

# Novel Pd<sup>II</sup>-Mediated Cascade Carboxylative Annulation to Construct Benzo[*b*]furan-3-Carboxylic Acids

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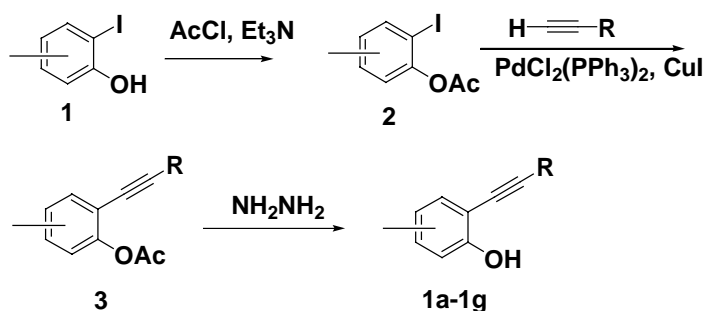
### ***I. General Methods***

Materials: Reaction solvents were commercially purchased from *Acros* and *Aldrich* without further purification and reagents were used as received. Reactions for the synthesis of the starting material were monitored by thin-layer chromatography (TLC) on 0.25 mm precoated Merck Silica Gel 60 F<sub>254</sub>, visualizing with ultraviolet light or phosphomolybdic acid stain. Flash column chromatography was performed on Merck Silica Gel 60 (230-400 mesh) using reagent grade hexanes, dichloromethane, methanol and ethyl acetate.

Analysis: <sup>1</sup>H NMR spectra were recorded on a INOVA plus Varian 500 MHz spectrometer and are referenced to residual solvents peaks (DMSO-d<sub>6</sub>: <sup>1</sup>H: δ 2.50 ppm (DMSO-d<sub>6</sub>)). Other peaks shown in the blank: δ 3.31 ppm (H<sub>2</sub>O in DMSO-d<sub>6</sub>) and δ 1.22 ppm (poly/oligopropylene dissolved in DMSO-d<sub>6</sub> from polypropylene 96-well plate). <sup>1</sup>H-<sup>1</sup>H couplings are assumed to be first order, and peak multiplicity is reported as s (single), d (doublet), t (triplet), q (quartet), m (multiplet), or b (broad). In regards to the products cleaved from the beads (10 macrobeads), their <sup>1</sup>H NMR spectra were recorded after 16 scans. All LC-MS spectra were obtained on a Micromass

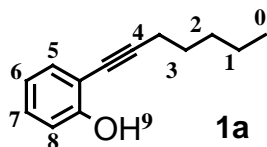
ZQ mass spectrometer in electrospray positive ionization (ES+) mode in line with a Waters 2790 HPLC system (Separations Module, Alliance<sup>TM</sup>). LC-MS chromatography was performed on a Waters Symmetry C18 Column (3.5  $\mu$ m, 2.1X 50 mm, W93491F 26) using a flow rate of 0.4 mL/min in a gradient of 15-100% CH<sub>3</sub>CN in H<sub>2</sub>O in 9 min with 1 min wash. Column temperature: 30 °C. [ES<sup>+</sup>]: Capillary (kV): 3.5; Cone (V): 70; Extractor (V): 5; RF Lens (V): 0.3; Source temperature (°C): 150; Cone temperature (°C): 20; Desolvation temperature (°C): 400; Cone gas flow (L/Hr): 114; Desolvation gas flow (L/Hr): 466. Injection Volume: 10  $\mu$ L. Software: Masslynx. Normally, product cleaved from one bead is sufficient for LC-MS analysis. After the product was dried completely, it was dissolved in 0.15 mL THF (HPLC grade) for LC-MS test, which was reported as: LC-MS (retention time, [M+1]<sup>+</sup>/ [M+Na]<sup>+</sup> (ES+)).

## II. Starting materials synthesis.

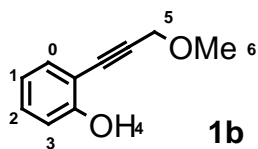


### General synthetic procedures for making the starting materials

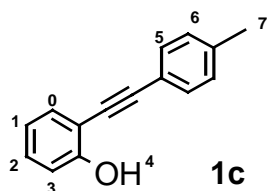
Please see the supporting information from *Org. Lett.* **2000**, 2, 297-299.



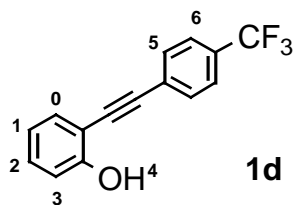
2-Hept-1-ynyl-phenol (**1a**) <sup>1</sup>H NMR (500 MHz, d<sub>6</sub>-DMSO):  $\delta$  9.64 (s, 1 H<sub>9</sub>), 7.19 (d, 1 H<sub>5</sub>,  $J$  = 7.5 Hz), 7.09 (t, 1 H<sub>6</sub>,  $J$  = 5.75 Hz), 6.84 (d, 1 H<sub>8</sub>,  $J$  = 8.0 Hz), 6.71 (t, 1 H<sub>7</sub>,  $J$  = 8.5 Hz), 2.40-2.37 (m, 2 H<sub>4</sub>), 1.53-1.50 (m, 2 H<sub>3</sub>), 1.40-1.36 (m, 2 H<sub>2</sub>), 1.32-1.28 (m, 2 H<sub>1</sub>), 0.89-0.85 (m, 3 H<sub>0</sub>).



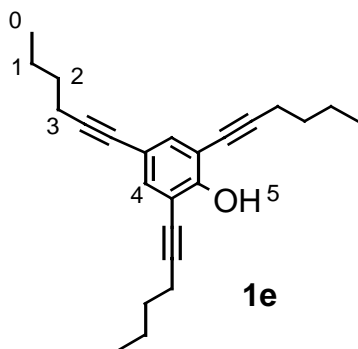
2-(3-Methoxy-prop-1-ynyl)-phenol (**1b**) <sup>1</sup>H NMR (500 MHz, d<sub>6</sub>-DMSO):  $\delta$  7.36 (d, 1 H<sub>0</sub>,  $J$  = 5.0 Hz), 7.25 (t, 1 H<sub>1</sub>,  $J$  = 7.5 Hz), 6.95 (d, 1 H<sub>3</sub>,  $J$  = 8.5 Hz), 6.87 (t, 1 H<sub>2</sub>,  $J$  = 7.5 Hz), 5.92 (s, 1 H<sub>4</sub>), 4.39 (s, 2 H<sub>5</sub>), 3.47 (s, 3 H<sub>6</sub>).



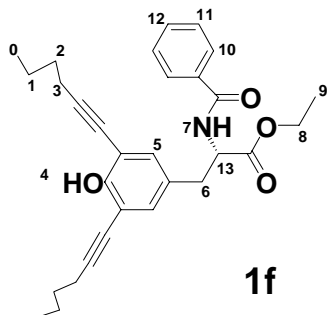
2-p-Tolylethynyl-phenol (**1c**)  $^1\text{H}$  NMR (500 MHz,  $\text{d}_6\text{-DMSO}$ ):  $\delta$  7.49-7.47 (m, 2  $\text{H}_5$  & 2  $\text{H}_6$ ), 7.30 (t, 1  $\text{H}_1$ ,  $J = 8.0$  Hz), 7.21 (d, 1  $\text{H}_0$ ,  $J = 8.0$  Hz), 7.05 (d, 1  $\text{H}_3$ ,  $J = 8.0$  Hz), 6.95 (t, 1  $\text{H}_2$ ,  $J = 7.5$  Hz), 5.98 (s, 1  $\text{H}_4$ ), 2.42 (s, 3  $\text{H}_7$ ).



2-(4-Trifluoromethyl-phenylethynyl)-phenol (**1d**)  $^1\text{H}$  NMR (500 MHz,  $\text{d}_6\text{-DMSO}$ ):  $\delta$  7.66-7.62 (m, 2  $\text{H}_5$  & 2 $\text{H}_6$ ), 7.45 (d, 1  $\text{H}_0$ ,  $J = 7.5$  Hz), 7.32 (t, 1  $\text{H}_1$ ,  $J = 7.0$  Hz), 7.01 (d, 1  $\text{H}_3$ ,  $J = 8.5$  Hz), 6.94 (t, 1  $\text{H}_2$ ,  $J = 7.5$  Hz), 5.82 (s, 1  $\text{H}_4$ ).

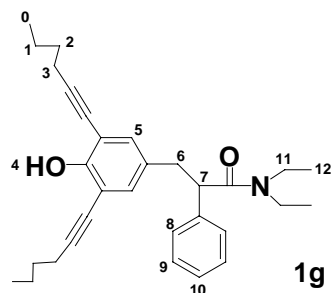


2,4,6-Tri-hex-1-ynyl-phenol (**1e**)  $^1\text{H}$  NMR (500 MHz,  $\text{d}_6\text{-DMSO}$ ):  $\delta$  9.44 (s, 1  $\text{H}_5$ ), 7.14 (s, 2  $\text{H}_4$ ), 2.41 (t, 6  $\text{H}_3$ ,  $J = 6.0$  Hz), 2.34 (t, 6  $\text{H}_2$ ,  $J = 6.0$  Hz), 1.51-1.40 (m, 6  $\text{H}_1$ ), 0.89 (t, 9  $\text{H}_0$ ,  $J = 6.0$  Hz).



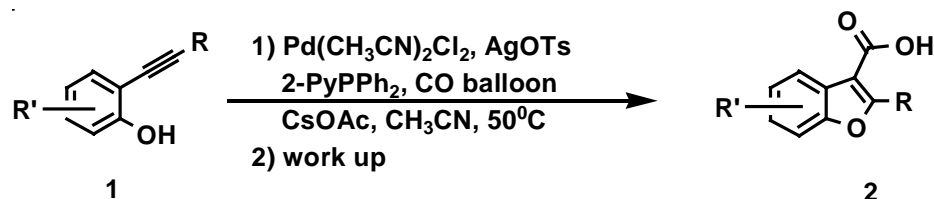
2-Benzoylamino-3-(3,5-di-hex-1-ynyl-4-hydroxy-phenyl)-propionic acid ethyl ester (**1f**)  $^1\text{H}$  NMR (500 MHz,  $\text{d}_6\text{-DMSO}$ ):  $\delta$  8.92 (s, 1  $\text{H}_4$ ), 8.75 (d, 2  $\text{H}_7$ ,  $J = 8.0$  Hz), 7.78 (d, 1  $\text{H}_{10}$ ,  $J = 7.5$  Hz), 7.53 (t, 2  $\text{H}_{12}$ ,  $J = 7.5$  Hz), 7.44 (t, 2  $\text{H}_{11}$ ,  $J = 7.5$  Hz), 7.12 (s, 1  $\text{H}_5$ ), 4.56-4.50 (m, 1  $\text{H}_{13}$ ), 4.10-

4.05 (m, 2 H<sub>8</sub>), 3.00-2.88 (m, 2 H<sub>6</sub>), 2.4 (t, 4 H<sub>3</sub>,  $J = 7.0$  Hz), 1.52-1.47 (m, 4 H<sub>2</sub>), 1.44-1.37 (m, 4 H<sub>1</sub>), 1.13 (t, 3 H<sub>9</sub>,  $J = 7.5$  Hz), 0.89 (t, 6 H<sub>0</sub>,  $J = 7.5$  Hz).

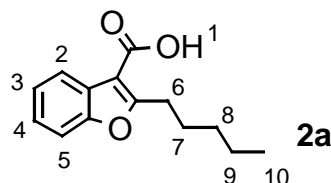


3-(3,5-Di-hex-1-ynyl-4-hydroxy-phenyl)-N,N-diethyl-2-phenyl-propionamide (**1g**)  $^1\text{H}$  NMR (500 MHz, d<sub>6</sub>-DMSO):  $\delta$  8.81 (s, 1 H<sub>4</sub>), 7.35 (d, 2 H<sub>8</sub>,  $J = 7.5$  Hz), 7.28 (t, 2 H<sub>9</sub>,  $J = 7.5$  Hz), 7.20 (t, 1 H<sub>10</sub>,  $J = 7.5$  Hz), 7.01 (s, 2 H<sub>5</sub>), 4.09-4.06 (m, 1 H<sub>7</sub>), 3.23-3.09 (m, 4 H<sub>11</sub>), 2.50-2.48 (m, 2 H<sub>6</sub>), 2.40 (t, 4 H<sub>3</sub>,  $J = 7.0$  Hz), 1.53-1.47 (m, 2 H<sub>2</sub>), 1.45-1.39 (m, 4 H<sub>1</sub>), 0.91-0.88 (m, 6 H<sub>0</sub> & 6 H<sub>12</sub>).

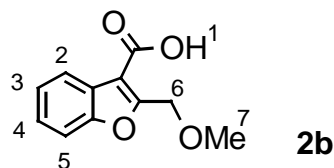
### III. Carboxylative Annulation (general stoichiometric method).



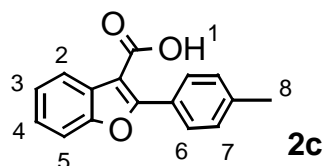
To proceed with carbonylative annulation reaction, Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub> (1.1 equiv), 2-Py-PPh<sub>3</sub> (1.1 equiv), AgOTs (4 equiv) and CsOAc (20 equiv) were mixed and degassed under high vacuum, and then charged with CO followed by addition of the dry CH<sub>3</sub>CN. The mixtures were then stirred at 50 °C under balloon pressure of CO for 10 min before the deprotected starting materials (**1a-1g**) (1 equiv) dissolved in CH<sub>3</sub>CN was added. After 2 hrs, the mixtures were filtered through a short plug of silica gel with CH<sub>3</sub>CN washings, followed by chromatographic purification to give the product (**2a-2g**).



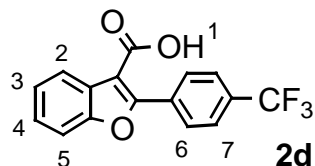
**2-Pentyl-benzofuran-3-carboxylic acid (2a):**  $^1\text{H}$  NMR (500 MHz, d<sub>6</sub>-DMSO):  $\delta$  12.90 (s, br, 1 H<sub>1</sub>), 7.90 (m, 1 H<sub>2</sub>), 7.57 (m, 1 H<sub>5</sub>), 7.29 (m, 1 H<sub>3</sub> & 1 H<sub>4</sub>), 3.13 (t, 2 H<sub>6</sub>,  $J = 7.5$  Hz), 1.70 (m, 2 H<sub>7</sub>), 1.29 (m, 2 H<sub>8</sub> & 1 H<sub>9</sub>), 0.84 (t, 3 H<sub>10</sub>,  $J = 6.5$  Hz).  $^{13}\text{C}$  NMR (500 MHz, d<sub>6</sub>-DMSO):  $\delta$  (ppm) 167.17, 165.66, 153.73, 126.81, 125.14, 124.49, 122.19, 111.67, 109.42, 31.46, 27.88, 27.76, 22.41, 14.48. LC-MS: 5.97 min, [M-H<sub>2</sub>O+1]<sup>+</sup> 215 (ES<sup>+</sup>). Melting Point: 78-80 °C.



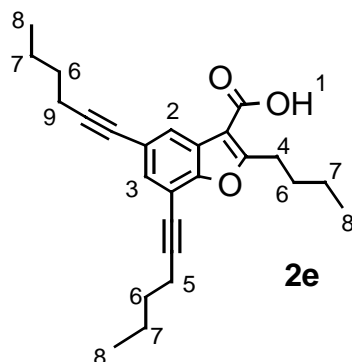
**2-Methoxymethyl-benzofuran-3-carboxylic acid (2b):**  $^1\text{H}$  NMR (500 MHz,  $\text{d}_6\text{-DMSO}$ ):  $\delta$  13.28 (s, br,  $1\text{H}_1$ ), 7.98 (d,  $1\text{H}_2$ ,  $J = 7.5$  Hz), 7.64 (d,  $1\text{H}_5$ ,  $J = 8.5$  Hz), 7.37 (m,  $1\text{H}_3$  &  $1\text{H}_4$ ), 4.88 (s,  $2\text{H}_6$ ), 3.33 (s,  $3\text{H}_7$ ).  $^{13}\text{C}$  NMR (500 MHz,  $\text{d}_6\text{-DMSO}$ ):  $\delta$  (ppm) 165.19, 160.86, 154.24, 129.95, 129.23, 126.18, 124.77, 122.79, 112.12, 65.26, 58.69. LC-MS: 3.97 min,  $[\text{M}+1]^+$  207 (ES+). Melting Point: 96-98  $^\circ\text{C}$ .



**2-p-Tolyl-benzofuran-3-carboxylic acid (2c):**  $^1\text{H}$  NMR (500 MHz,  $\text{d}_6\text{-DMSO}$ ):  $\delta$  13.40 (s, br,  $1\text{H}_1$ ), 7.99 (dd,  $1\text{H}_2$   $J_1 = 2.0$  Hz,  $J_2 = 7.0$  Hz), 7.89 (d,  $2\text{H}_6$   $J = 8.0$  Hz), 7.66 (d,  $1\text{H}_5$   $J = 7.5$  Hz), 7.30-7.40 (m,  $1\text{H}_3$  &  $1\text{H}_4$  &  $2\text{H}_7$ ), 2.38 (s,  $3\text{H}_8$ ).  $^{13}\text{C}$  NMR (500 MHz,  $\text{d}_6\text{-DMSO}$ ):  $\delta$  (ppm) 165.33, 160.40, 153.73, 140.95, 129.90, 129.51, 127.78, 127.02, 126.00, 124.79, 122.98, 111.91, 109.48, 21.75. LC-MS: 5.31 min,  $[\text{M}-\text{H}_2\text{O}+1]^+$  235 (ES+). Melting Point: 183-185  $^\circ\text{C}$ .

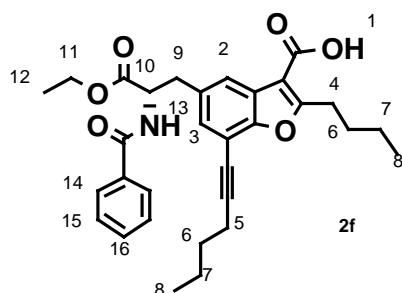


**2-(4-Trifluoromethyl-phenyl)-benzofuran-3-carboxylic acid (2d):**  $^1\text{H}$  NMR (500 MHz,  $\text{d}_6\text{-DMSO}$ ):  $\delta$  13.10 (s, br,  $1\text{H}_1$ ), 8.21 (d,  $2\text{H}_7$   $J = 8.0$  Hz), 8.00 (d,  $1\text{H}_2$   $J = 8.0$  Hz), 7.89 (d,  $2\text{H}_7$   $J = 8.0$  Hz), 7.89 (d,  $1\text{H}_5$   $J = 8.0$  Hz), 7.35-7.50 (m,  $1\text{H}_3$  &  $1\text{H}_4$ ).  $^{13}\text{C}$  NMR (500 MHz,  $\text{d}_6\text{-DMSO}$ ):  $\delta$  (ppm) 165.00, 158.12, 154.14, 133.71, 130.80, 127.40, 126.73, 125.82, 125.79, 125.76, 125.10, 123.31, 112.18, 111.58. LC-MS: 5.57 min,  $[\text{M}-\text{H}_2\text{O}+1]^+$  289 (ES+). Melting Point: 103-105  $^\circ\text{C}$ .

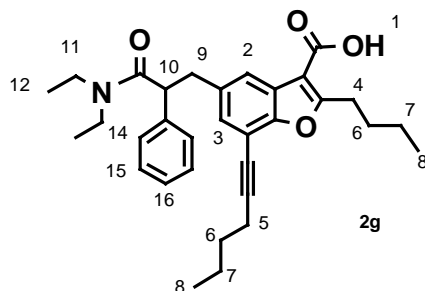


**2-Butyl-5,7-di-hex-1-ynyl-benzofuran-3-carboxylic acid (2e):**  $^1\text{H}$  NMR (500 MHz,  $\text{d}_6\text{-DMSO}$ ):  $\delta$  13.20 (s, br,  $1\text{H}_1$ ), 7.82 (s,  $1\text{H}_2$ ), 7.27 (s,  $1\text{H}_3$ ), 3.15 (t,  $2\text{H}_4$ ,  $J = 8.0$  Hz), 2.51 (t,  $2\text{H}_5$ ,  $J = 7.0$  Hz), 2.40 (t,  $2\text{H}_9$ ,  $J = 7.0$  Hz), 1.30-1.80 (m,  $6\text{H}_6$  &  $6\text{H}_7$ ), 0.88-0.95 (m,  $9\text{H}_8$ ).  $^{13}\text{C}$  NMR (500 MHz,  $\text{d}_6\text{-DMSO}$ ):  $\delta$  (ppm) 168.32, 165.18, 152.71, 130.75, 127.43, 124.78, 119.90, 109.66, 108.31, 97.42,

90.59, 80.45, 74.50, 30.92, 30.70, 30.03, 27.61, 22.47, 22.14, 21.98, 19.22, 18.94, 14.23, 14.16. LC-MS: 7.78 min,  $[M+1]^+$  379 (ES+). Melting Point: 122-124 °C.



**5-(2-Benzoylamino-2-ethoxycarbonyl-ethyl)-2-butyl-7-hex-1-ynyl-benzofuran-3-carboxylic acid (2f):**  $^1\text{H}$  NMR (500 MHz, d6-DMSO):  $\delta$  13.04 (s, br, 1H<sub>1</sub>), 8.83 (d, ,  $J = 7.5$  Hz), 7.82 (s, 1H<sub>2</sub>), 7.78 (d, 2H<sub>14</sub>,  $J = 7.0$  Hz), 7.30-7.60 (m, 1H<sub>16</sub>& 2H<sub>15</sub>), 7.29 (s, 1H<sub>3</sub>), 4.61 (m, 1H<sub>10</sub>), 4.08 (m, 2H<sub>11</sub>), 3.20 (m, 2H<sub>9</sub>), 3.13 (t, 2H<sub>4</sub>,  $J = 8.0$  Hz), 2.49 (m, 2H<sub>5</sub>), 1.10-1.70 (m & m & m & m, 4H<sub>6</sub>& 4H<sub>7</sub>), 1.12 (t, 2H<sub>12</sub>,  $J = 7.0$  Hz), 0.88-0.95 (m, 6H<sub>8</sub>).  $^{13}\text{C}$  NMR (500 MHz, d6-DMSO):  $\delta$  (ppm) 172.17, 167.62, 167.28, 165.47, 152.44, 134.54, 134.25, 132.11, 129.94, 129.42, 129.22, 128.92, 128.08, 127.07, 122.69, 107.36, 96.43, 75.35, 61.28, 55.41, 41.41, 41.37, 36.74, 30.79, 30.15, 27.63, 22.46, 21.97, 19.20, 14.67, 14.23, 14.16. LC-MS: 6.45 min,  $[M+1]^+$  518 (ES+). Melting Point: 166-168 °C.



**2-Butyl-5-(2-diethylcarbamoyl-2-phenyl-ethyl)-7-hex-1-ynyl-benzofuran-3-carboxylic acid (2g):**  $^1\text{H}$  NMR (500 MHz, d6-DMSO):  $\delta$  12.97 (s, br, 1H<sub>1</sub>), 7.68 (s, 1H<sub>2</sub>), 7.38 (d, 2H<sub>14</sub>,  $J = 7.0$  Hz), 7.29 (m, 1H<sub>16</sub>& 2H<sub>15</sub>), 7.20 (s, 1H<sub>3</sub>), 4.65 (m, 1H<sub>10</sub>), 2.80-3.40 (m, 4H<sub>11</sub>& 2H<sub>9</sub>& 2H<sub>4</sub>), 2.49 (t, 2H<sub>5</sub>,  $J = 6.5$  Hz), 1.10-1.70 (m & m & m & m, 4H<sub>6</sub>& 4H<sub>7</sub>), 0.80-1.00 (m, 6H<sub>5</sub>& 3H<sub>8</sub>), 0.71 (t, 3H<sub>8</sub>,  $J = 7.0$  Hz).  $^{13}\text{C}$  NMR (500 MHz, d6-DMSO):  $\delta$  (ppm) 171.30, 167.36, 165.50, 152.20, 141.19, 136.42, 129.94, 129.26, 129.21, 129.14, 128.48, 127.41, 126.82, 122.51, 109.74, 107.11, 96.10, 75.53, 49.87, 41.90, 40.72, 30.92, 30.84, 30.28, 30.18, 27.65, 22.49, 22.00, 19.21, 14.97, 14.27, 14.24, 14.18, 14.16, 14.08, 13.39. LC-MS: 6.87 min,  $[M+Na]^+$  524 (ES+).

#### ***IV. Table of Spectra***

- 1.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of compound 1a. (Page 1-2) (S8-S9)**
- 2.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of compound 1b. (Page 3-4) (S10-S11)**
- 3.  $^1\text{H}$  NMR of compound 1c. (Page 5) (S12)**
- 4.  $^1\text{H}$  NMR of compound 1d. (Page 6) (S13)**
- 5.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of compound 1e. (Page 7-8) (S14-S15)**
- 6.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of compound 1f. (Page 9-10) (S16-S17)**
- 7.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of compound 1g. (Page 11-12) (S18-S19)**
- 8.  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and LC-MS spectra of compound 2a. (Page 13-16) (S20-S23)**
- 9.  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and LC-MS spectra of compound 2b. (Page 17-20) (S24-S27)**
- 10.  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and LC-MS spectra of compound 2c. (Page 21-24) (S28-S31)**
- 11.  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and LC-MS spectra of compound 2d. (Page 25-28) (S32-S35)**
- 12.  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and LC-MS spectra of compound 2e. (Page 29-32) (S36-S39)**
- 13.  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and LC-MS spectra of compound 2f. (Page 33-36) (S40-S43)**
- 14.  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and LC-MS spectra of compound 2g. (Page 37-40) (S44-S47)**
- 15.  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and LC-MS spectra of  $^{18}\text{O}$ -labeled compound 2. (Page 41-43) (S48-S50)**

b36-2

Pulse Sequence: s2pu1

Solvent: DMSO

Ambient temperature

INOVA-500 "Vivoquest"

Relax. delay 2.000 sec

Pulse 45.4 degrees

Acq. Time 1.892 sec

Width 10000 Hz

X Resolution

OBSERVE: H1, 499.7200211 MHz

DATA PROCESSING 0.4 Hz

Line broadening 0.4 Hz

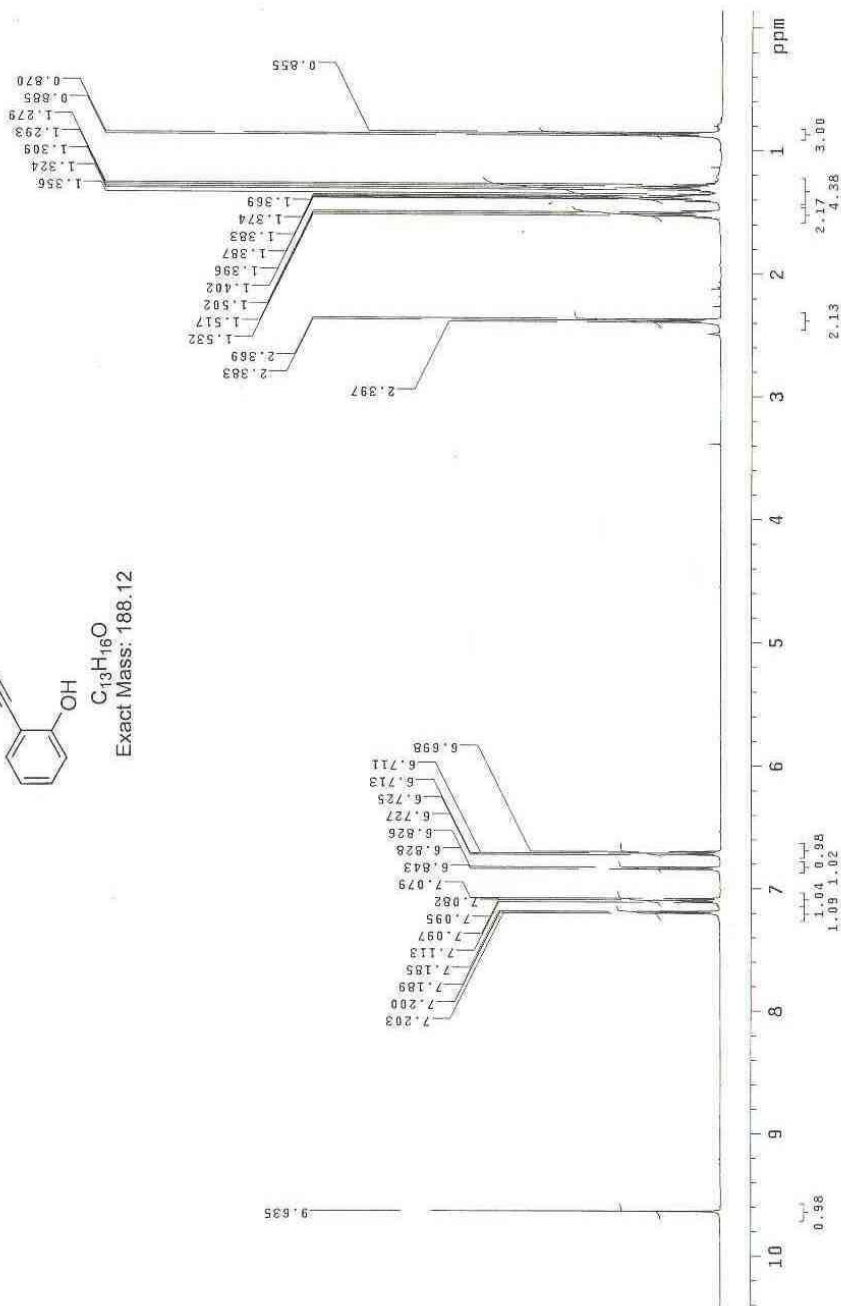
FT size 32768

Total time 0 min, 23 sec

1a



$C_{10}H_{10}O$   
Exact Mass: 188.12



835-2

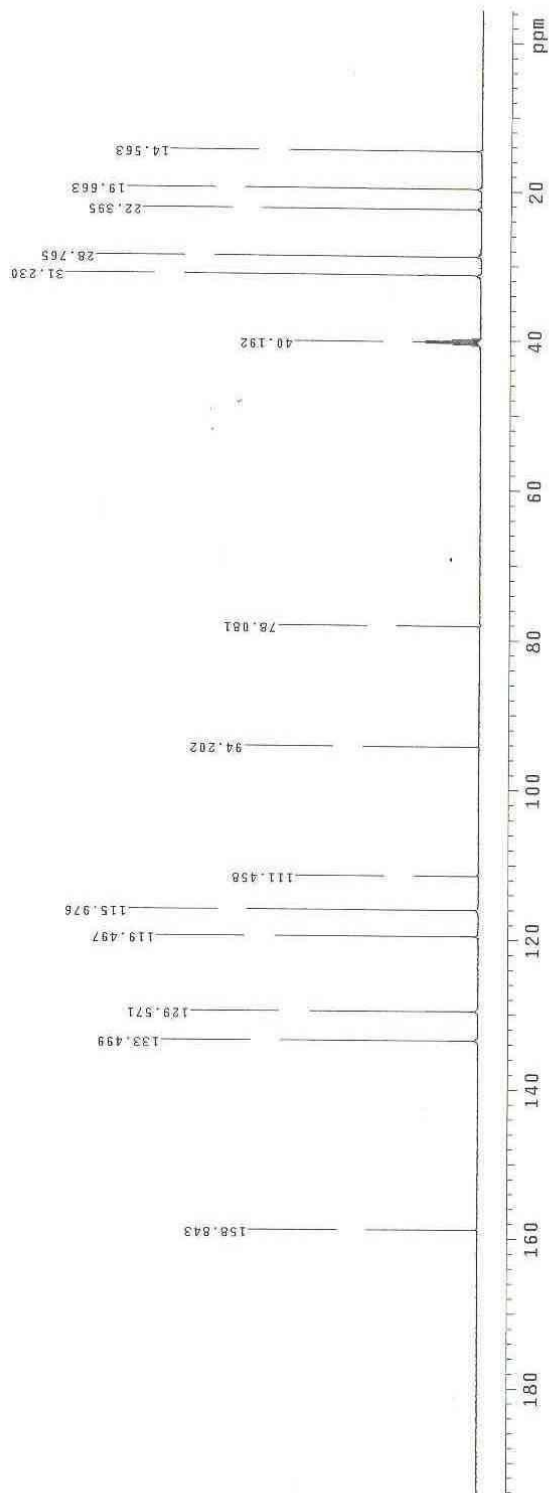
Pulse Sequence: s2pul  
Solvent: DMSO  
Ambient temperature  
User: 1-14-87  
INOVA-500 "Vivoquest"

Pulse 64.3 degrees  
Acq. time 1.300 sec  
Width 25000.0 Hz  
256 repetitions  
OBSERVE C13, 125.654693 MHz  
DECOUPLE H1, 499.725198 MHz  
PACIFIC  
CONTINUOUSLY ON  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 0.5 Hz  
FT size 65536  
Total time 3 hr, 38 min, 16 sec

1a



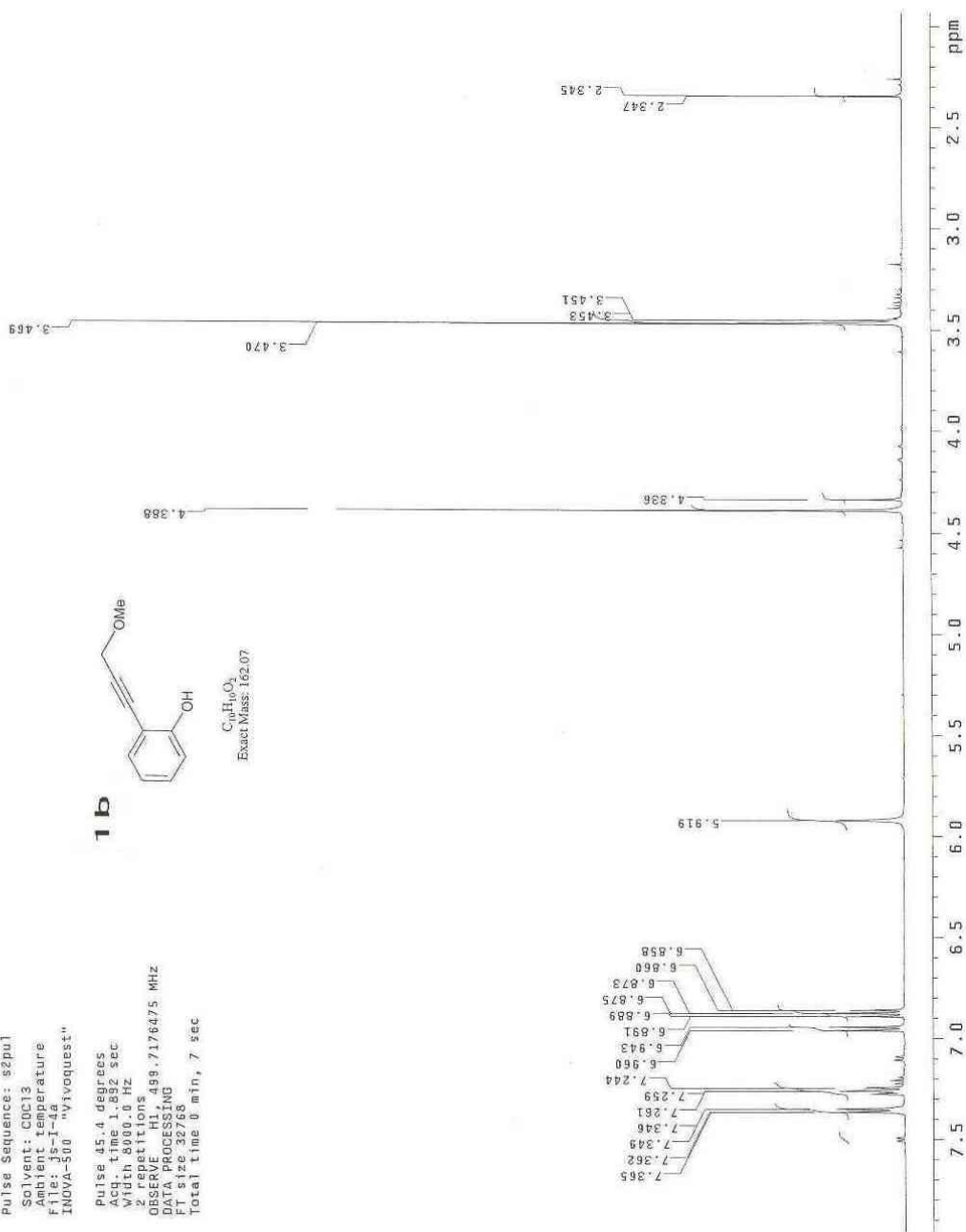
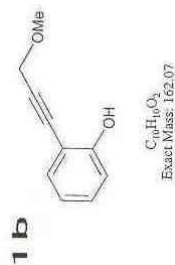
$C_{13}H_{16}O$   
Exact Mass: 188.12



js-I-4a

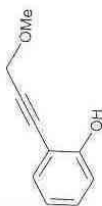
Pulse Sequence: s2pul  
Solvent: CDCl3  
Ambient temperature  
File: js-I-4a  
INOVA-500 "vivoquest"

Pulse 45.4 degrees  
Acq. time 1.882 sec  
Width 2000.0 Hz  
F2 (MHz) 499.7176475  
OBSERVE H1  
DATA PROCESSING  
FT size 32768  
Total time 0 min, 7 sec

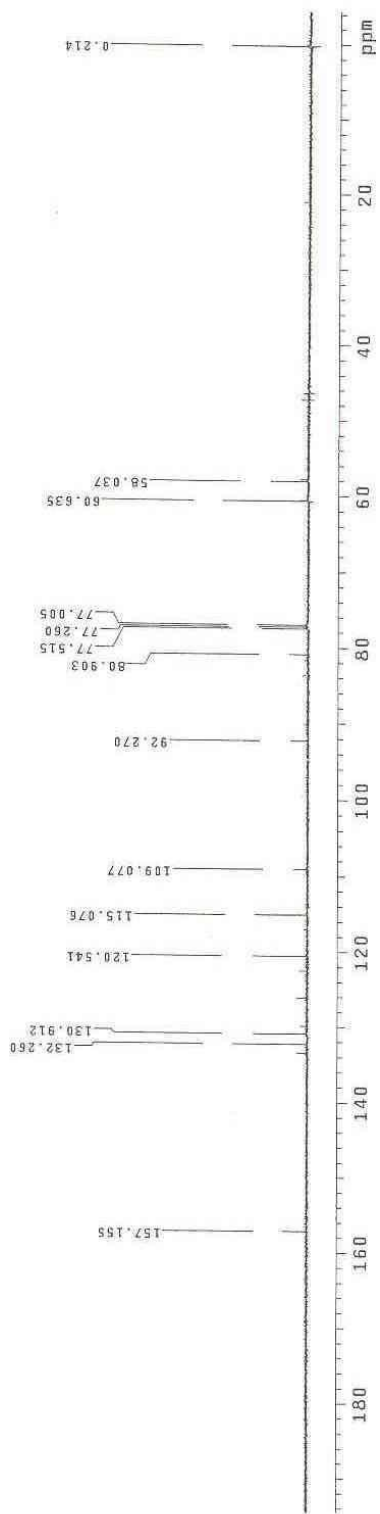


js-i-4a-c13  
Pulse Sequence: szpul  
Solvent: CDCl3  
Temperature: 125.8540724 MHz  
File: js-i-4a-c13  
INNOVA-500 "Vivoquest"  
Pulse 64.3 degrees  
Acq: time 1.300 sec  
Width 25000.0 Hz  
256 repetitions  
OBSERVE C13, 125.8540724 MHz  
DECOUPLE H1, 499.7201462 MHz  
Power 41 dB  
continuously on  
continuously on  
DATA PROCESSING  
Line broadening 0.5 Hz  
FT size 65536  
Total time 21 min, 52 sec

1b



$C_{16}H_{16}O_2$   
Exact Mass: 162.07



js-1-4c

Pulse Sequence: s0pul

Solvent: CCl<sub>3</sub>

Ambient temperature

INOVA-500 "vivoquest"

Pulse 45.4 degrees

Acq. time 1.892 sec

Width 8000.0 Hz

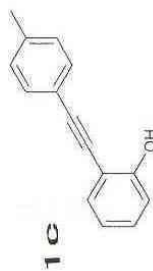
2 repetitions

OBSERVE H1, 499.7176475 MHz

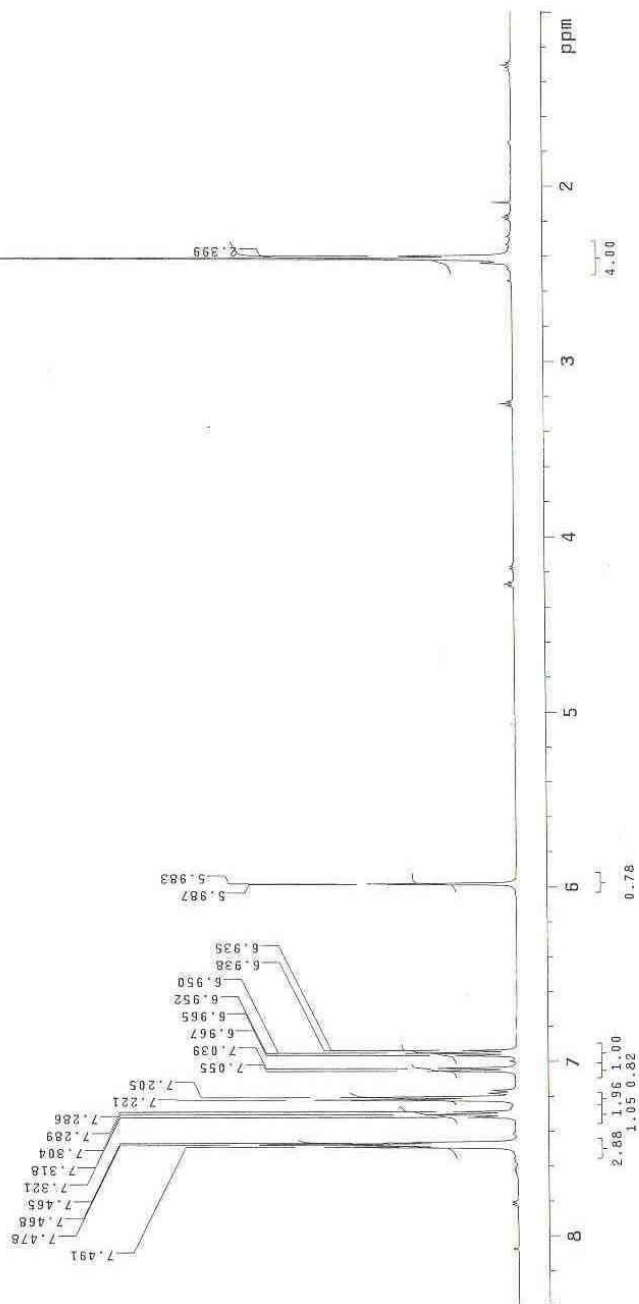
DATA PROCESSING

File size 32788

Total time 0 min, 7 sec



C<sub>14</sub>H<sub>10</sub>O  
Exact Mass: 208.09



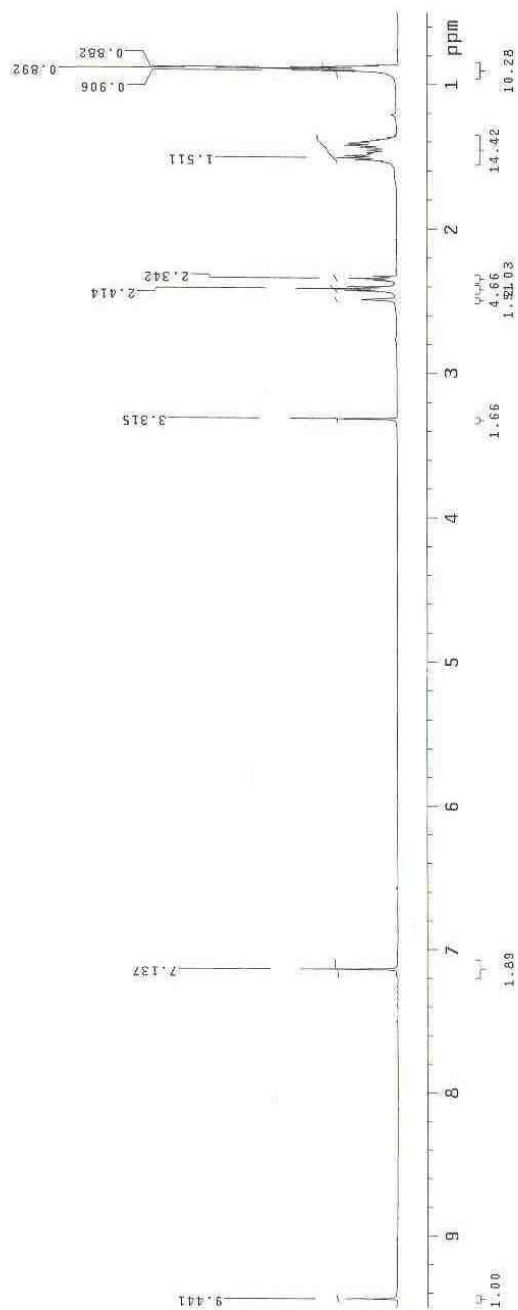
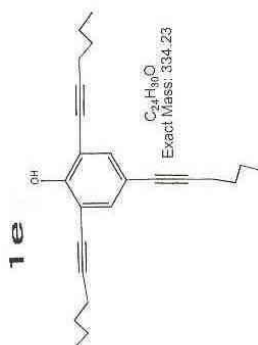


js-1-21b

Pulse Sequence: s2pu1  
 Solvent: DMSO  
 Ambient Temperature  
 File: js-1-21b  
 INOVA-300 "N1voquest"

Relax. delay 2.00 sec  
 Pulse 4.00 sec  
 Acq. time 1.892 sec  
 Width 4499.9 Hz  
 6 repetitions

OBSERVE H1, 499.7200211 MHz  
 DATA PROCESSING  
 Line broadening 0.4 Hz  
 FT size 32768  
 Total time 0 min, 31 sec



js-1-24b-cl3

Pulse Sequence: s2pul

Solvent: DMSO

Ambient temperature

User: 1-14-87

INNOVA-500 "Vivoquest"

Pulse 64.3 degrees

Acq. time 1.300 sec

Width 25000.0 Hz

Resolution

OBSERVE C13, 65.46693 MHz

DECOUPLE H1, 480.7225198 MHz

Power 41 dB

continuously on

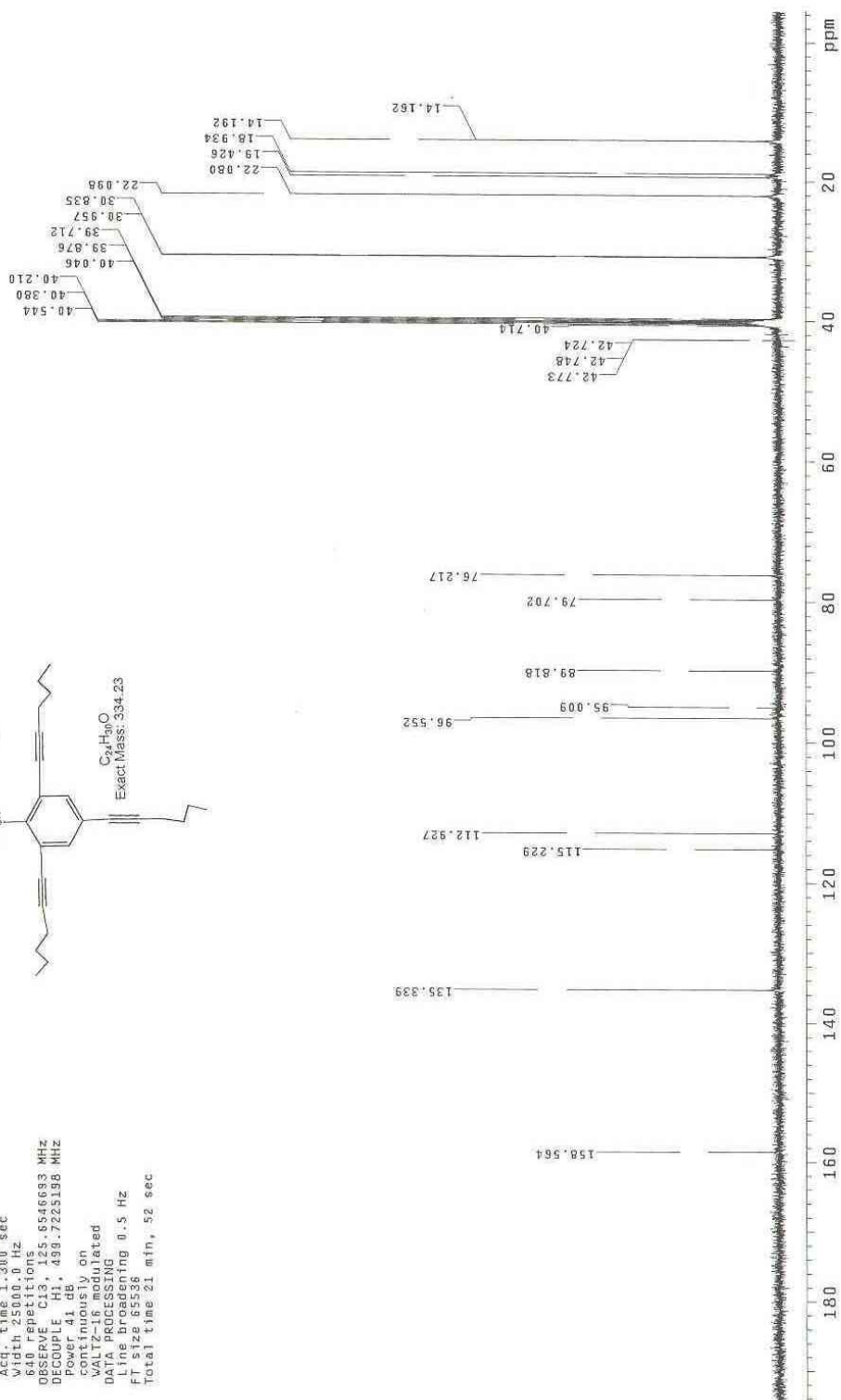
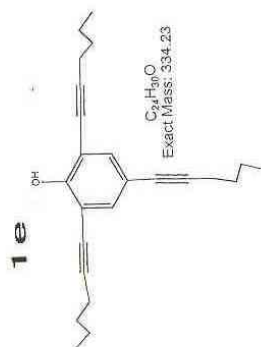
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 65536

Total time 21 min, 52 sec





js-1-23c

Pulse Sequence: s2pu1

Solvent: DMSO

Ambient temperature

User: 1-14-87

INNOVA-500 "vivoquest"

Pulse 54.3 degrees

Acq. time 1.300 sec

Width 25000.0 Hz

1280 repetitions

DECOUPLE CH2, 100.62546593 MHz

DECOUPLE CH, 400.7225198 MHz

Power 41 dB

continuously on

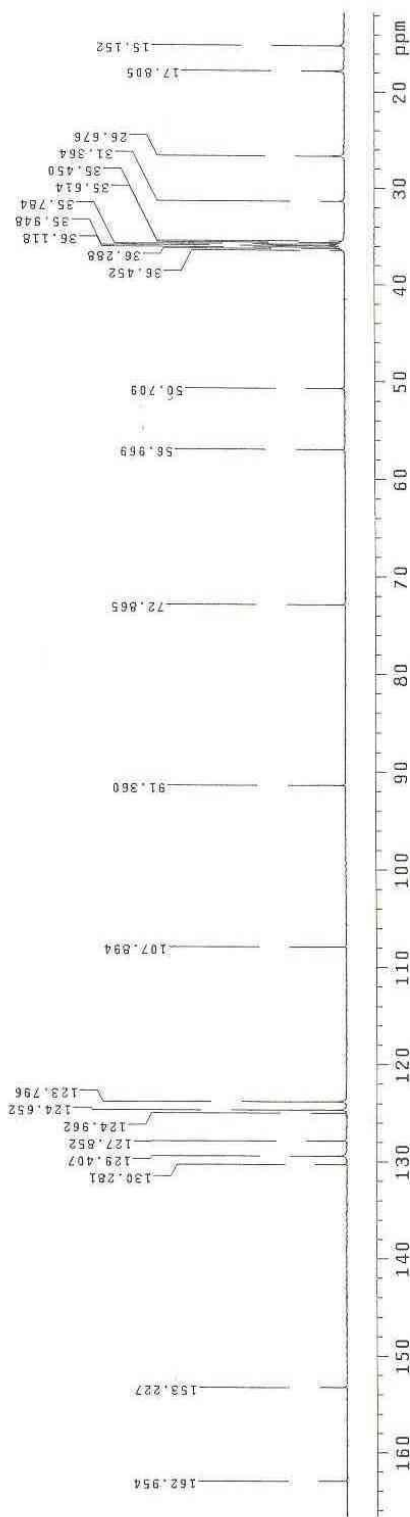
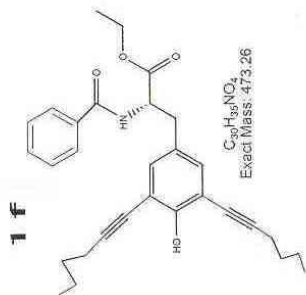
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 65536

Total time 21 min, 52 sec



JS-1-23f

Pulse Sequence: s2pul

Solvent: DMSO

Ambient temperature

INUA-500 "Vivoquest"

Relax. delay 2.000 sec

Pulse 45.4 degrees

Acq. time 1.893 sec

Width 5000.0 Hz

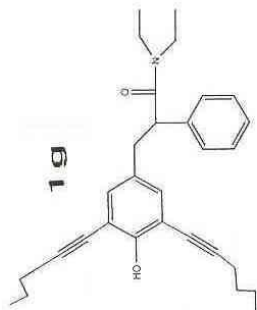
Observed 1H 499.720211 MHz

DATA PROCESSING

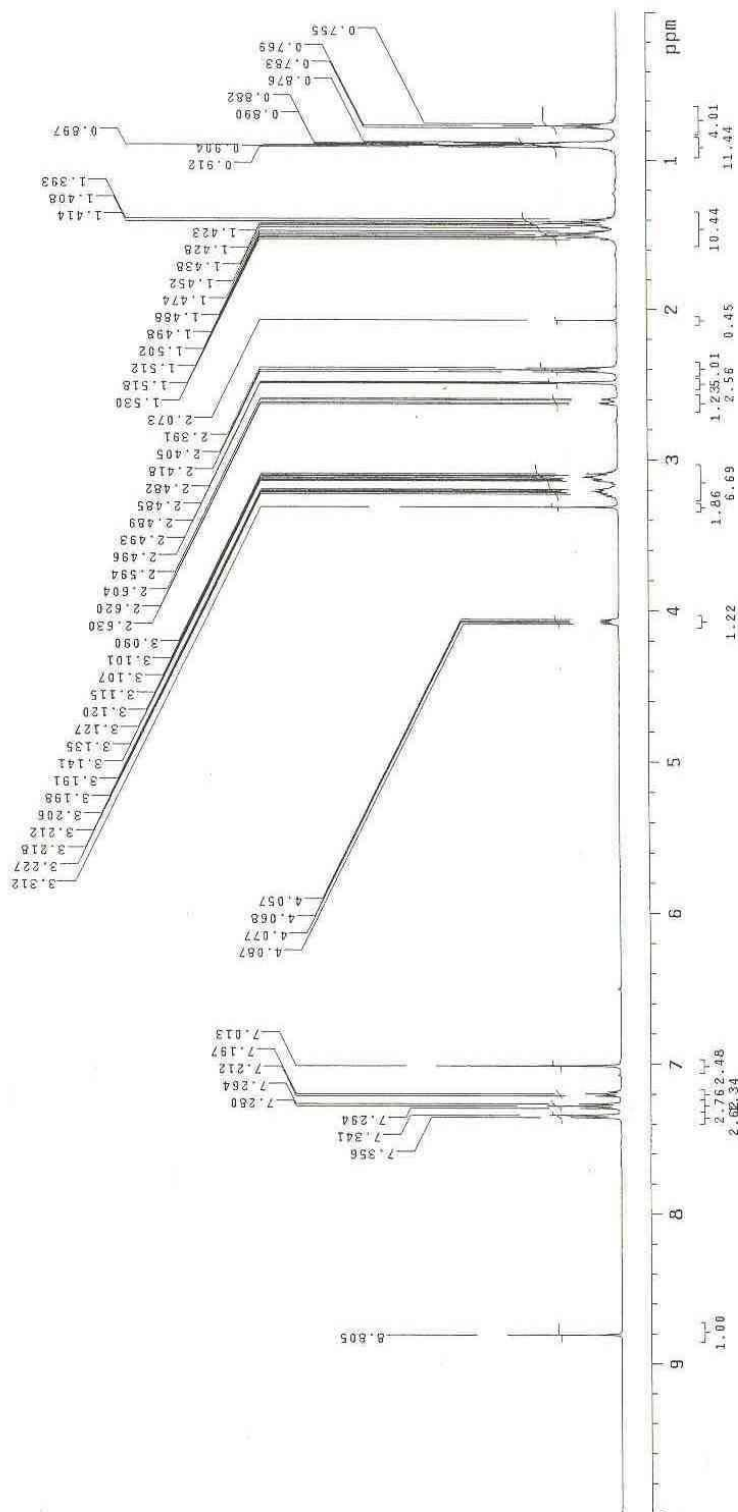
Line broadening 0.4 Hz

FT size 32768

Total time 0 min, 23 sec



$C_{21}H_{29}NO_2$   
Exact Mass: 457.30



js-1-23f-c13

Pulse Sequence: zgpg30

Solvent: DMSO

Ambient temperature

User: 1-14-87

File: js-1-23f-c13

INOVA-500 "vivoquest"

Pulse 64.3 degrees

Acq. time 1.300 sec

Width 25000.0 Hz

896 repetitions

OBSERVE C13, 125.854663 MHz

DECOUPLE H1, 499.7223196 MHz

Continuously on

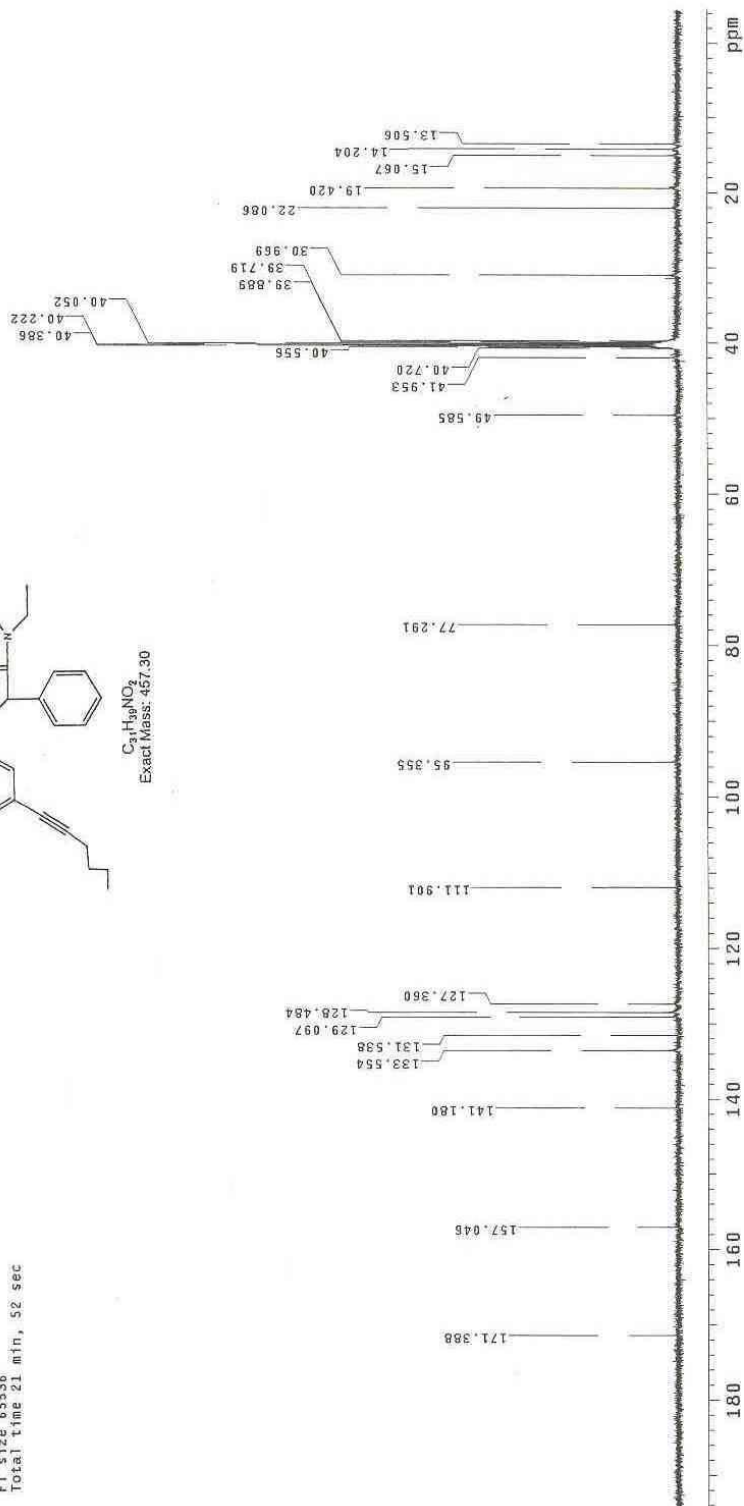
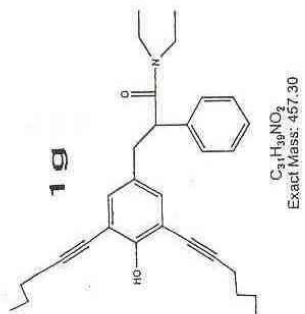
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 65536

Total time 21 min, 52 sec



b43-1-3

Pulse Sequence: s2pul

Solvent: DMSO

Ambient temperature

File: b43-1-3

INOVA-500 "vivoquest"

Relax. delay 2.000 sec

Pulse 45.4 degrees

Acq. time 1.892 sec

Width 5000.0 Hz

4 repetitions

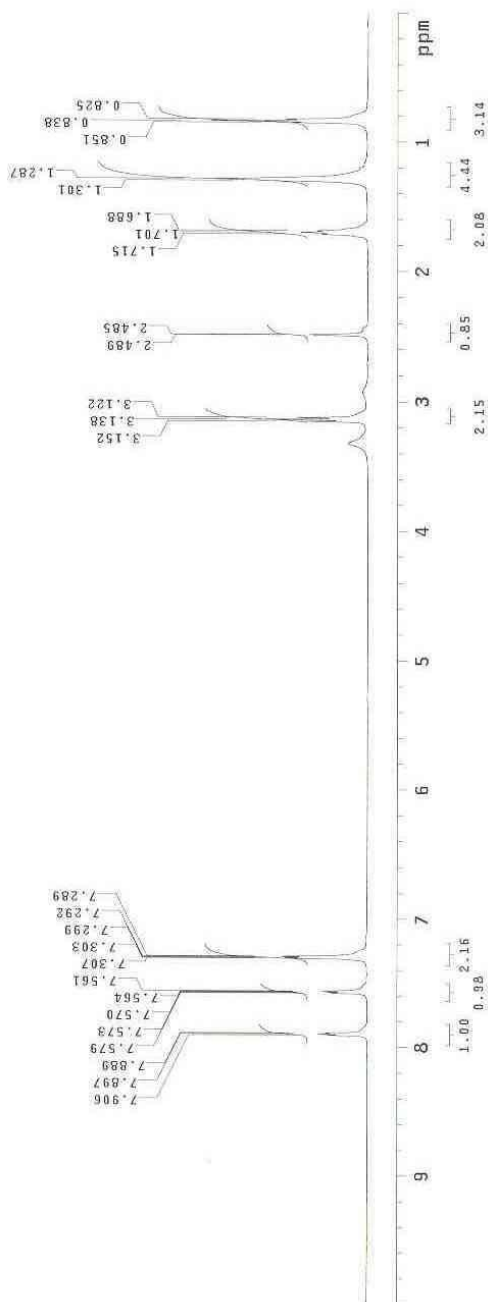
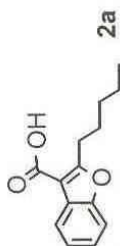
OBSERVED FID 99.7200211 MHz

DATA PROCESSING

Line Processing 0.4 Hz

FT size 32768

Total time 0 min, 23 sec



YLJS-43-3

Pulse Sequence: s2pu1

Solvent: DMSO

Ambient temperature

INNOVA-500 "Vivoquest"

Relax. delay 2.000 sec

Pulse 45.4 degrees

Acq. time 1.593 sec

Wdth 1000.0 Hz

Wdth 1000.0 Hz

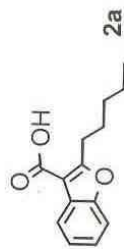
OBSERVE F1 499.720211 MHz

DATA PROCESSING

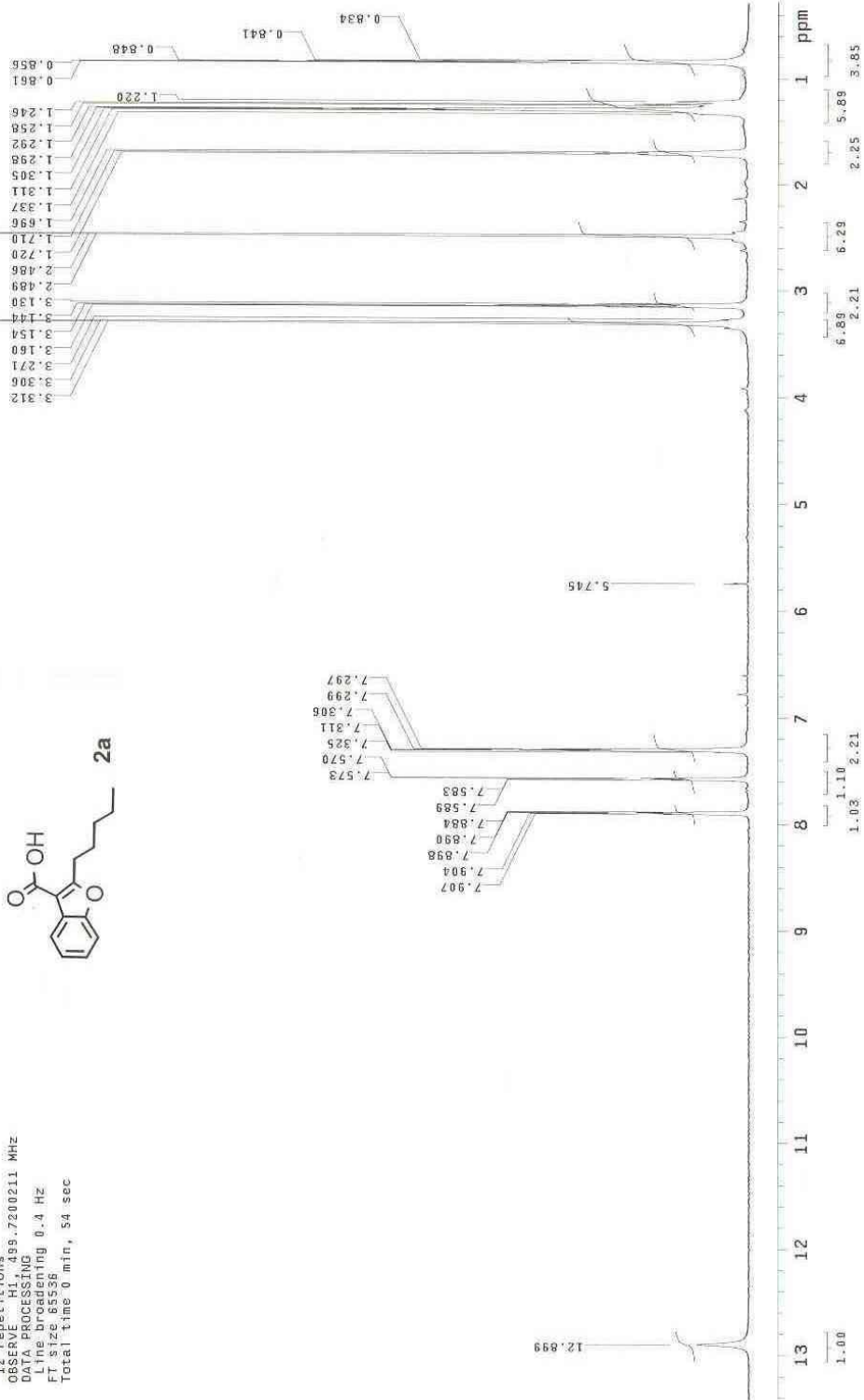
Line broadening 0.4 Hz

FT size 8536

Total time 0 min, 54 sec



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## STANDARD CARBON PARAMETERS

Pulse Sequence: zgpg30

Solvent: DMSO

Ambient temperature

P1: 12.00

P2: 12.00

INQVA-500 "Vivoquest"

Pulse 64.3 degrees

Acq. time 1.00 min

Width 2000.0 Hz

576 repetitions

OBSERVE C13, 125.6546693 MHz

DECOUPLE H1, 499.7225198 MHz

Power 41 dB

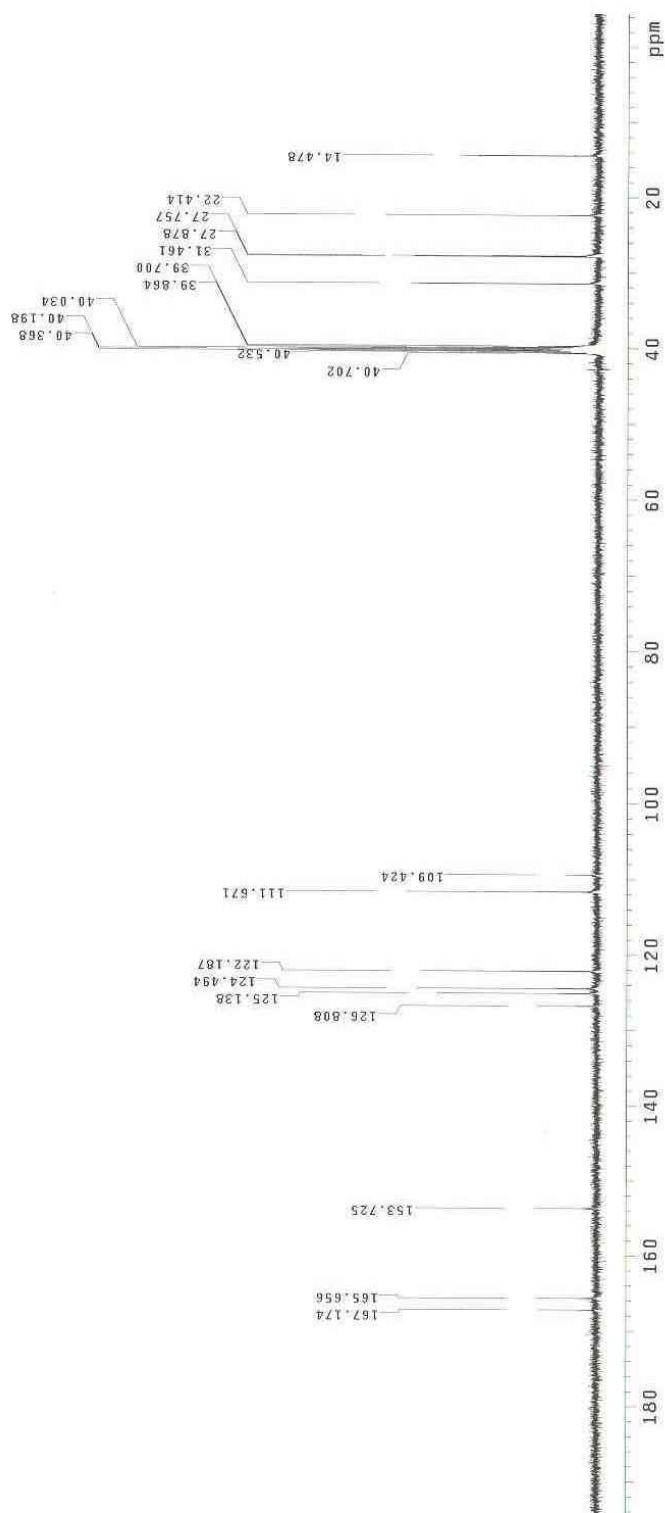
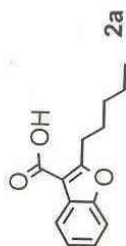
continuously on

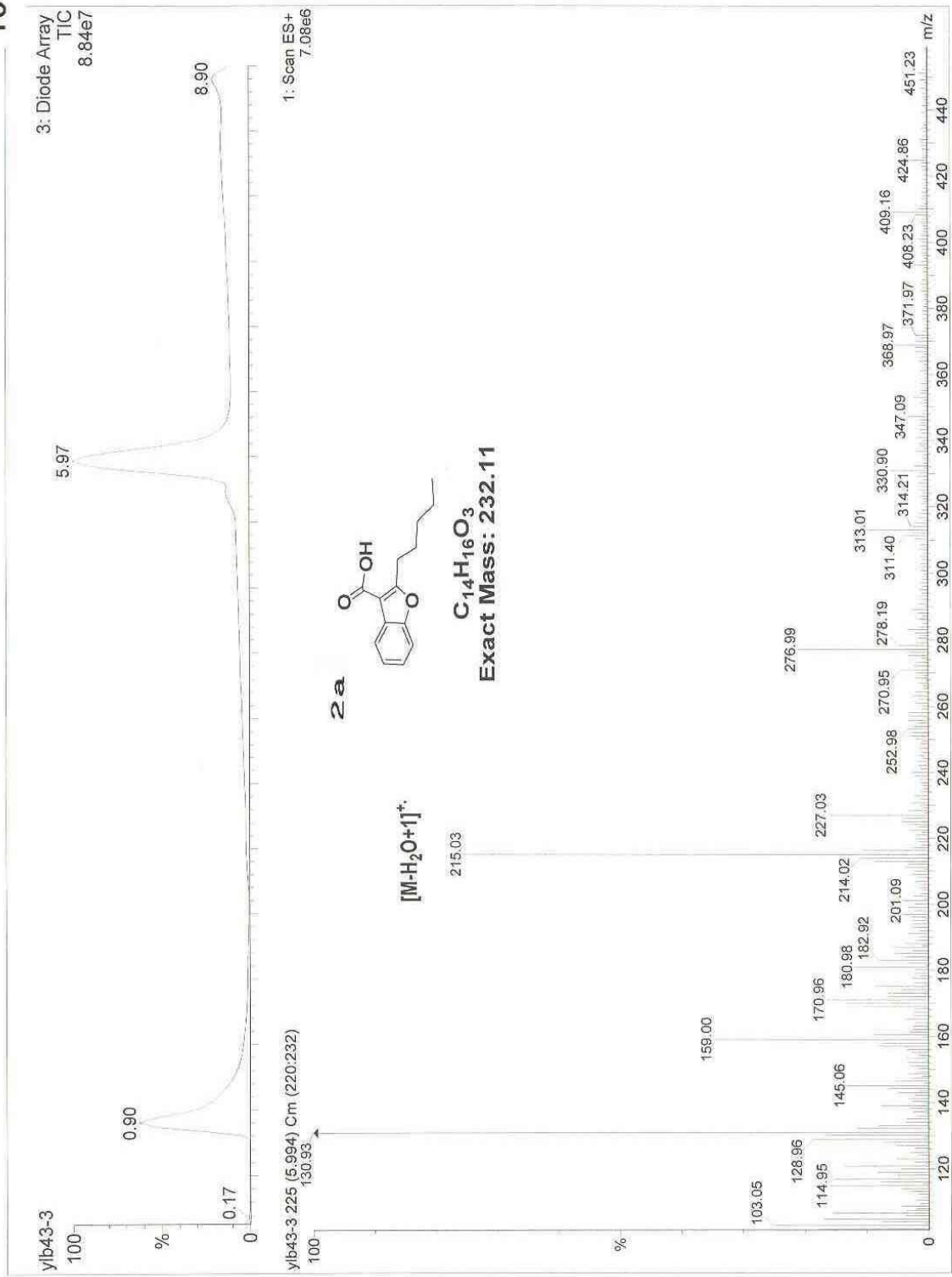
WALTZ-16 modulated

DATA ACQUISITION

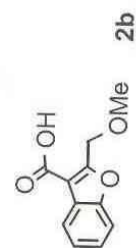
F1 size 65536

Total time 21 min, 52 sec

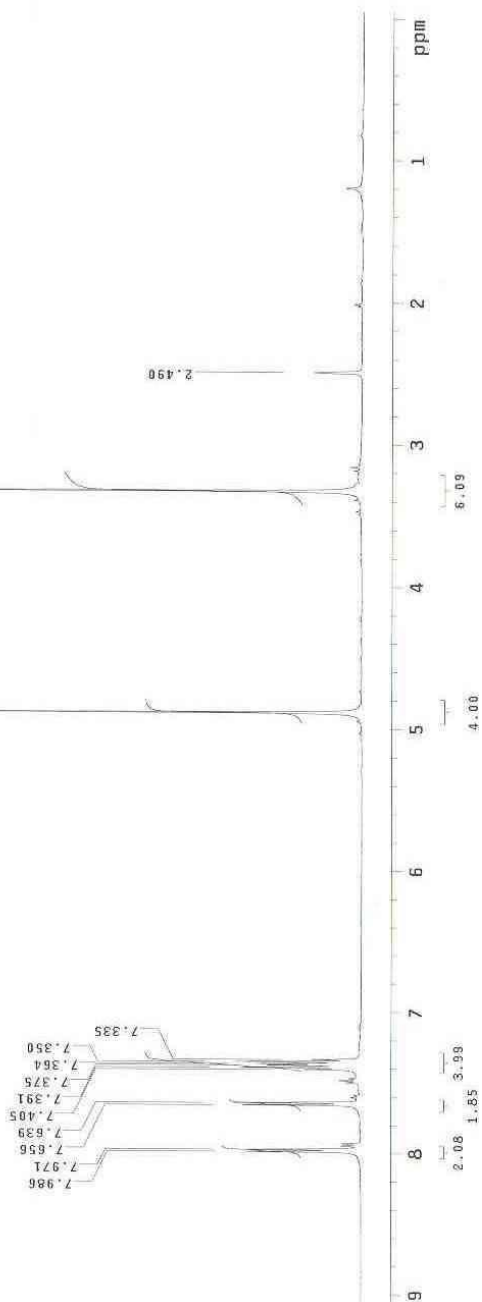




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y1b87-1  
Pulse Sequence: s2pu1  
Solvent: DMSO  
Ambient temperature  
INDVA-500 "Vivoquest"  
Relax. delay 2.000 sec  
Pulse 45.4 degrees  
Acq. time 1.832 sec  
Width 8000.0 Hz  
Observer: JCH  
QNP: 499.7200211 MHz  
DATA PROCESSING  
Line broadening 0.4 Hz  
FT size 32768  
Total time 0 min, 15 sec



YLJS-87-1

Pulse Sequence: s2pu1

Solvent: DMSO

Ambient temperature

INNOVA-500 "Vivoquest"

Relax. delay 2.000 sec

Pulse 45.4 degrees

Acq. time 1.892 sec

Width 10000.0 Hz

12 repetitions

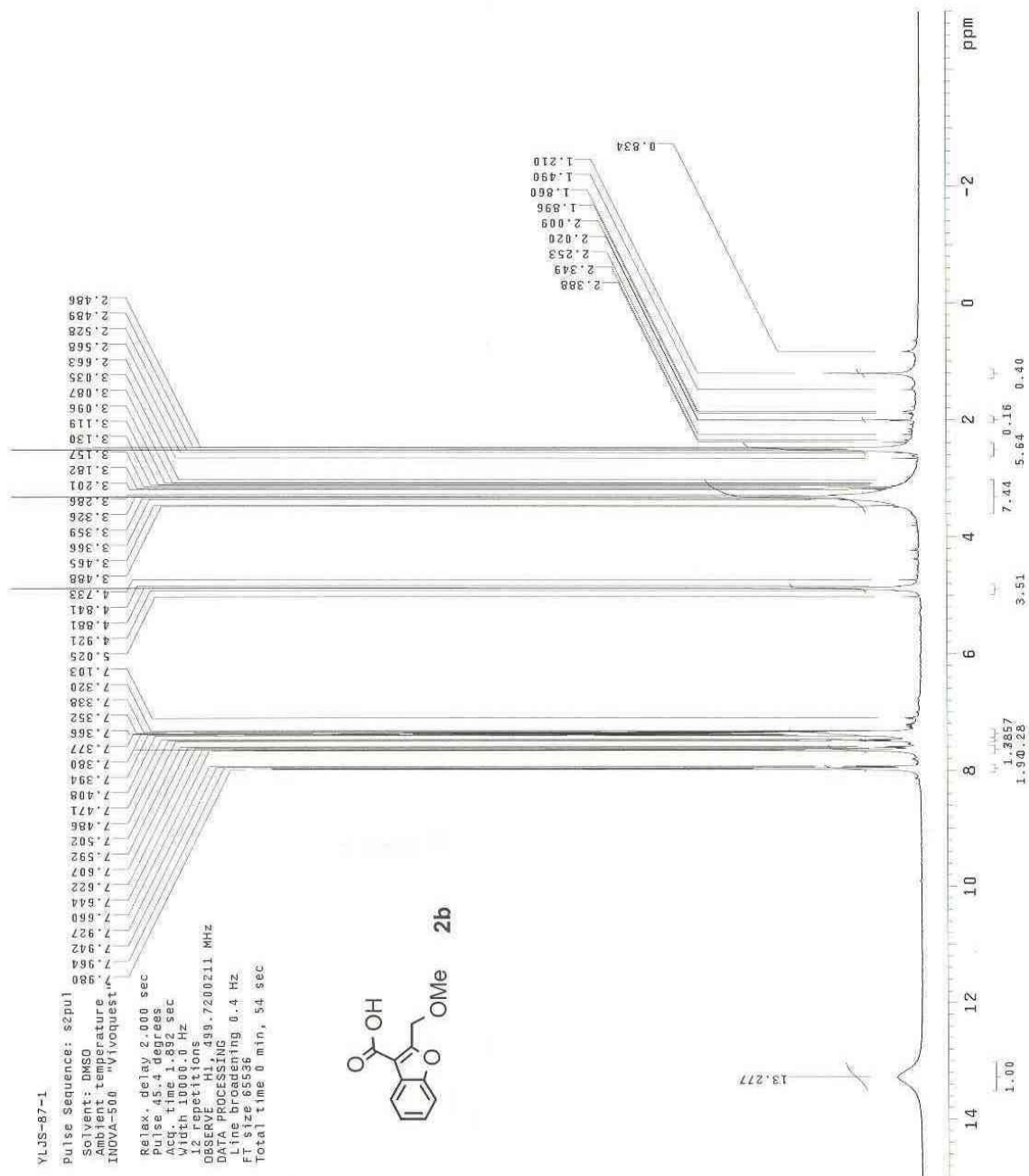
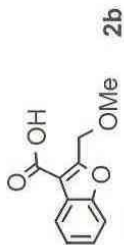
OBSERVE H1, 499.7200211 MHz

DATA PROCESSING

F1: fine processing 0.4 Hz

F2: size 65536

Total time 0 min, 54 sec



y1b27-1

Pulse Sequence: s2pul

Solvent: DMSO

Ambient temperature

User: 1-14-97

INOVA-500 "Vivoquest"

Pulse 64.3 degrees

Acq. time 1.300 sec

Width 2500.0 Hz

385.500 MHz

OBSERVE C13, 125.6546693 MHz

DECOUPLE H1, 459.7225198 MHz

Power 41 dB

continuously on

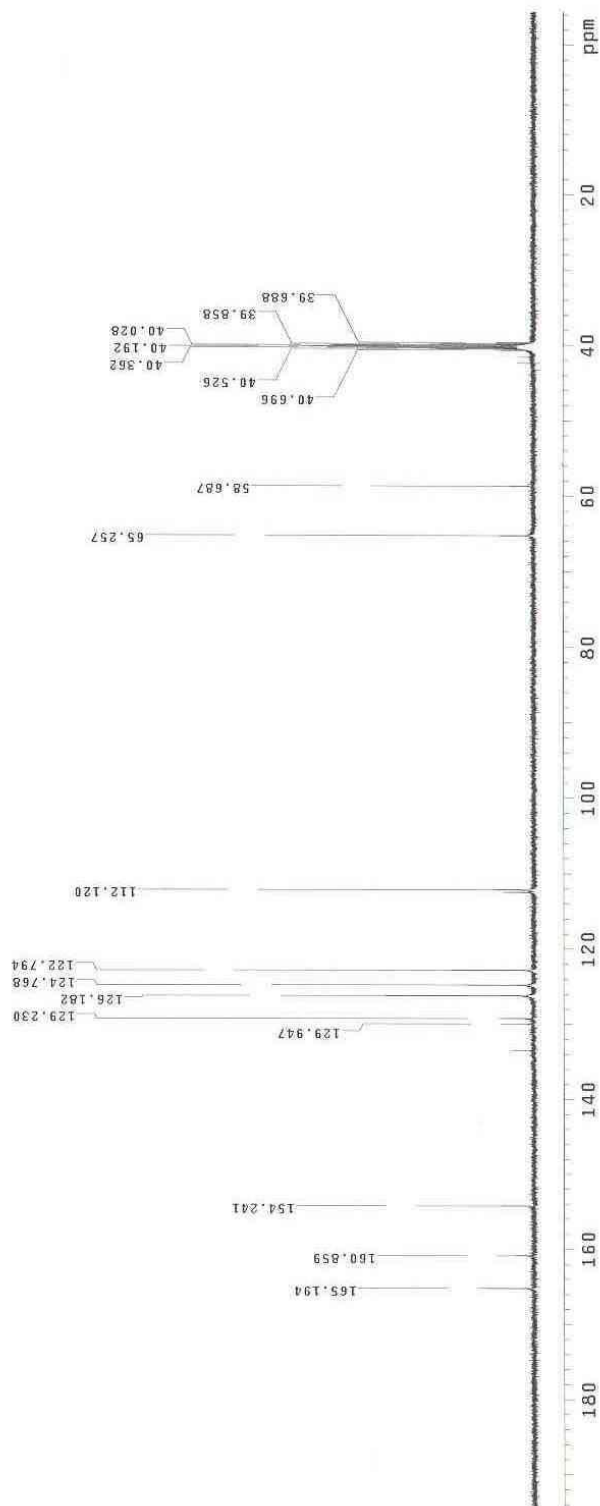
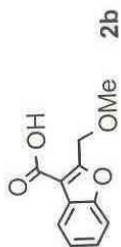
WALTZ-16 modulated

DATA PROCESSING

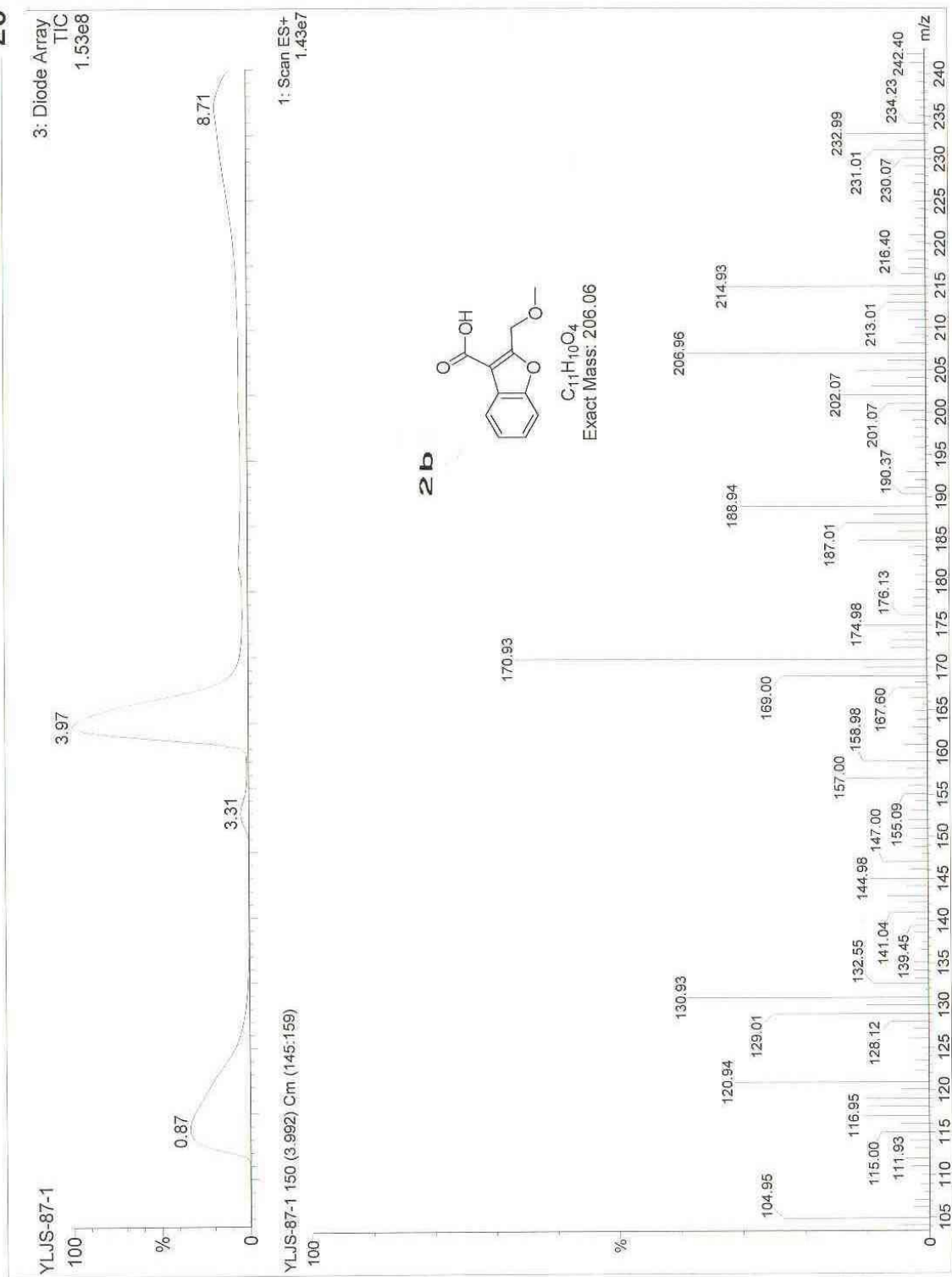
Line broadening 0.5 Hz

Ft size 65536

Total time 21 min, 52 sec



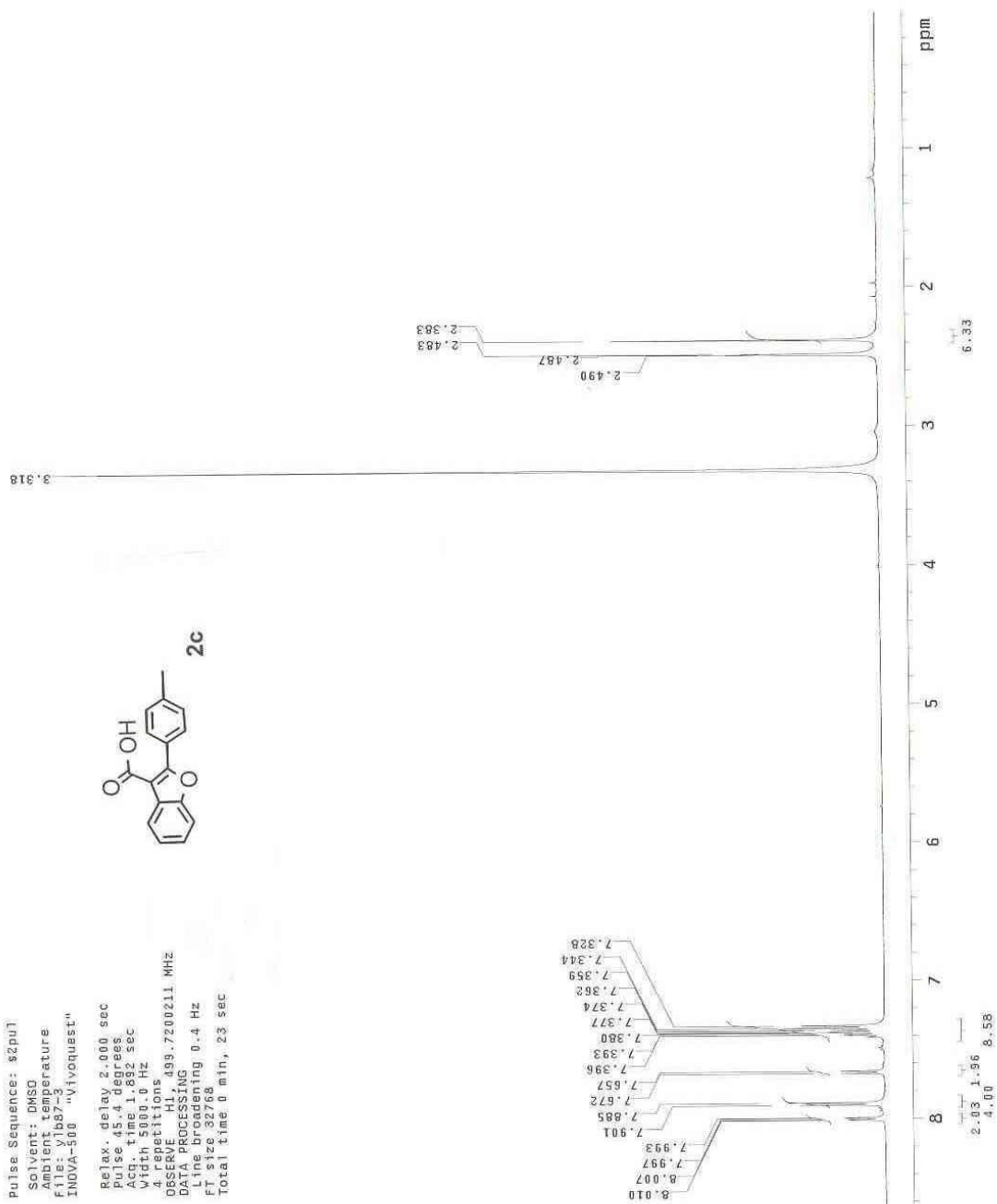
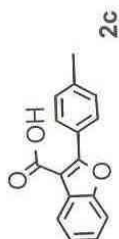
20



v1b87-3

Pulse Sequence: zgpg30  
 Solvent: DMSO  
 Ambient Temperature  
 File: v1b87-3  
 INOVA-500 "Vivoquest"

Relax. delay 2.000 sec  
 Pulse 45.4 degrees  
 Acq. time 1.892 sec  
 Width 5000.0 Hz  
 4 repetitions  
 OBSERVE H1, 499.7200211 MHz  
 DATA PROCESSING  
 F1: zgpg30  
 F2: zgpg30  
 Total time 0 min, 23 sec



YLSJ-87-3

Pulse Sequence: s2pu1

Solvent: DMSO

Acquisition temperature

INDRA-500 "Vivoquest"

Relax. delay 2.000 sec

Pulse 45.4 degrees

Acq. time 1.892 sec

Width 10000.0 Hz

12 repetitions

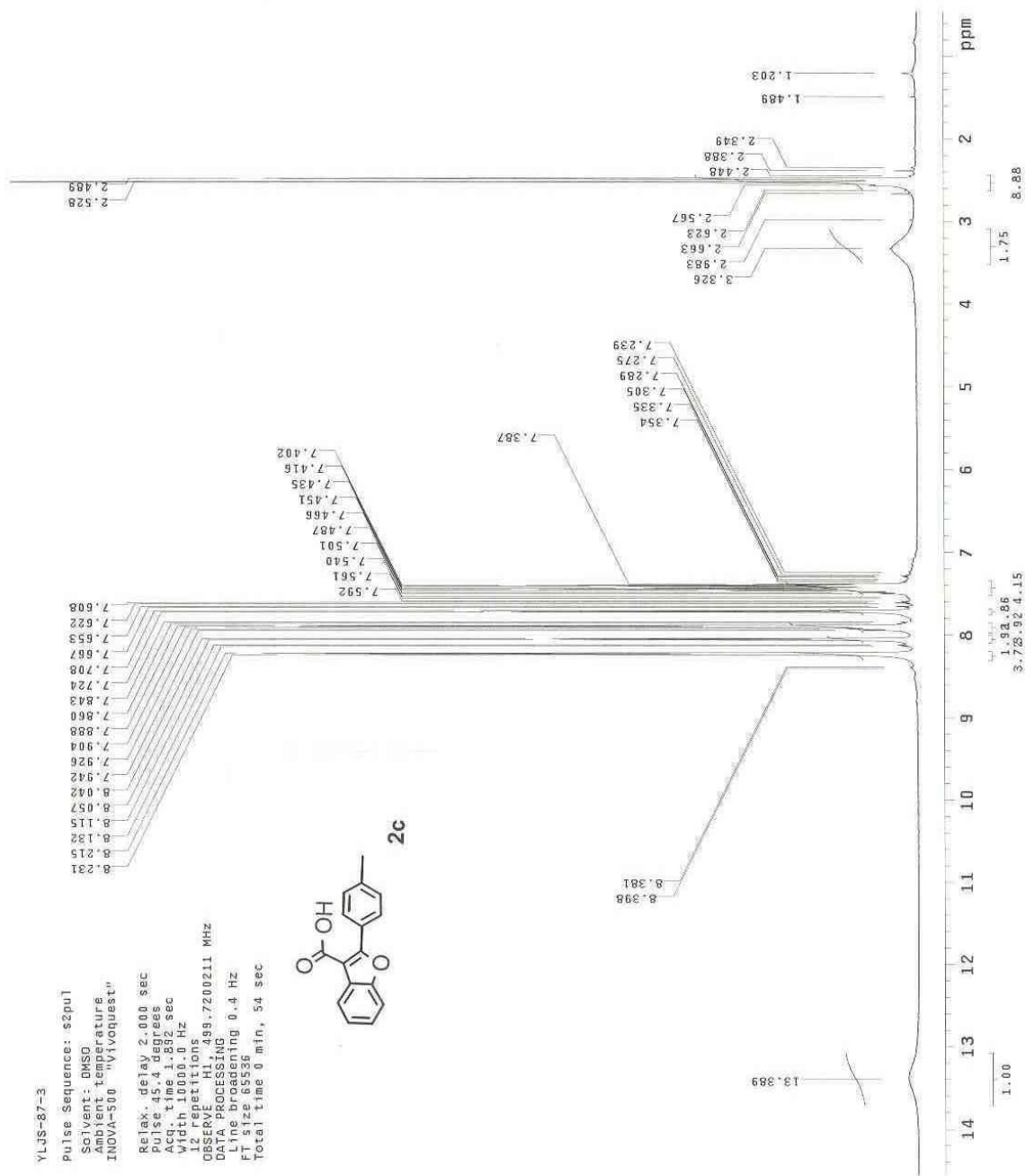
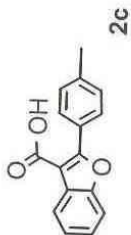
OBSERVE H1, 499.7200211 MHz

DATA PROCESSING

Line broadening 0.4 Hz

FI size 65536

Total time 0 min, 54 sec



y1b07-3

Pulse Sequence: s2pul

Solvent: DMSO

Ambient temperature

User: 1-14-87

INOVA-500 "vivoquest"

Pulse 64.3 degrees

Acq. time 1.300 sec

Width 3495.6 Hz

3356 repetitions

OBSERVE C13, 125.5546693 MHz

DECOUPLE H1, 499.725198 MHz

Continuously on

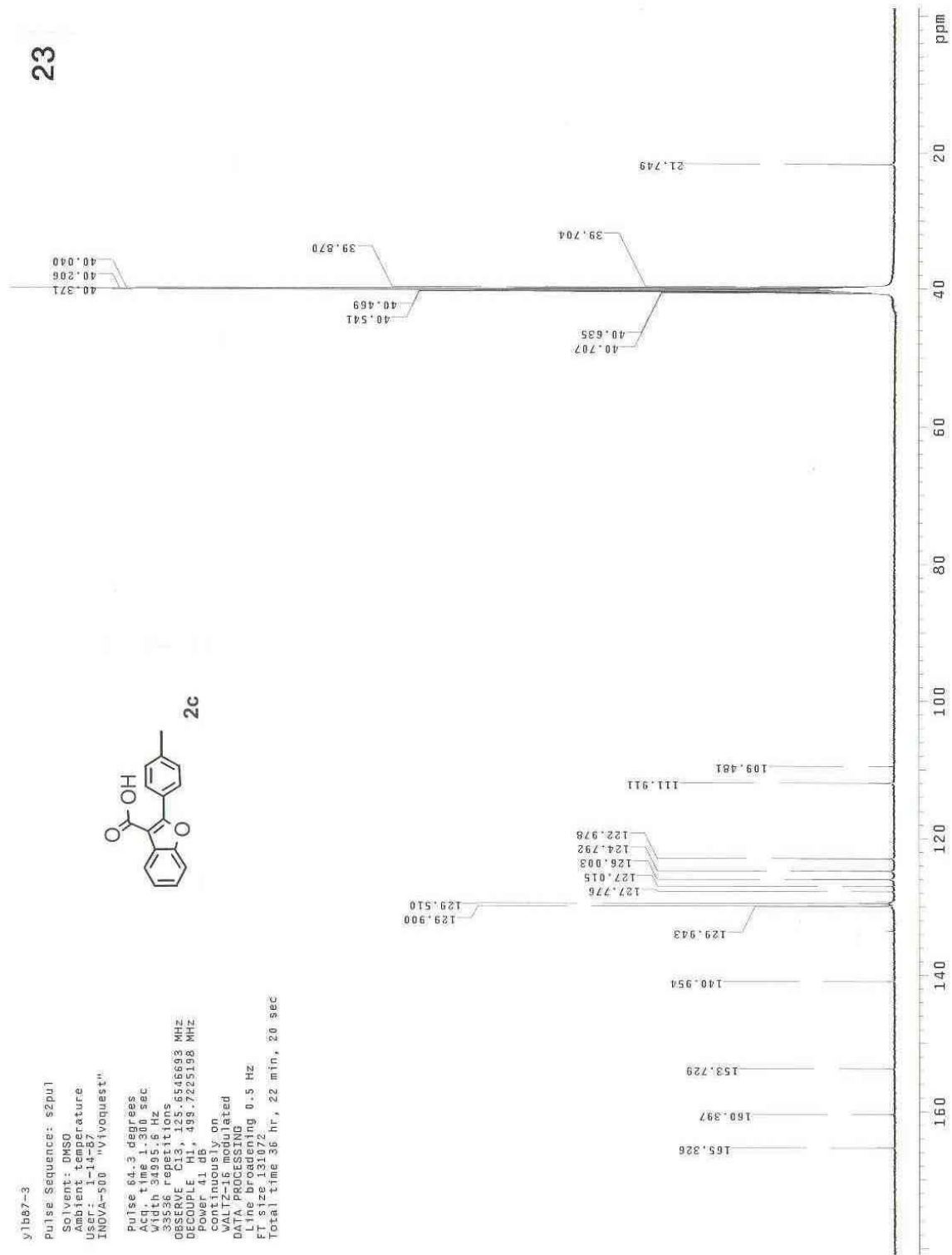
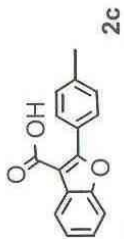
WALTZ-16 modulated

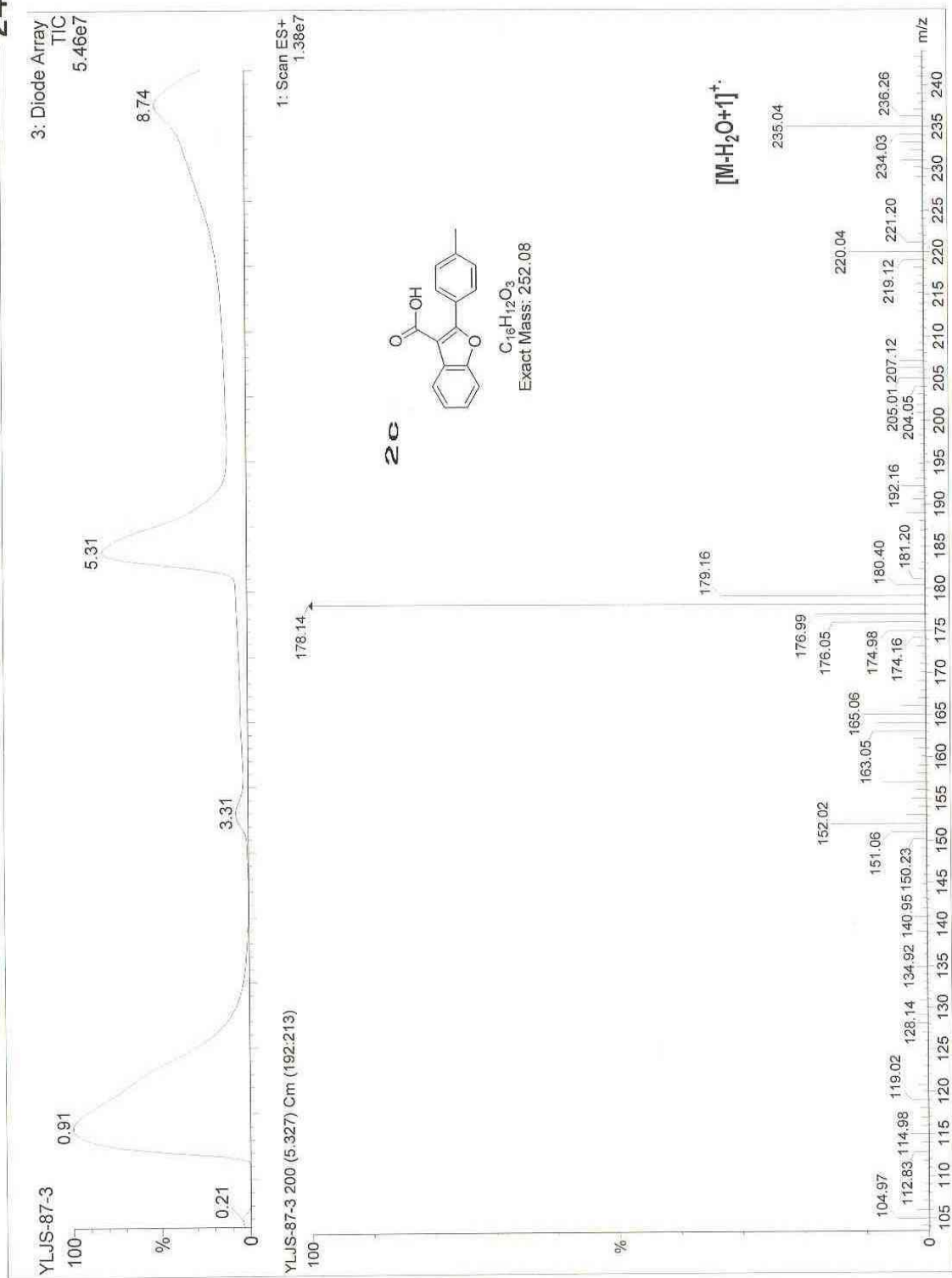
DATA PROCESSING

Line broadening 0.5 Hz

FT size 131072

Total time 36 hr, 22 min, 20 sec



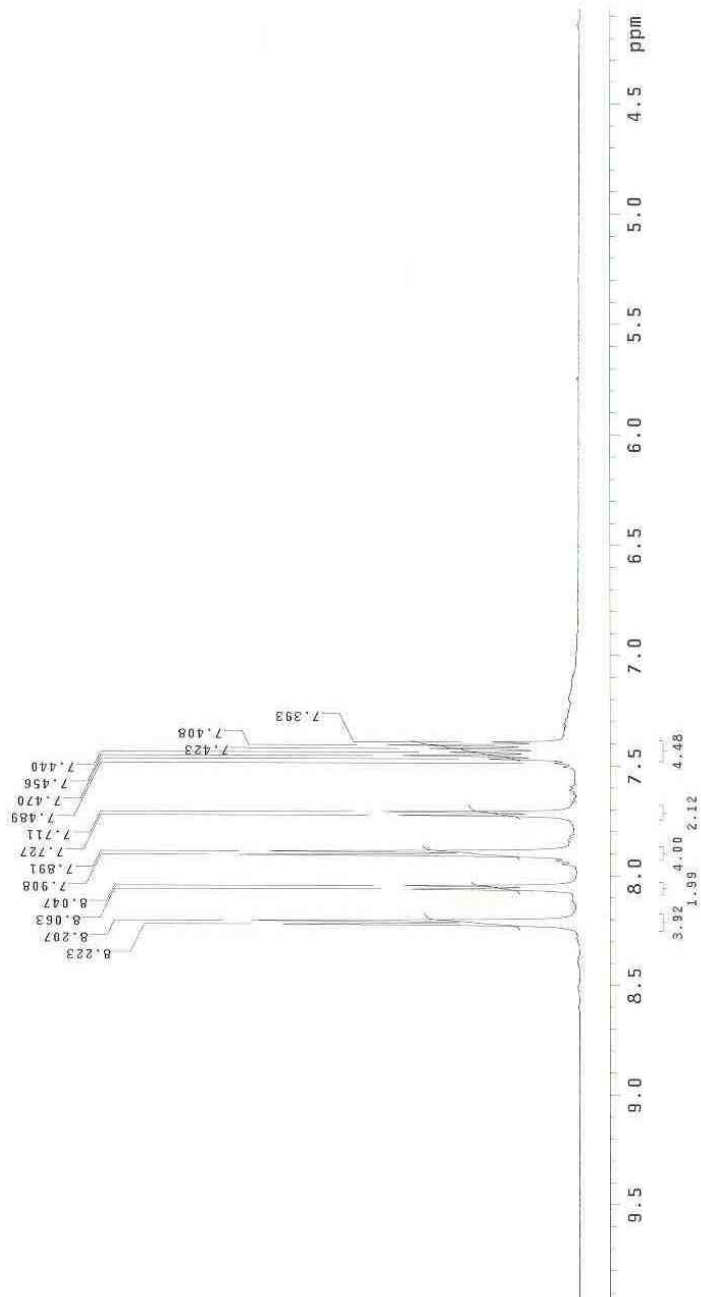
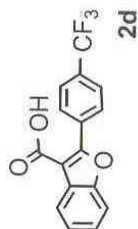


y1b87-4

Pulse Sequence: s2pul  
 Solvent: DMSO  
 Ambient temperature  
 INOVA-500 "Vivoquest"

Relax. delay 2.000 sec  
 Pulse 45.4 degrees  
 Acq. time 1.892 sec  
 Width 5000.0 Hz  
 4 repetitions

OBSERVE H1, 499.7200211 MHz  
 DATA PROCESSING  
 Line broadening 0.4 Hz  
 F1 size 32768  
 Total time 0 min, 23 sec



YLJS-87-4

Pulse Sequence: zgpg30

Solvent: DMSO

Ambient temperature

File: YLJS-87-4

INOVA-500 "vivoquest"

Relax. delay 2.000 sec

Pulse 15.000000000000000

Acq. time 1.000000000000000

Width 10000.0 Hz

12 repetitions

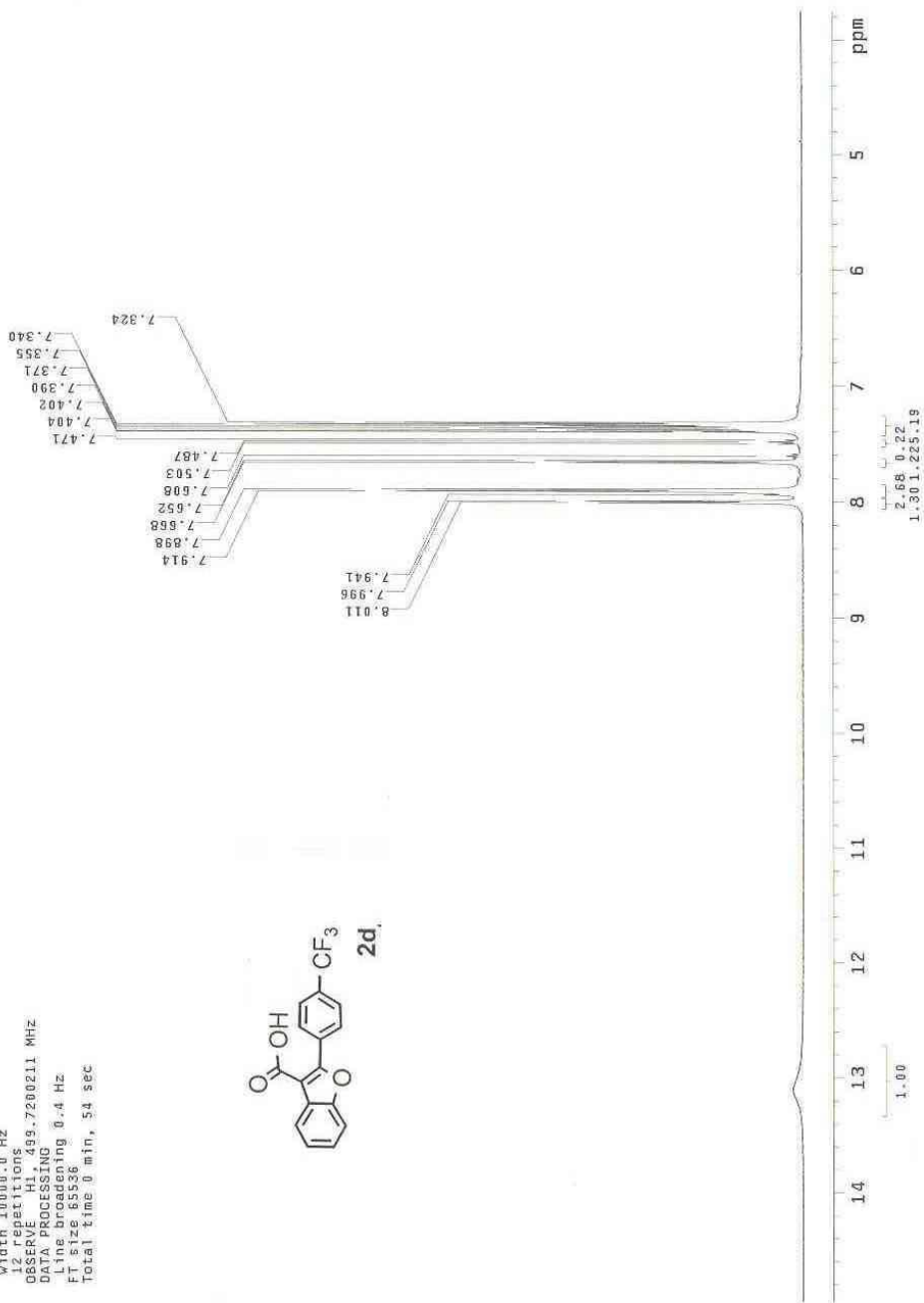
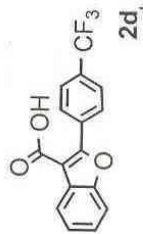
OBSERVE H1, 499.7200211 MHz

DATA PROCESSING

Line broadening 0.4 Hz

FT size 65536

Total time 0 min, 54 sec



27

y1b87-4

Pulse Sequence: zgpg30

Solvent: DMSO

Ambient temperature

User: 1-14-87

INOVA-500 "Vivoquest"

Pulse 64.3 degrees

Acq. time 1.300 sec

Width 25000.0 Hz

576 repetitions

OBSERVE C13, 125.654693 MHz

DECOUPLE H1, 499.725198 MHz

Power 11.00 W

Controlled by on

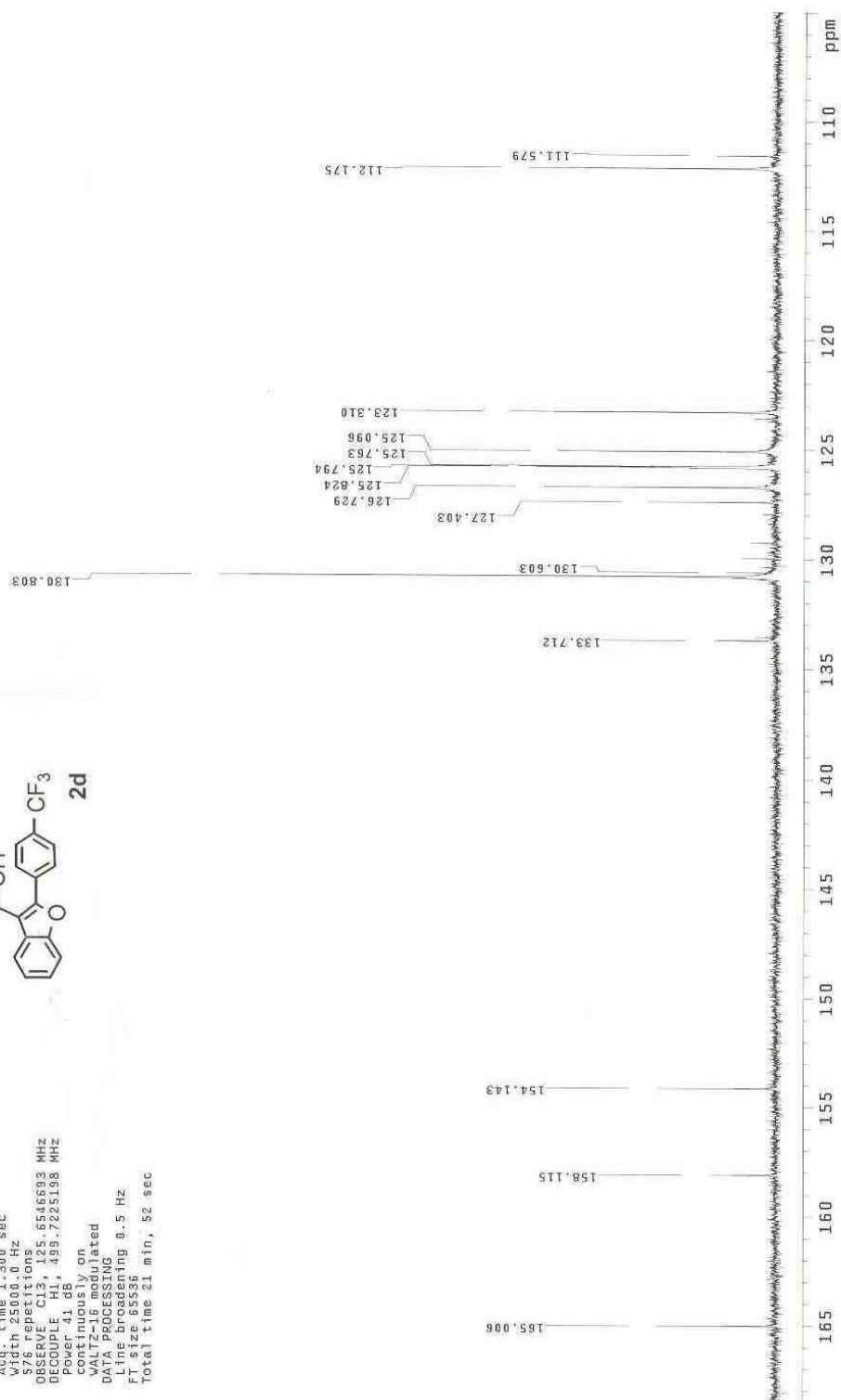
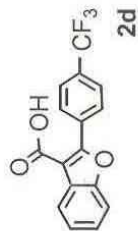
WALTZ-16 modulated

DATA PROCESSING

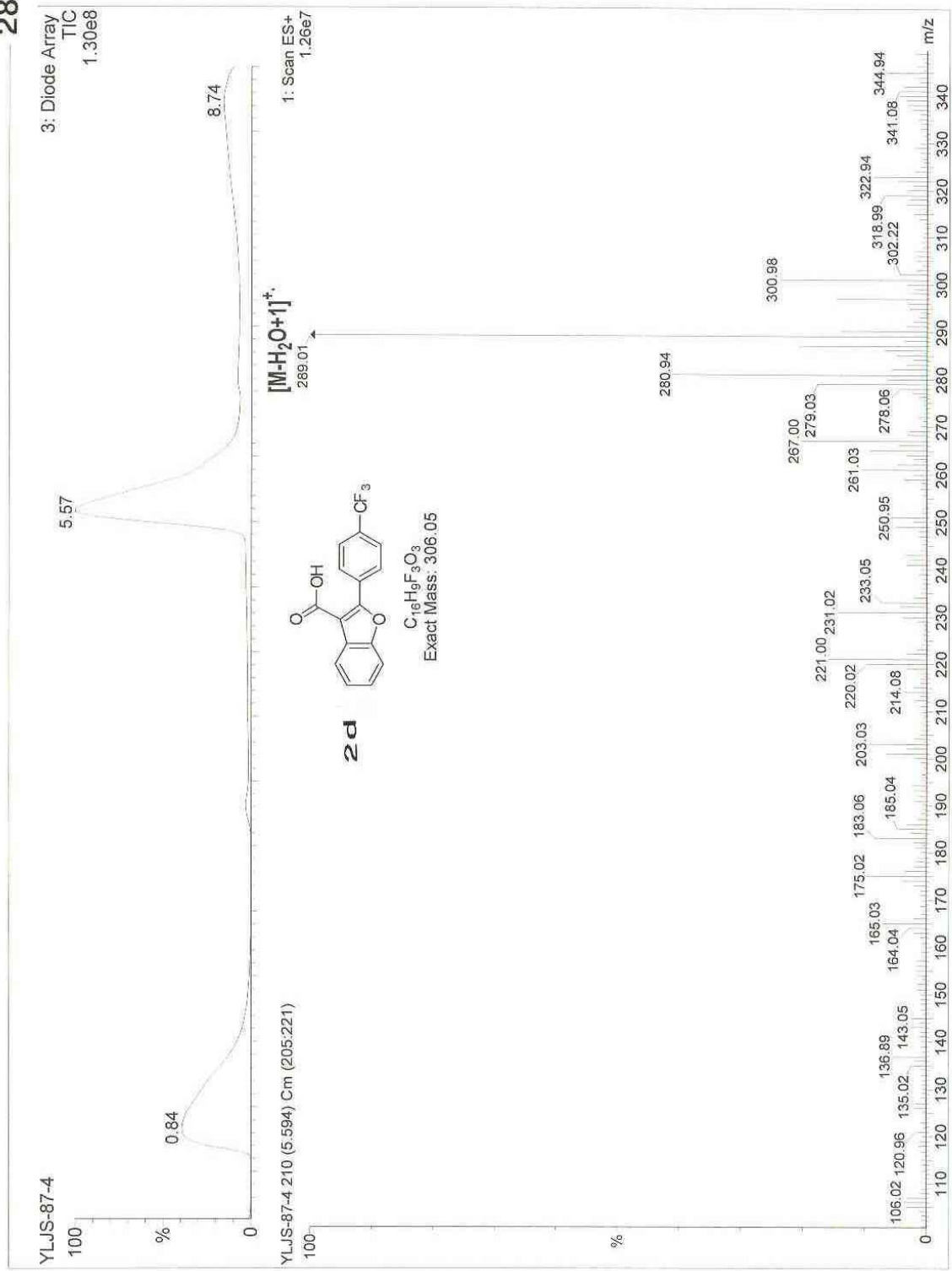
Line broadening 0.5 Hz

F1 size 65536

Total time 21 min, 52 sec



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ylb91-1

Pulse Sequence: s2pul

Solvent: DMSO

Acquire temperature

INDVA-300 Vivoquest

Relax. delay 2.000 sec

Pulse 15.00 degrees

Acq. time 1.000 sec

Width 5000.0 Hz

2 repetitions

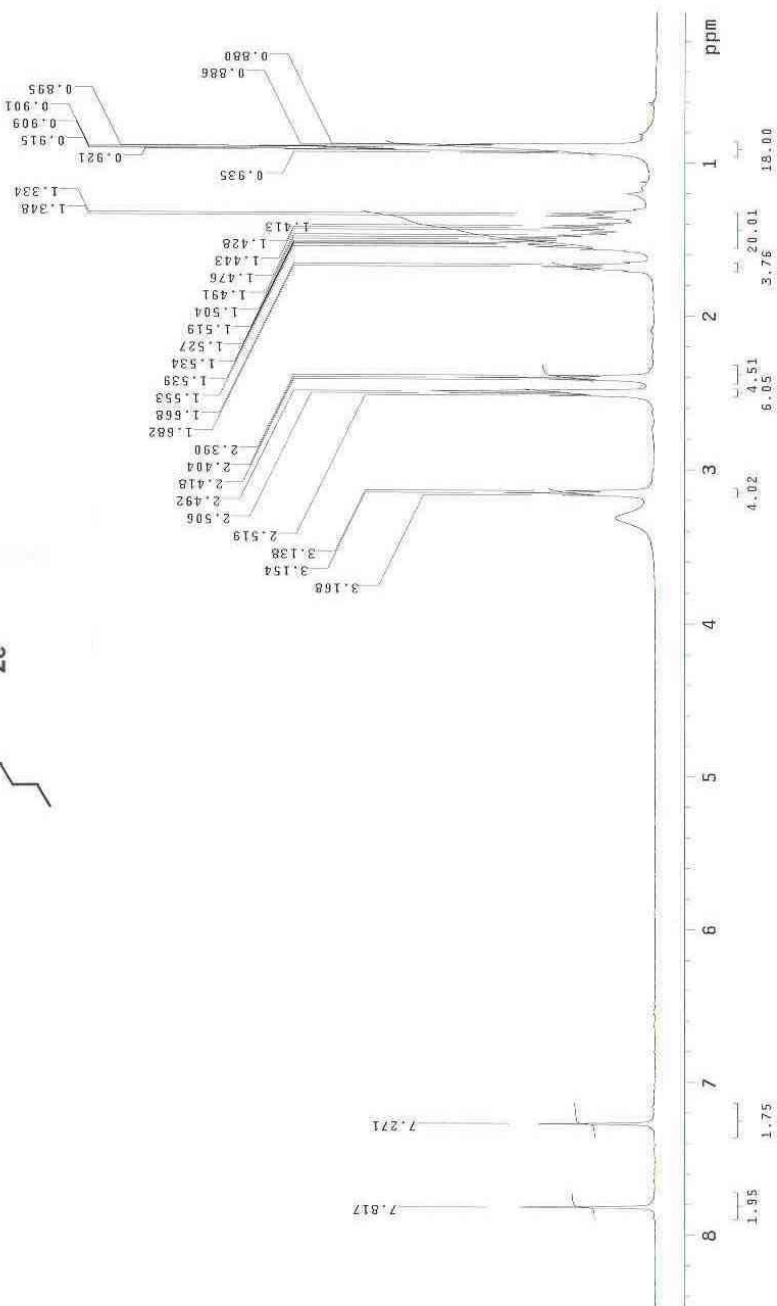
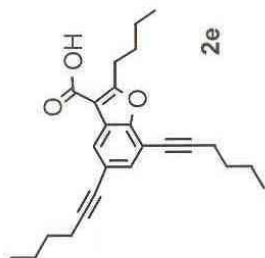
OBSERVE H1, 499.7200211 MHz

DATA PROCESSING

Line broadening 1.0 Hz

FT size 32768

Total time 0 min, 15 sec



y1b91-1

Pulse Sequence: szpul

Solvent: DMSO

Ambient temperature

INNOVA-300 "vivoquest"

Relax. delay 2.000 sec

Pulse 15.4 degrees

Acquire time 1.000 sec

Width 10000.0 Hz

2 repetitions

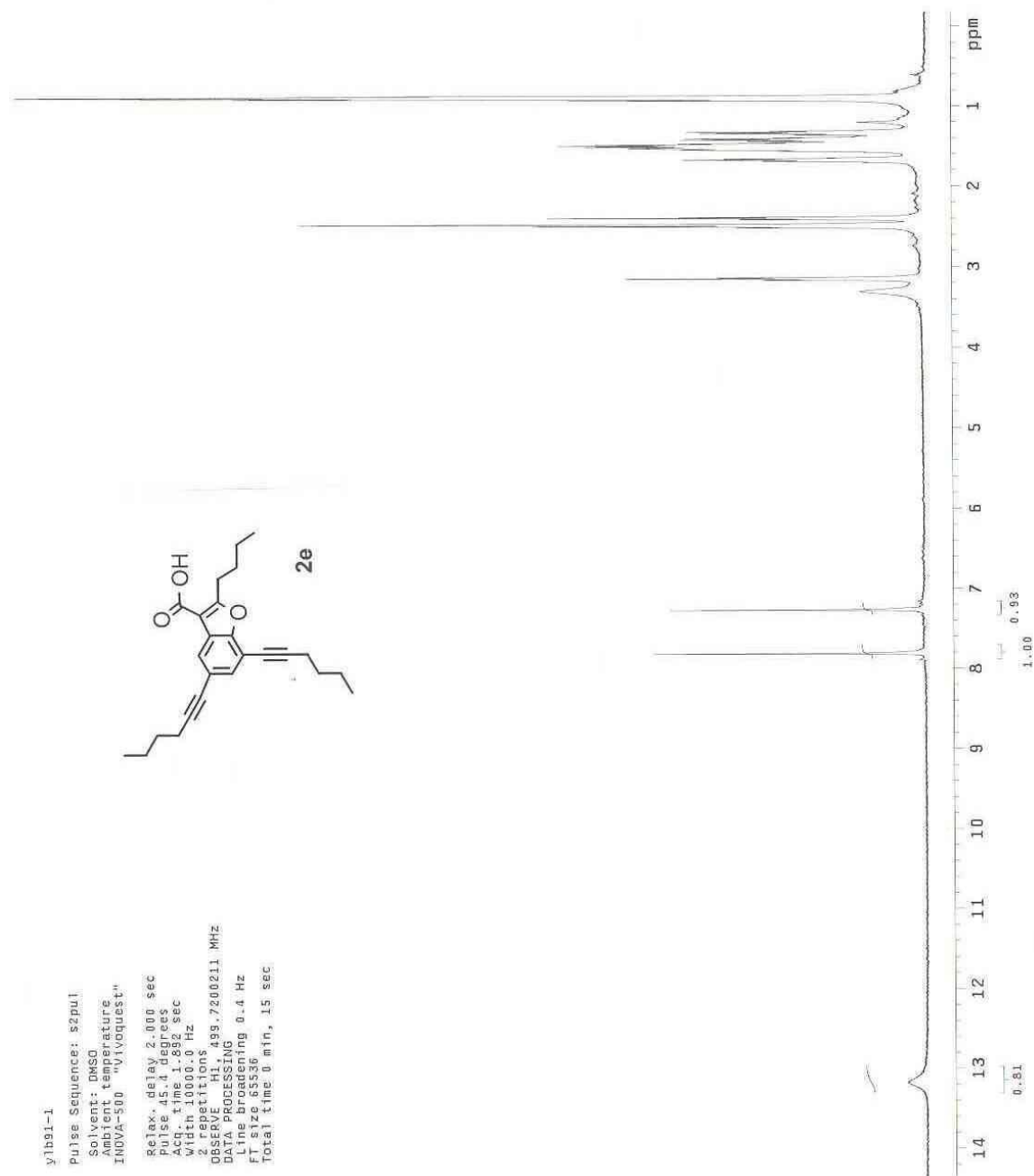
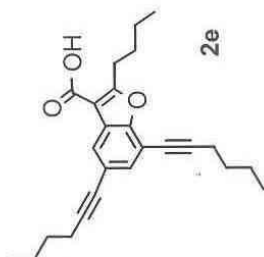
OBSERVE H1, 499.7200211 MHz

DATA PROCESSING

Line broadening 0.4 Hz

FT size 65536

Total time 0 min, 15 sec



Y1b31-1

Pulse Sequence: s2pul

Solvent: DMSO

Ambient temperature

User: 1-14-87

INNOVA-500 "Vivoquest"

Pulse 64.3 degrees

Acq. time 1.300 sec

Width 34955.6 Hz

868 repetitions

DECOUPLE CH1, 125.654563 MHz

DECOUPLE CH2, 459.722519 MHz

Power 41 dB

continuously on

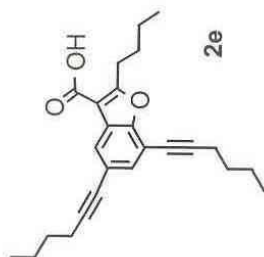
WALTZ-16 modulated

DATA PROCESSING

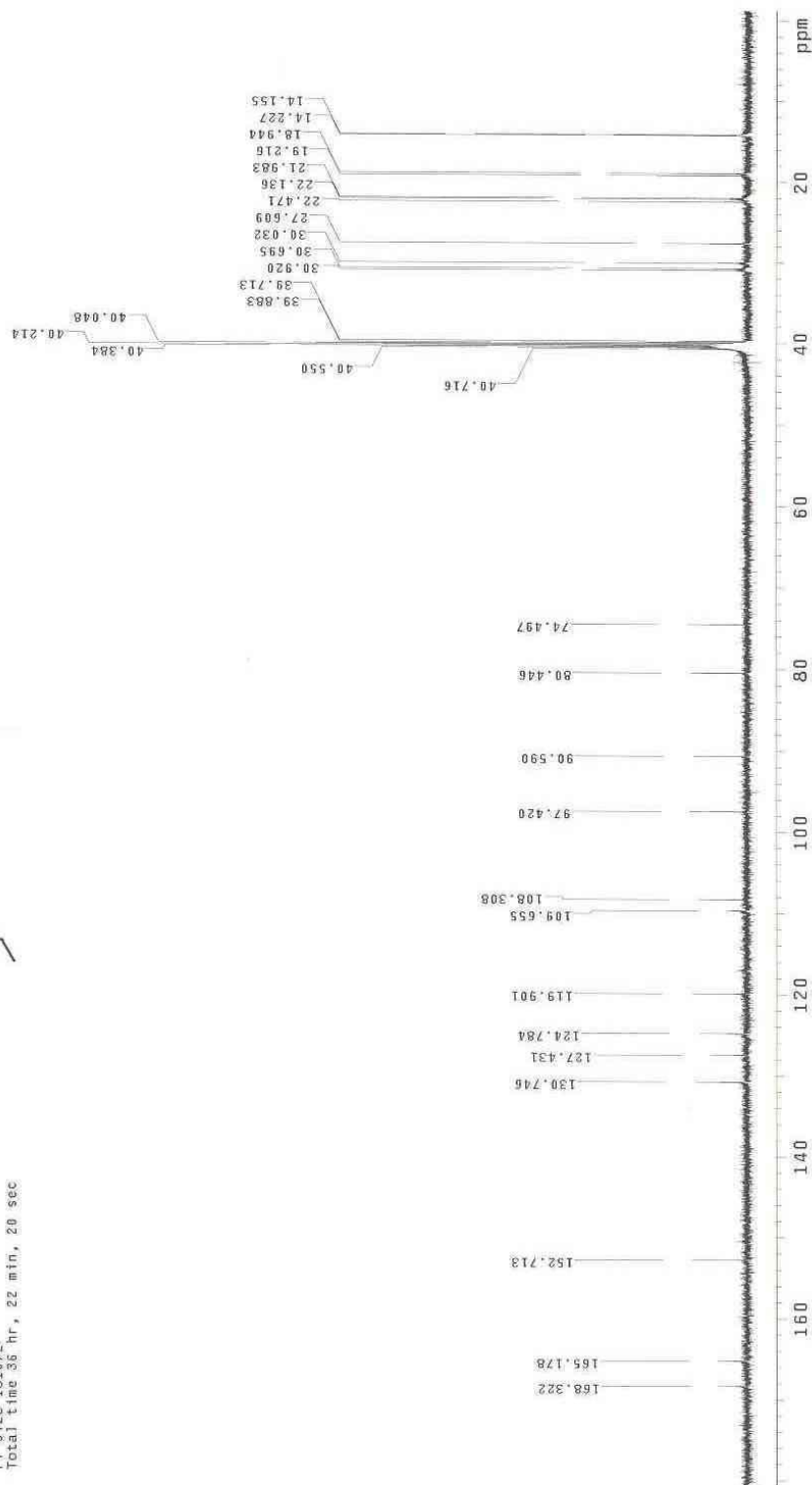
Line broadening 0.5 Hz

FT size 131072

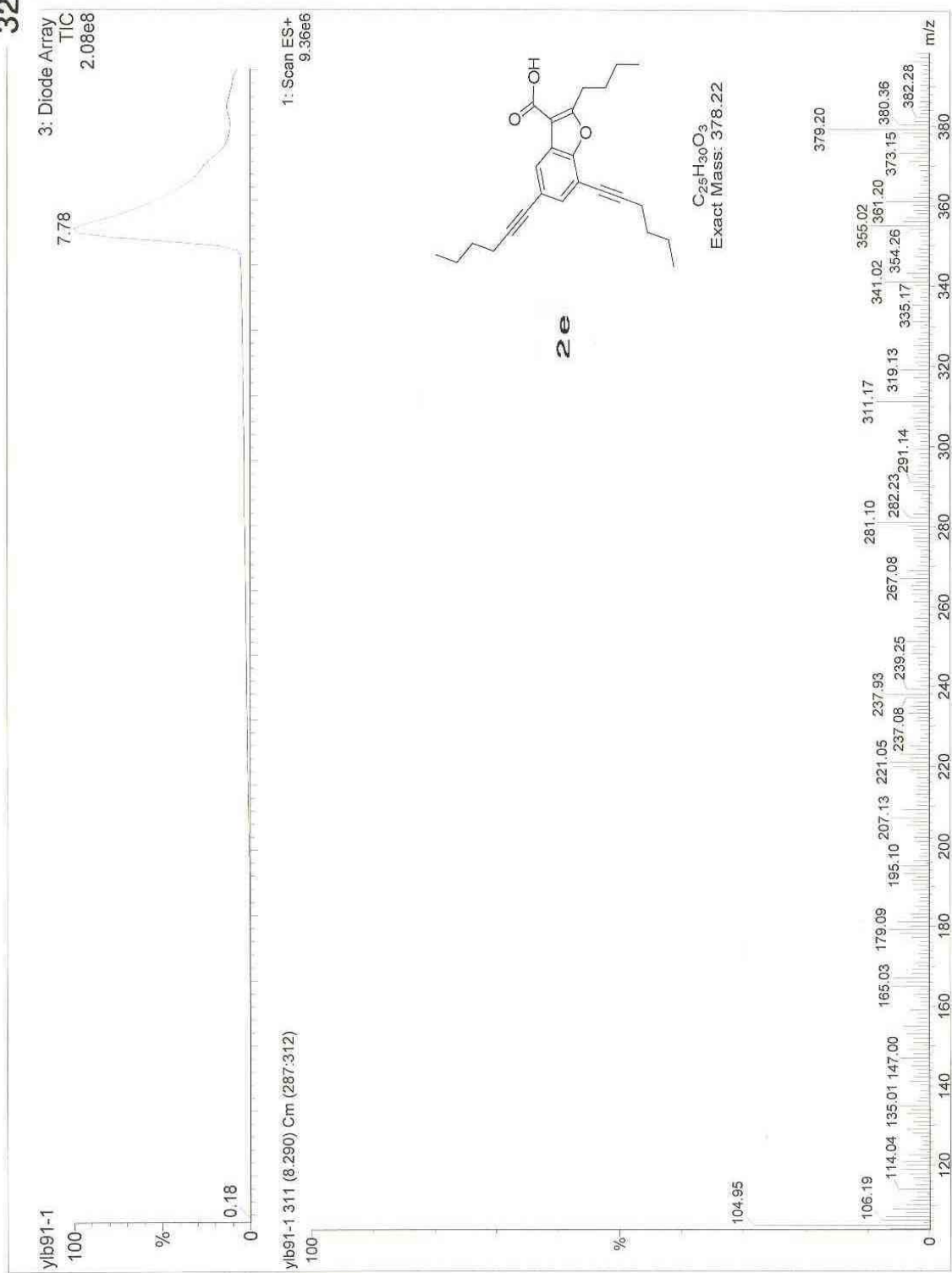
Total time 36 hr, 22 min, 20 sec



2e



32



y1b91-2

Pulse Sequence: zgpg30

Solvent: DMSO

Ambient temperature

INNOVA-500 "Vivoquest"

Relax. delay 2.000 sec

Pulse 45.4 degrees

Acq. time 1.803 sec

Width 5000.0 Hz

2 repetitions

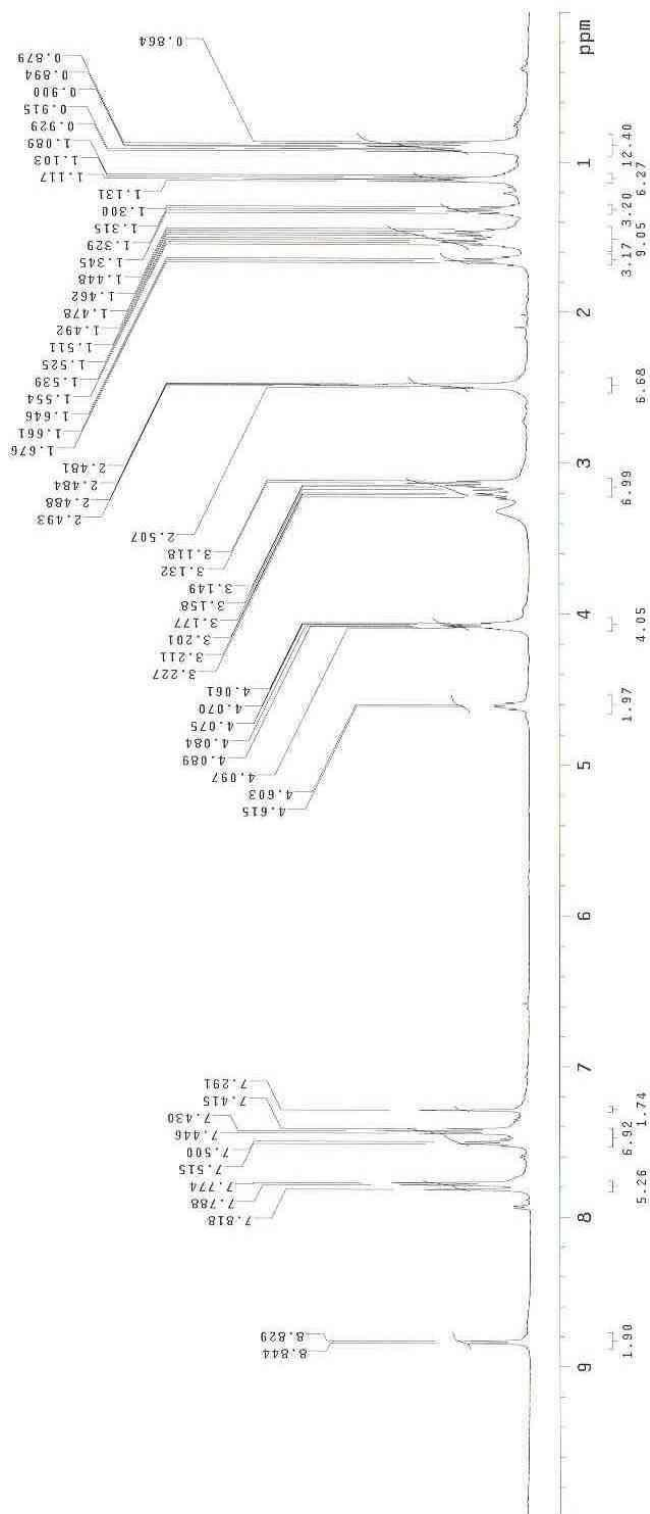
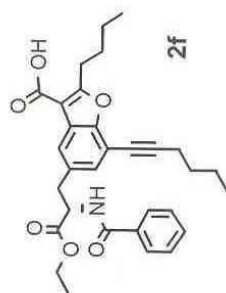
OBSERVE F1 499.720211 MHz

LINE PROCESSING

Line broadening 0.4 Hz

FI size 32768

Total time 0 min, 15 sec



YLS-91-2

Pulse Sequence: s2pul

Solvent: DMSO

Ambient temperature

INNOVA-300 "Vivoquest"

Relax. delay 2.000 sec

Pulse 45.4 degrees

Acq. time 0.893 sec

Width 0.000 Hz

12 repetitions

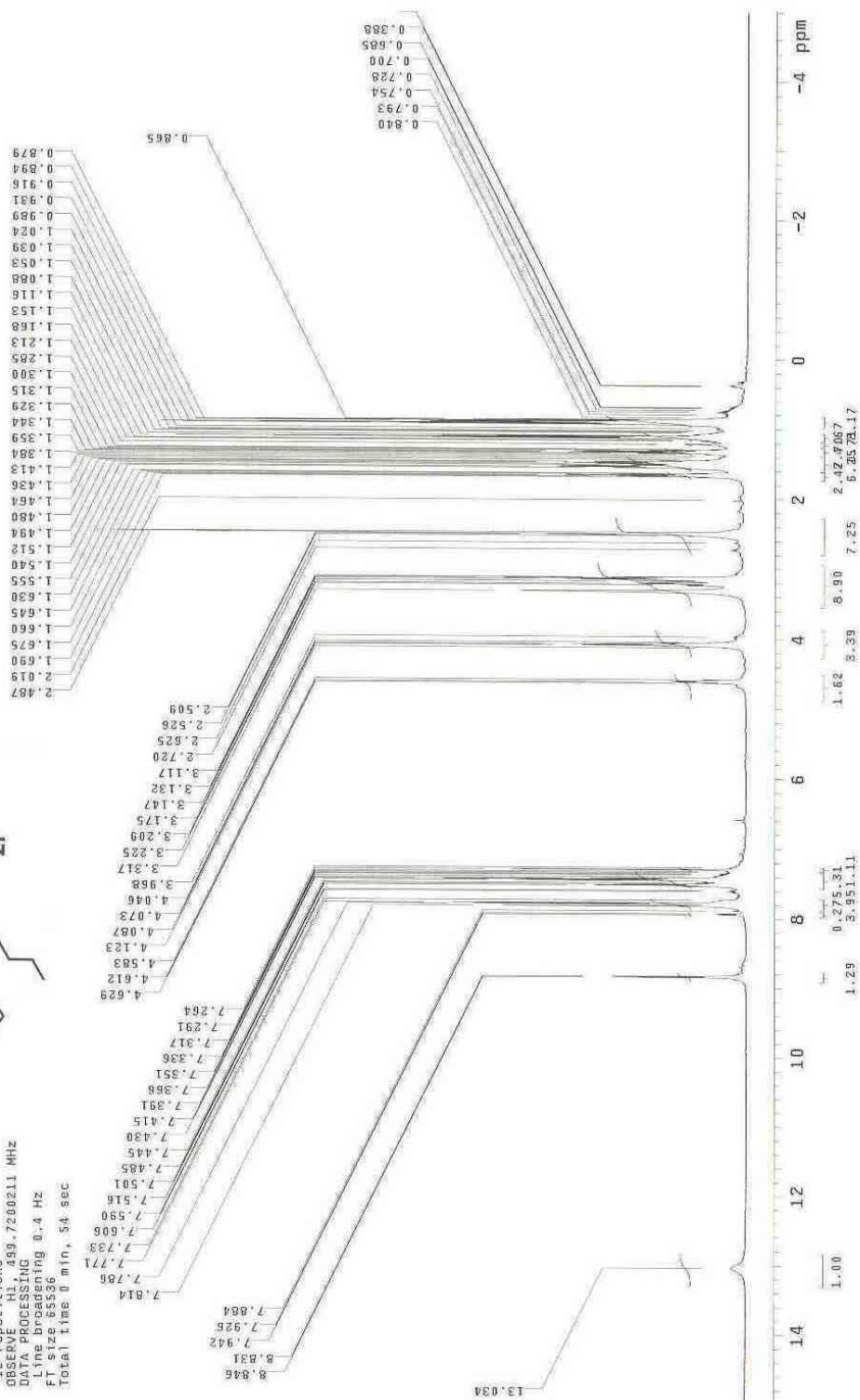
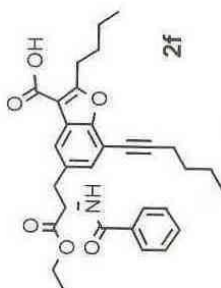
OBSERVE H1, 499.7200211 MHz

DATA PROCESSING

Line broadening 0.4 Hz

FT size 65536

Total time 0 min, 54 sec



y1b91-2

Pulse Sequence: zgpg30

Solvent: DMSO

Ambient temperature

User: 1-14-87

INNOVA-500 "Vivoquest"

Pulse 64.3 degrees

Acq. time 1.300 sec

Width 34995.6 Hz

Size 1024

Repetitions 5

DECOUPLE CH, 125.654663 MHz

DECOUPLE CH, 459.7225198 MHz

Power 41 dB, continuously on

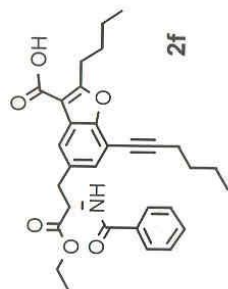
WALTZ-16 modulated

DATA PROCESSING

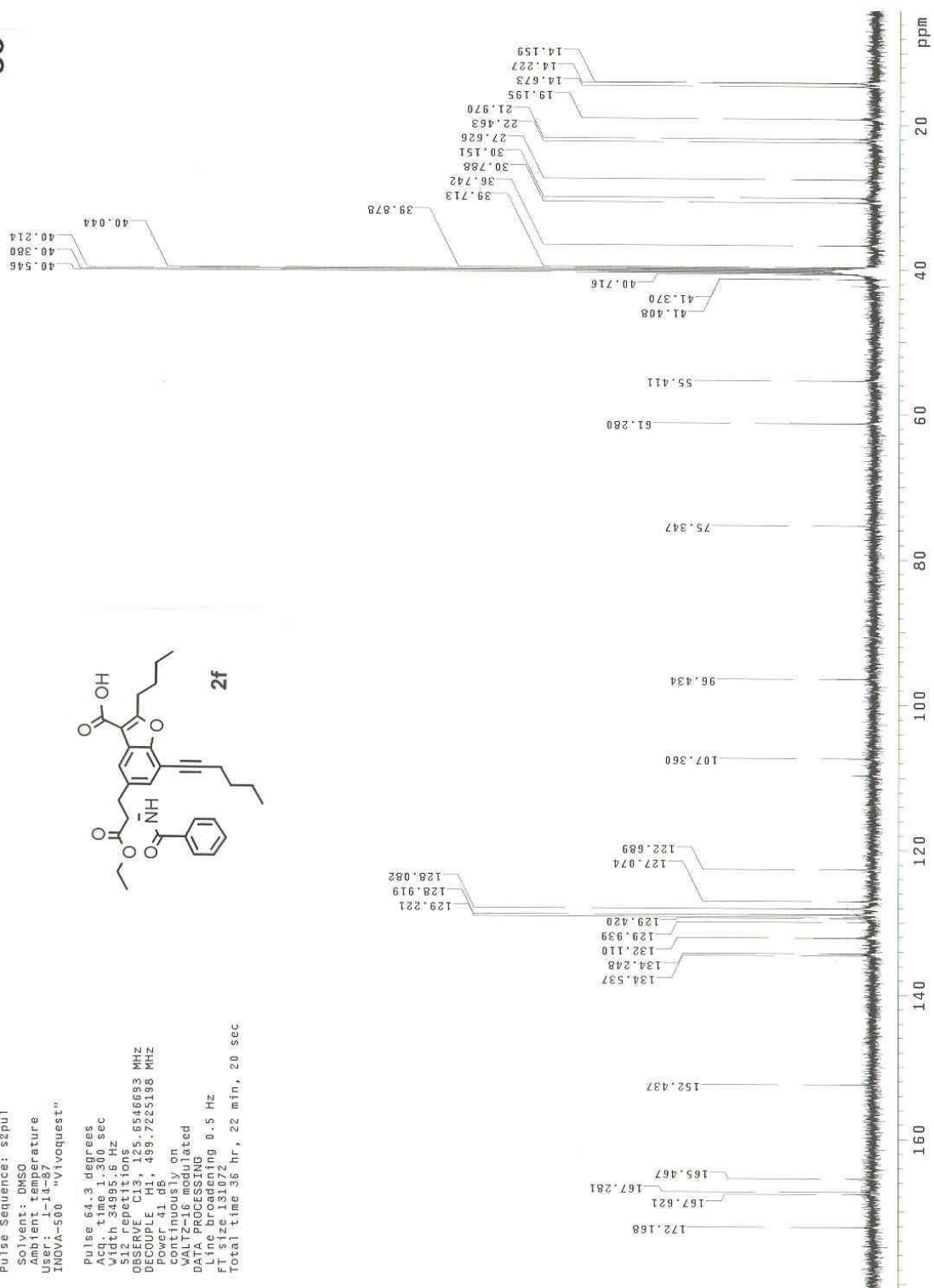
Line broadening 0.5 Hz

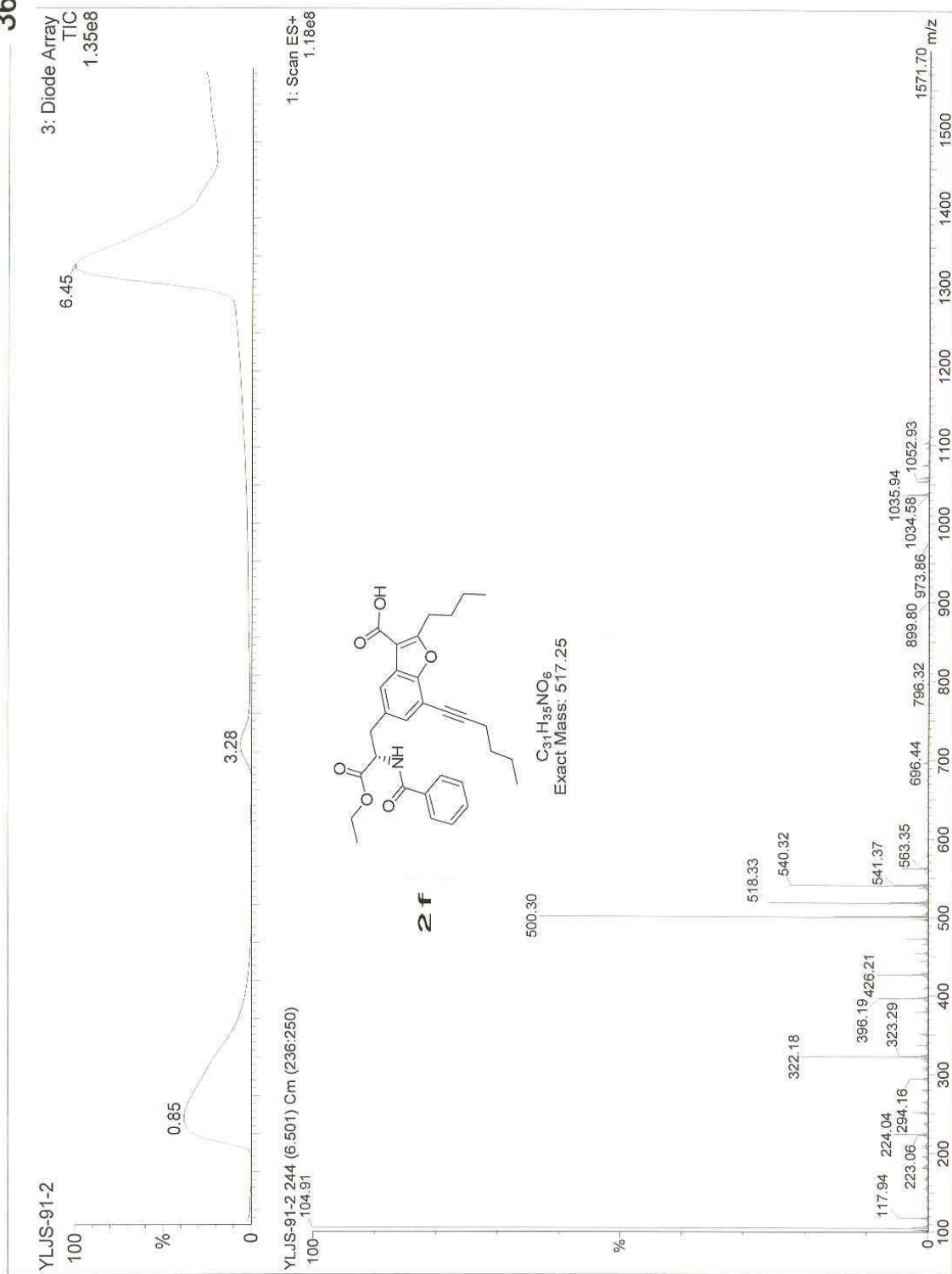
FT size 131072

Total time 36 hr, 22 min, 20 sec



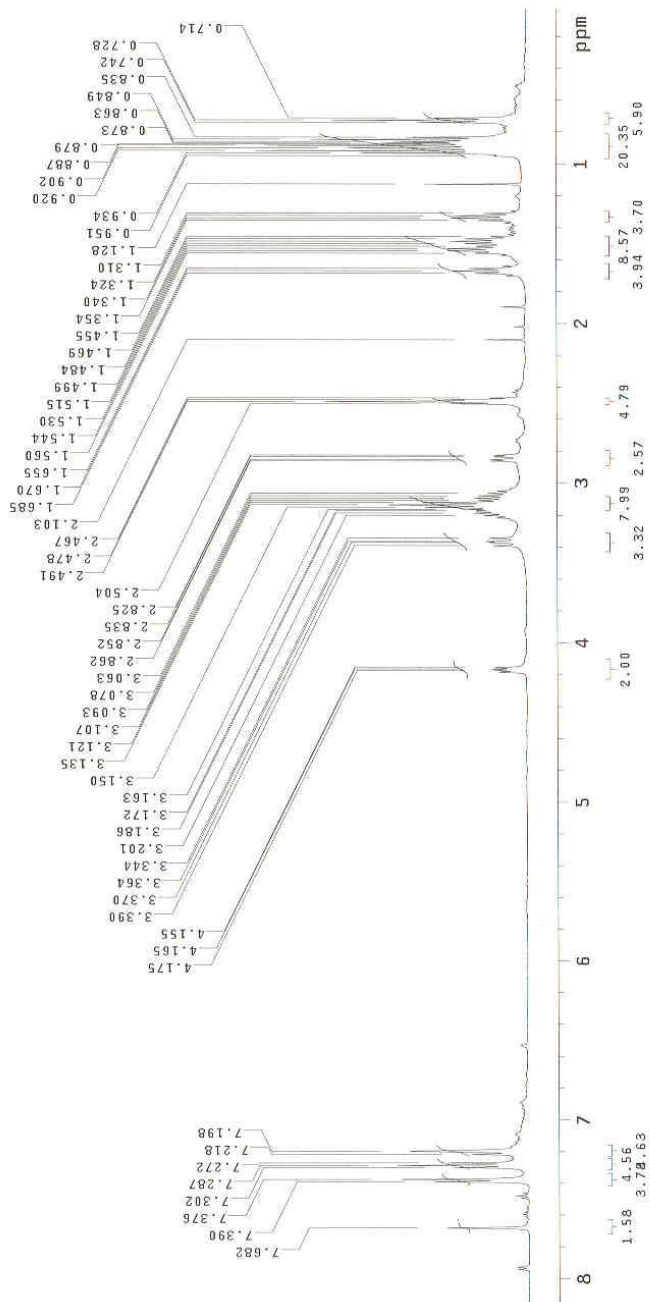
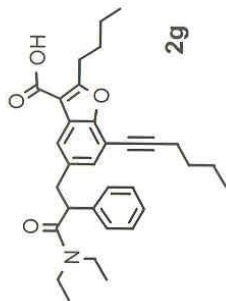
35

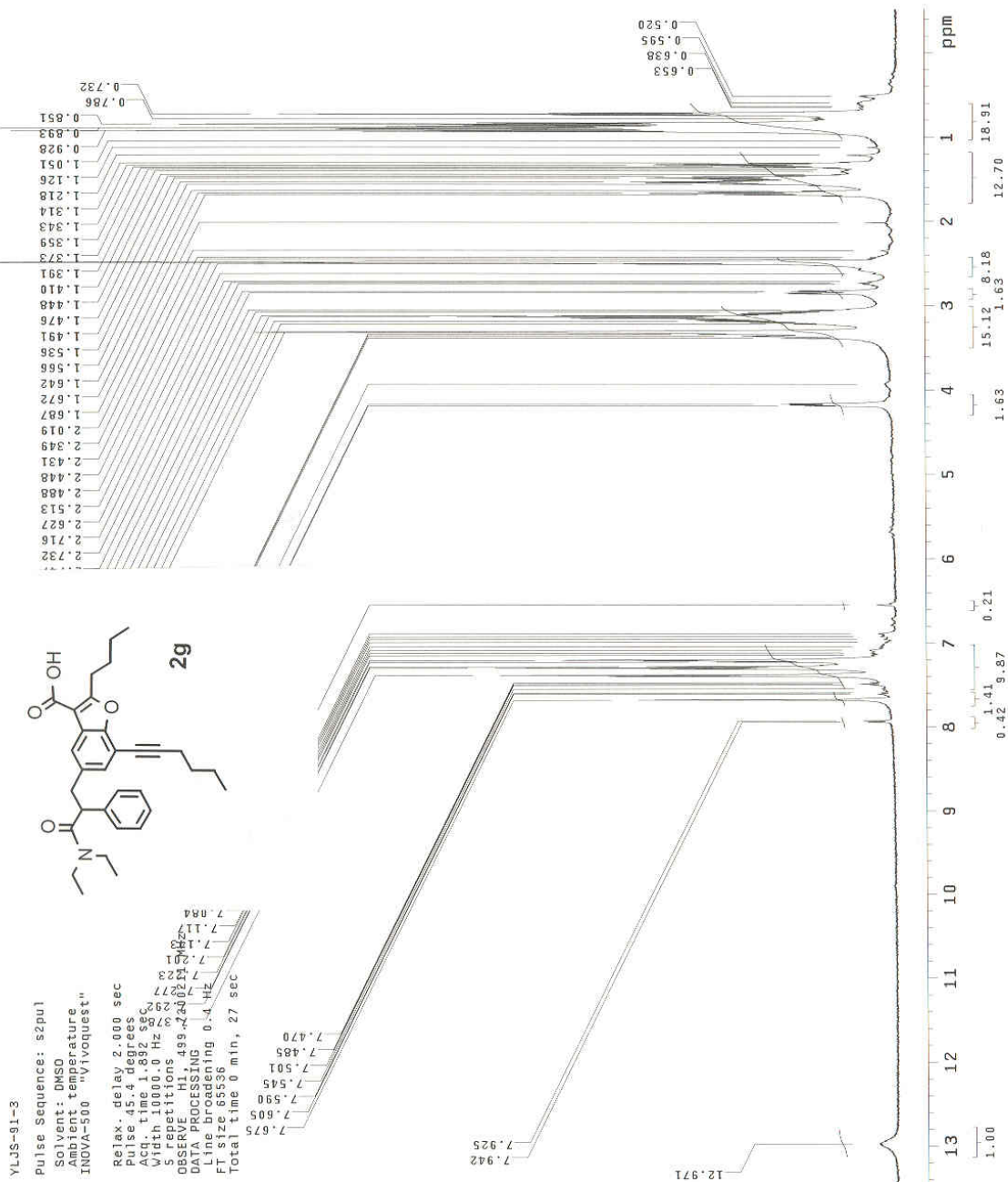




y1b91-3

Pulse Sequence: s2pul  
 Solvent: DMSO  
 Ambient temperature  
 INOVA-500 "Vivoquest"  
 Relax. delay 2.000 sec  
 Pulse 45.4 degrees  
 Acq. time 1.892 sec  
 Width 5000.0 Hz  
 2 repetitions  
 OBSERVED F1 99.7200211 MHz  
 PROCESSED F1 99.7200211 MHz  
 Line broadening 0.4 Hz  
 FT size 32768  
 Total time 0 min, 15 sec





y'lb91-3

Pulse Sequence: s2pul

Solvent: DMSO

Ambient temperature

INNOVA-500 "Vivoquest"

Pulse 64.3 degrees

Acq. time 1.00 sec

Width 3095.6 Hz

3840 repetitions

OBSERVE C13, 125.6546693 MHz

DECOUPLE H1, 499.7225198 MHz

Power 41 dB

continuously on

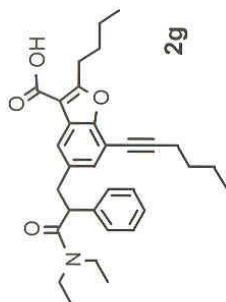
WALTZ-16 modulated

DATA PROCESSING

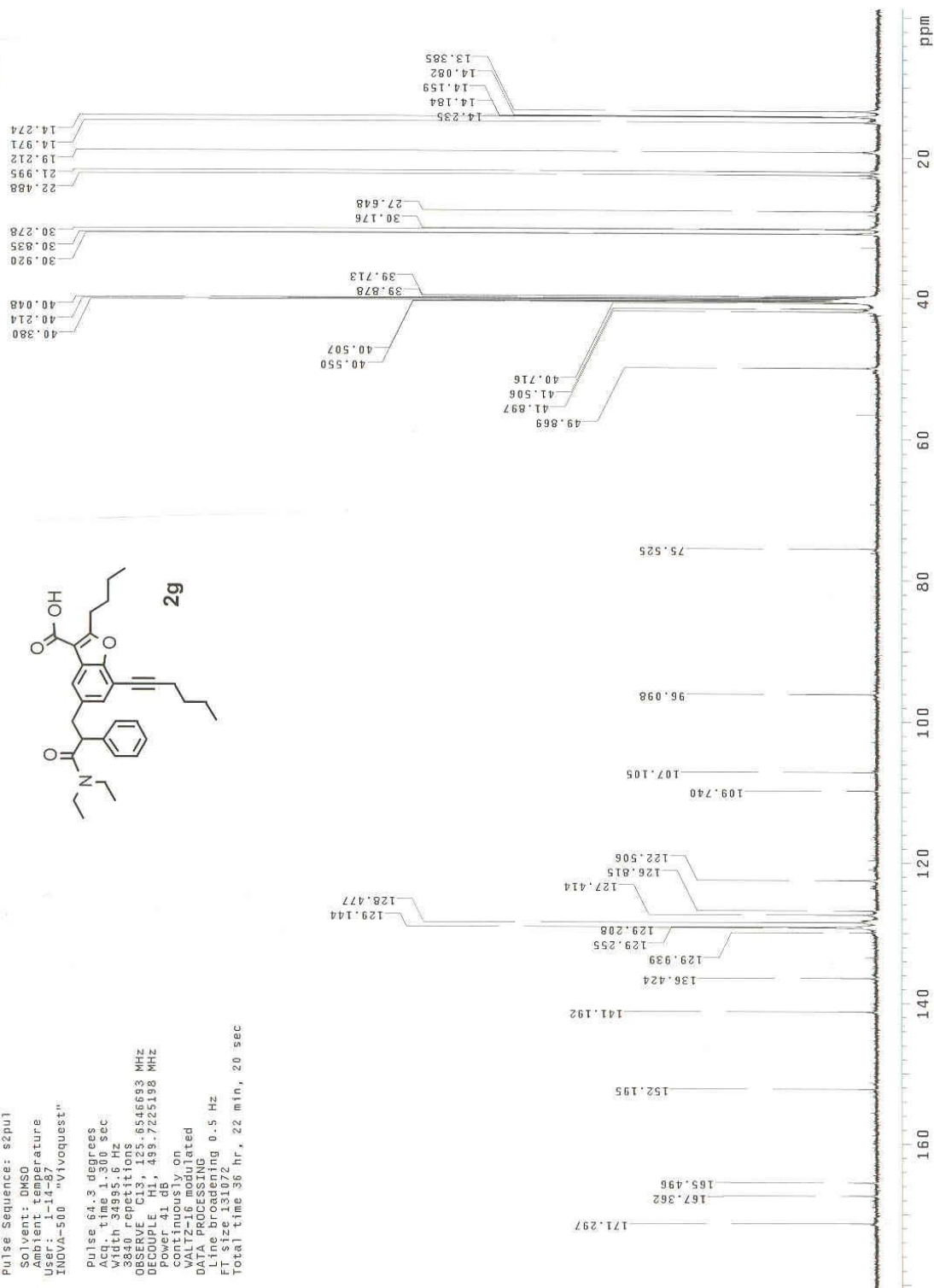
File processing 0.5 Hz

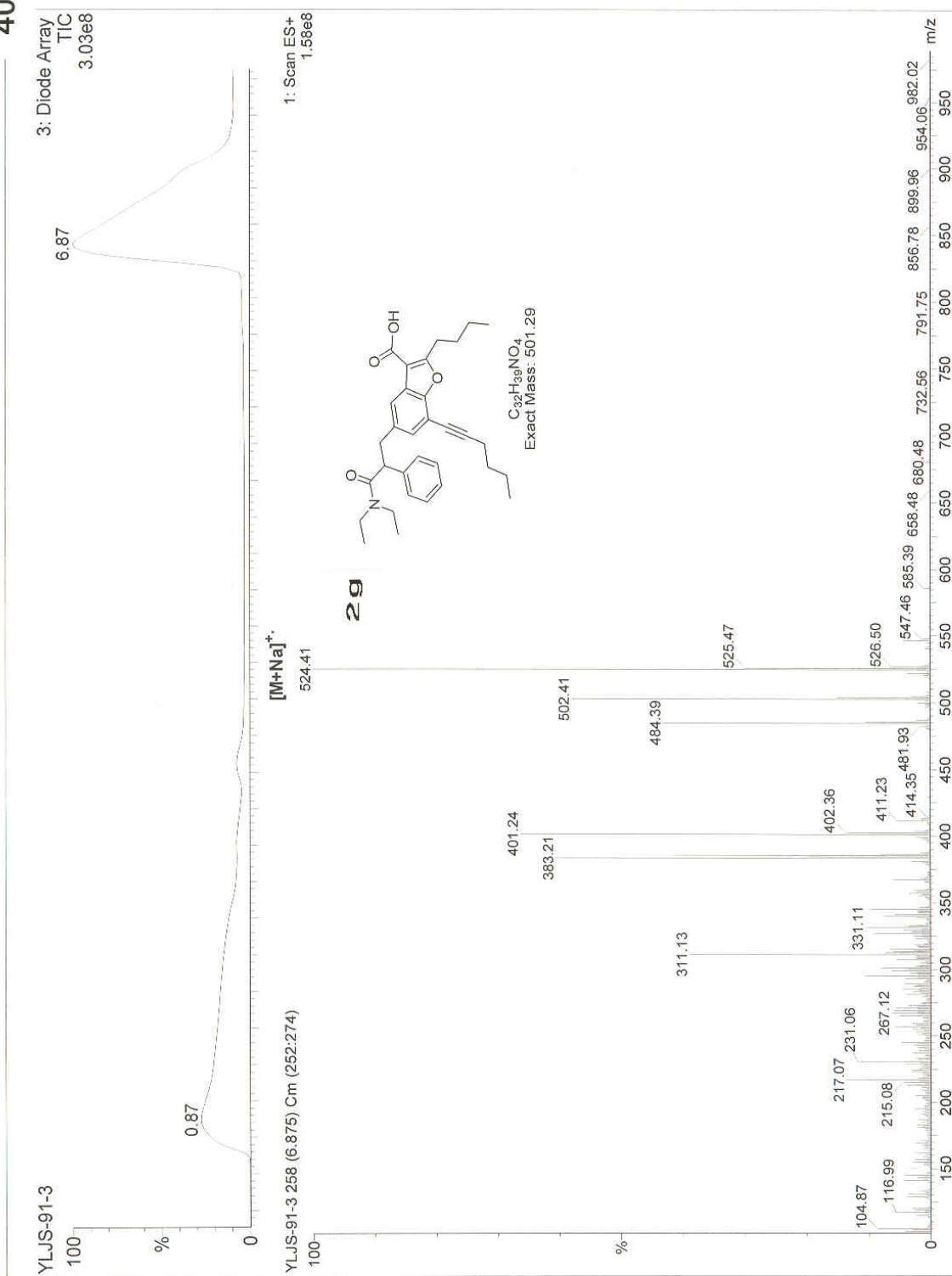
File size 31072

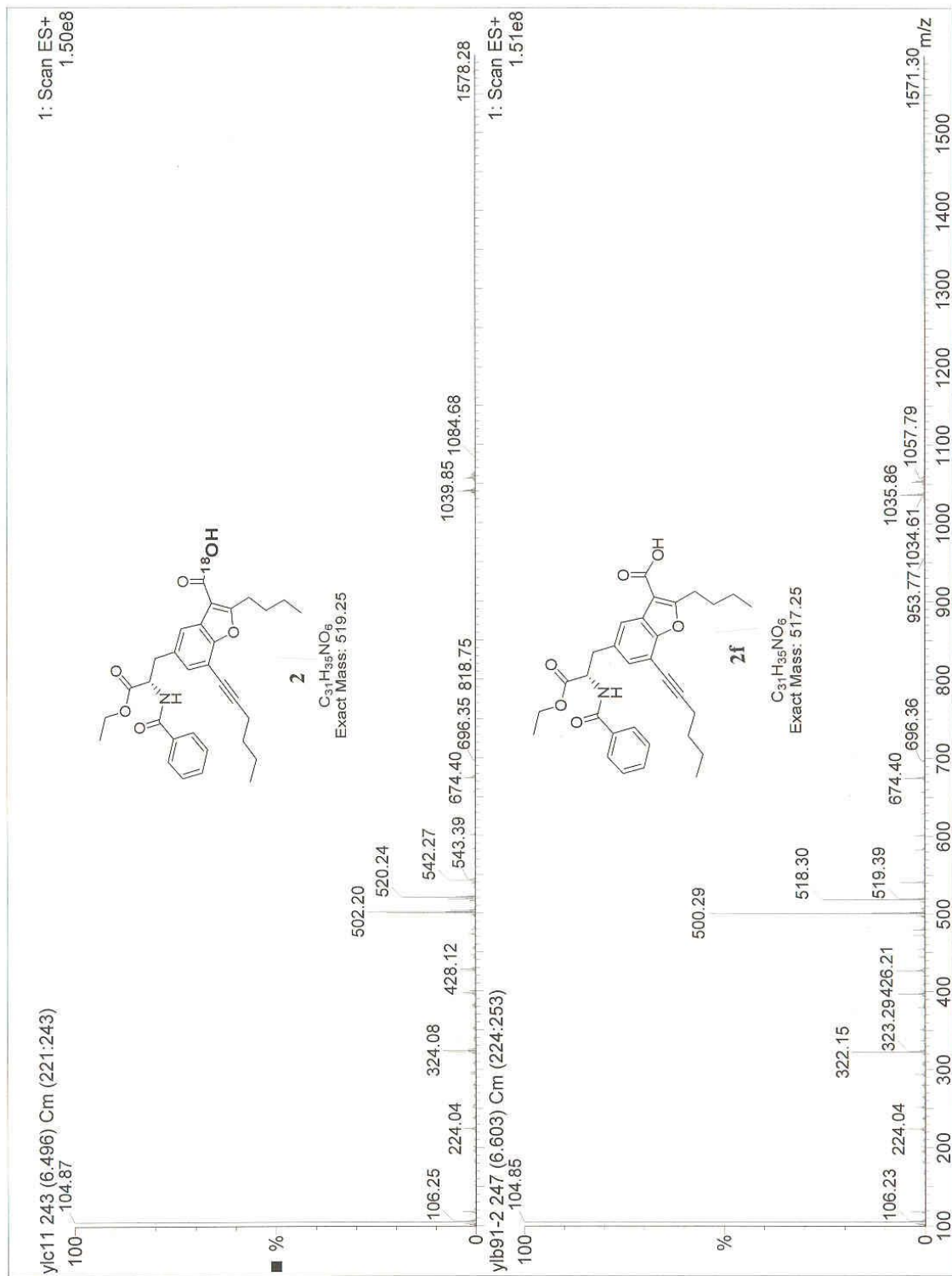
Total time 36 hr, 22 min, 20 sec



39







c11

Pulse Sequence: s2pu1

Solvent: DMSO

Ambient temperature

INOVA-500 "Vivoquest"

Relax. delay 2.000 sec

Pulse 45.4 degrees

Acq. time 1.893 sec

Width 10000.0 Hz

2 repetitions

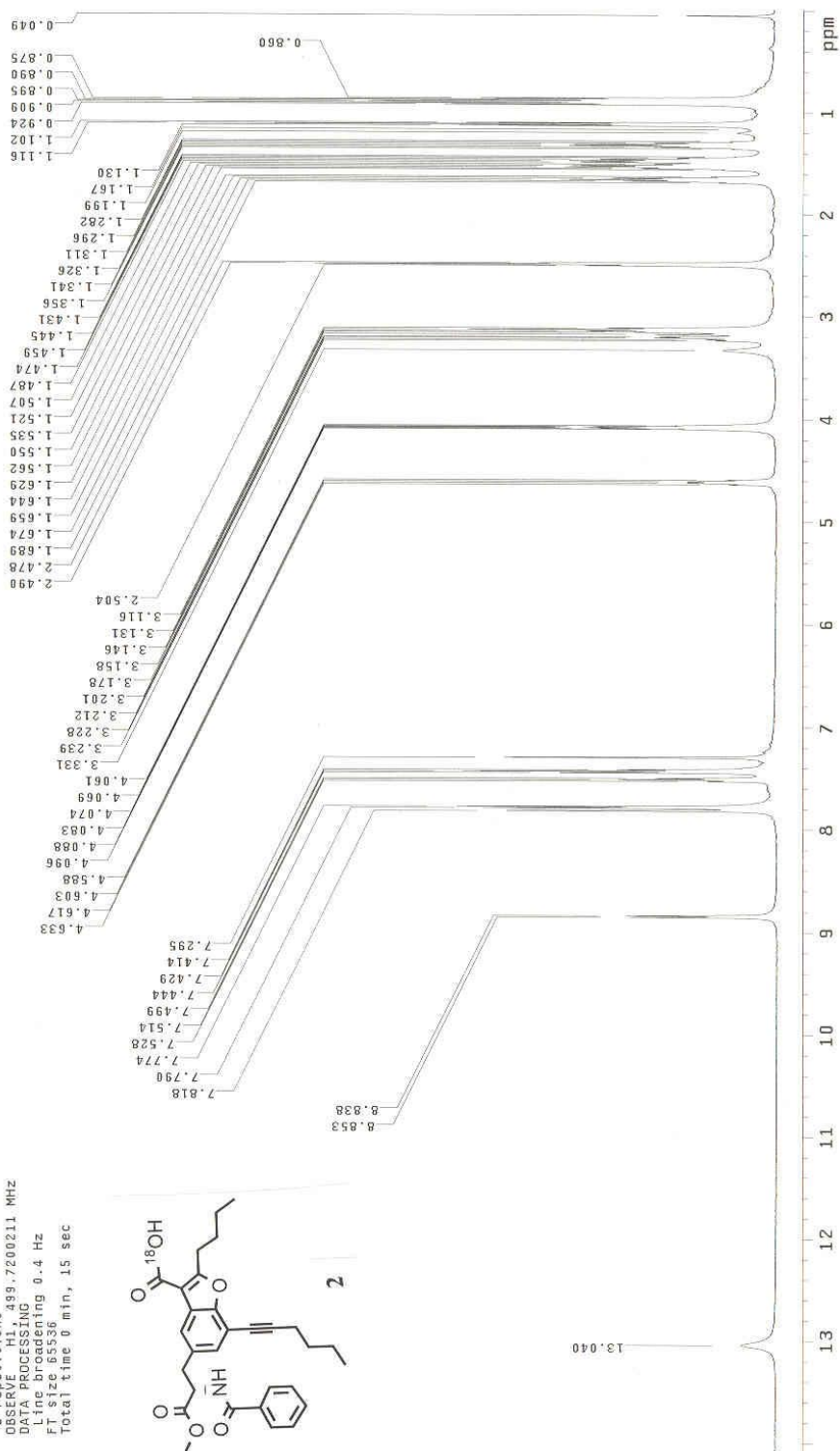
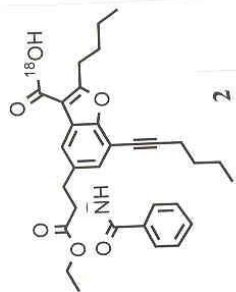
OBSERVE Hz, 499.7200211 MHz

DATA PROCESSING

F1 processing 0.4 Hz

FT size 65536

Total time 0 min, 15 sec



c11-c13

Pulse Sequence: s2pul

Solvent: DMSO

Ambient temperature

User: 1-14-87

INOVA-500 "Vivoquest"

Pulse 64.3 degrees

Acq. time 1.300 sec

Width 25000.0 Hz

Observed F1 505.6546693 MHz

Observed F2 125.7225198 MHz

Decouple CH1 499.7225198 MHz

Power 41 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 65536

Total time 21 min, 52 sec

