

**Supplementary information for**

**2,5-Bis(azulenyl)pyrrolo[3,2-*b*]pyrroles – the key influence of the linkage position on the  
linear and non-linear optical properties**

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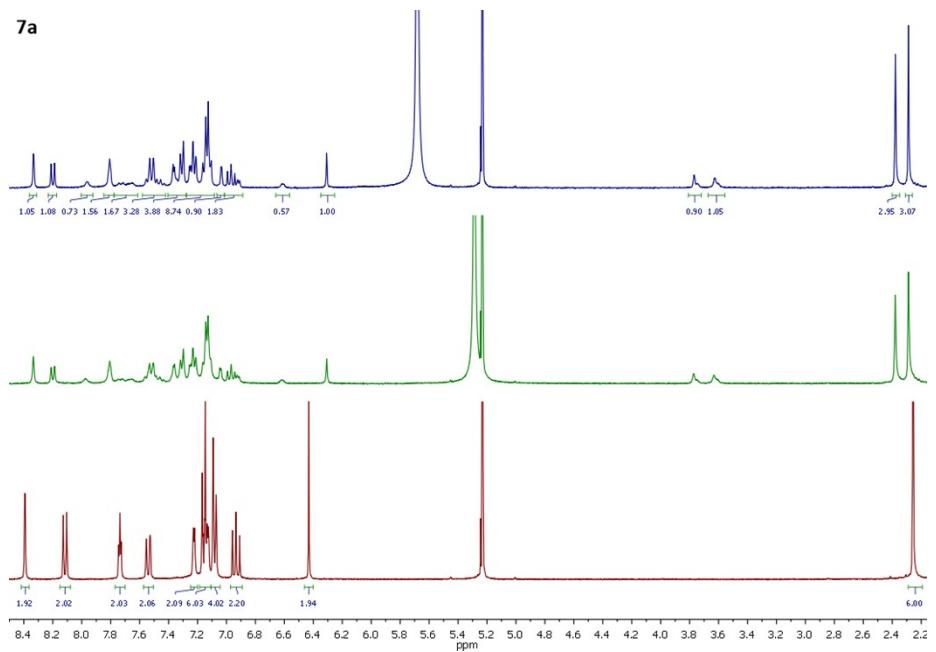


Figure S1.  $^1\text{H}$  NMR titration of compound **7a** in  $\text{CD}_2\text{Cl}_2$  solution with  $\text{CF}_3\text{COOD}$

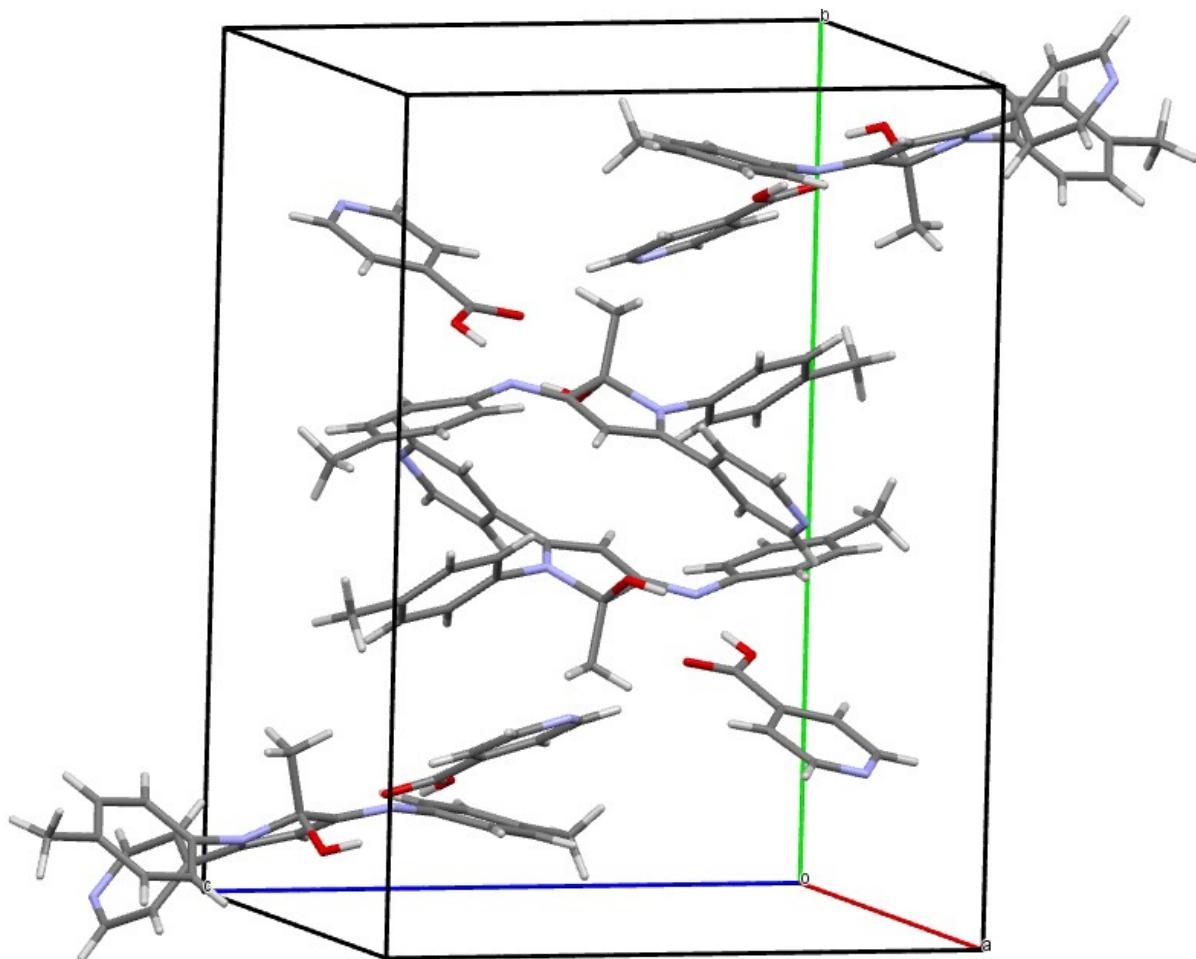


Figure S2. Crystal packing for compound **4bbb**

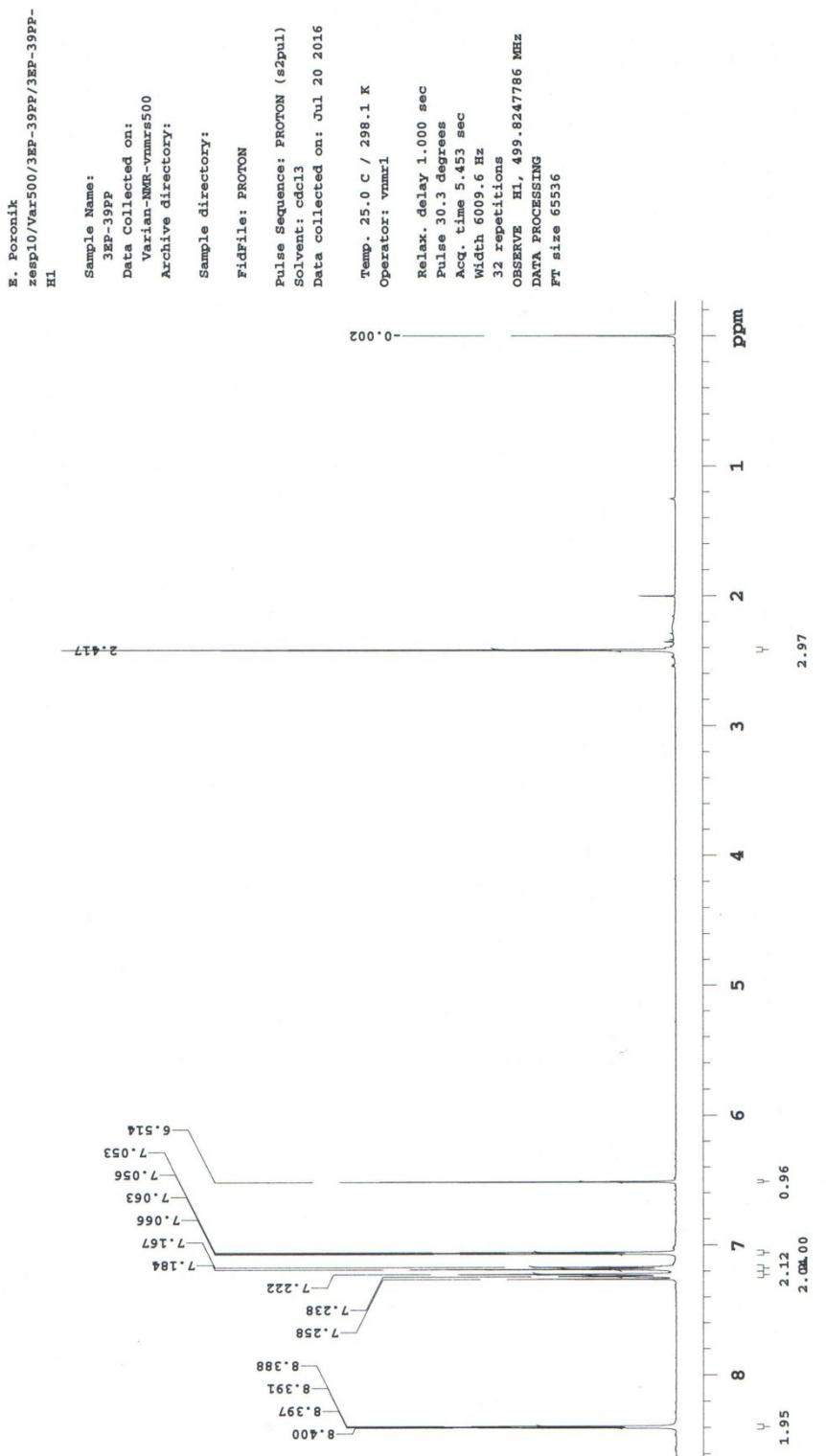


Figure S3.  $^1\text{H}$  NMR spectrum of **4b** in  $\text{CDCl}_3$

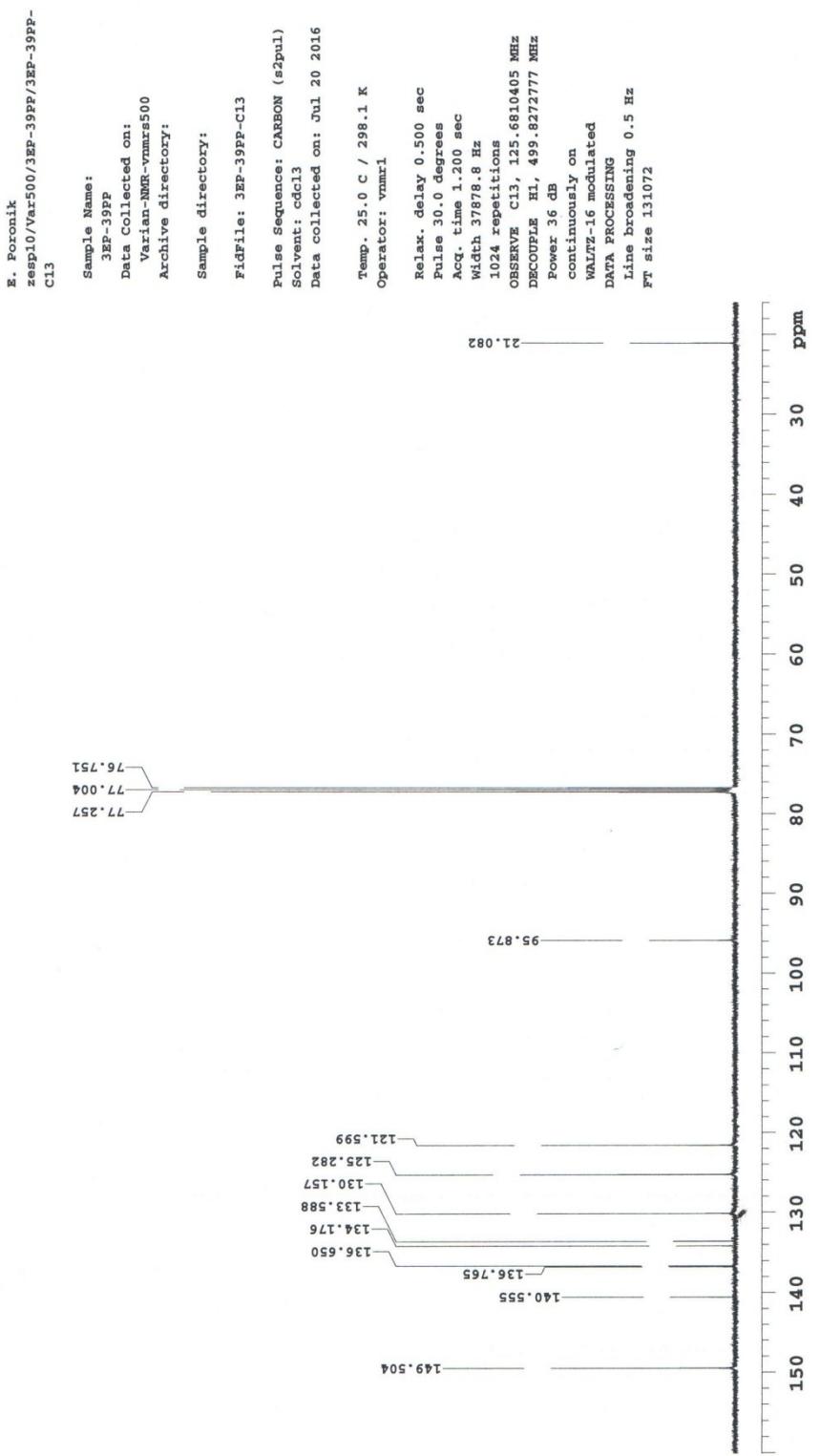
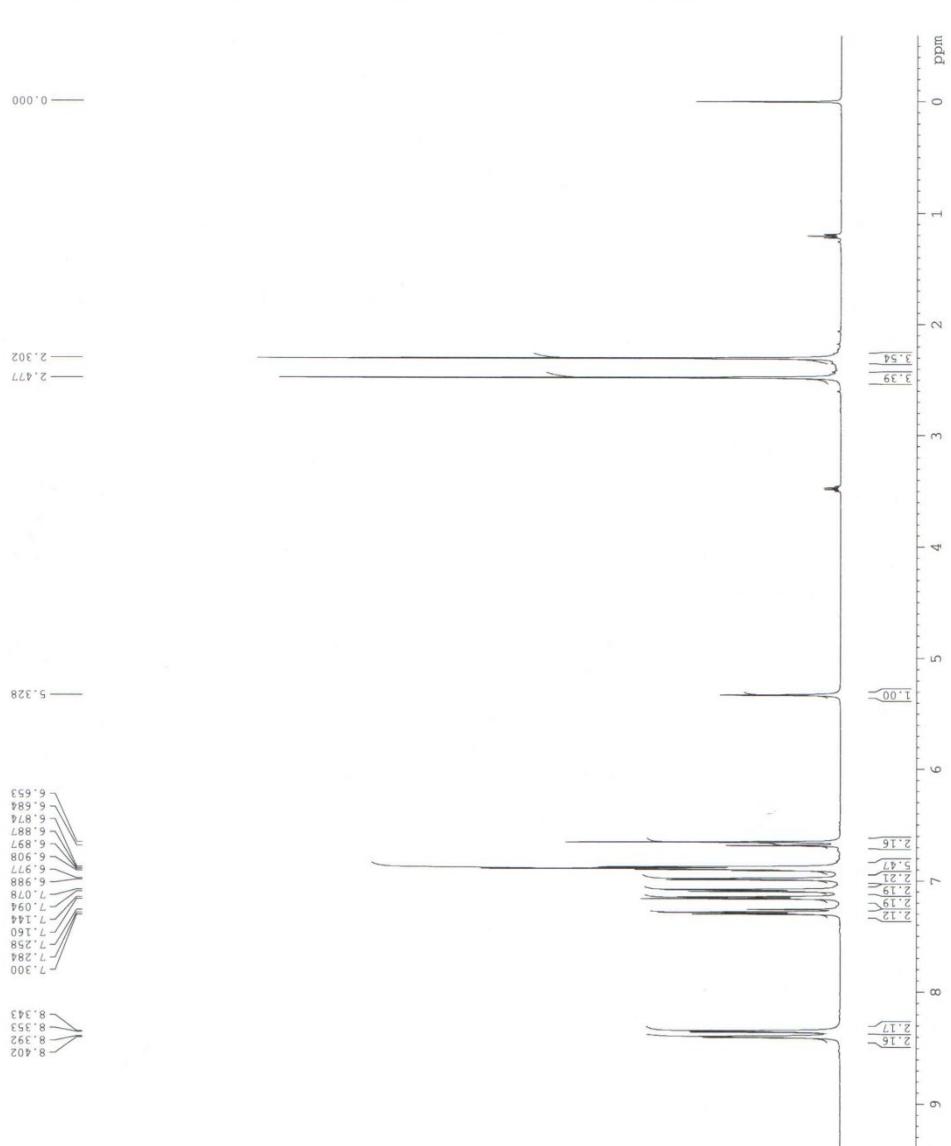


Figure S4.  $^{13}\text{C}$  NMR spectrum of **4b** in  $\text{CDCl}_3$



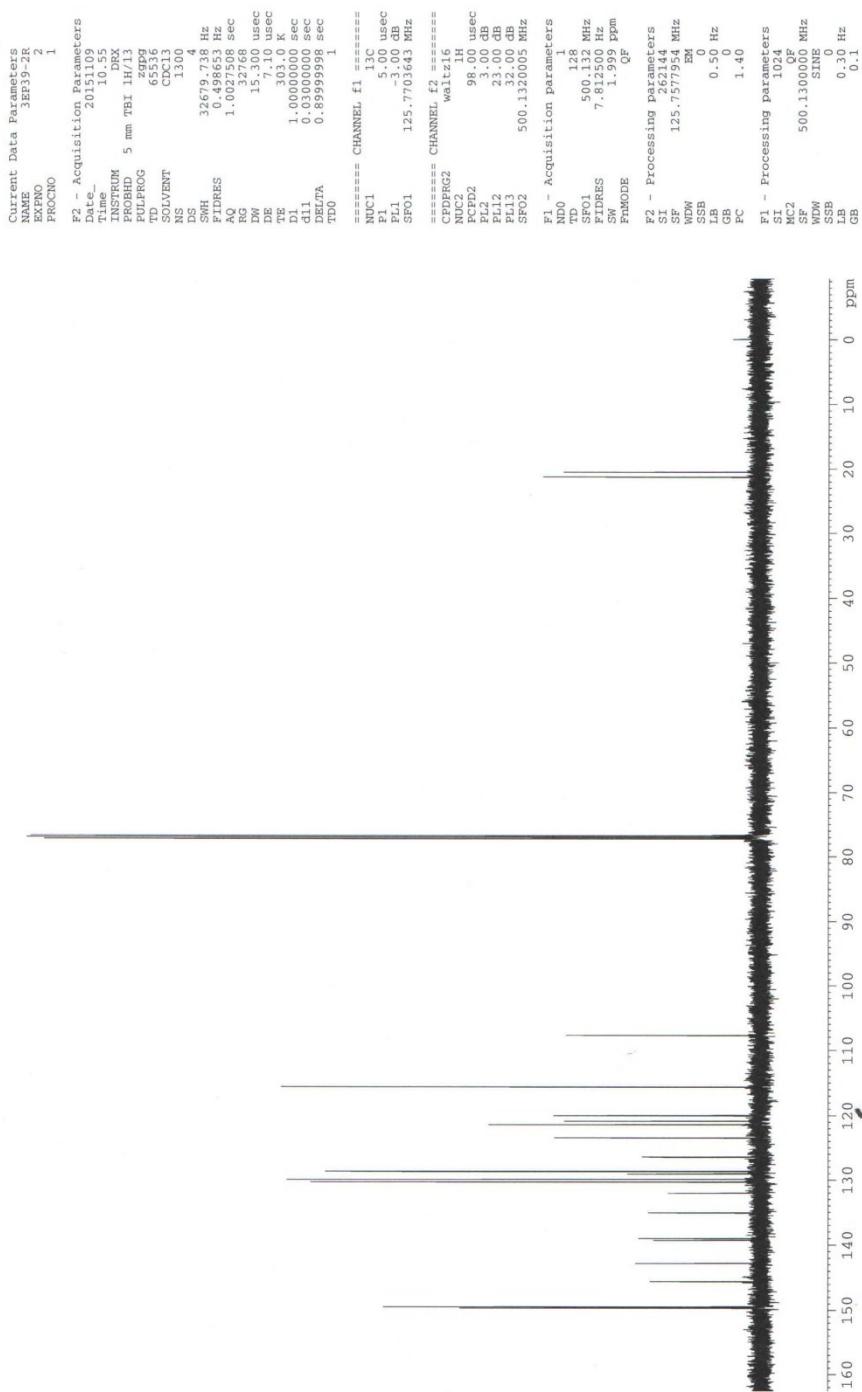


Figure S6. <sup>13</sup>C NMR spectrum of **4bb** in CDCl<sub>3</sub>

**Agilent Technologies**

Y. Poronik  
zespi0/Var600/3ER-39-red/3ER-39  
red-H1  
zespi0/Var600/3ER-39-red/3ER-39  
red-H1

Sample Name:  
3ER-39-red  
Data Collected on:  
Varian-NMR-vnmrs600  
Archive directory:

Sample directory:  
FidFile: PROTON

Pulse Sequence: PROTON (s2pul)  
Solvent: cdd13  
Data collected on: Jun 1 2015  
  
Solvent: cdd13  
Temp. 25.0 C / 298.1 K  
Operator: vnmr1  
VNMR-S-600 "Varian-NMR"

Relax. delay 1.000 sec  
Pulse 90.0 degrees  
Acq. time 5.000 sec  
Width 9058.0 Hz  
16 repetitions  
OBSERVE H1, 599.8350742 MHz  
DATA PROCESSING  
FT size 131072

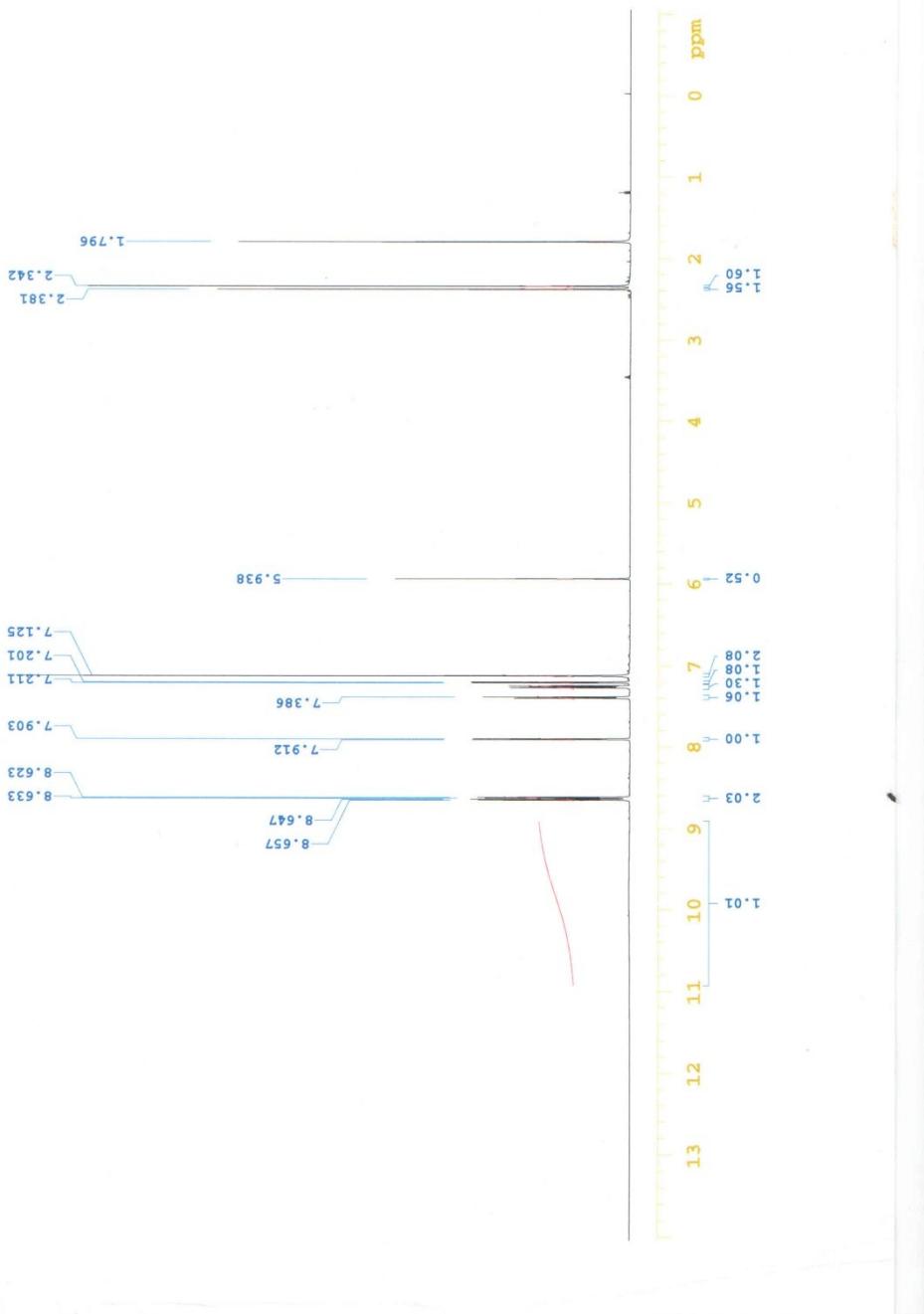


Figure S7.  $^1\text{H}$  NMR spectrum of **4bbb** in  $\text{CDCl}_3$

Agilent Technologies

Y. Poronik  
zep10/Var600/3ER-39-red/3ER-39  
red-C13

Sample Name:

3ER-39-red

Data Collected on:

Varian-NMR-vnmrs600

Archive directory:

Sample directory:

Fidfile: CARBON

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Jun 1 2015

Solvent: cdcl3

Temp. 25.0 C / 298.1 K

Operator: vnmr1

VNMR-S-600 "Varian-NMR"

Relax. delay 0.500 sec

Pulse 30.0 degrees

Acq. time 1.200 sec

width 37878.8 Hz

8000 repetitions

OBSERVE C13, 150.8286494 MHz

DECOUPLE H1, 599.8380734 MHz

Power 34 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 13102



Figure S8.  $^{13}\text{C}$  NMR spectrum of **4bbb** in  $\text{CDCl}_3$

Y. Poronik  
zesp10/var600/3ER-39-red/3ER-39-red-gCOSY  
  
Sample Name:  
3ER-39-zed  
Data Collected on:  
Varian-NMR-vnmrs600  
Archive directory:  
  
Sample directory:  
  
FidFile: gCOSY  
Pulse Sequence: gCOSY  
Solvent: cdcl3  
Data collected on: Jun 1 2015

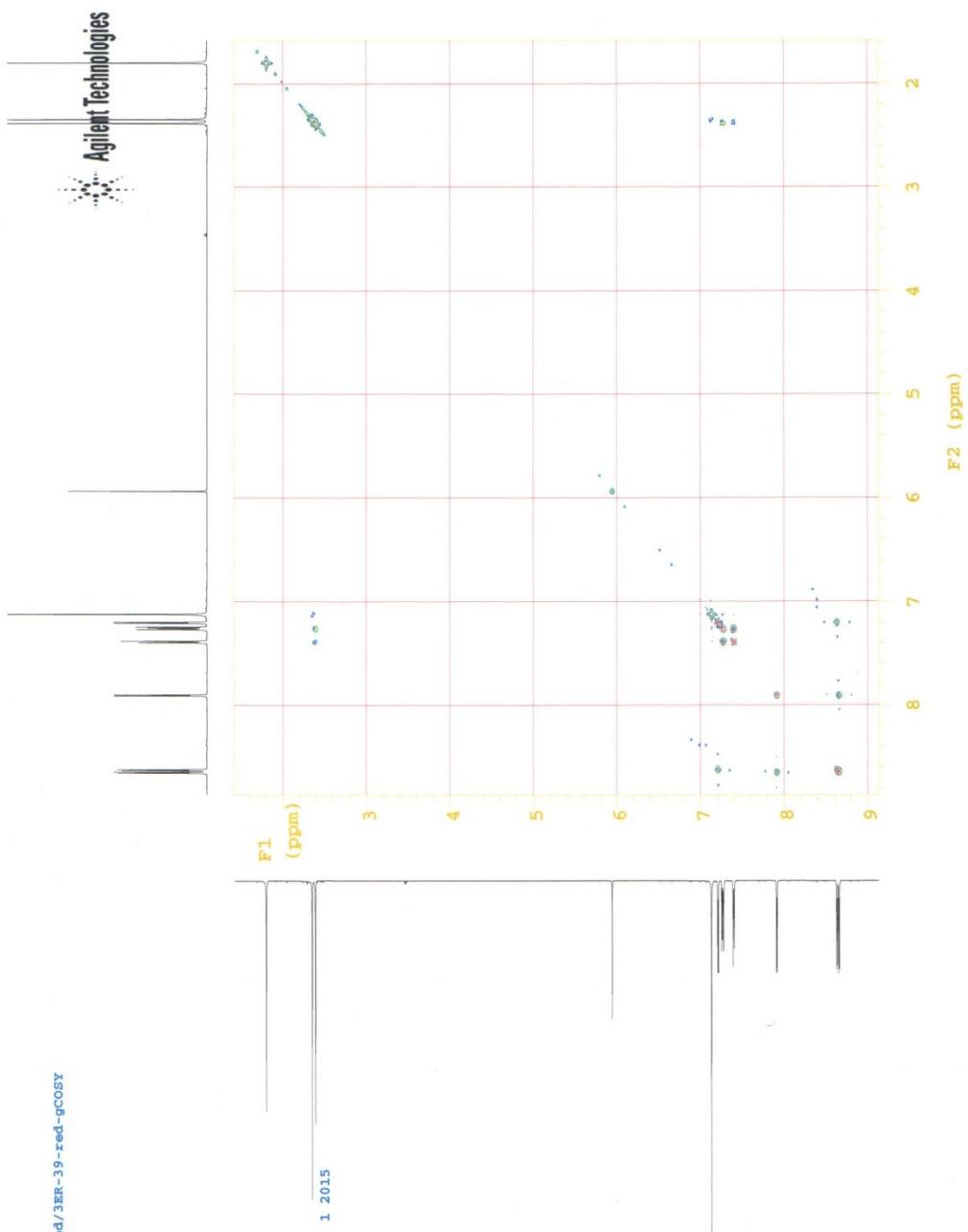


Figure S9. COSY experiment for **4bbb** in  $\text{CDCl}_3$

Agilent Technologies

Y. Poronik  
zespi0/Var600/3ER-39-red/3ER-39  
red-NOESY1D

Sample Name:  
3ER-39-red  
Data Collected on:  
Varian-NMR-vnmrs600  
Archive directory:

Sample directory:

Fidfile: NOESY1D

Pulse Sequence: NOESY1D  
Solvent: cdcl3  
Data collected on: Jun 1 2015

Solvent: cdcl3  
Temp. 25.0 C / 298.1 K  
Operator: vnmrl  
VNMRs-600 "Varian-NMR"

Relax. delay 1.000 sec  
Pulse 90.0 degrees  
Acq. time 2.386 sec  
Width 6868.1 Hz  
128 repetitions  
OBSERVE H1, 599.8350742 MHz  
DATA PROCESSING  
Line broadening 2.0 Hz  
FT size 131072



Agilent Technologies

Y. Poronik  
zespi0/Var600/3ER-39-red/3ER-39  
red-NOESY1D

Sample Name:  
3ER-39-red  
Data Collected on:  
Varian-NMR-vnmrs600  
Archive directory:

Sample directory:

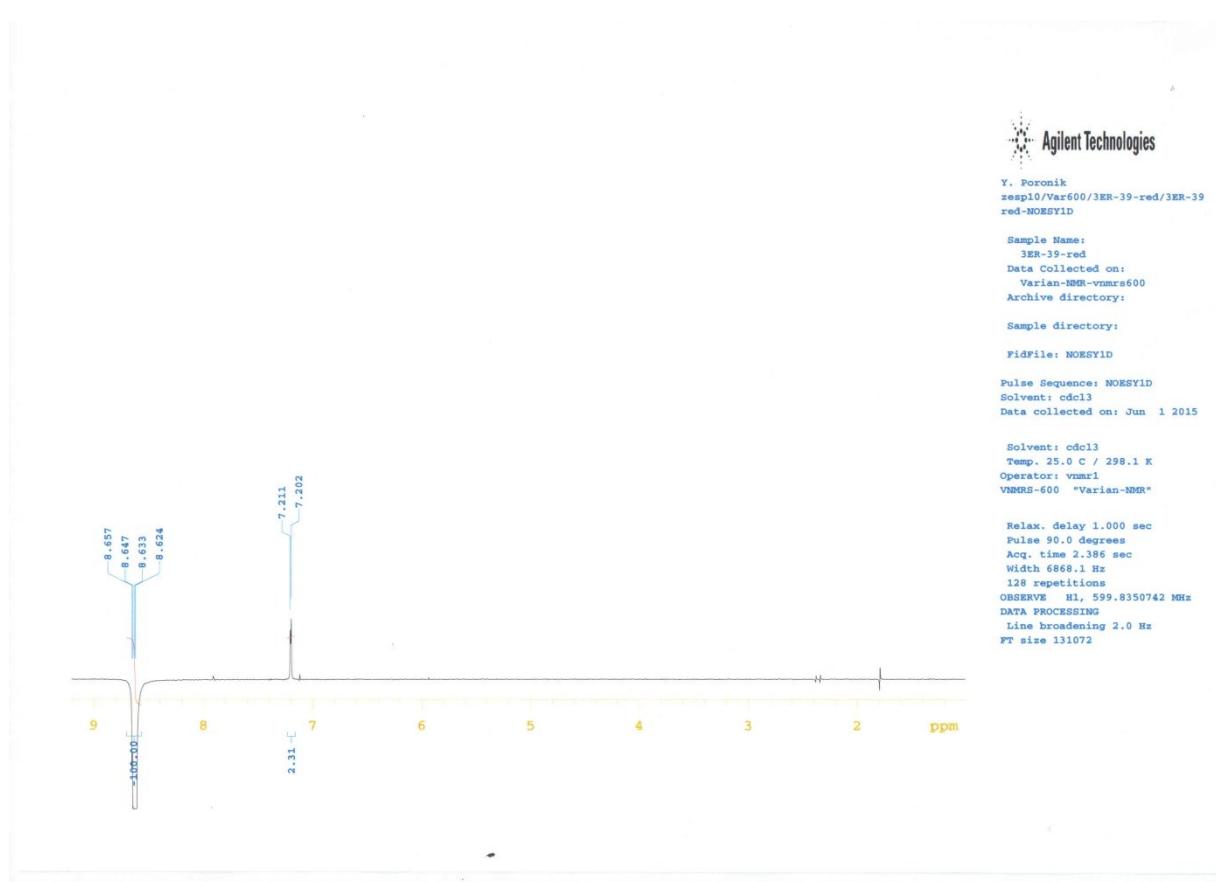
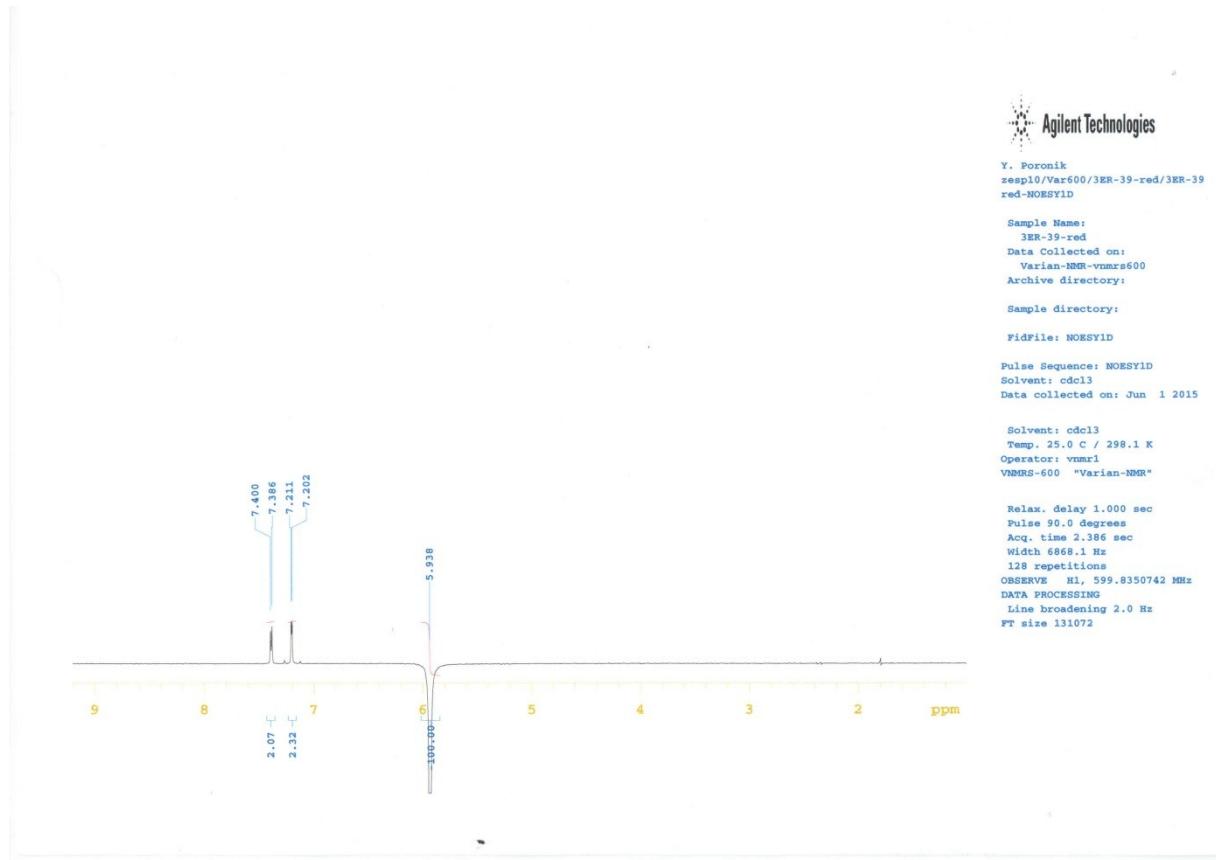
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Pulse Sequence: NOESY1D  
Solvent: cdcl3  
Data collected on: Jun 1 2015

Solvent: cdcl3  
Temp. 25.0 C / 298.1 K  
Operator: vnmrl  
VNMRs-600 "Varian-NMR"

Relax. delay 1.000 sec  
Pulse 90.0 degrees  
Acq. time 2.386 sec  
Width 6868.1 Hz  
128 repetitions  
OBSERVE H1, 599.8350742 MHz  
DATA PROCESSING  
Line broadening 2.0 Hz  
FT size 131072







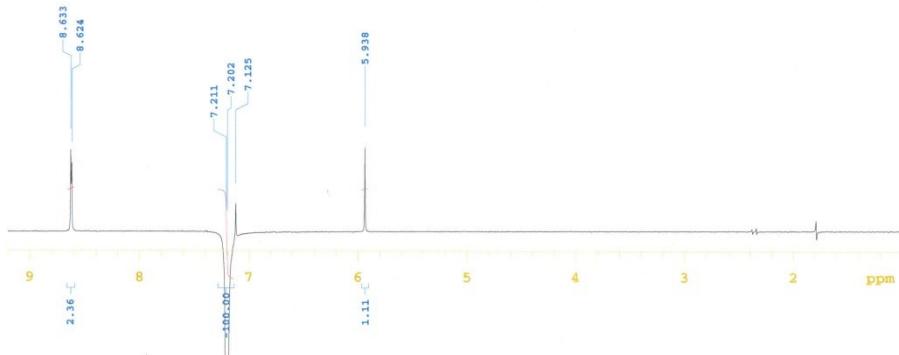
Y. Poronik  
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red-NOESY1D

Sample Name:  
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Data Collected on:  
Varian-NMR-vnmrs600  
Archive directory:

Sample directory:  
Fidfile: NOESY1D  
Pulse Sequence: NOESY1D  
Solvent: cdcl3  
Data collected on: Jun 1 2015

Solvent: cdcl3  
Temp. 25.0 C / 298.1 K  
Operator: vnmr1  
VNMRs-600 "Varian-NMR"

Relax. delay 1.000 sec  
Pulse 90.0 degrees  
Acc. time 2.386 sec  
Width 6868.1 Hz  
128 repetitions  
OBSERVE H1, 599.8350742 MHz  
DATA PROCESSING  
Line broadening 2.0 Hz  
FT size 131072



Y. Poronik  
zespl0/Var600/3ER-39-red/3ER-39  
red-NOESY1D

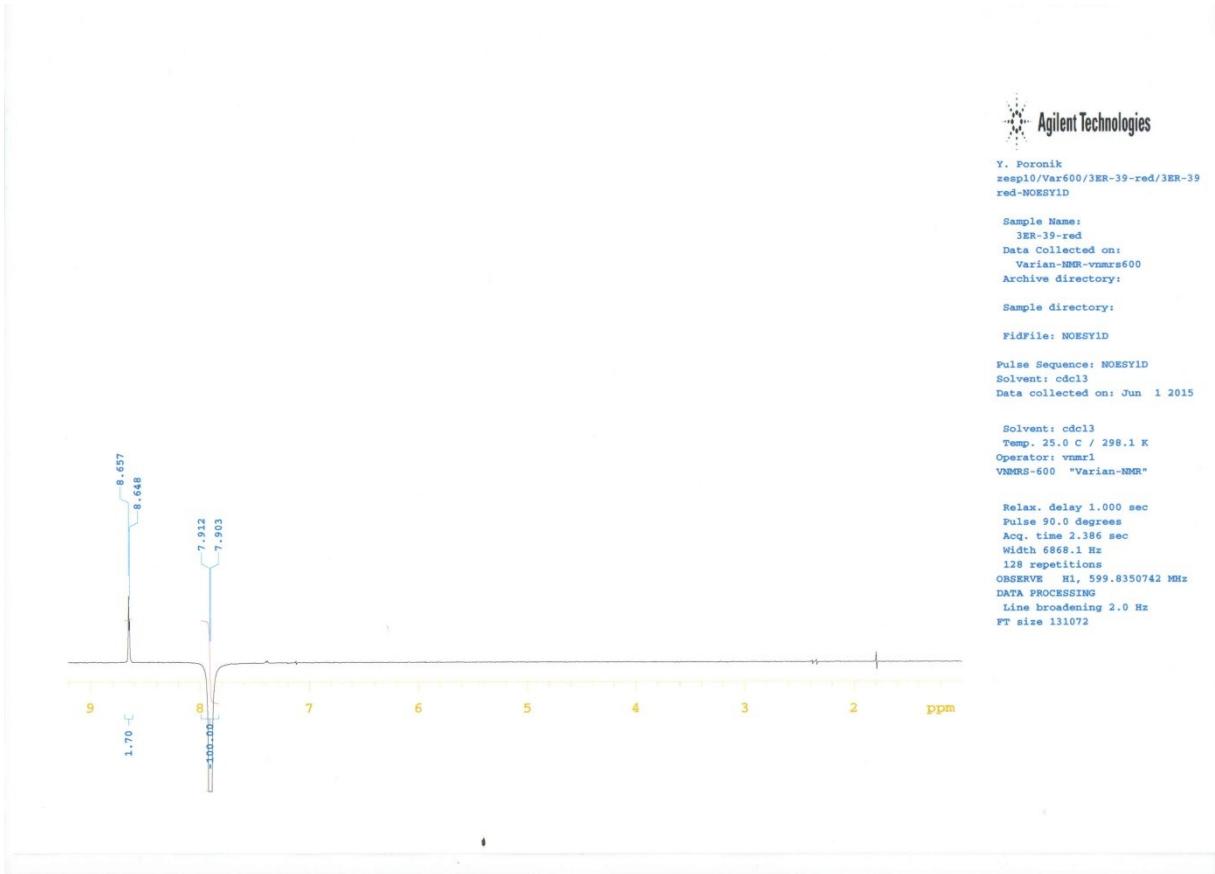
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Data Collected on:  
Varian-NMR-vnmrs600  
Archive directory:

Sample directory:  
Fidfile: NOESY1D  
Pulse Sequence: NOESY1D  
Solvent: cdcl3  
Data collected on: Jun 1 2015

Solvent: cdcl3  
Temp. 25.0 C / 298.1 K  
Operator: vnmr1  
VNMRs-600 "Varian-NMR"

Relax. delay 1.000 sec  
Pulse 90.0 degrees  
Acc. time 2.386 sec  
Width 6868.1 Hz  
128 repetitions  
OBSERVE H1, 599.8350742 MHz  
DATA PROCESSING  
Line broadening 2.0 Hz  
FT size 131072





Figures S10a-g. A set of NOESY experiments for **4bbb** in  $\text{CDCl}_3$

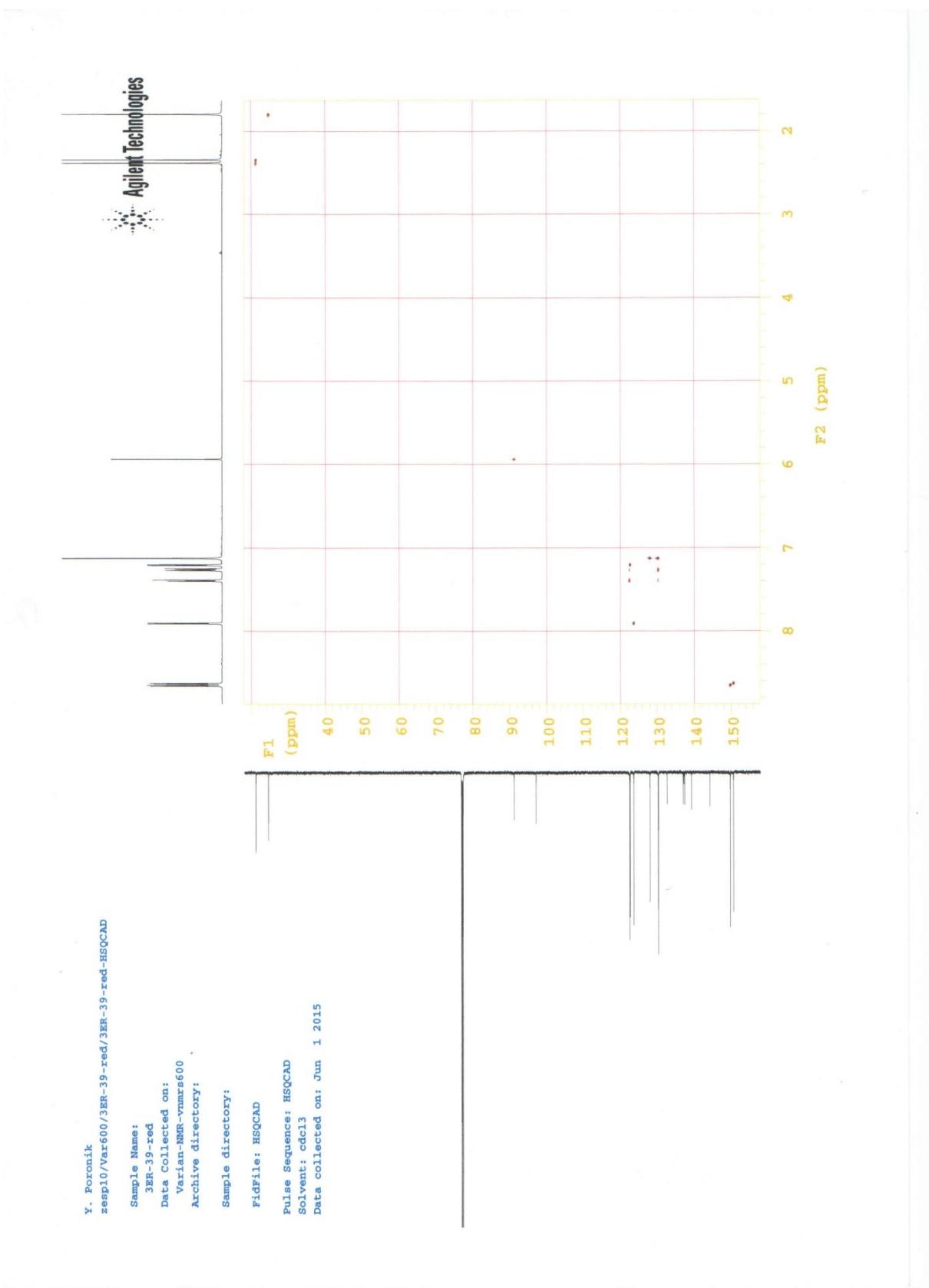


Figure S11. HSQC experiment for **4bbb** in  $\text{CDCl}_3$

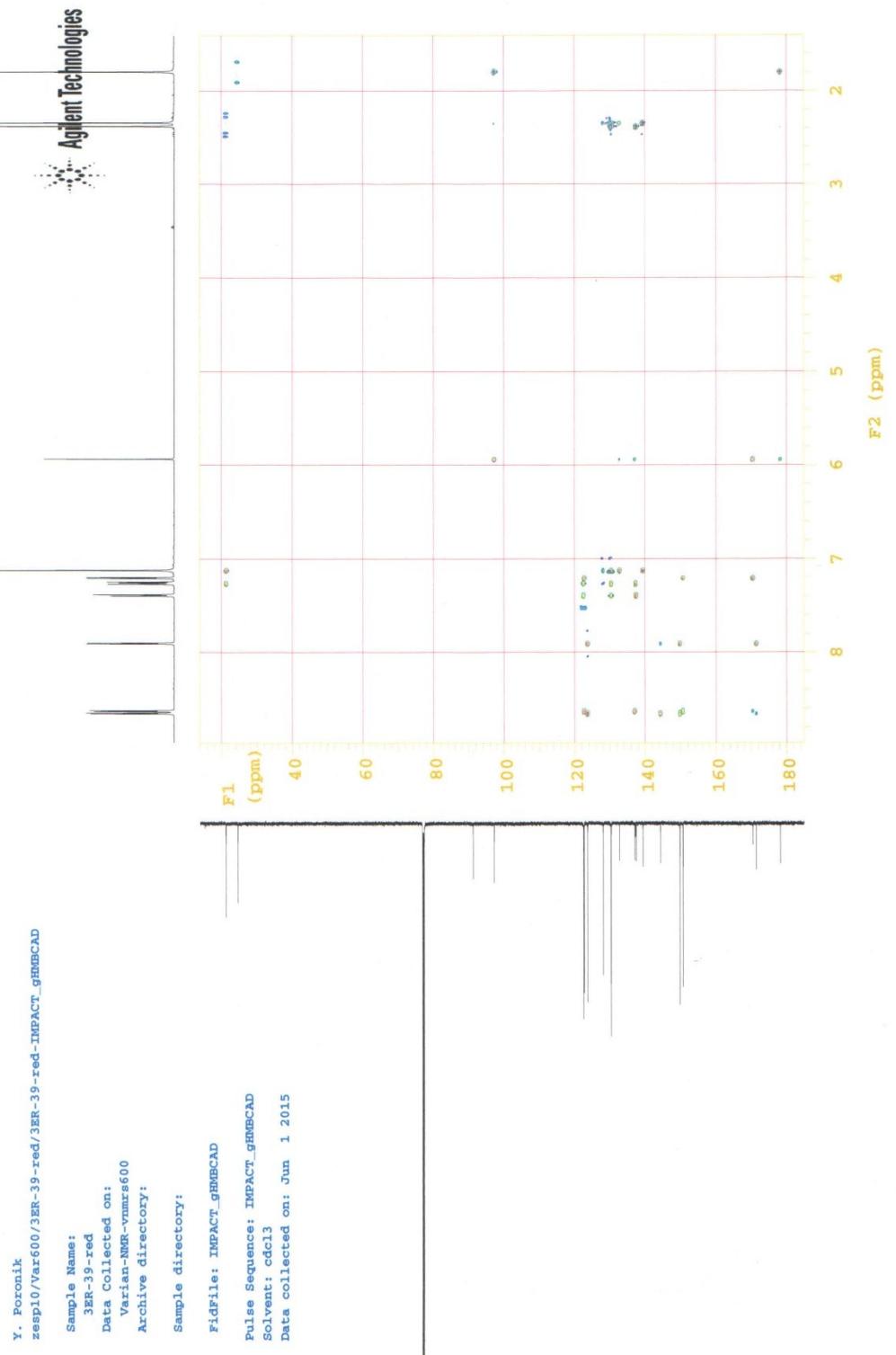


Figure S11. HMBC experiment for **4bbb** in  $\text{CDCl}_3$

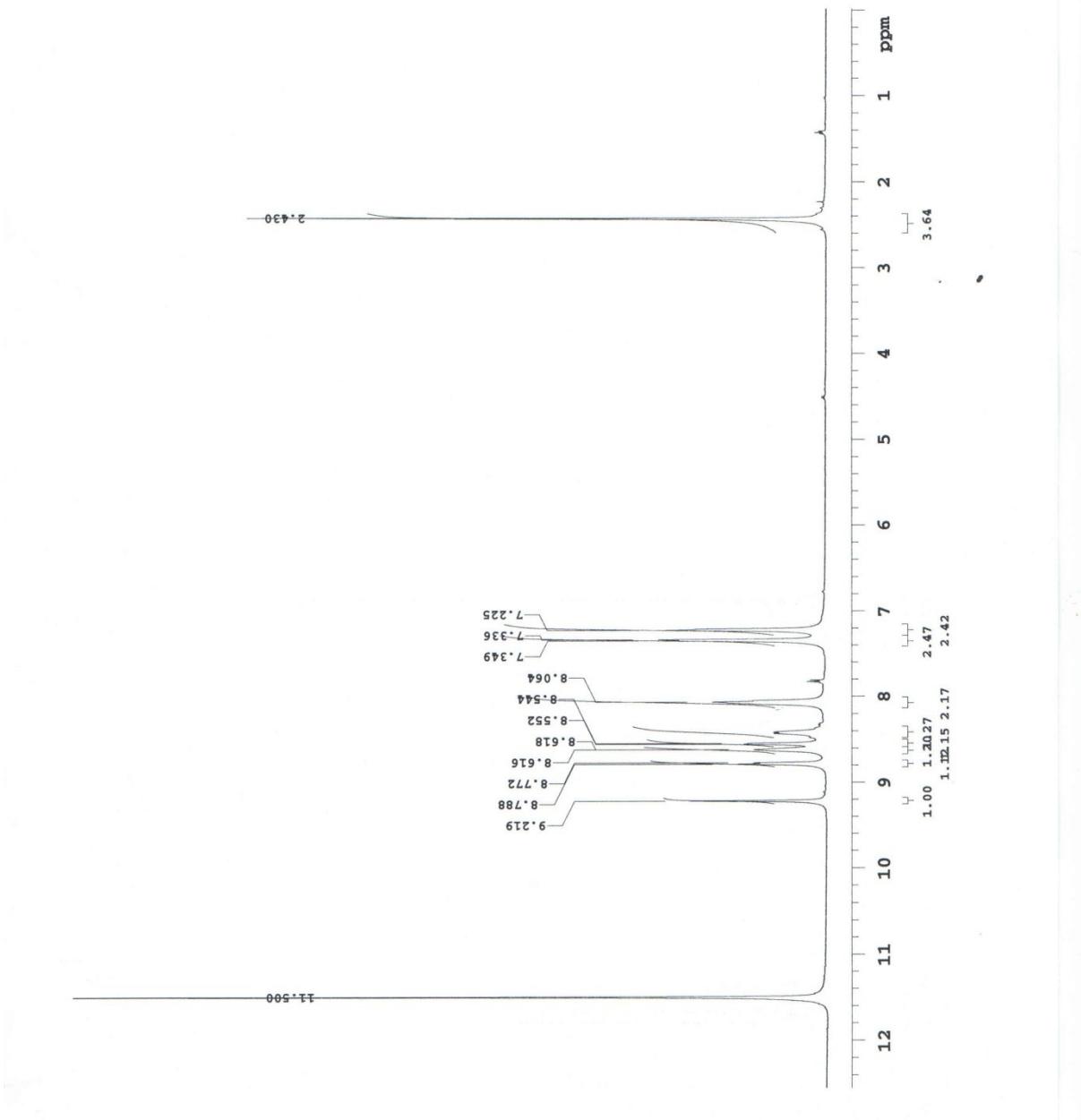


Figure S12.  $^1\text{H}$  NMR spectrum of **5a** in  $\text{CF}_3\text{COOD}$

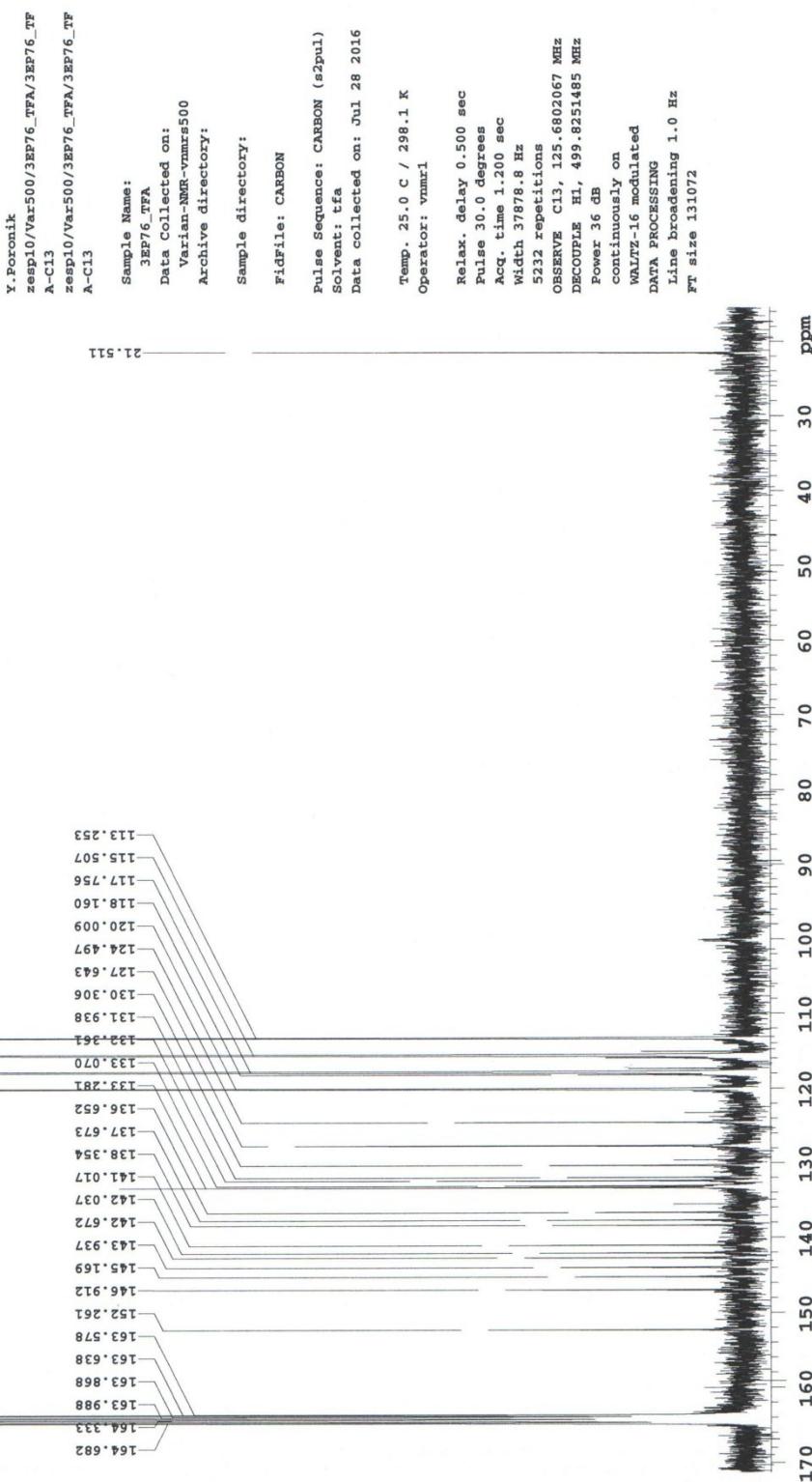


Figure S13.  $^{13}\text{C}$  NMR spectrum of **5a** in  $\text{CF}_3\text{COOD}$



0.001

2.448  
2.497  
2.500  
2.504

3.319

7.452  
7.479  
7.500  
7.520  
7.562  
7.596  
7.620  
7.652  
8.374  
8.392  
8.398  
8.403  
8.406  
8.430  
8.433  
8.435  
8.438  
8.453  
8.456  
8.463  
8.466  
8.473  
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9.037  
9.042  
9.052  
9.062  
9.072  
9.082

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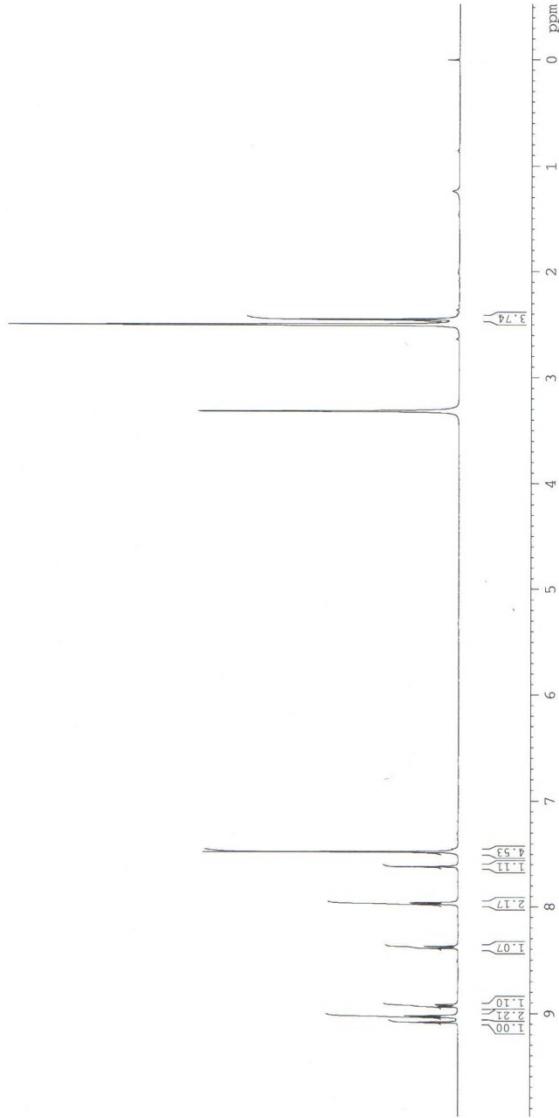
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TD       6536
SOLVENT DMSO
NS      64
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FIDRES 0.157632 Hz
AQ     3.171923 sec
RG      203.2
DW      48.400 usec
DE      6.78 usec
TE      303.0 K
D1     1.0000000 sec
TDO    1

===== CHANNEL E1 =====
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PL      2.50 usec
PL1     0.00 dB
SF01   500.1330985 MHz

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GB      1.00
PC      1.00

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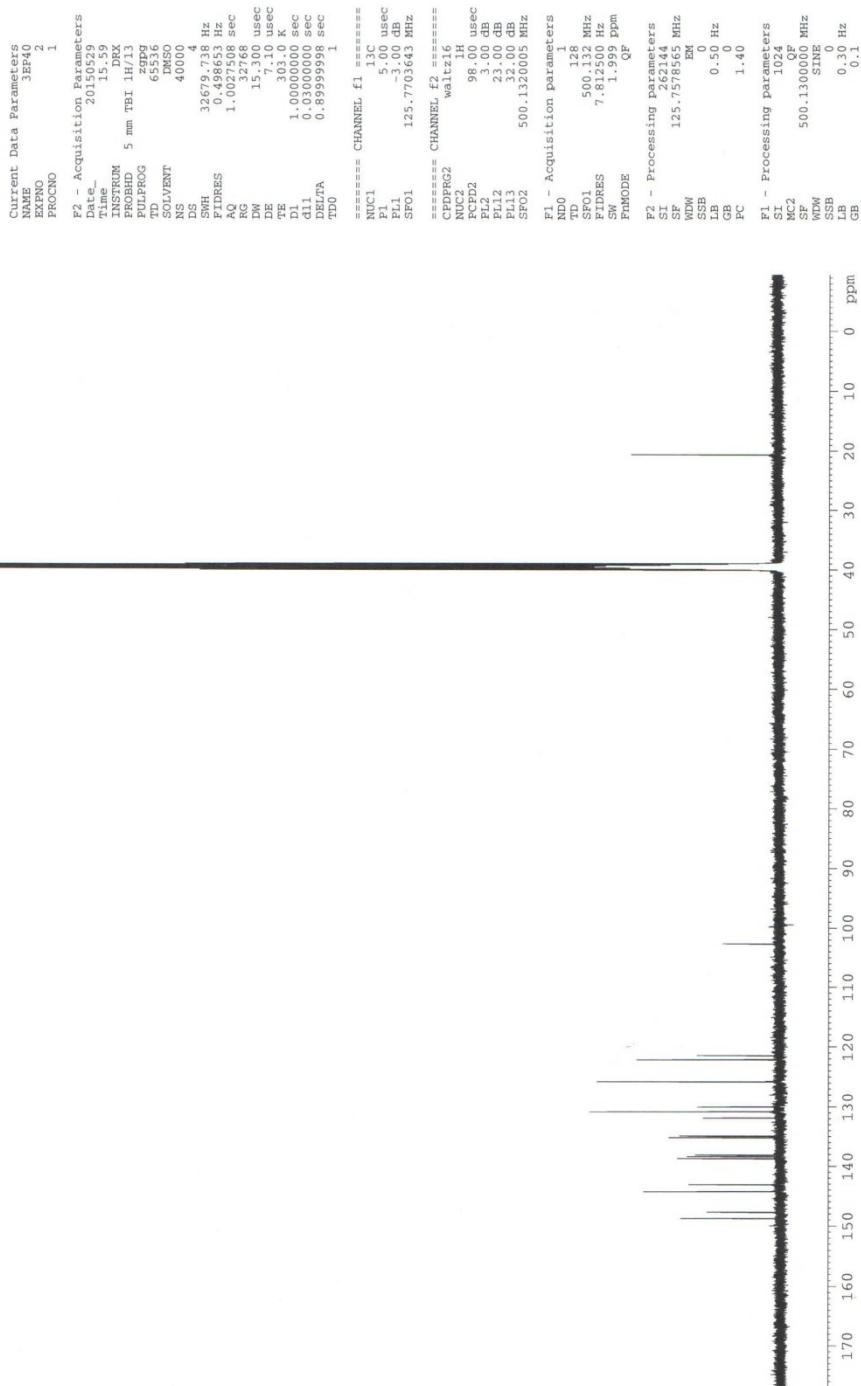


Figure S15.  $^{13}\text{C}$  NMR spectrum of **5b** in  $\text{DMSO-d}_6$

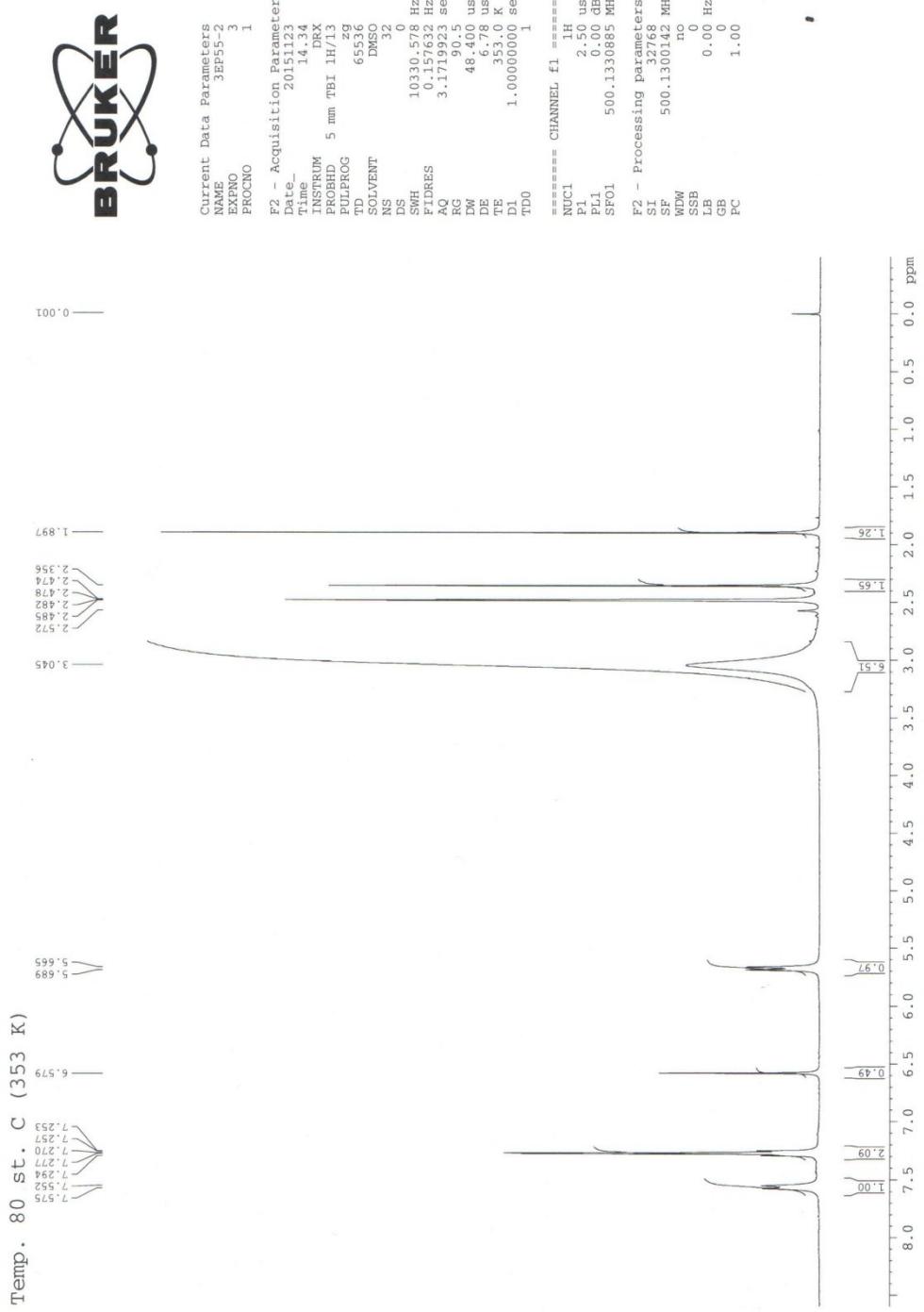


Figure S16.  $^1\text{H}$  NMR spectrum of **6b** in  $\text{DMSO-d}_6$



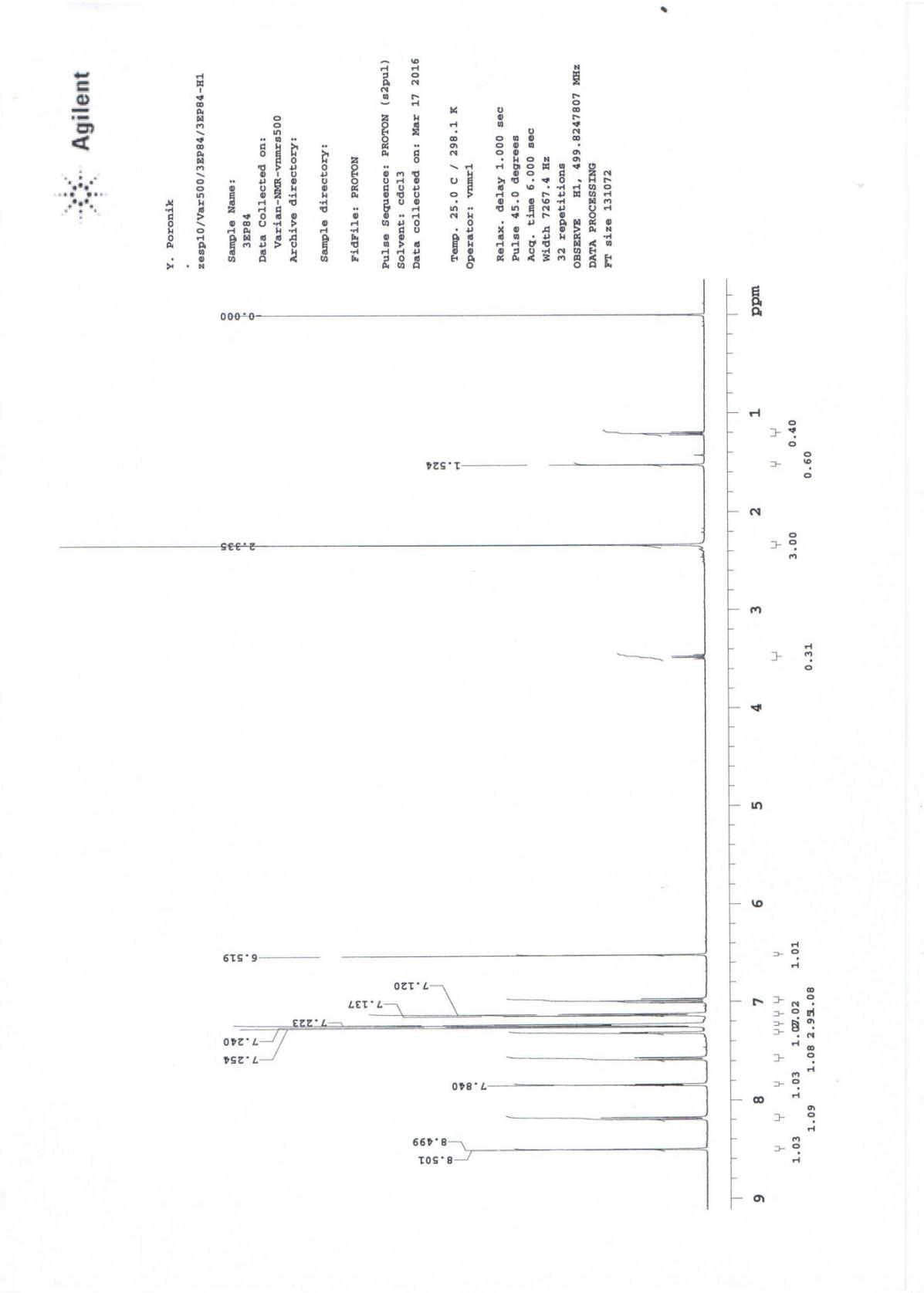


Figure S18.  $^1\text{H}$  NMR spectrum of **7a** in  $\text{CDCl}_3$

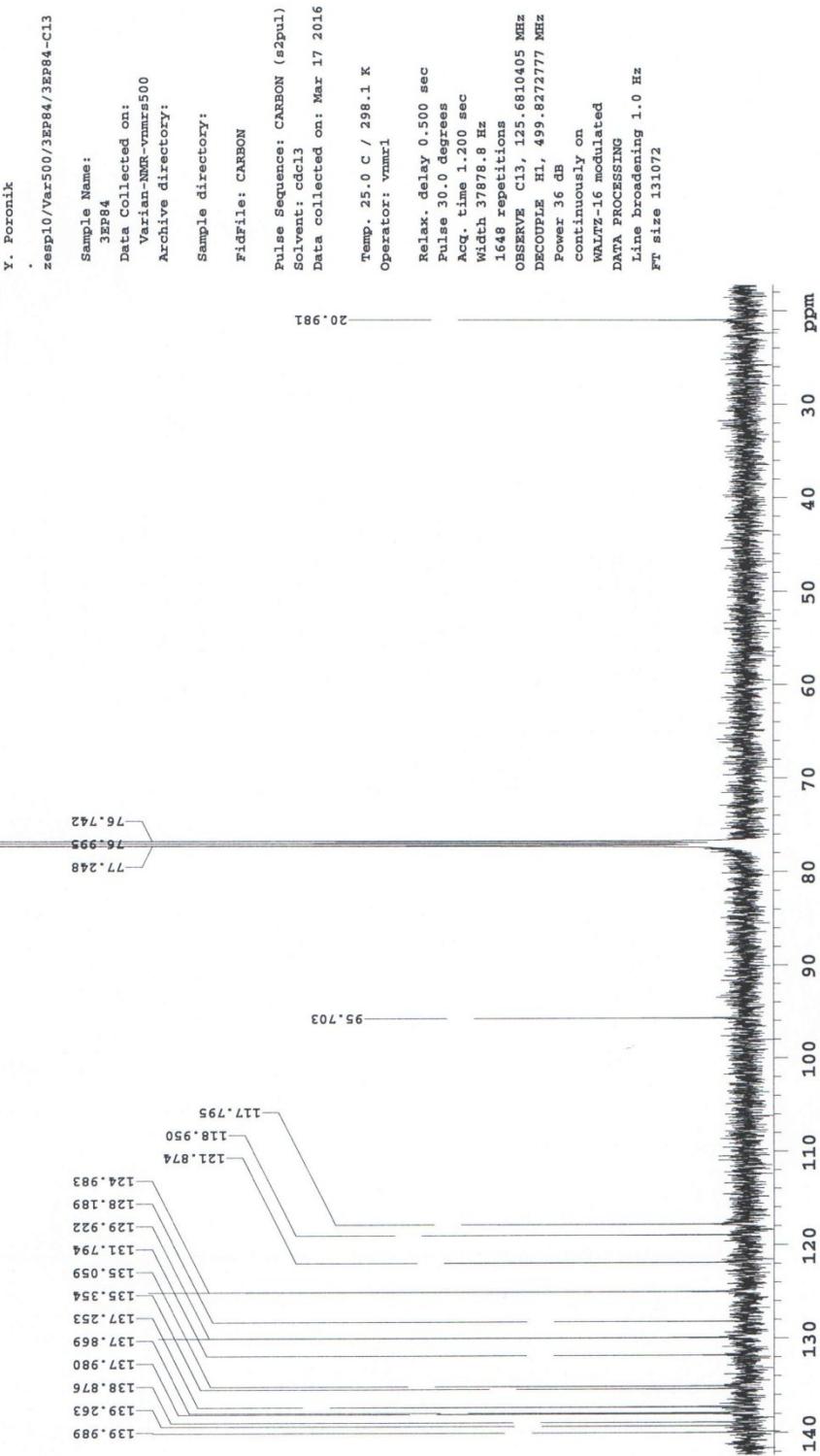
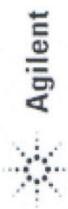


Figure S19.  $^{13}\text{C}$  NMR spectrum of **7a** in  $\text{CDCl}_3$

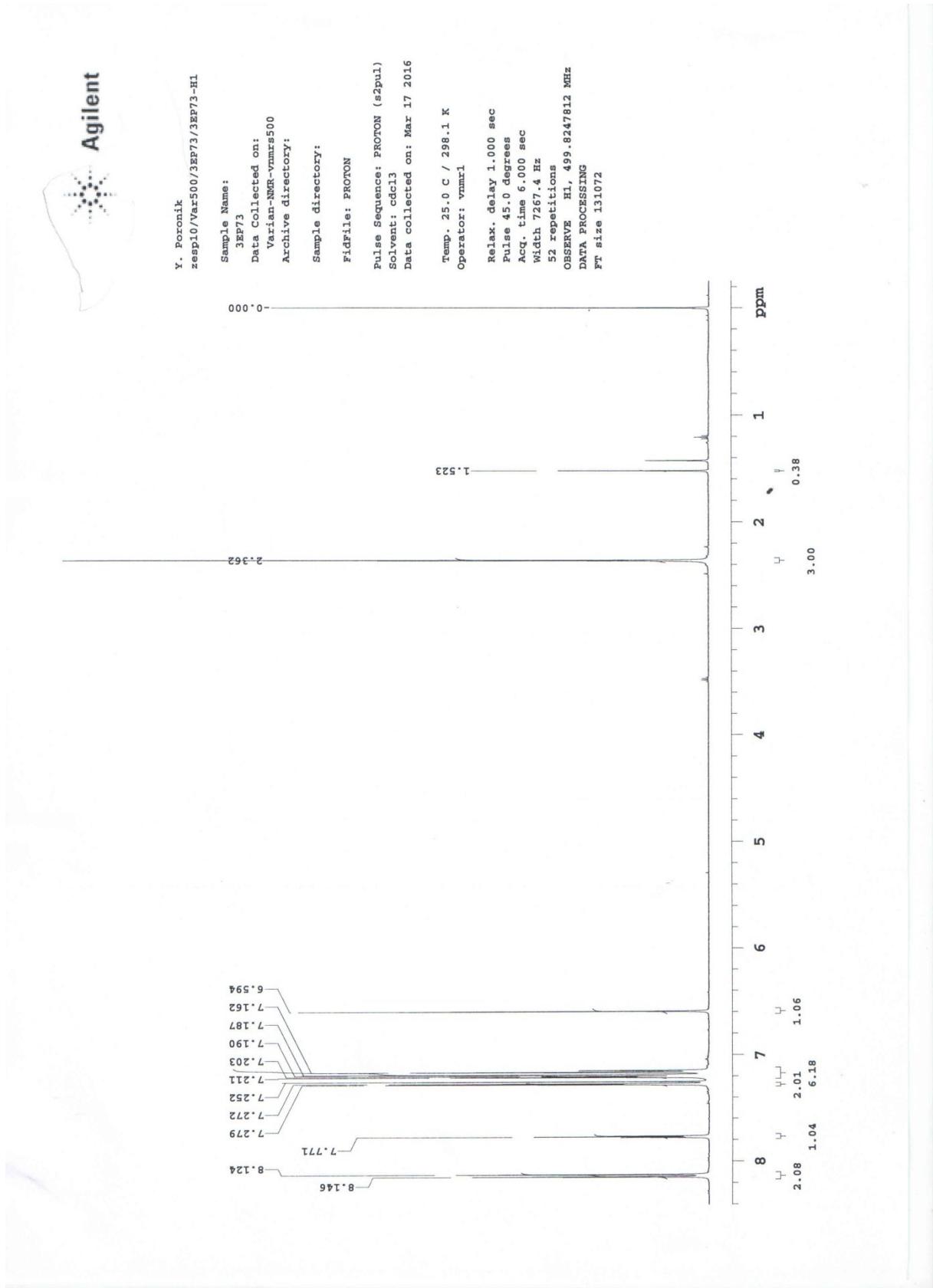
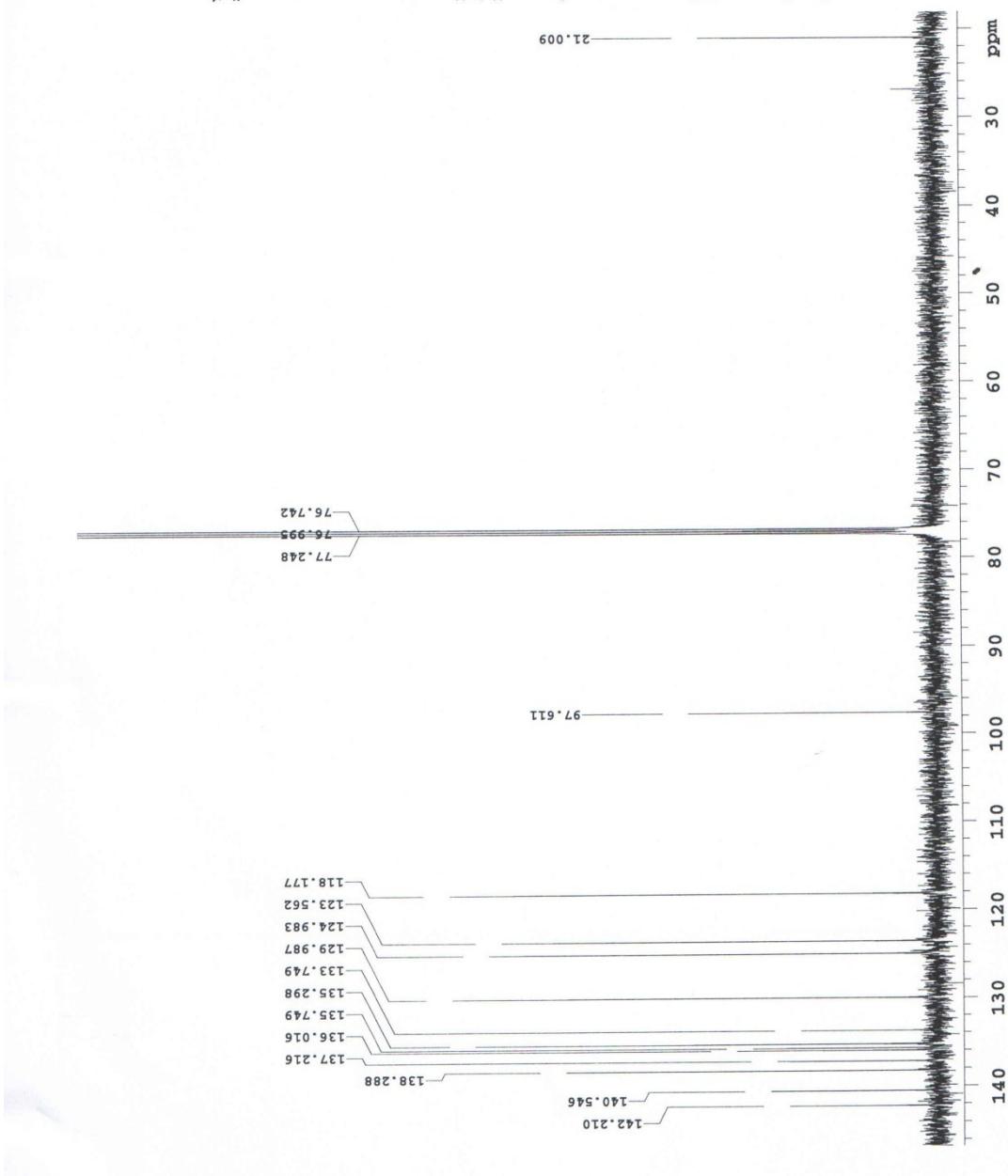


Figure S20.  $^1\text{H}$  NMR spectrum of **7b** in  $\text{CDCl}_3$

Figure S21.  $^{13}\text{C}$  NMR spectrum of **7a** in  $\text{CDCl}_3$