

## Supporting Information

### Synthesis of Near-Infrared Fluorescent Two-Photon Absorbing Fluorenyl Benzothiadiazole and Benzoselenadiazole Derivatives

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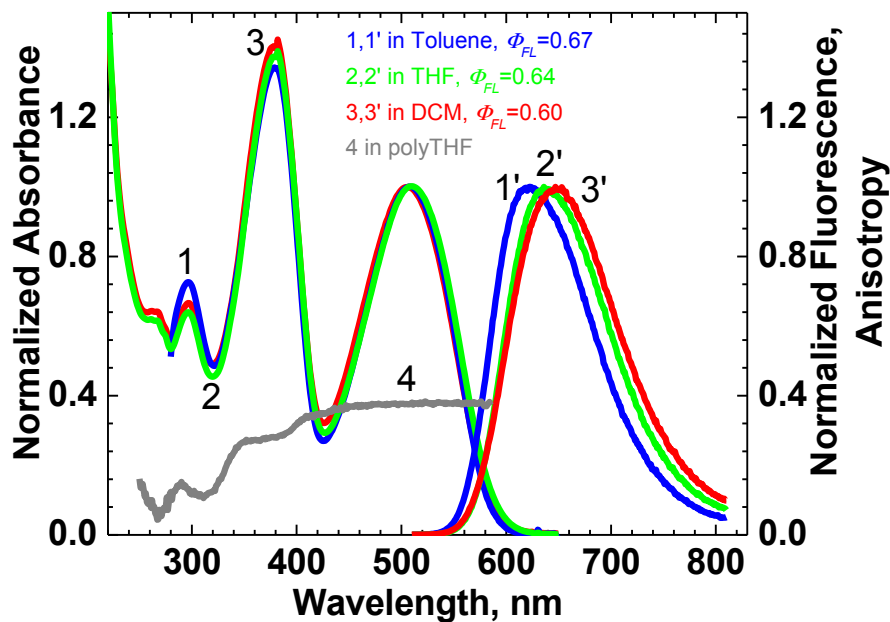
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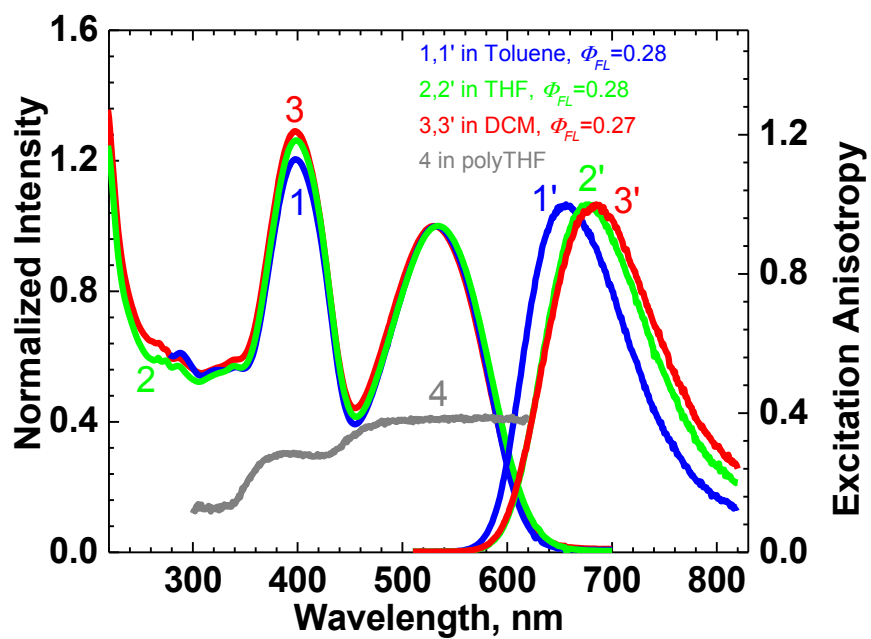
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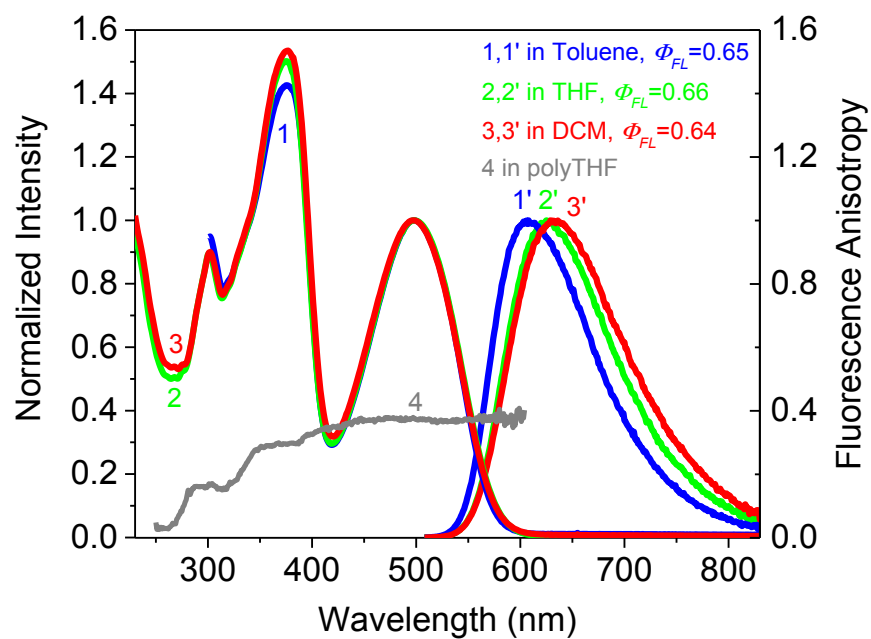
**Linear optical properties of dyes 2-5 in toluene, THF and methylene chloride.**



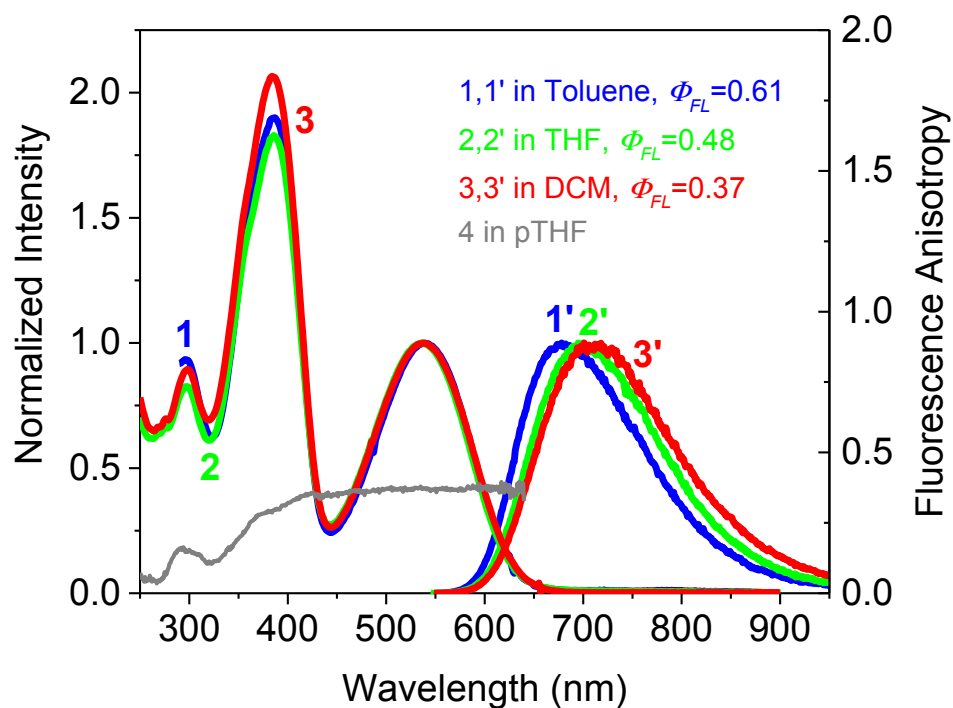
**Figure S1.** Absorption spectra (1, blue, in toluene; 2, green, in THF; 3, red, in dichloromethane (DCM)), fluorescence spectra (1', blue, in toluene; 2', green, in THF; 3', red, in DCM), and excitation anisotropy (4, grey, in polyTHF) of dye 2.



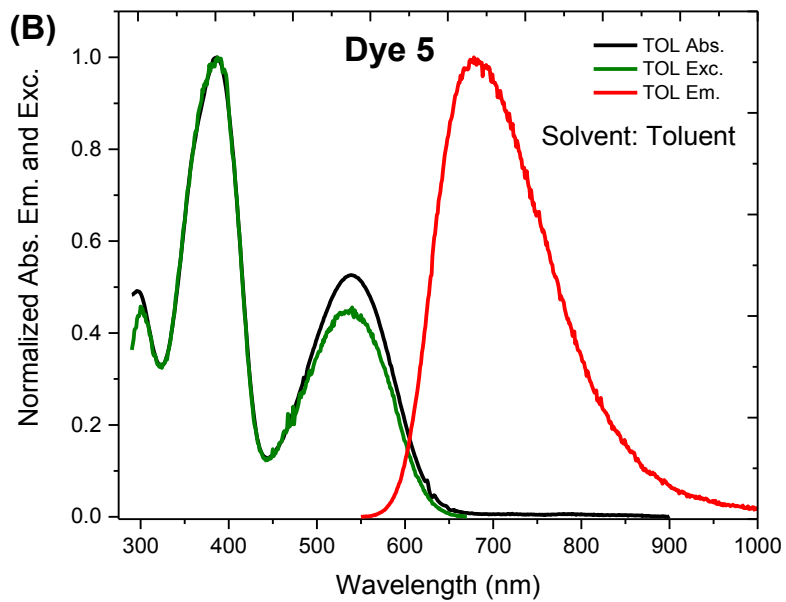
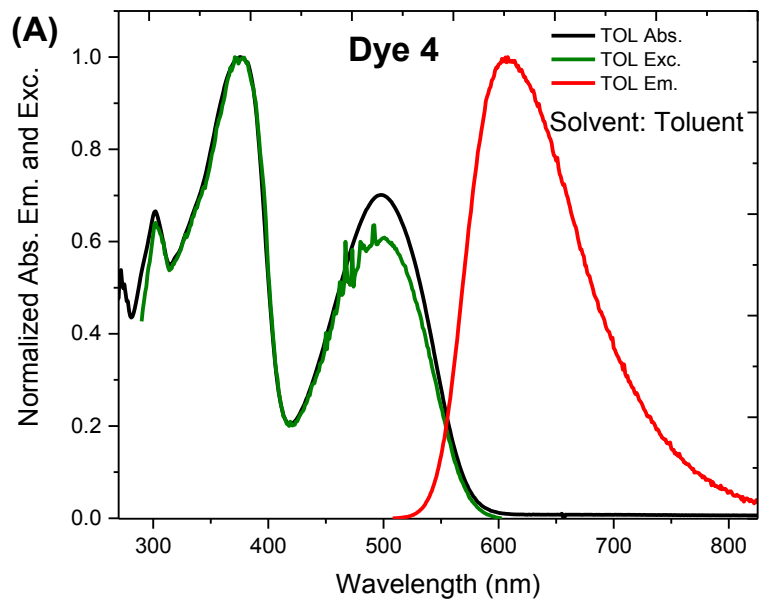
**Figure S2.** Absorption spectra (1, blue, in toluene; 2, green, in THF; 3, red, in DCM), fluorescence spectra (1', blue, in toluene; 2', green, in THF; 3', red, in DCM), and excitation anisotropy (4, grey, in polyTHF) of dye 3.



**Figure S3.** Absorption spectra (1, blue, in toluene; 2, green, in THF; 3, red, in DCM), fluorescence spectra (1', blue, in toluene; 2', green, in THF; 3', red, in DCM), and excitation anisotropy (4, grey, in polyTHF) of dye 4.



**Figure S4.** Absorption spectra (1, blue, in toluene; 2, green, in THF; 3, red, in DCM), fluorescence spectra (1', blue, in toluene; 2', green, in THF; 3', red, in DCM), and excitation anisotropy (4, grey, in polyTHF) of dye 5.



**Figure S5.** Absorption (black), excitation (green) and fluorescence (red) spectra of dye **4** (A) and dye **5** (B) in toluene.

# $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra

## Compound 9 $^1\text{H}$ NMR

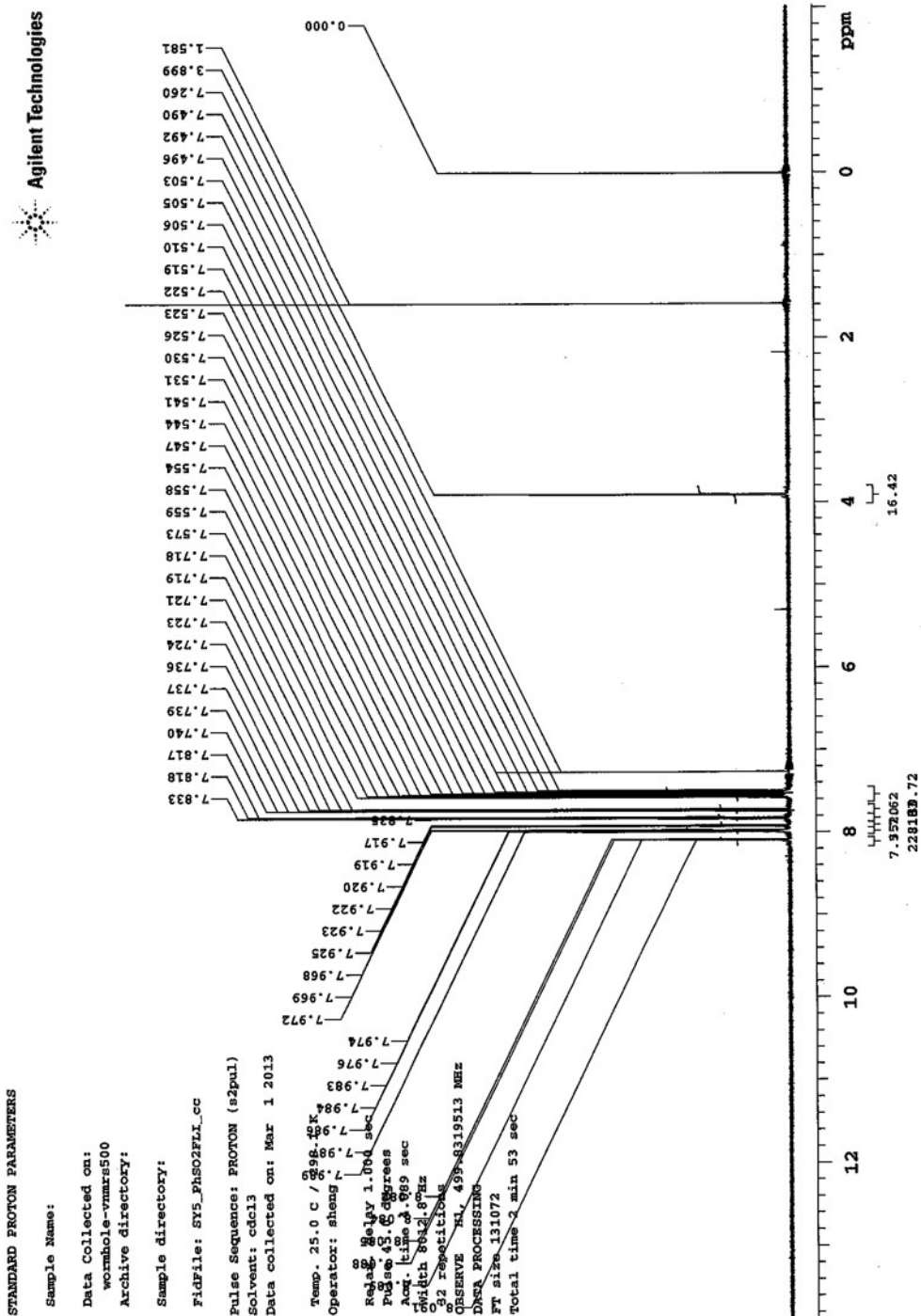


Figure S6a.  $^1\text{H}$  NMR spectra of 9.

# Compound 9 <sup>13</sup>C NMR

## STANDARD PROTON PARAMETERS

Sample Name:

Data Collected on:  
wormhole-vnmr500

Archive directory:

Sample directory:

FidFile: SVS\_FHS02FLI\_C

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Mar 1 2013

Temp. 25.0 C / 298.1 K

Operator: sheng

Relax. delay 1.000 sec

Pulse 45.0 degrees

Accr. time 1.022 sec

Width 32051.3 Hz

16 repetitions

OBSERVE C13, 125.6828439 MHz

DECOUPLE H1, 499.8344436 MHz

Power 40 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 131072

Total time 1 hr, 26 min

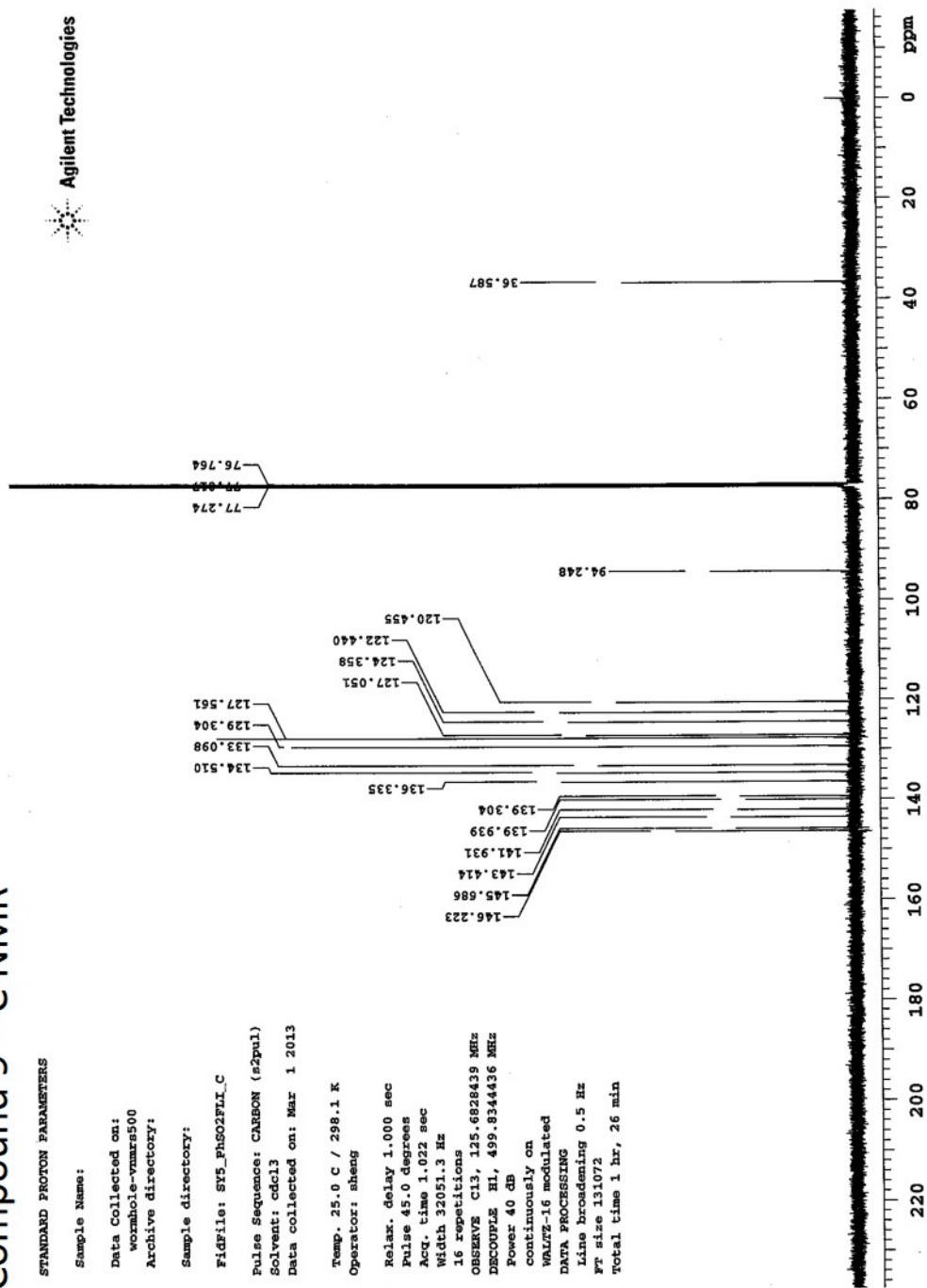
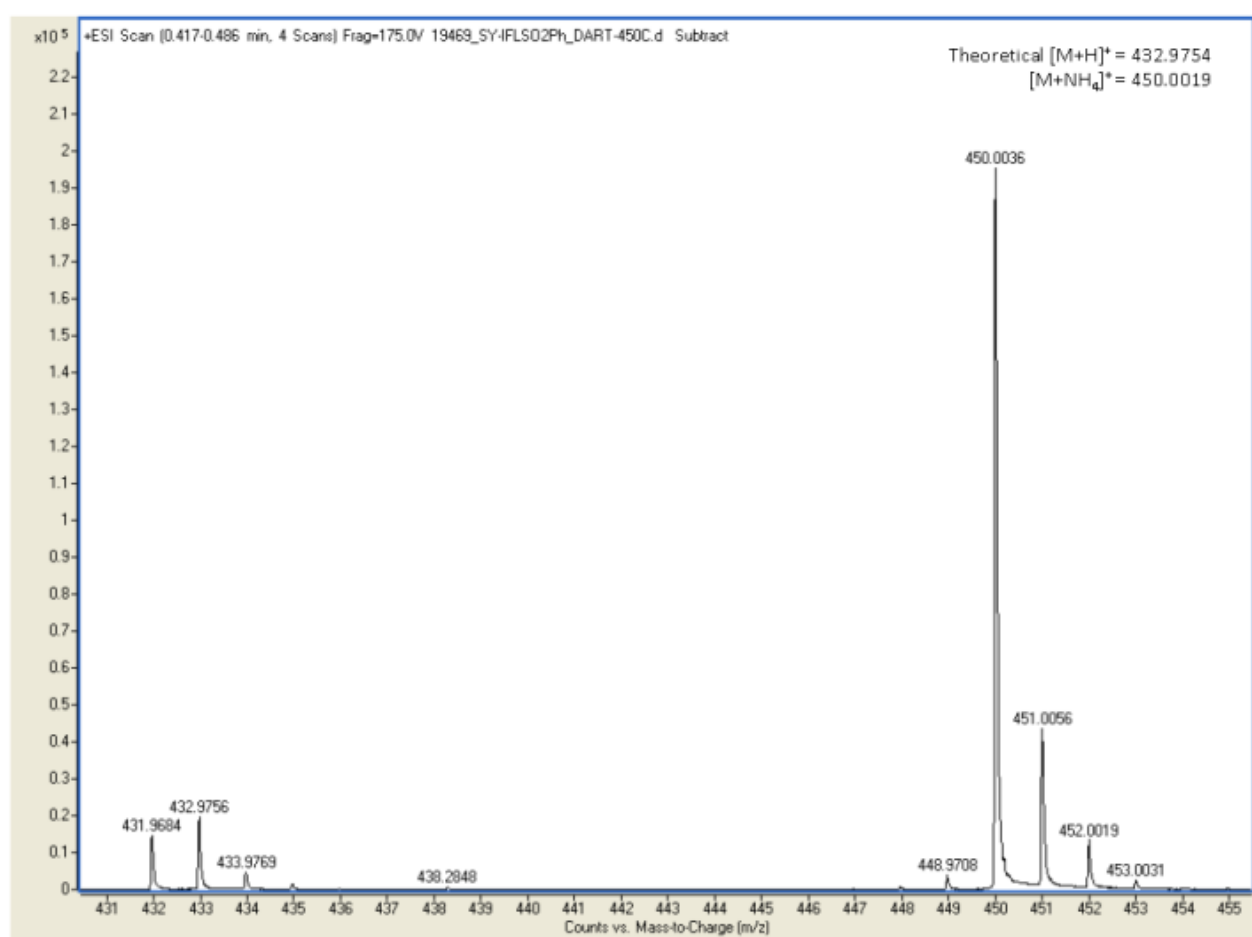
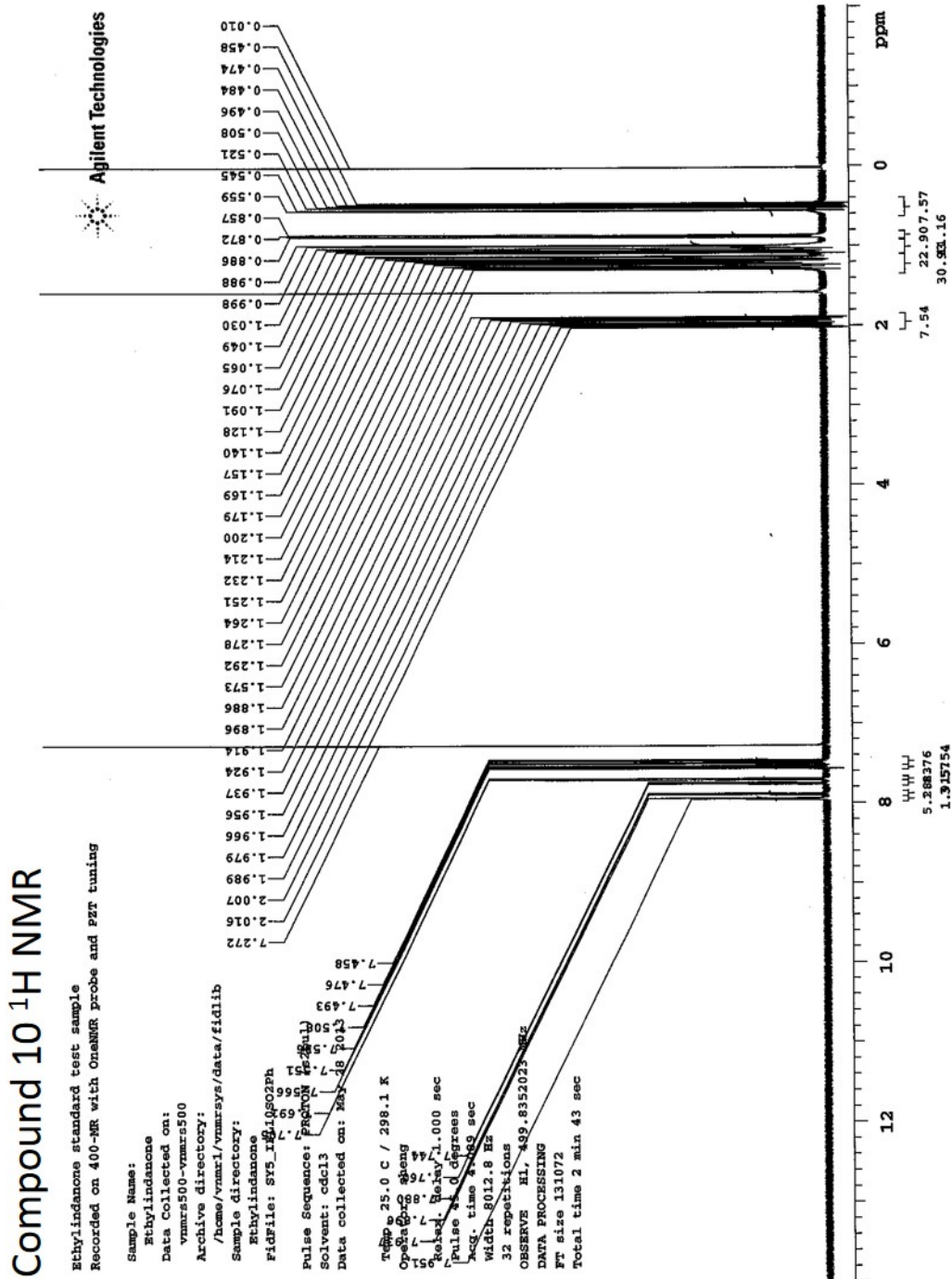


Figure S6b. <sup>13</sup>C NMR spectra of 9.



**Figure S6c.** HRMS spectrum of **9**.





# Compound 10 <sup>13</sup>C NMR

## STANDARD PROTON PARAMETERS

Sample Name:

Data Collected on:  
wormhole-vmar2500  
Archive directory:  
Sample directory:  
F10File: SV5\_IFL10S02Ph\_C  
Pulse Sequence: CARBON (s2pul)  
Solvent: cdcl3  
Data collected on: Jan 17 2013

Temp. 25.0 C / 298.1 K  
Operator: sheng

Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 1.022 sec  
Width 32051.3 Hz  
1792 repetitions  
OBSERVE C13, 125.6828426 MHz  
DECOUPLE H1, 499.8344436 MHz  
Power 40 dB  
continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 0.5 Hz  
FT size 131072  
Total time 1 hr, 26 min

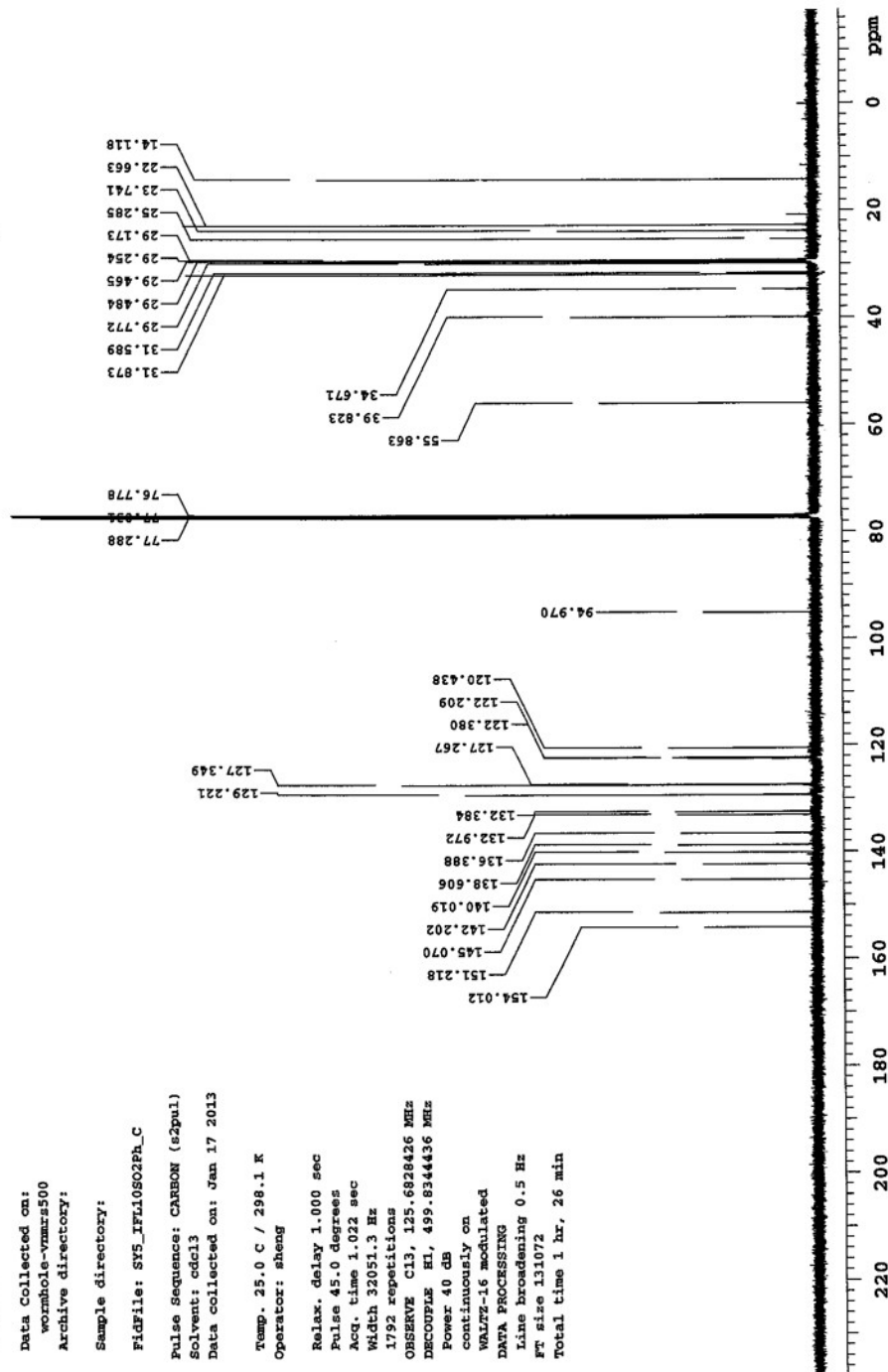
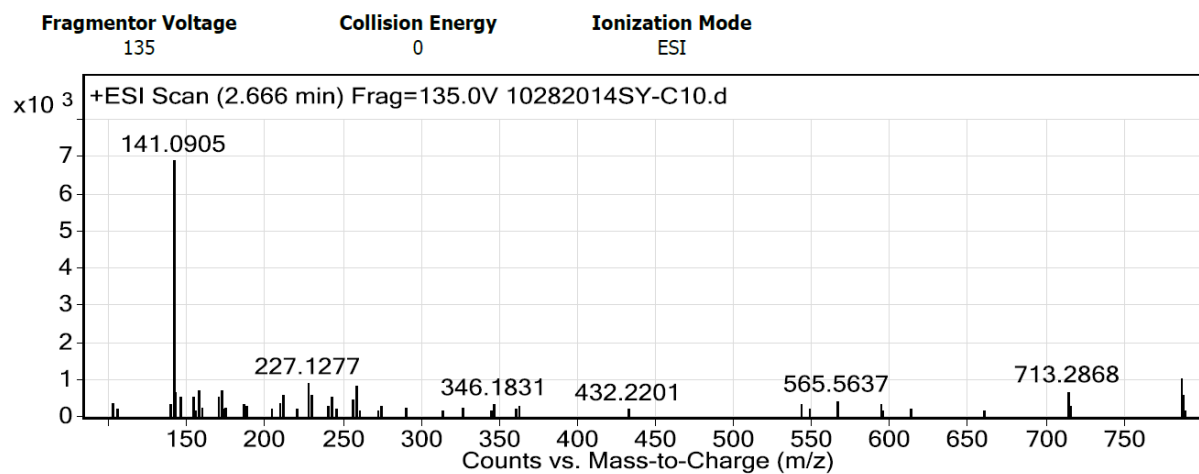


Figure S7b. <sup>13</sup>C NMR spectra of 10.



**Figure S7c.** HRMS spectrum of **10**.

# Compound 12 <sup>1</sup>H NMR

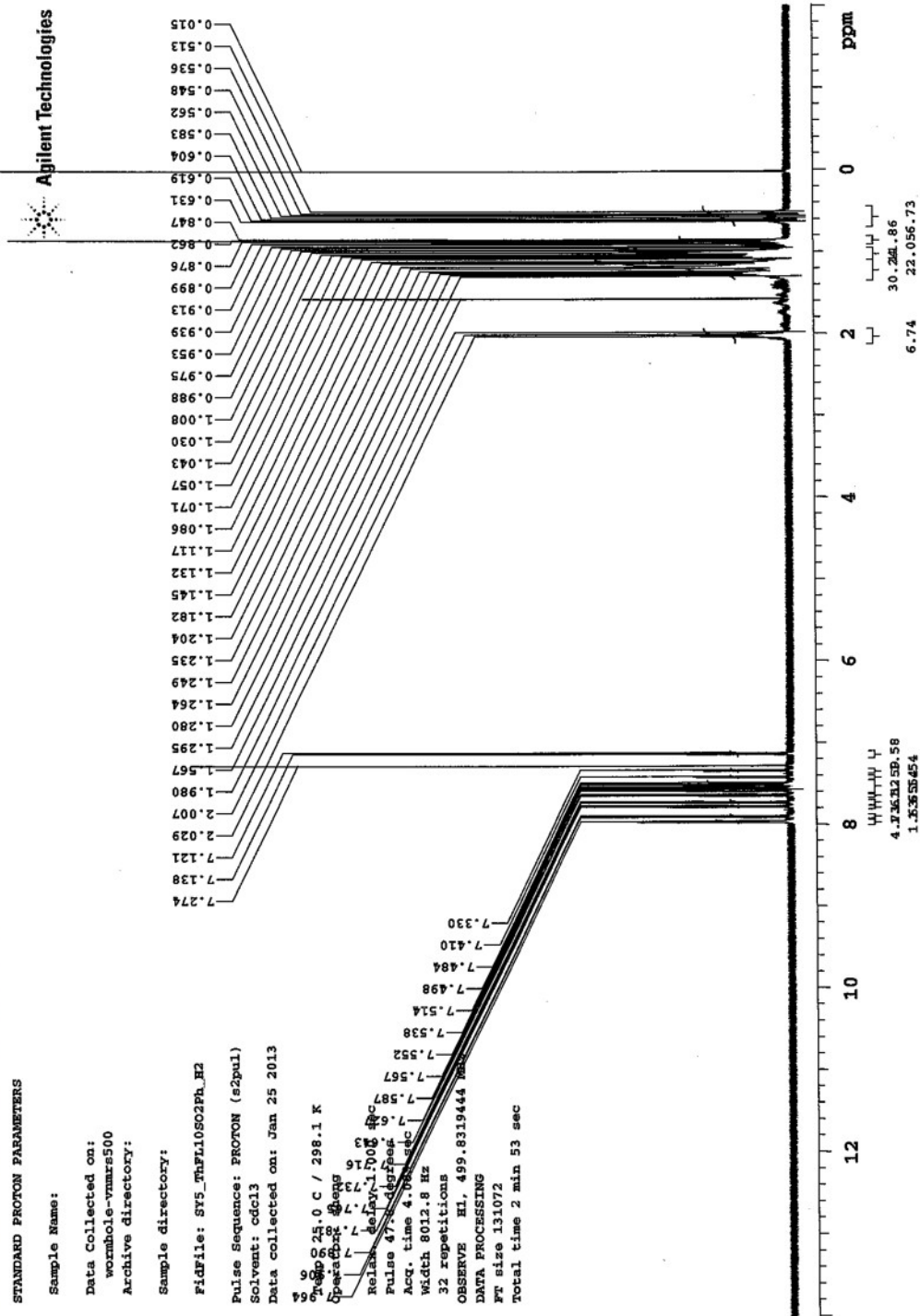


Figure S8a. <sup>1</sup>H NMR spectra of 12.

# Compound 12 <sup>13</sup>C NMR

## Gradient Shimming

Sample Name:

Data Collected on:

vmrs500-vmrs500

Archive directory:

/export/home/chmback/vmrsys/data

Sample directory:

FidFile: SYS\_TbFL10SO2Ph\_C2

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Nov 7 2013

Temp. 25.0 C / 298.1 K

Operator: sheng

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 1.049 sec

Width 31250.0 Hz

256 repetitions

OBSERVE C13, 125.6836615 MHz

DECOUPLE H1, 499.8377008 MHz

Power 41 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 65536

Total time 8 min 44 sec

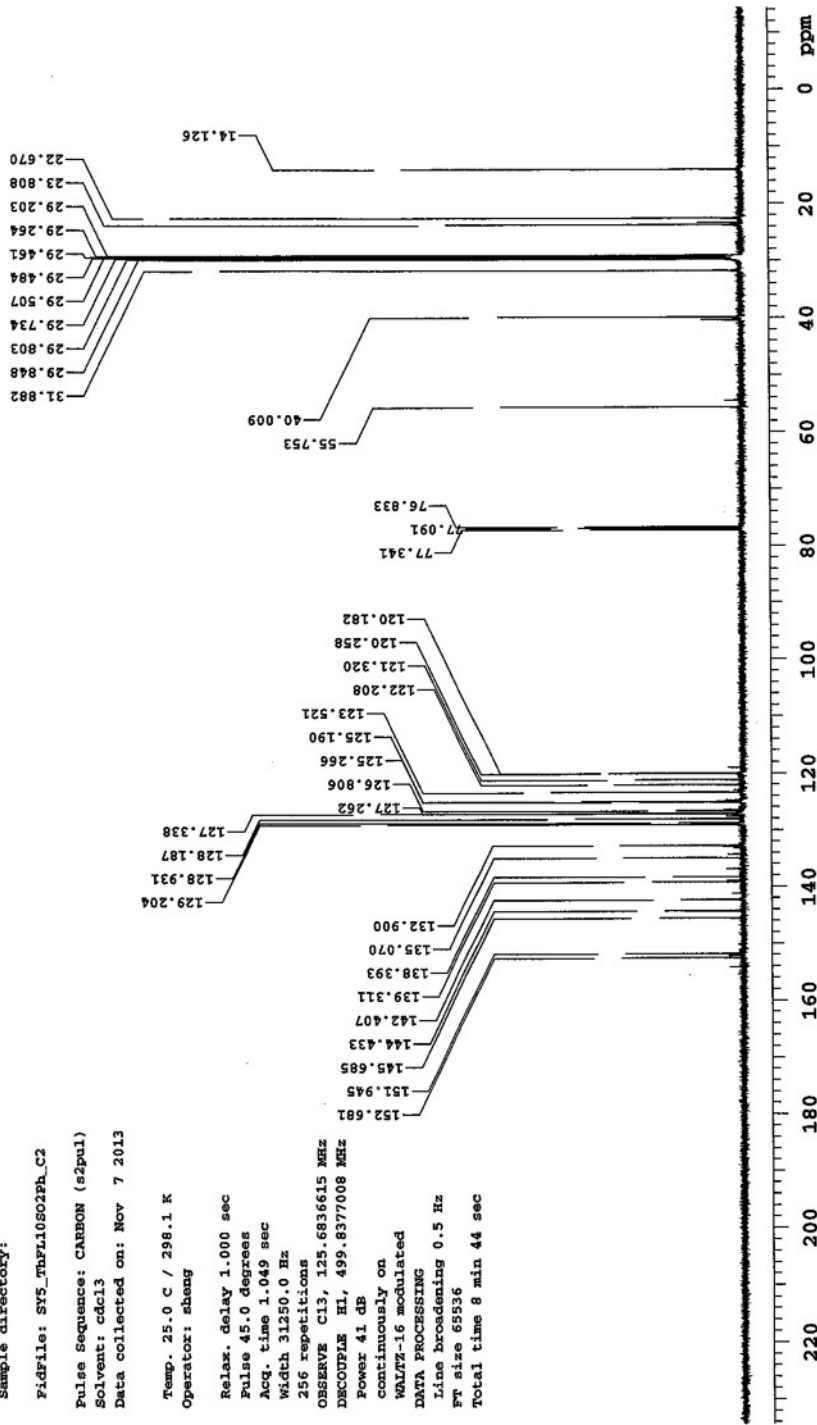
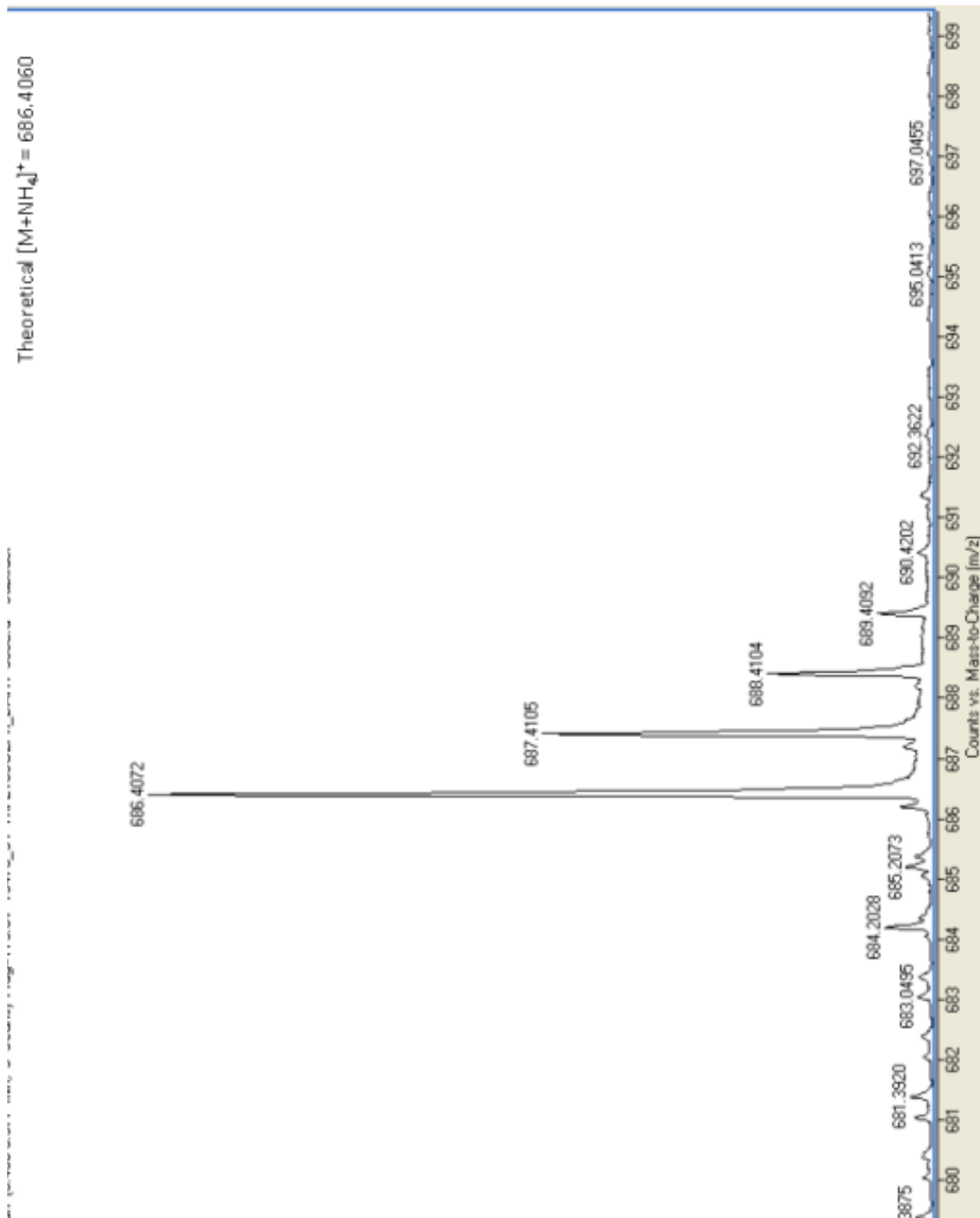


Figure S8b. <sup>13</sup>C NMR spectra of 12.



**Figure S8c.** HRMS spectrum of **12**.

# Compound 13 <sup>1</sup>H NMR

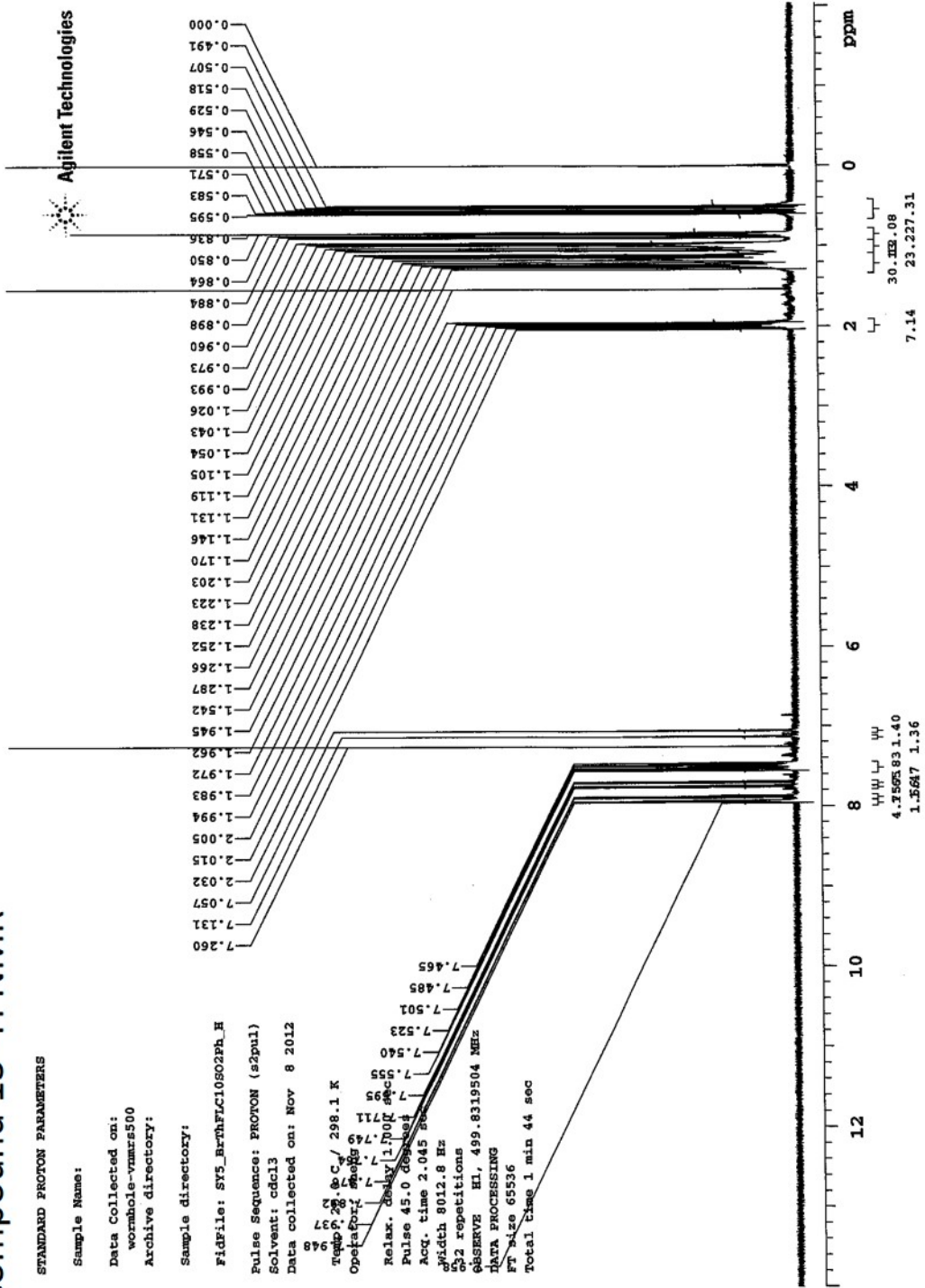


Figure S9a. <sup>1</sup>H NMR spectra of 13.



# Compound 13 <sup>13</sup>C NMR

## STANDARD PROTON PARAMETERS

### Sample Name:

Data Collected on:  
wormhole-vmars500  
Archive directory:  
Sample directory:  
FidFile: SV5\_BrTbFLC10S02Pb\_C  
Pulse Sequence: CARBON (s2pul)  
Solvent: cdcl3  
Data collected on: Nov 8 2012

Temp. 25.0 C / 298.1 K  
Operator: sheng

Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 1.022 sec  
Width 32051.3 Hz  
2320 repetitions  
OBSERVE C13, 125.6828407 MHz  
DECOUPLE H1, 499.8344436 MHz  
Power 41 dB  
continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 0.5 Hz  
FT size 131072  
Total time 2 hr, 48 min

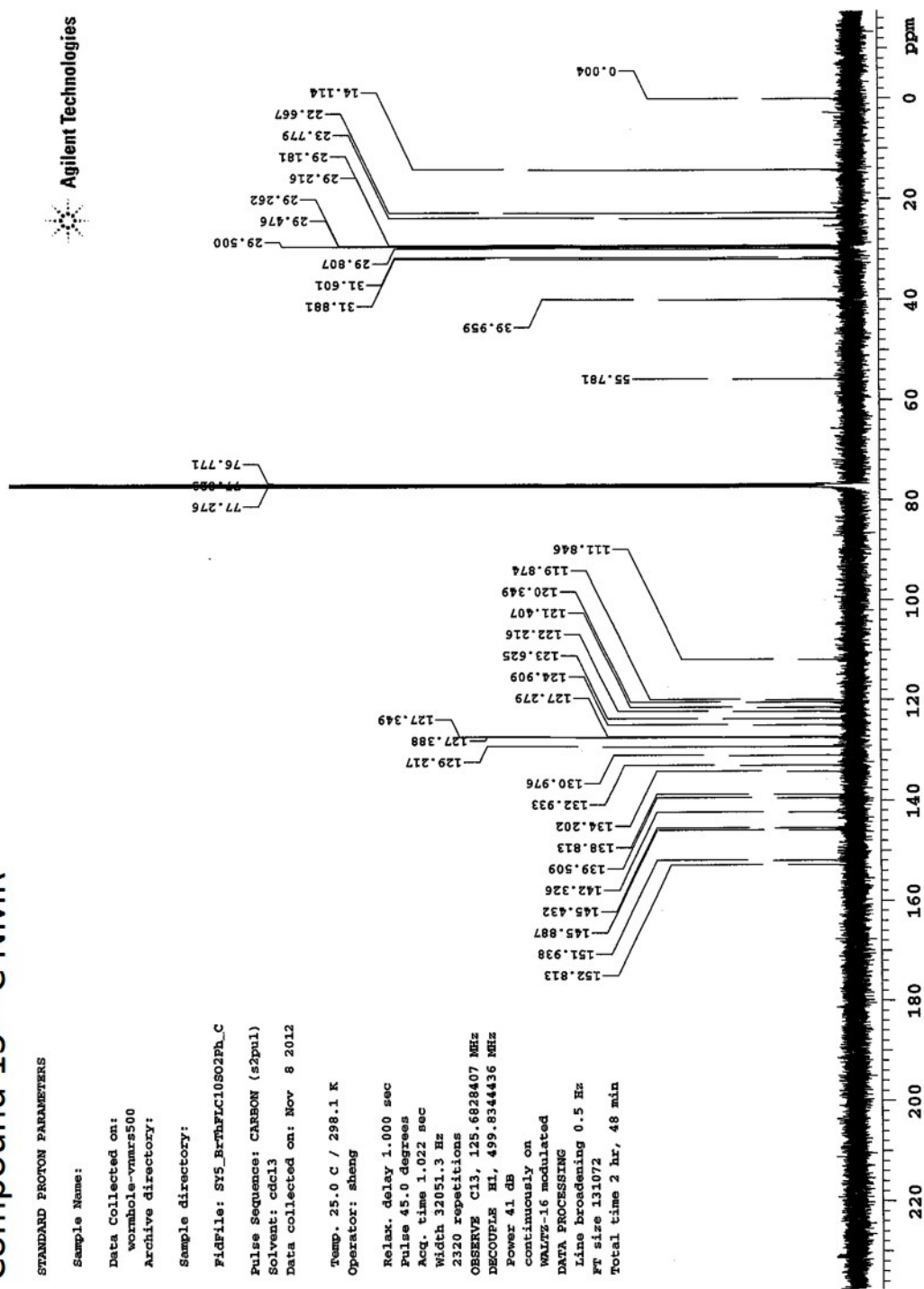
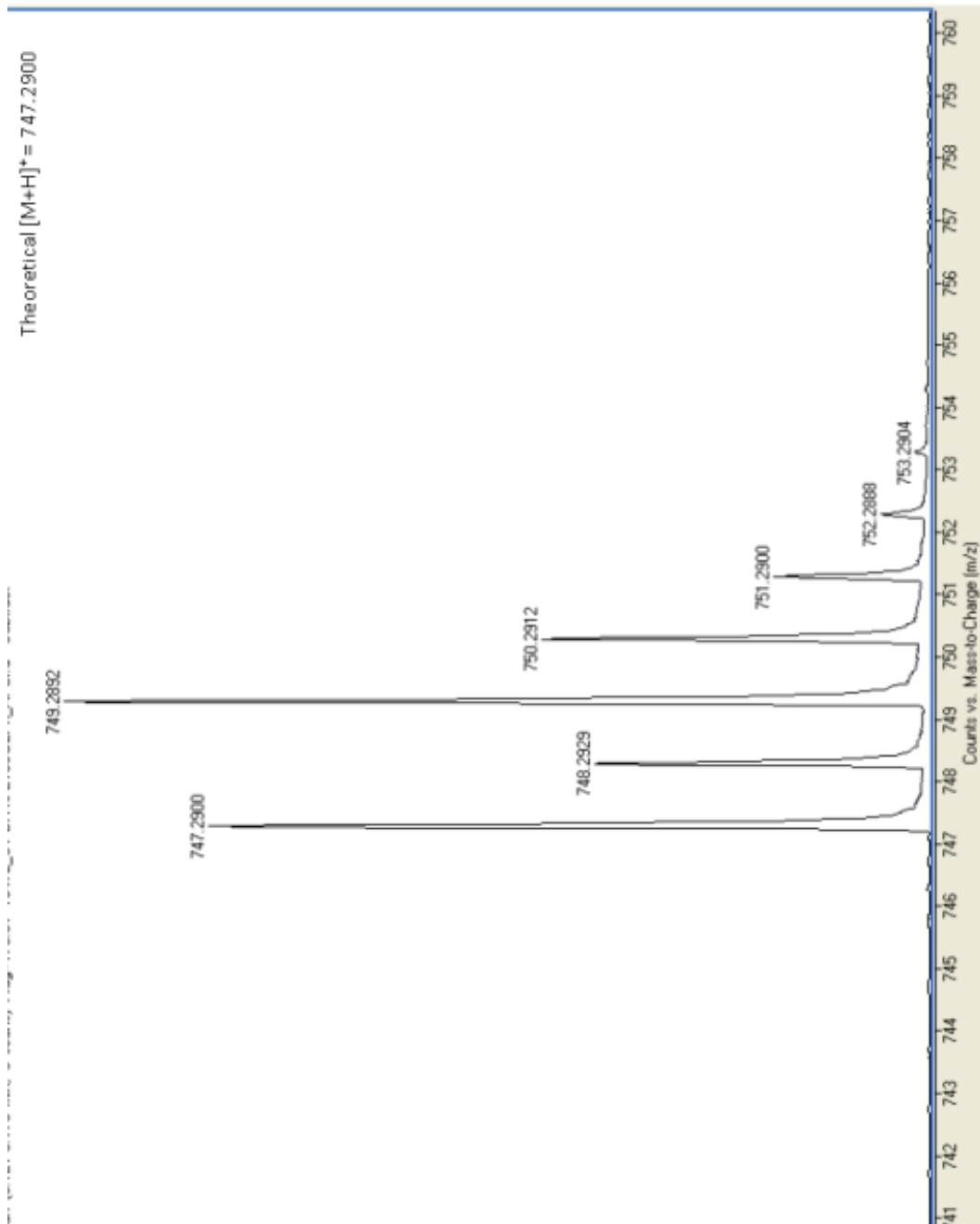


Figure S9b. <sup>13</sup>C NMR spectra of 13.





**Figure S9c.** HRMS spectrum of **13**.



# Compound 2 <sup>13</sup>C NMR

## STANDARD PROTON PARAMETERS

Sample Name:

Data Collected on:  
wormhole-vmrms500

Archive directory:

Sample directory:

Fidfile: SYS\_PHSO2FL10TANBDYHFL1DSO2PA\_C

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Feb 15 2013

Temp. 25.0 C / 298.1 K

Operator: sheng

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 1.022 sec

Width 32051.3 Hz

720 repetitions

OBSERVE C13, 125.6828425 MHz

DECOUPLE H1, 499.8344436 MHz

Power 40 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

Ft size 131072

Total time 1 hr, 26 min

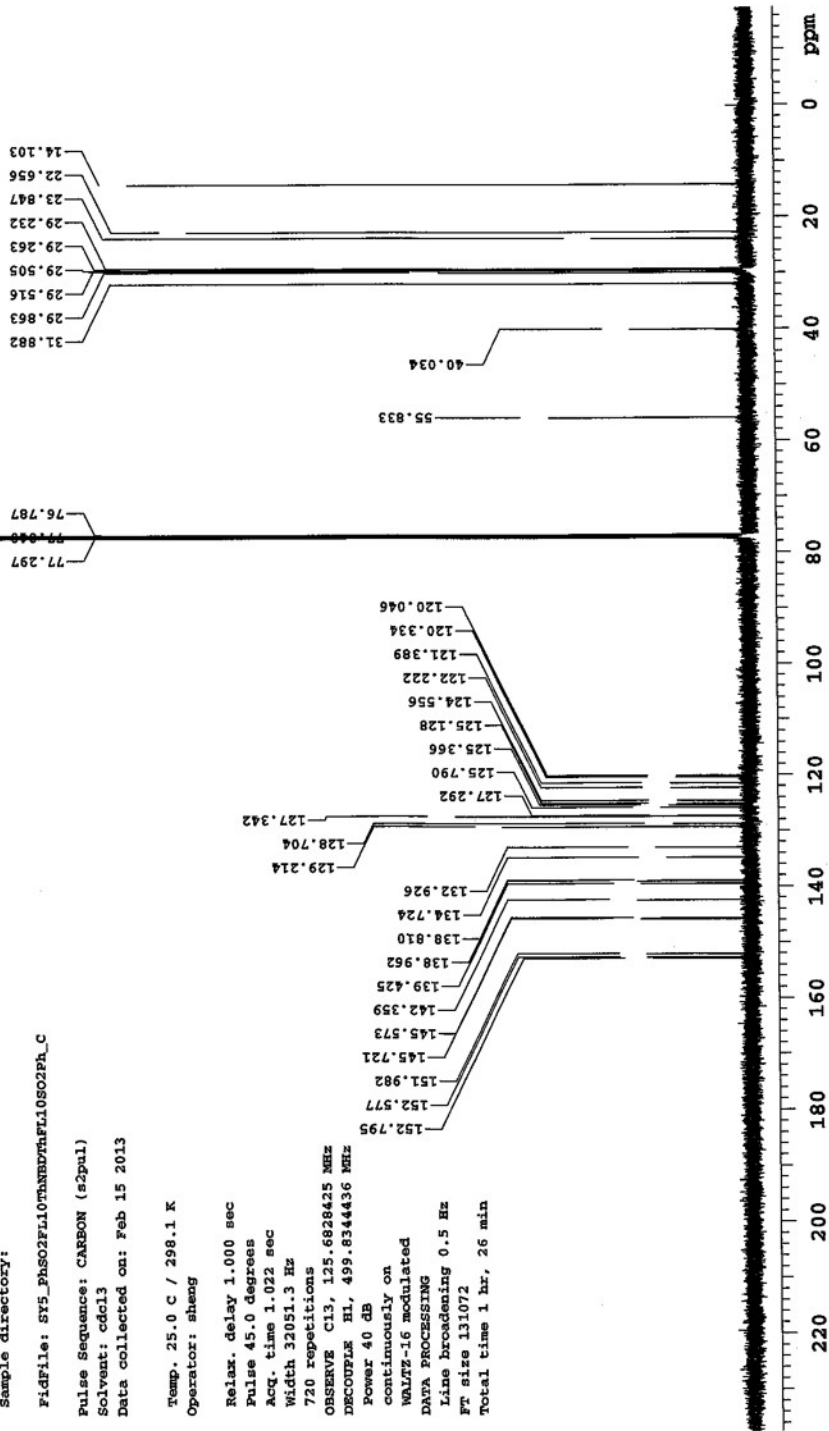


Figure S10b. <sup>13</sup>C NMR spectra of 2.

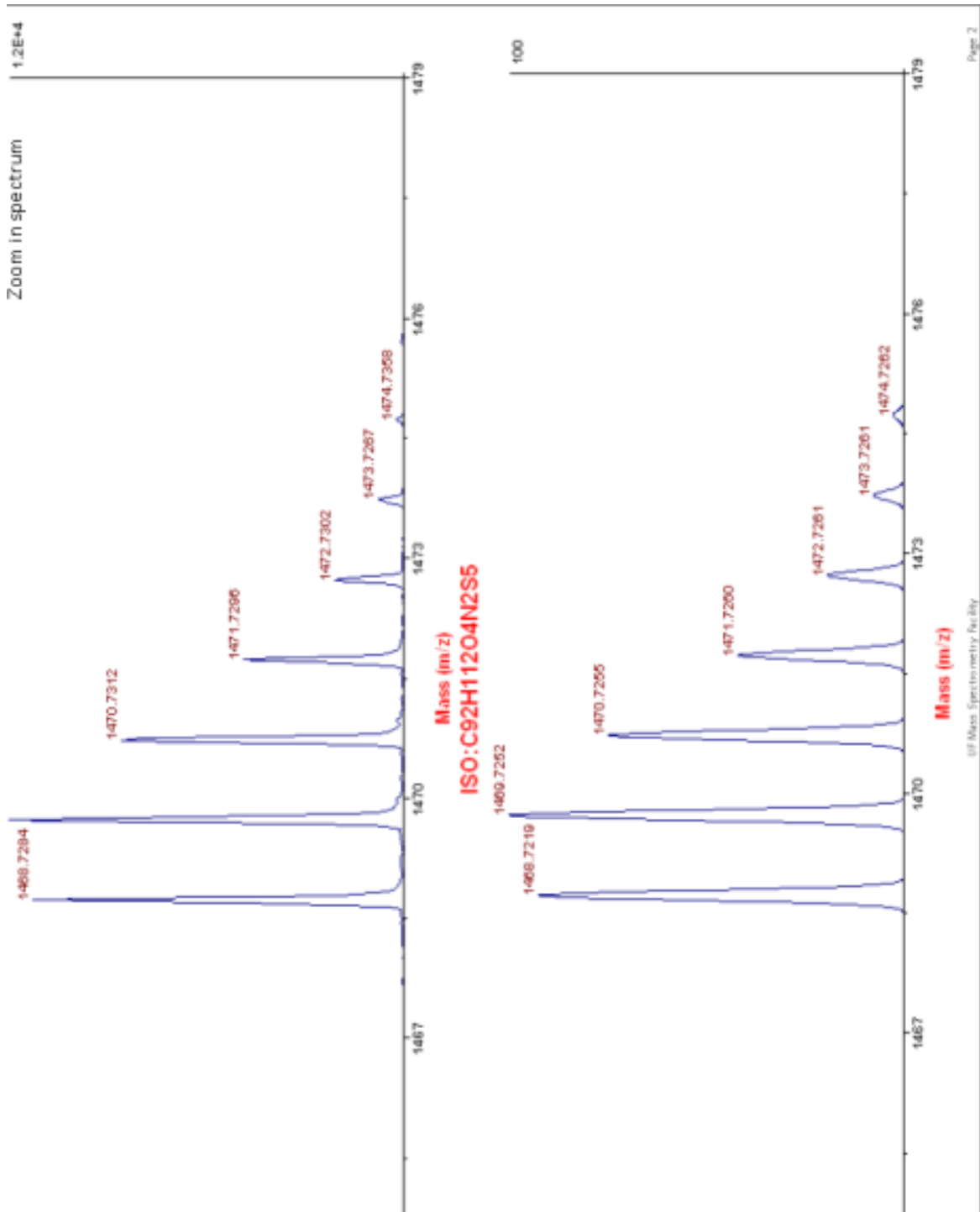


Figure S10c. HRMS spectrum of 2.

# Compound 3 <sup>1</sup>H NMR

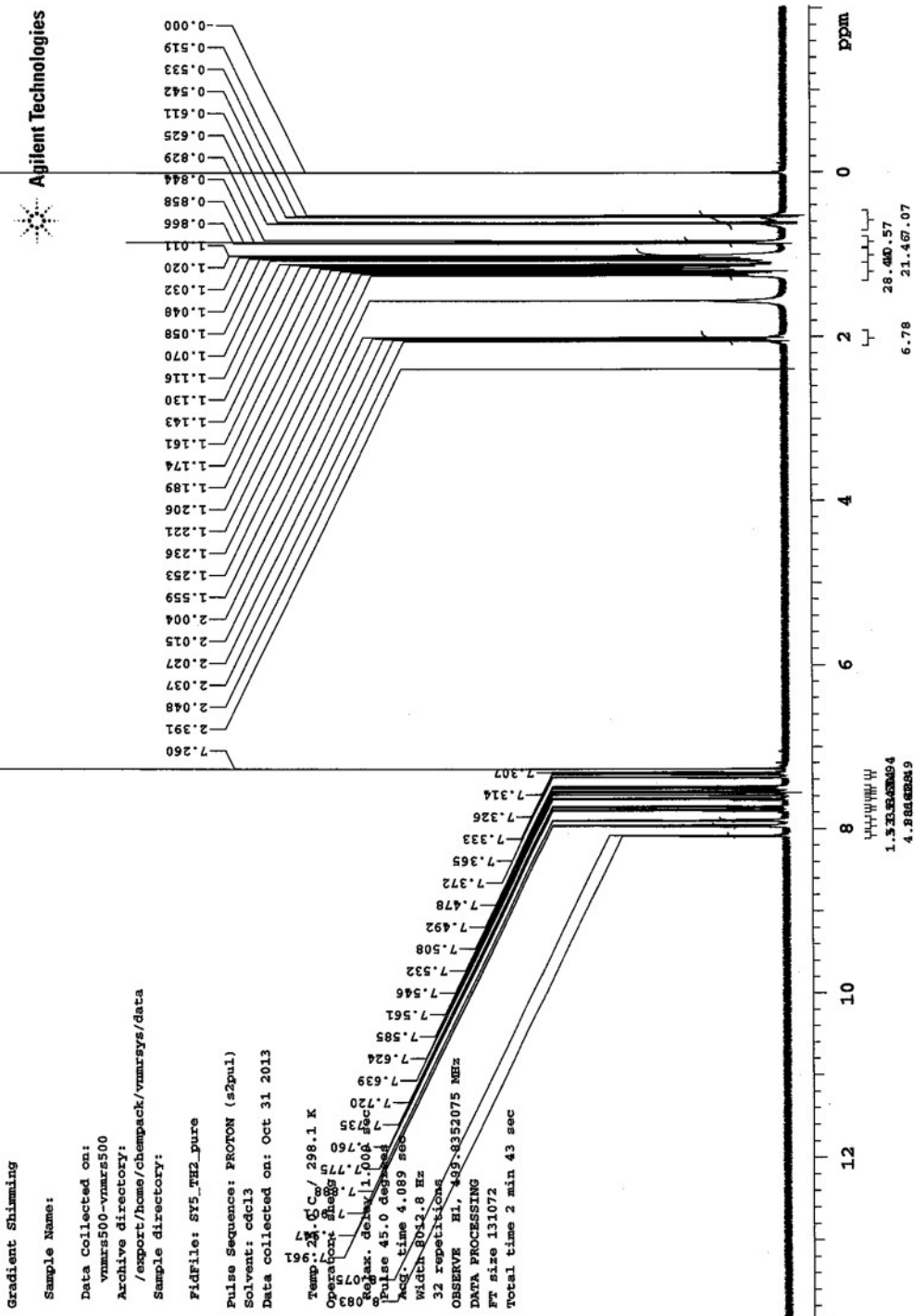


Figure S11a. <sup>1</sup>H NMR spectra of 3.

# Compound 3 <sup>13</sup>C NMR

## STANDARD PROTON PARAMETERS

Sample Name:

Data Collected on:  
wormhole-vnmrs500

Archive directory:

Sample directory:

FidFile: SYS\_PhS02FL10THNBDTHTAF10S02Ph\_C

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Feb 15 2013

Temp. 25.0 C / 298.1 K

Operator: sheng

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 1.022 sec

Width 32051.3 Hz

2560 repetitions

OBSERVE C13, 125.6829705 MHz

DECOUPLE H1, 499.8344436 MHz

Power 40 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

Ft size 131072

Total time 1 hr, 26 min

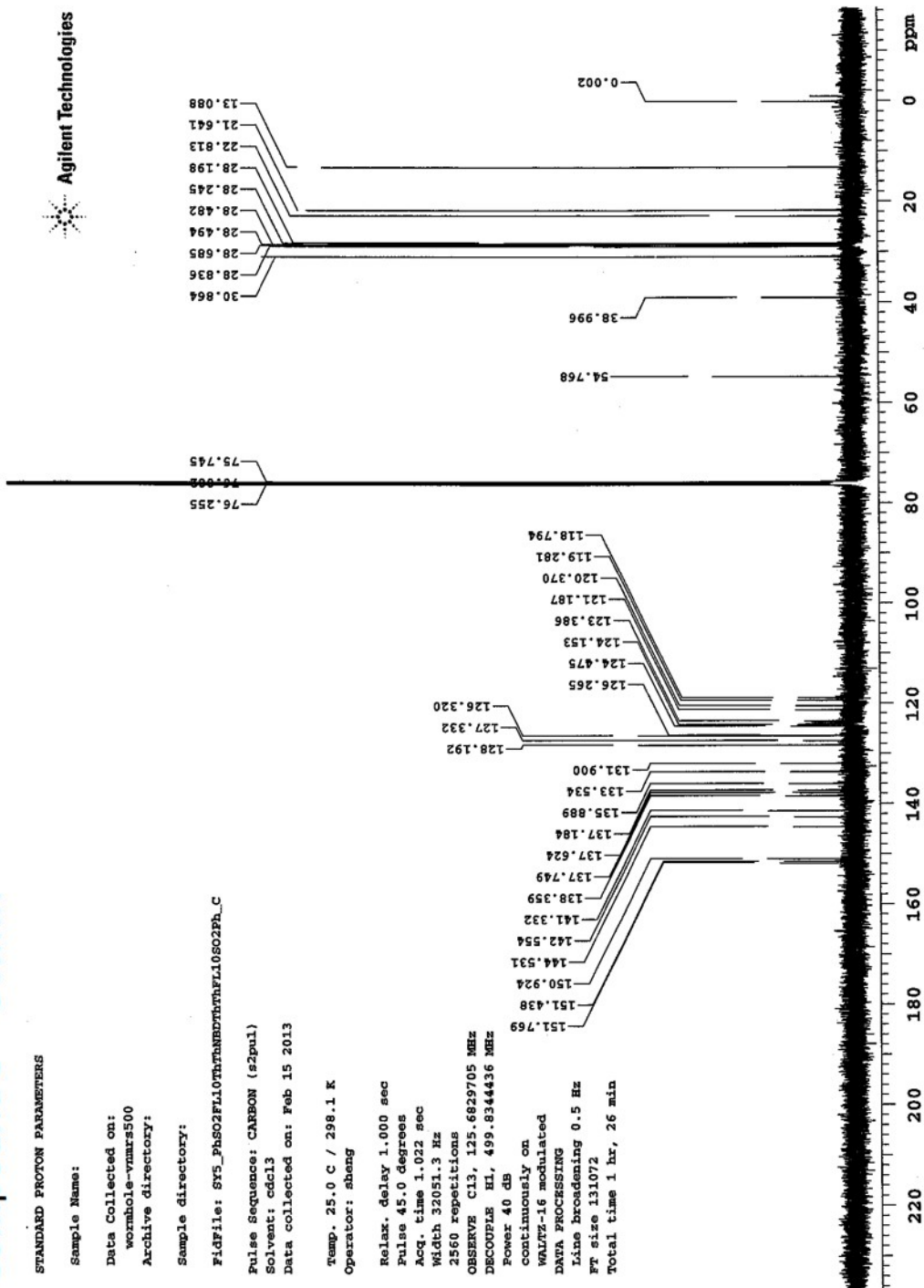


Figure S11b. <sup>13</sup>C NMR spectra of 3.

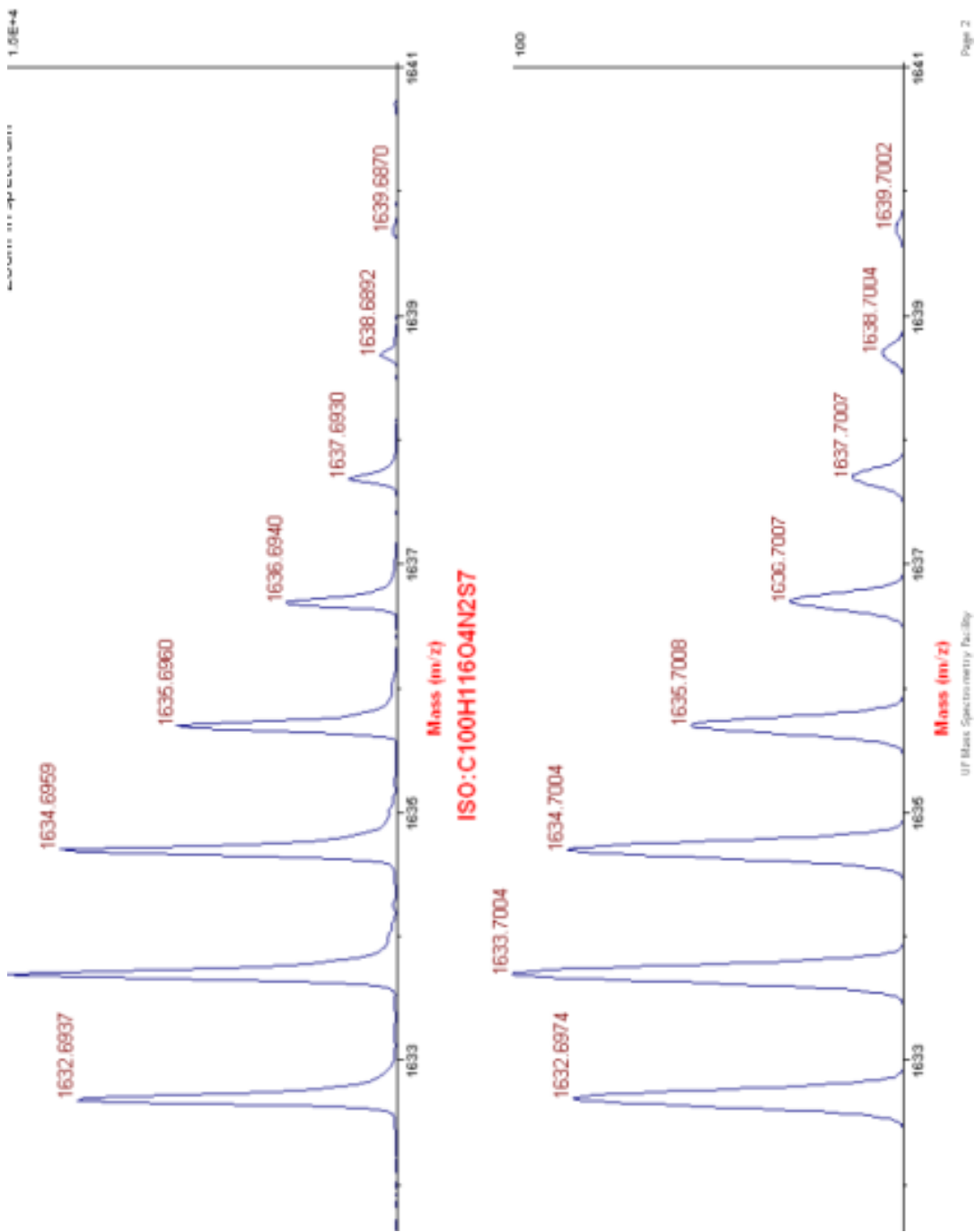


Figure S11c. HRMS spectrum of 3.

# Compound 14 <sup>1</sup>H NMR

Ethylindanone standard test sample  
Recorded on 400-MR with OneNMN probe and PZT tuning

Sample Name:  
Ethylindanone  
Data Collected on:  
mercury300-mercury300  
Archive directory:  
/home/vmar1/vnmr/sys/data/fidlib  
Sample directory:  
Ethylindanone  
File: SY3\_PhSO2FL10yneSims3  
Pulse Sequence: PROTON (s2pul)  
Solvent: cdc13  
Data collected on: Jun 17 2013

Temp. 25.0 C / 298.1 K  
Operator: sheng

Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 1.706 sec  
Width 4800.8 Hz  
64 repetitions  
OBSERVE HL, 299.9865892 MHz  
DATA PROCESSING  
FT size 16384  
Total time 2 min 53 sec

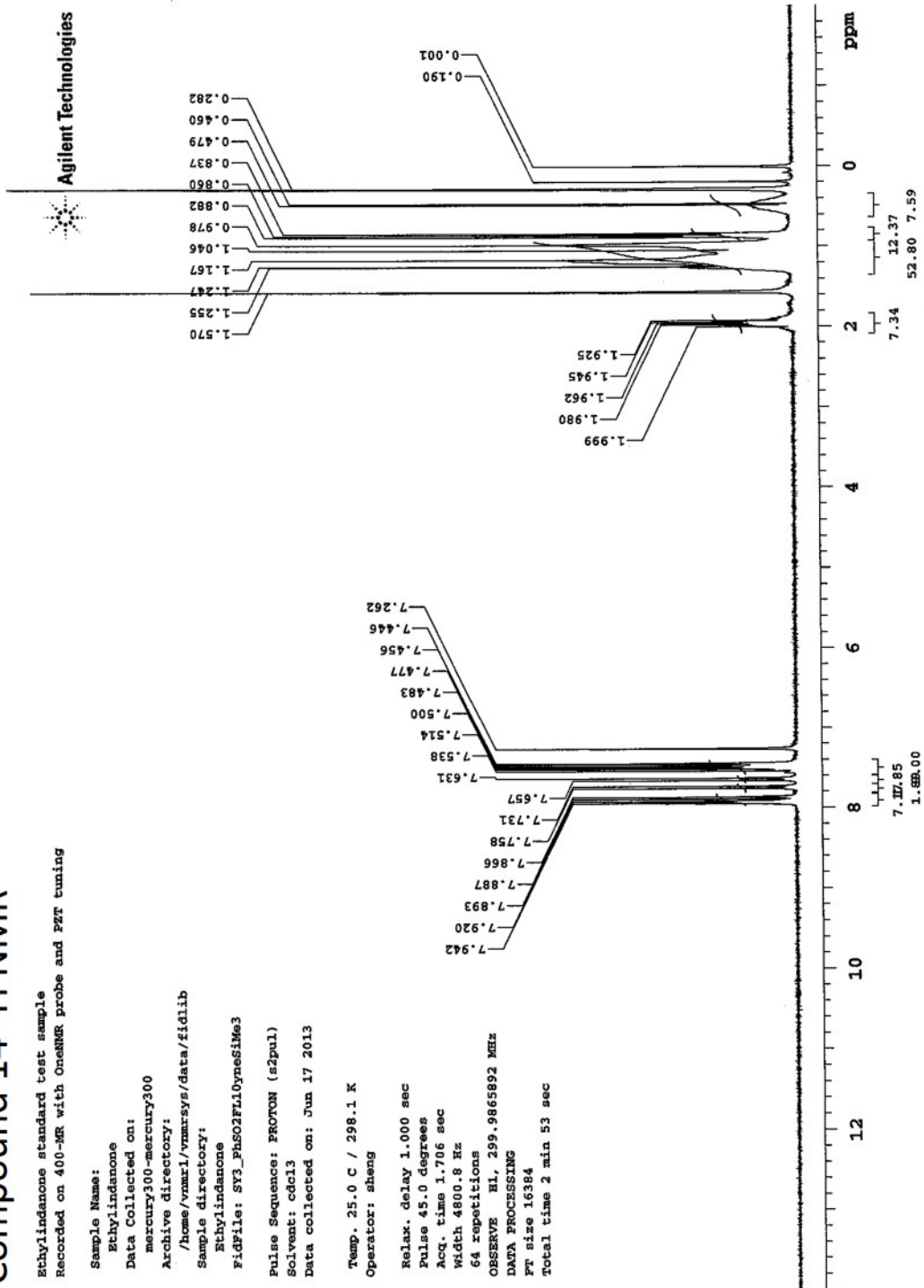


Figure S12a. <sup>1</sup>H NMR spectra of 14.



# Compound 14 <sup>13</sup>C NMR

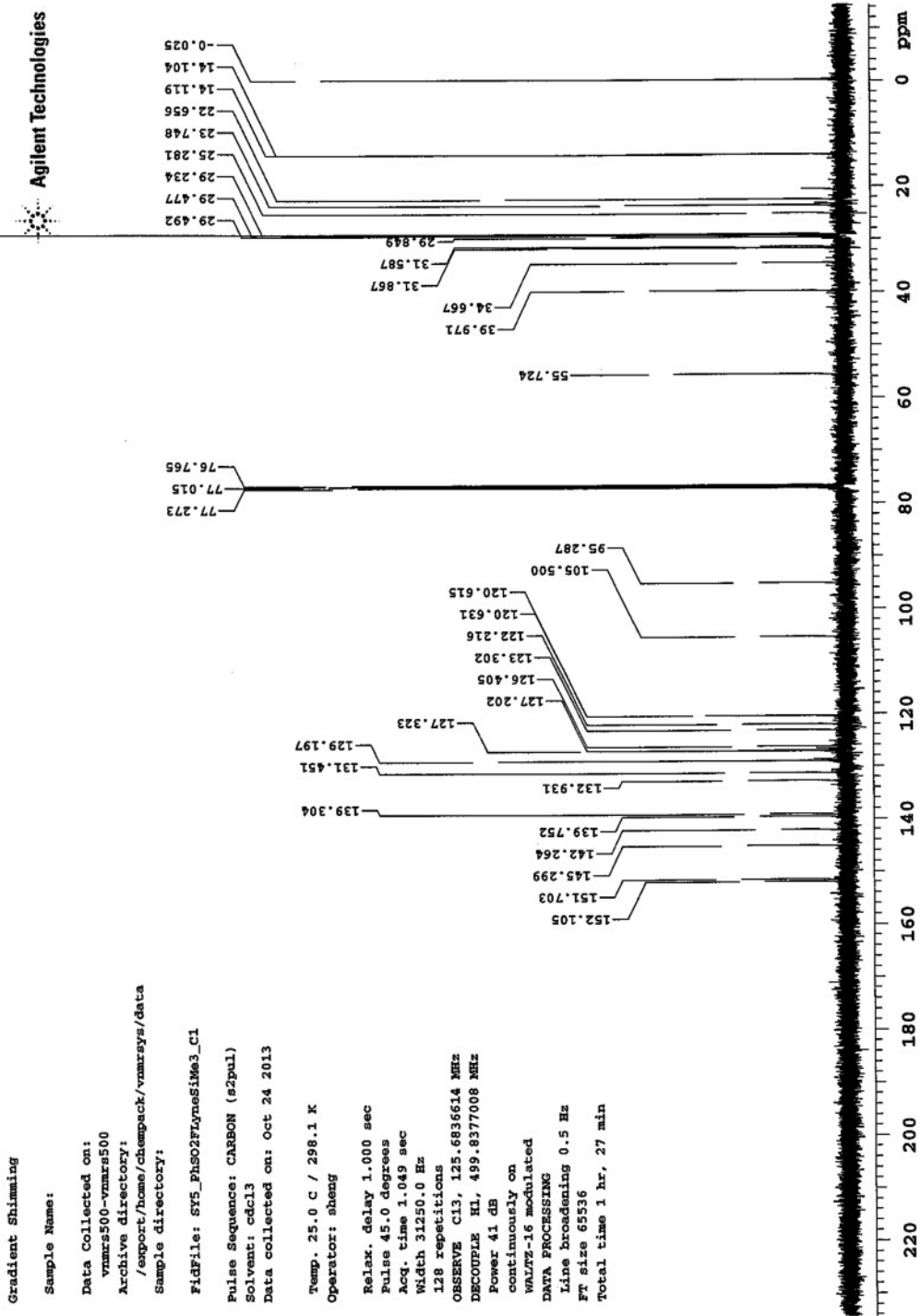


Figure S12b. <sup>13</sup>C NMR spectra of 14.

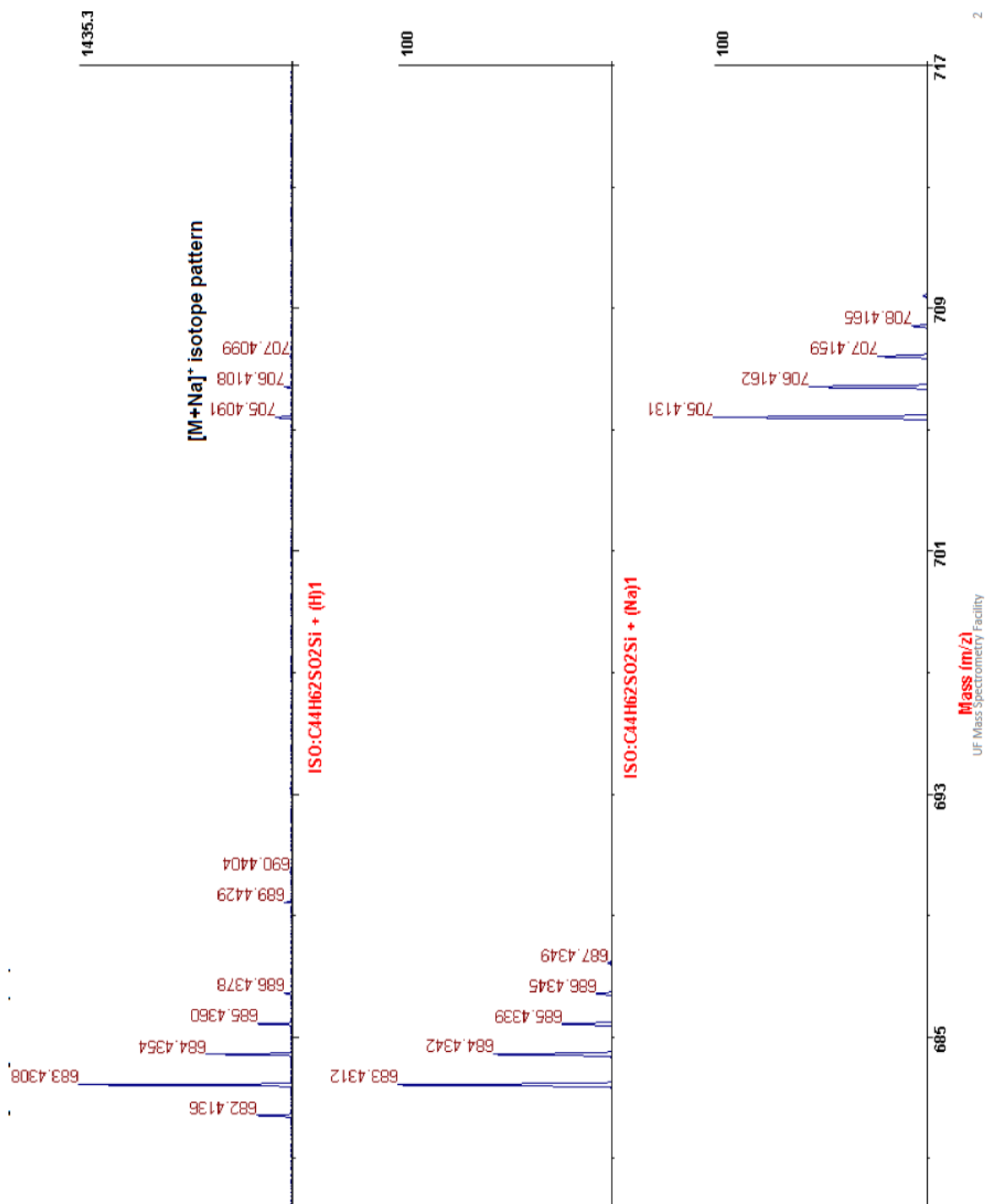


Figure S12c. HRMS spectrum of 14.

# Compound 15 <sup>1</sup>H NMR

Ethylindanone standard test sample  
Recorded on 400-MR with OneNMN probe and PZT tuning

Sample Name: Ethylindanone  
Data Collected on: vmars500-vmars500  
Archive directory: /home/vmars1/vmarsys/data/fidlib  
Sample directory: Ethylindanone  
Fidfile: SYS\_PHSO2F110yne

Pulse Sequence: PROTON (s2pul)  
Solvent: cdc13  
Data collected on: Jun 20 2013

Temp. 25.0 C / 298.1 K  
Operator: sheag

Relax. delay 1.000 sec  
cpulse 45.0 degrees  
scf-time 4.089 sec  
width 6812.8 Hz  
[64] repeats 1.000 sec  
OBSERVE 400.145000000 MHz  
DATA PROCESSING  
FT size 131072  
Total time 5 min 58 sec

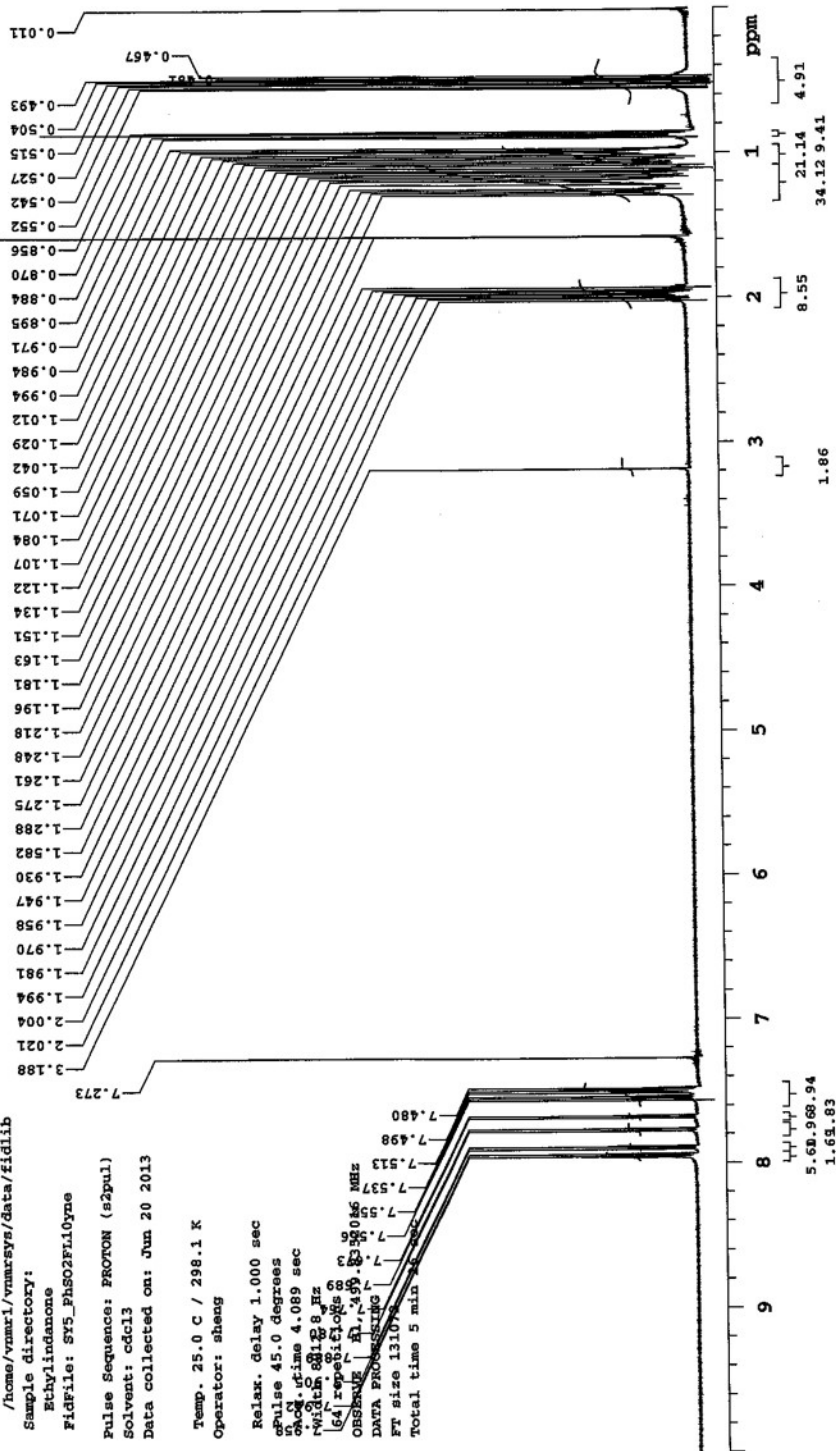


Figure S13a. <sup>1</sup>H NMR spectra of 15.

# Compound 15 <sup>13</sup>C NMR



## Gradient Shimming

Sample Name:

Data Collected on:  
vnmrs500-vnmrs500  
Archive directory:  
/export/home/chempack/vnmrsys/data  
Sample directory:

FidFile: SY5\_PhS02Flyne\_C1

Pulse Sequence: CARBON (s2pul)  
Solvent: cdcl3  
Data collected on: Oct 31 2013

Temp. 25.0 C / 298.1 K  
Operator: sheng

Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 1.049 sec  
Width 31250.0 Hz  
128 repetitions  
OBSERVE C13, 125.6836615 MHz  
DECOUPLE H1, 499.8377008 MHz  
Power 41 dB  
continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 0.5 Hz  
Ft size 65536  
Total time 1 hr, 27 min

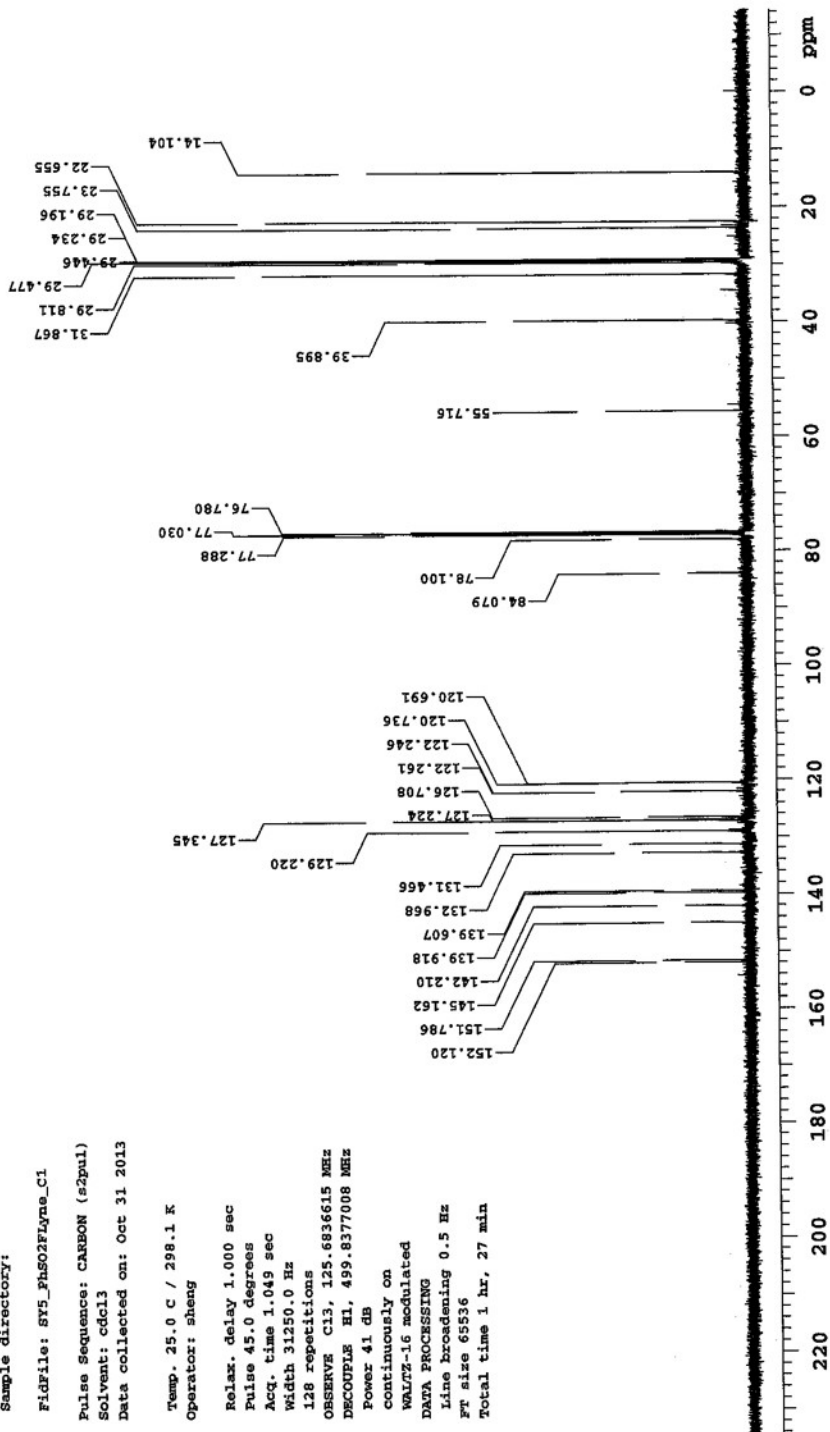


Figure S13b. <sup>13</sup>C NMR spectra of 15.

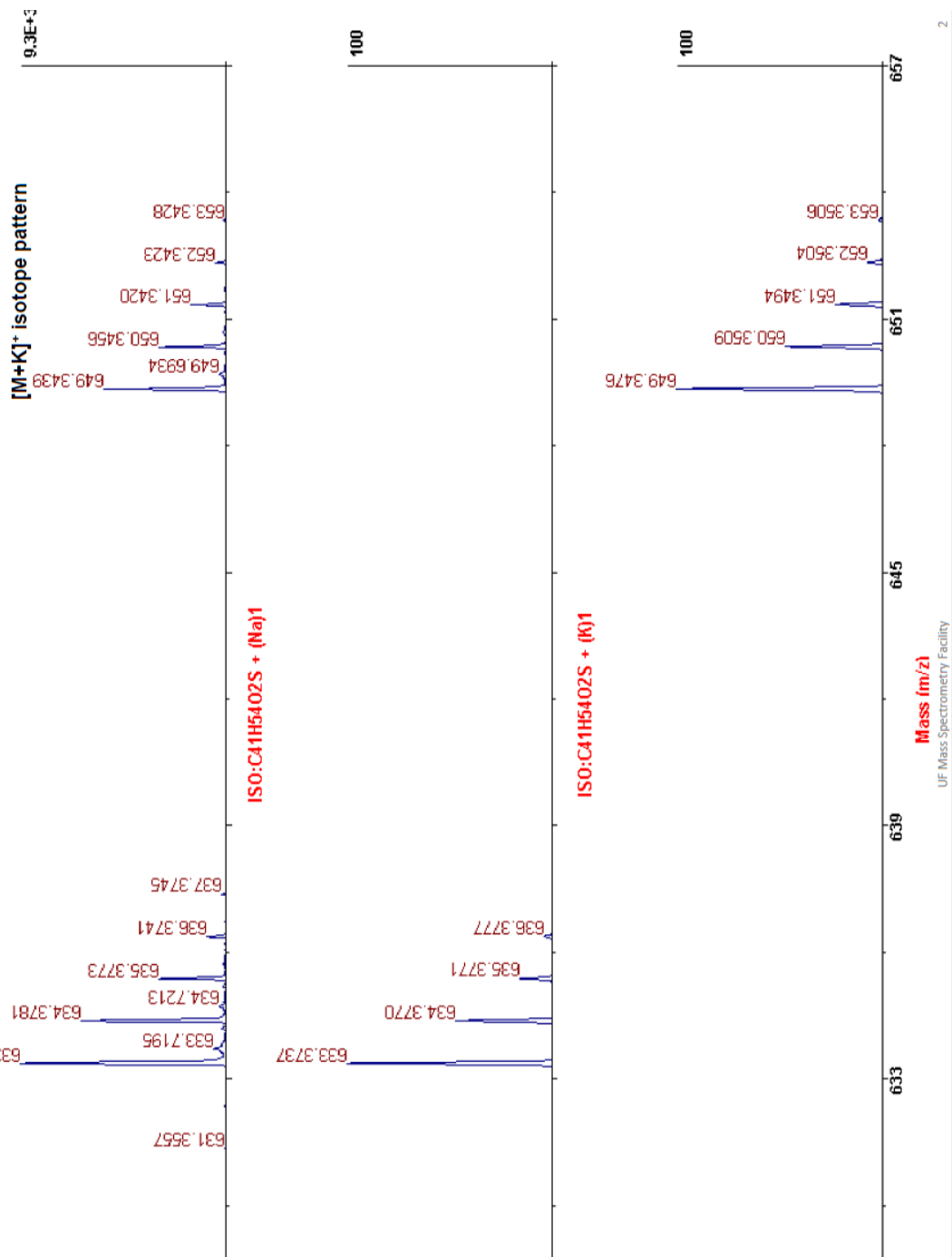


Figure S13c. HRMS spectrum of 15.

# Compound 4 <sup>1</sup>H NMR

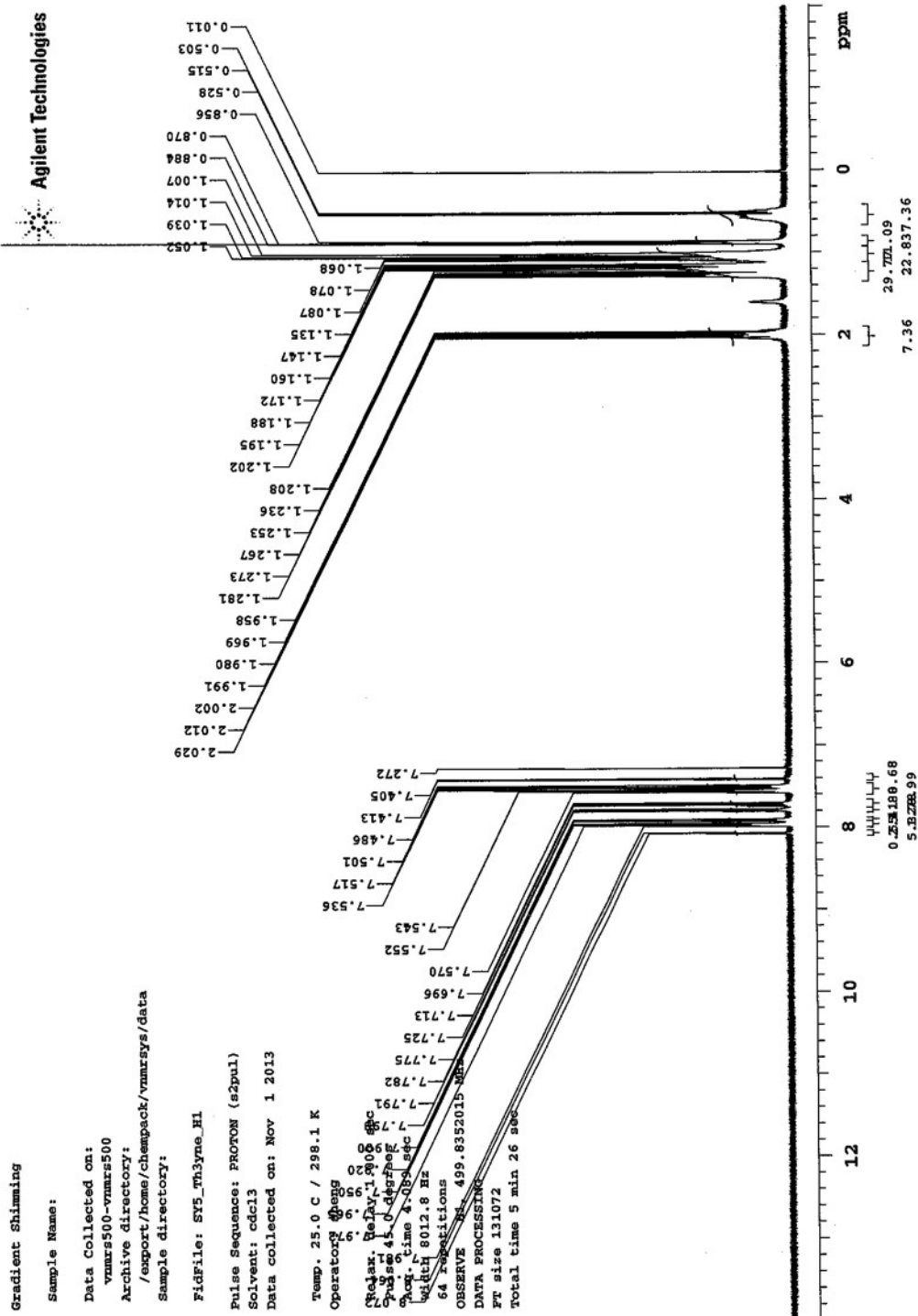


Figure S14a. <sup>1</sup>H NMR spectra of 4.

# Compound 4 <sup>13</sup>C NMR



Gradient Shimming

Sample Name:

Data Collected on:  
 vnmrs500-vnmrs500  
 Archive directory:  
 /export/home/chempack/vnmrsys/data  
 Sample directory:

Fidfile: SYS\_Th3yne\_C1

Pulse Sequence: CARBON (s2pul)  
 Solvent: cdcl3  
 Data collected on: Nov 1 2013

Temp. 25.0 C / 298.1 K  
 Operator: sheng

Relax. delay 1.000 sec  
 Pulse 45.0 degrees  
 Acq. time 1.049 sec  
 Width 31250.0 Hz

640 repetitions  
 OBSERVE C13, 125.6836614 MHz  
 DECOUPLE H1, 499.8377008 MHz  
 Power 41 dB  
 continuously on  
 WALTZ-16 modulated  
 DATA PROCESSING  
 Line broadening 0.5 Hz  
 FT size 65536  
 Total time 1 hr, 27 min

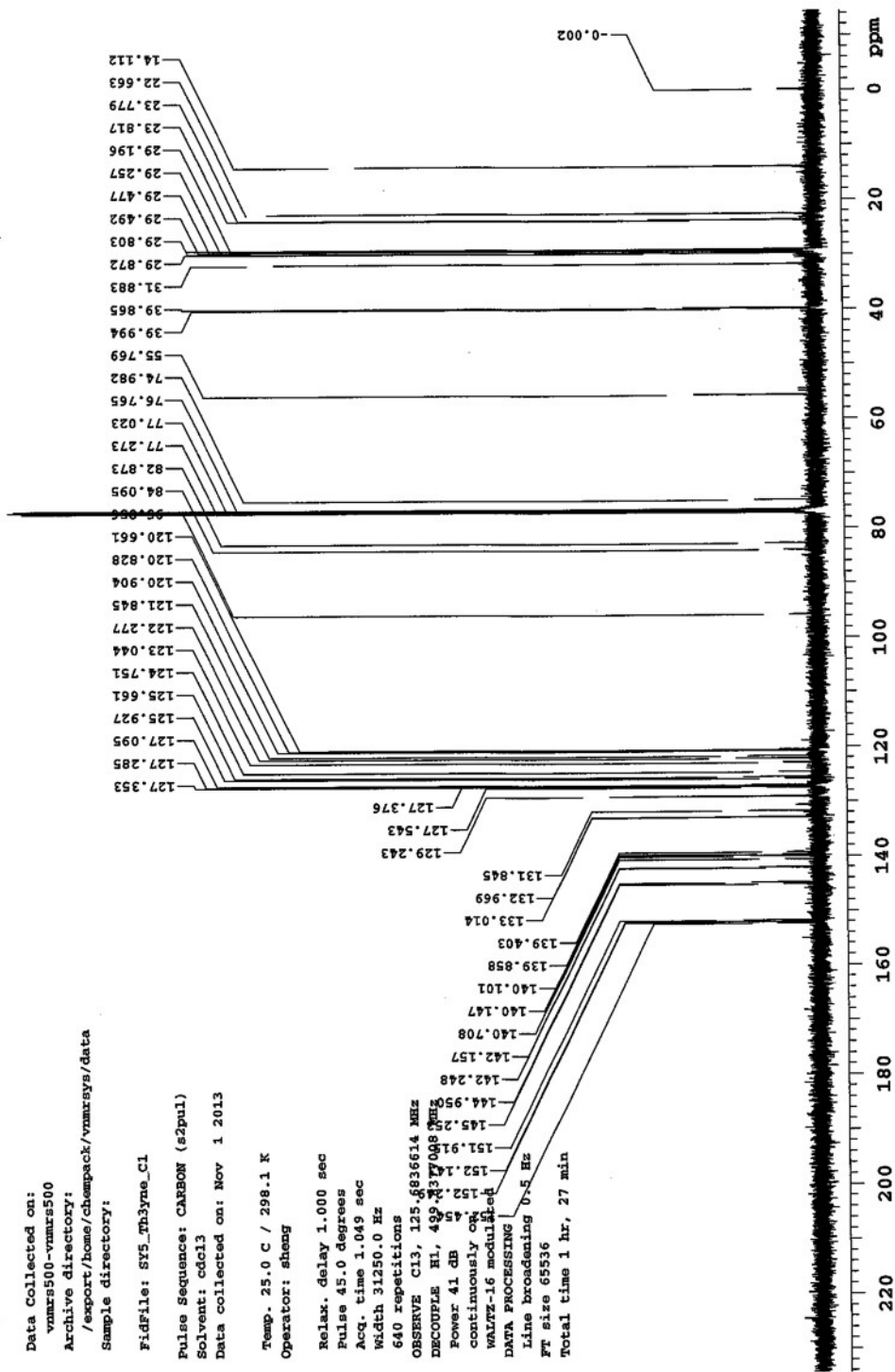


Figure S14b. <sup>13</sup>C NMR spectra of 4.

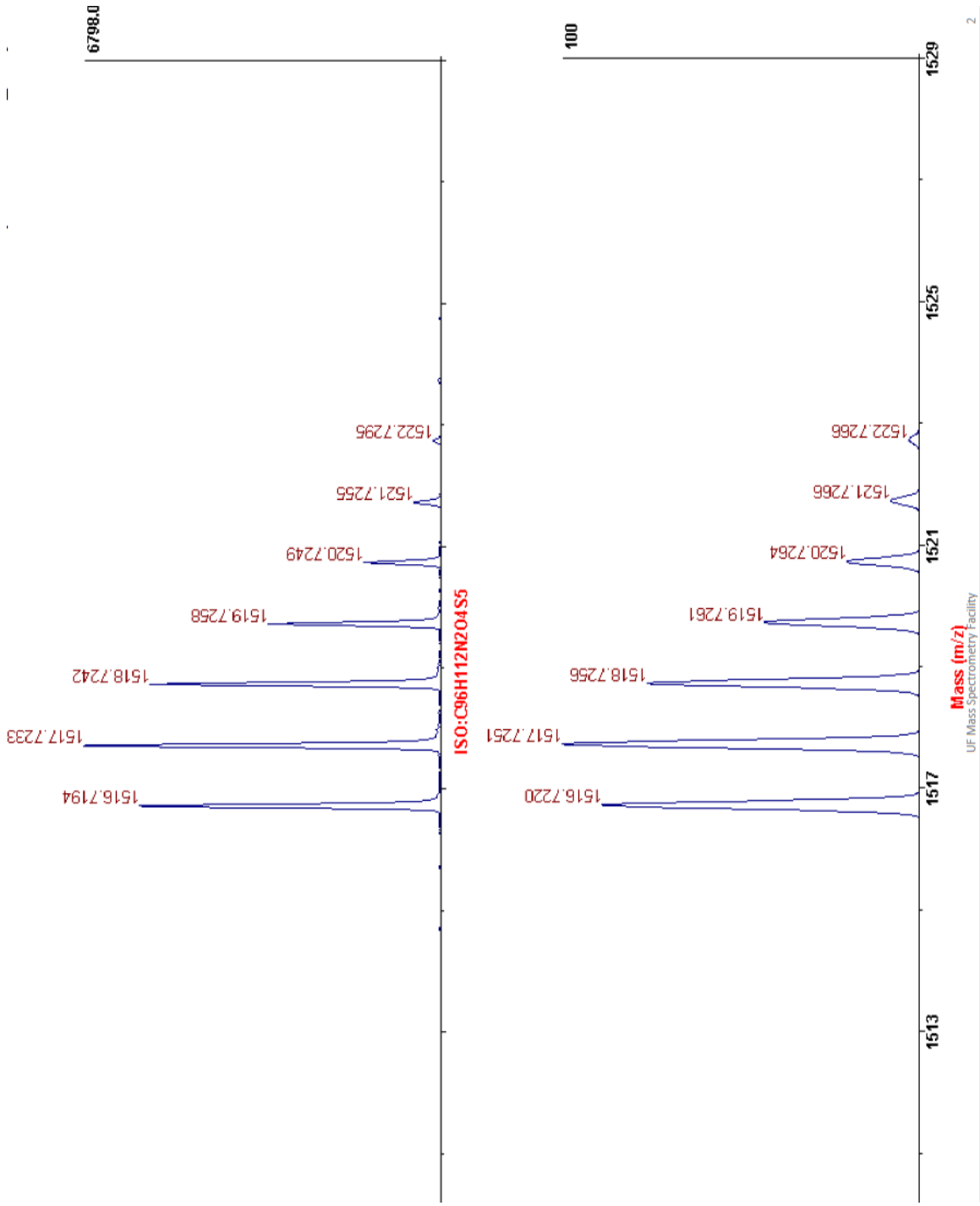


Figure S14c. HRMS spectrum of 4.



# Compound 5 <sup>1</sup>H NMR

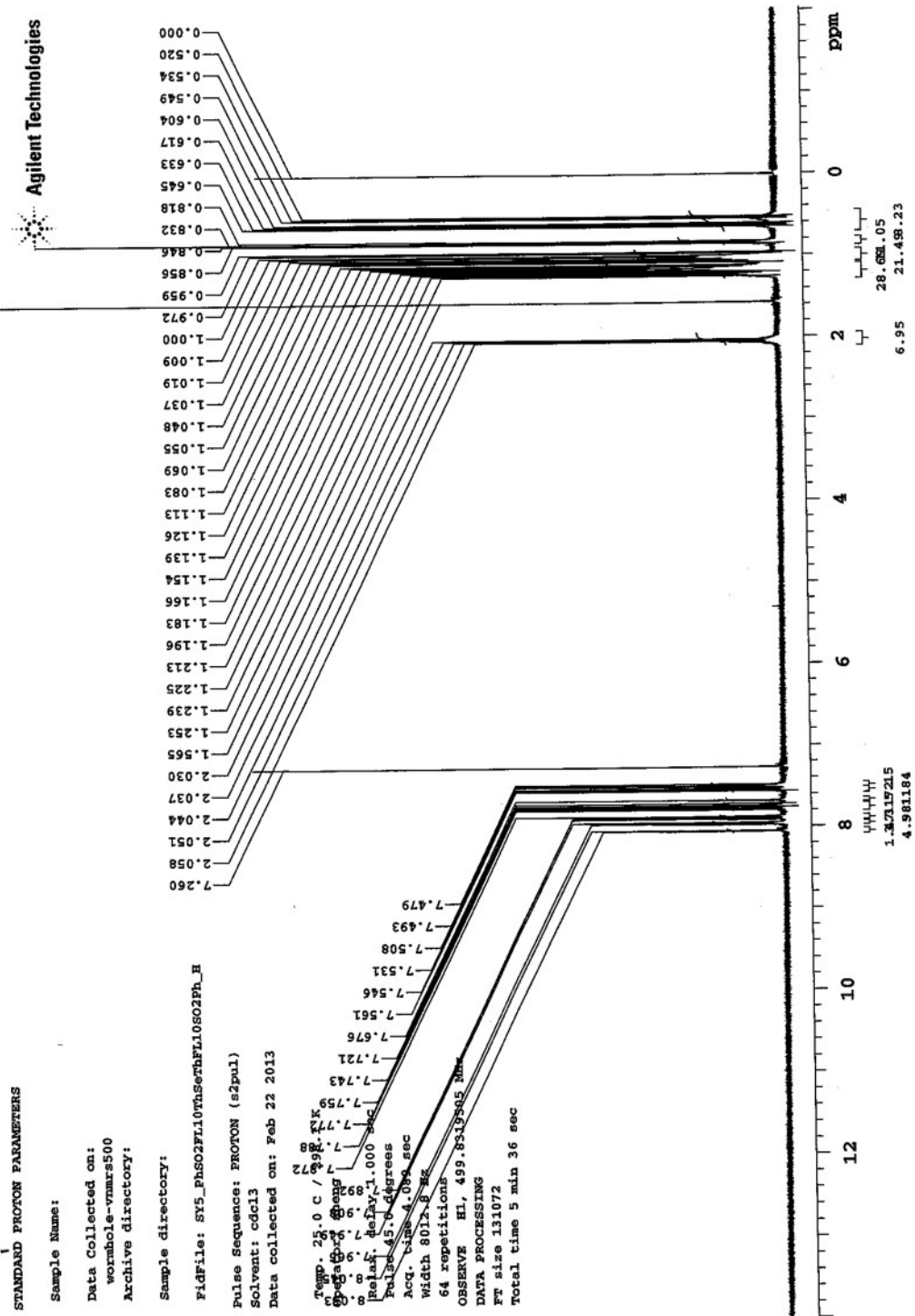


Figure S15a. <sup>1</sup>H NMR spectra of 5.

# Compound 5 <sup>13</sup>C NMR



## Gradient Shimming

Sample Name:

Data Collected on:

vmrs500-vmrs500

Archive directory:

/export/home/chempack/vmrsys/data

Sample directory:

FidFile: SY5\_Th3Se\_C2

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Nov 14 2013

Temp. 25.0 C / 298.1 K

Operator: sheng

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 1.049 sec

Width 31250.0 Hz

256 repetitions

OBSERVE C13, 125.6836614 MHz

DECOUPLE H1, 499.8377008 MHz

Power 41 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 65536

Total time 1 hr, 27 min

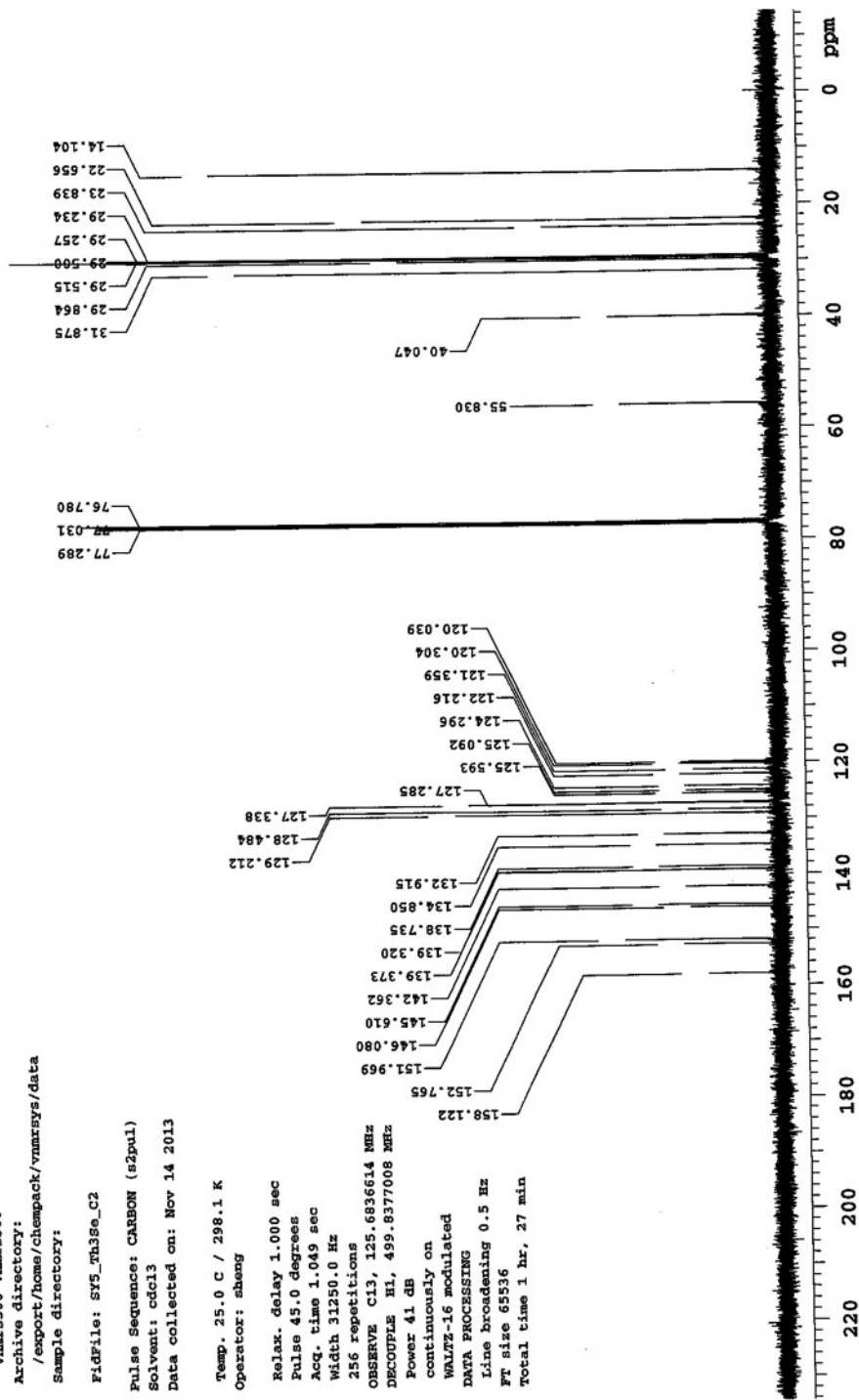


Figure S15b. <sup>13</sup>C NMR spectra of 5.

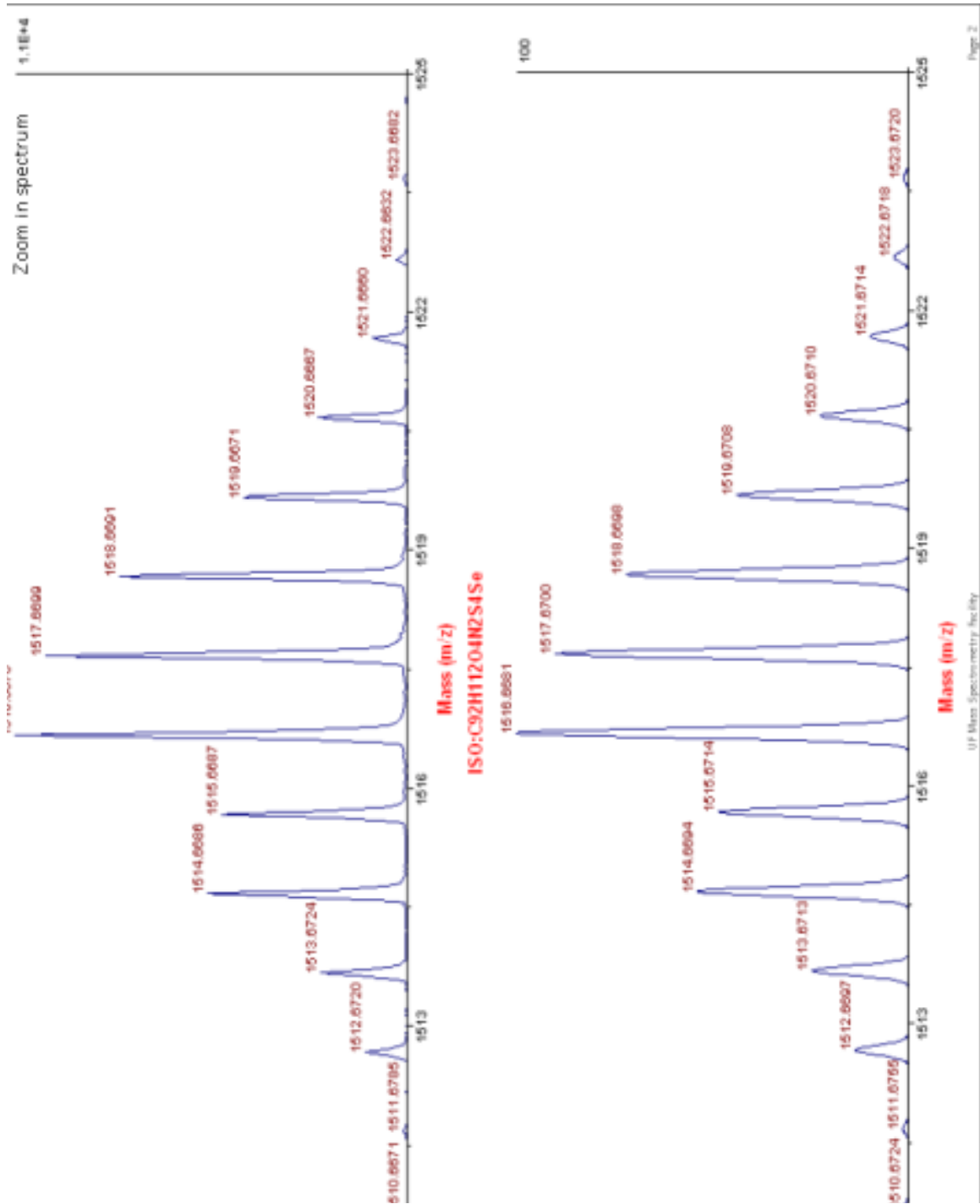


Figure S15c. HRMS spectrum of 5.