

## Supporting Information

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

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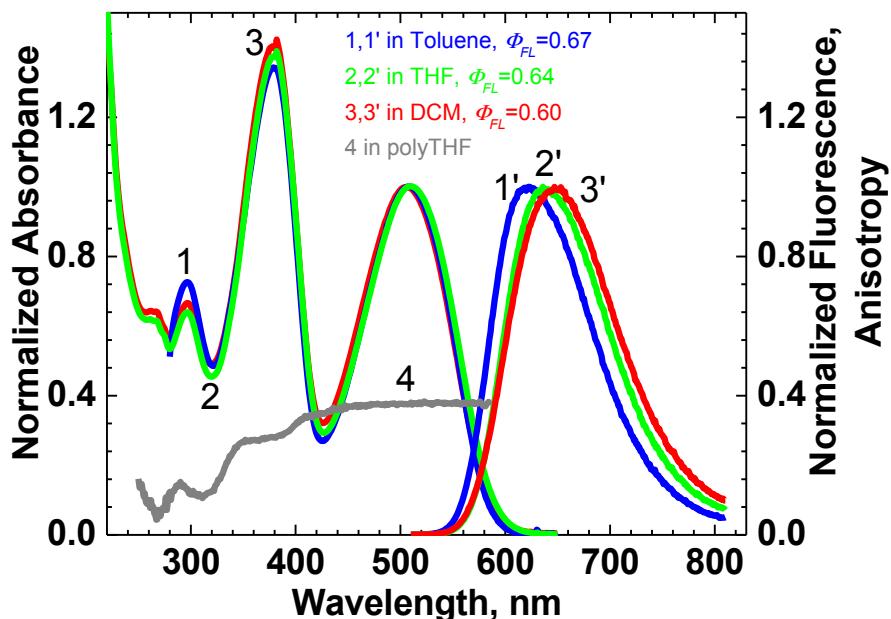
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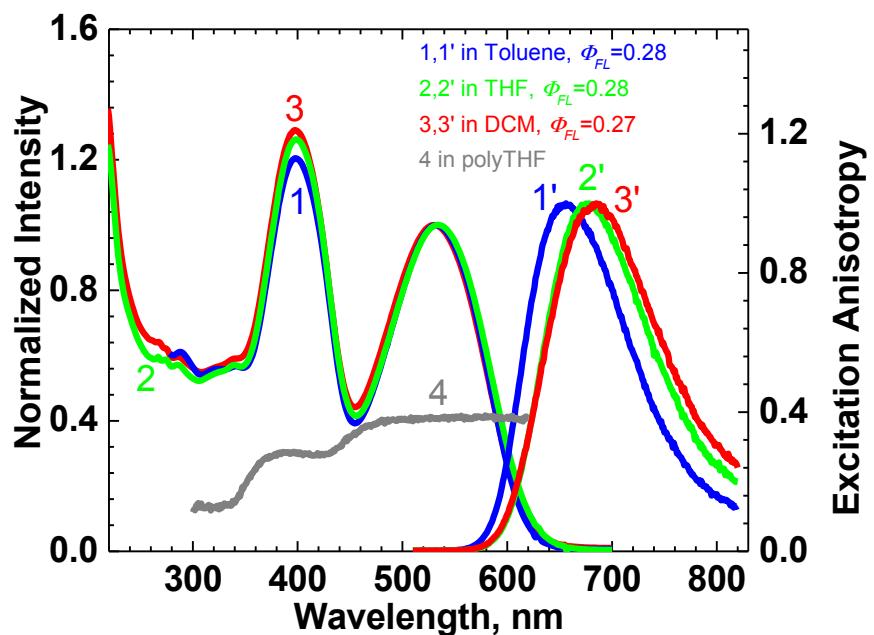
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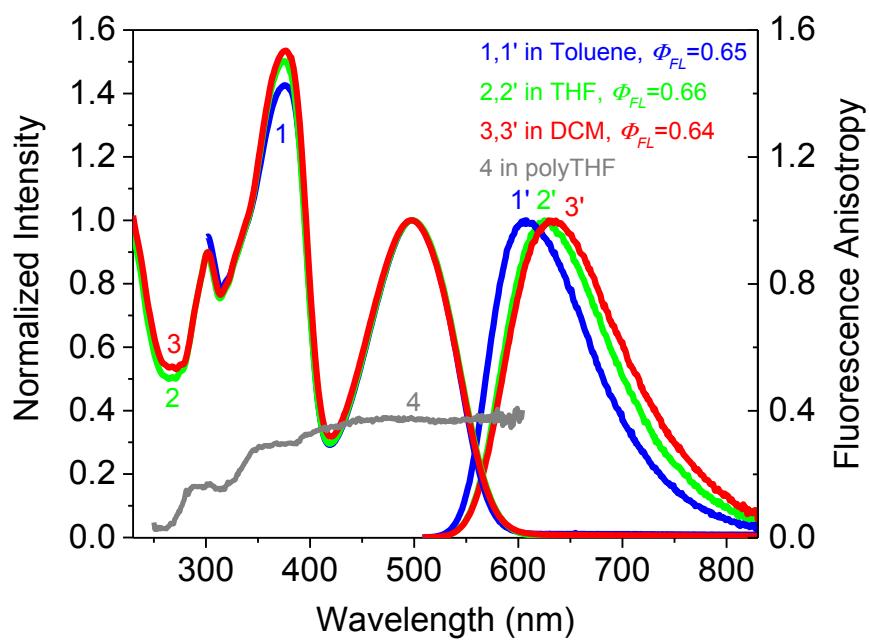
Linear optical properties of dyes **2-5** in toluene, THF and methylene chloride.



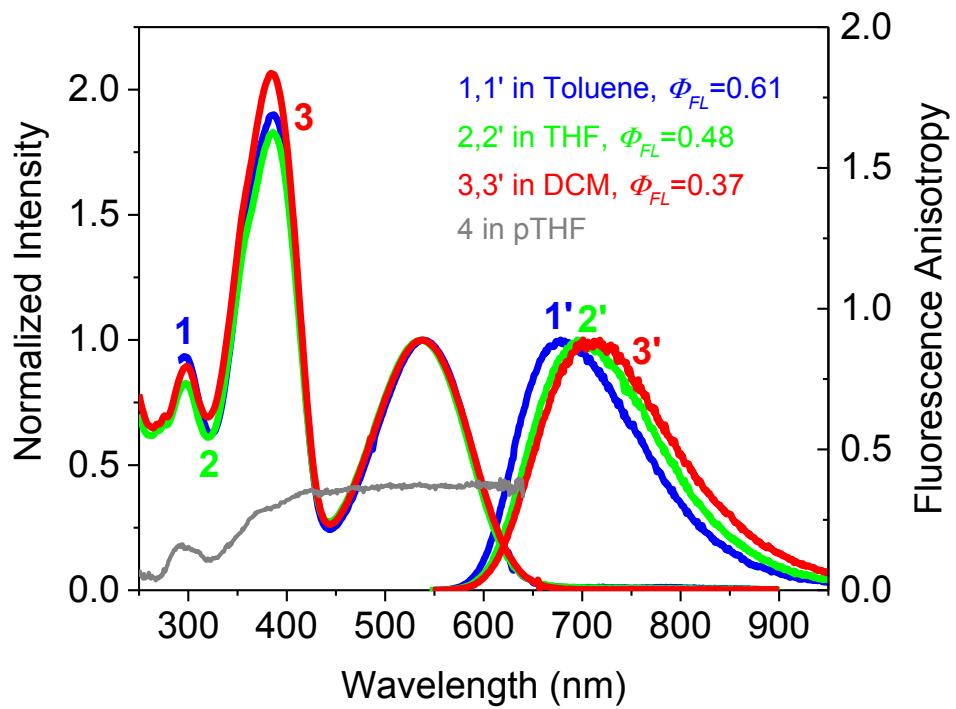
**Figure S1.** Absorption spectra (1, blue, in toluene; 2, green, in THF; 3, red, in dichloromethane (DCM)), fluorescence spectra (1', blue, in toluene; 2', green, in THF; 3', red, in DCM), and excitation anisotropy (4, grey, in polyTHF) of dye **2**.



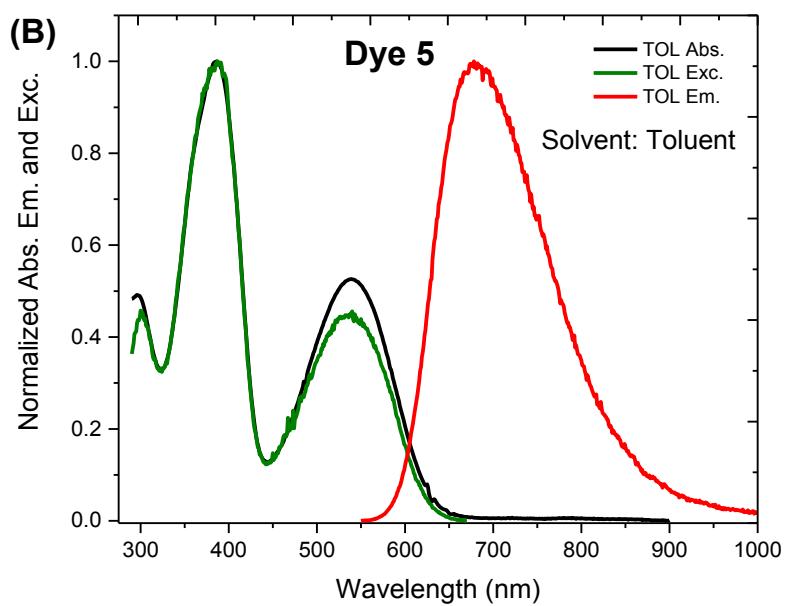
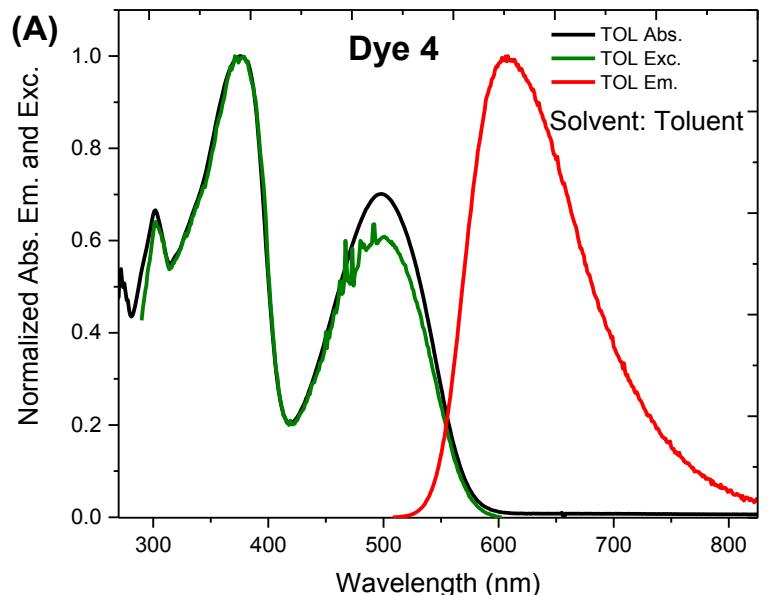
**Figure S2.** Absorption spectra (1, blue, in toluene; 2, green, in THF; 3, red, in DCM), fluorescence spectra (1', blue, in toluene; 2', green, in THF; 3', red, in DCM), and excitation anisotropy (4, grey, in polyTHF) of dye **3**.



**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.

## <sup>1</sup>H and <sup>13</sup>C NMR Spectra

### Compound 9 <sup>1</sup>H NMR

#### STANDARD PROTON PARAMETERS

Sample Name:

Data Collected on:

wormhole-ynmr500

Archive directory:

Sample directory:

Pulse Sequence: PROTON (32pul)

Solvent: cdcl3

Data collected on: Mar 1 2013

Temp. 25.0 C / 69.8 K  
Operator: shang . sec

Reps: 8192 1.000 sec

Progs: 45.0 degrees

Acq. Time: 0.069 sec

Width: 864.0-872.0 Hz

Q32 Tolerances: 0.0000000000000000 MHz

Observe: H, 499.031513 MHz

DSP: PROCESSING

FT size: 131072

total time: 2 min 53 sec

Agilent Technologies

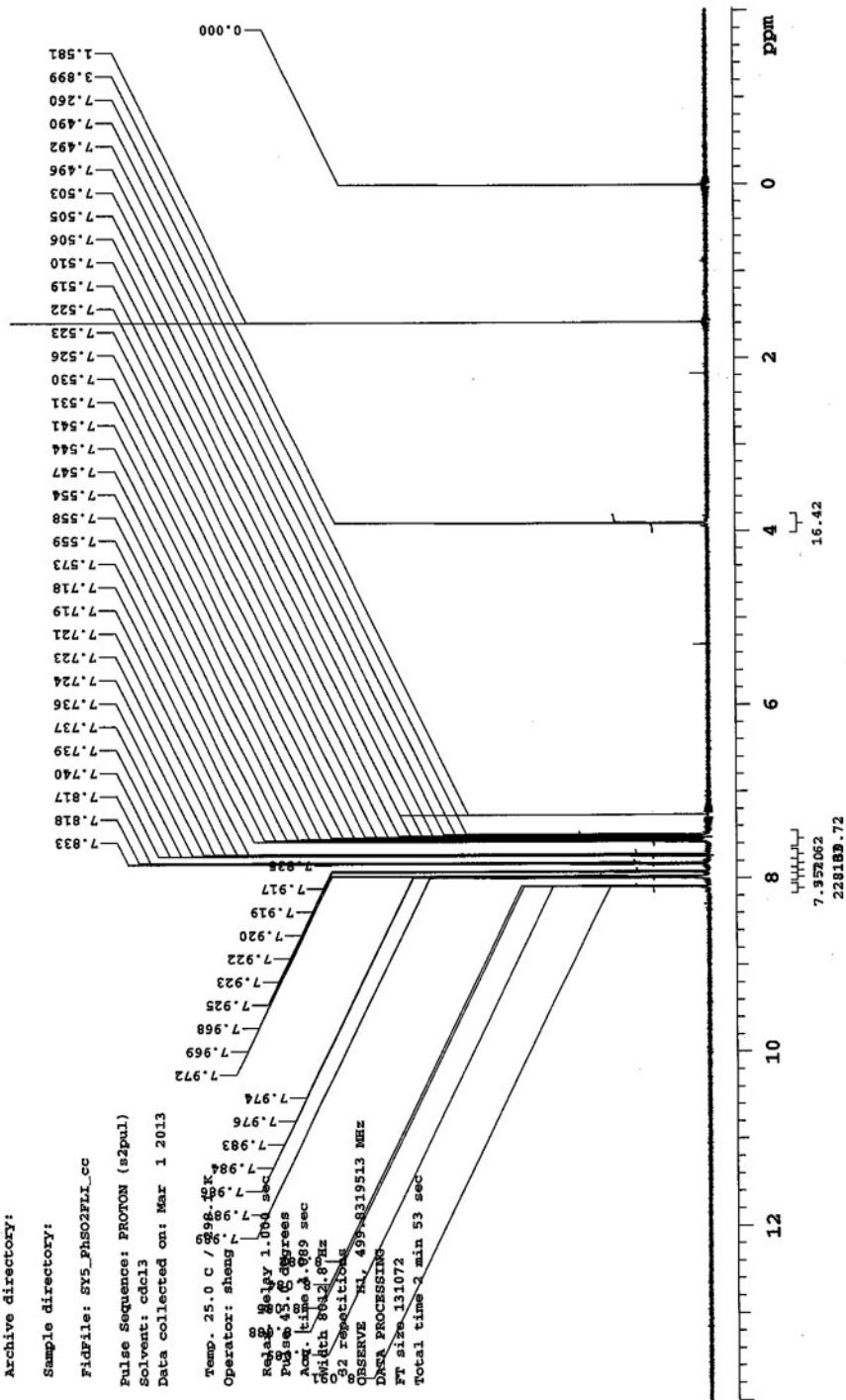


Figure S6a. <sup>1</sup>H NMR spectra of 9.

# Compound 9 $^{13}\text{C}$ NMR

## STANDARD PROTON PARAMETERS

### Sample Name:

Data Collected on:  
woxhole-vms500  
Archive directory:

### Sample directory:

FidFile: SV5\_Ph502FLI\_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  
Acc. time 1.032 sec  
Width 32051.3 Hz  
16 repetitions  
OBSERVE Cl3, 125.6828439 MHz  
DECcouple H1, 499.8344436 MHz  
Power 40 dB  
continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 0.5 Hz  
FID size 131072  
Total time 1 hr, 26 min

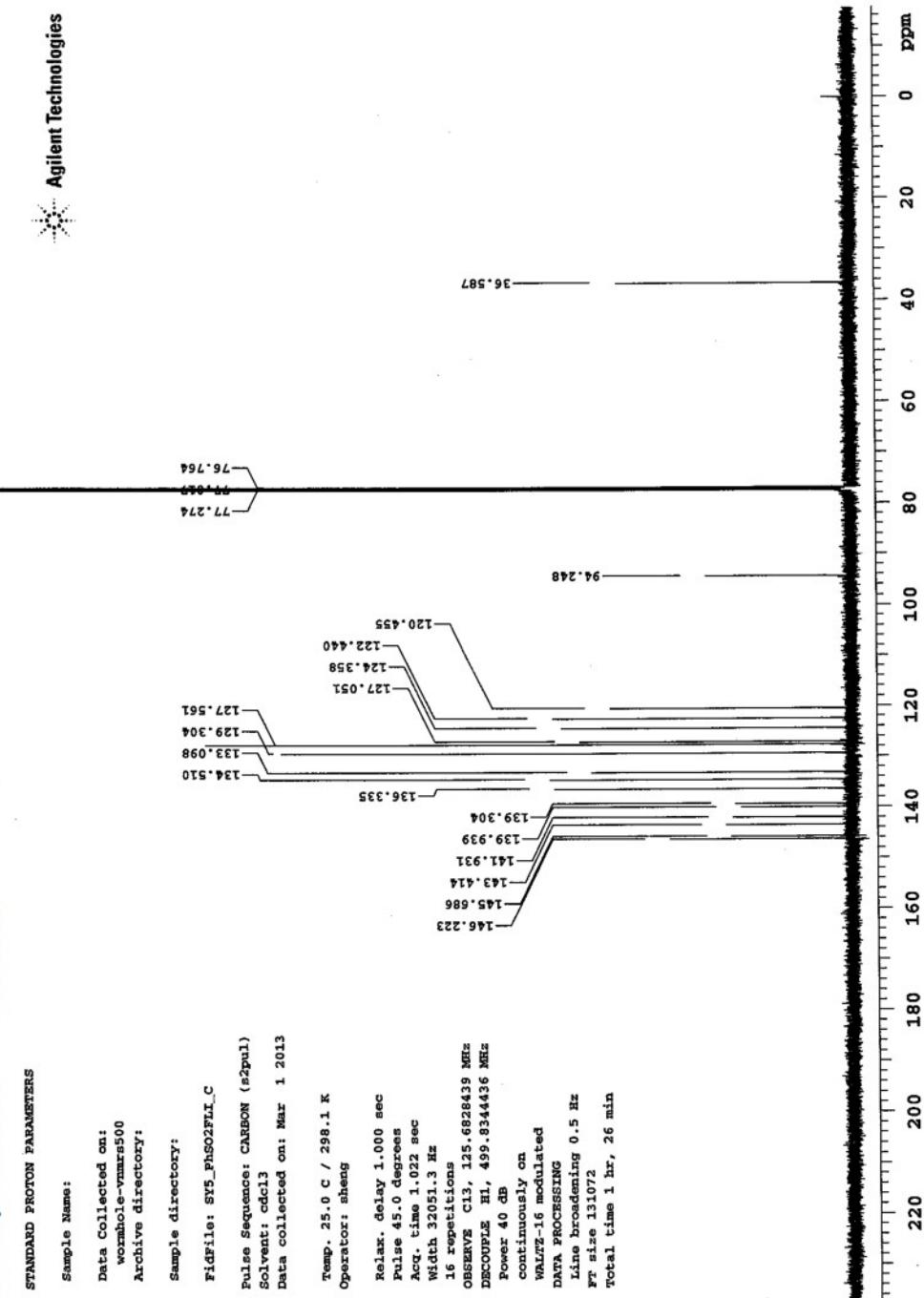
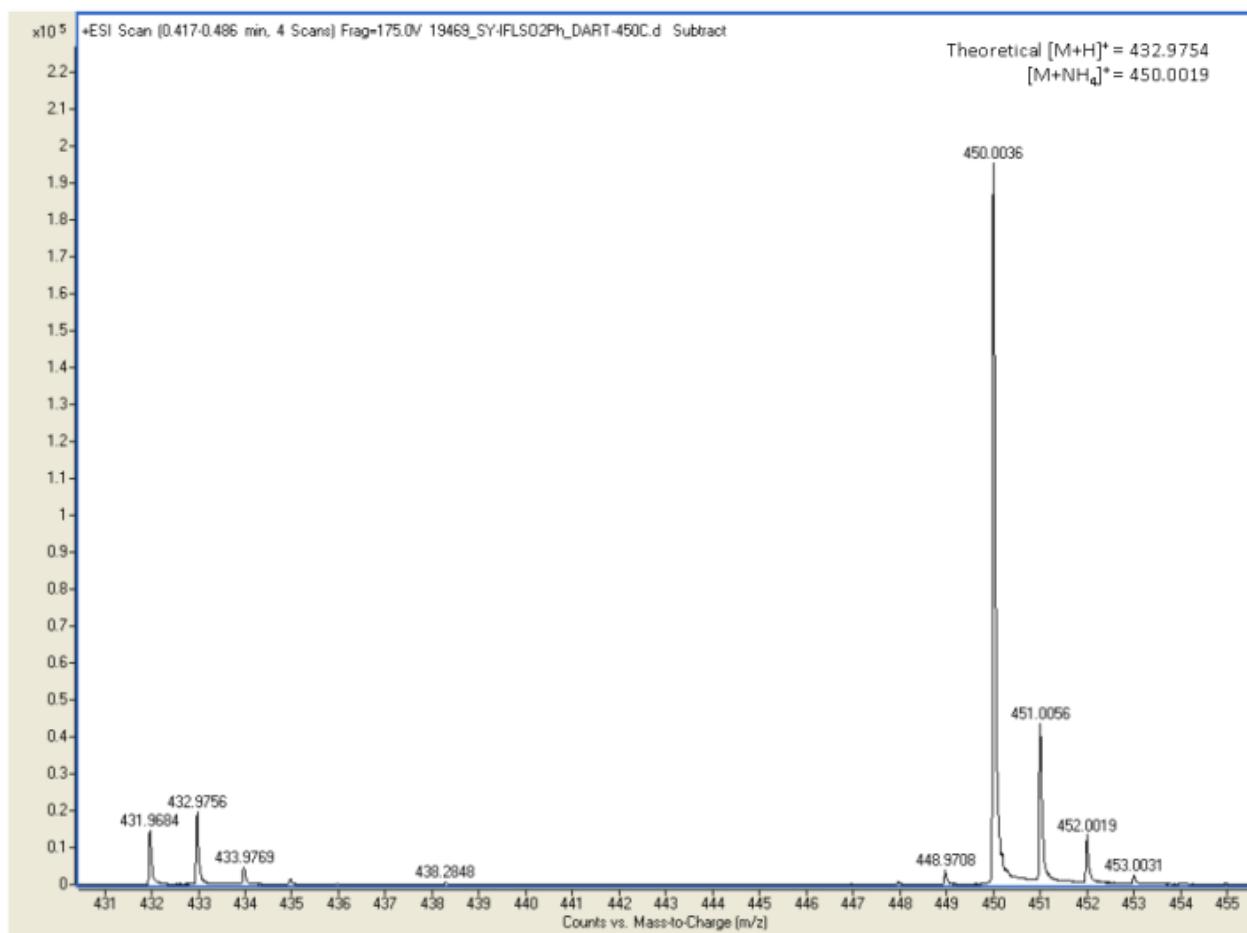


Figure S6b.  $^{13}\text{C}$  NMR spectra of 9.

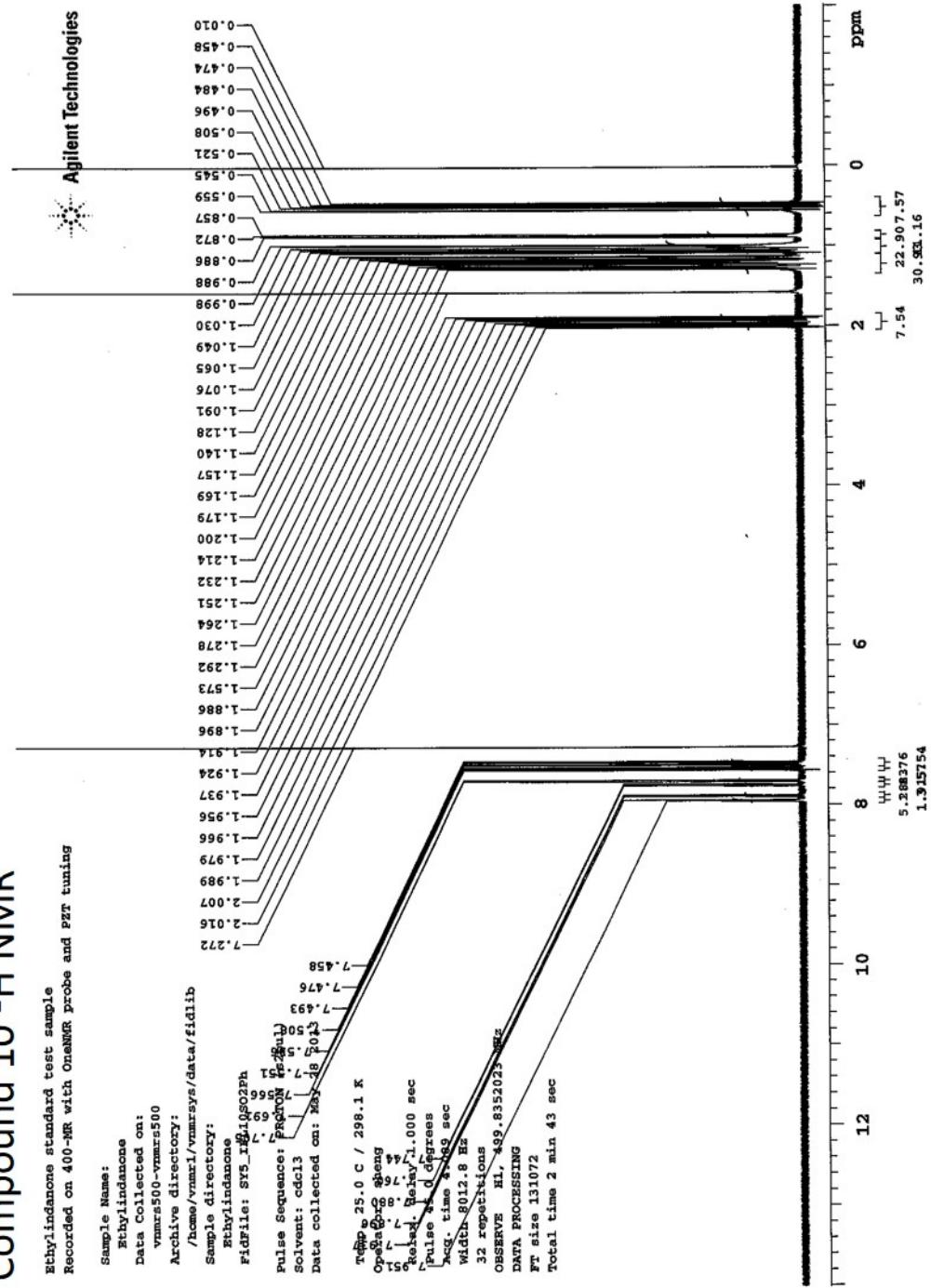


**Figure S6c.** HRMS spectrum of **9**.

# Compound 10 $^1\text{H}$ NMR

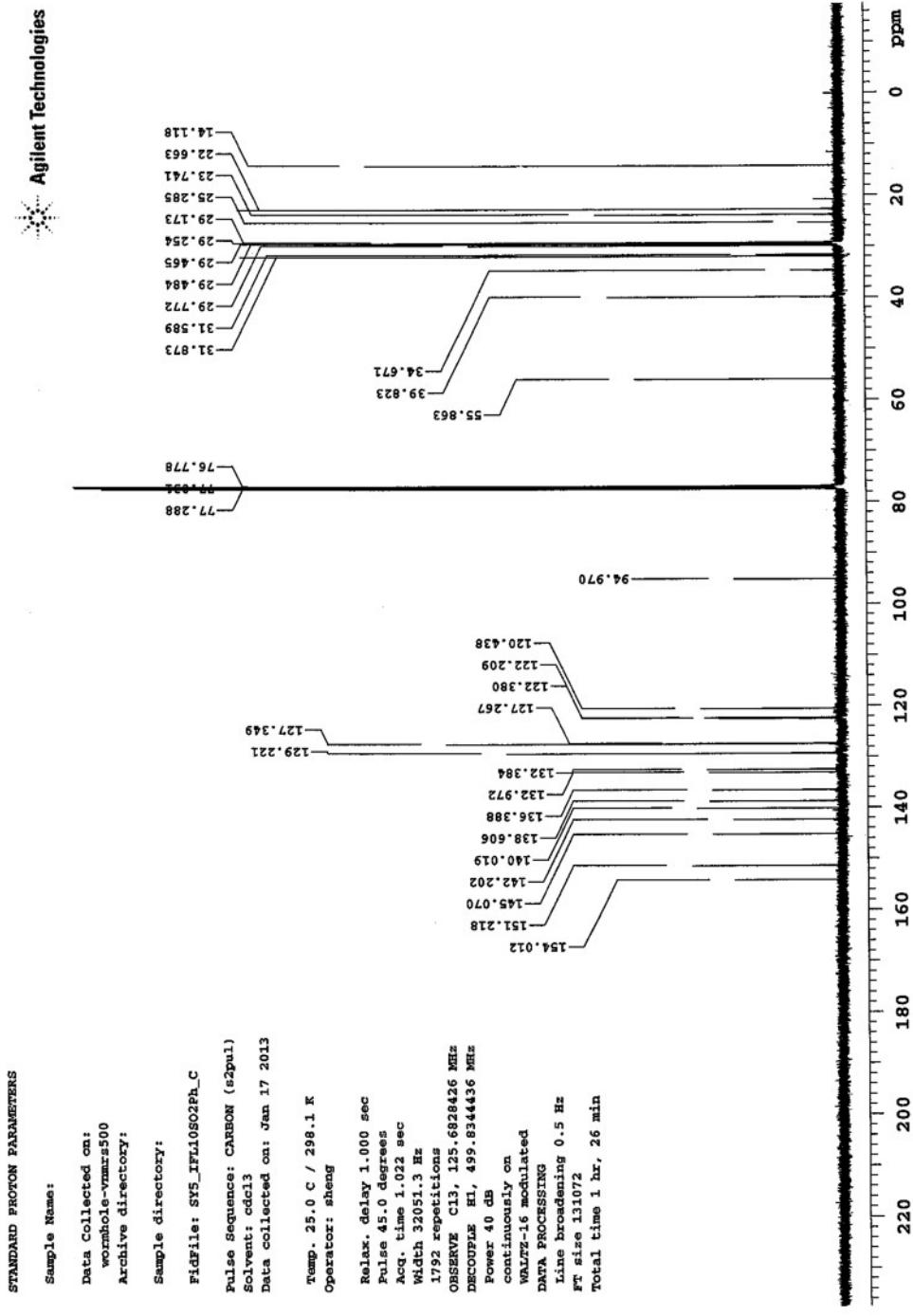
Ethylindanone standard test sample  
Recorded on 400-NMR with OmNMR probe and P2T tuning

Sample Name: Ethylindanone  
Data Collected on: vnmr350-vnmr350  
Archive directory: /home/vnmr1/vnmrsys/data/fidlib  
Sample directory: Ethylindanone  
FidFile: ST5\_R010902PH  
Pulse Sequence: FID013  
Solvent: Proton  
Data collected on: 2013-01-18  
Temp: 25.0 C / 298.1 K  
Op: S2202, sheng  
PS: 1.000 sec  
Relax: 1.000 sec  
Pulse: 90 degrees  
Acq. time: 4.000 sec  
Width: 8012.8 Hz  
32 repetitions  
OBSERVE: HI, 499.833203 Hz  
DATA PROCESSING  
Ft size: 131072  
Total time: 2 min 43 sec

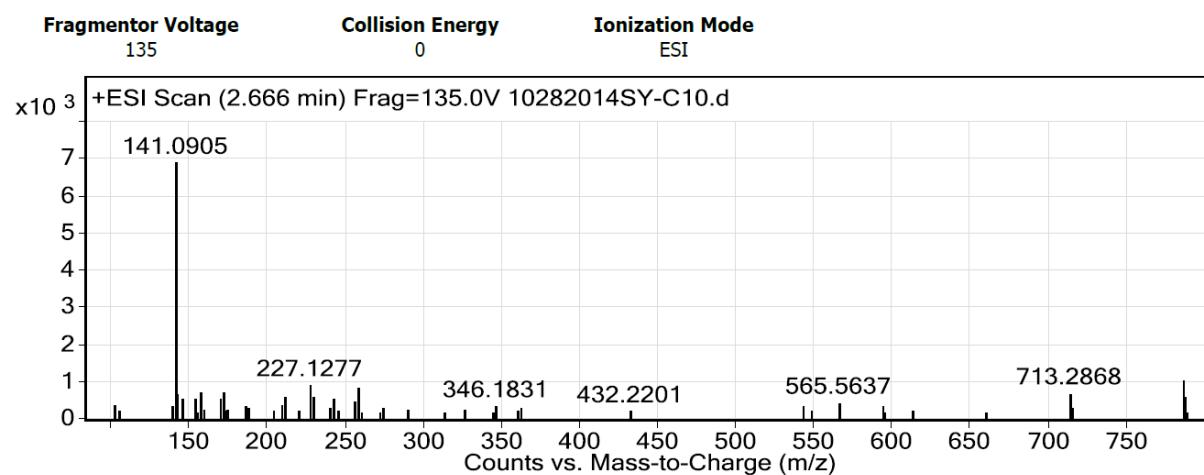


**Figure S7a.**  $^1\text{H}$  NMR spectra of **10**.

## Compound 10 $^{13}\text{C}$ NMR



**Figure S7b.**  $^{13}\text{C}$  NMR spectra of **10**.



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

## Compound 12 $^1\text{H}$ NMR

### STANDARD PROTON PARAMETERS

Sample Name:

Data Collected on:  
wormhole-vnmrs500  
Archive directory:

Sample directory:

Fidfile: S12\_Proton (s2pul)

Pulse Sequence: PROTON (s2pul)

Solvent: odc13

Data collected on: Jan 25 2013

Temp 25.0 C / 298.1 K

Operating freq 400

Relax delay 1.000 sec

Pulse 47.0 degrees

Acq. time 4.000 sec

Width 8013.8 Hz

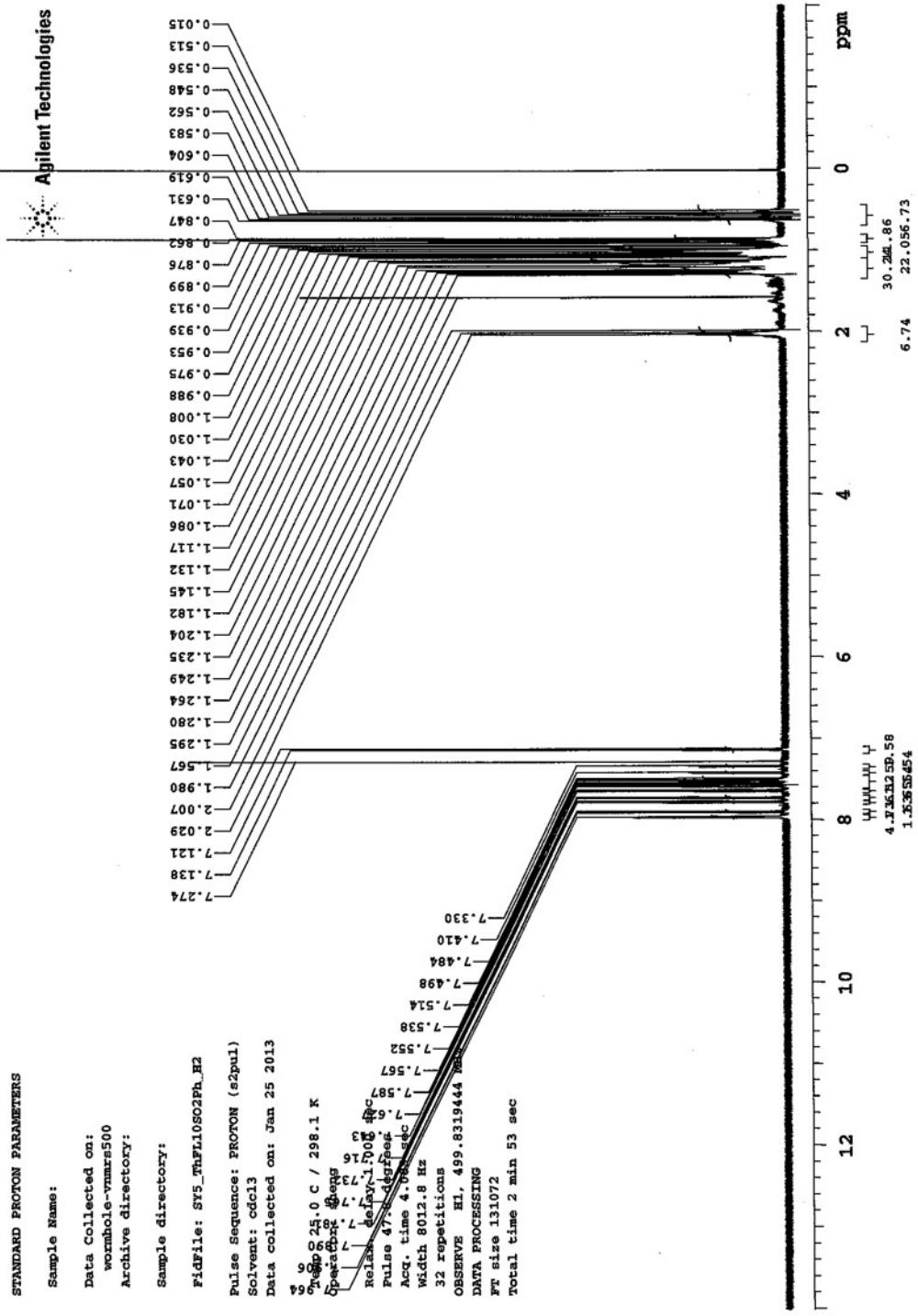
32 repetitions

OBSERVE HI, 499.831944 sec

DATA PROCESSING

RF size 131072

Total time 2 min 53 sec



**Figure S8a.**  $^1\text{H}$  NMR spectra of 12.

# Compound 12 $^{13}\text{C}$ NMR

## Gradient Shimming

### Sample Name:

Data Collected on:  
vnmrs500-vnmrs500

Archive directory:  
/export/home/chempack/vnmrsys/data  
Sample directory:

Fidfile: S75\_TMSPL1002Ph\_C2

Pulse Sequence: CARBON (s2pul1)

Solvent: cdc13

Data collected on: Nov 7 2013

Temp. 25.0 C / 298.1 K  
Operator: sheaq

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 1.049 sec

Width 31250.0 Hz

256 repetitions

OBSERVE Cl3, 125.6836615 MHz

DECOPPLE 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

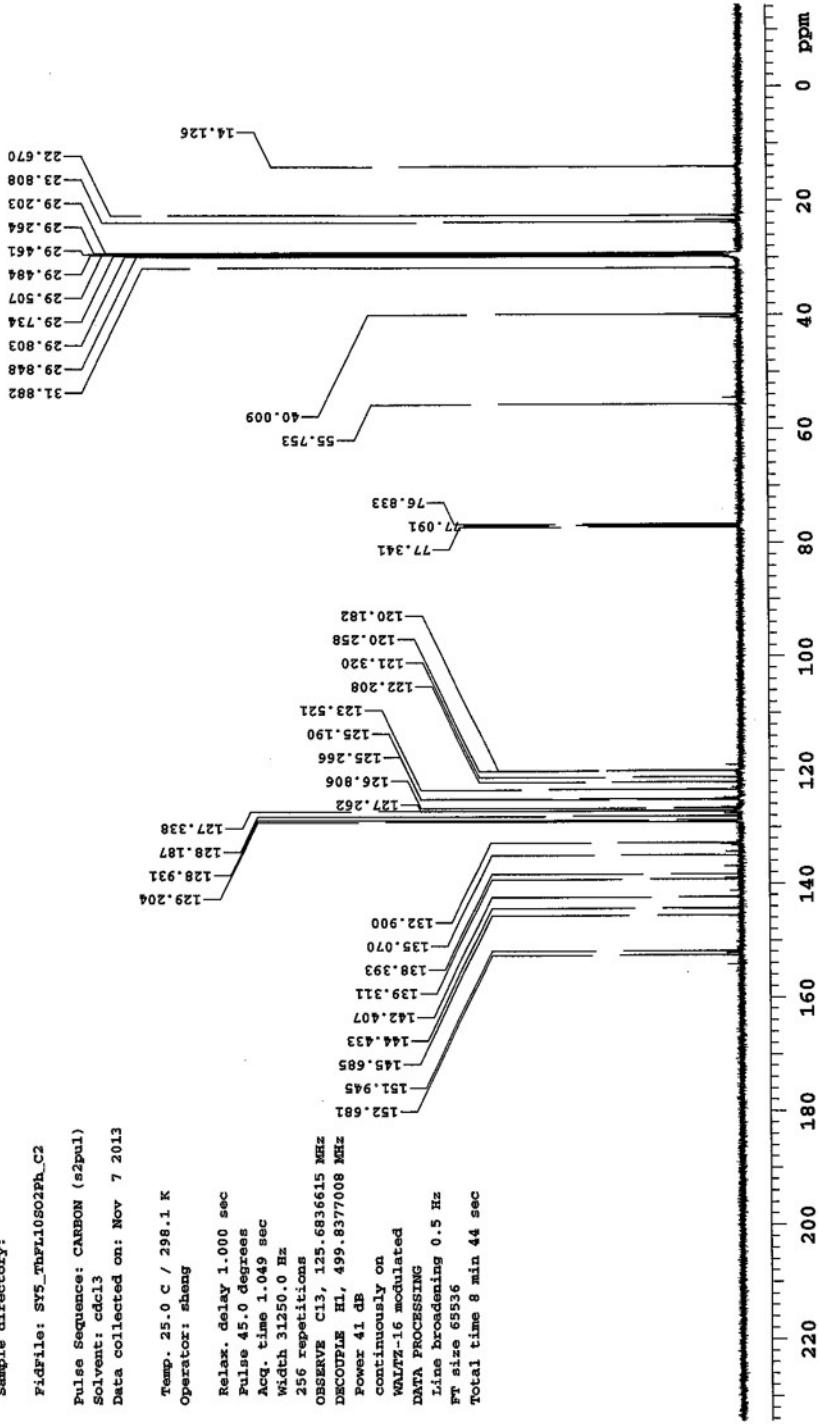
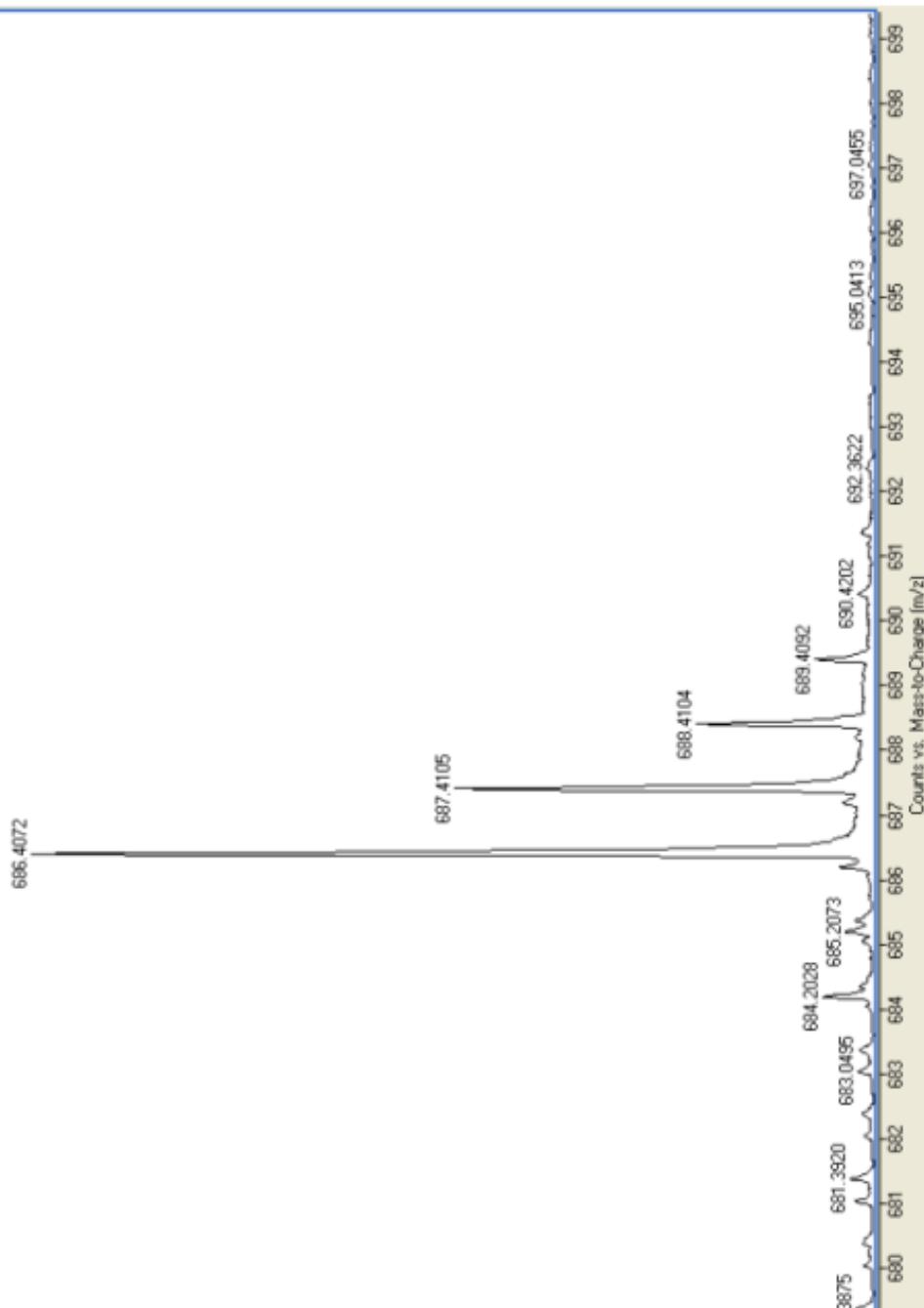


Figure S8b.  $^{13}\text{C}$  NMR spectra of 12.



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

# Compound 13 $^1\text{H}$ NMR

## STANDARD PROTON PARAMETERS

### Sample Name:

Data Collected on:

wormhole-vnmr500  
Archive directory:

### Sample directory:

FidFile: S75\_BirthFLC108025h\_H

Pulse Sequence: PROTON (S2spn1)

Solvent: cddc13

Data collected on: Nov 8 2012

temp 35.0 °C / 298.1 K

Optical filter: 25.0 °C / 298.1 K

Relax. delay 1.000 sec

Pulse 45.0 deg

Acq. time 2.045 sec

width 8012.8 Hz

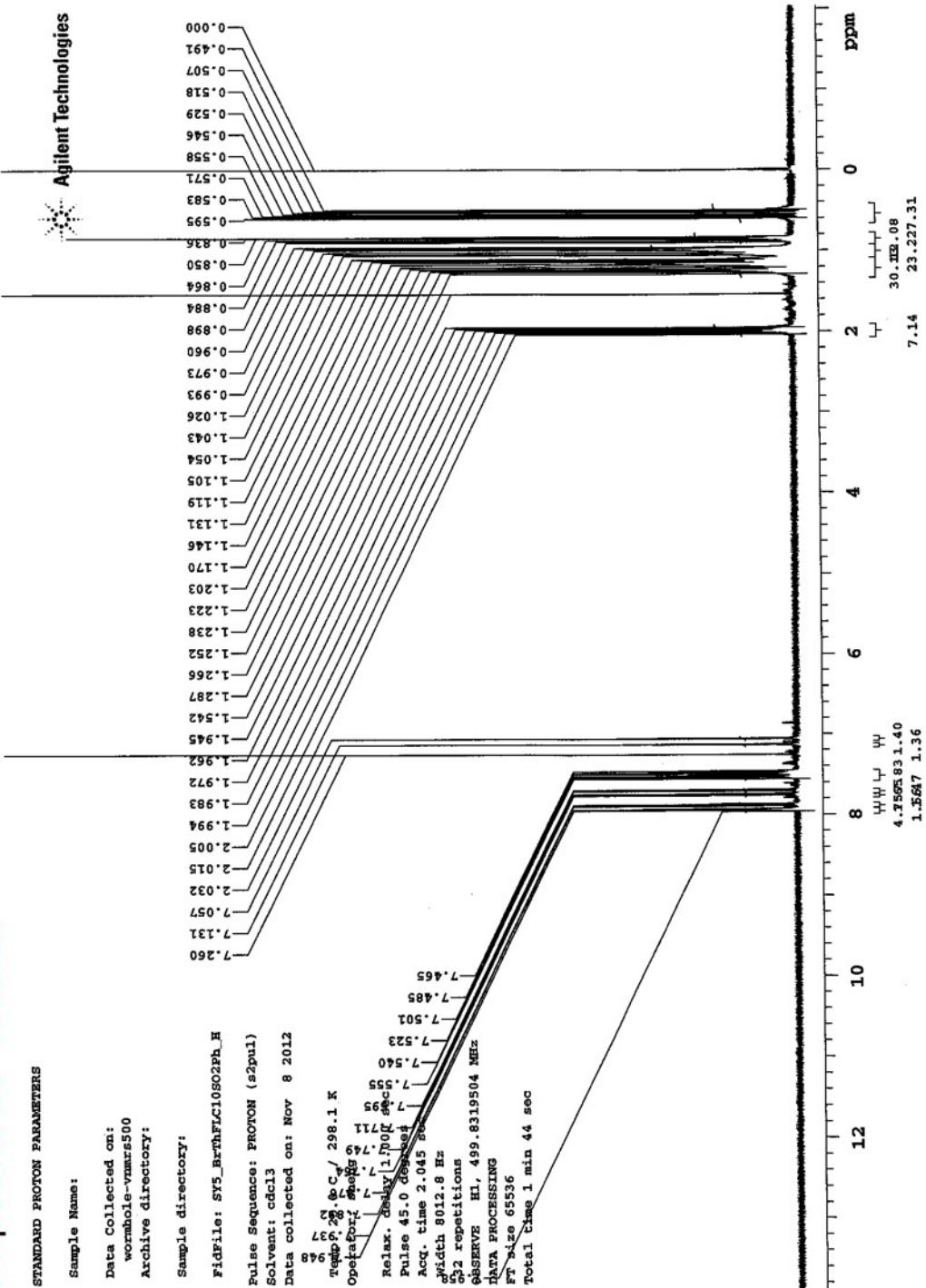
652 repetitions

OBSERVE H1, 499.8319504 MHz

DATA PROCESSING

FT size 65536

Total time 1 min 44 sec



**Figure S9a.**  $^1\text{H}$  NMR spectra of 13.

## Compound 13 $^{13}\text{C}$ NMR

### STANDARD PROTON PARAMETERS

#### Sample Name:

Data Collected on:  
wormhole~vnarrs500  
Archive directory:

#### Sample directory:

#### Fidfile: SIS\_BrtnFLC10SO2Pb\_C

#### Pulse Sequence: CARBON (42ppm)

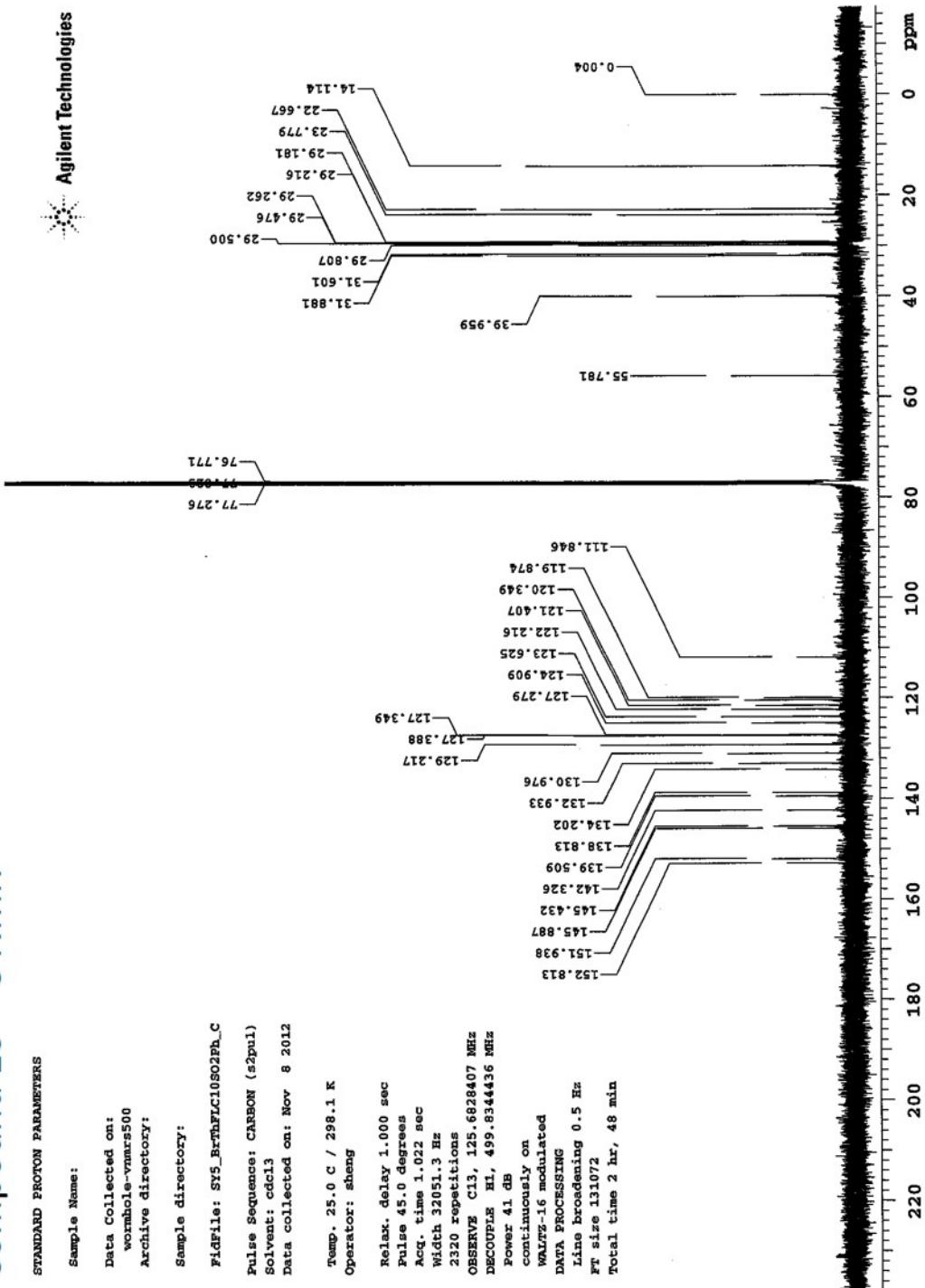
Solvent: cdcl<sub>3</sub>

Data collected on: Nov 8 2012

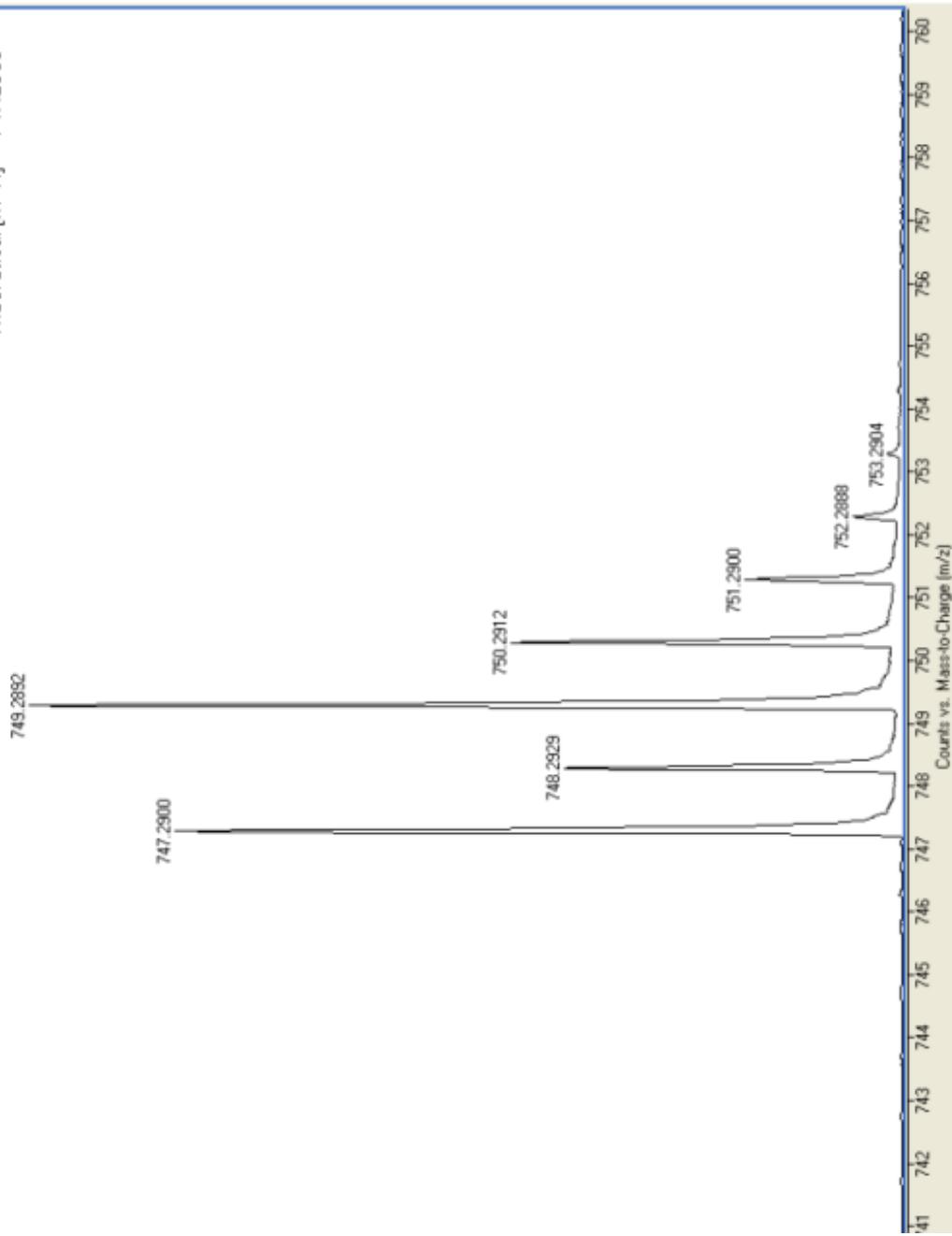
Temp. 25.0 C / 298.1 K  
Operator: shang  
Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acc. time 1.022 sec  
Width 32051.3 Hz

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  
ff size 121072  
Total time 2 hr, 48 min

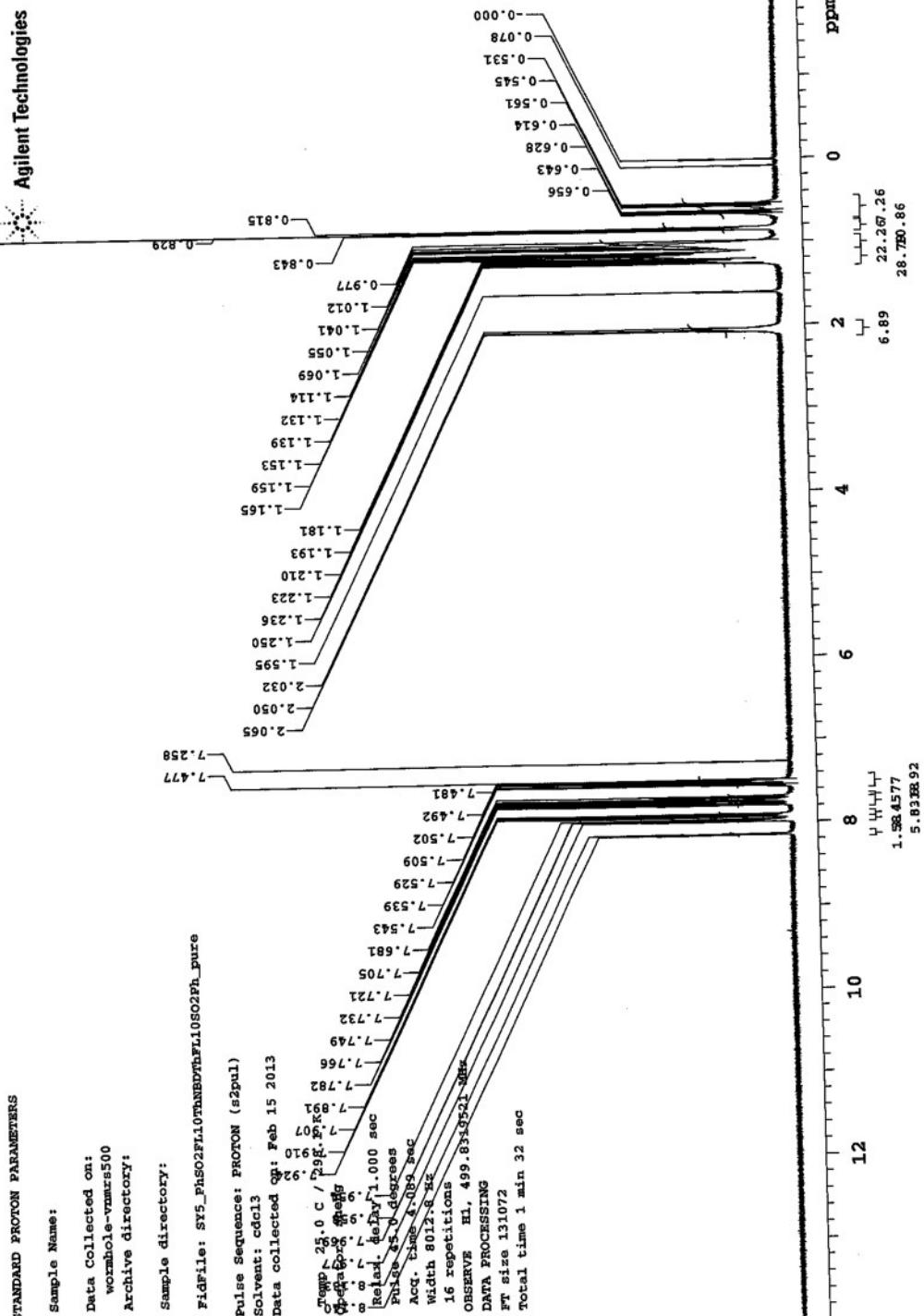


**Figure S9b.**  $^{13}\text{C}$  NMR spectra of 13.



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

# Compound 2 $^1\text{H}$ NMR



## Compound 2 $^{13}\text{C}$ NMR

### STANDARD PROTON PARAMETERS

#### Sample Name:

Data Collected on:  
wmmhole-vmr500  
Archive directory:

#### Sample directory:

#### Pulse Sequence: CARBON (s2pul)

Solvent: cdd13  
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 33051.3 Hz

720 repetitions  
OBSERVE C13, 125.688425 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

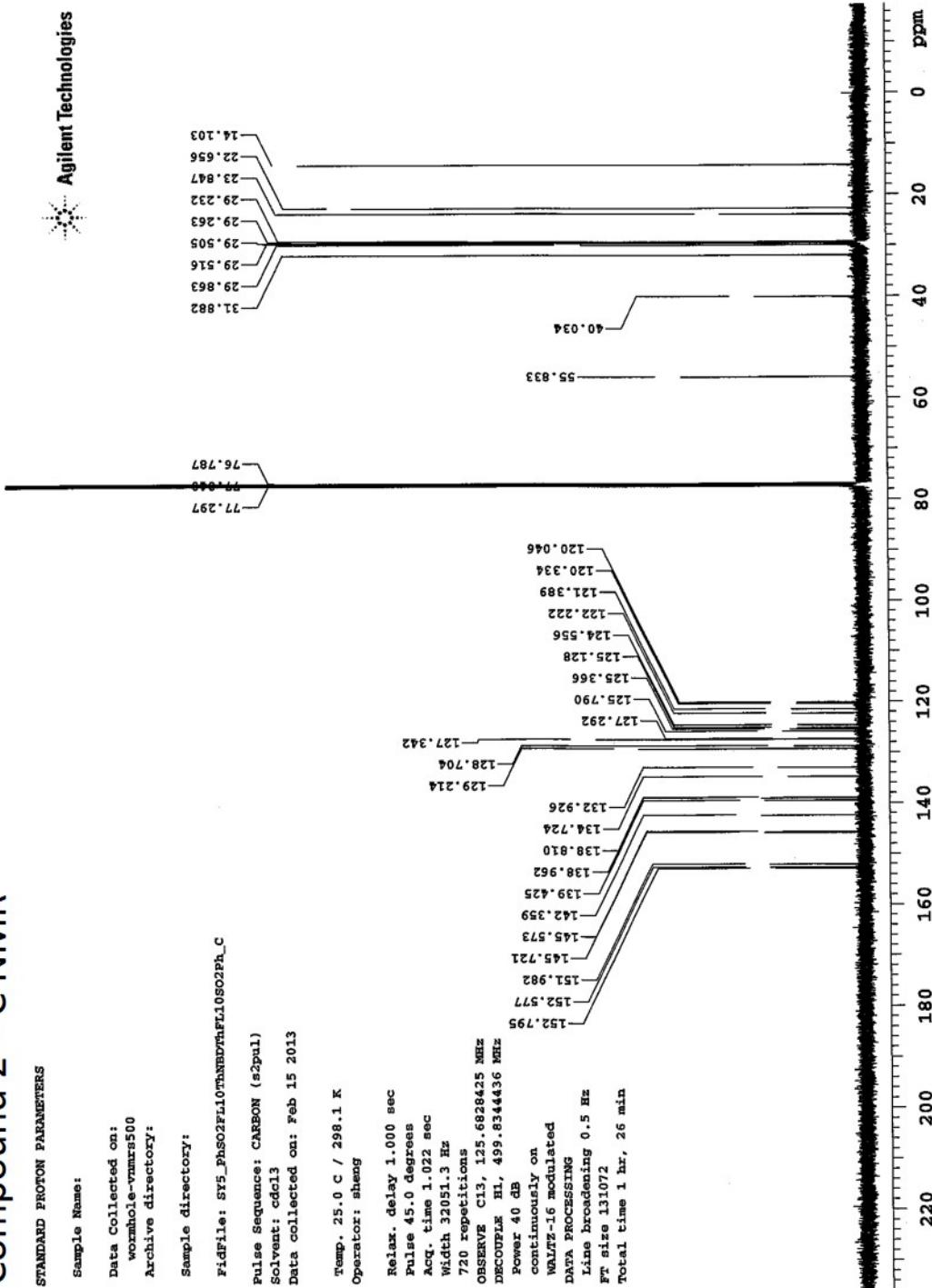
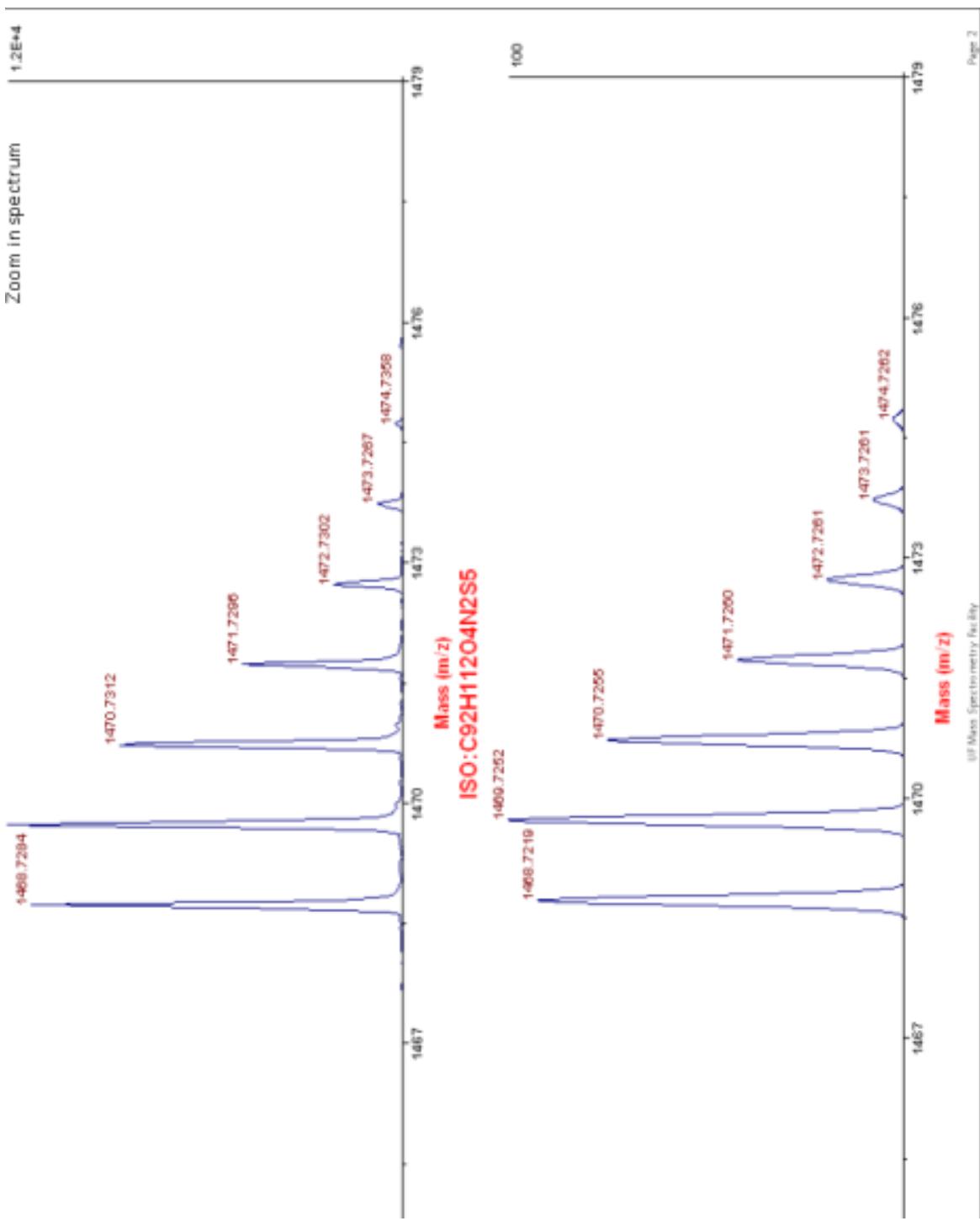


Figure S10b.  $^{13}\text{C}$  NMR spectra of 2.



**Figure S10c.** HRMS spectrum of **2**.

# Compound 3 $^1\text{H}$ NMR

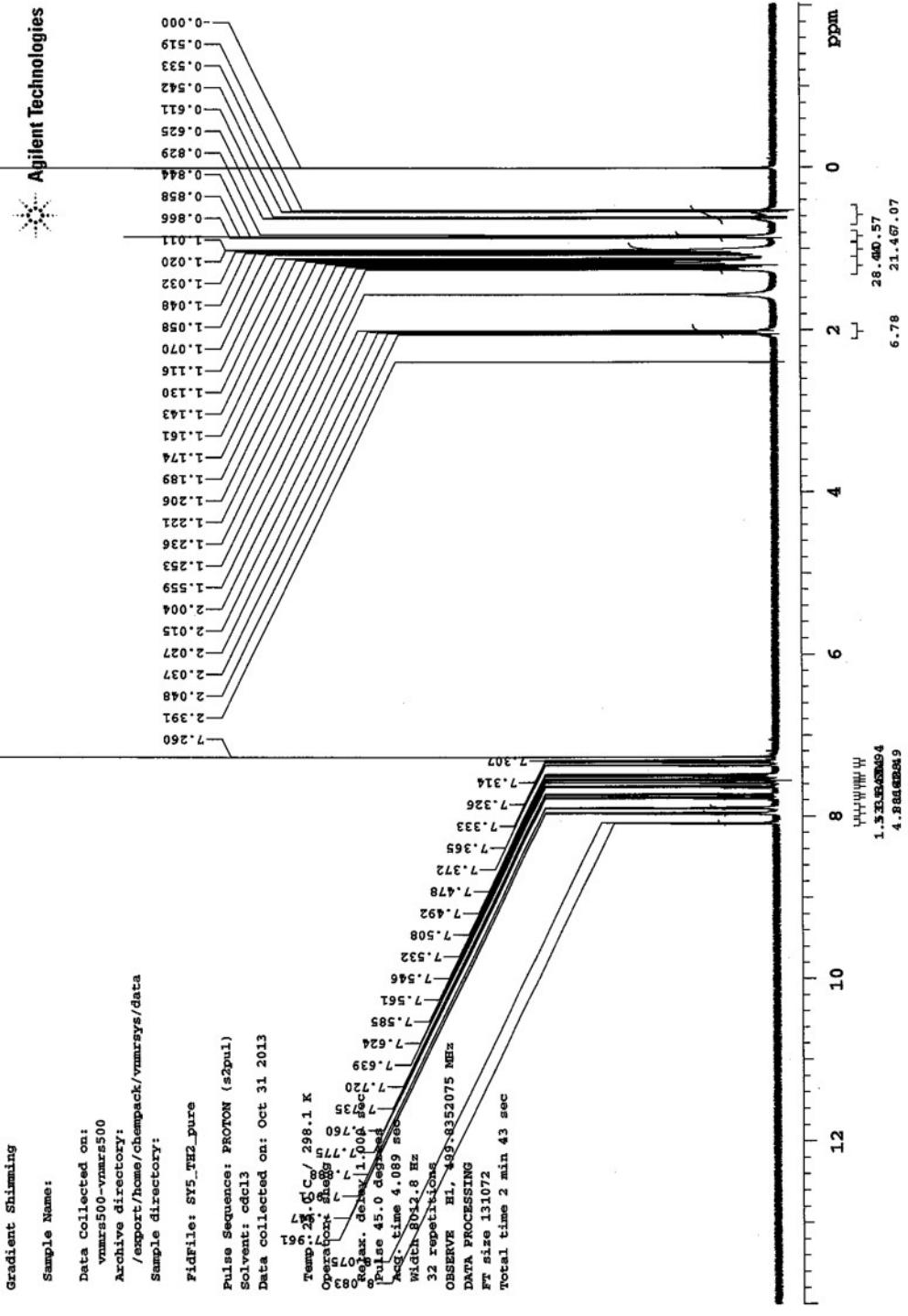


Figure S11a.  $^1\text{H}$  NMR spectra of 3.

## Compound 3 $^{13}\text{C}$ NMR

### STANDARD PROTON PARAMETERS

Sample Name:

Data Collected on:  
wormhole-vmar500

Archive directory:

Sample directory:

FidFile: S11b\_SbSO2Ph1.0THFNaBorborhrl10SO2Ph.C

Pulse Sequence: CARBON (s2pul)

Solvent: cdc13

Data collected on: Feb 15 2013

TEMP. 25.0 C / 298.1 K

Operator: sheng

Relax. delay 1.000 sec

Pulse 45.0 degrees

Aqc. time 1.032 sec

Width 32051.3 Hz

2560 repetitions

OBSERVE C13, 125.6829705 MHz

DECOUPLE H1, 499.8344436 MHz

Power 40 dB

continuously on

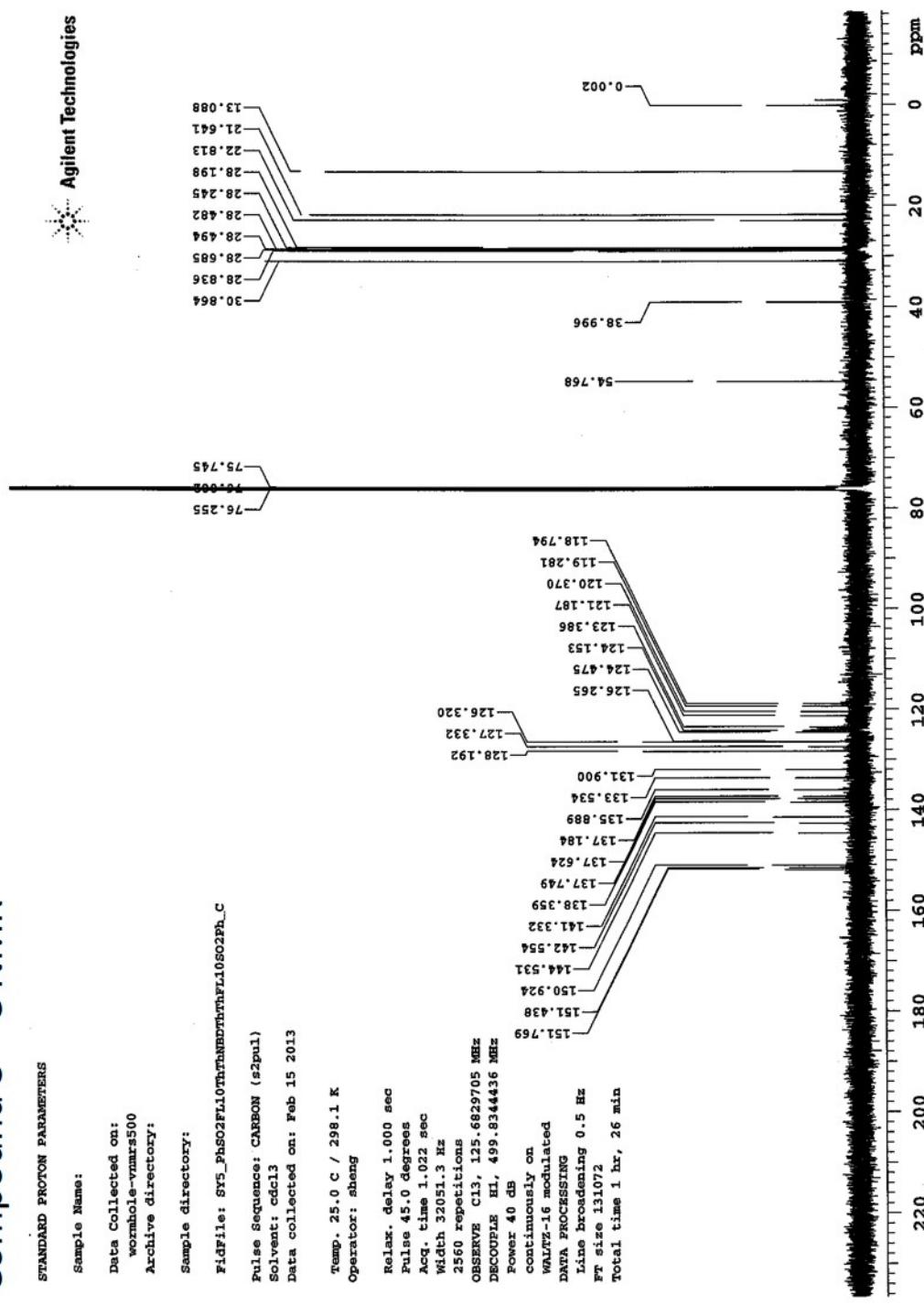
WALTZ-16 modulated

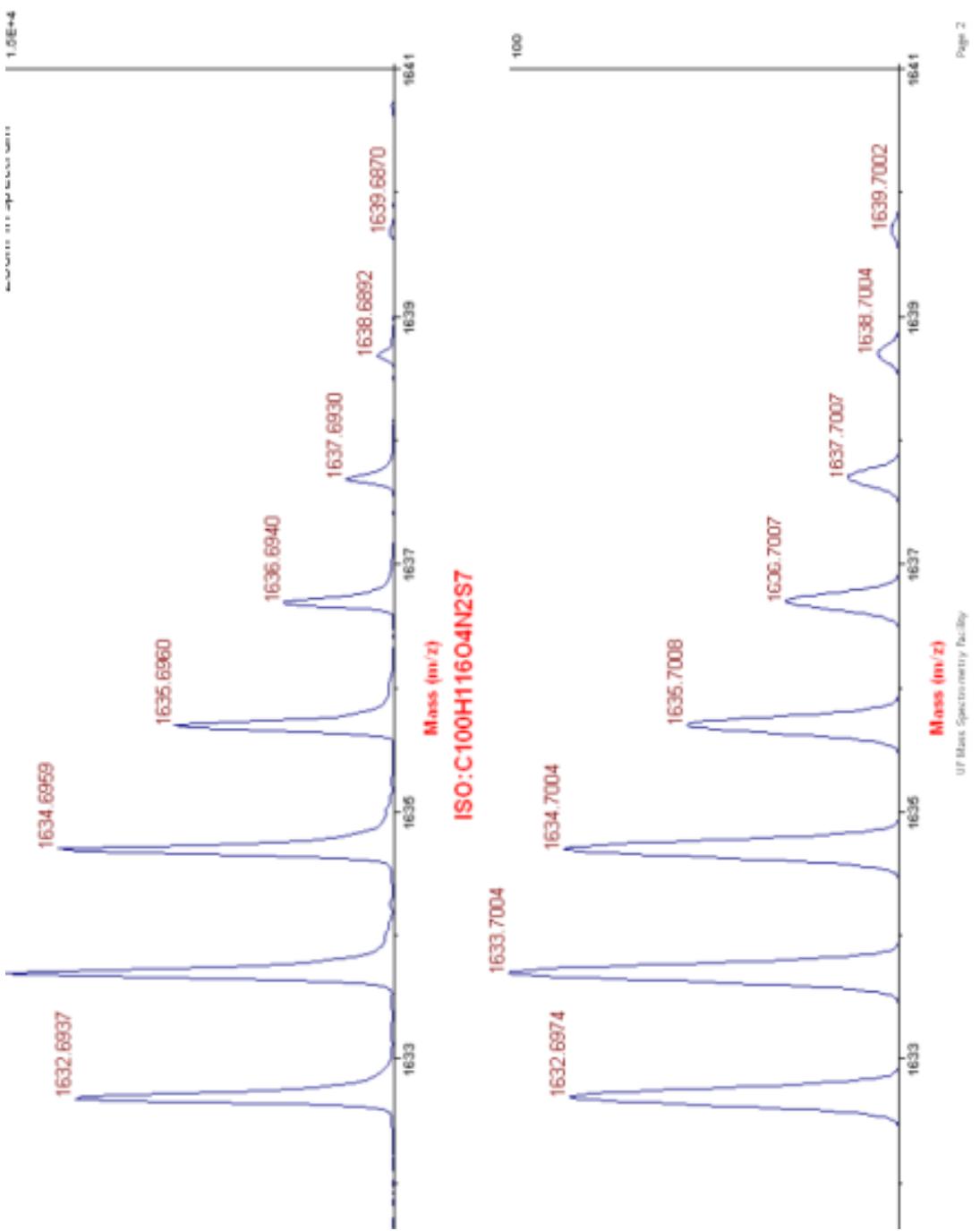
DATA PROCESSING

Line broadening 0.5 Hz

FF size 131072

Total time 1 hr, 26 min





**Figure S11c.** HRMS spectrum of **3**.

## Compound 14 $^1\text{H}$ NMR

Ethylindanone standard test sample  
Recorded on 400-MR with Omega probe and P2T tuning

Sample Name: Ethylindanone

Data Collected on: mercury300-mercury300

Archive directory: /home/vmarc1/rmnrssys/data/fidlib

Sample directory: /home/vmarc1/rmnrssys/data/fidlib

PidFile: ST3\_PHSO2FL10ynesim3

Pulse Sequence: PROTON (s2pul)

Solvent: ccd13

Date collected on: Jun 17 2013

Temp. 25.0 C / 298.1 K

Operator: shang

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acd. time 1.016 sec

Width 4800.8 Hz

64 repetitions

OBSERVE H1, 299.9865992 MHz

DATA PROCESSING

FR size 16384

Total time 2 min 53 sec

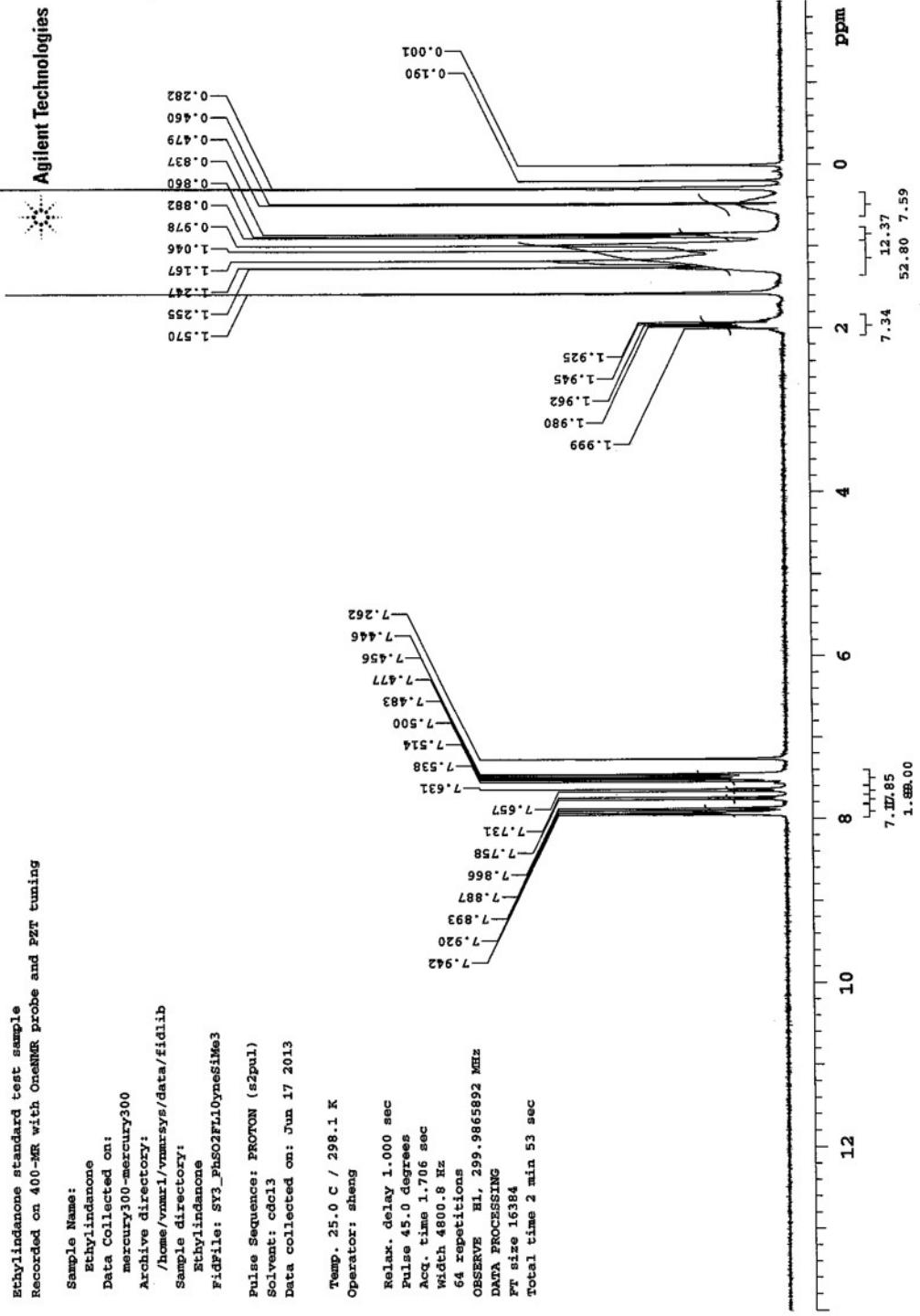


Figure S12a.  $^1\text{H}$  NMR spectra of 14.

# Compound 14 $^{13}\text{C}$ NMR

## Gradient Shimming

### Sample Name:

Data Collected on:  
vnmrs500-vnmrs500

Archive directory:  
/export/home/champack/vnmrsys/data

Sample directory:

Pulse Sequence: CARBON (32pul)

Solvent: cdcl3

Data collected on: Oct 24 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, 125.6836614 MHz

DECOUPLE H1, 499.8377008 MHz

Power 41 dB

continuously on

WALFZ-16 modulated

## DATA PROCESSING

Line broadening 0.5 Hz

FT size 65536

Total time 1 hr, 27 min

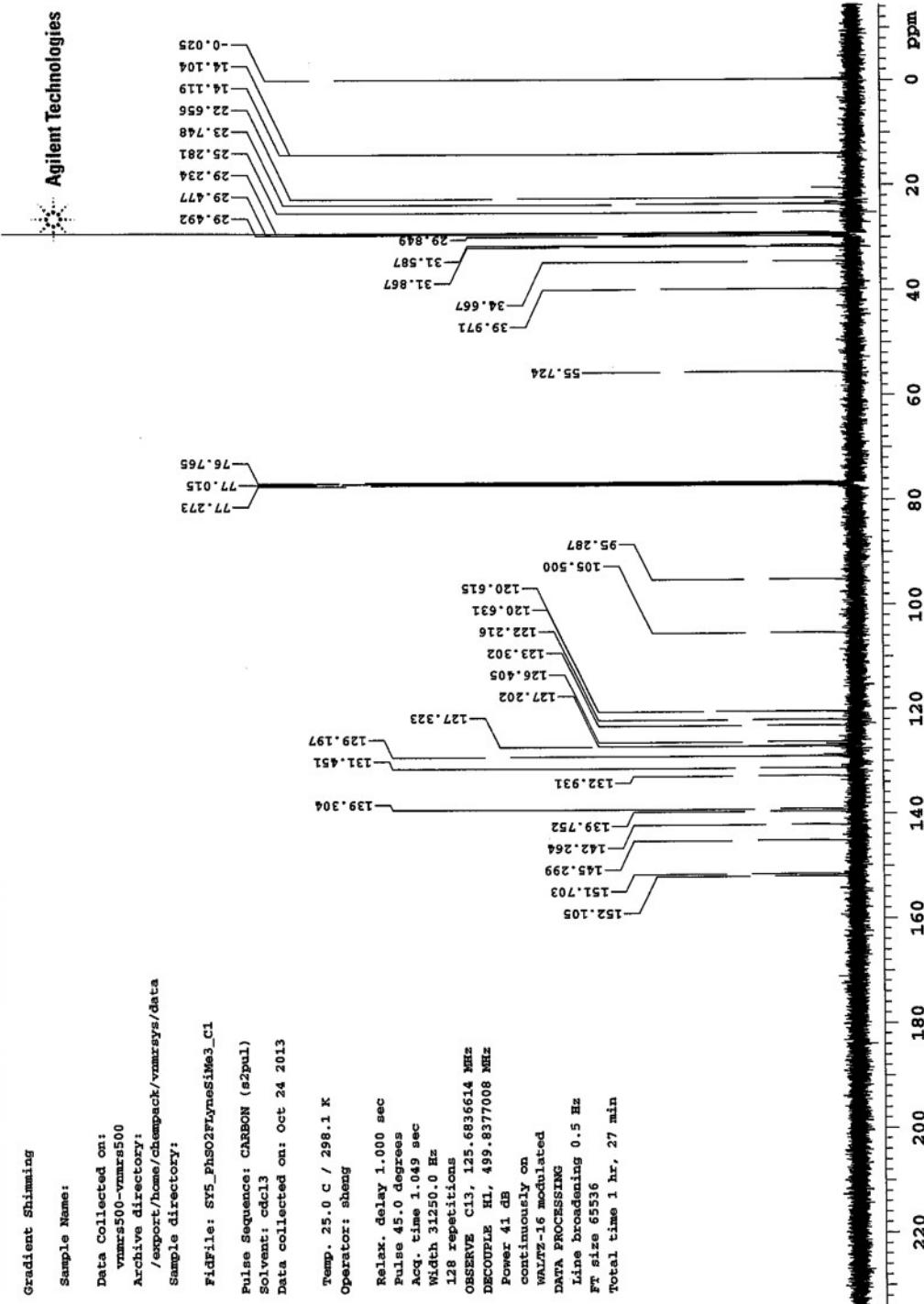


Figure S12b.  $^{13}\text{C}$  NMR spectra of 14.

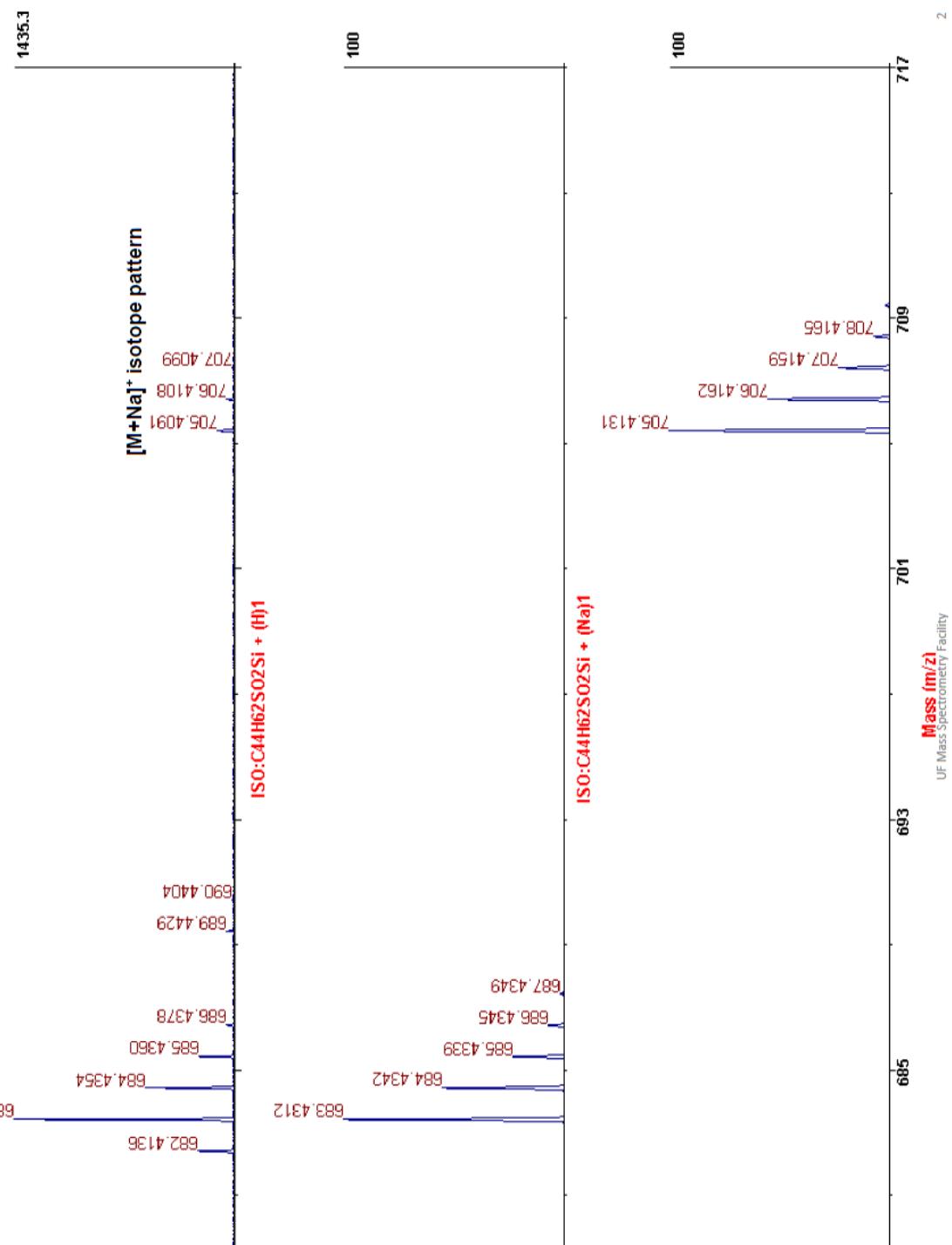


Figure S12c. HRMS spectrum of **14**.

# Compound 15 $^1\text{H}$ NMR

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

Sample Name: Ethylindanone  
 Data Collected on: vnmr500-vnmr500  
 Archive directory: /home/vnmr1/vnmrsys/data/fidlib  
 Sample directory: Ethylindanone  
 Fidfile: S75\_Fhs02Fl10yne  
 Pulse Sequence: PROTON (s2pul)  
 Solvent: ccd13  
 Data collected on: Jun 20 2013  
 Temp. 25.0 C / 298.1 K  
 Operator: sheqg

Relax. delay 1.000 sec  
 pulse 45.0 degrees  
 scan. time 4.09 sec  
 wait 0.0128 sec  
 (64) acquisition 0.95 sec  
 observe 0.95 sec  
 DATA PROCESSING  
 FT size 131072  
 Total time 5 min

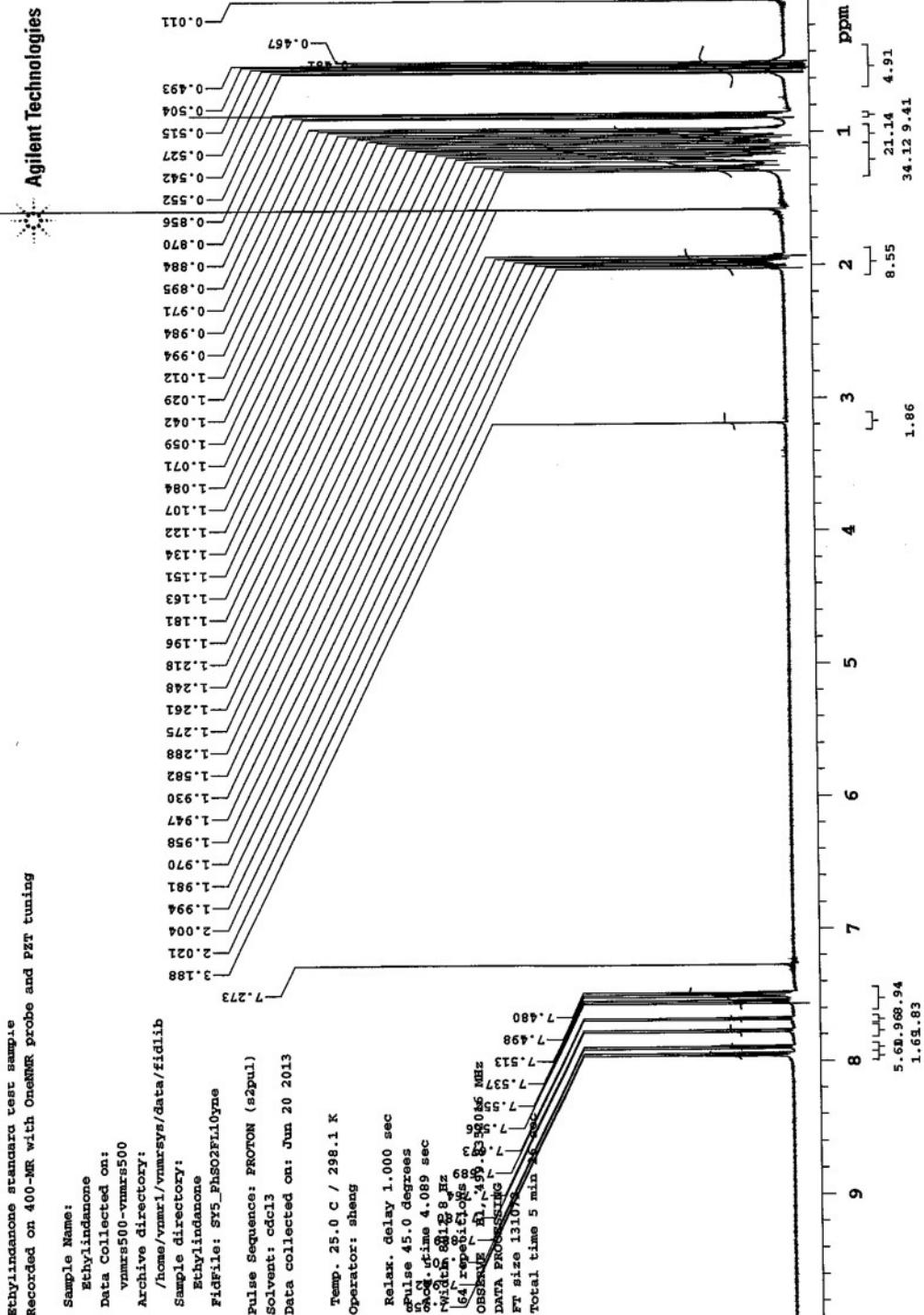


Figure S13a.  $^1\text{H}$  NMR spectra of 15.

# Compound 15 $^{13}\text{C}$ NMR

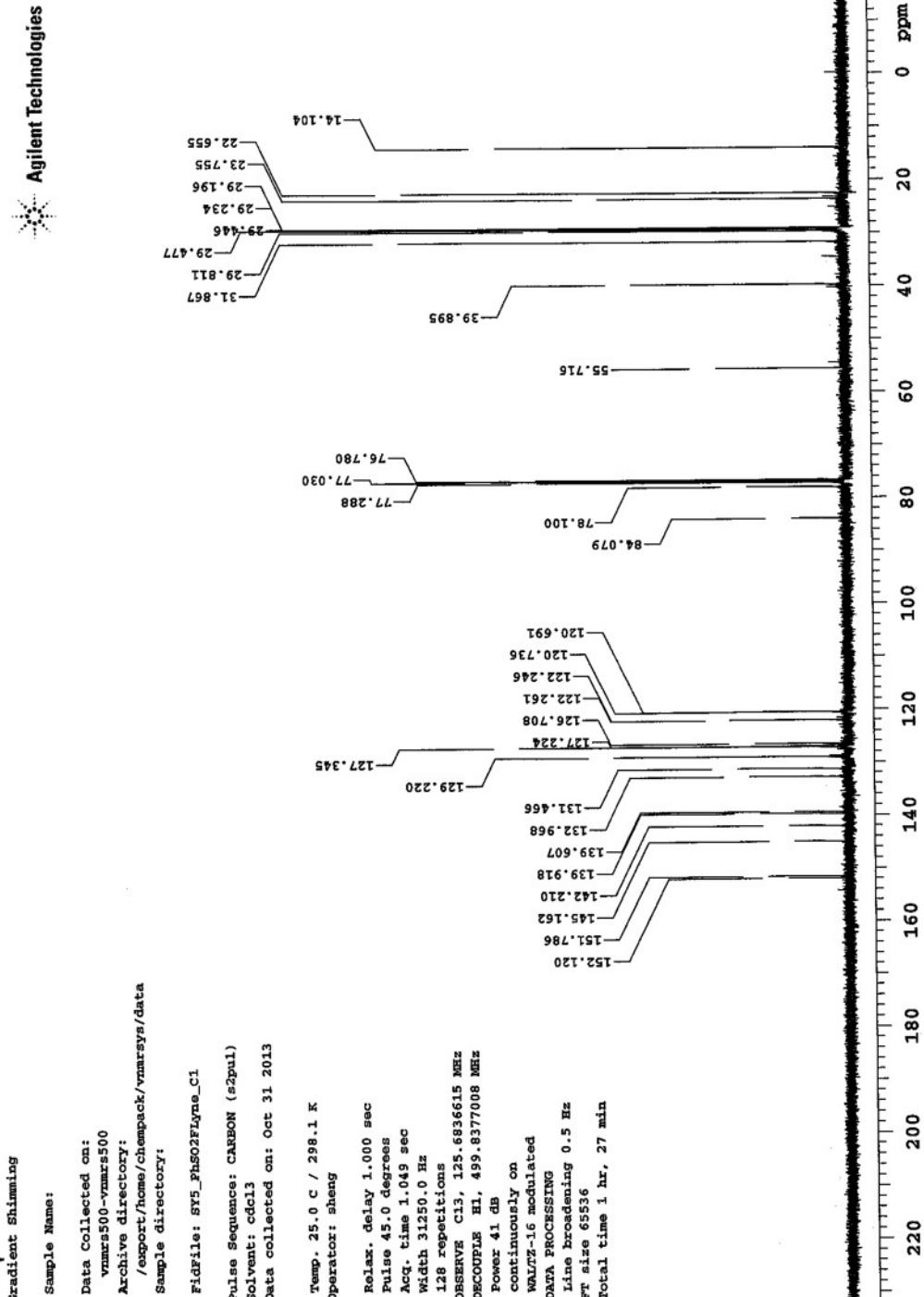
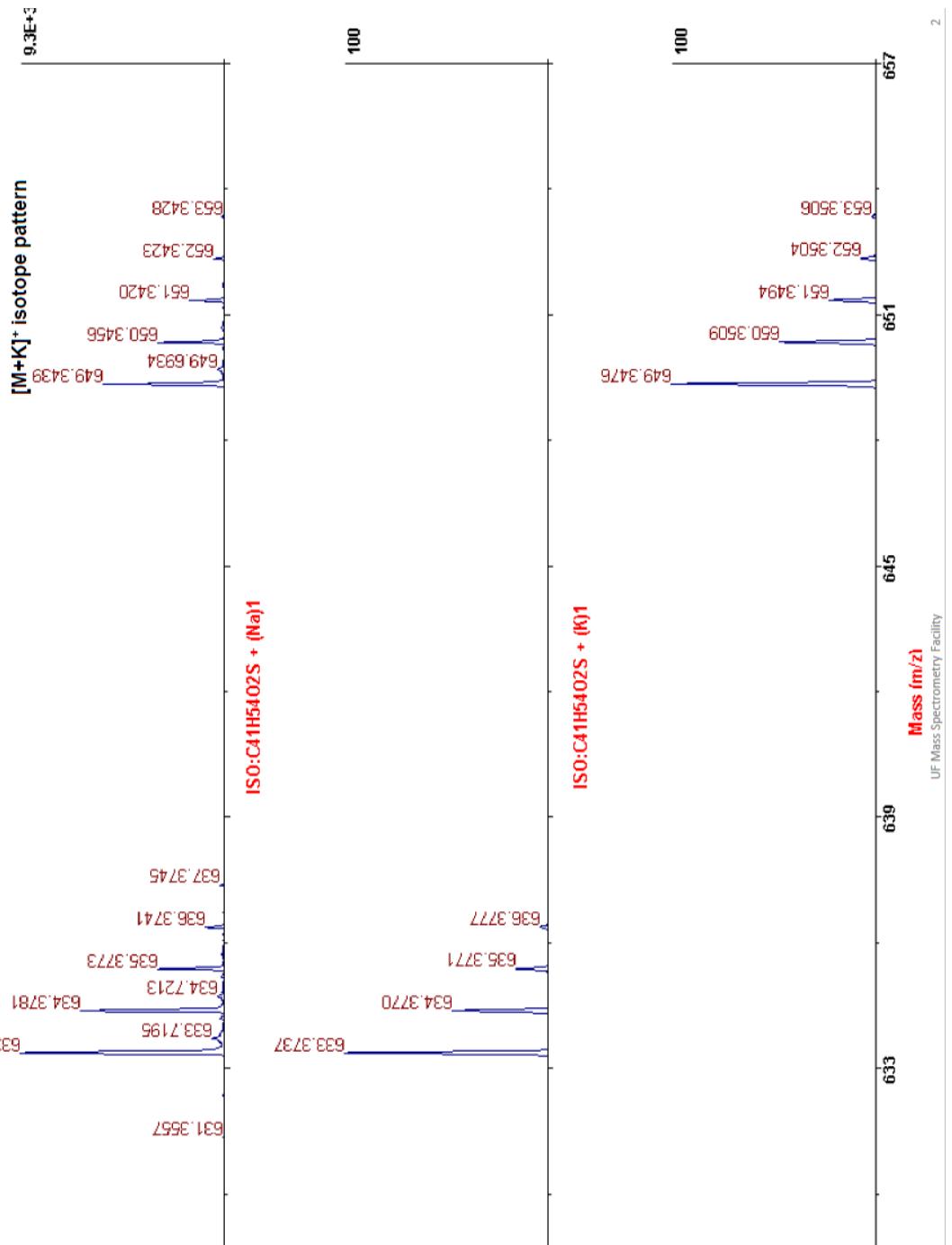
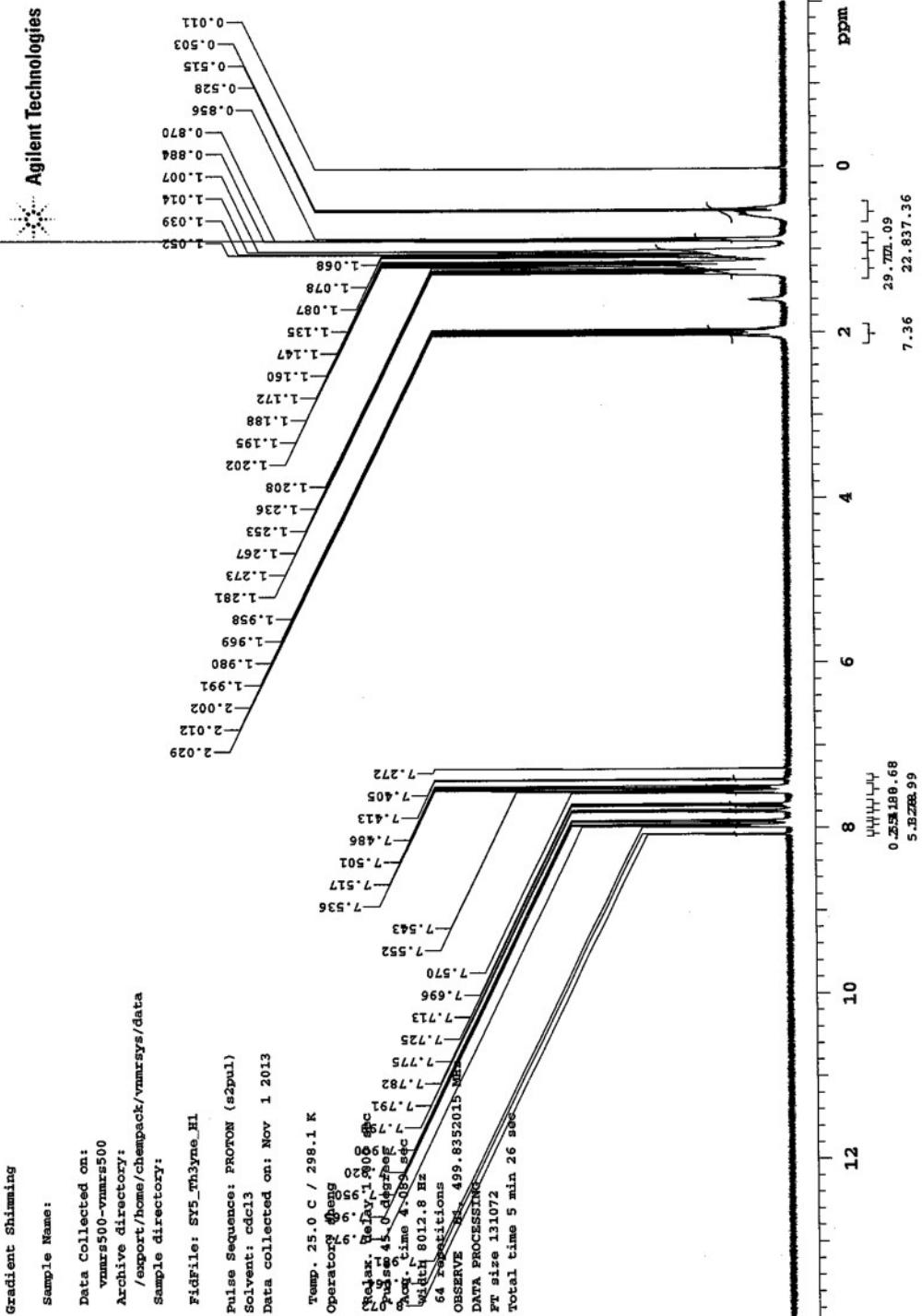


Figure S13b.  $^{13}\text{C}$  NMR spectra of **15**.



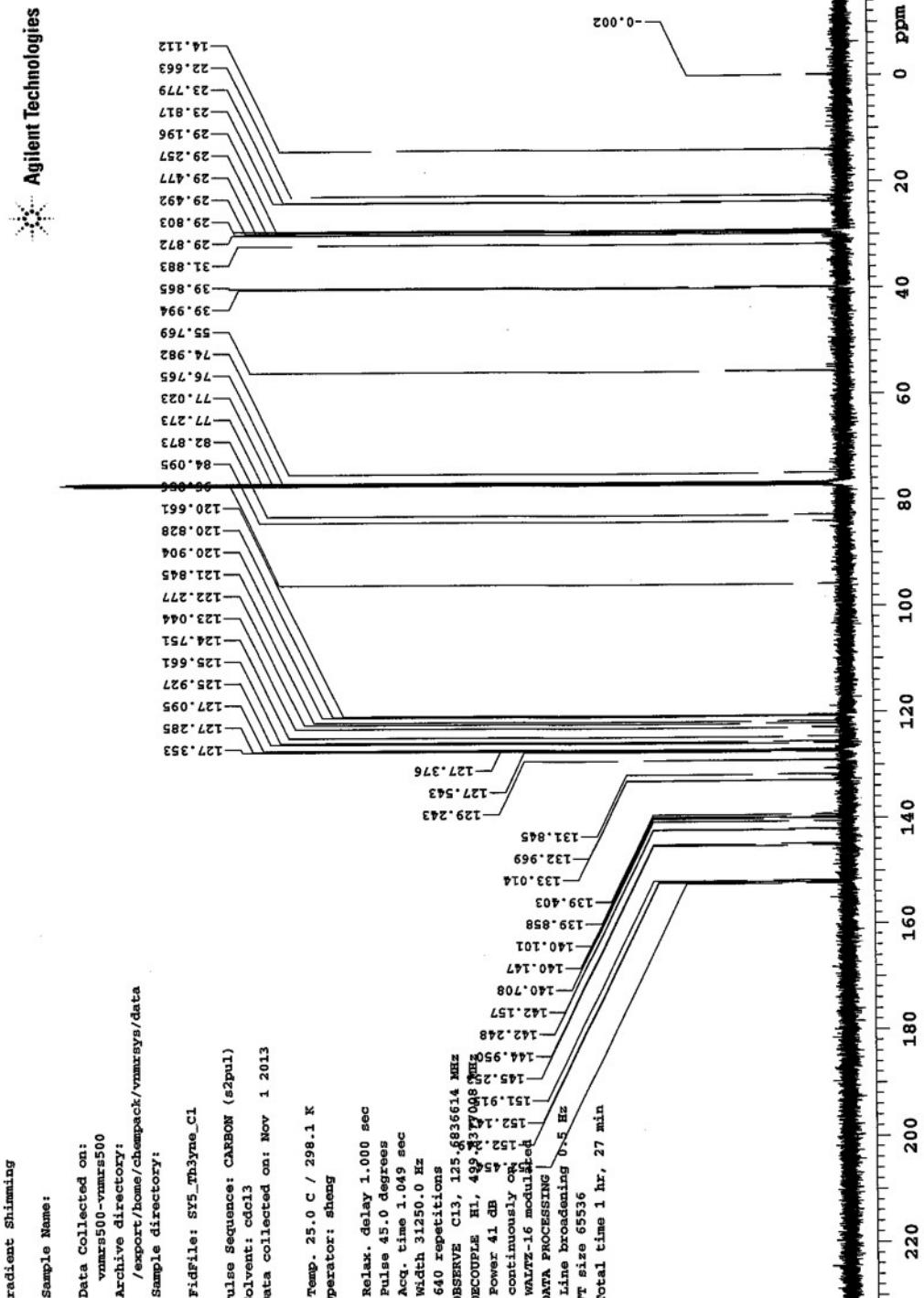
**Figure S13c.** HRMS spectrum of **15**.

# Compound 4 $^1\text{H}$ NMR

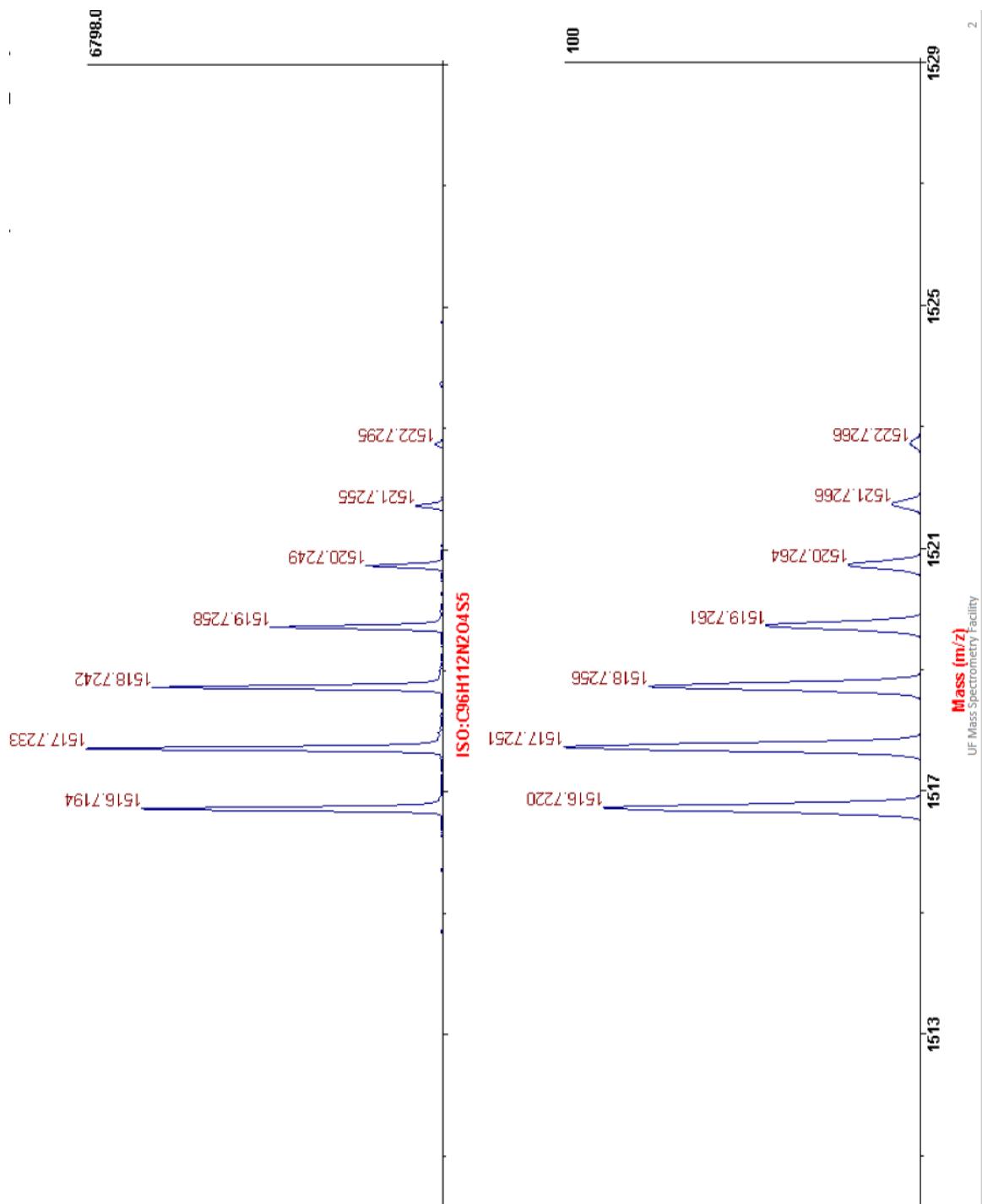


**Figure S14a.**  $^1\text{H}$  NMR spectra of 4.

# Compound 4 $^{13}\text{C}$ NMR



**Figure S14b.**  $^{13}\text{C}$  NMR spectra of 4.



**Figure S14c.** HRMS spectrum of **4**.

### Compound 5 $^1\text{H}$ NMR

STANDARD PROTON PARAMETERS

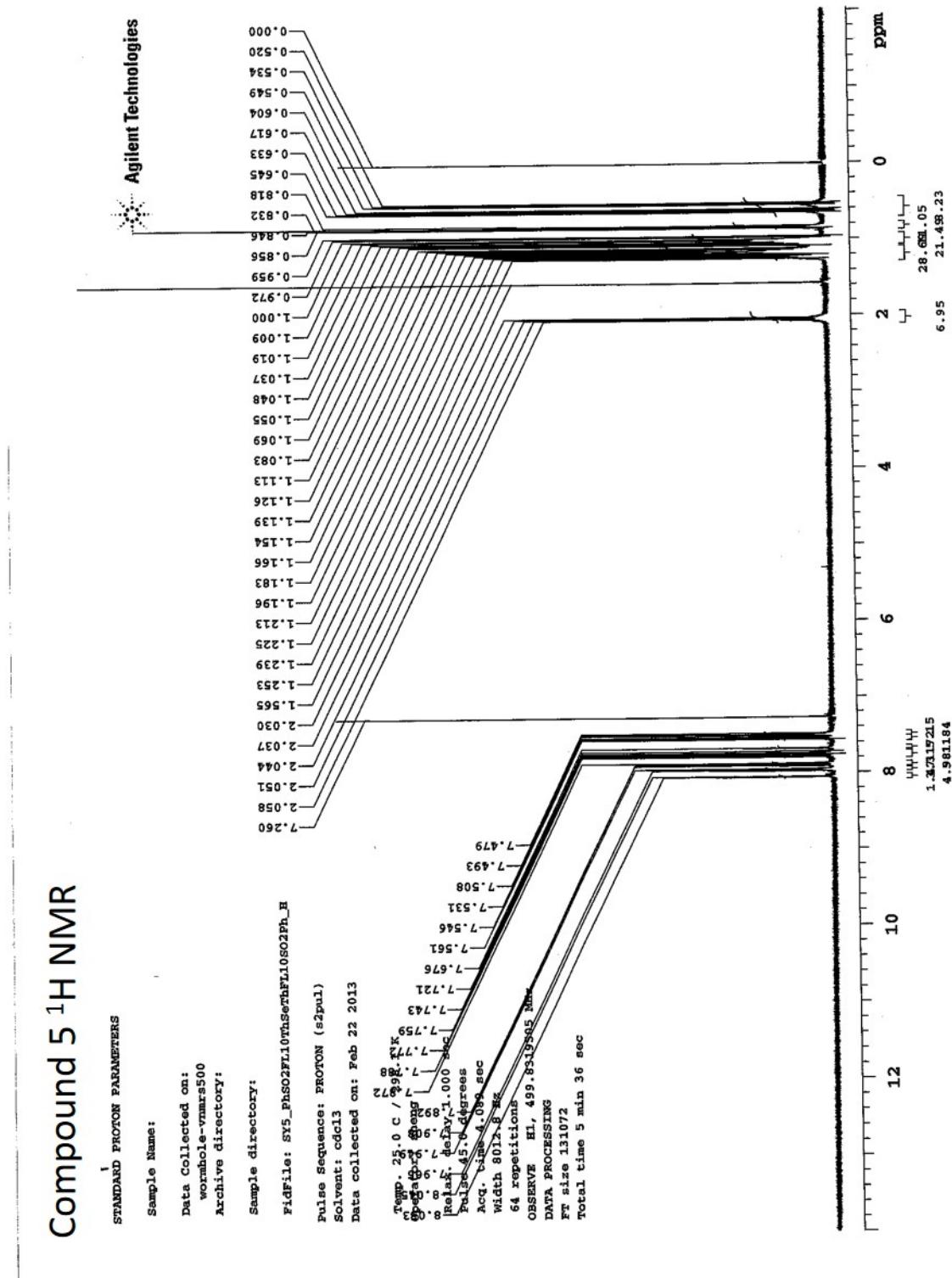
Sample Name:

Data Collected on:  
wormhole-vnmr500  
Archive directory:

Glossary

Pidfile: sy5\_PhsO2F10rnsErhfr10sO2Ph\_H  
Pulse Sequence: PROTON (s2p1)  
Solvent: cdc13  
Data collected on: Feb 22 2013

Temp. 25.0 C / 69.8 F  
 P.D. 4.5 cm  
 Relax. 1.00 sec  
 P.D. 4.5 cm  
 64 repetitions  
 Width 8012.8 Hz  
 Acq. time 4.096 sec  
 DATA PROCESSING  
 File size 131072  
 Total time 5 min 36 sec



**Figure S15a.**  $^1\text{H}$  NMR spectra of **5**.

## Compound 5 $^{13}\text{C}$ NMR

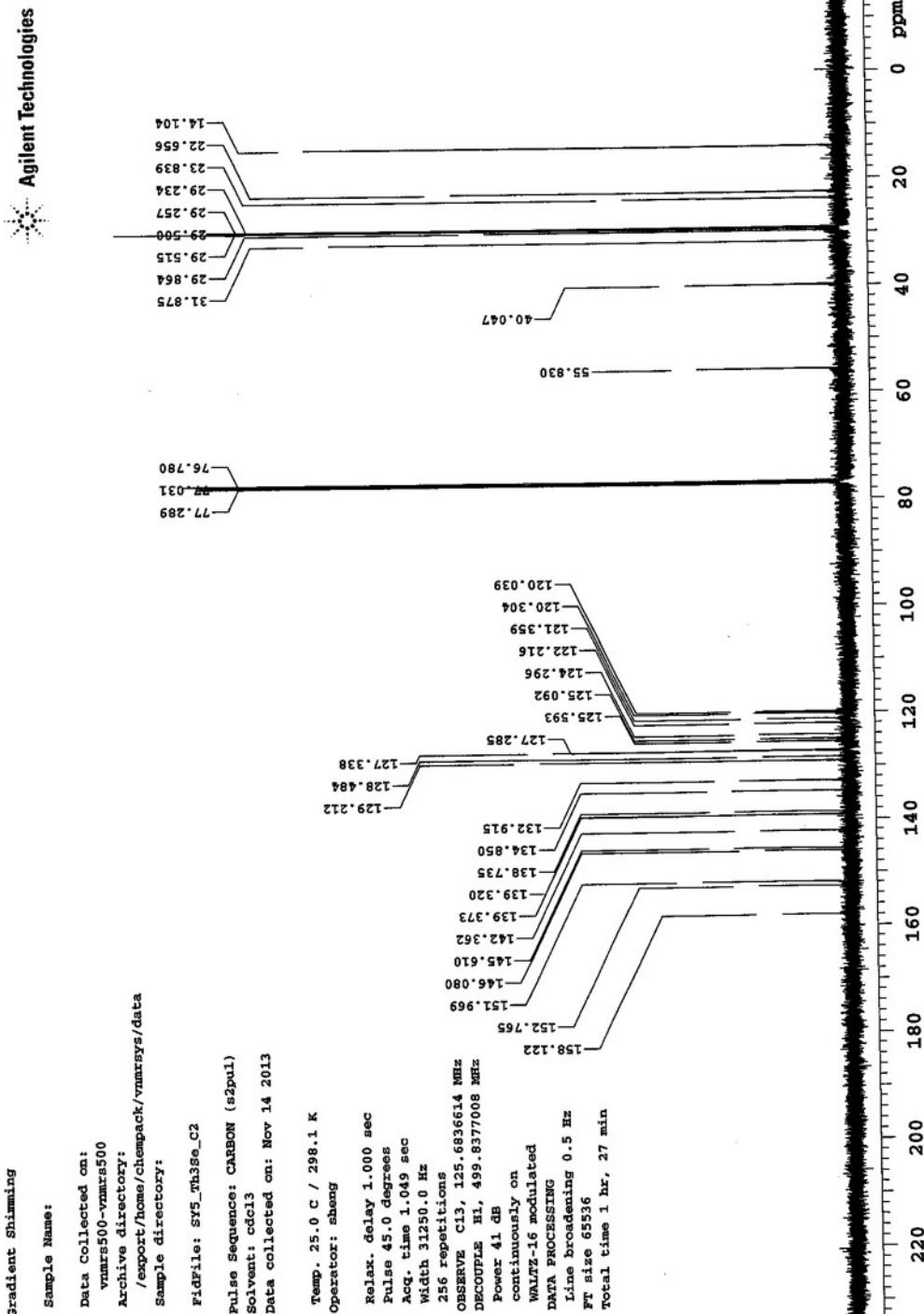
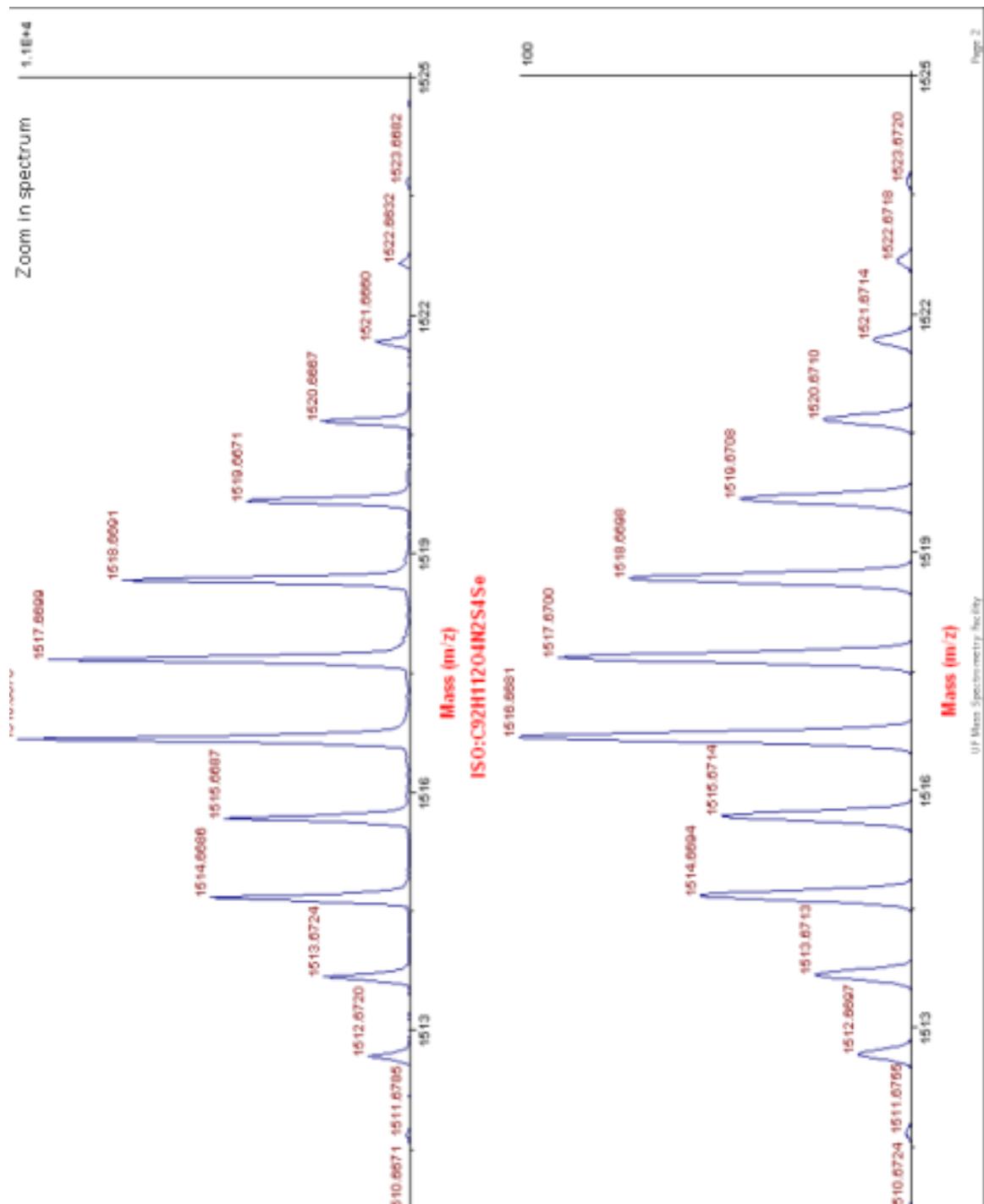


Figure S15b.  $^{13}\text{C}$  NMR spectra of 5.



**Figure S15c.** HRMS spectrum of **5**.