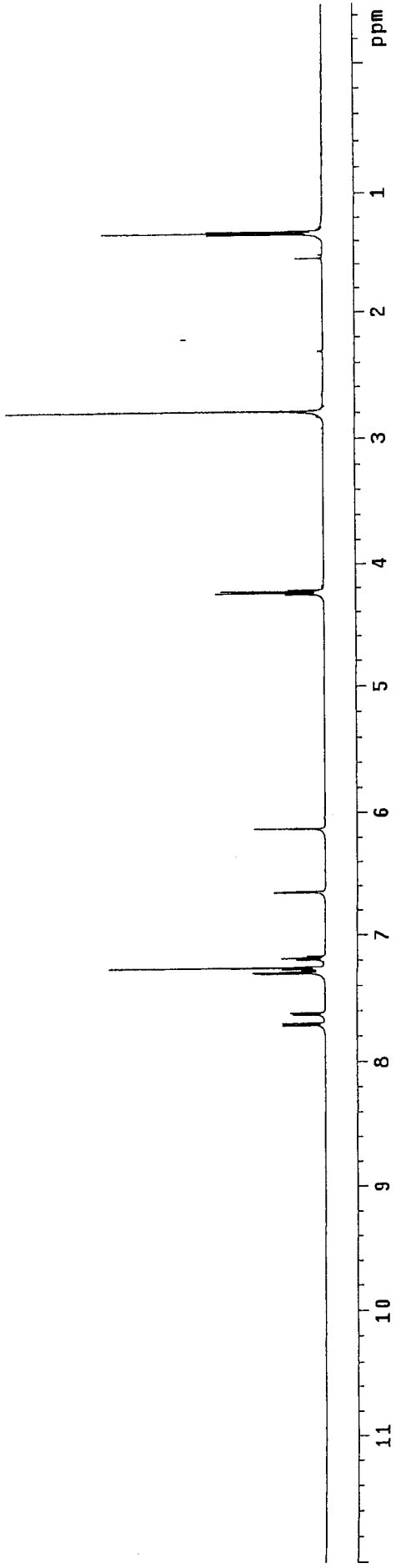
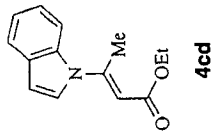


4cc



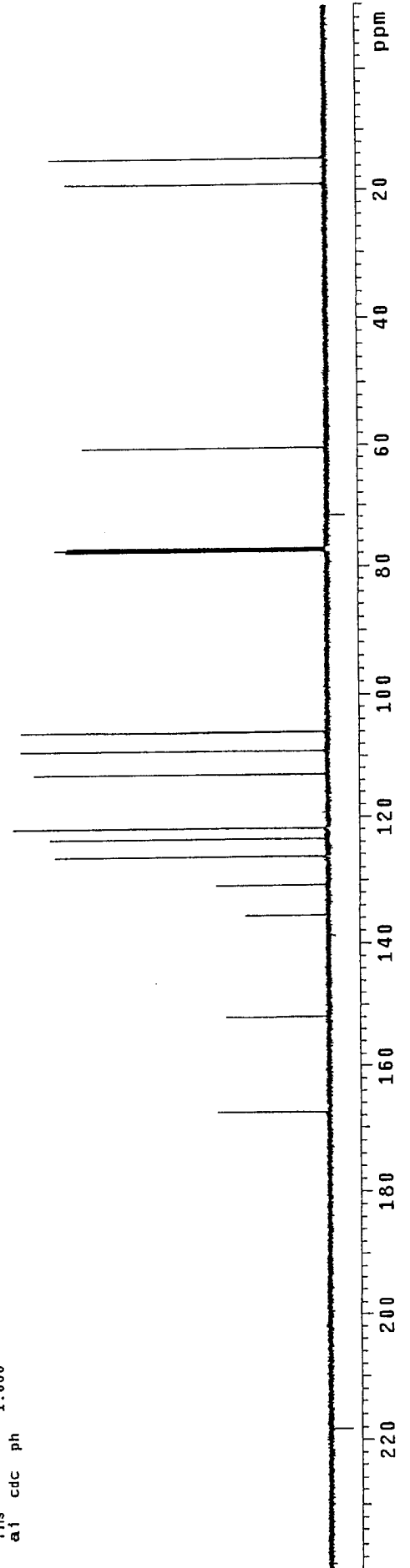
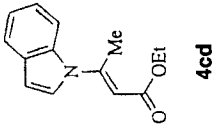
```

exp1 s2pul
SAMPLE DEC. & VT
date Apr 25 2005 dfrq 125.674
solvent CDC13 dn C13
file /data/export/~ dpwr 34
home/moyassag/Mco/~ dof 1498.1
bullwinkle/Mco_042~ dm nmh
505_A01164_in.fid dmm w
ACQUISITION dmf 10000
sfrq 499.749 dseq
tn H1 dres 1.0
at 3.277 homo n
np 65536 PROCESSING
sw 9998.8 wfile
fb not used proc ft
bs 4 fn 65536
tpwr 56 math f
pw 8.2
d1 2.000 verr
tof 1498.1 wexp
nt 18 wbs
ct 18 wnt
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY -250.1
sp 6246.8
vs 32
sc 0
wc 250
hzmm 4.87
ls 840.27
rfl 1015.4
rfp 0
th 7
ins 2.000
al cdc ph
    
```

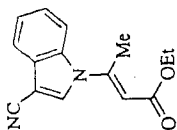


```

exp2 s2pul
SAMPLE DEC. & VT
date Apr 30 2005 dfrq 499.747
solvent CDC13 dn H1
file /data/export/~ dpwr 34
home/movassag/Mao/~ dof 0
bu1lwinkle/Mao.043~ dm yyy
005_AQI1164_13C.f1~ dmm W
dmf 10000
ACQUISITION
sfrq 125.673 dseq
tn 125.673 dres 1.0
at C13 homo n
np 65536 lb PROCESSING 1.00
sw 37718.1 wfile ft
fb not used proc 131072
bs 16 fn
ss 1 math
tpwr 58
pw 7.5 werr
d1 3.000 wexp
tof 615.5 wbs
nt 10000 wnt
ct 1168
alock n
gain not used
FLAGS
f1 n
in n
dp y
hs nn
DISPLAY
sp -1256.8
wp 31414.3
vs 447
sc 0
wc 250
hzmm 150.87
ls 500.00
rfl 6304.2
rfp 0
th 8
ims 1.000
at cdc ph
  
```



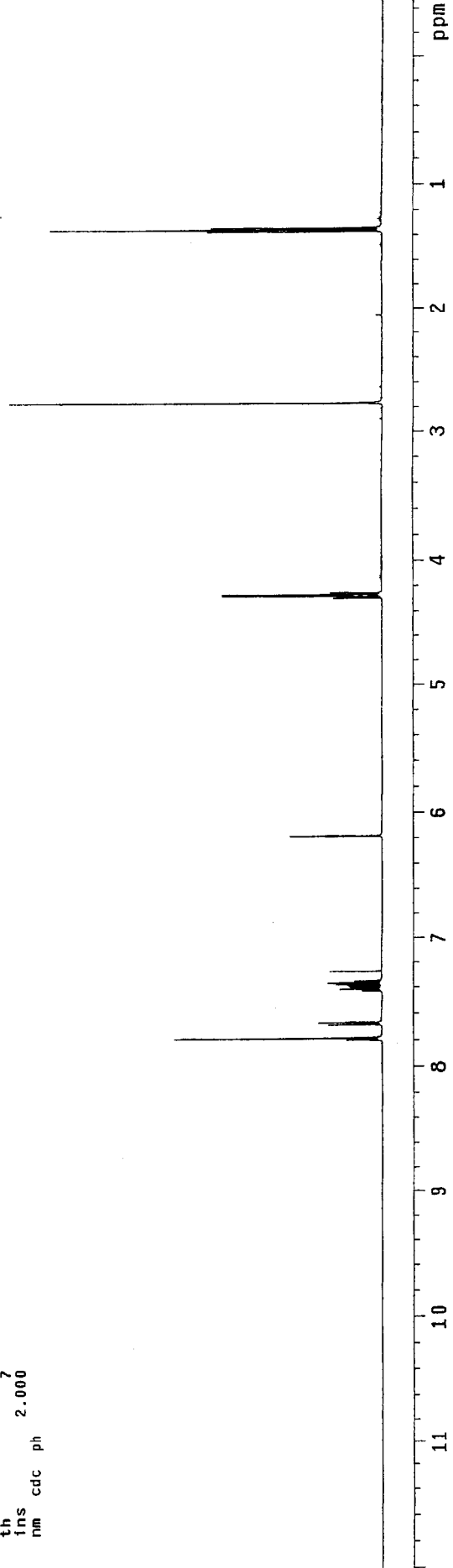


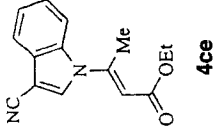


4ce

```

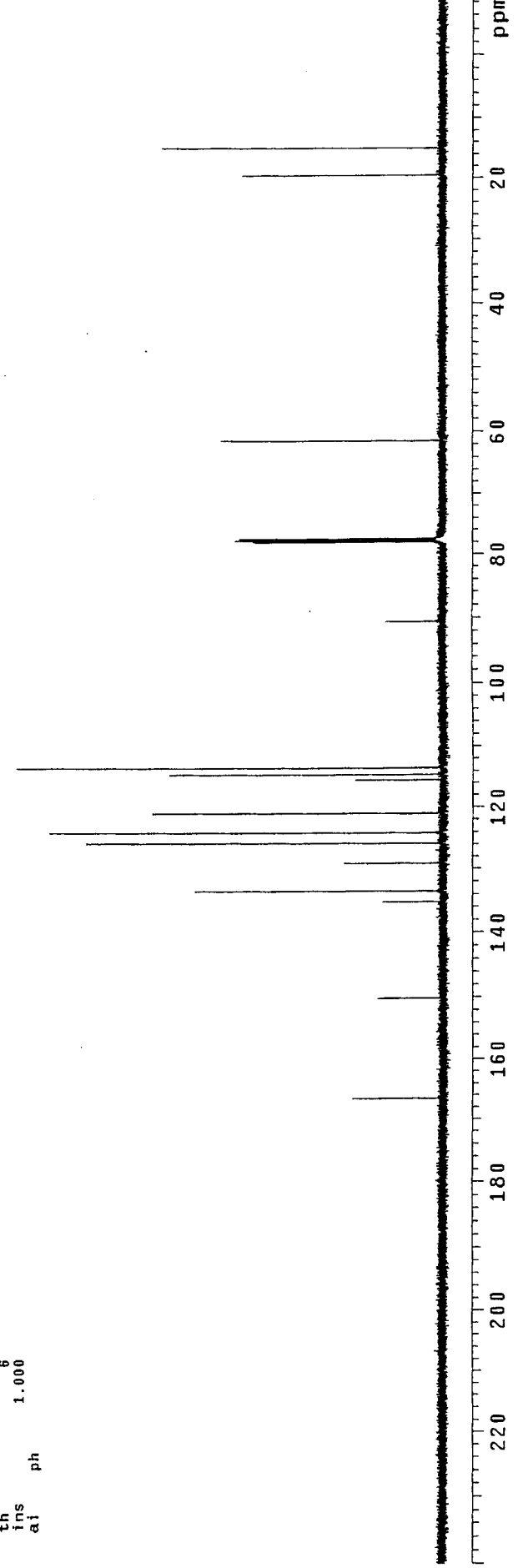
exp5 s2pul
SAMPLE          DEC. & VT
date  feb 5 2005  dfrq      125.677
solvent  CDC13      dn      C13
file /data/export/~ dpwr      34
home/movassag/Mao/~ dof      1498.1
bullwinkle/Mao_020~ dm      nnn
505_A011084_1H_fid  dmw      w
ACQUISITION     dmf      10000
sfrq  499.758      dseq
tn      H1          dres      1.0
at      3.277      homo      n
np      65536      PROCESSING
sw      9998.8      wtfile
fb      not used   proc      ft
bs      4          fn      65536
tpwr    56        math      f
pw      8.2
d1      2.000     werr
tof     1488.1   wexp
nt      18       wbs
ct      18       wnt
alock   not used
gain    not used
FLAGS   n
il      n
in      n
dp      y
hs      nn
DISPLAY -250.1
sp      6246.8
vs      59
sc      0
wc      250
hzamm   2.36
is      33.57
rfl     1002.0
th      7
ins     2.000
nm      cdc      ph
  
```

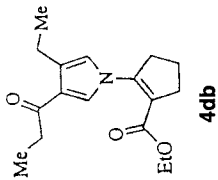




```

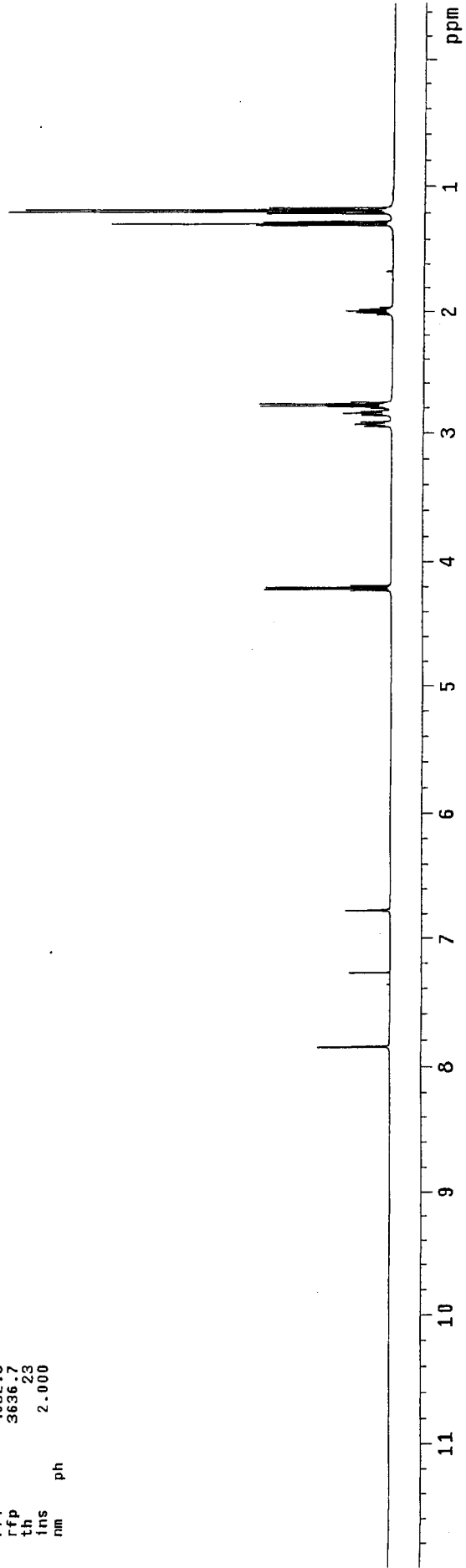
exp5 s2pu)
SAMPLE
date Feb 15 2005 dfrq DEC. & VT 500.233
solvent CDC13 dn H1
file /data/export/~ dpwr 37
home/movassag/Mao/~ dof -500.0
rocky/Mao.021505.A~ dm y
011084_13C.fid dmm w
ACQUISITION dmf 10000
sfrq 125.786 dseq
tn C13 dres 1.0
at 1.736 homo n
np 131010
sw 37795.8 lb PROCESSING 0.30
fb not used wtfile ft
bs 8 fn 131072
ss l math f
tpwr 53
pw 6.9
d1 0.763 werr
tof 631.4 wexp
nt 10000 wbs
ct 896 wnt
atock n
gain not used
flags
il n
in n
dp y
hs nm
sp -1258.3
wp 31448.1
vs 315
sc 0
wc 250
hzmm 125.78
is 500.00
rf1 15311.8
rff 9686.0
th 6
ins 1.000
ai ph
  
```

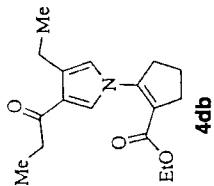




```

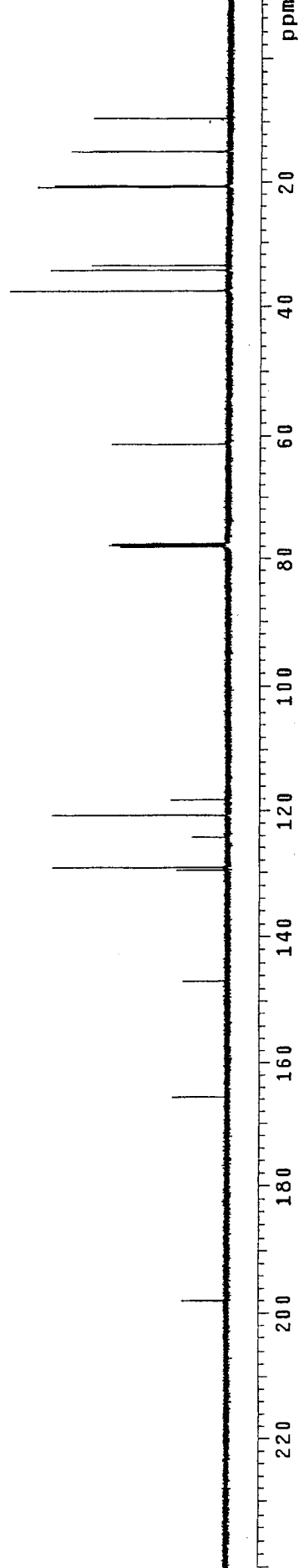
exp1 s2pu1
SAMPLE
date Feb 15 2005 dfrq DEC. & VI 125.785
solvent CDC13 dn C13
file /data/export/~ dpwr 37
home/movassag/Mao/~ dof 0
rocky/Mao_021505_A~ dm nnn
OII087_1H.fid dmm C
ACQUISITION dmf 10000
sfrq 500.235 dseq
tn H1 dres 1.0
at 3.200 homo n
np 64000
sw 10000.0 wtfile
fb not used proc ft
bs 4 fn 131072
ss 1 math f
tpwr 59
pw 9.8 werr
dl 2.000 wexp
tof 1498.2 wbs
nt 20 wnt
ct 20
atlock n
gain not used
flags
it n
in n
dp Y
hs nn
DISPLAY
sp -250.4
wp 6246.3
vs 61
sc 0
wc 250
hzmm 3.57
ls 119.21
rf1 4632.8
rfp 3636.7
th 23
ins 2.000
nm ph
  
```

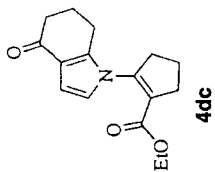




```

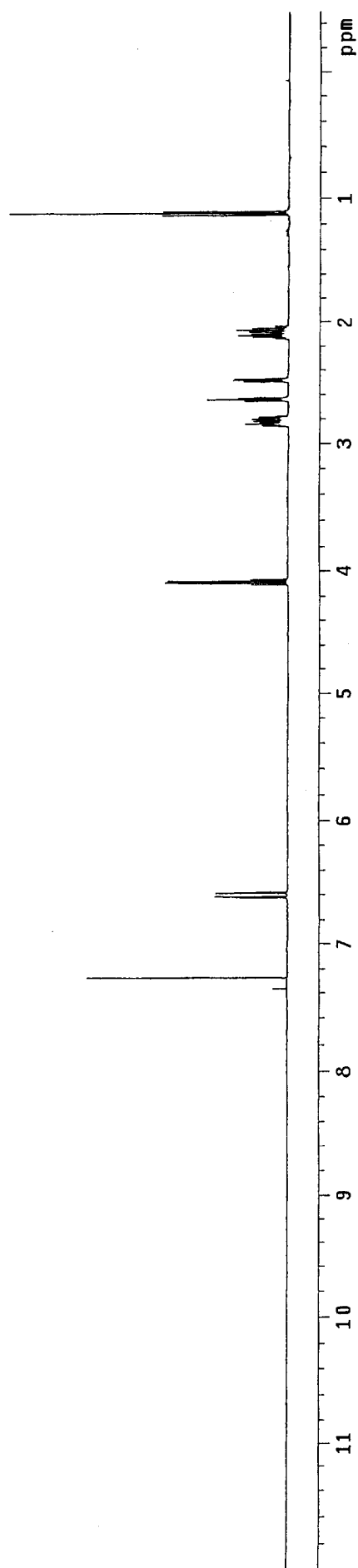
exp1 s2pul
SAMPLE
date Feb 15 2005 dfrq DEC. & VT 500.233
solvent CDC13 dn H1
file /data/export/~ dpwr 37
home/movassag/Mao/~ dof -500.0
rocky/Mao.021505.A~ dm Y
011087_13c.fid dmm W
ACQUISITION dmf 10000
sfrq 125.796 dseq
tn C13 dres 1.0
ap 1.736 homo n
np 131010
sw 37735.8 lb PROCESSING 0.30
fb not used wfile
bs 8 proc ft
ss 1 fn 131072
tpwr 53 math f
pw 6.9
d1 0.763 werr
tof 631.4 wexp
nt 10000 wbs
ct 584 wnt
atock n
gain not used
flags
  il n
  in n
  dp y
  hs nn
DISPLAY
sp -1258.3
wp 31448.1
vs 35
sc 0
wc 250
hzmm 125.79
is 500.00
rfl 15911.8
rfp 9686.0
th 5
ins 1.000
nm ph
  
```

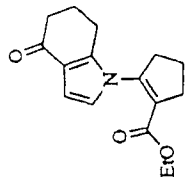




```

exp1 s2pul
SAMPLE
date Feb 12 2005
solvent CDC13
file /data/export/~ dpwr
home/movassag/Mac/~ dof
bulwinkle/Mac_021~ dmm
205_AQII088_1H.fid dmf
ACQUISITION dmf 10000
sfrq 499.758 dseq
tn H1 dres 1.0
at 3.277 homo
np 65536
sw 9998.8 wtfile
fb not used proc ft
bs 4 fn 65536
tpwr 56 math
pw 8.2
dl 2.000 werr
tof 1498.1 wexp
nt 18 wbs
ct 18 wnt
alock n
gain not used
flags
il n
in n
dp y
hs nn
DISPLAY
sp -250.4
wp 6246.5
vs 45
sc 0
wc 250
hzmm 40.00
is 33.57
rfl 1002.5
rfp 0
th 7
ins cdc
nm ph 2.000
    
```

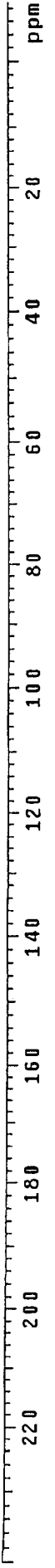


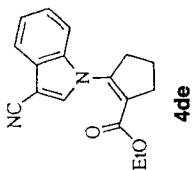


4dc

```

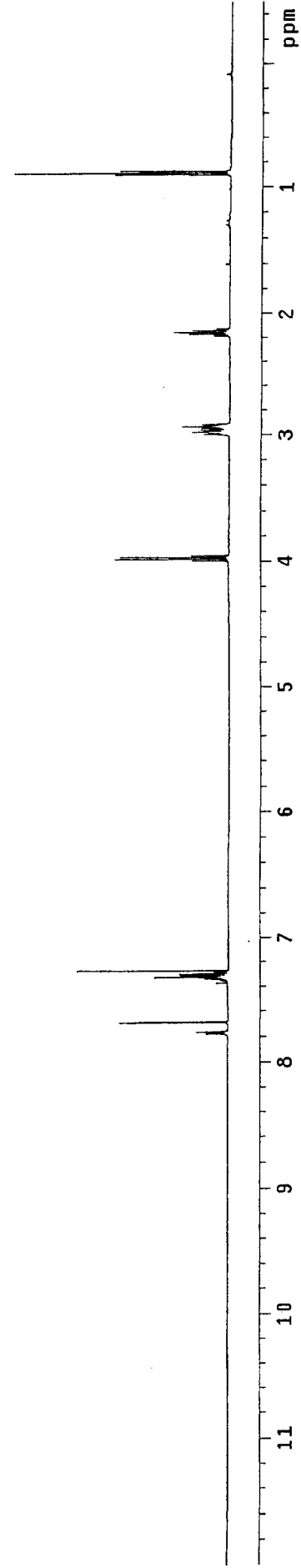
exp1 s2pu1
SAMPLE DEC. & VT
date Feb 12 2005 dfrq 499.756
solvent CDCl3 dn H1
file /data/movassa~ dpwr 34
g/Mac/Mac_021205.A~ dof 0
OII088_13C.fid dm YYY
ACQUISITION W 10000
sfrq 125.676 dmf 1.0
tn C13 dseq n
at 0.869 dres n
sp 65536 homo DEC2
sw 37718.1 dfrq2 0
fb not used dn2 1
bs 16 dn2 1
ss 1 dpwr2 0
tpwr 58 dof2 0
pw 7.5 dm2 n
d1 3.000 dmm2 C
tof 615.5 dmf2 10000
nt 10000 dseq2 n
ct 832 dres2 1.0
alock not used dn2 n
gain not used dfrq3 DEC3 0
FLAGS dn3 n
il in n dpwr3 1
dp in y dof3 0
hs nm dn3 n
DISPLAY dmm3 C
SP -1257.2 dmfs 10000
wp 31415.3 dseq3 n
vs 677 dres3 1.0
sc homo3 n
WC 250 PROCESSING
hzm 125.66 lb 1.00
fs 500.00 wtfile
rfl 8304.1 proc ft
th g fn 131072
tms 7 math f
al cdc ph 1.000 werr
wexp
wbs
wnt
  
```

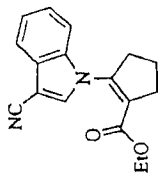




```

exp1 s2pu1
SAMPLE DEC. & VT
date Feb 12 2005 dfrq 125.677
solvent CUC13 dn C13
file /data/export/~ dpwr 34
home/movassag/Mao/~ dof 1498.1
bul1winkle/Mao_021~ dm nnn
205_AQII089_1H_fid dmm v
ACQUISITION dmf 10000
sfrq 499.758 dseq
tn HI dres 1.0
at 3.277 homo n
np 65536 PROCESSING
sw 9998.8 wfile
fb not used 4 proc ft
bs 56 fn 65536
tpwr 56 math f
pw 8.2
d1 2.000 werr
tof 1498.1 wexp
nt 18 wbs
ct 18 wnt
alock n
gain not used
FLAGS
il n
in n
dp y
hs mn
DISPLAY
sp -250.4
wp 6246.5
vs 35
sc 0
wc 250
h2mm 40.00
ls 33.57
rf1 4635.5
rfp 3633.2
th ins
nm cdc ph 2.000
  
```

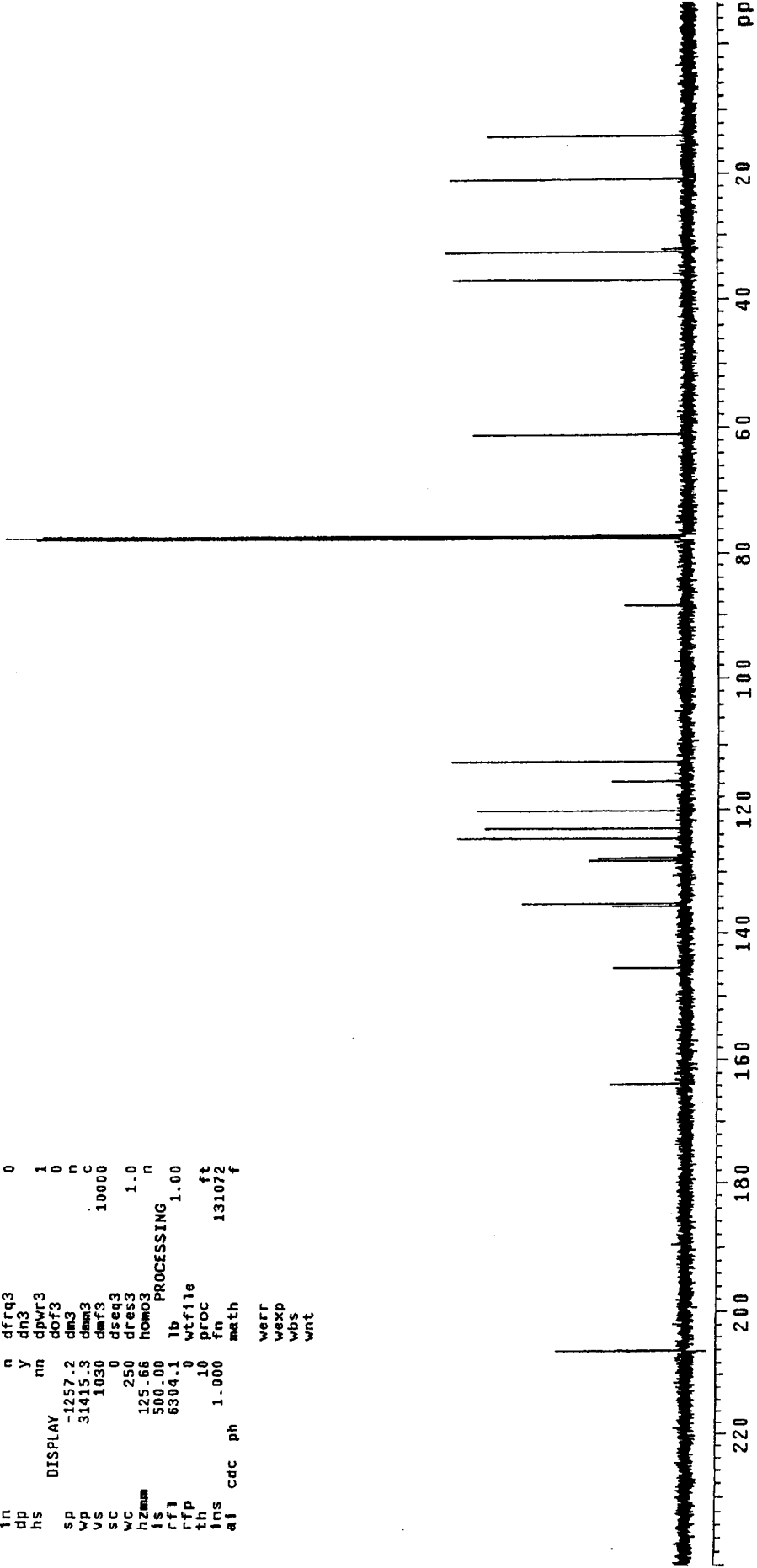




4de

```

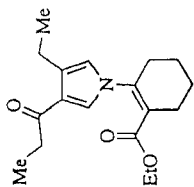
exp3 s2pu1
SAMPLE DEC. 5 VT
date Feb 12 2005 dfrq 499.756
solvent CDC13 dn HI
file ACQUISITION exp dpwr 34
sfrq 125.676 dm VVY 0
in 0.869 dmf W 10000
at 65536 dseq 1.0 n
sw 37718.1 dres homo DEC2
fb not used 16
bs 1 dfrq2 0
ss 58 dn2
tpwr 7.5 dpwr2 1
d1 3.000 dof2 0
tof 615.5 dm2 n
nt 10000 dmm2 C
ct 800 dmf2 10000
atlock n
gain not used
FLAGS n
11 n dfrq3 0
in n dn3
dp y
hs nn
DISPLAY -1257.2 dm3
sp 31415.3 dmm3 n
vs 1030 dmf3 C
sc 0 dseq 10000
wc 250 dres3 1.0
hzmm 125.68 homo3 n
ls 500.09 PROCESSING
rf1 6304.1 lb wtfile 1.00
rfp 10 proc ft
th 131072 fn
ins ai cdc ph math 131072 f
werr
wexp
wbs
wnt
  
```



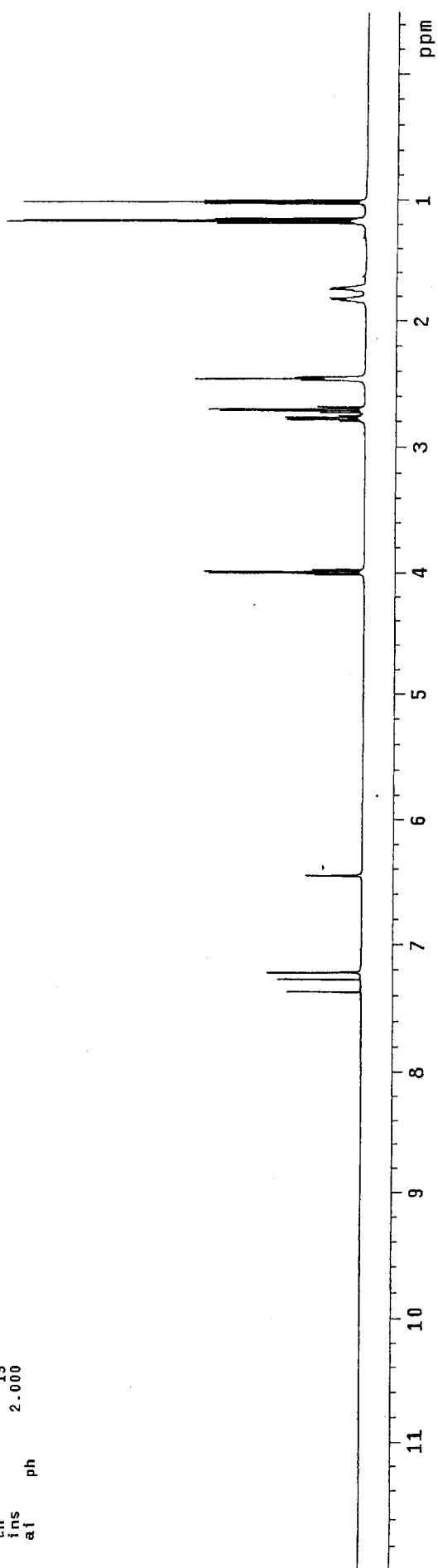


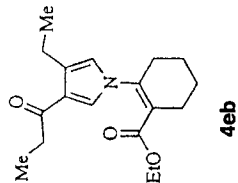
```

exp1 s2pu1
SAMPLE DEC. & VT
date Feb 15 2005 dfrq 125.795
solvent CDC13 dn C13
file /data/export/~ dpwr 37
home/movassag/Mao/~ dof 0
rocky/Mao_021505_A~ dm nnn
OII05_1H.fid dmm C
ACQUISITION dmf 10000
sfrq 500.235 dseq
tn HI dres 1.0
at 3.200 homo n
np 64000
sw 10000.0 wfile
fb not used proc ft
bs 4 fn 131072
ss 1 math
tpwr 59
pw 9.8 werr
d1 2.000 wexp
tof 1498.2 wbs
ct 20 wnt
atock n
gain not used
FLAGS
f1 n
in n
dd y
hs nm
DISPLAY
sp -250.1
wp 6246.6
vs 37
sc 0
wc 250
hzmm 7.04
is 119.21
rf1 4632.9
rffp 3636.7
th 15
ins 2.000
ai ph
  
```



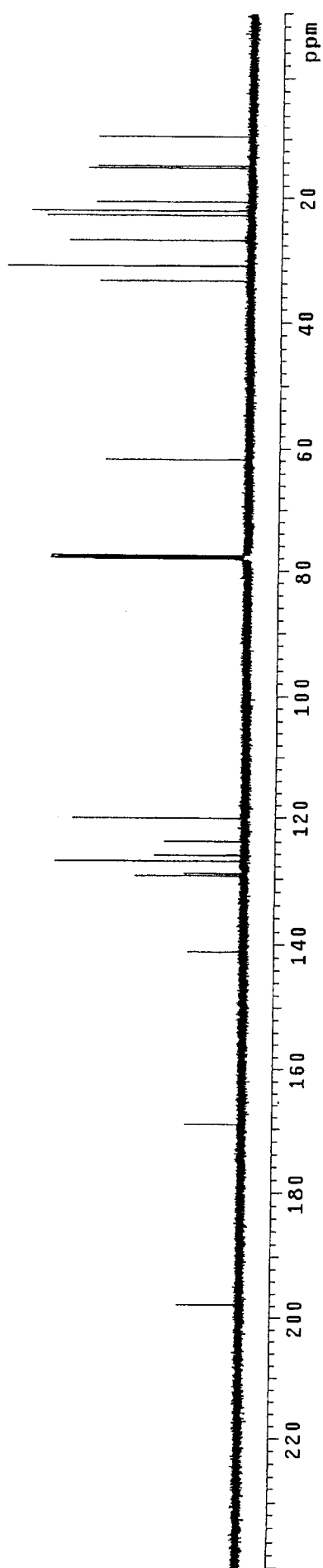
4eb

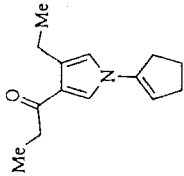




```

exp1 s2pu1
SAMPLE DEC. & VT
date Feb 15 2005 dfrq 500.233
solvent CDC13 dn H1
file /data/export/~ dpwr 37
home/movassag/Mao/~ dof -500.0
rocky/Mao_021505_A~ dn
011055_13C.fid dnm w
ACQUISITION dmf 10000
sfrq 125.796 dseq
tn C13 dres 1.0
at 1.736 homo n
np 131010 PROCESSING 0.30
sw 37735.8 lb
fb not used wtfile
bs 8 proc
ss 1 fn 131072
tpwr 53 math ft
pw 6.9 werr f
di 0.763 werr
tof 631.4 wexp
nt 10000 wbs
ct 736 wnt
alock n
gain not used
FLAGS
i1 n
in n
dp y
hs nn
DISPLAY
sp -1258.3
wp 31448.1
vs 39
sc 0
wc 250
hzmm 125.79
is 500.00
rfl 15311.8
rfp 9686.0
th 6
ins 1.000
nm ph
  
```





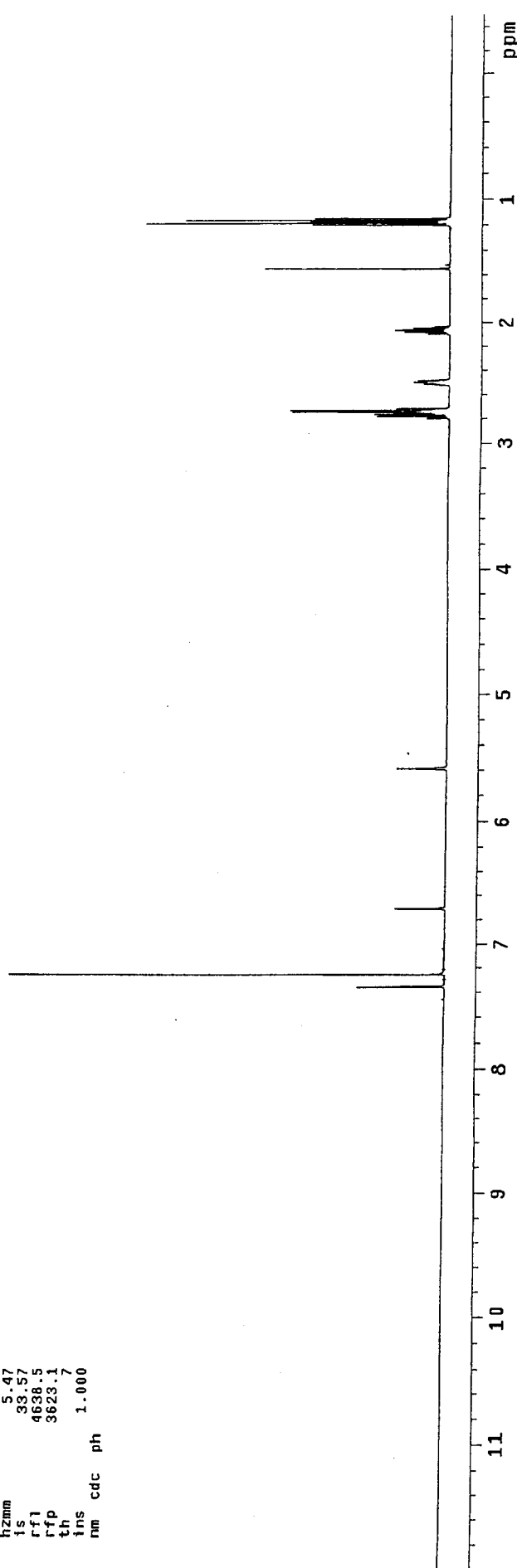
4fb

```

expi s2pu1
SAMPLE
date Apr 30 2005
solvent CDC13
file /data/export/~
home/movassag/Mac/~
bulwinkle/Mac_043~
005_A01189_in.fid
ACQUISITION
sfrq 499.749
in H1
at 3.277
np 65536
sw 9998.8
fb not used
bs 4
tpwr 56
pw 8.2
d1 2.000
tof 1498.1
nt 20
ct 20
alock not used
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.1
wp 6246.5
vs 69
sc 0
wc 250
hzmm 57.47
is 38.57
rf1 4638.5
rfp 3623.1
th 7
ins 1.000
nm cdc
ph
    
```

```

DEC. & VT
dfrq 125.674
dn C13
dpwr 34
dof 1498.1
dm nnn
dmm w
dmf 10000
dseq 1.0
dres n
homo
PROCESSING
wtfile ft
proc 65536
fn f
math
werr
wexp
wbs
wnt
    
```



exp2 s2pu1

SAMPLE DEC. & VT  
 date Apr 30 2005 dfrq 499.747  
 solvent CDC13 dn H1  
 file /data/export/~ dpwr 34  
 home/movassag/Mac/~ dof 0  
 builwinkle/Mac\_043~ dm VVY  
 005\_A011169\_13C.f1~ dmm w  
 dmf 10000  
 ACQUISITION d  
 sfrq 125.673 dseq  
 tn 125.673 dres 1.0  
 at 0.869 homo n  
 np 65536 lb PROCESSING  
 sw 37718.1 wtfile 1.00  
 fb not used proc ft  
 bs 16 fn 131072  
 ss 1 math f  
 tpwr 58  
 pw 7.5 werr  
 dl 3.000 wexp  
 tof 615.5 wbs  
 nt 100000 wnt  
 ct 432  
 alock n  
 gain not used  
 flags

ll n  
 ln n  
 dp y  
 hs nn  
 DISPLAY  
 sp -1256.8  
 wp 31414.3  
 vs 328  
 sc 0  
 wc 250  
 hzmm 125.66  
 fs 500.00  
 rfl 6304.2  
 rfp 0  
 th 10  
 lms 1.000  
 al cdc ph

