

SUPPORTING INFORMATION

FOR

Redox and Lewis Acid Relay Catalysis: A Titanocene/Zinc Catalytic Platform in the Development of Multicomponent Coupling Reactions

Joseph B. Gianino, Catherine A. Campos, Antonio J. Lepore, David M. Pinkerton,
and Brandon L. Ashfeld*

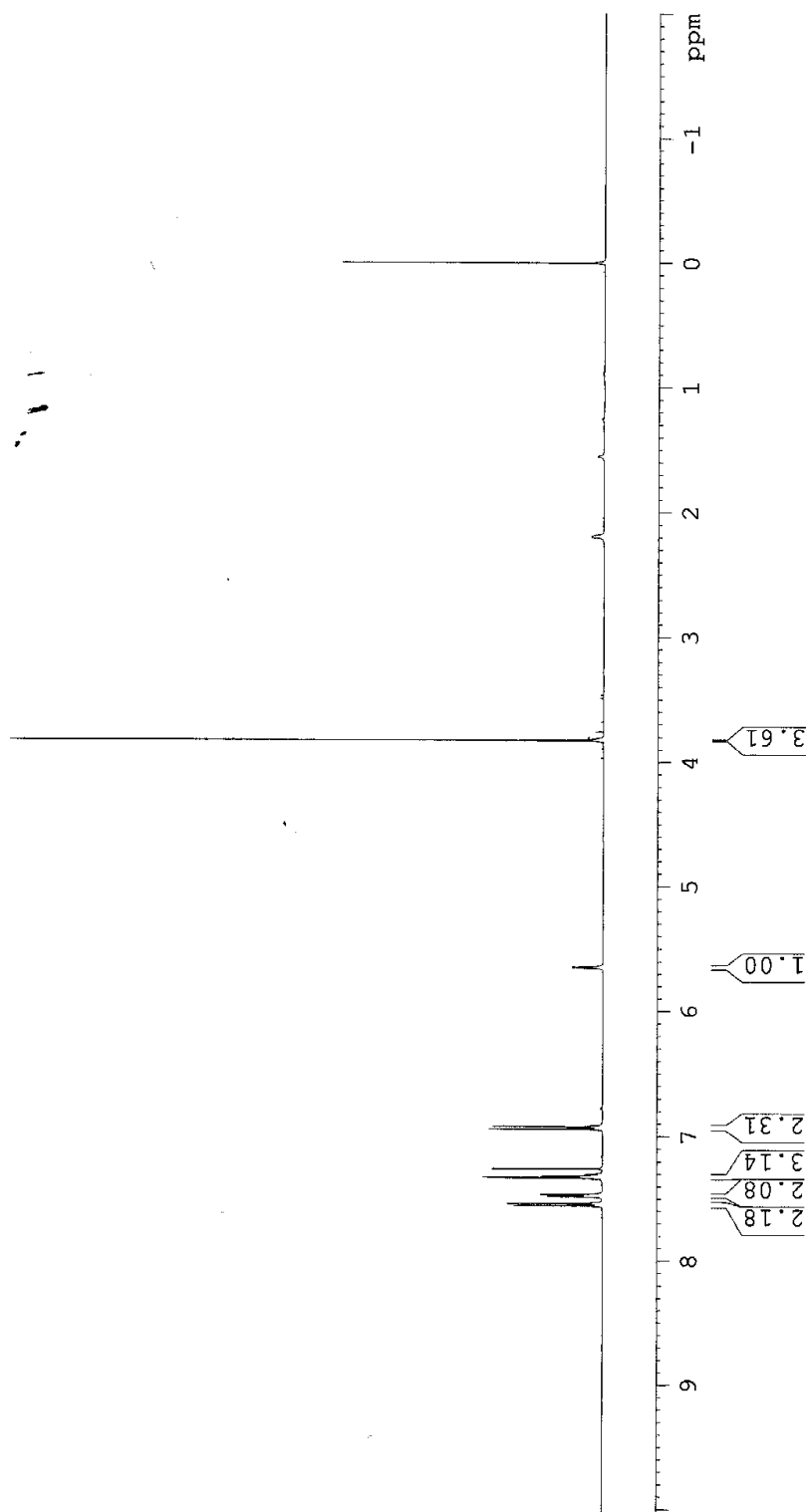
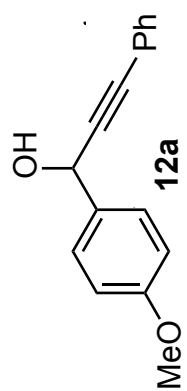
*Department of Chemistry and Biochemistry, University of Notre Dame
251 Nieuwland Science Hall, Notre Dame, IN 46556*

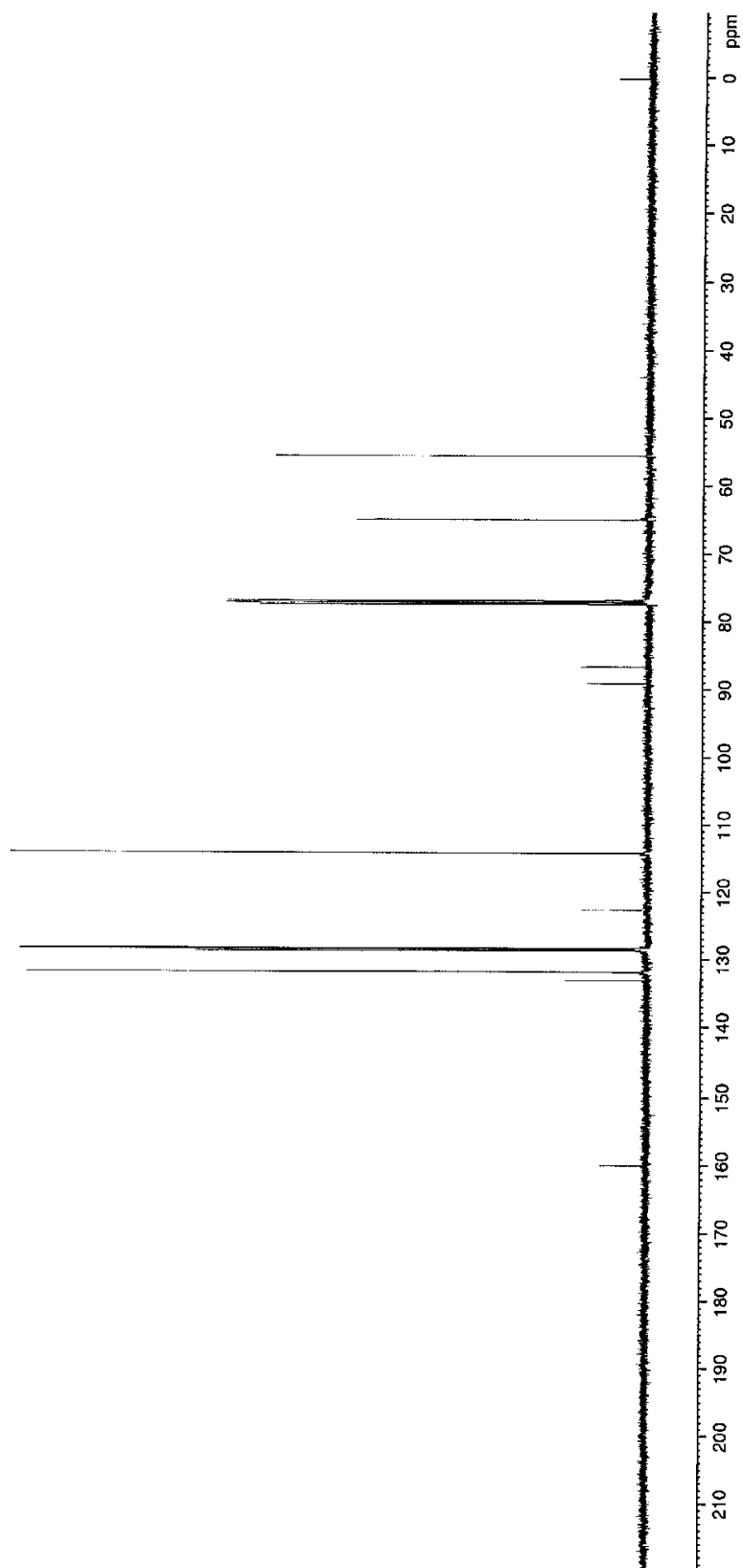
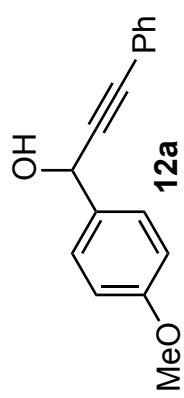
bashfeld@nd.edu

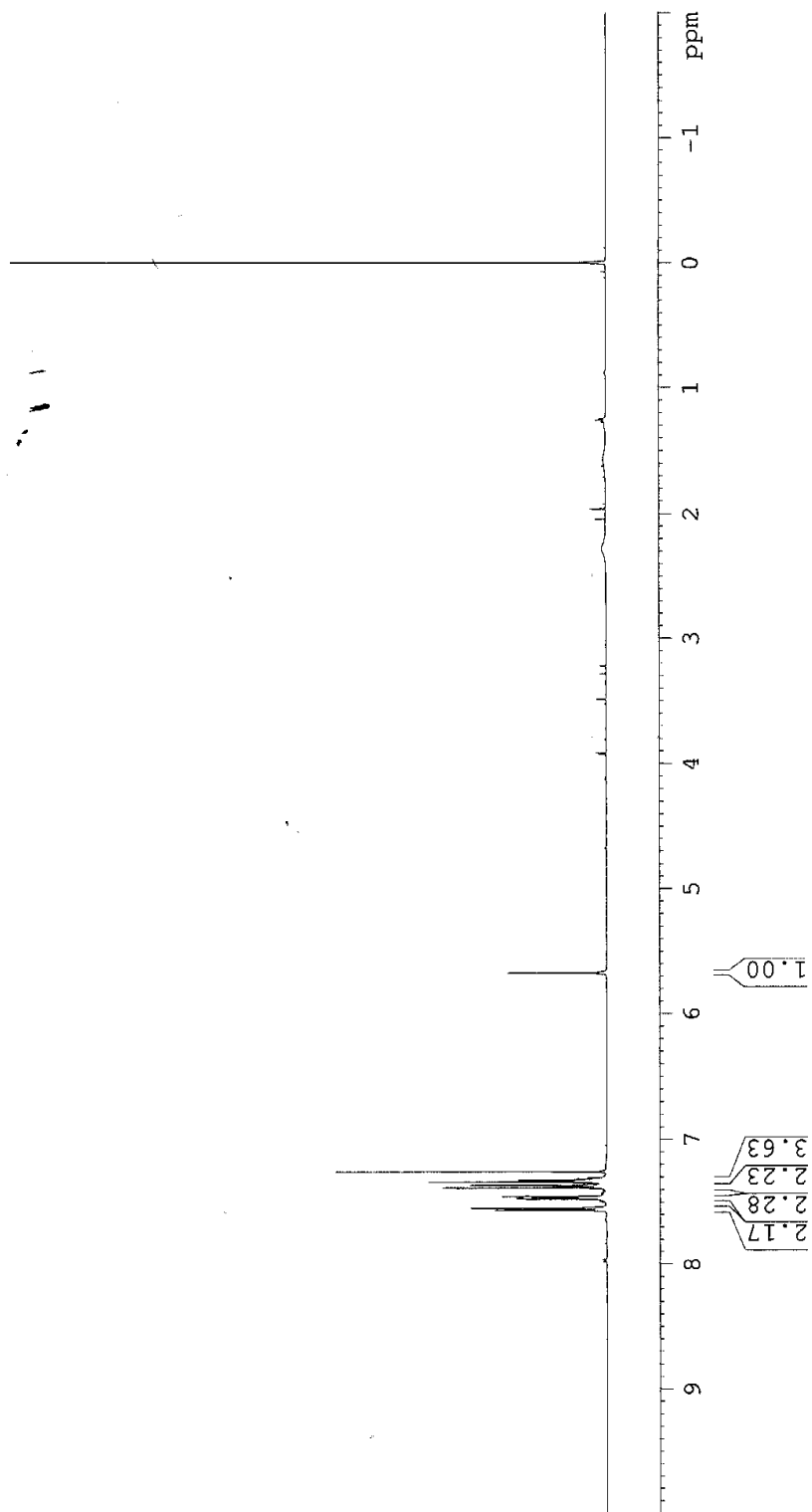
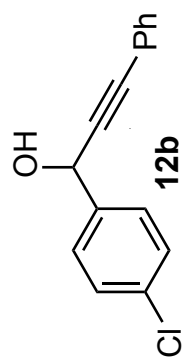
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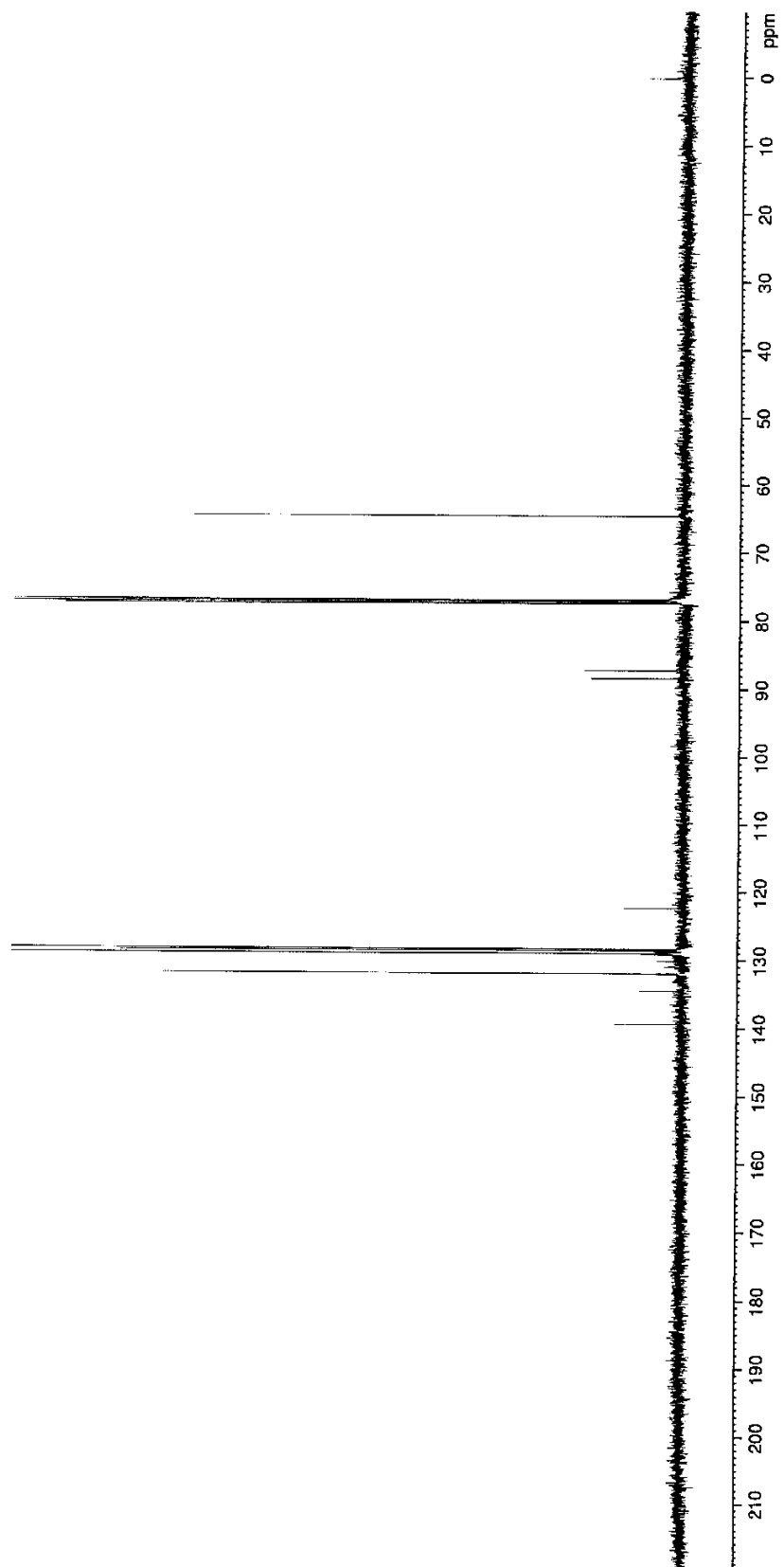
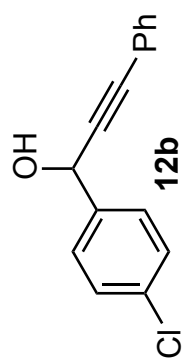
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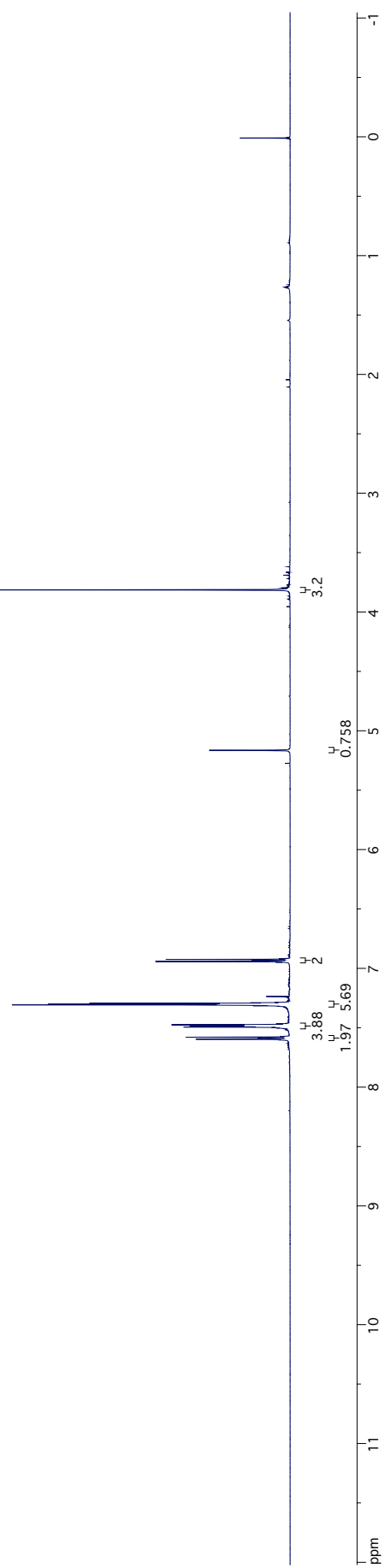
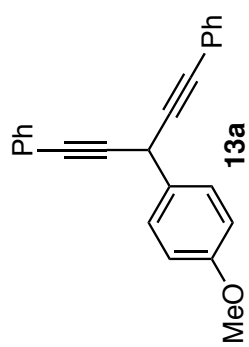
S2-S90



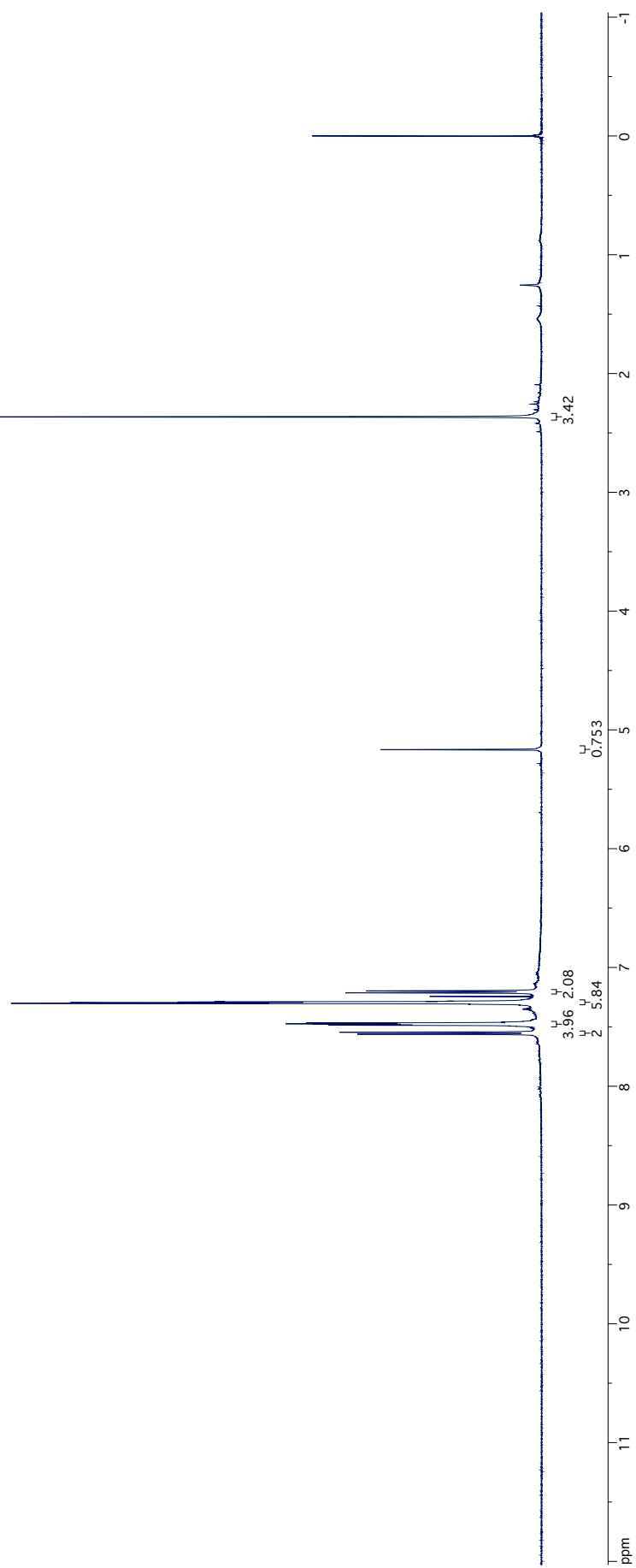
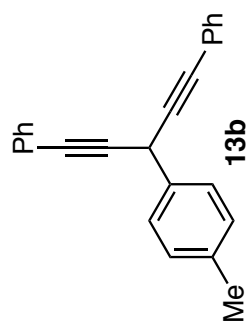


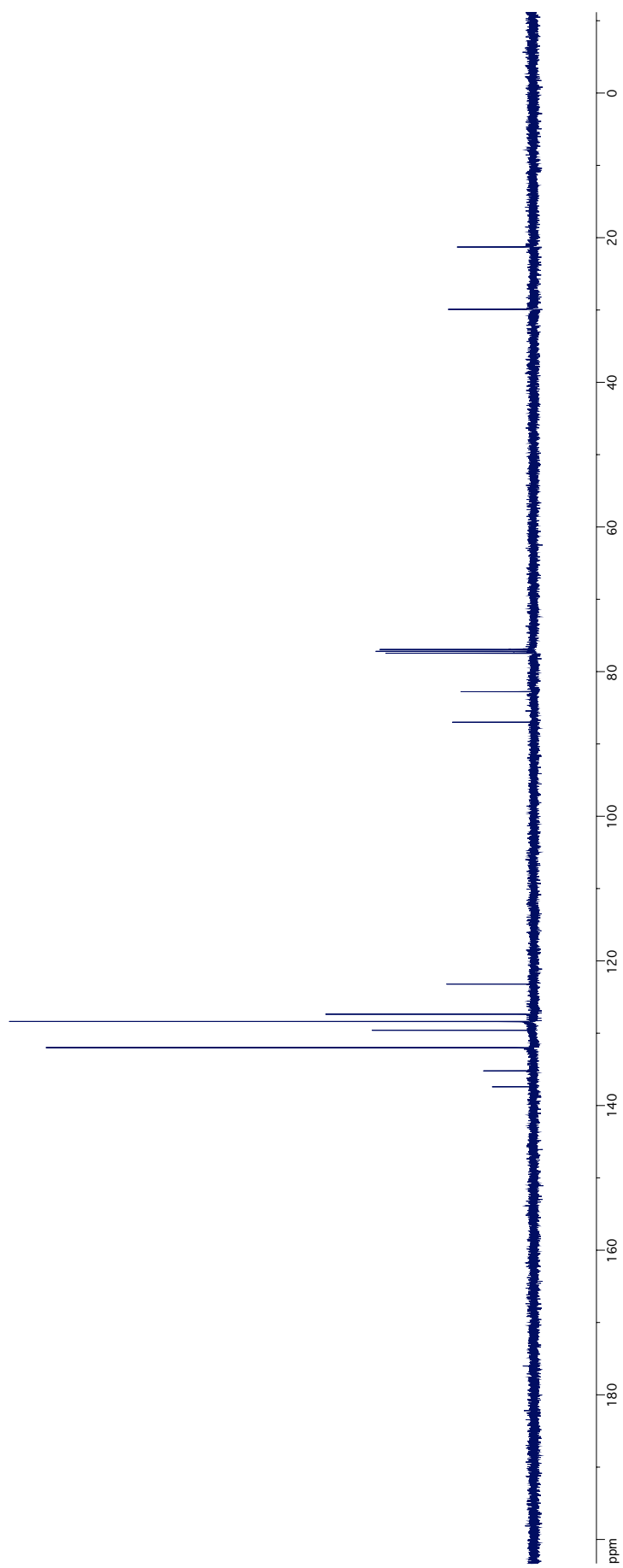
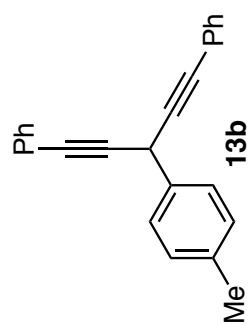


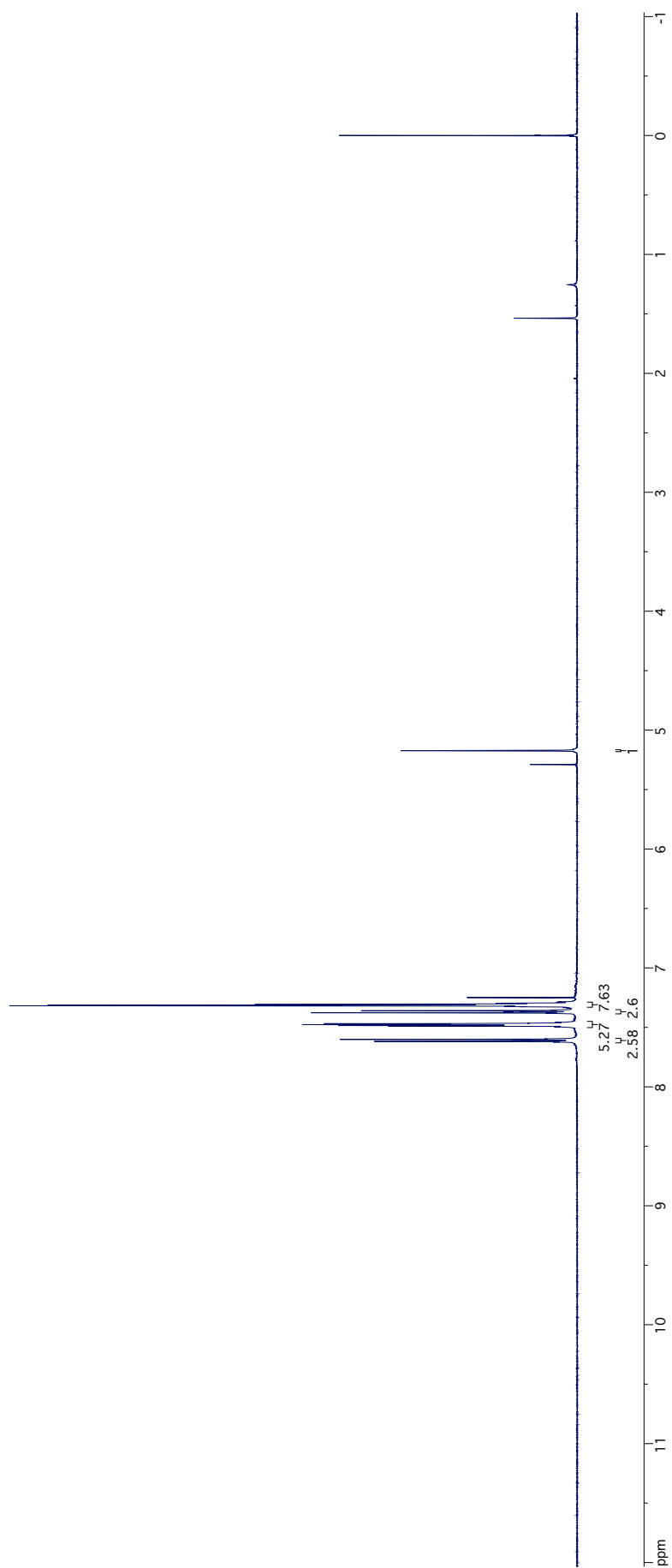
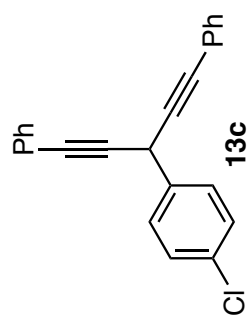


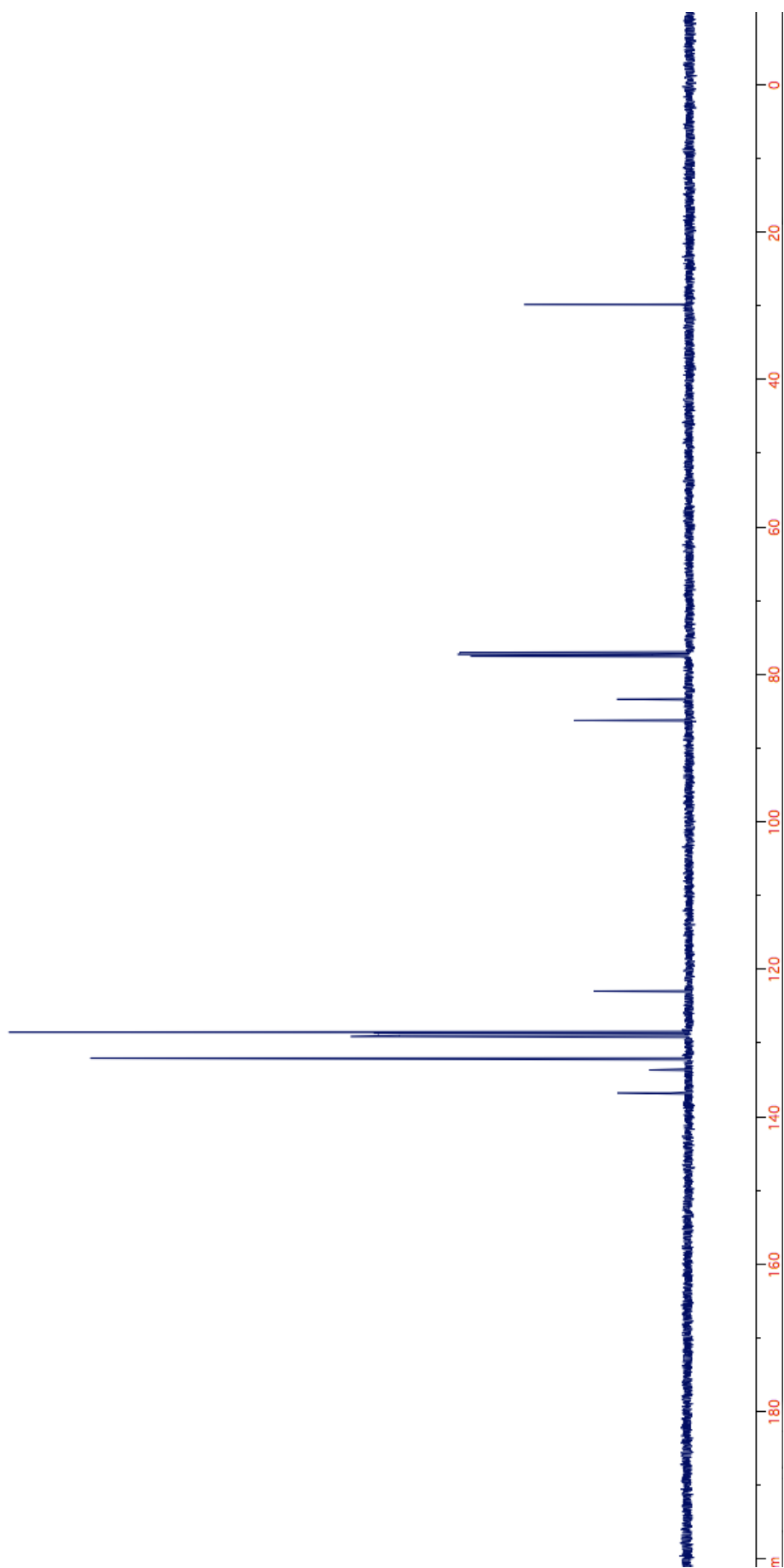
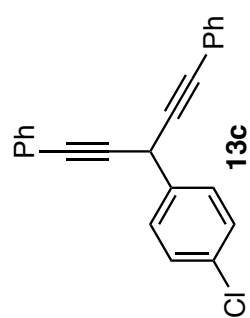


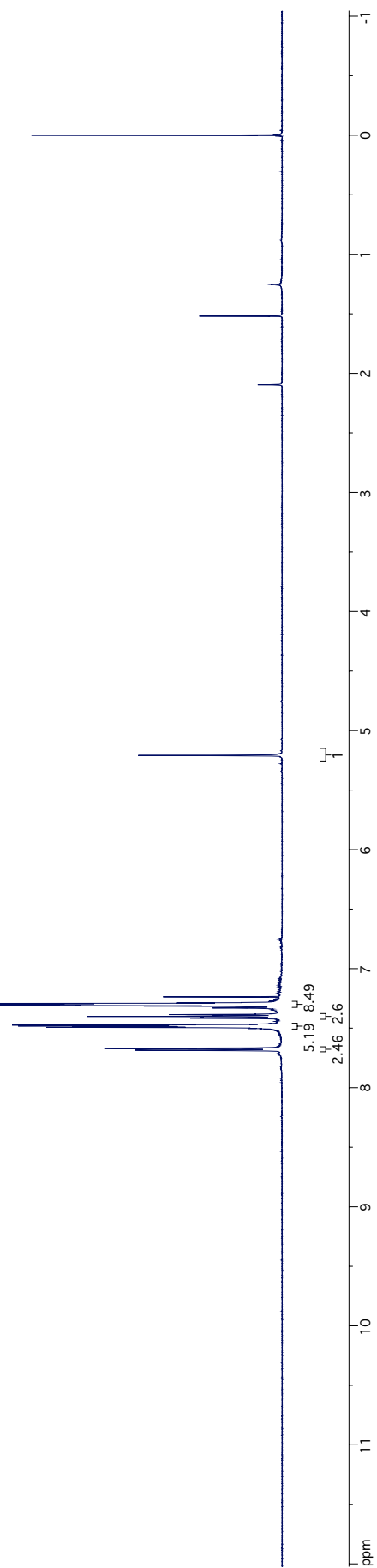
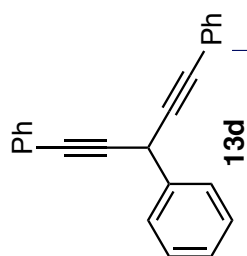


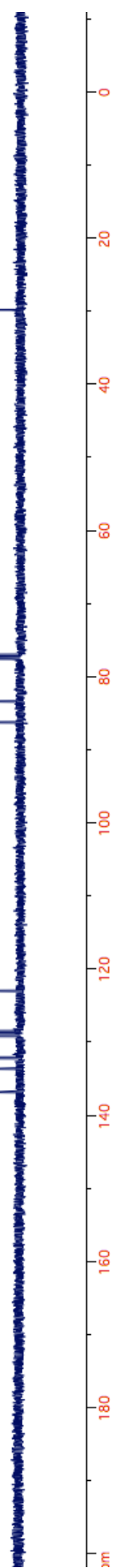
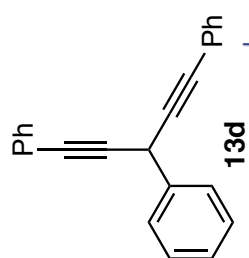


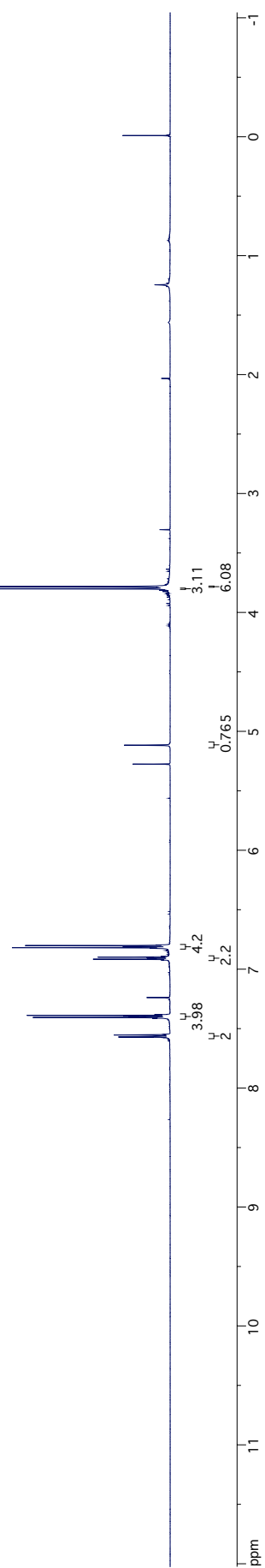
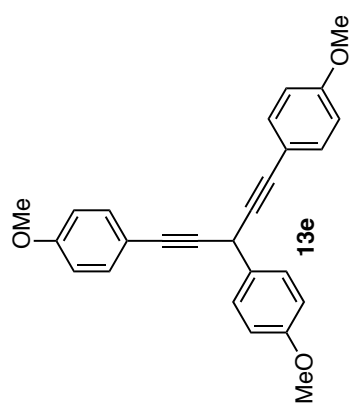


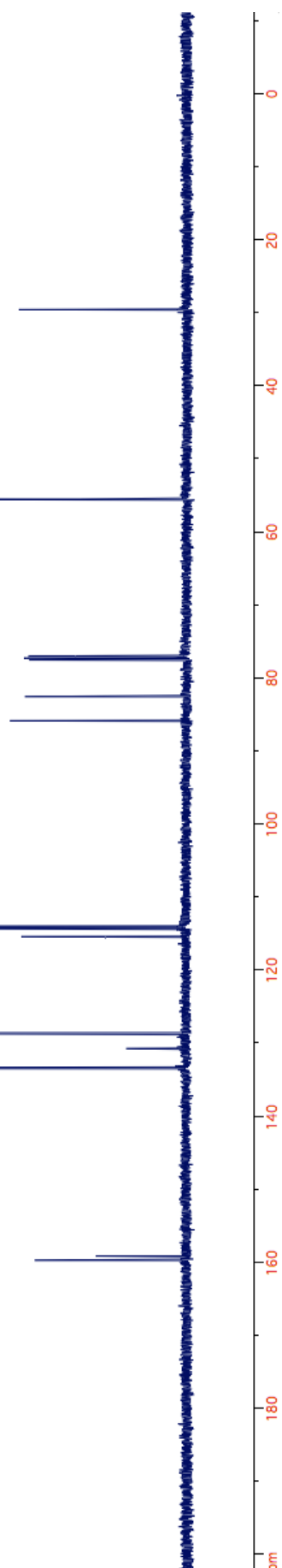
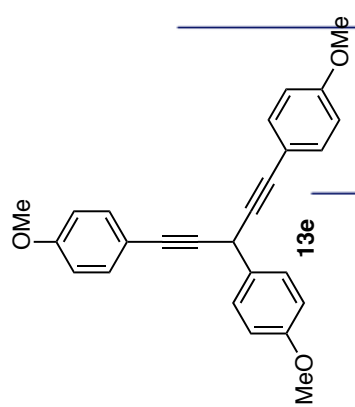


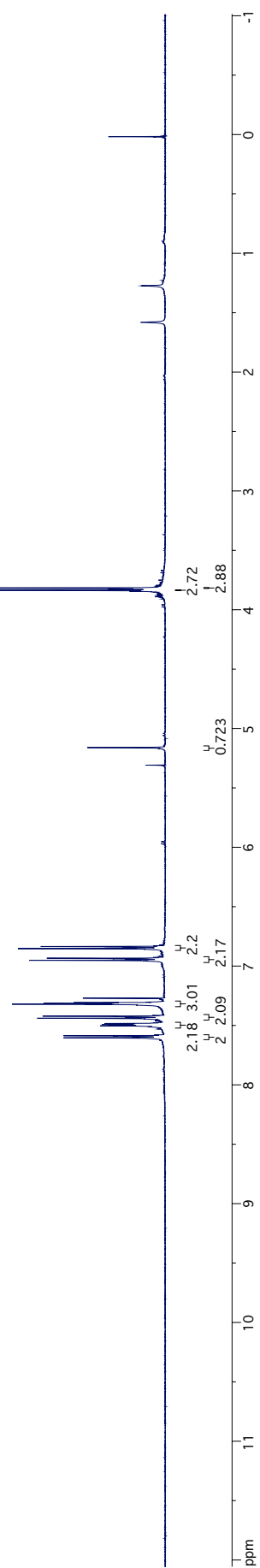
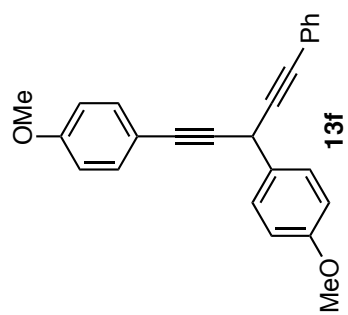


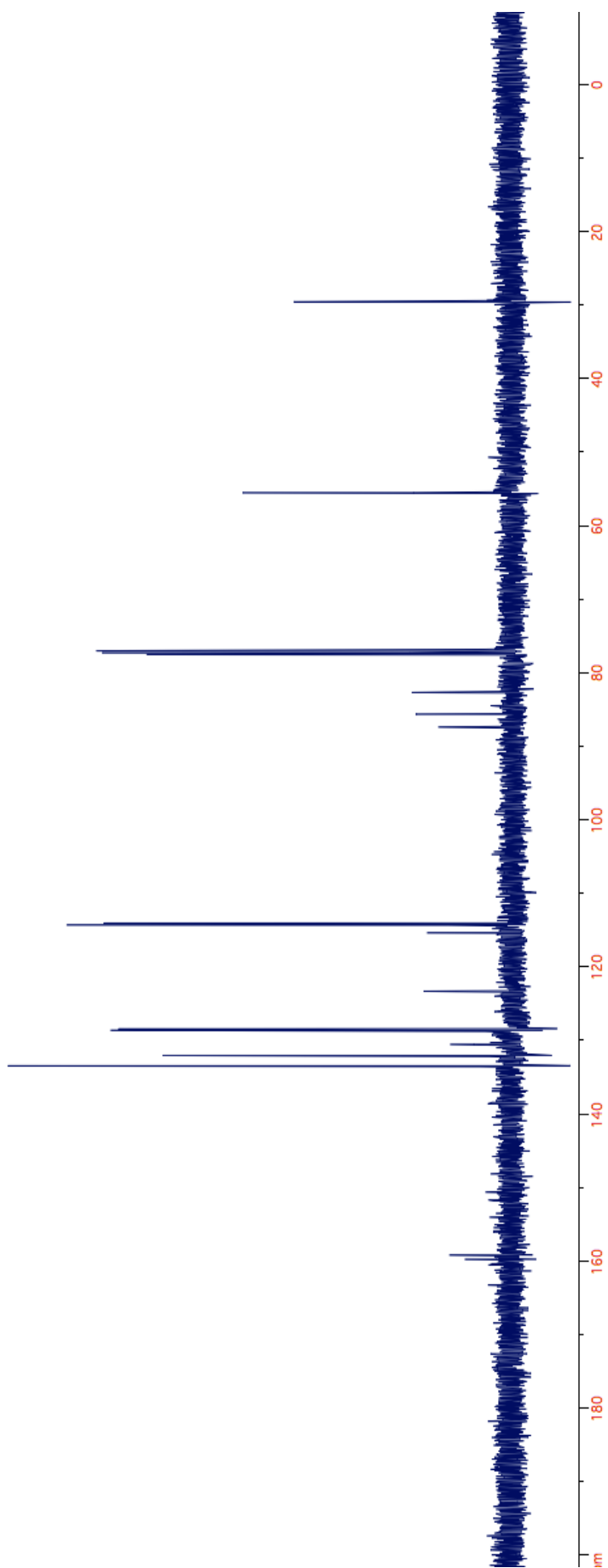
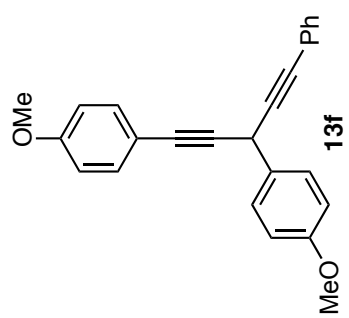


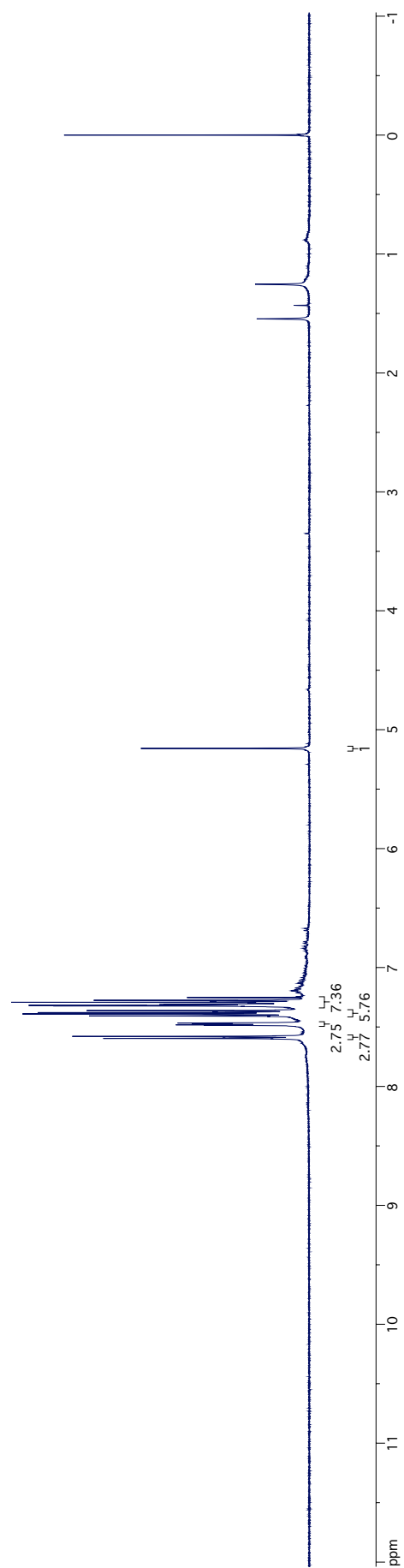
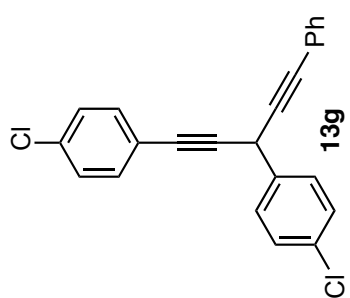


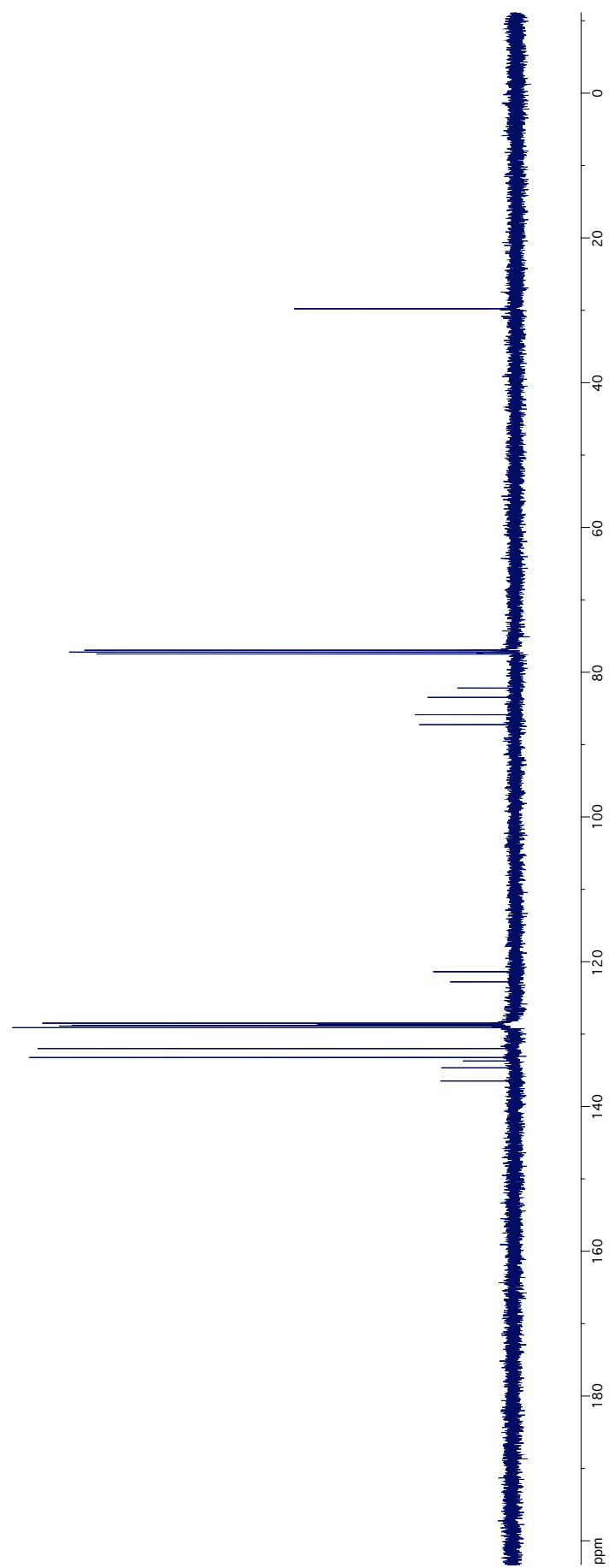
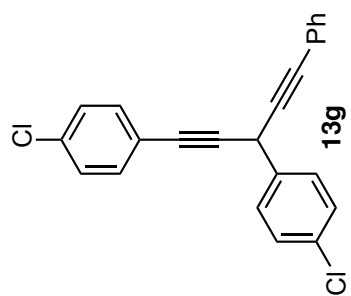


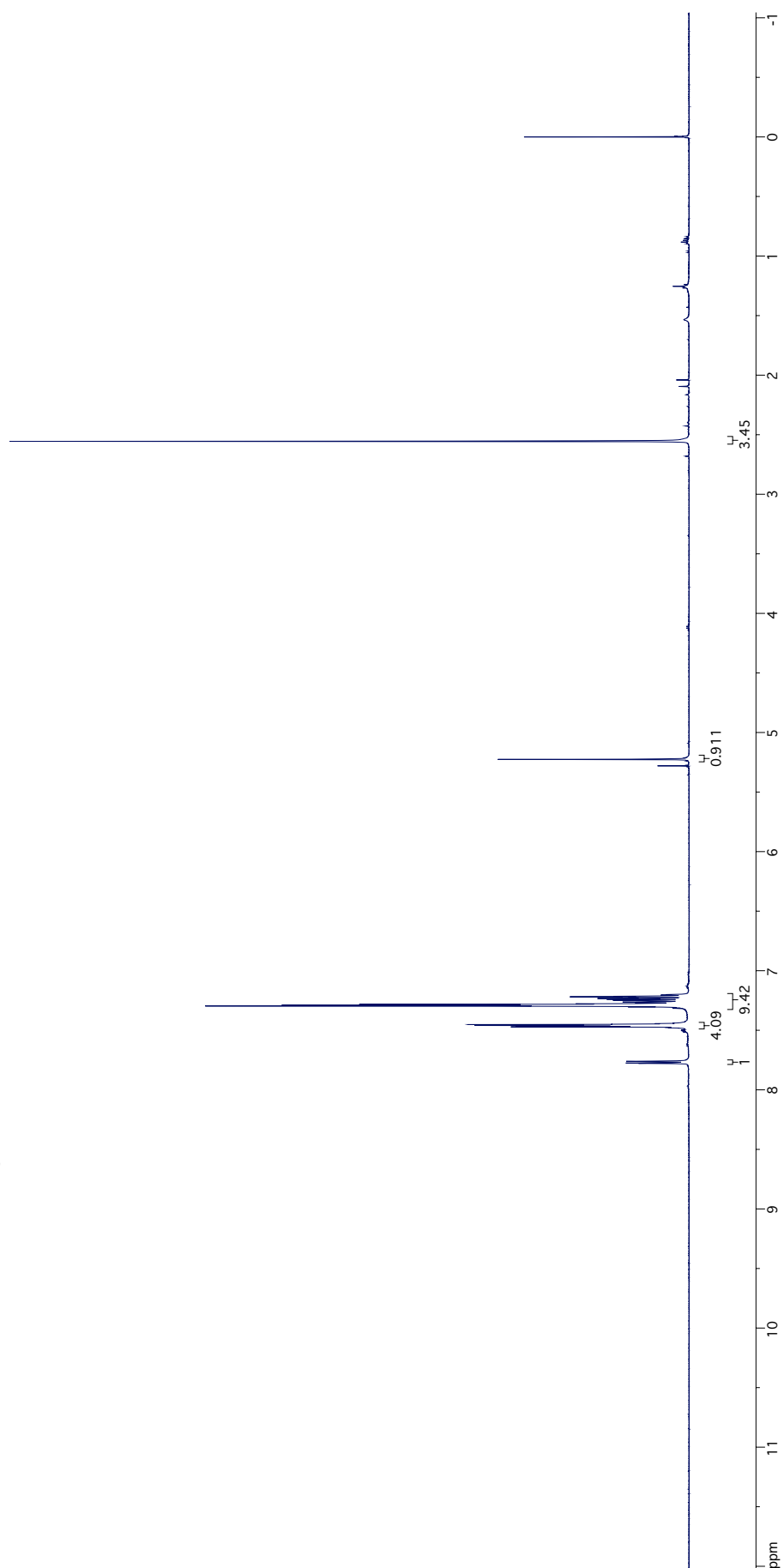
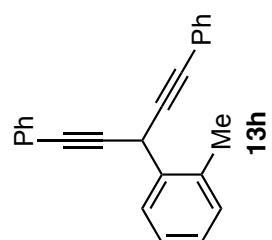


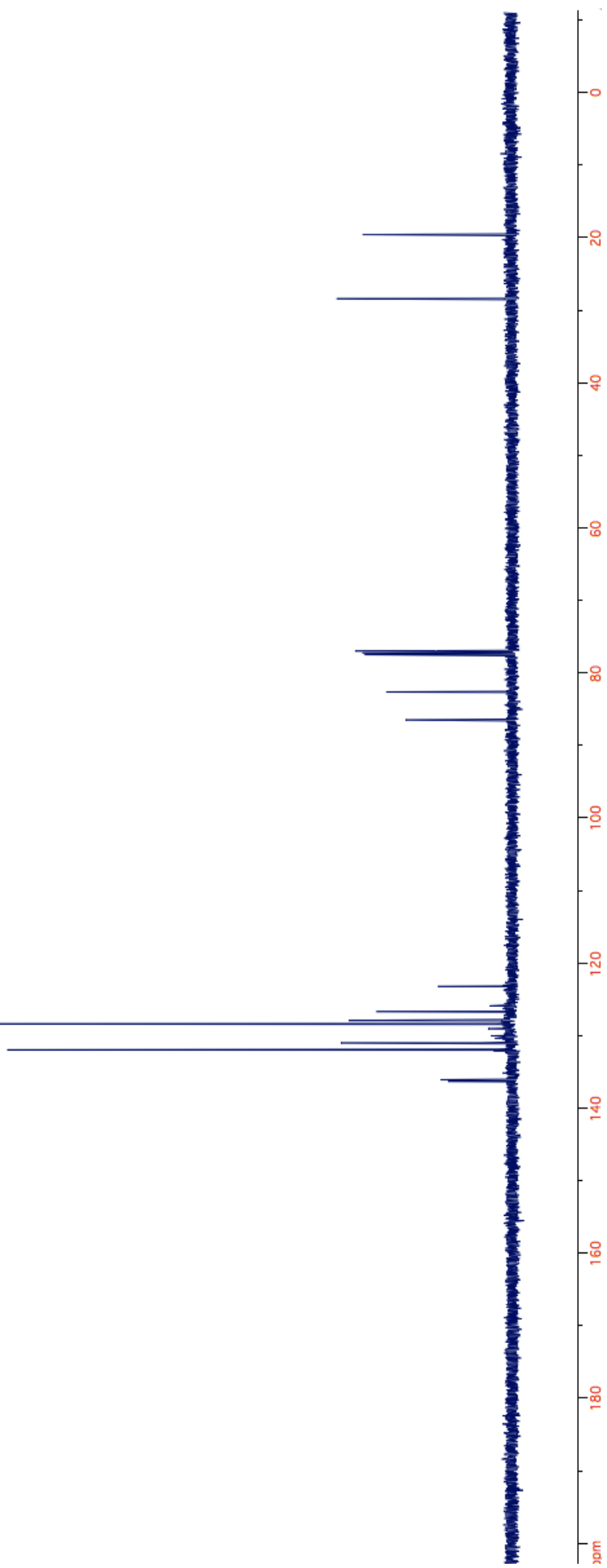
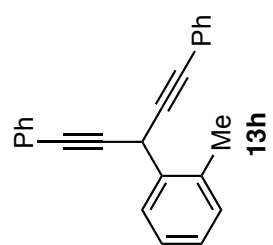


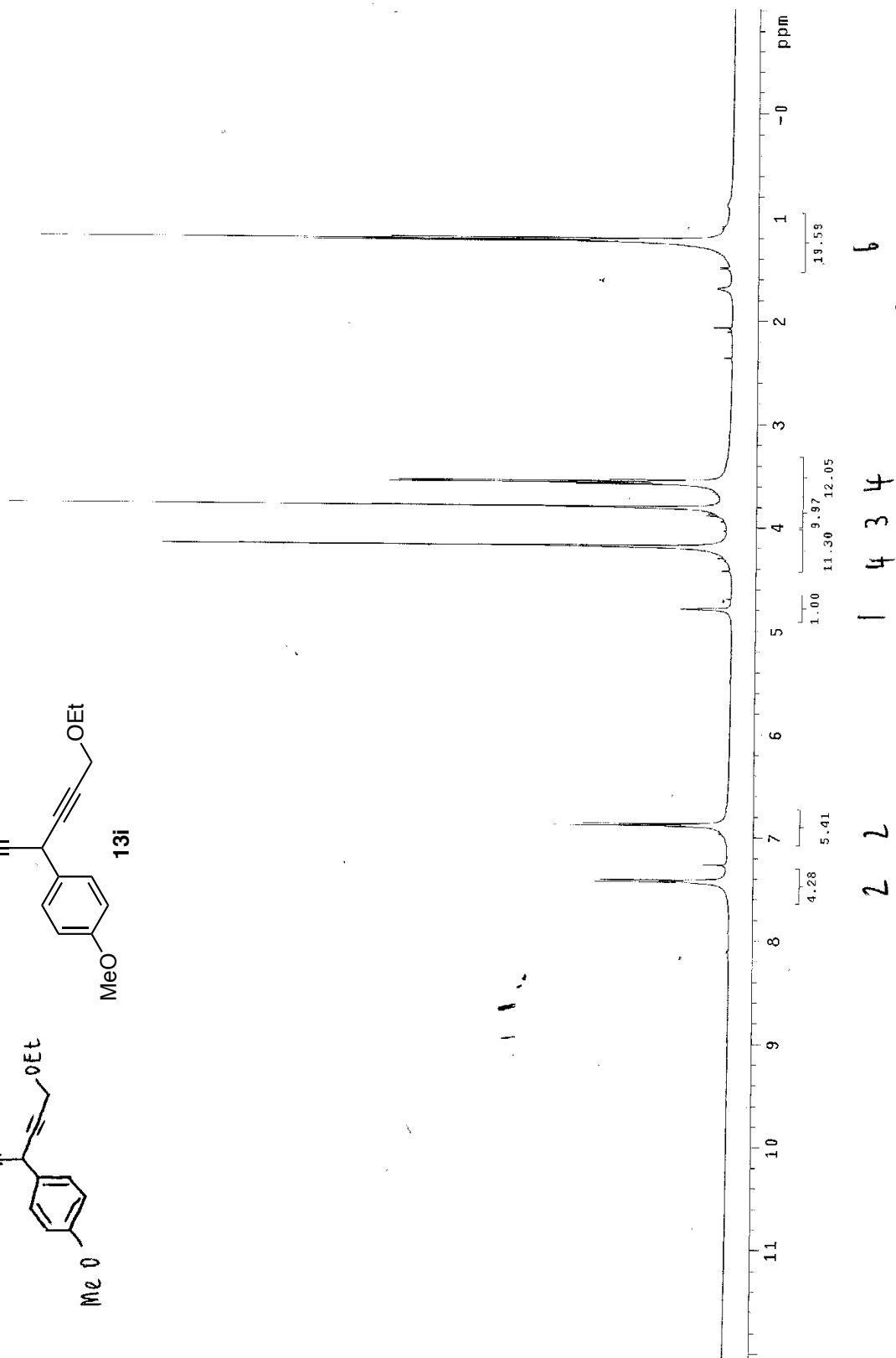
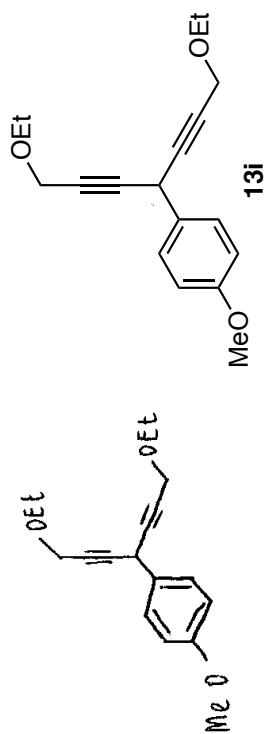










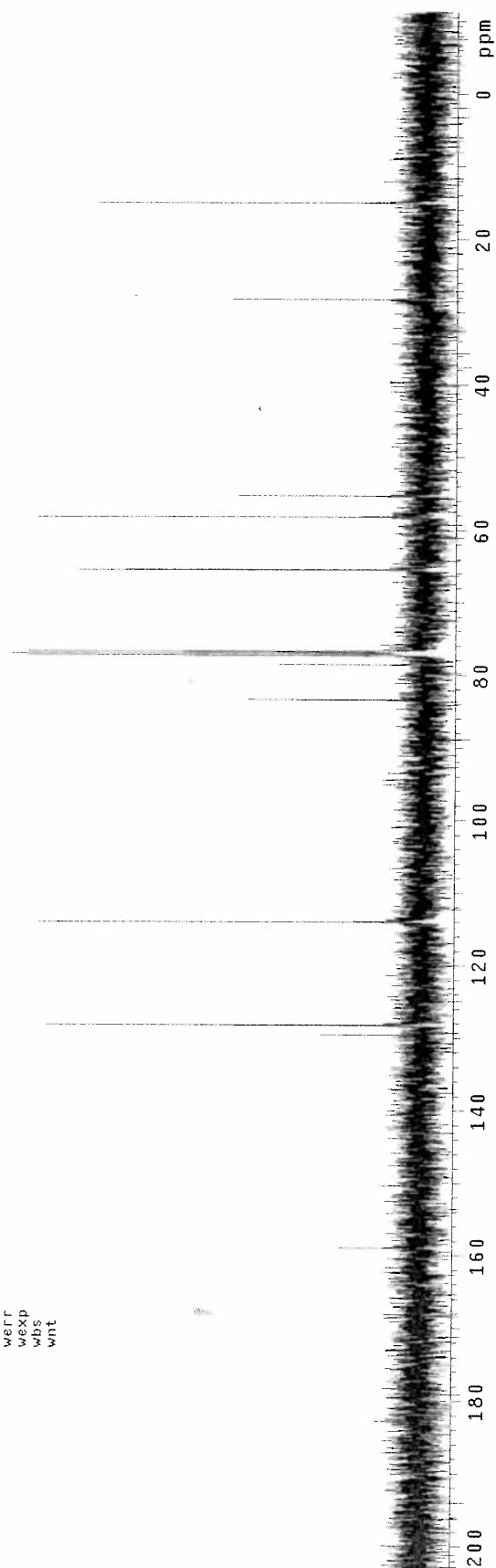
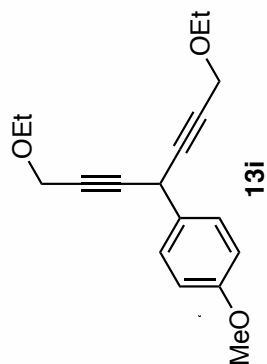


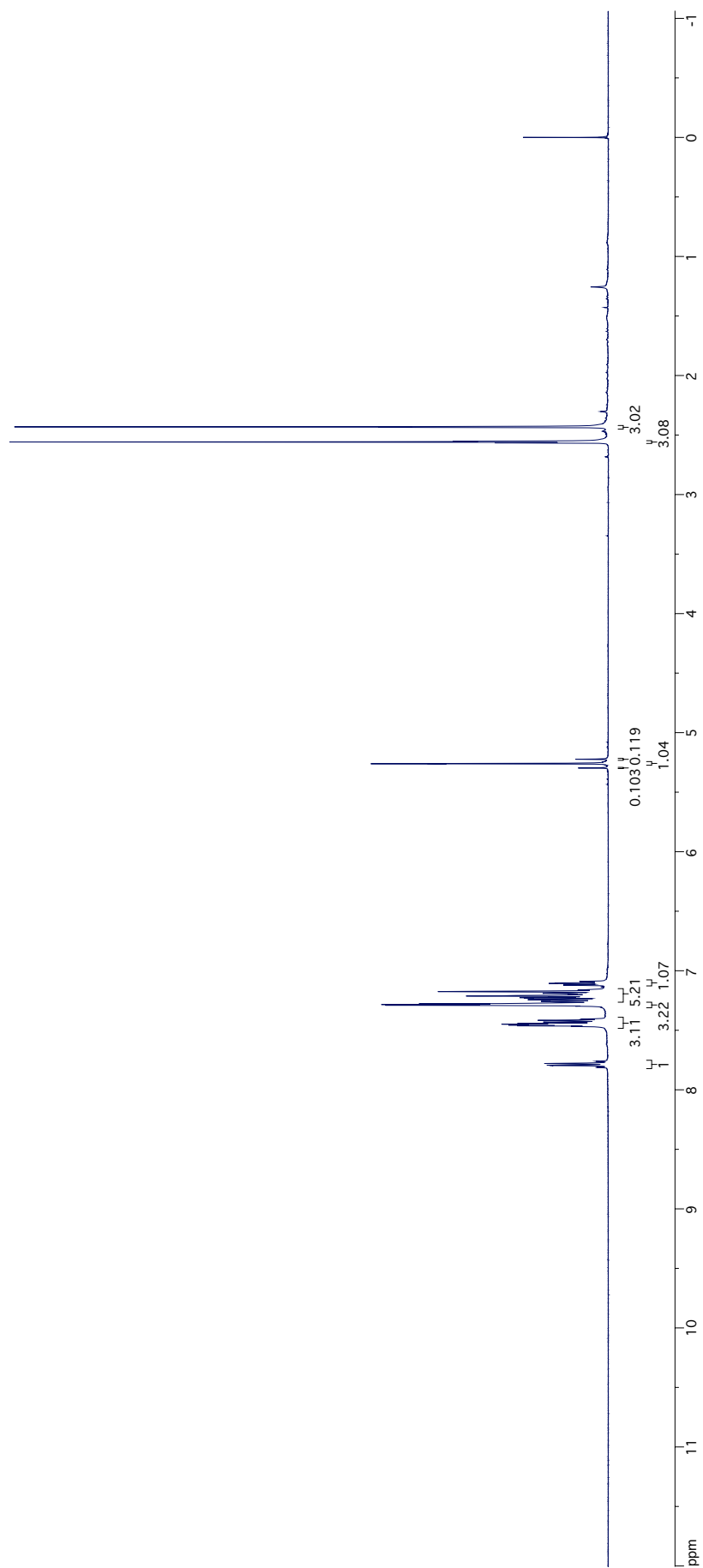
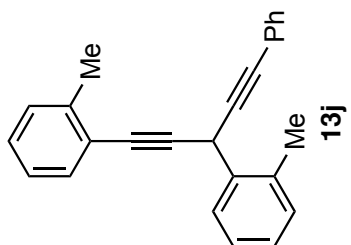
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at       1.215
np       65536
sw       26963.3
fb       15000
ls        4
tpwr     52
pw       10.2
d1       5.000
tof      144.5
nt       100
ct       48
alock    not used
gain     10000
FLAGS   n
il       n
in       n
dp       y
hs       n
DISPLAY
sp       -1433.3
wp       26962.9
vs       901
sc       0
wc       250
h2nm     107.85
is       500.00
rfl      11111.8
rfp      9678.1
th       131072
ins      100.000
ai       131072
cdc      ph
ph       math
werr     wexp
wexp     wds
wds      wnt
wnt

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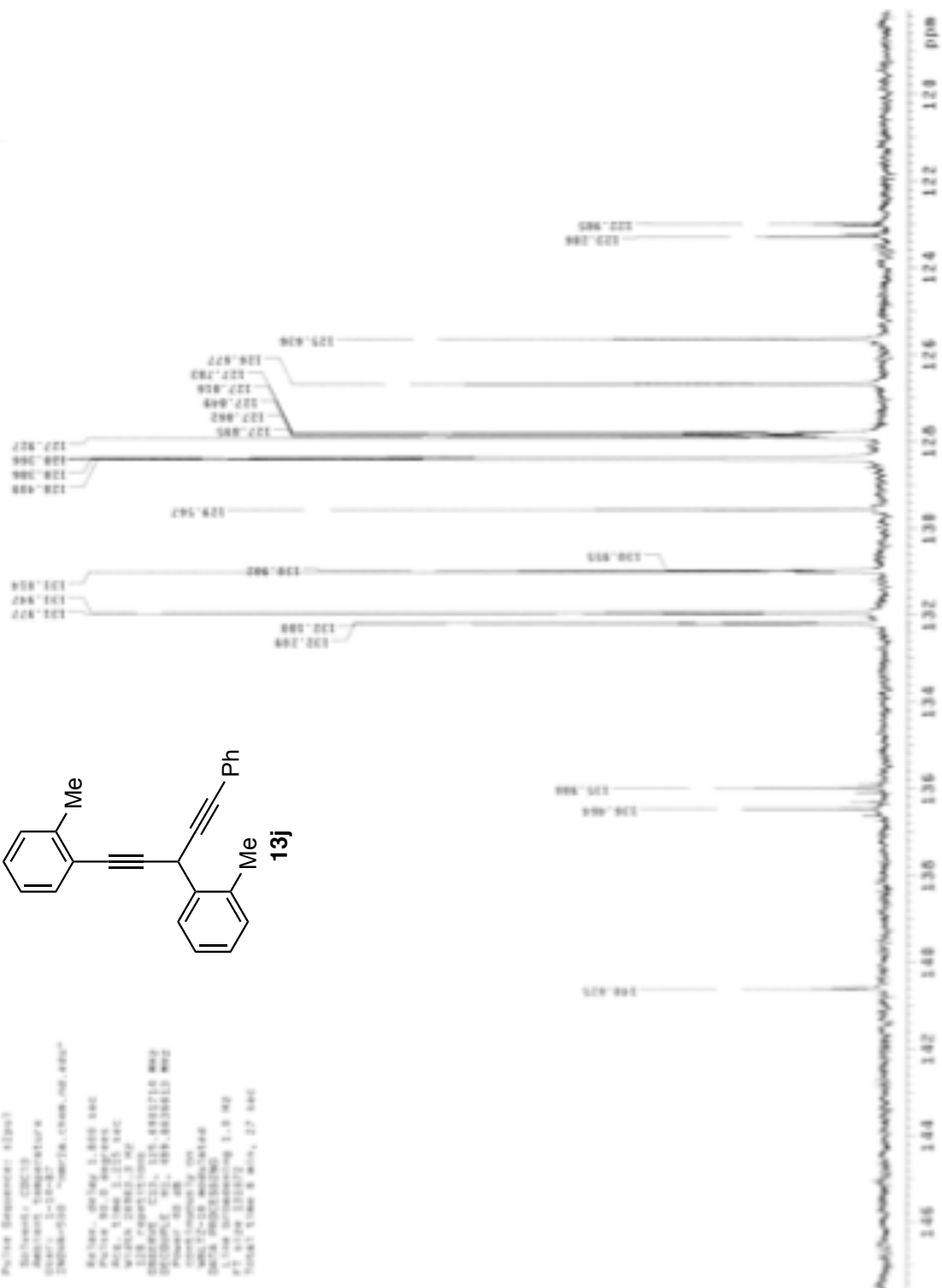


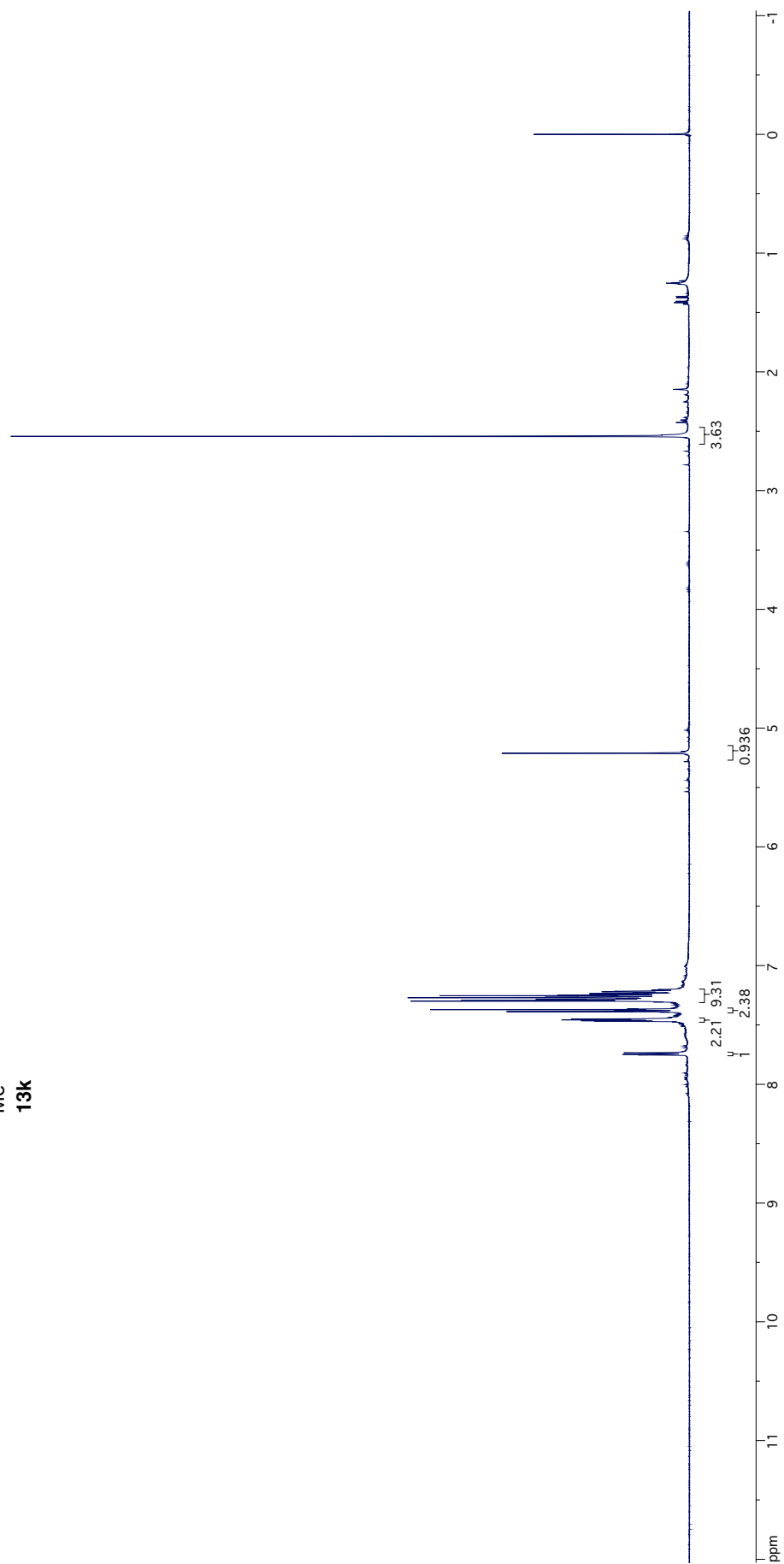
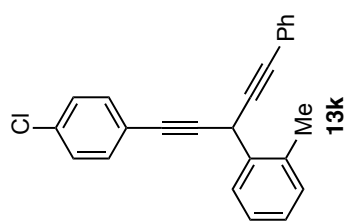


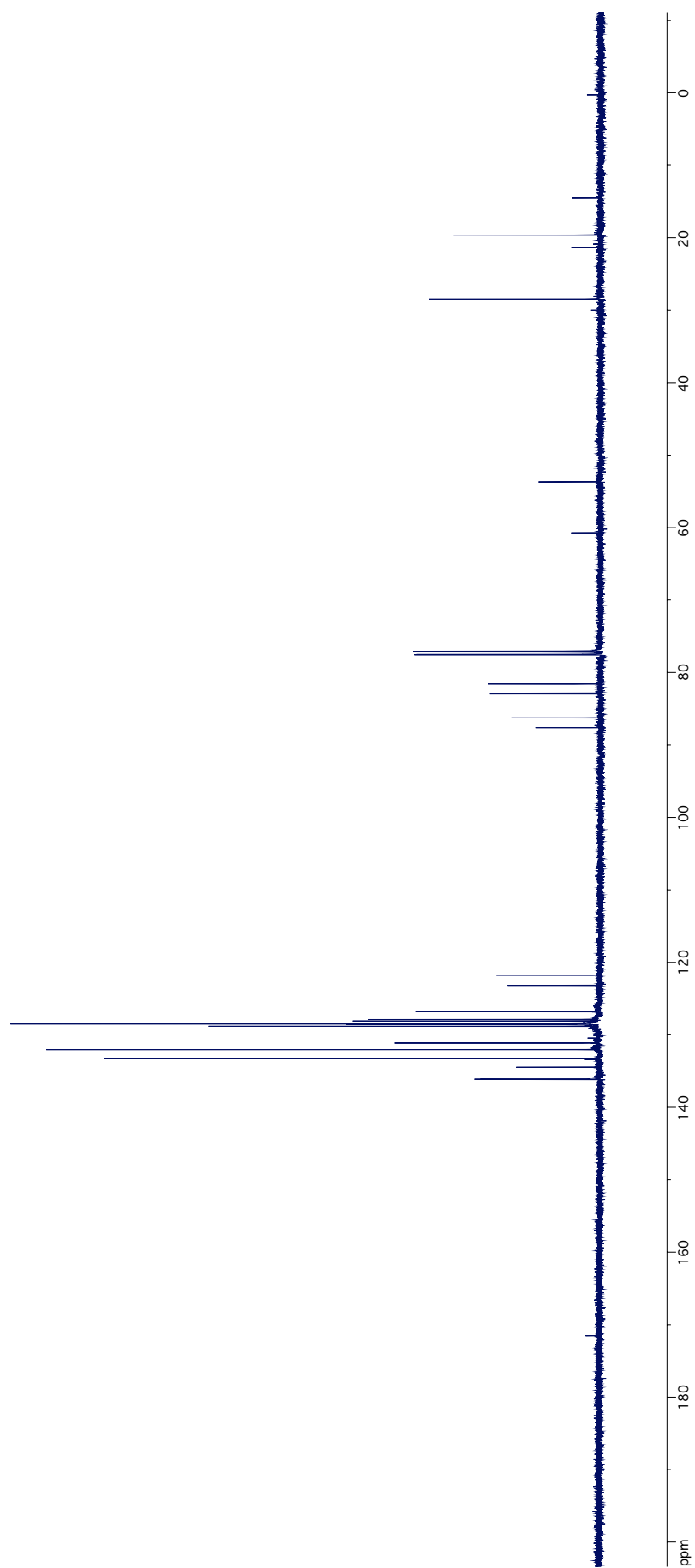
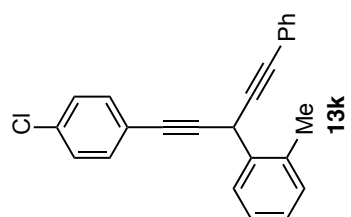
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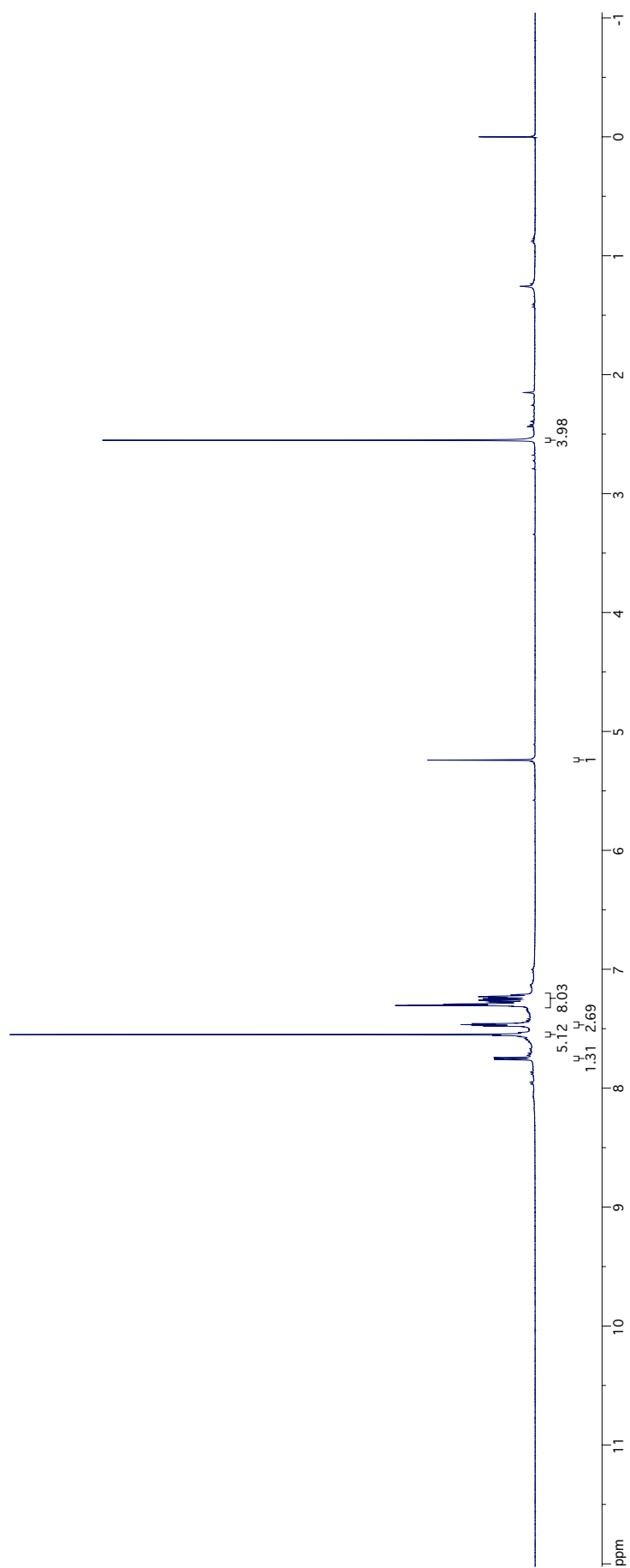
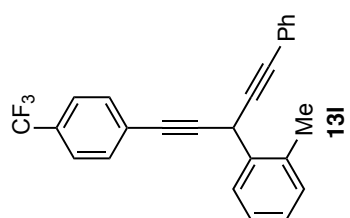
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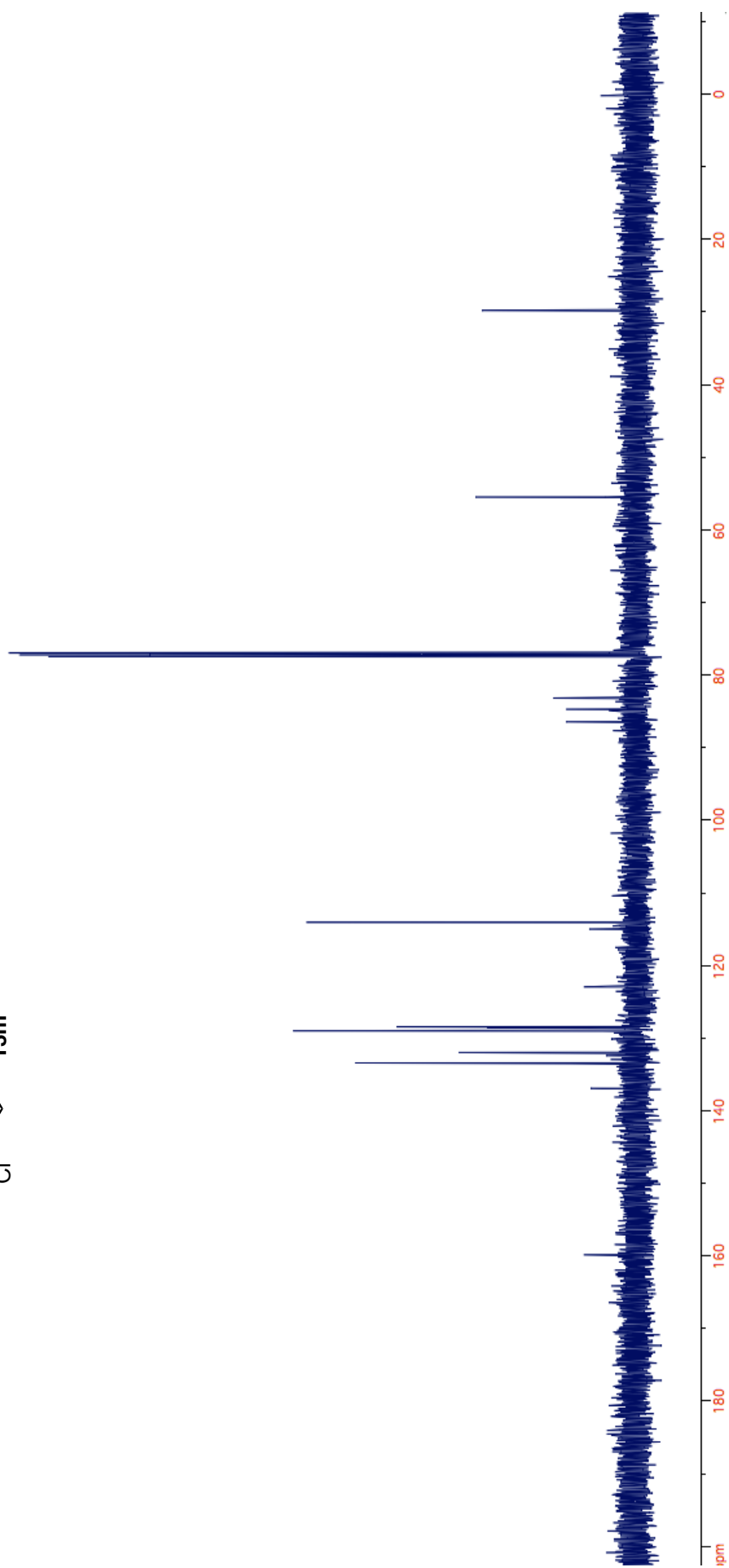
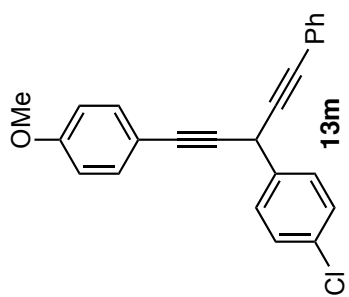


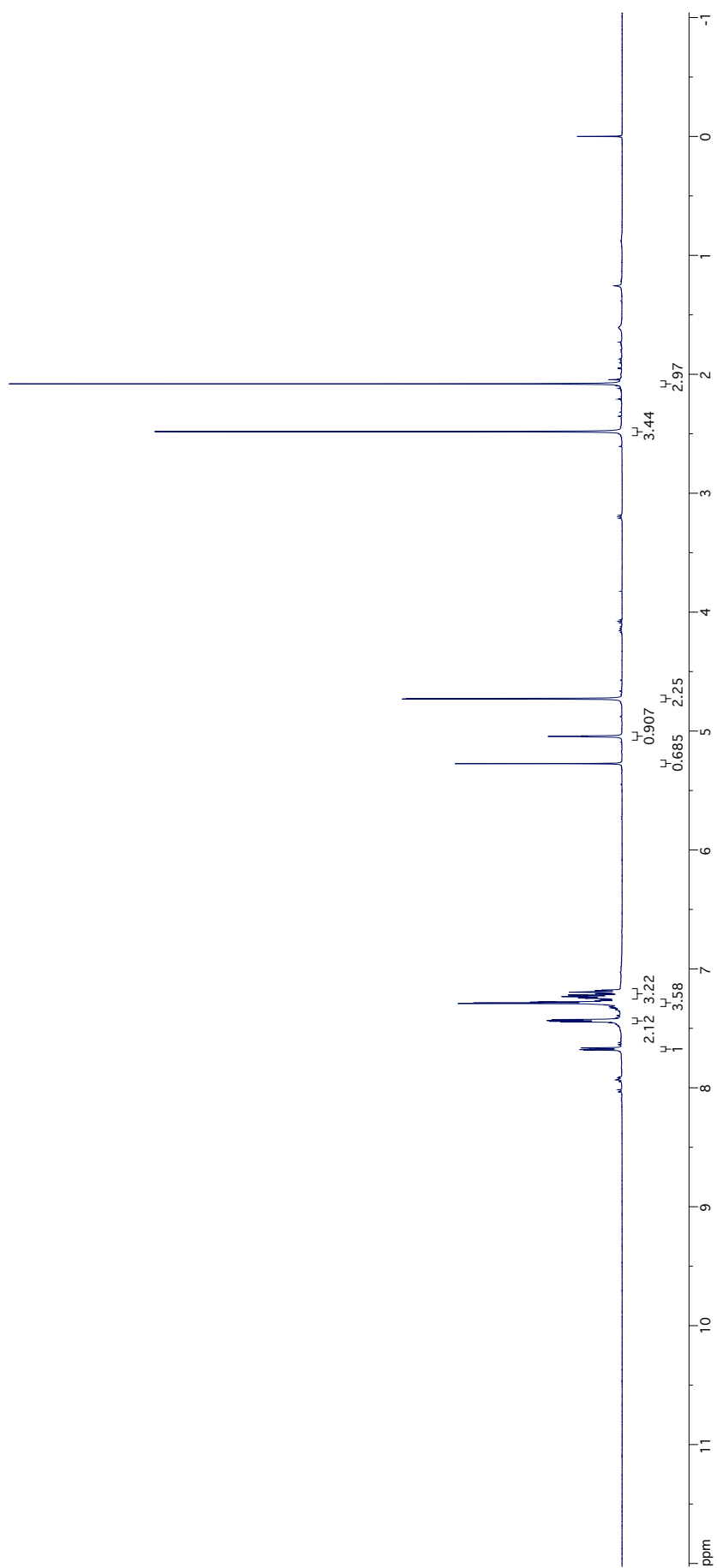
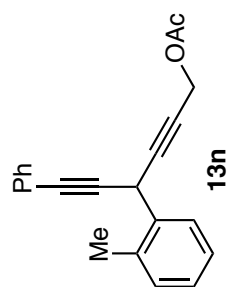


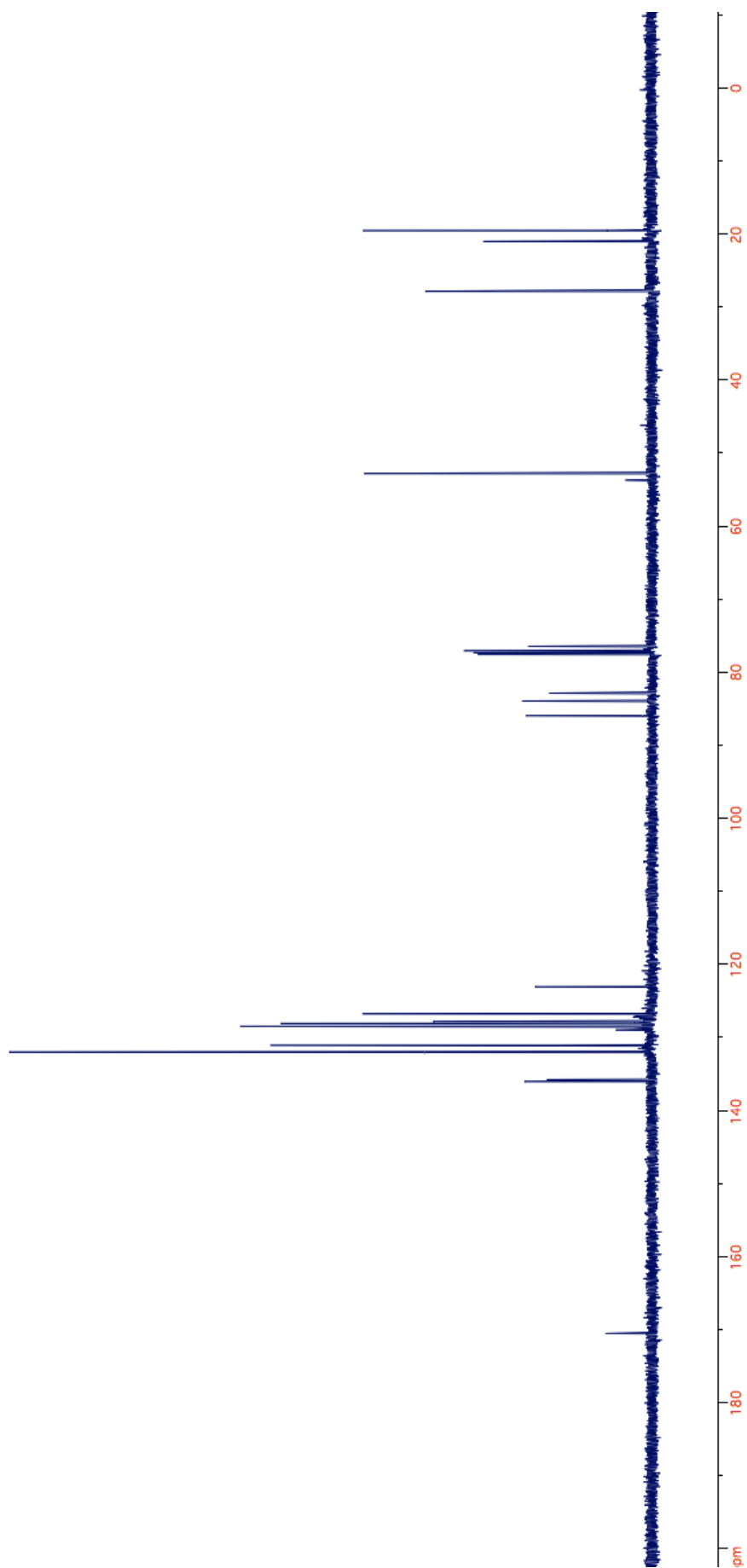
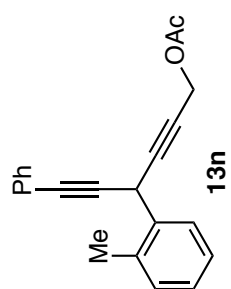


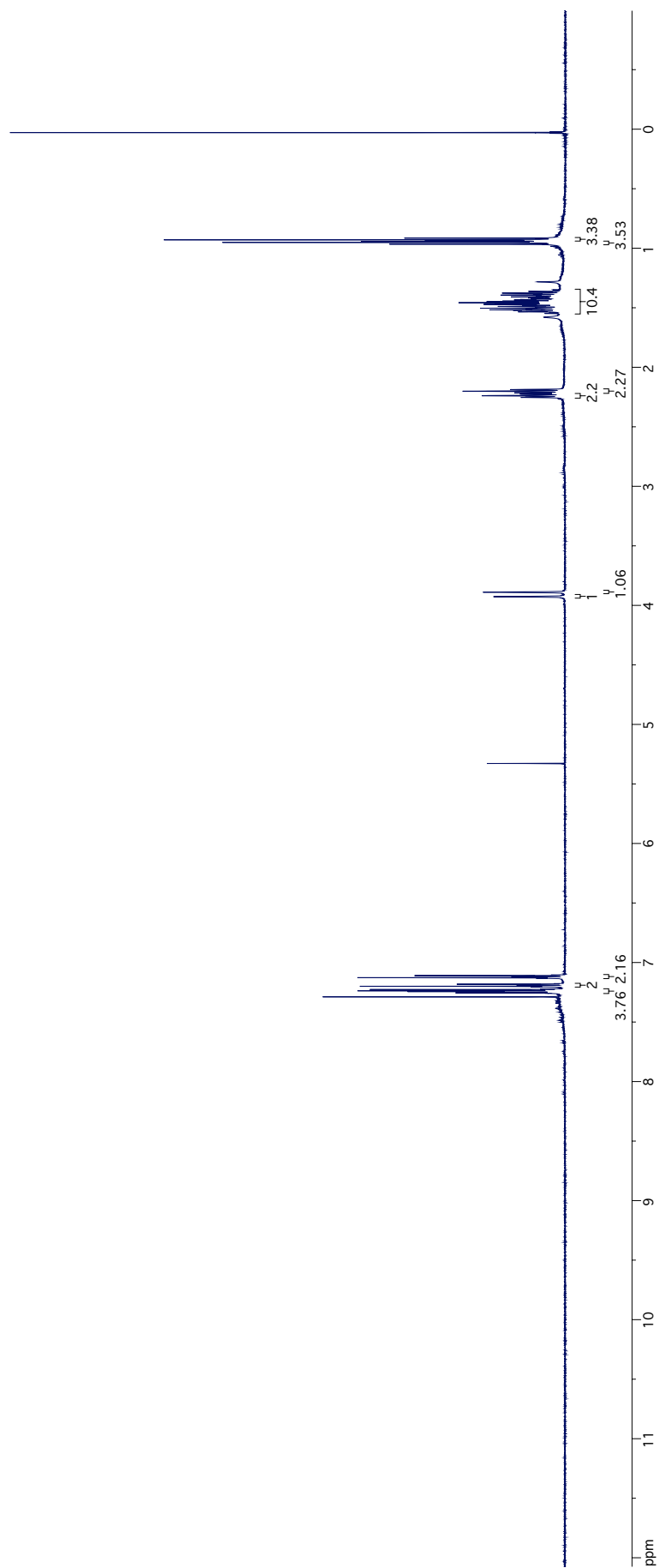
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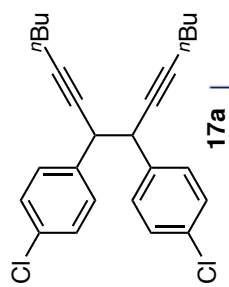




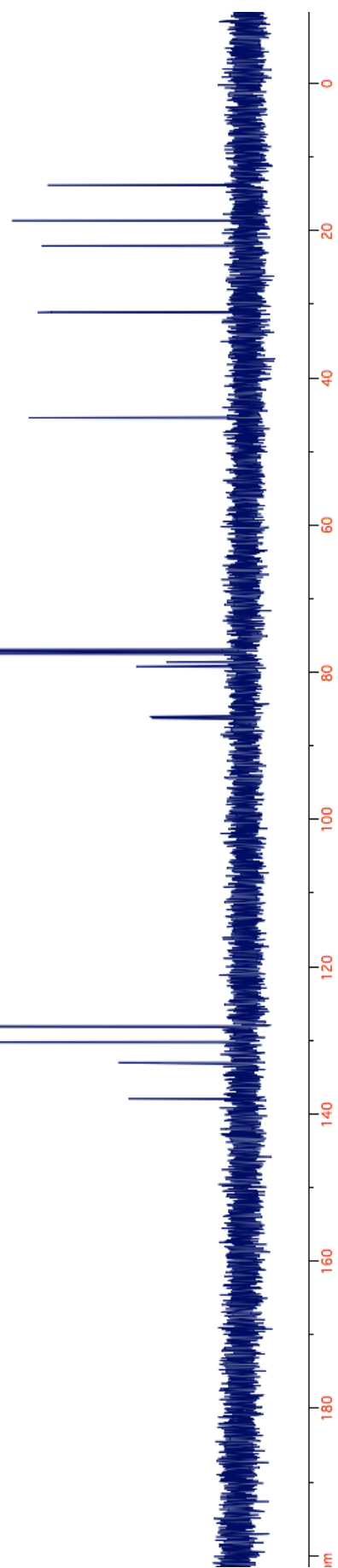


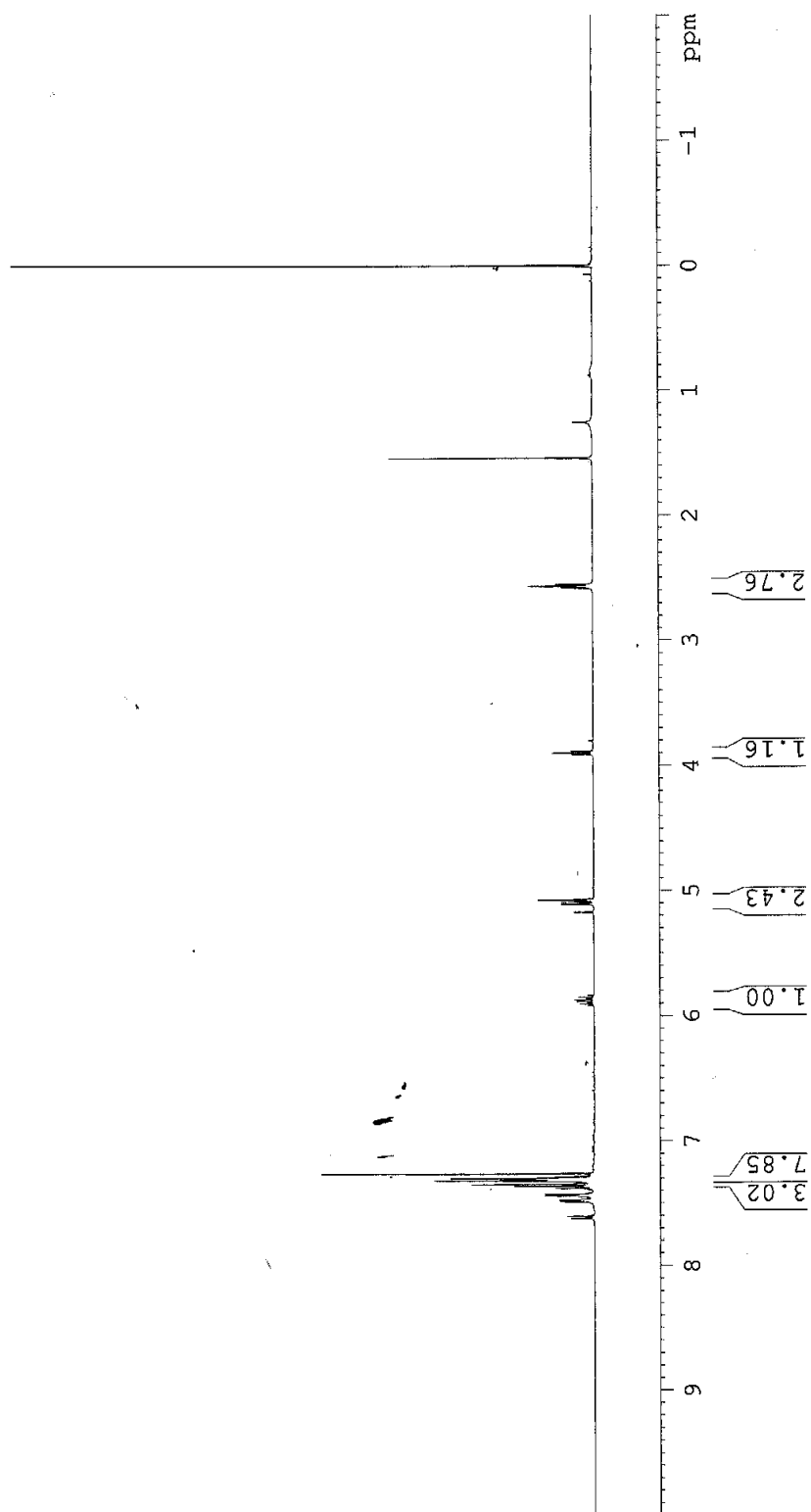
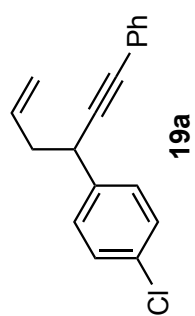


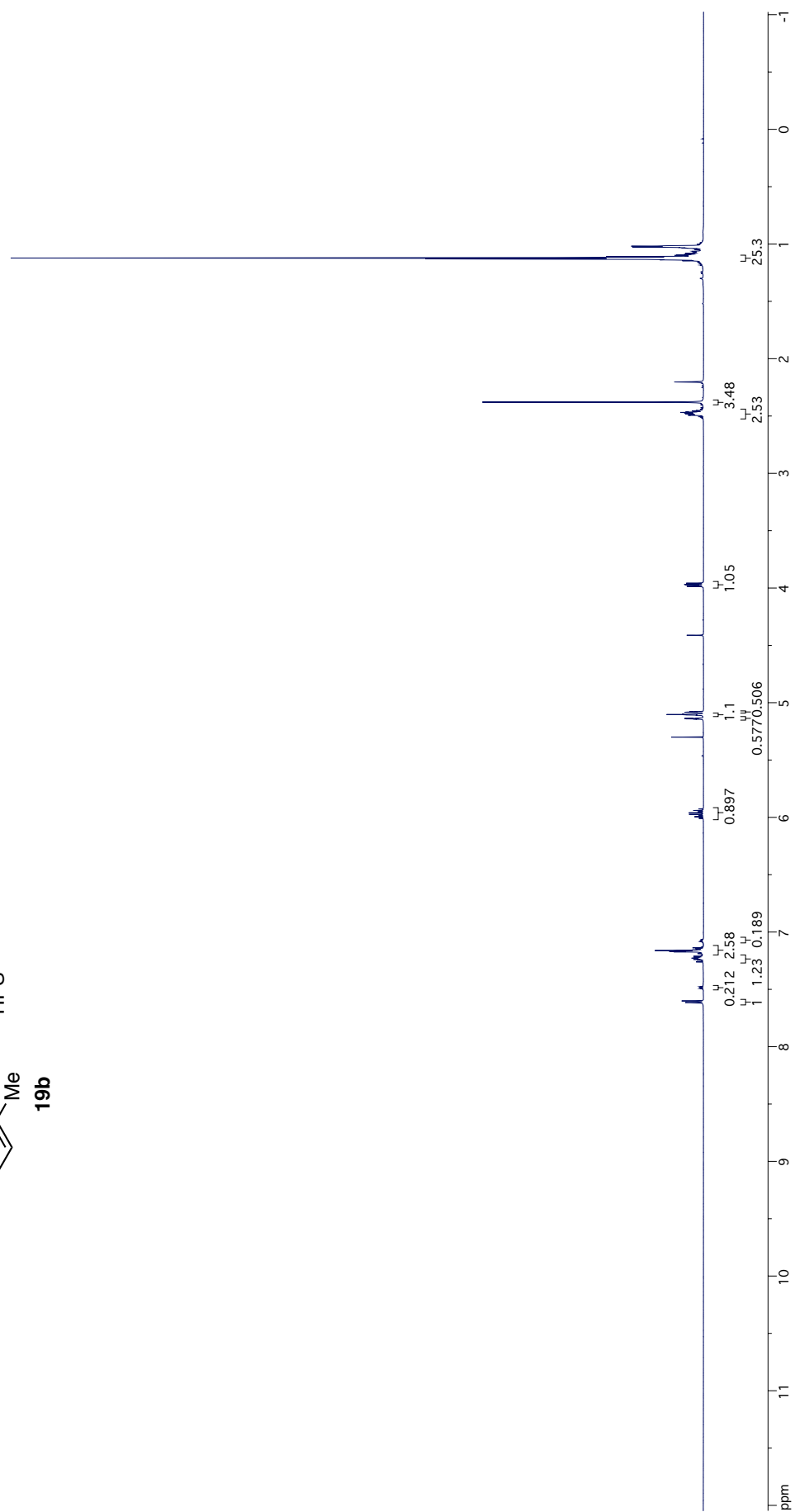
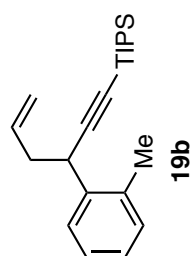




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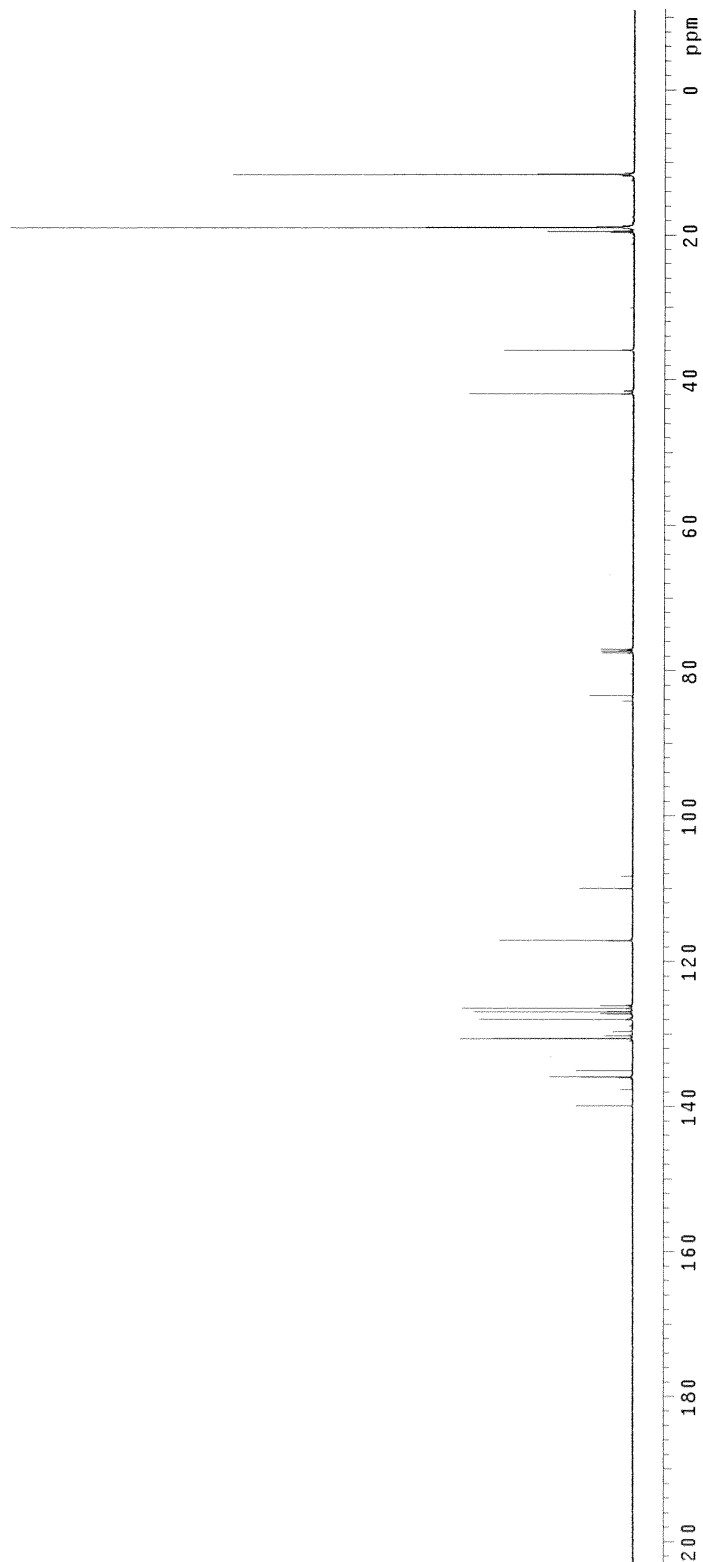
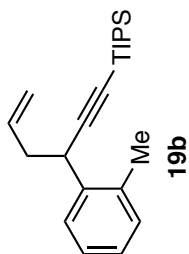


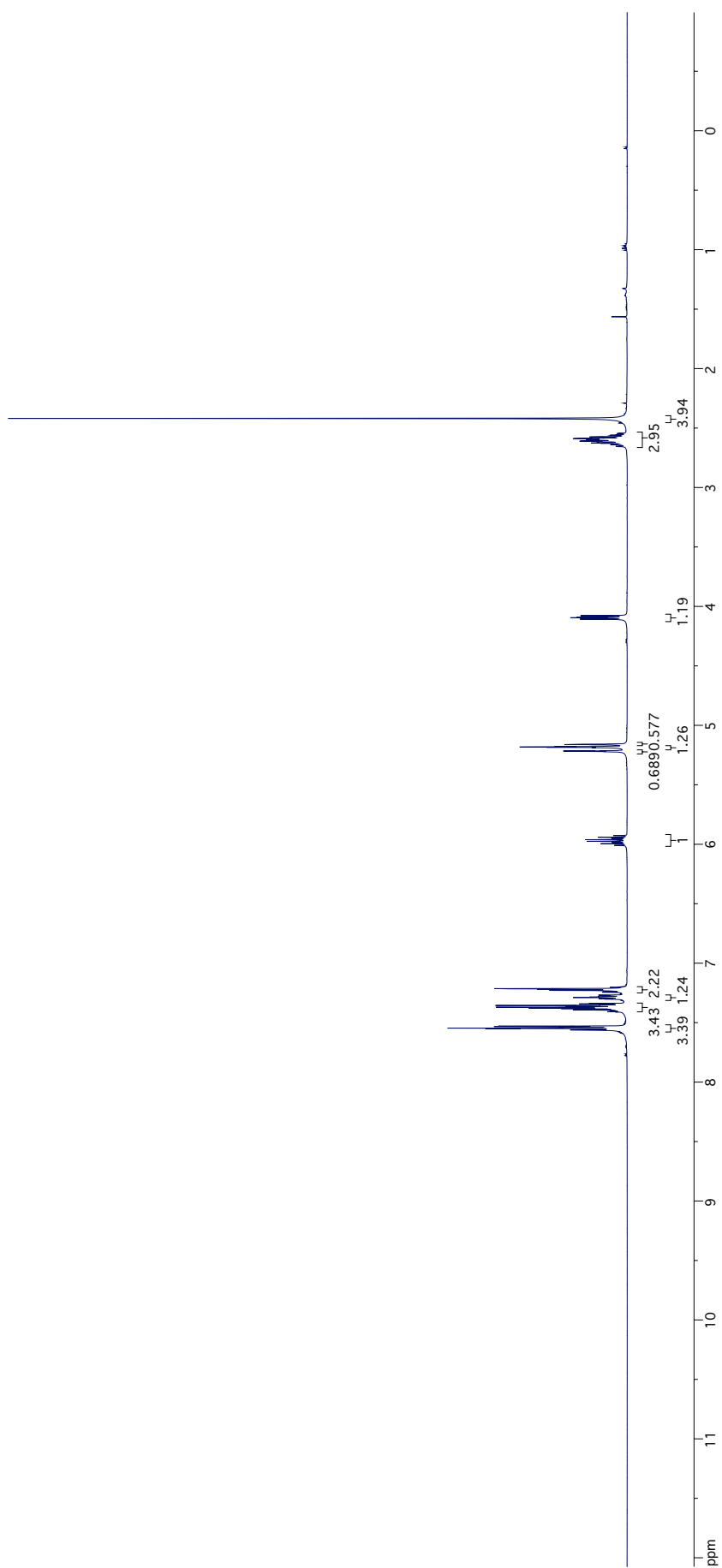
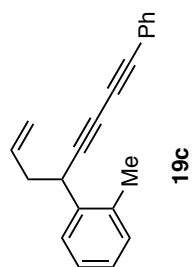


STANDARD PROTON PARAMETERS

Pulse Sequence: s2pul
 Solvent: CDCl₃
 Ambient temperature
 User: 1-14-87
 File: AL1-229-13C
 INOVA-500 "bioch.chem.nd.edu"

Relax. delay 1.800 sec
 Pulse 90.0 degrees
 Acq. time 1.215 sec
 Width 28963.3 Hz
 Observation 13C
 Observation 125.5801591 MHz
 DECOUPLE CH, 493.8636613 MHz
 Power 40 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 131072
 Total time 25 min, 49 sec

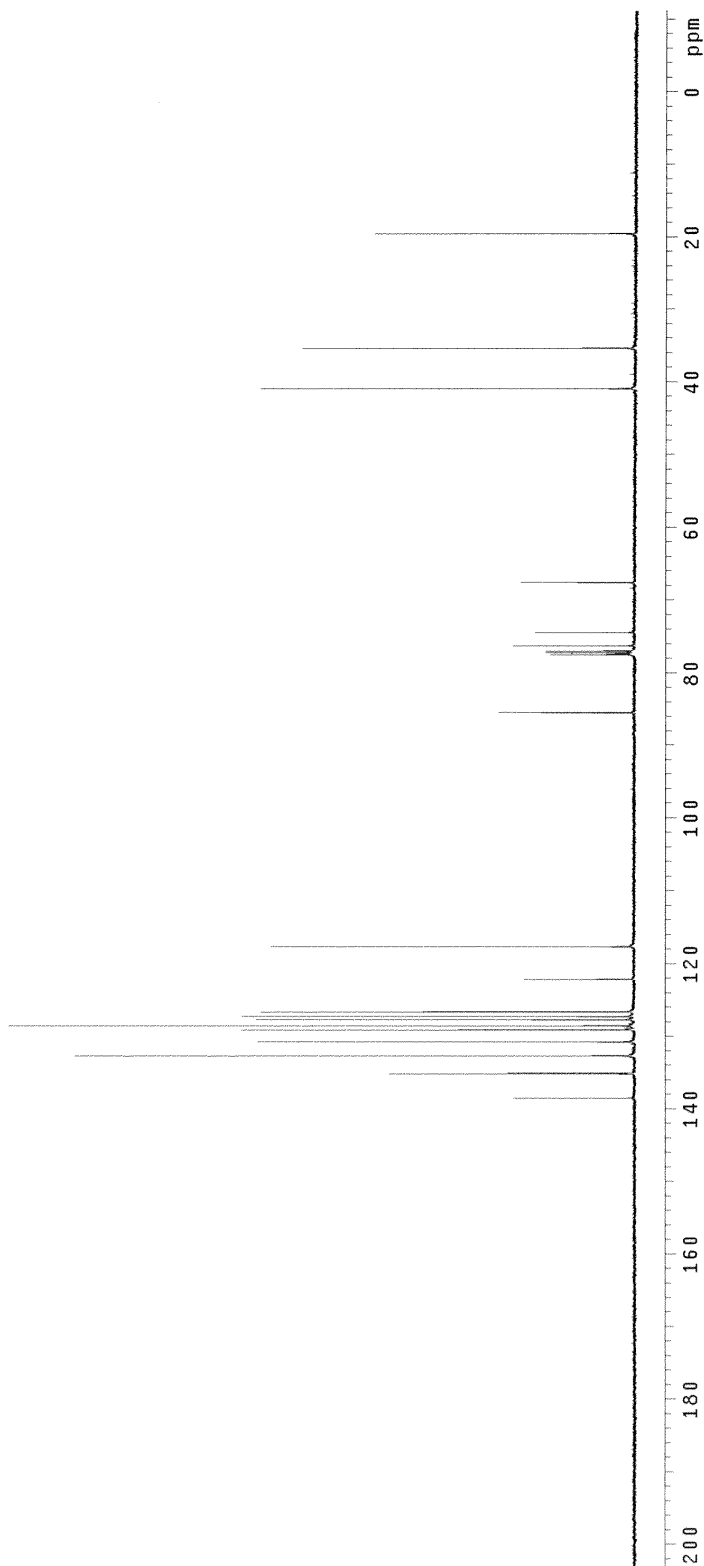
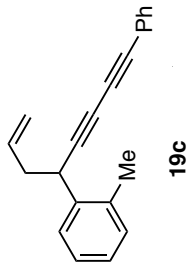


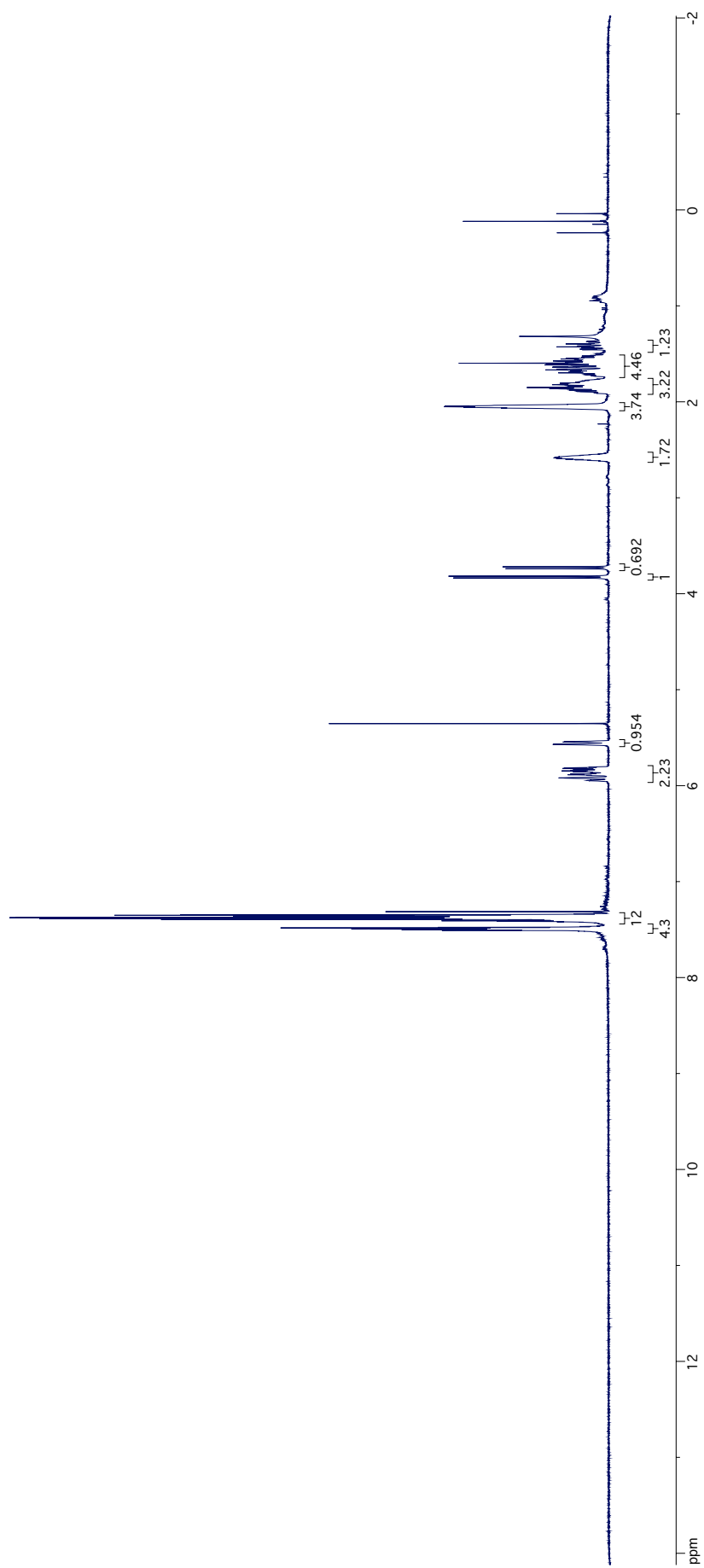
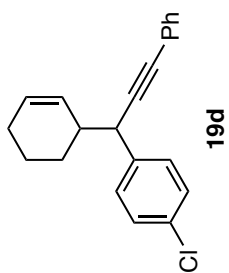


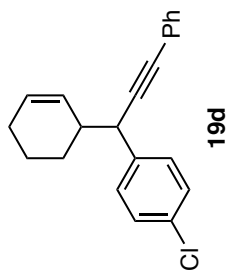
STANDARD PROTON PARAMETERS

Pulse Sequence: s2pu1
 Solvent: CDCl3
 Acquisition time: 1.00 min
 Acquisition temperature: 300 K
 File: AL-2-43.13C
 INOVA-500 "bToch.chem.nd.edu"

Relax. delay 1.800 sec
 Pulse program: zgpg30
 Acquisition: 1.00 min
 Width 28963.3 Hz
 1024 Repetitions
 OBSERVE C13, 125.8901724 MHz
 DECOUPLE H1, 499.8636613 MHz
 Power 40 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 131072
 Total time 51 min, 38 sec







```

F2 - Acquisition Parameters
Date_ 20121016
Time_ 12.49
INSTRUM spect
PROBHD 5 mm Nalorac B
PULPROG zgdc
TD 65536
SOLVENT CDCl3
NS 261
DS 2
SWH 24271.844 Hz
FIDRES 0.370359 Hz
AQ 1.3500416 sec
RG 1149.4
DE 20.600 usec
TE 294.7 K
D1 1.6499998 sec
d11 0.0300000 sec
TD0 1

```

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===== CHANNEL f1 =====
NUC1 13C
P1 10.30 usec
PL1 1.00 dB
SFO1 100.6238269 MHz

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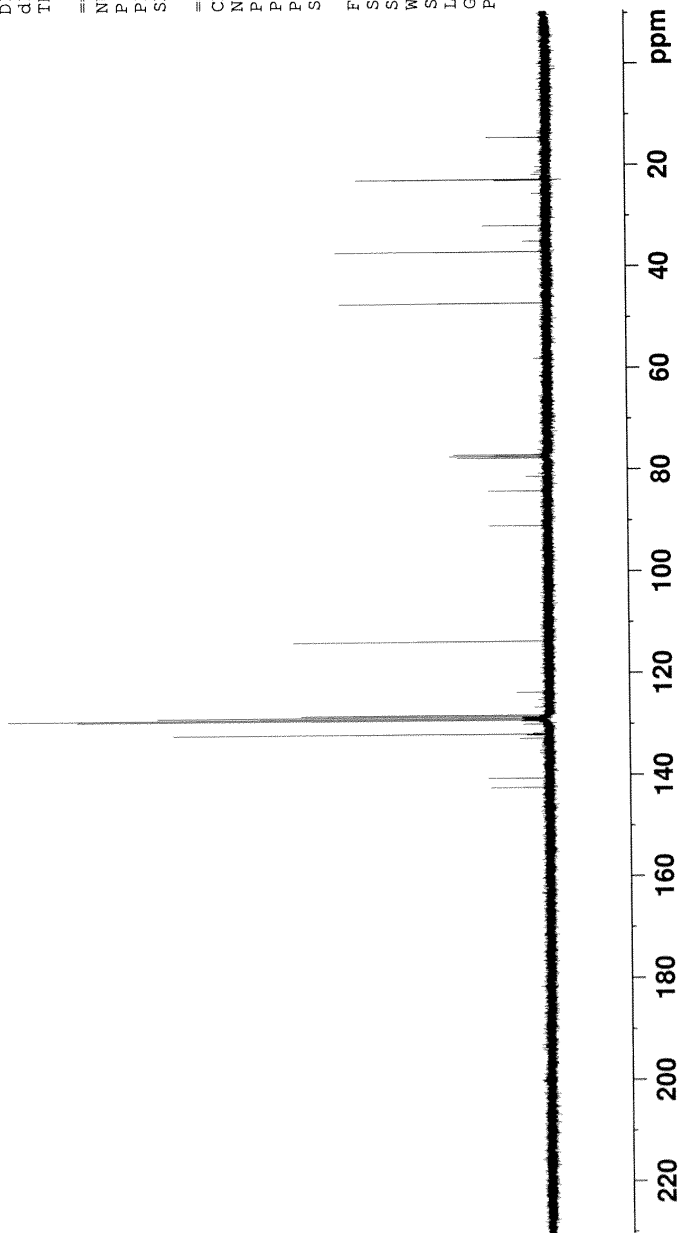
===== CHANNEL f2 =====
CPDPRG[2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.75 dB
PL12 15.61 dB
SFO2 400.1316005 MHz

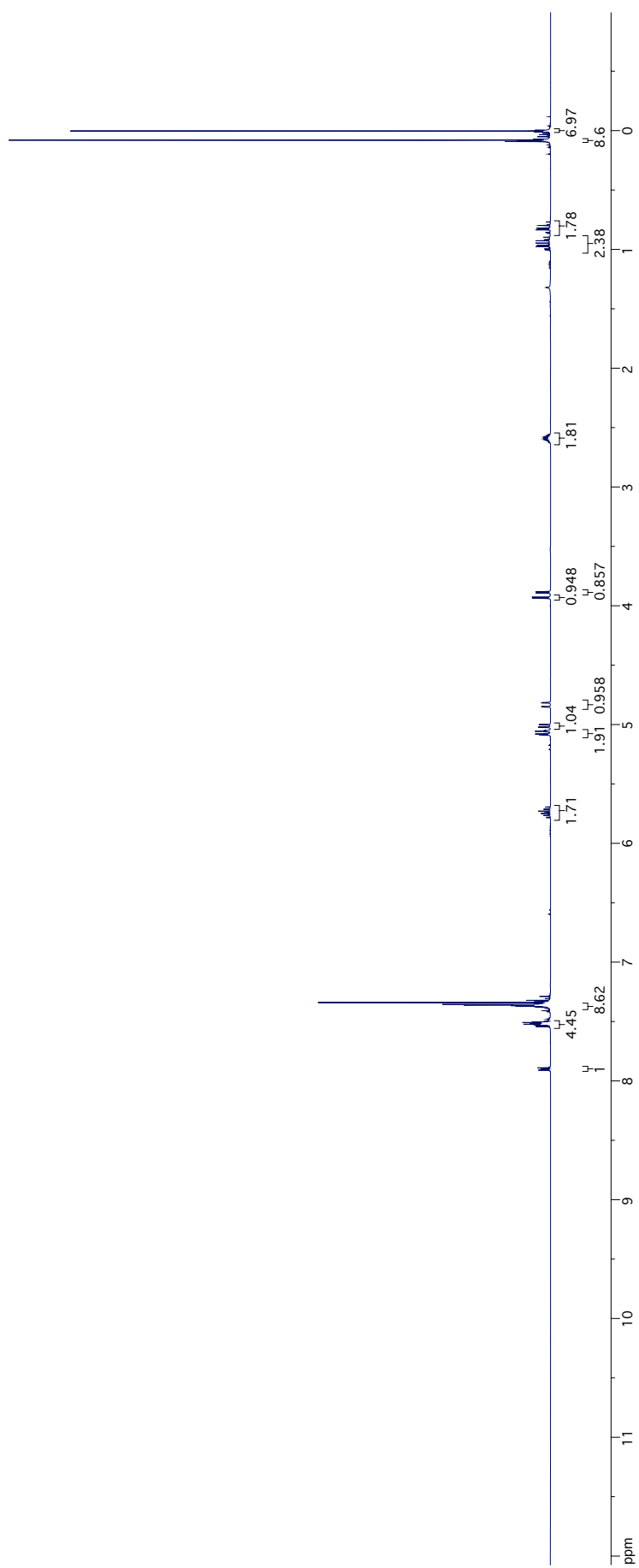
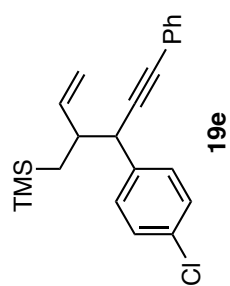
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F2 - Processing parameters
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WDW no
SSB 0
LB 0 Hz
GB 0
PC 1.00

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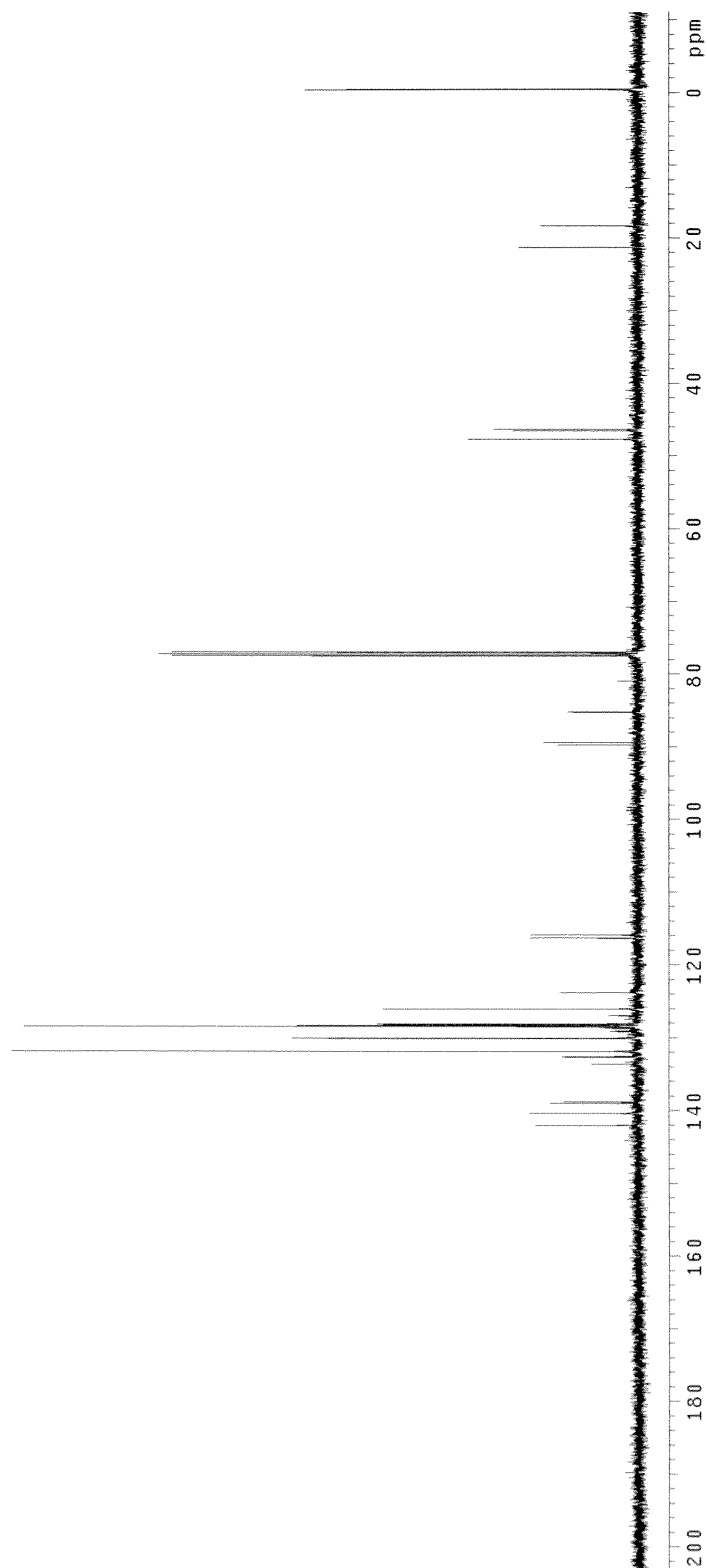
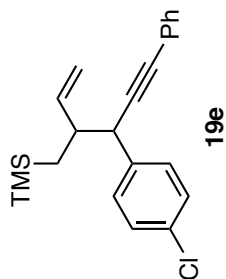


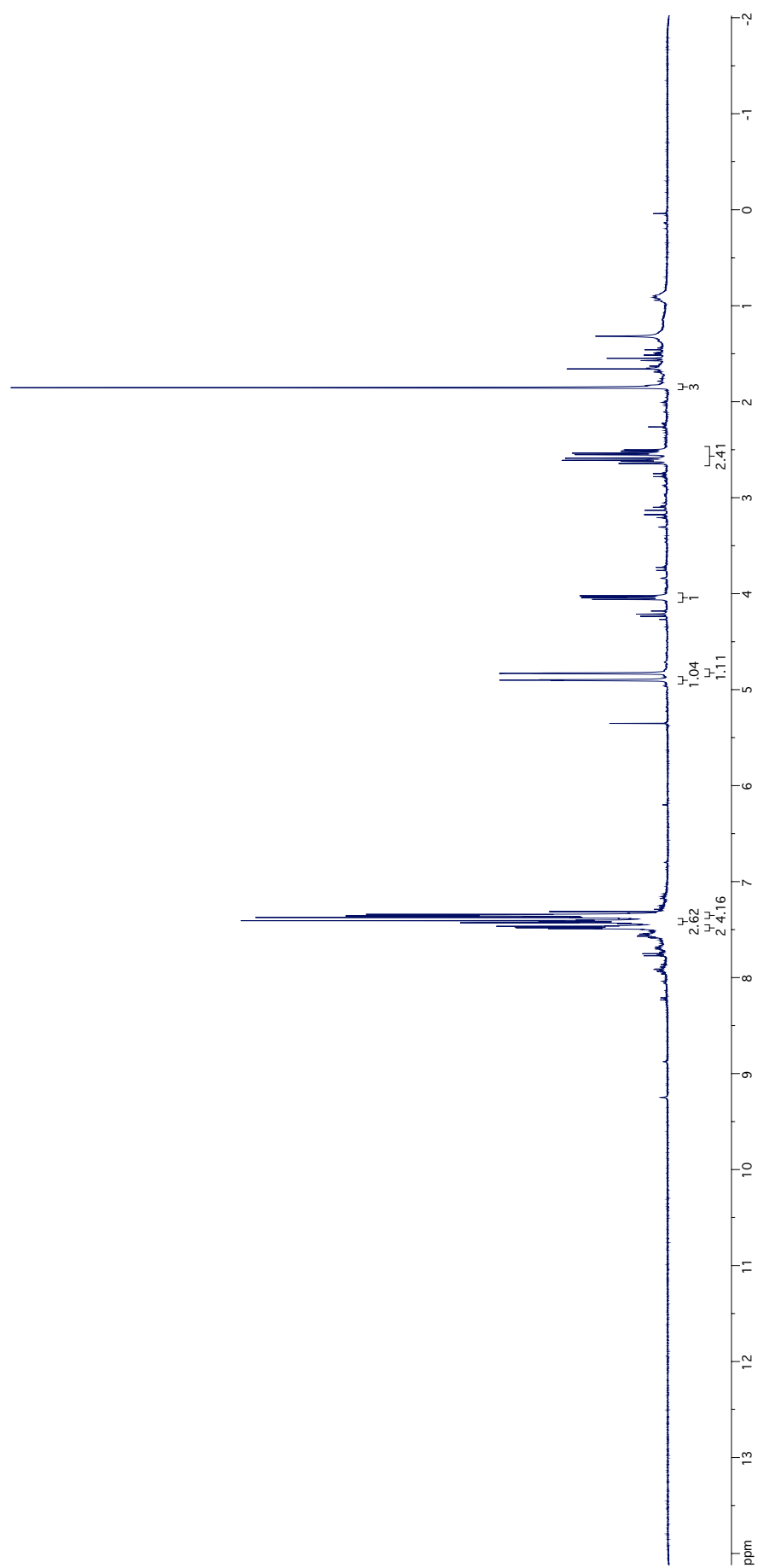
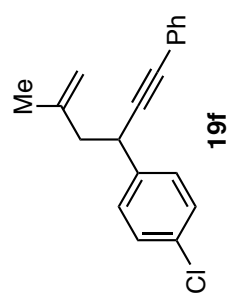


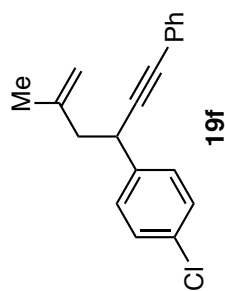
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Pulse Sequence: s2pu1
Solvent: CDCl3
Ambient temperature
User: 1-14-87
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Relax. delay 1.800 sec
Pulse 90.0 degrees
Acq. time 1.215 sec
Width 28903.3 Hz
SOLVENT DEPTHS 10
13C DEPT 135
DECOUPLE CH1, 155.6901588 MHz
Power 40 dB, 159.865613 MHz
CONTINUOUS IY ON
WAIT2=16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 51 min, 36 sec

```







```

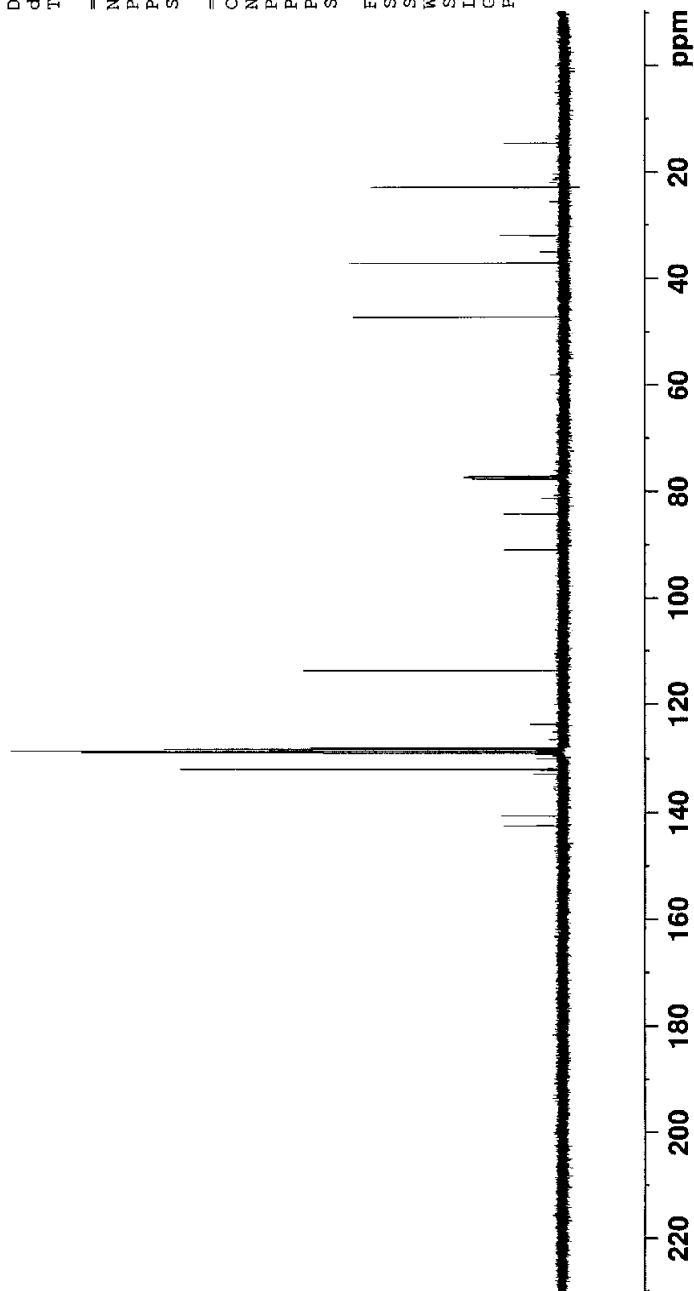
F2 - Acquisition Parameters
Date_      20121016
Time       12.49
INSTRUM    spect
PROBHD     5 mm Nalorac B
PULPROG    zgdc
TD         65536
SOLVENT    CDCl3
NS         261
DS         2
SWH        24271.844 Hz
FIDRES     0.370359 Hz
AQ         1.3500416 sec
RG         1149.4
DW         20.600 usec
DE         6.00 usec
TE         294.7 K
d1         1.64999998 sec
d11        0.03000000 sec
TD0        1

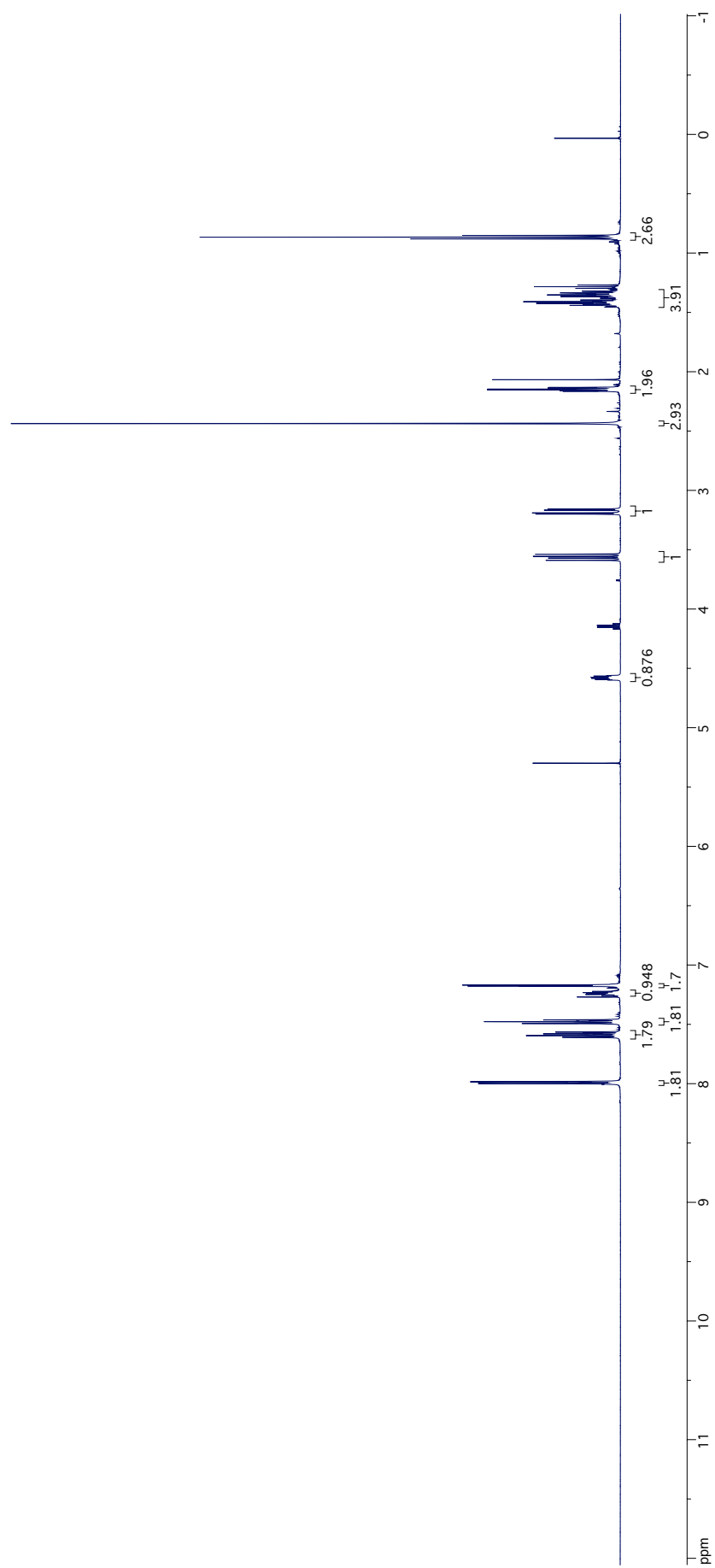
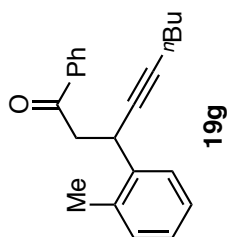
===== CHANNEL f1 =====
NUC1       13C
P1         10.30 usec
PL1        1.00 dB
SFO1       100.6238269 MHz

===== CHANNEL f2 =====
CPDPRG[2   waltz16
NUC2       1H
PCPD2      90.00 usec
PL2        -1.75 dB
PL12       15.61 dB
SFO2       400.1316005 MHz

F2 - Processing parameters
SI         65536
SF         100.6127496 MHz
WDW        no
SSB        0
LB         0 Hz
GB         0
PC         1.00

```

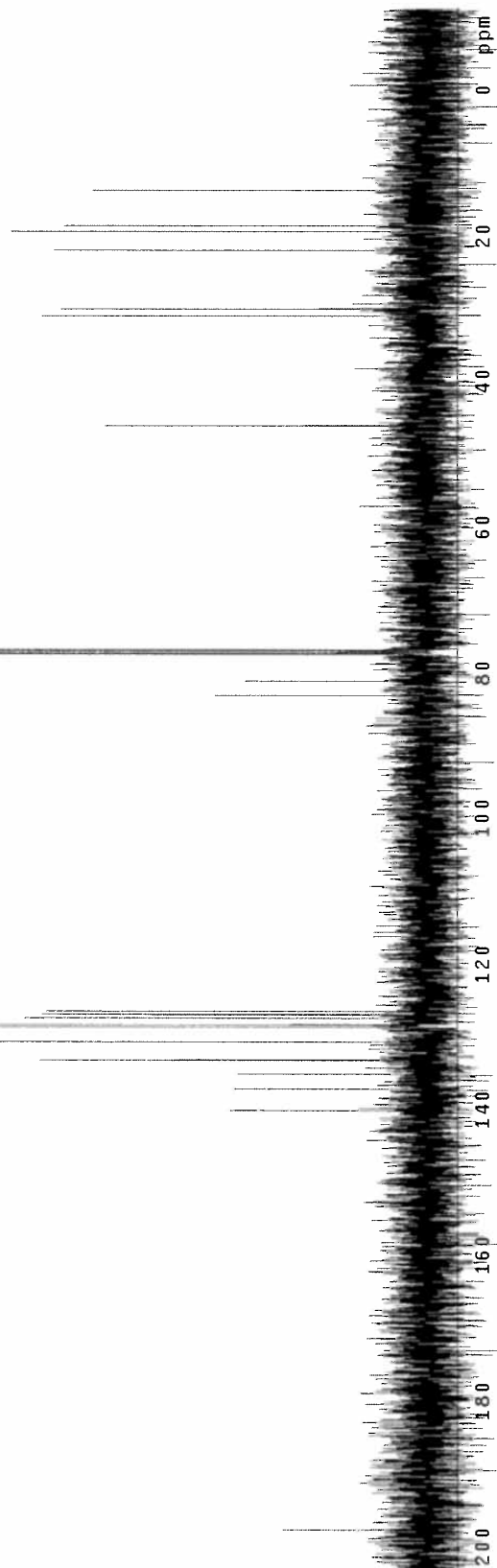
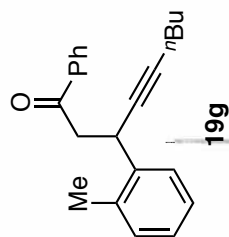


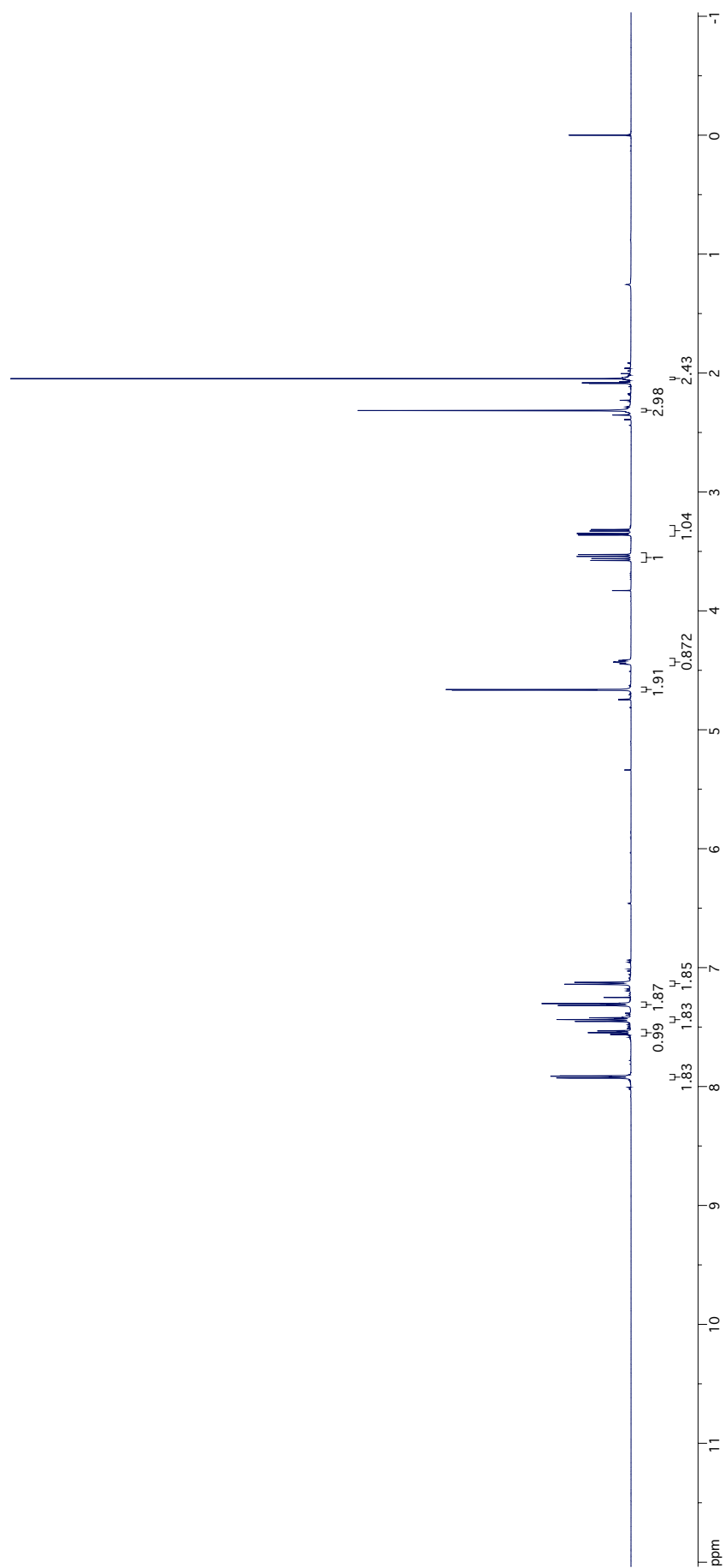
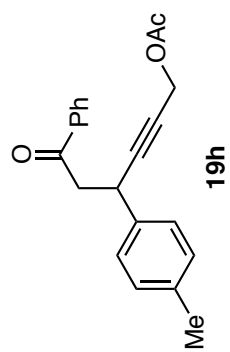


STANDARD PROTON PARAMETERS

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 User: 12-14-87
 INOVA-500 "nmr2a.chem.nd.edu"

Relax. delay 1.800 sec
 Pulse 90.0 degrees
 Acq. time 1.215 sec
 Width 26963.3 Hz
 128 repetitions
 OBSERVE C13, 125.6901698 MHz
 DECOUPLE H1, 499.8636613 MHz
 Power 40 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FI size 131072
 Total time 6 min, 27 sec

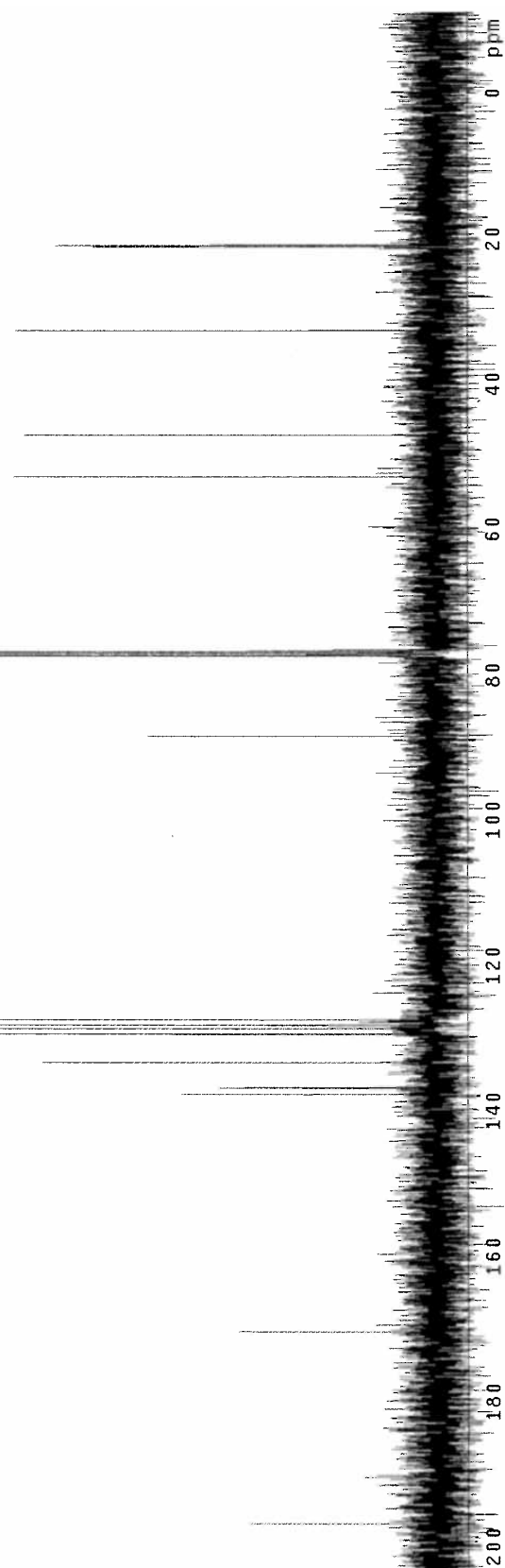
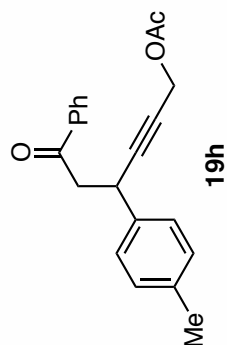


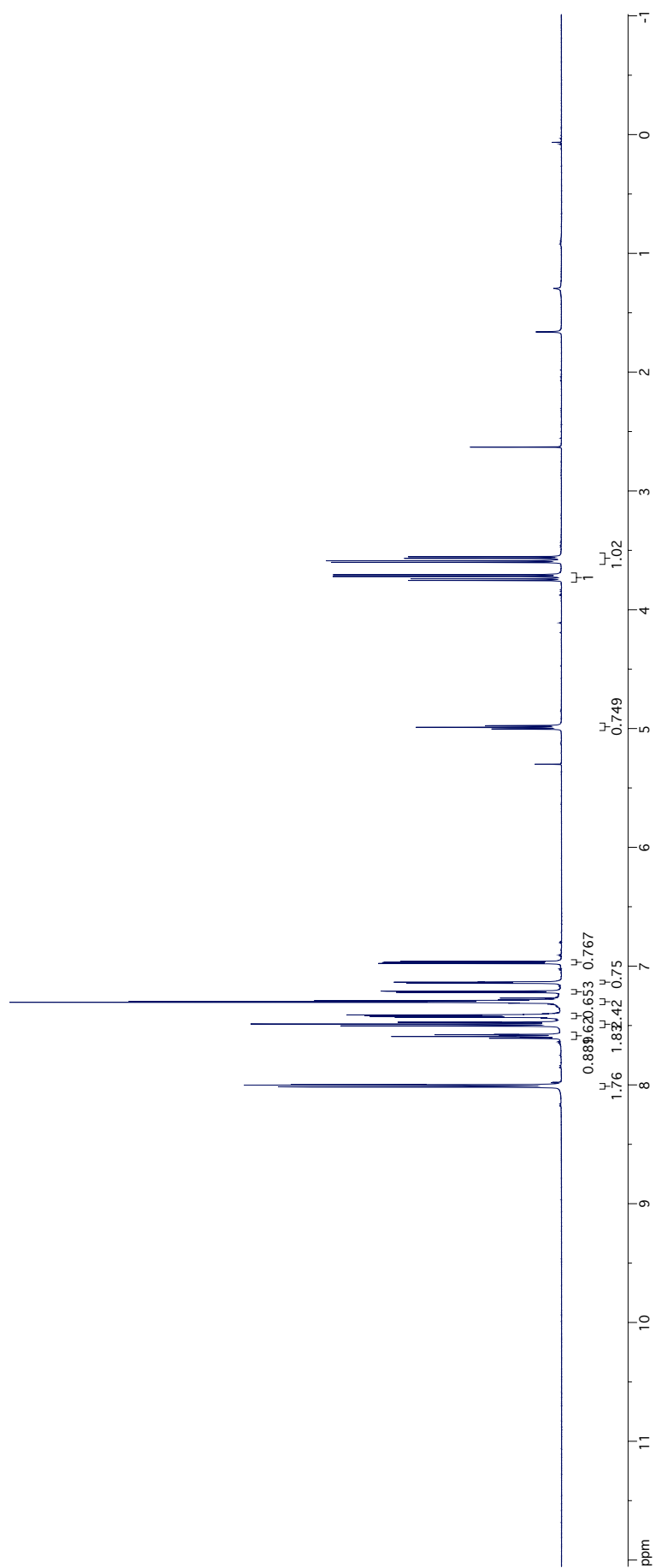
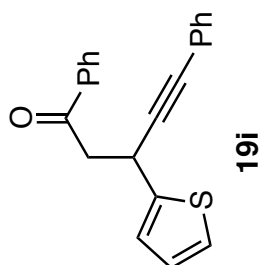


STANDARD PROTON PARAMETERS

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 User: 1-14-87
 INOVA-500 "nmr2a.chem.nd.edu"

Relax. delay 1.800 sec
 Pulse 90.0 degrees
 Acq. time 1.215 sec
 Width 26963.3 Hz
 128 repetitions
 OBSERVE C13, 125.6901714 MHz
 DECOUPLE H1, 499.8636613 MHz
 Power 40 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 131072
 Total time 6 min, 27 sec

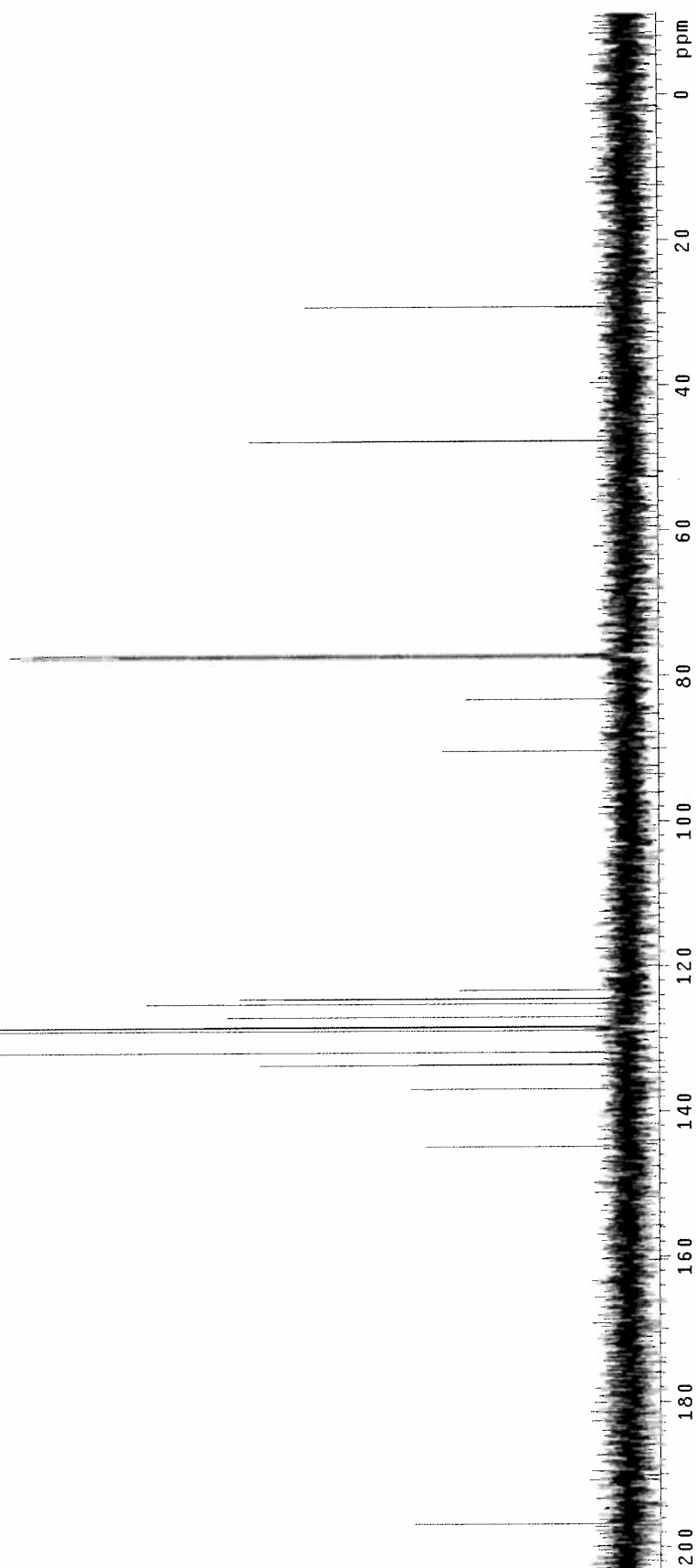
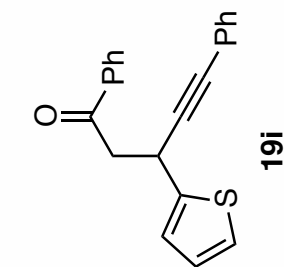


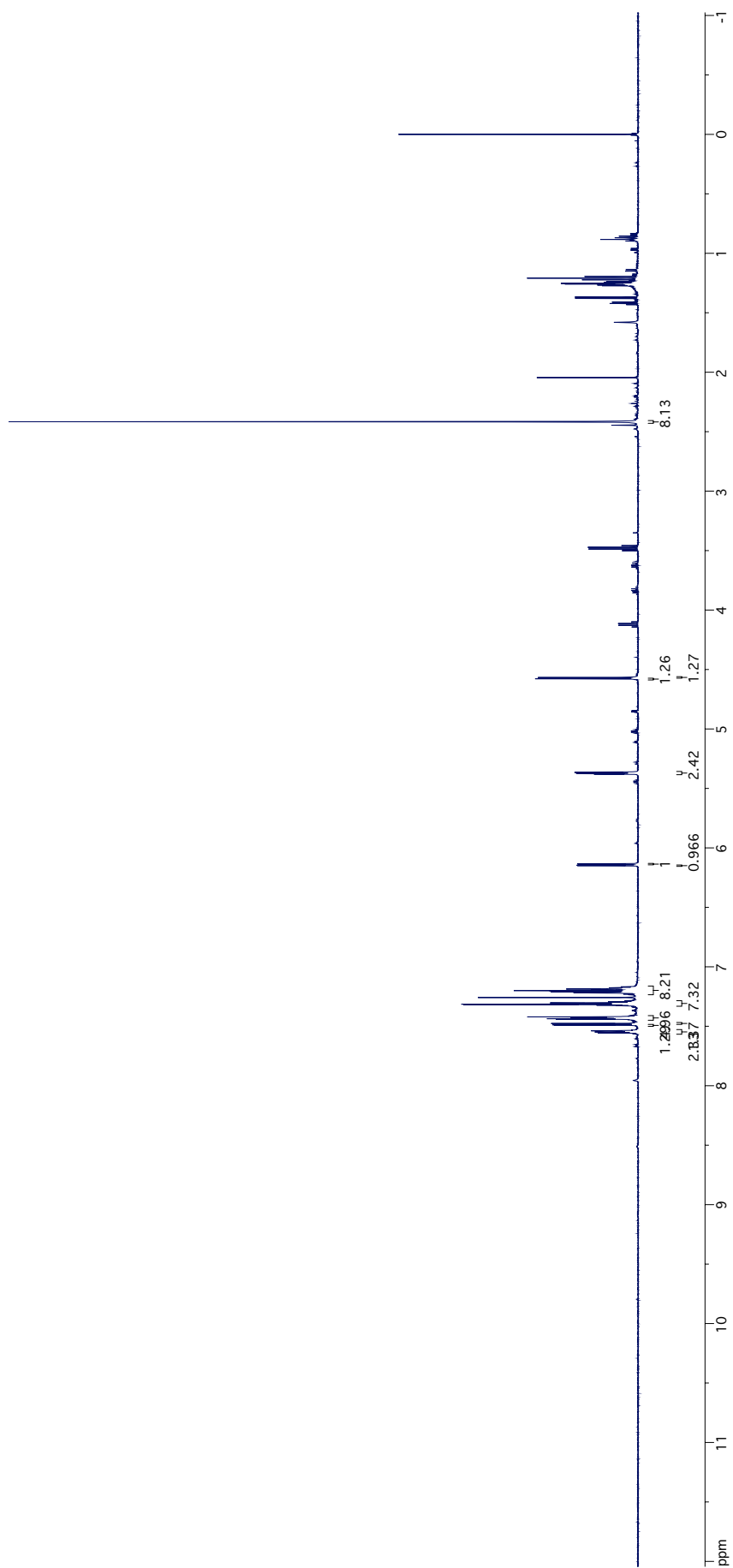
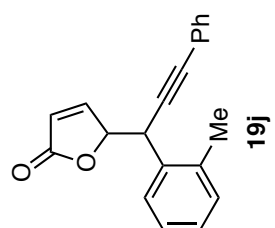


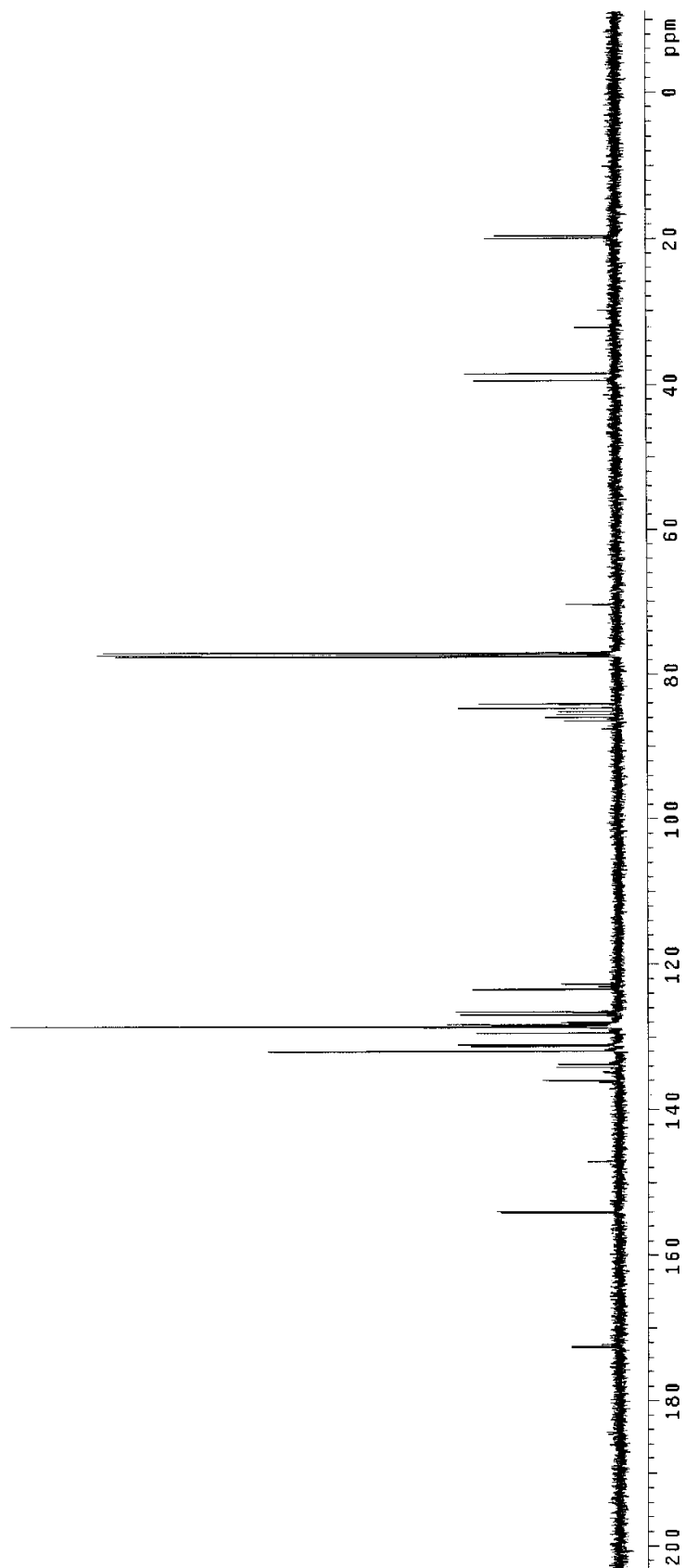
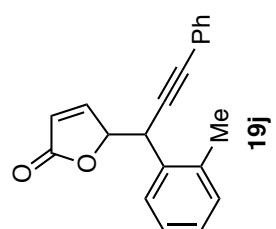
STANDARD PROTON PARAMETERS

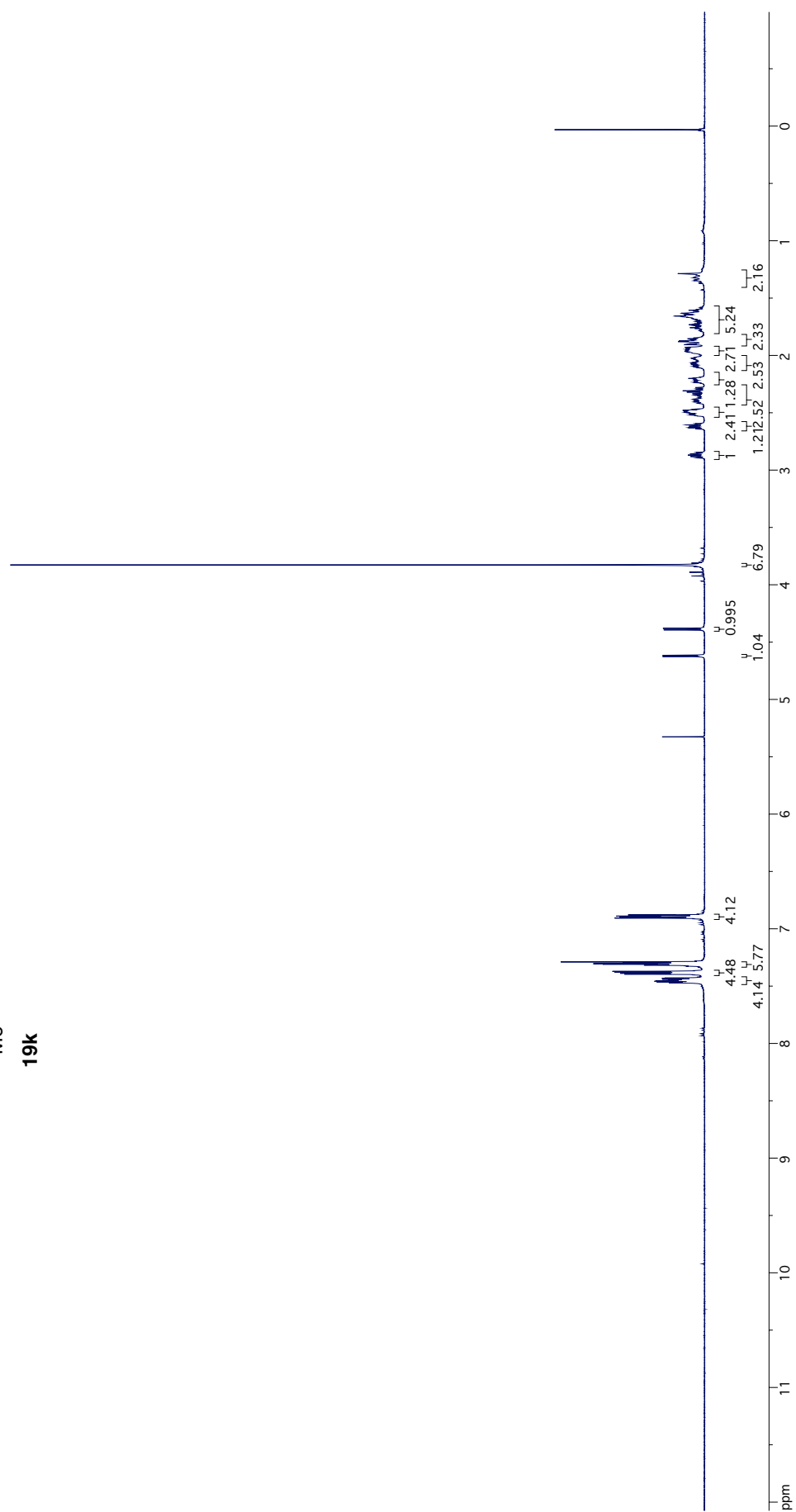
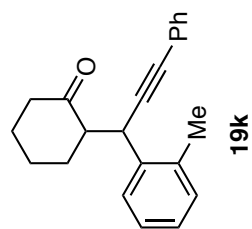
Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 User: 1-14-87
 INOVA-500 "nmr2a.chem.nd.edu"

Relax. delay 1.800 sec
 Pulse 90.0 degrees
 Acq. time 1.235 sec
 Width 28963.3 Hz
 128 repetitions
 OBSERVE C13, 125.6901747 MHZ
 DECOUPLE H1, 499.8636613 MHZ
 Power 10 dB
 Continuously on
 WALTZ16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FI size 131072
 Total time 6 min, 27 sec





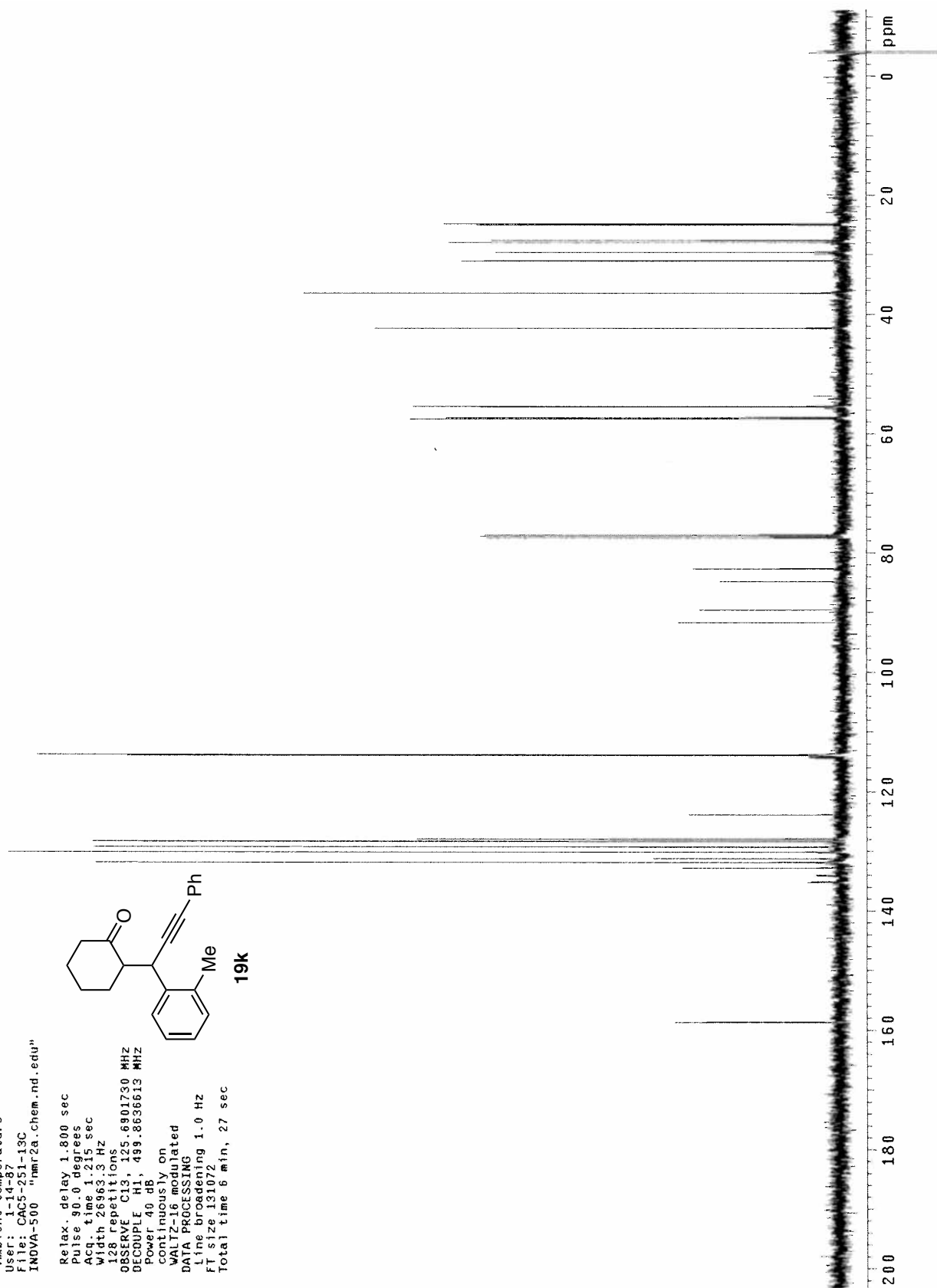
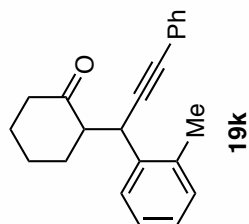


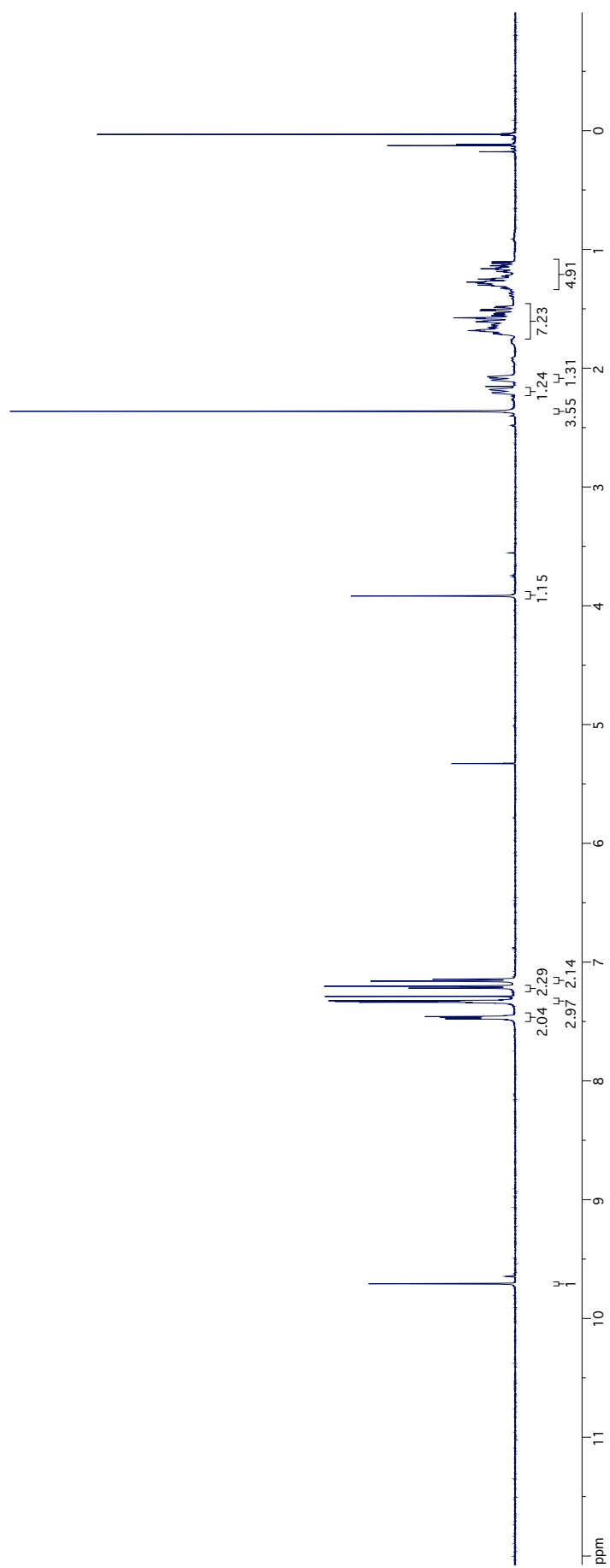
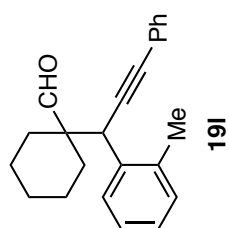


STANDARD PROTON PARAMETERS

Pulse Sequence: s2pu1
Solvent: CDCl3
Ambient temperature
User: 1-14-87
File: CAC5-251-13C
INOVA-500 "nmr2a.chem.nd.edu"

Relax. delay 1.800 sec
Pulse 90.0 degrees
Acq. time 1.215 sec
Width 28963.3 Hz
128 repetitions
OBSERVE C13, 125.6901730 MHz
DECOUPLE H1, 499.8636613 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 6 min, 27 sec

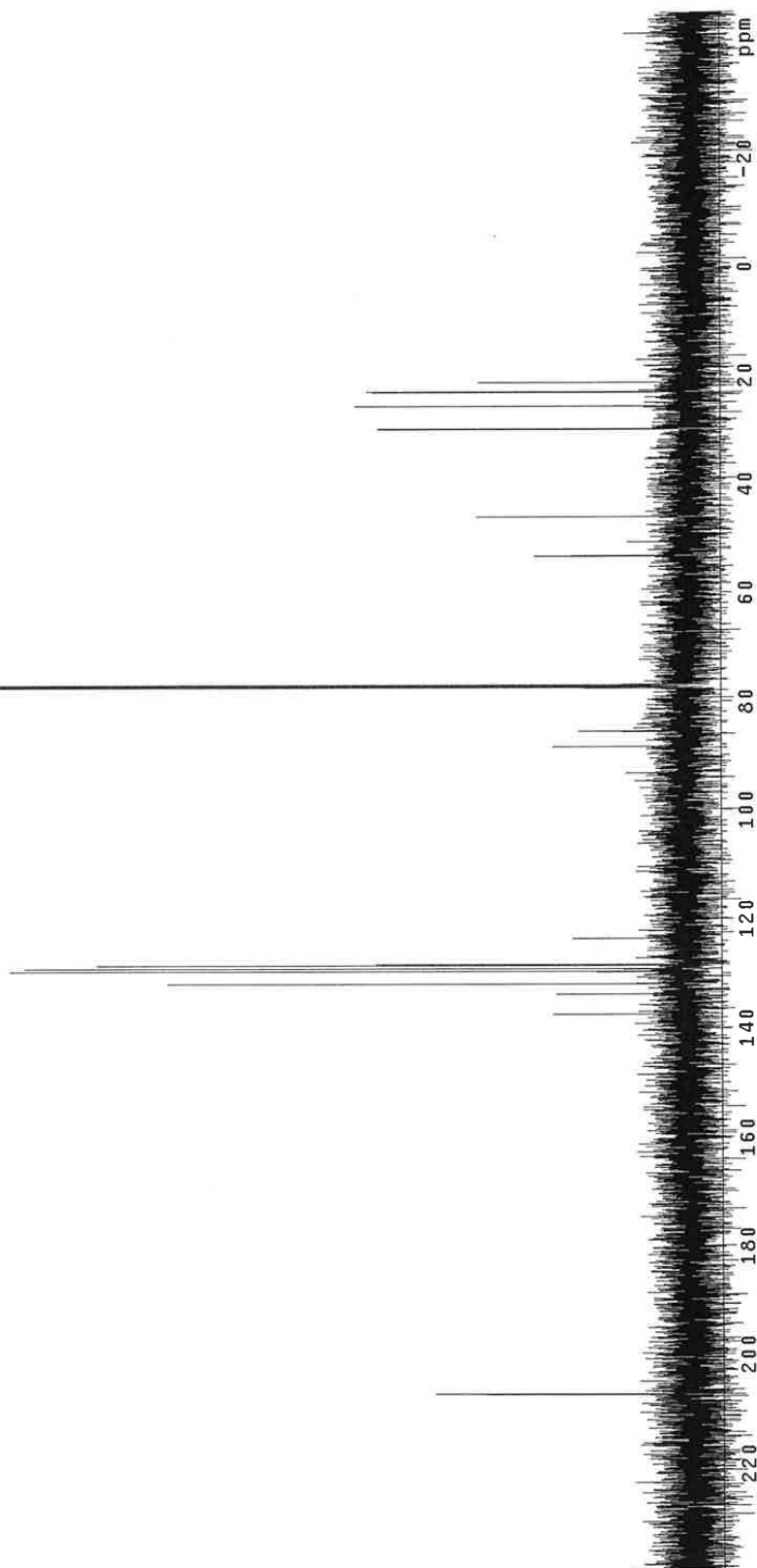
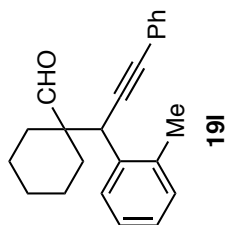


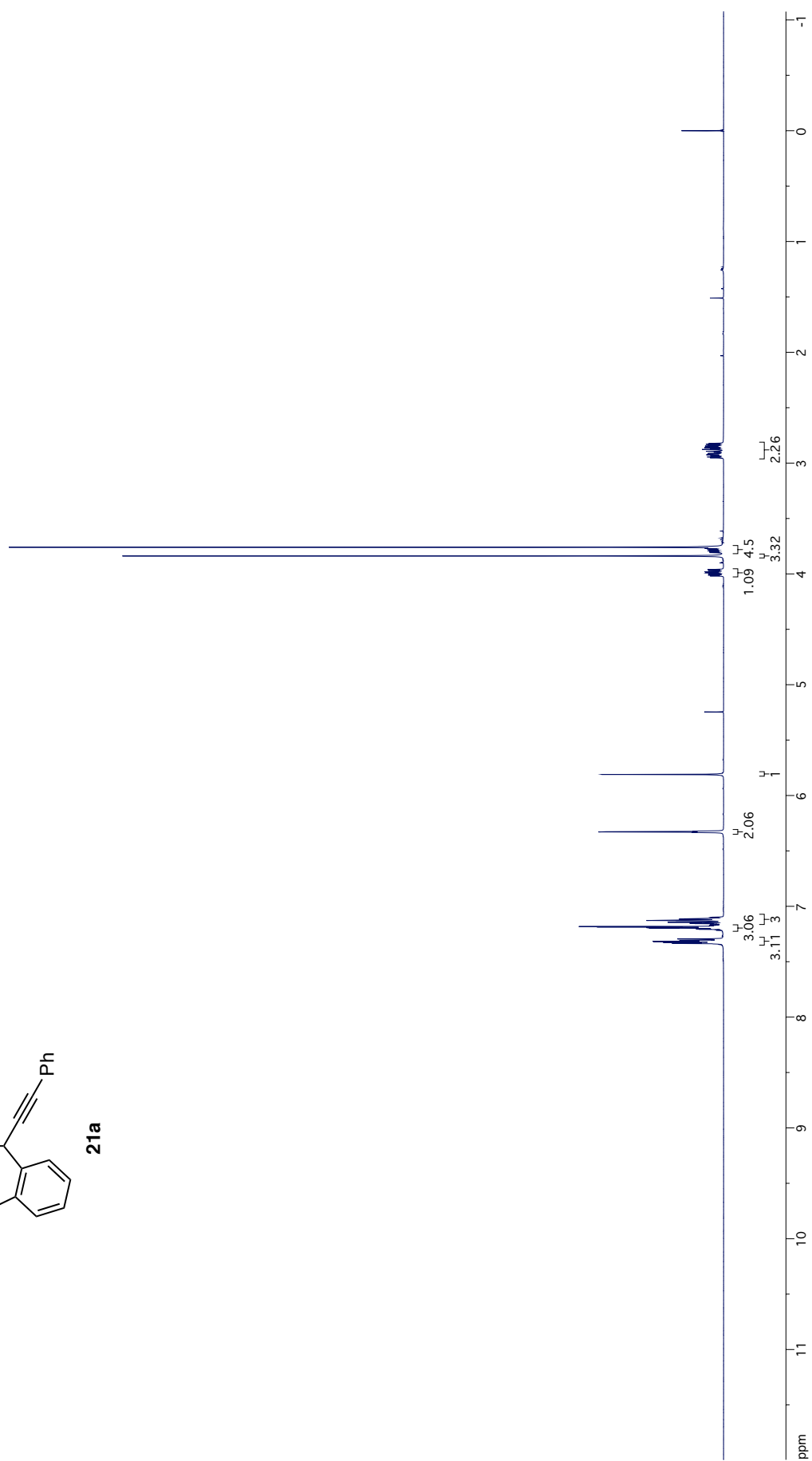
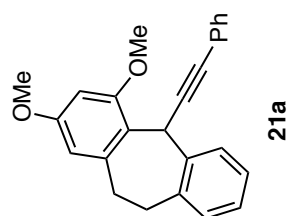


STANDARD PROTON PARAMETERS

Pulse Sequence: s2pul
 Solvent: CDCl₃
 Ambient temperature
 User: QAC7-37-13C
 File: 1448
 INOVA-500 "nmr2a.chem.nd.edu"

Relax. delay 1.800 sec
 Pulse 90.0 degrees
 Acq. time 1.215 sec
 Width 36003.6 Hz
 Spectroscopy
 OBSERVE C13, 425.6901644 MHZ
 DECOUPLE H1, 499.8636613 MHZ
 Power 40 dB,
 continuously on
 VOLTAGE-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 131072
 Total time 6 min, 27 sec

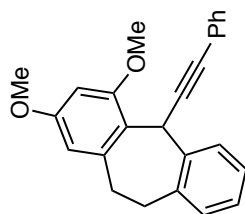




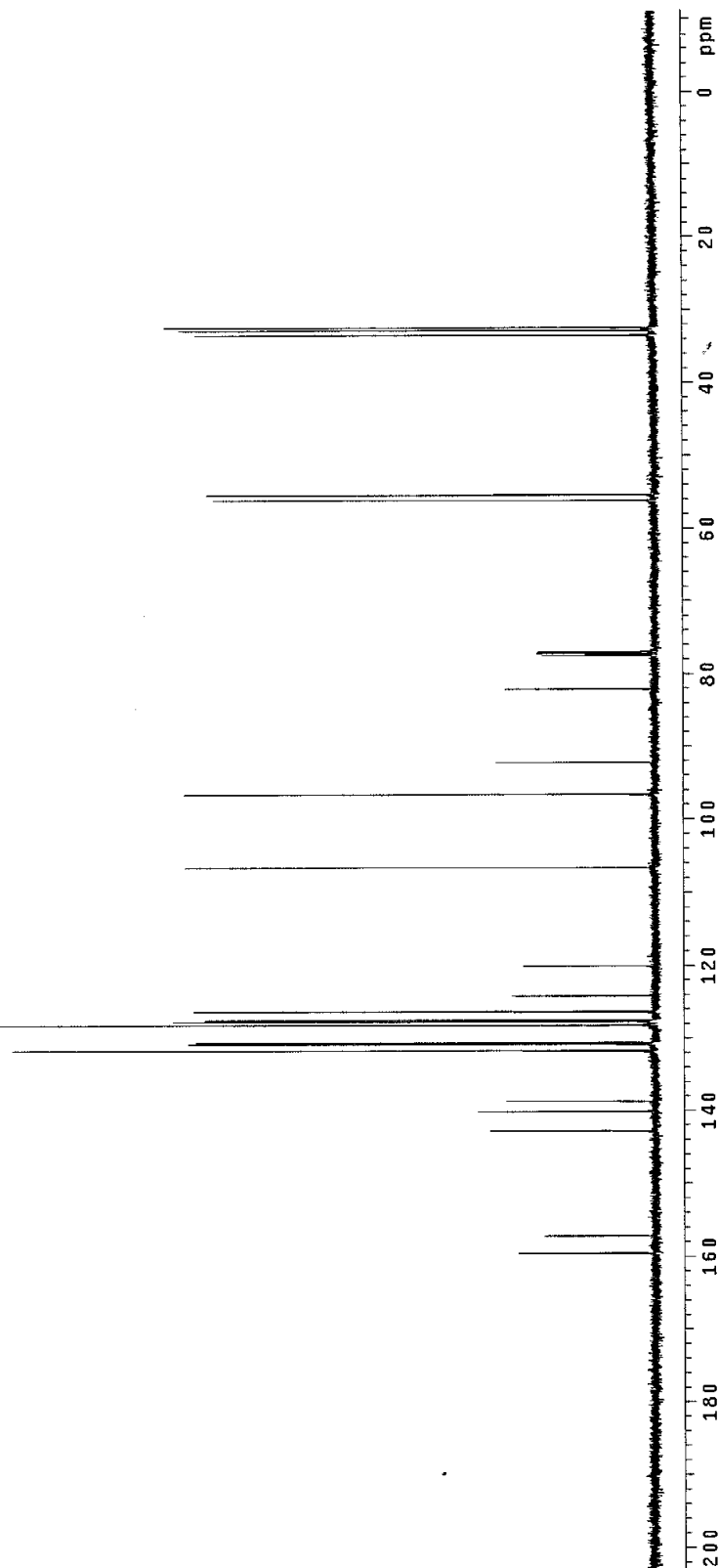
STANDARD PROTON PARAMETERS

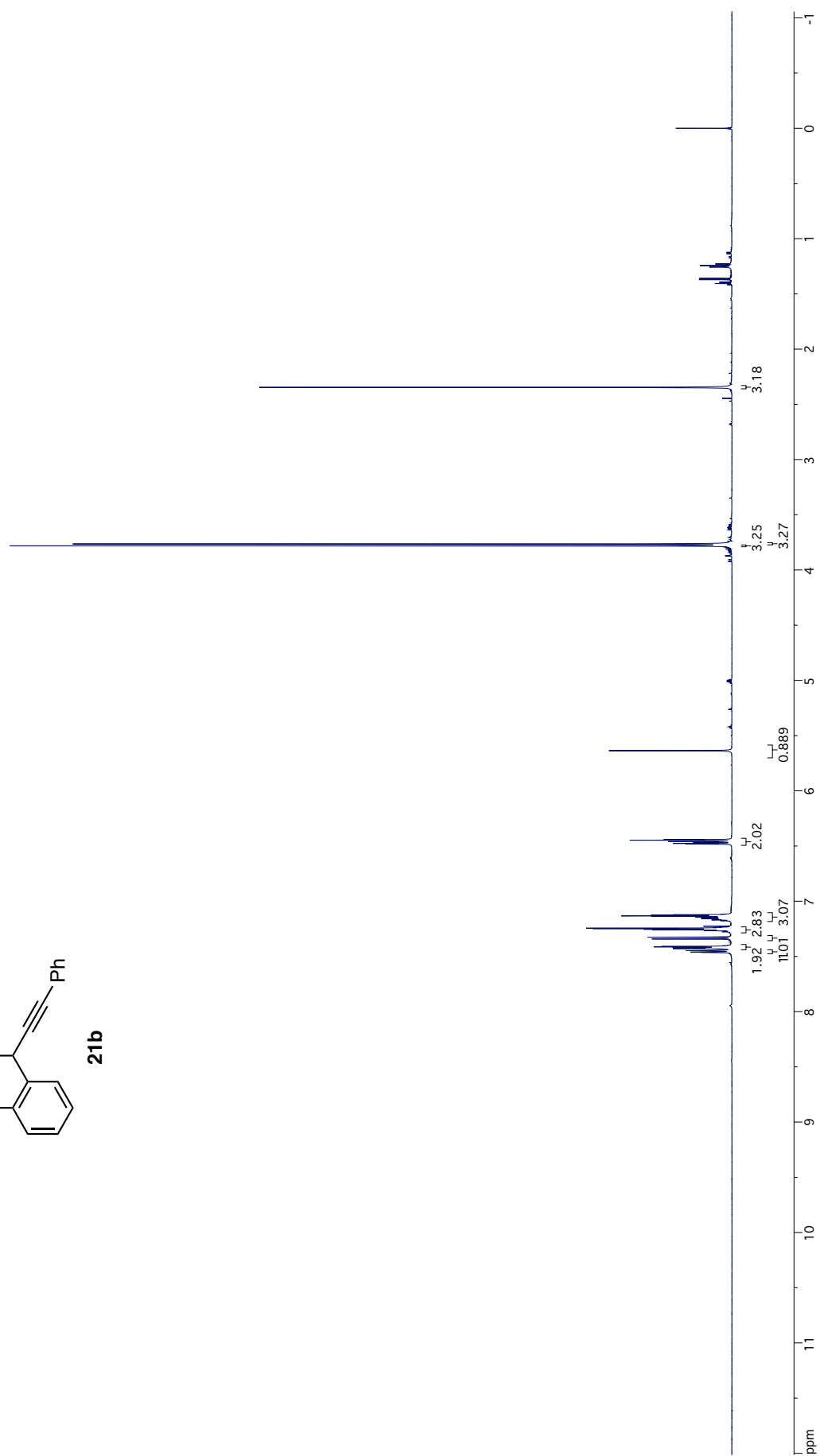
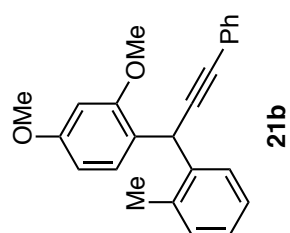
Pulse Sequence: s2pu1
 Solvent: CDCl3
 Ambient temperature
 User: 1-14-87
 File: JBGII181-C
 INOVA-500 "bloch.Chem.nd.edu"

Relax. delay 1.800 sec
 Pulse 90.0 degrees
 Acq. time 1.235 sec
 Width 26963.3 Hz
 128 repetitions
 OBSERVE C13, 125.6901743 MHz
 DECOUPLE H1, 499.8636613 MHz
 Power 40 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 Ft size 131072
 Total time 6 min, 27 sec



21a

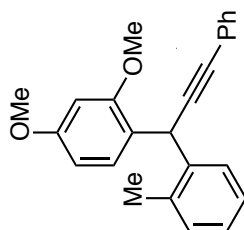




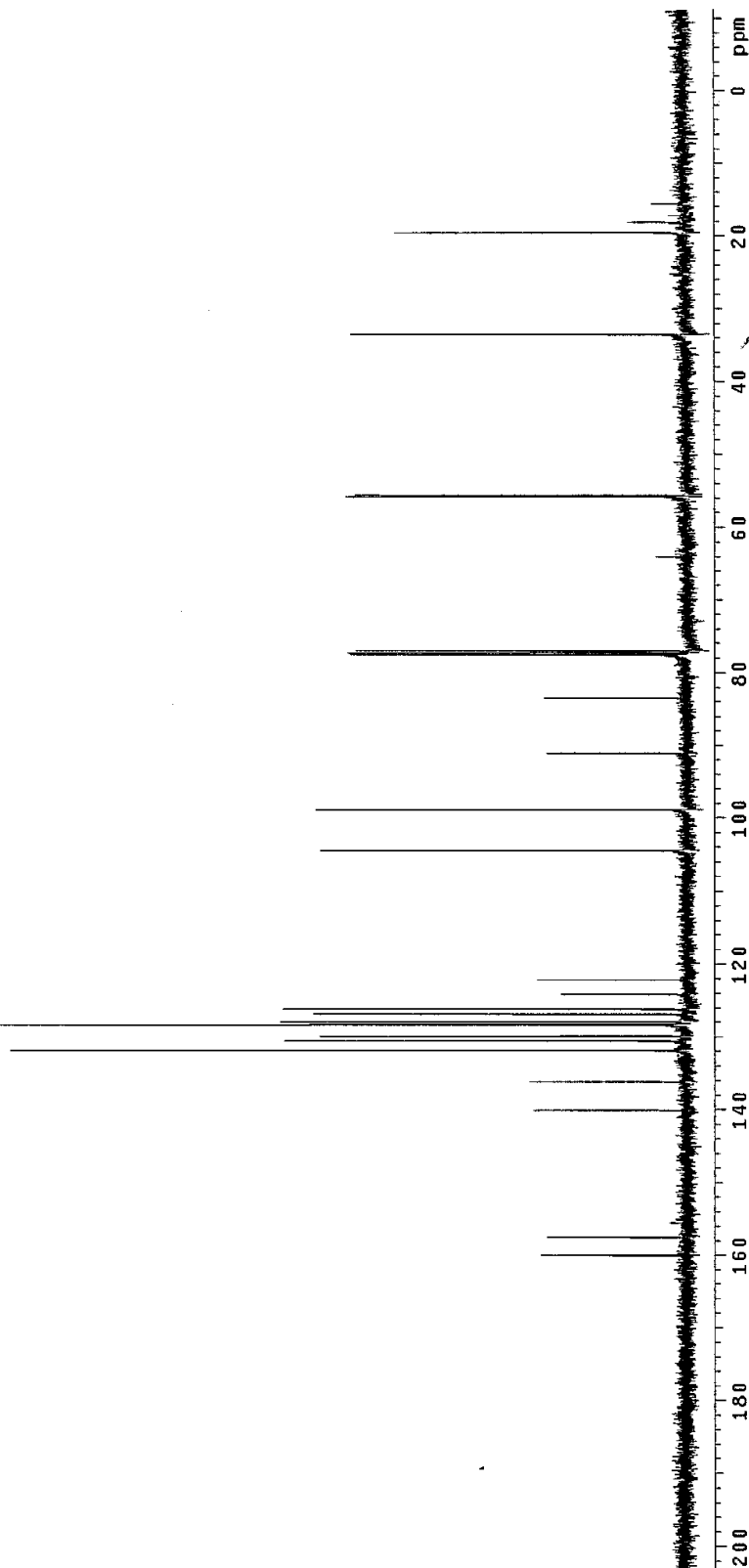
STANDARD PROTON PARAMETERS

Pulse Sequence: s2pu1
 Solvent: CDCl3
 Ambient temperature
 User: 1-10-87
 File: J8G11243-C
 INOVA-500 "bioc.chem.nd.edu"

Relax. delay 1.800 sec
 Pulse 90.0 degrees
 Acq. time 1.215 sec
 Width 28963.3 Hz
 128 repetitions
 OBSERVE C13, 125.8901698 MHz
 DECOUPLE H1, 499.8636613 MHz
 Power 40 dB,
 continuously on
 WAIT-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 131072
 Total time 6 min, 27 sec

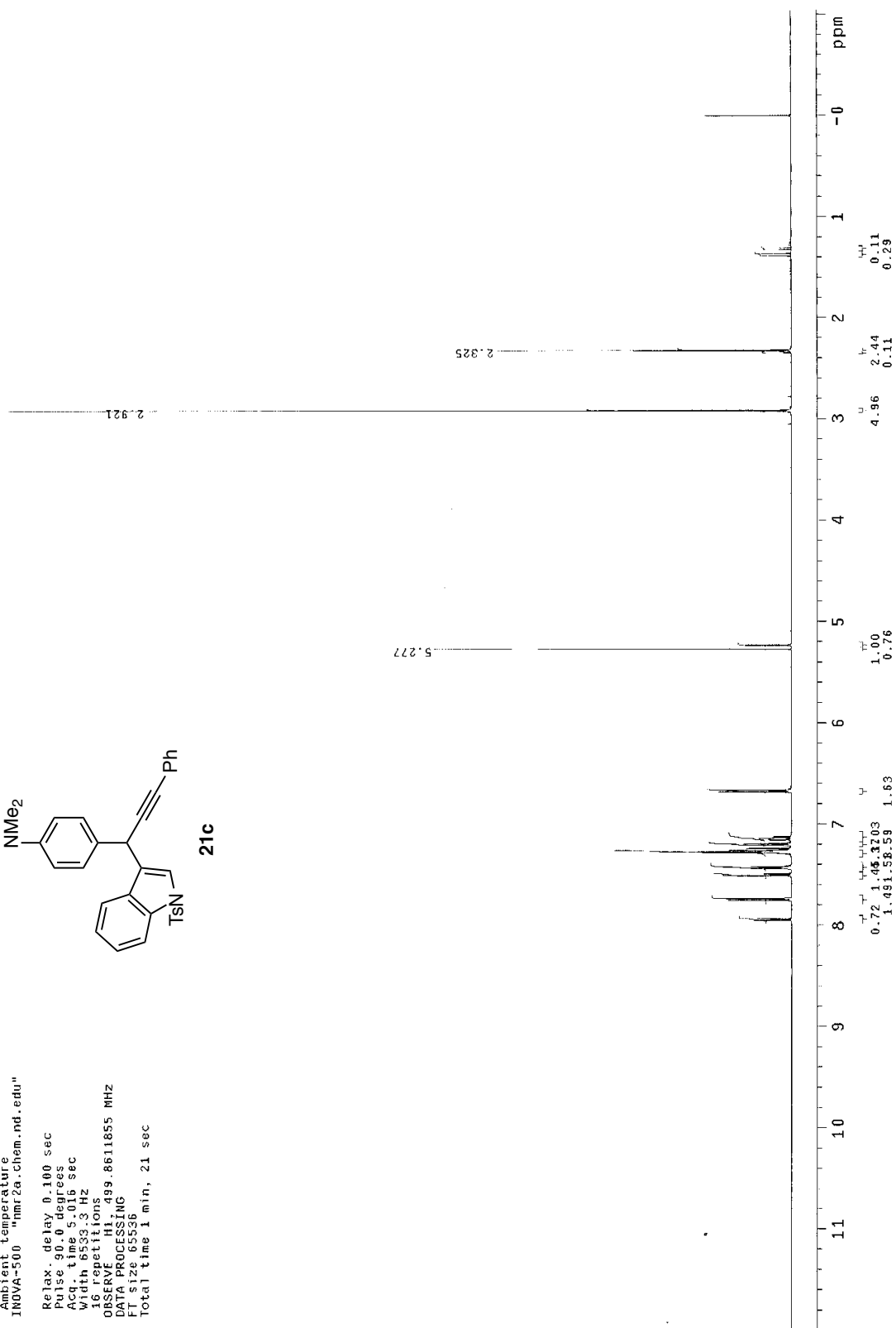
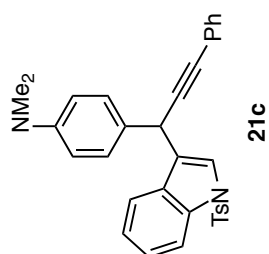


21b



STANDARD PROTON PARAMETERS

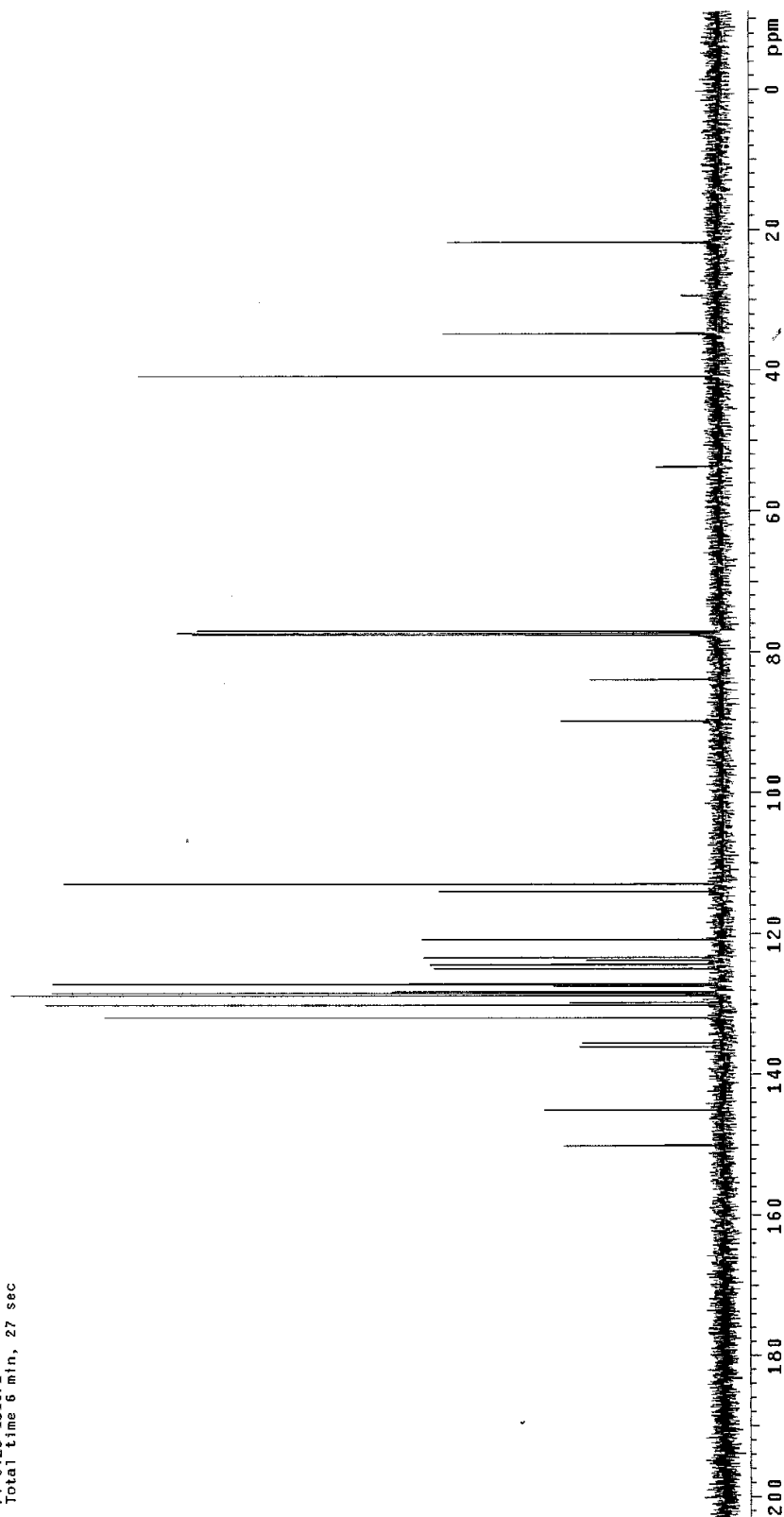
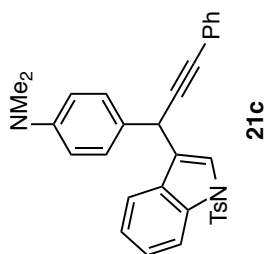
Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 INOVA-500 "nmr2a.Chem.nd.edu"
 Relax. delay 0.100 sec
 Pulse 90.0 degrees
 Acq. time 5.016 sec
 Width 6533.3 Hz
 16 repetitions
 OBSERVE H1, 499.8611855 MHz
 DATA PROCESSING
 FT size 65536
 Total time 1 min, 21 sec

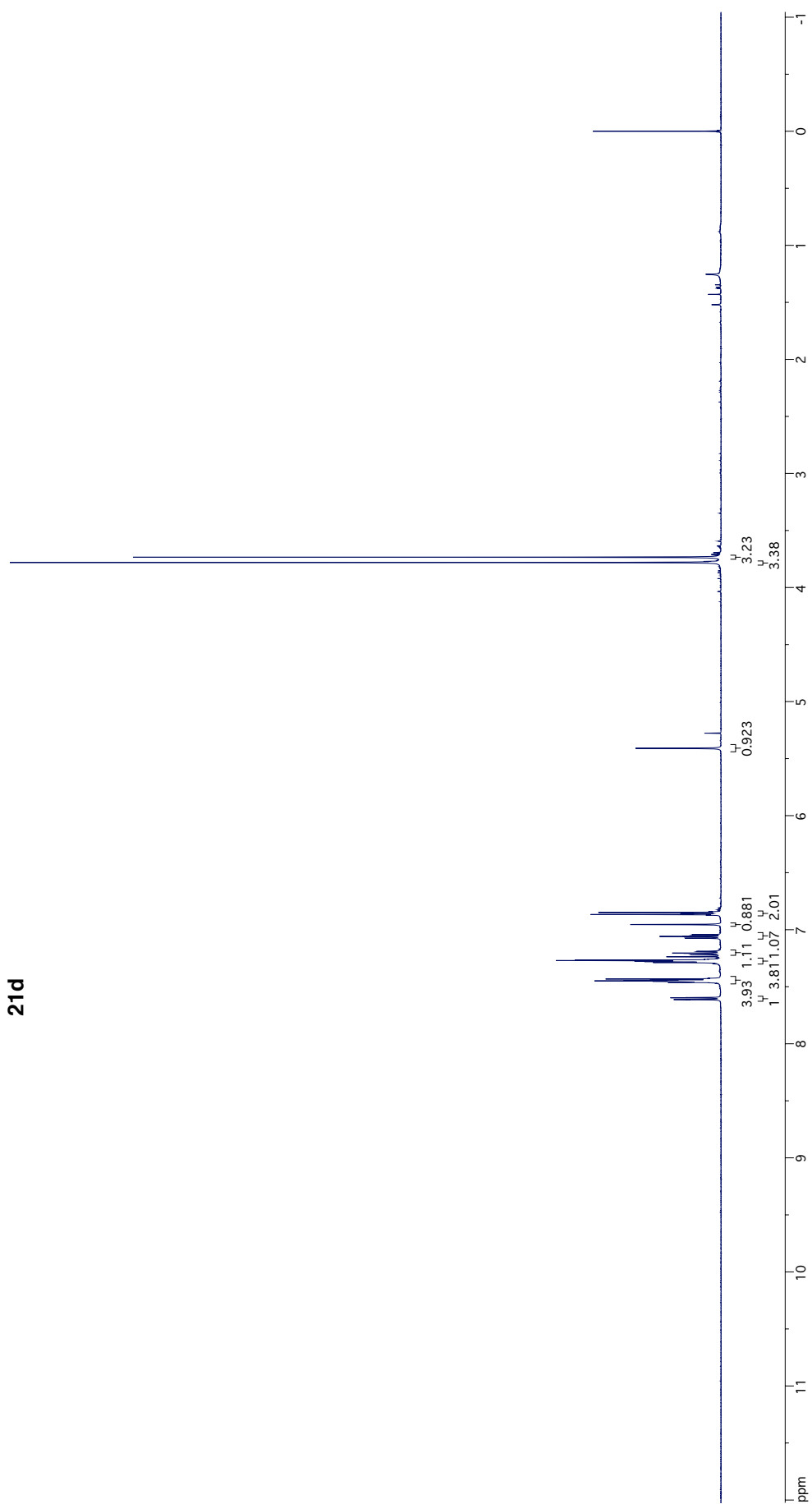
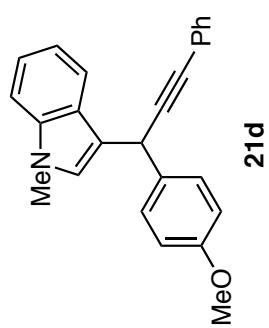


STANDARD PROTON PARAMETERS

Pulse Sequence: s2pu1
 Solvent: CDCl3
 Ambient temperature
 User: 1-14-87
 File: JBG11253p-C
 INOVA-500 "bloch.chem.nd.edu"

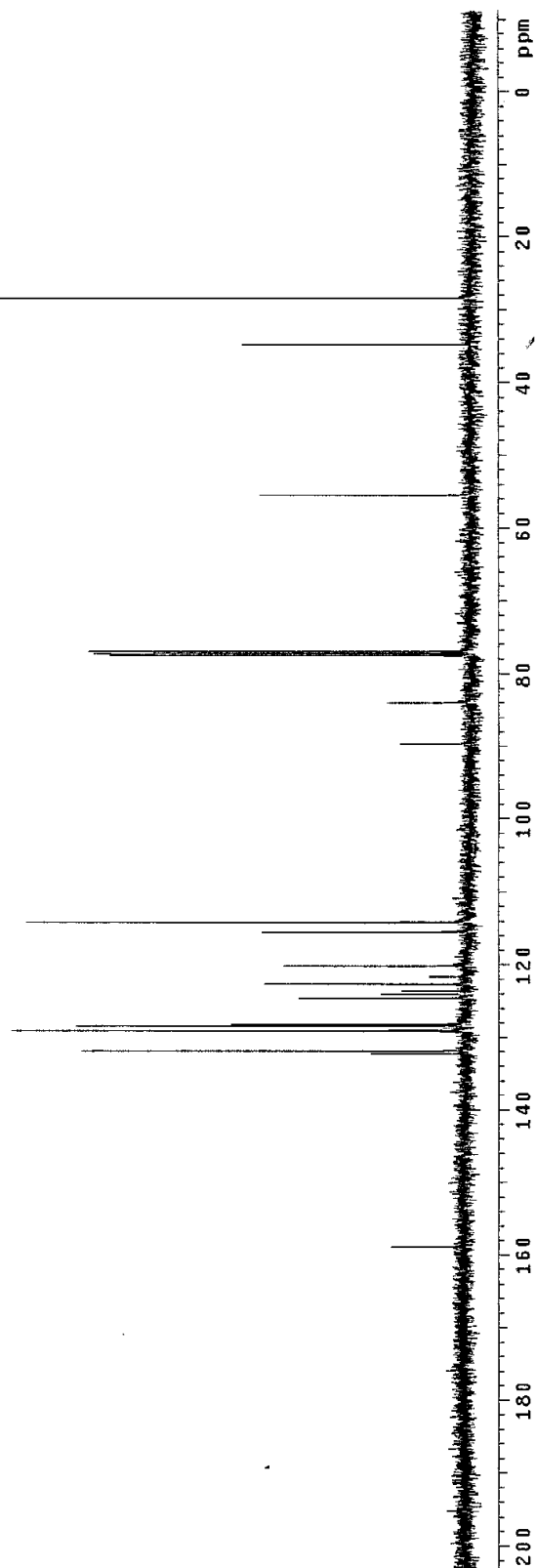
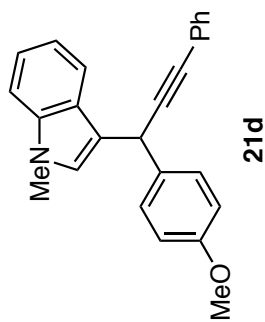
Relax. delay 1.800 sec
 Pulse 90.0 degrees
 Acq. time 1.215 sec
 Width 28963.3 Hz
 128 repetitions
 OBSERVE C13, 125.8901591 MHZ
 DECOUPLE H1, 499.8636613 MHZ
 Power 40 dB
 Continuously on
 Locking on
 VFA 12.0000000
 DATA PROCESSING
 Line broadening 1.0 Hz
 FI size 131072
 Total time 6 min, 27 sec

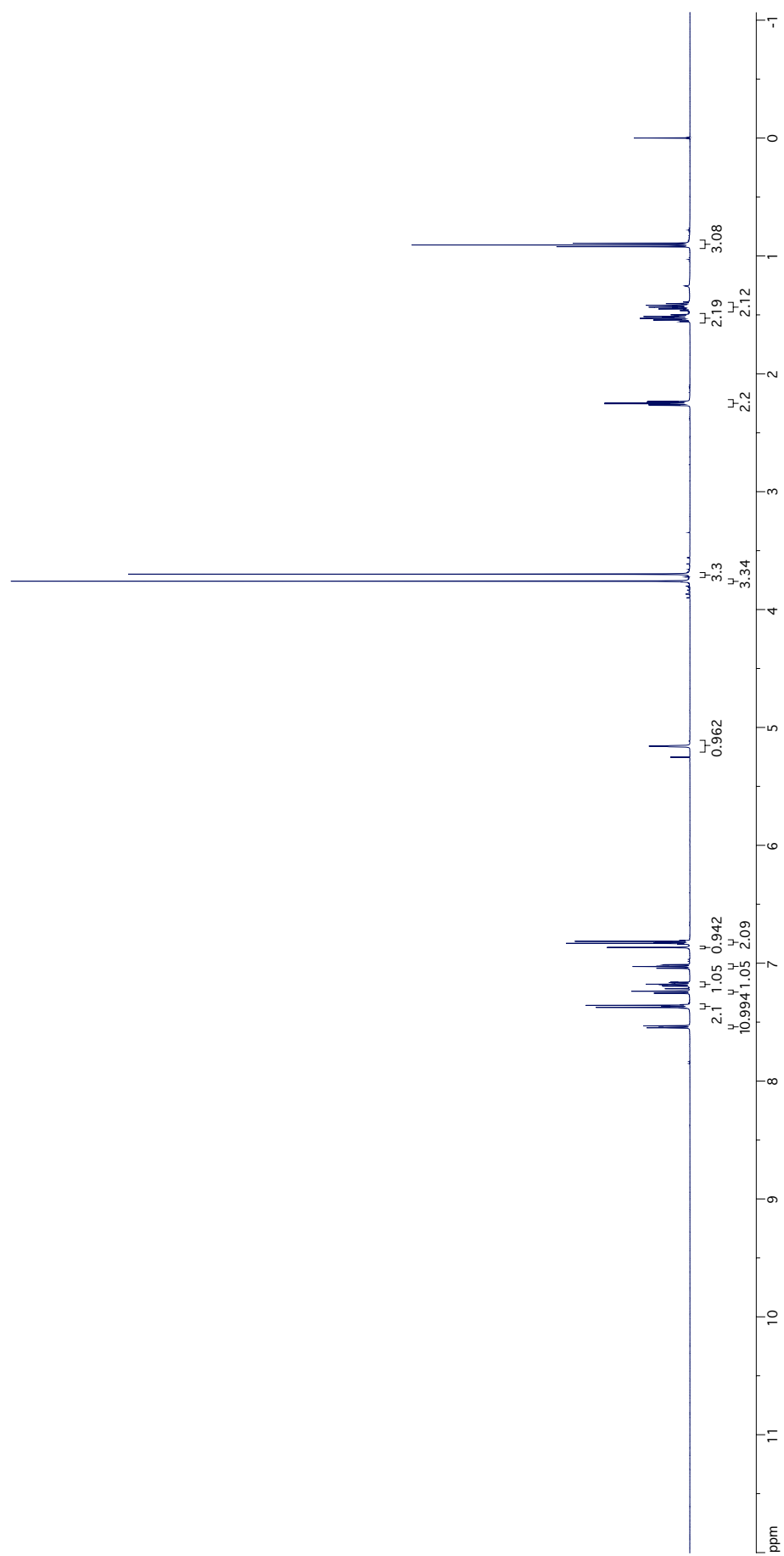
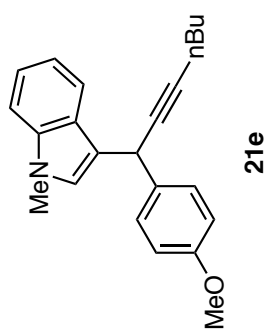




STANDARD PROTON PARAMETERS

Pulse Sequence: s2pu1
 Solvent: CDCl3
 Ambient temperature
 User: 1-14-87
 File: JBOIV244-2-C
 INOVA-S00 "Bioch.chem.nd.edu"
 Relax. delay 1.800 sec
 Pulse 90.0 degrees
 Acq. time 1.215 sec
 Width 26963.3 Hz
 Repetitions 640
 OBSERVE F1, 439.1668 MHz
 DECOUPLE F1, 439.863613 MHz
 Power 40 dB,
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 131072
 Total time 12 min, 54 sec

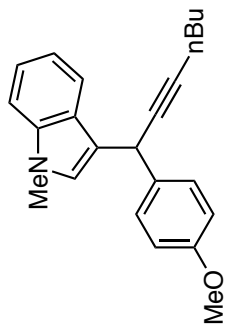




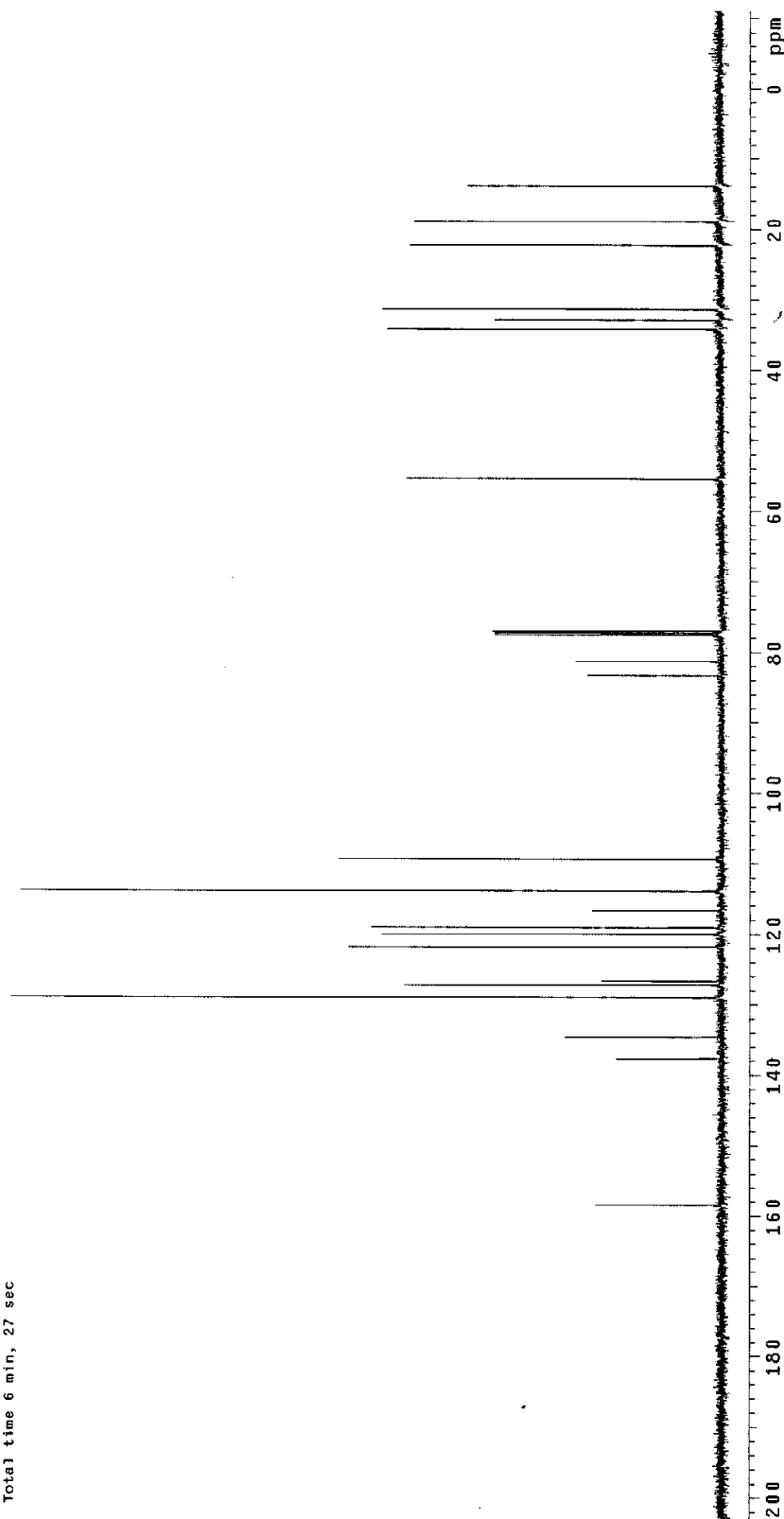
STANDARD PROTON PARAMETERS

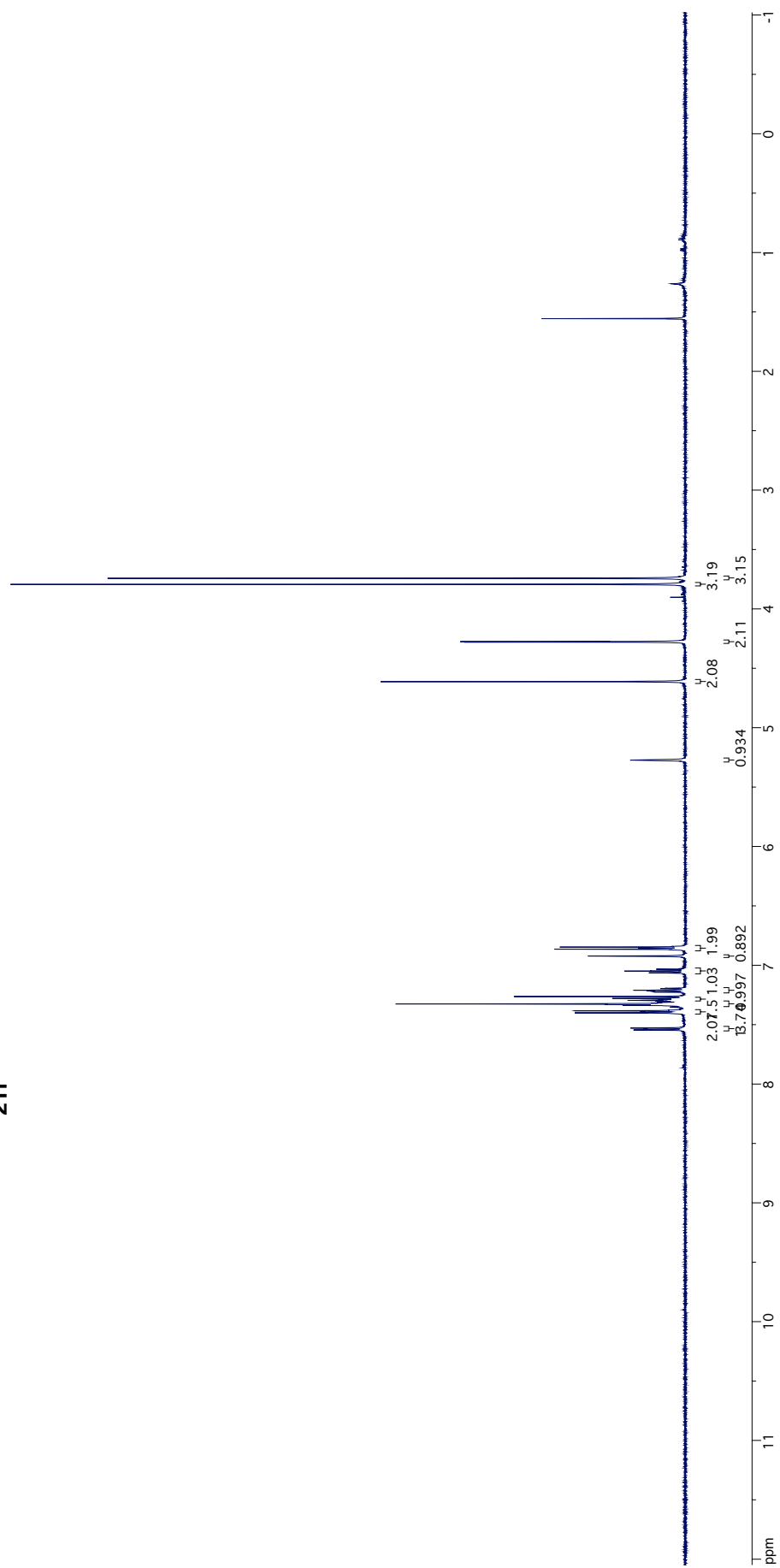
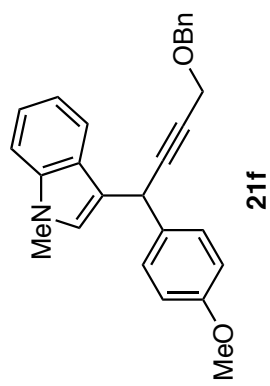
Pulse Sequence: s2pu1
 Solvent: CDCl3
 Ambient temperature
 User: 1-14-87
 File: JBG11285-C
 INOVA-500 "bioch.chem.nd.edu"

Relax. delay 1.800 sec
 Pulse 90.0 degrees
 Acq. time 1.215 sec
 Width 26963.3 Hz
 128 repetitions
 OBSERVE C13, 125.8901718 MHz
 DECOUPLE H1, 499.8636613 MHz
 Continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FI size 131072
 Total time 6 min, 27 sec



21e

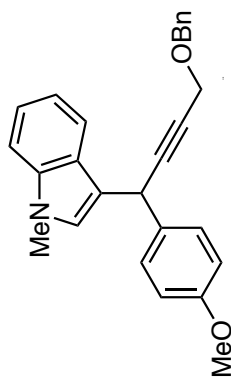




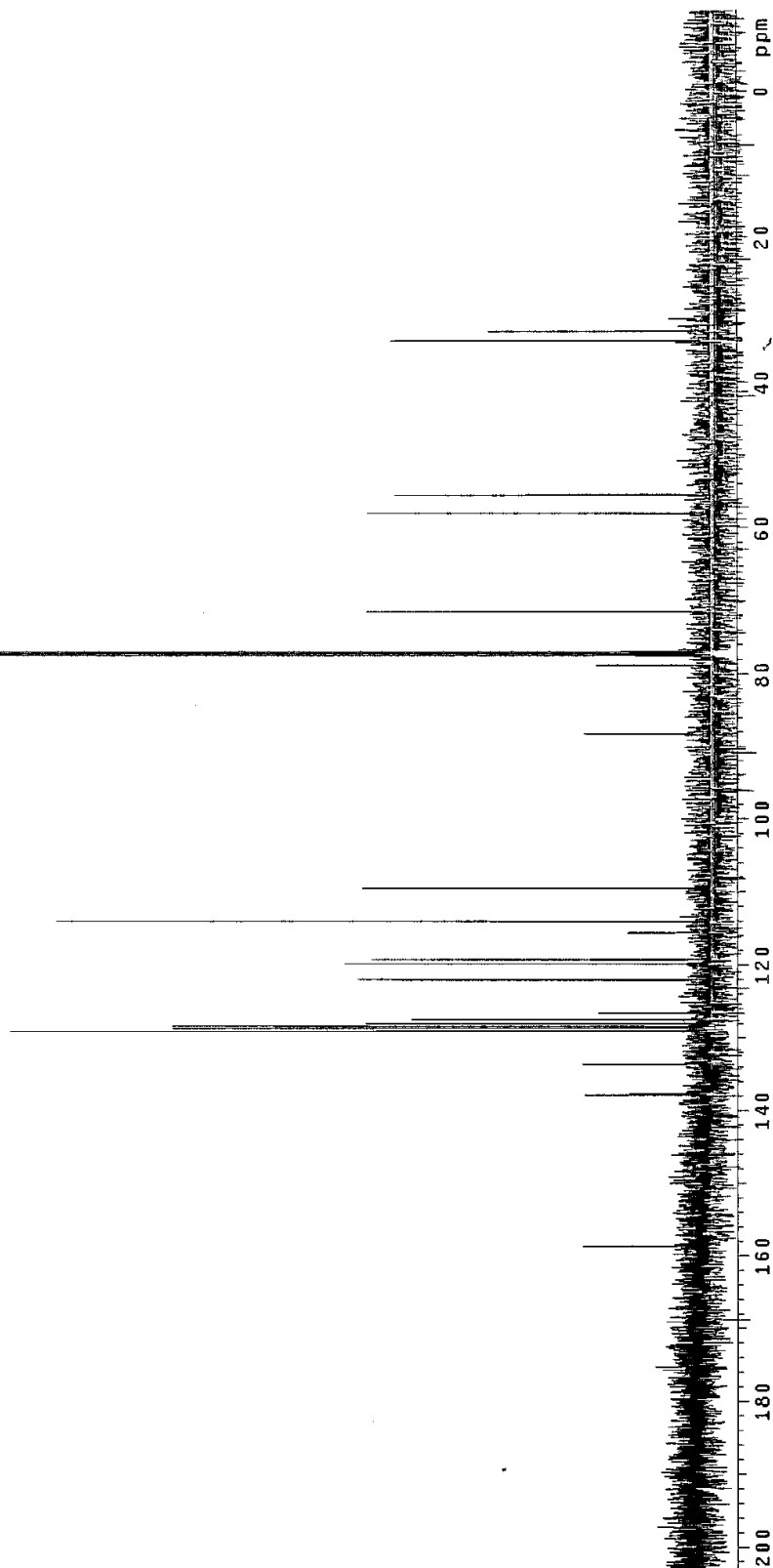
STANDARD PROTON PARAMETERS

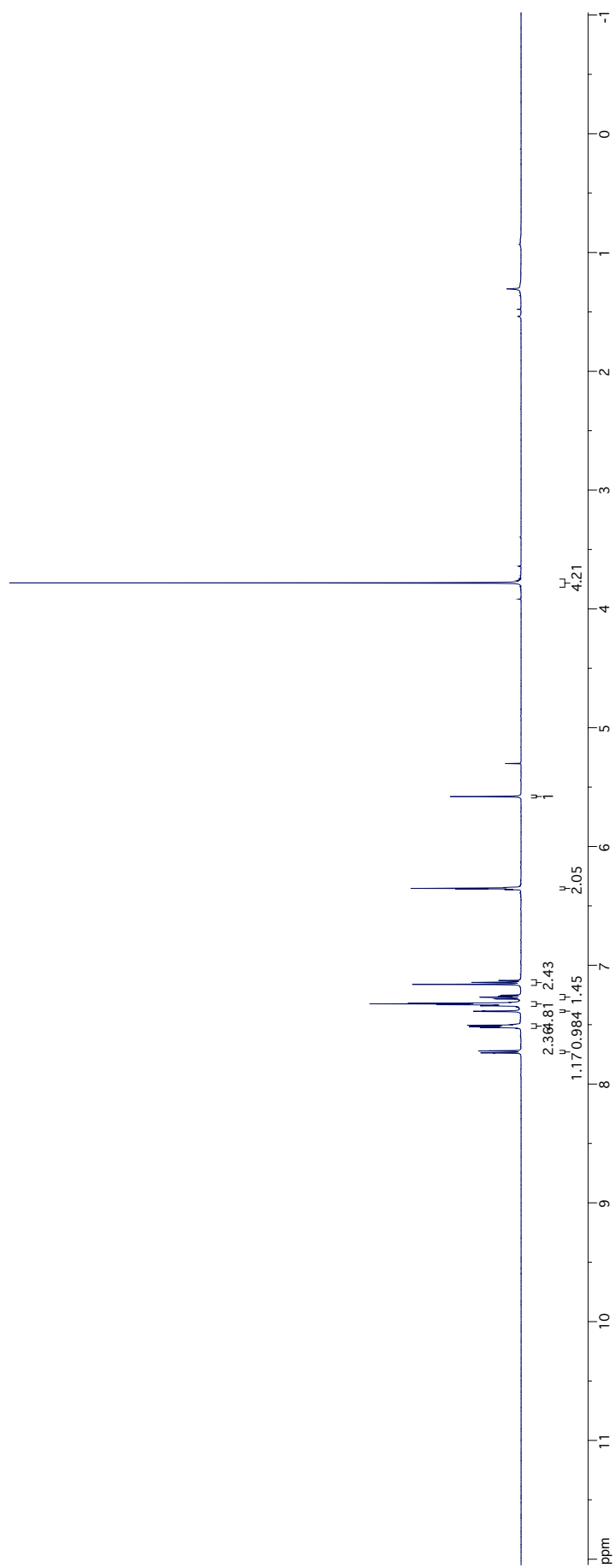
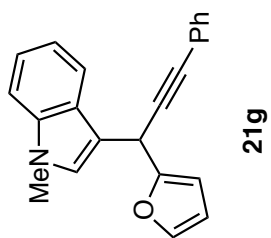
Pulse Sequence: s2pul
Solvent: CDCl₃
Ambient temperature
User: i-14-87
File: J8G1V245-2-C
INOVA-500 "bloch.chem.nd.edu"

Relax. delay 1.800 sec
Pulse 30.0 degrees
Acq. time 1.215 sec
Width 26963.3 Hz
276 repetitions
OBSERVE CH3, 125.6901655 MHz
PULSE PRG, 499.8636613 MHz
continuous on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 13 min, 55 sec



21f

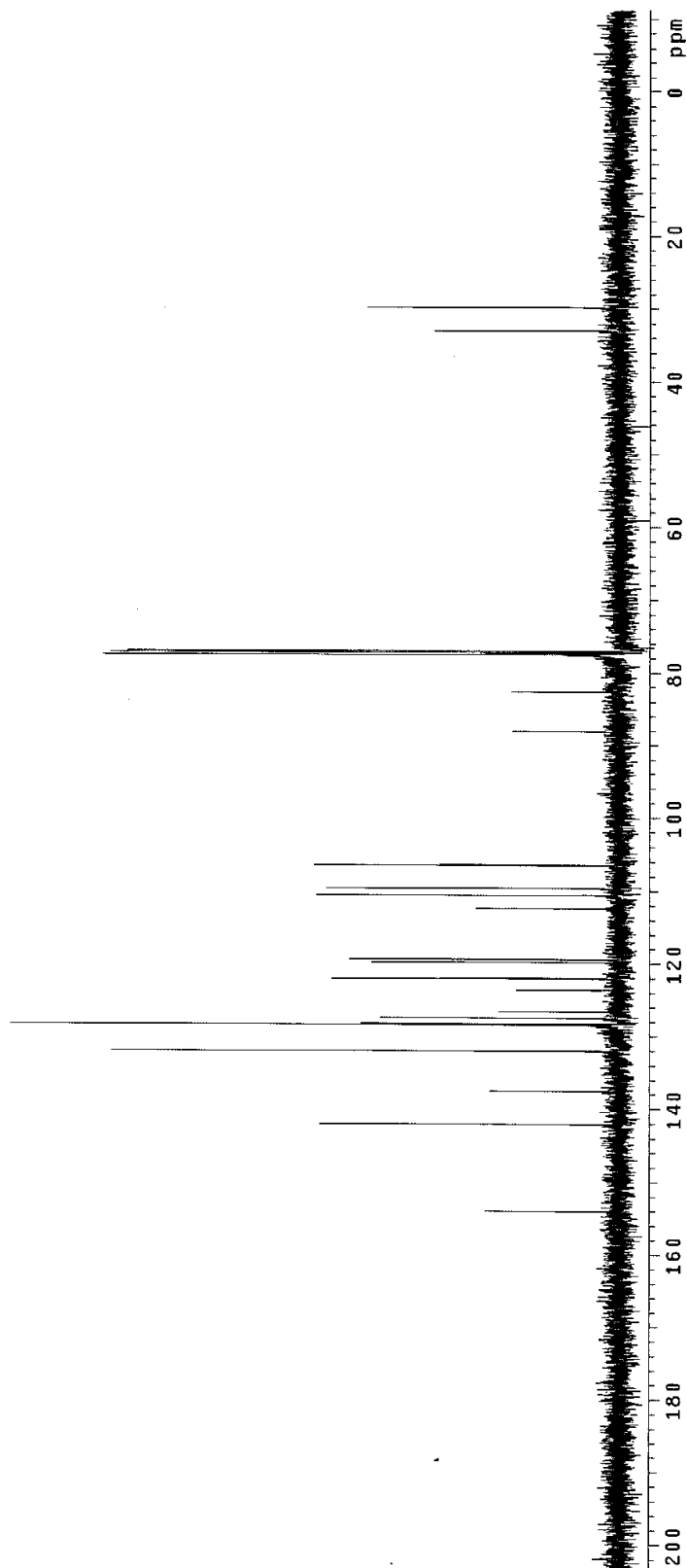
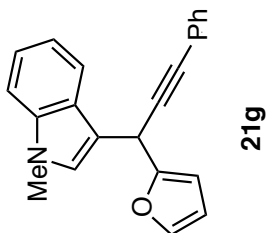


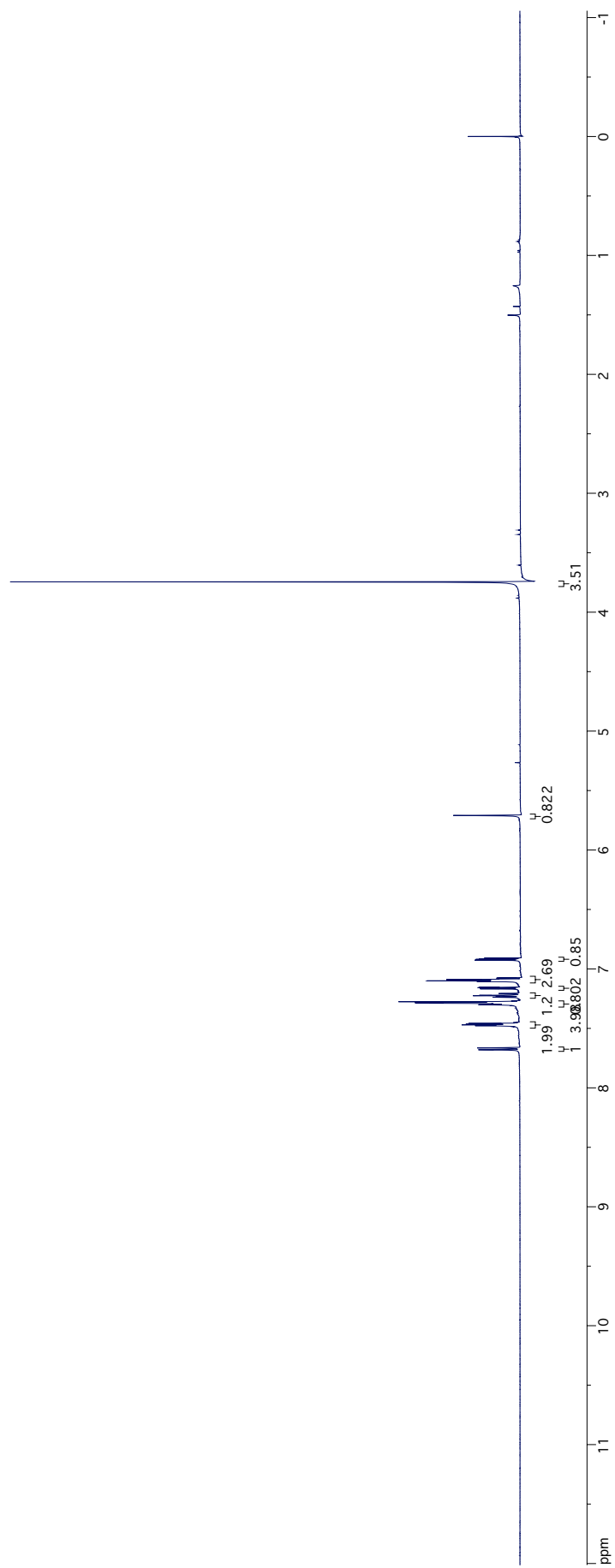
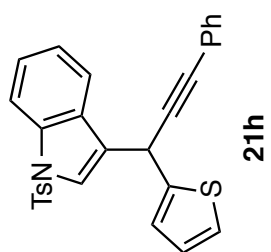


STANDARD PROTON PARAMETERS

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 User: jk
 INOVA-500 "nmr2a.chem.nd.edu"

Relax. delay 1.800 sec
 Pulse 90.0 degrees
 Width 18.219 sec
 Width 1863.5 Hz
 256 repetitions
 OBSERVE C13, 125.6901730 MHz
 DECOUPLE H1, 499.8636613 MHz
 Power 40 dB,
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 131072
 Total time 12 min, 54 sec

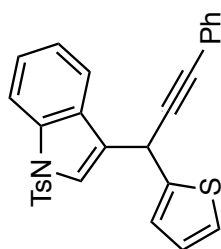




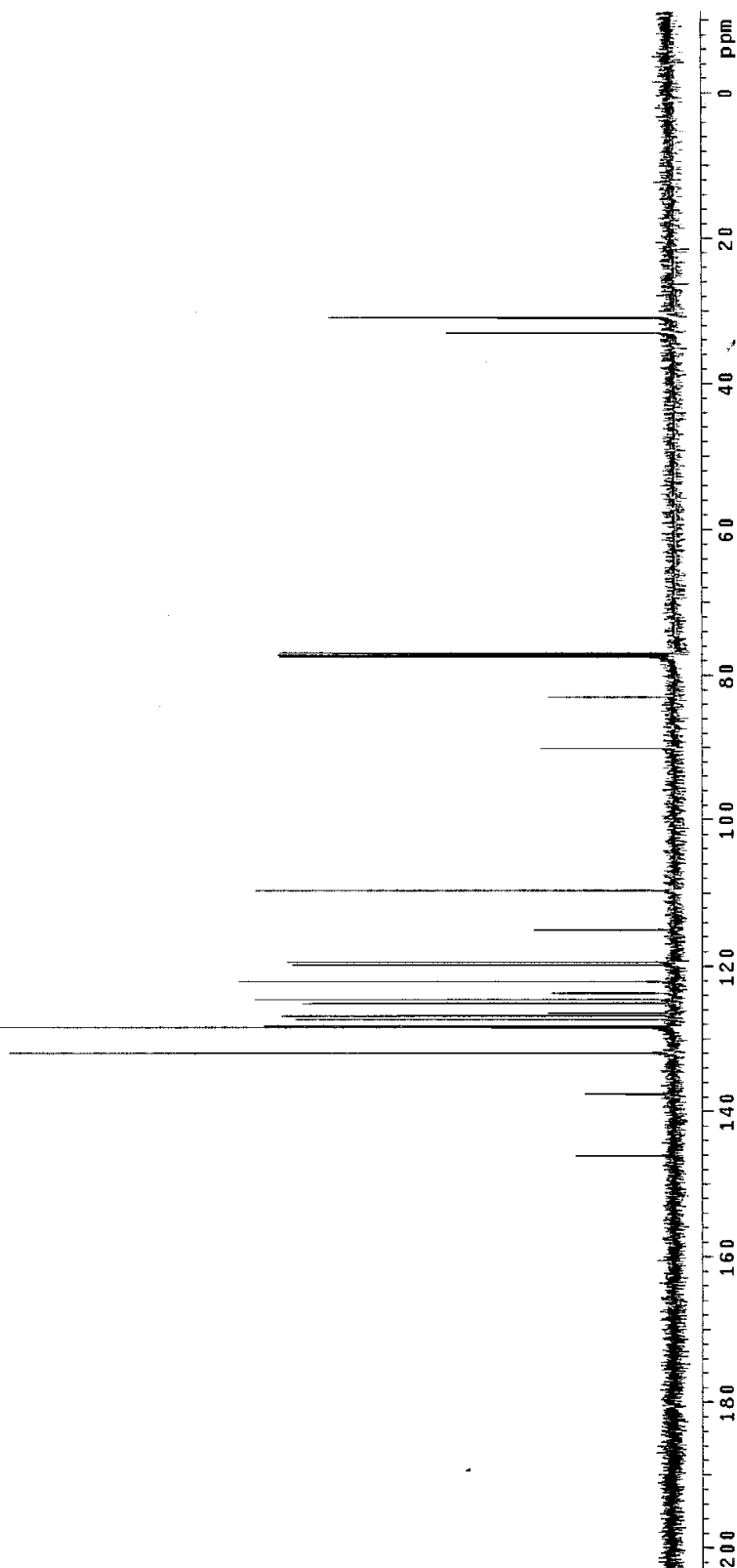
STANDARD PROTON PARAMETERS

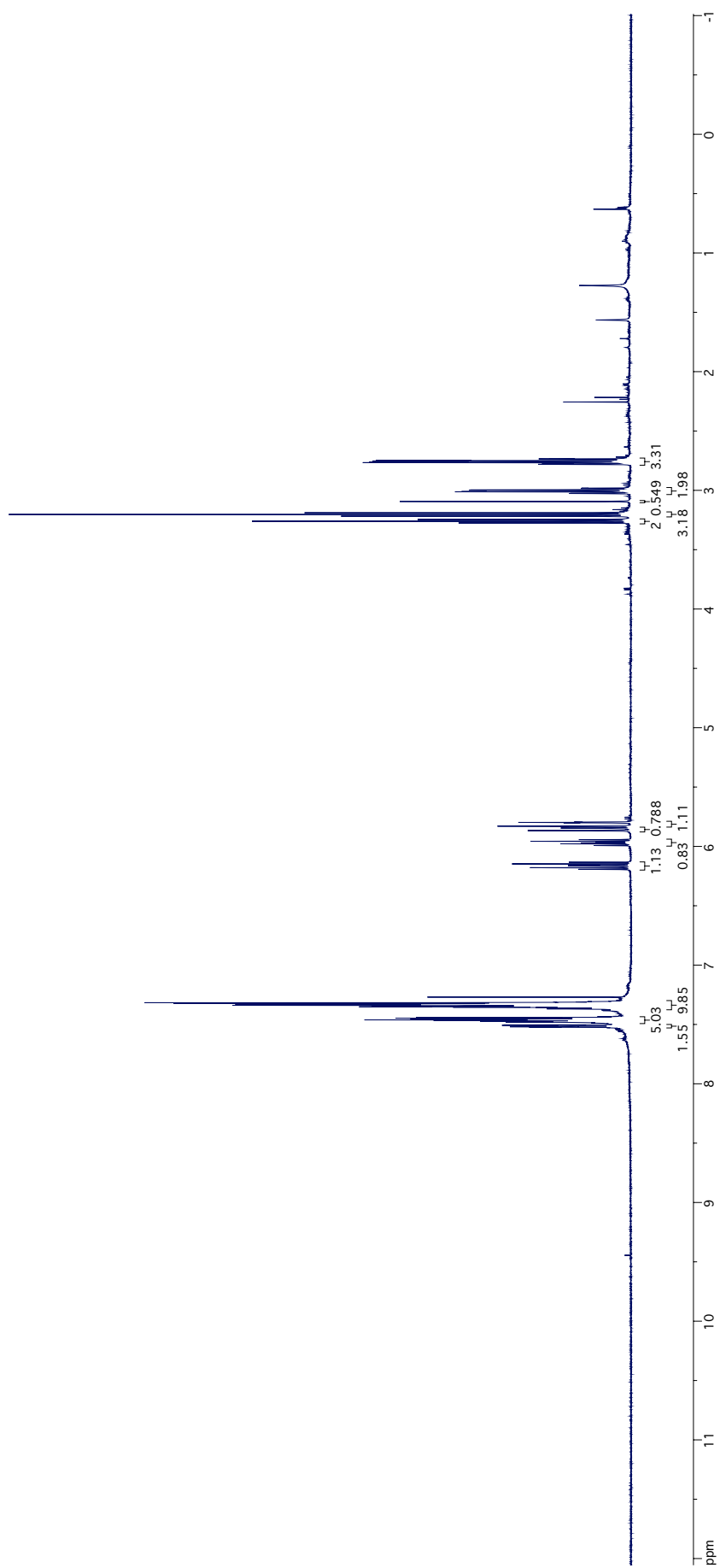
Pulse Sequence: s2pu1
 Solvent: CDCl3
 Ambient temperature
 User: 1-14-87
 File: JBG11280-C
 INOVA-500 "bioch.chem.nd.edu"

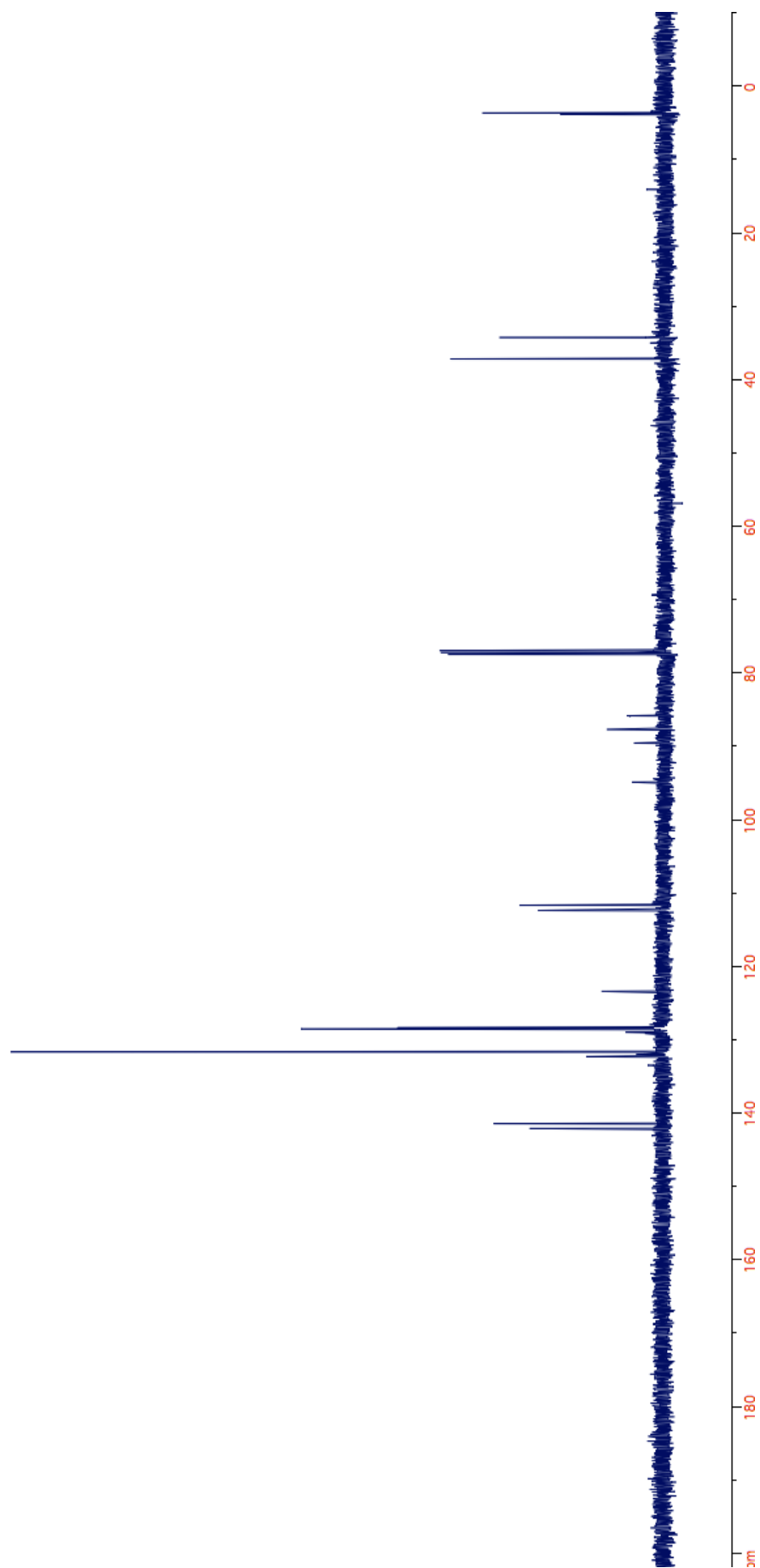
Relax. delay 1.800 sec
 Pulse 90.0 degrees
 Acq. time 1.215 sec
 Width 26963.3 Hz
 128 repetitions
 OBSERVE C13, 125.6901706 MHz
 DECOUPLE H1, 499.8636613 MHz
 Power 40 dB
 Continuously on
 VAL12-16, 1600 Hz
 DATA PROCESSING
 Line broadening 1.0 Hz
 FI size 131072
 Total time 6 min, 27 sec



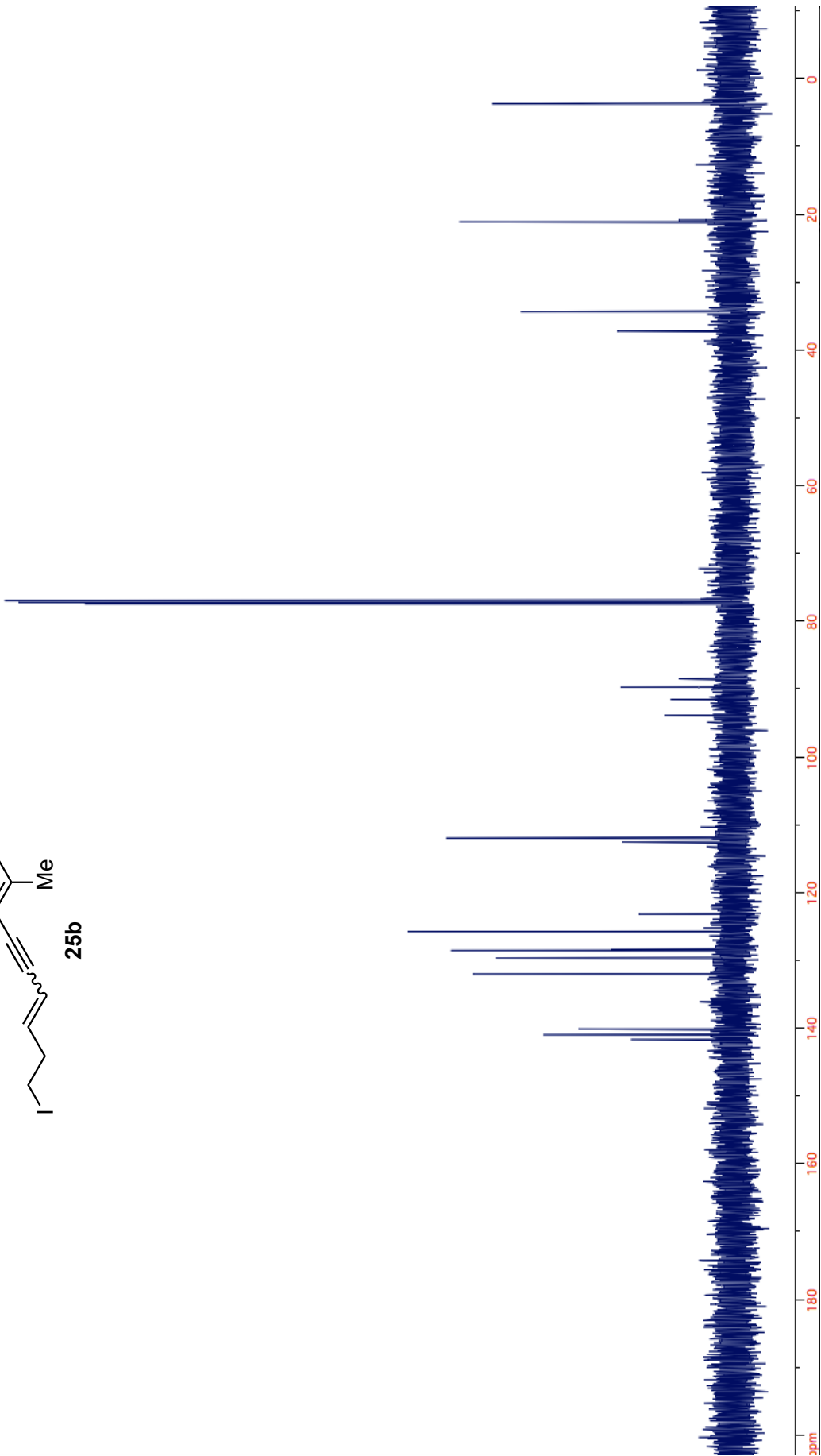
21h

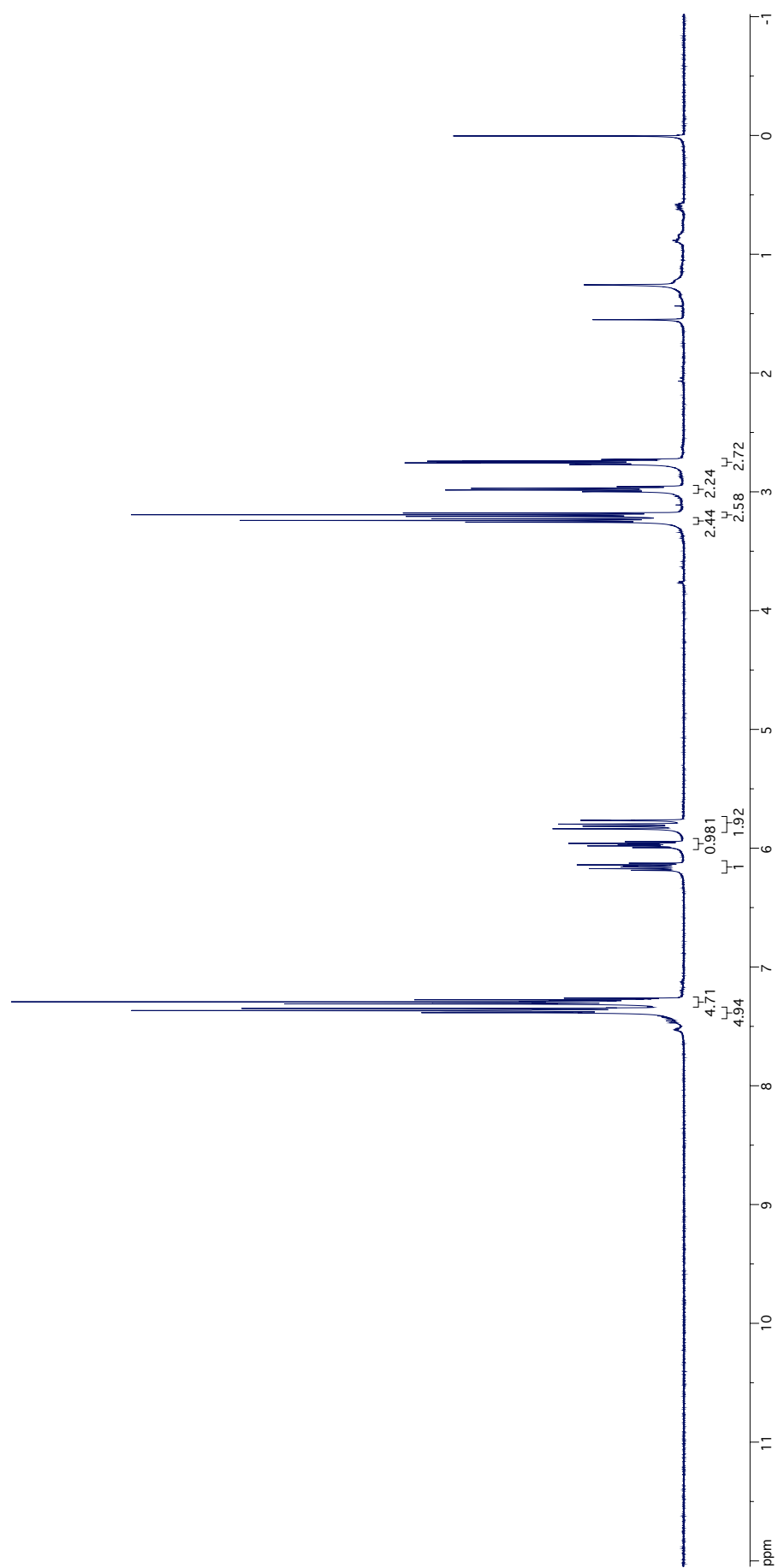
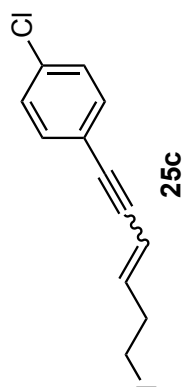


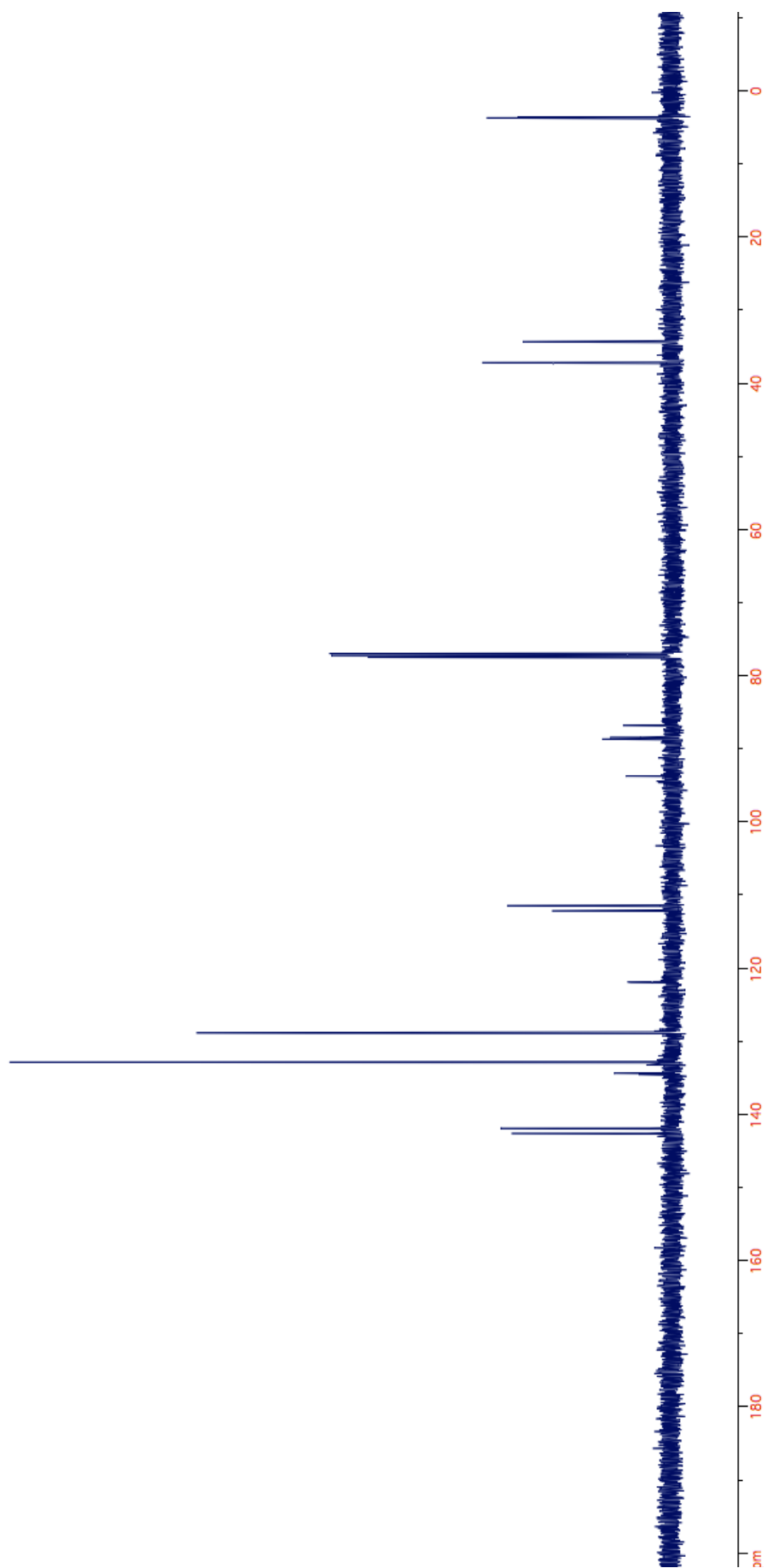
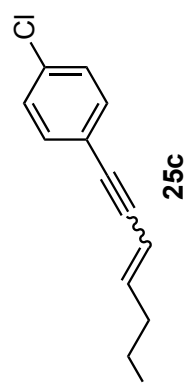


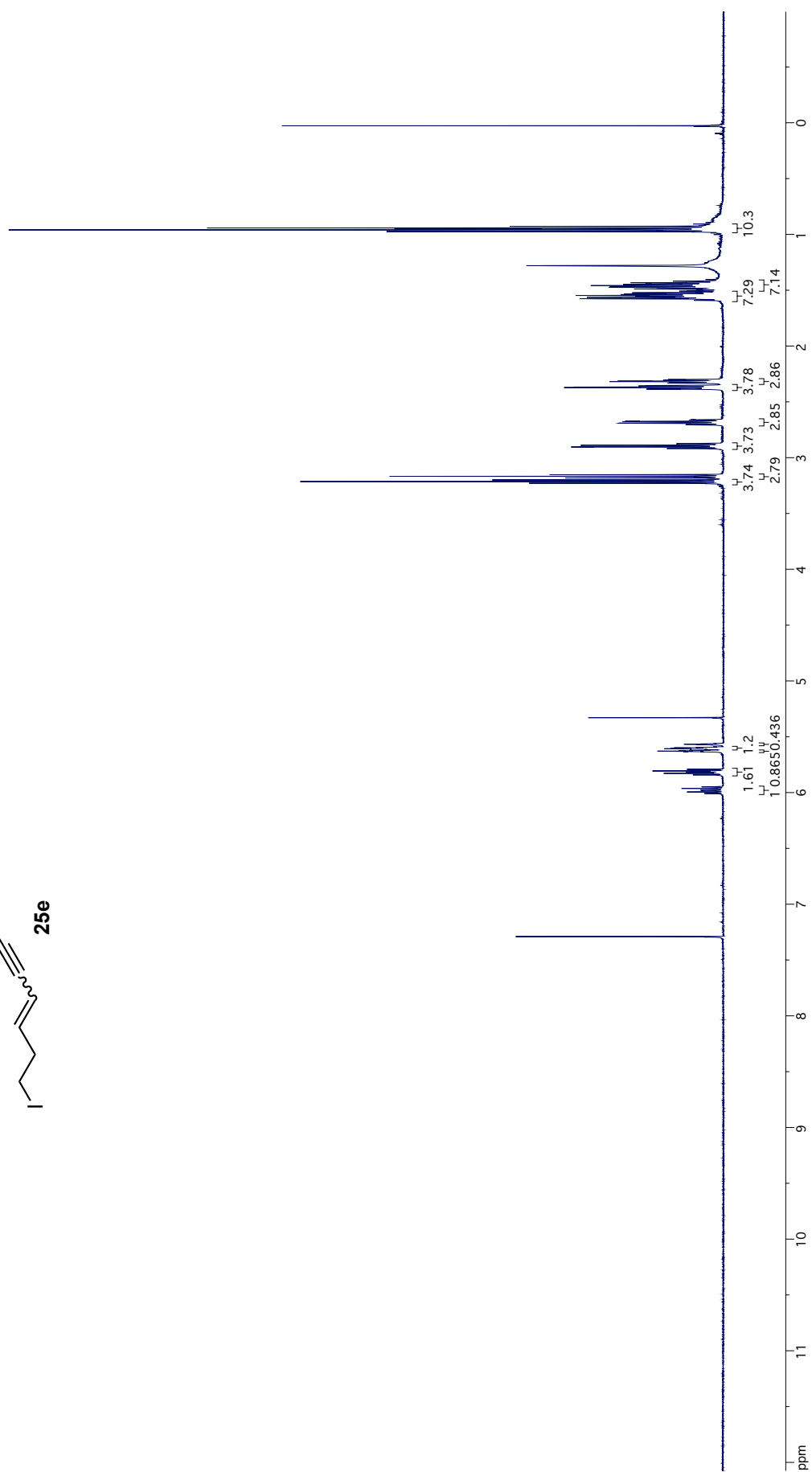






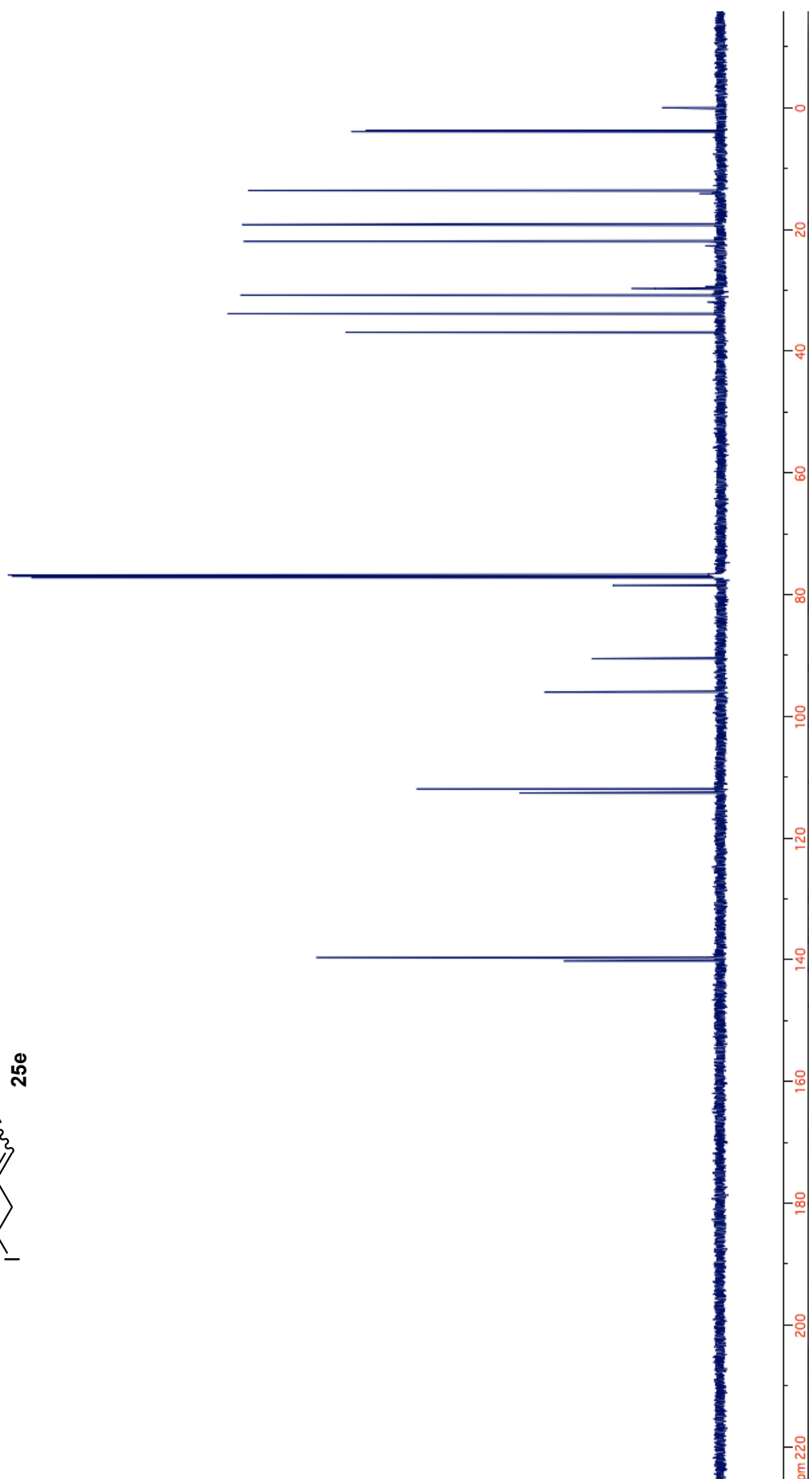


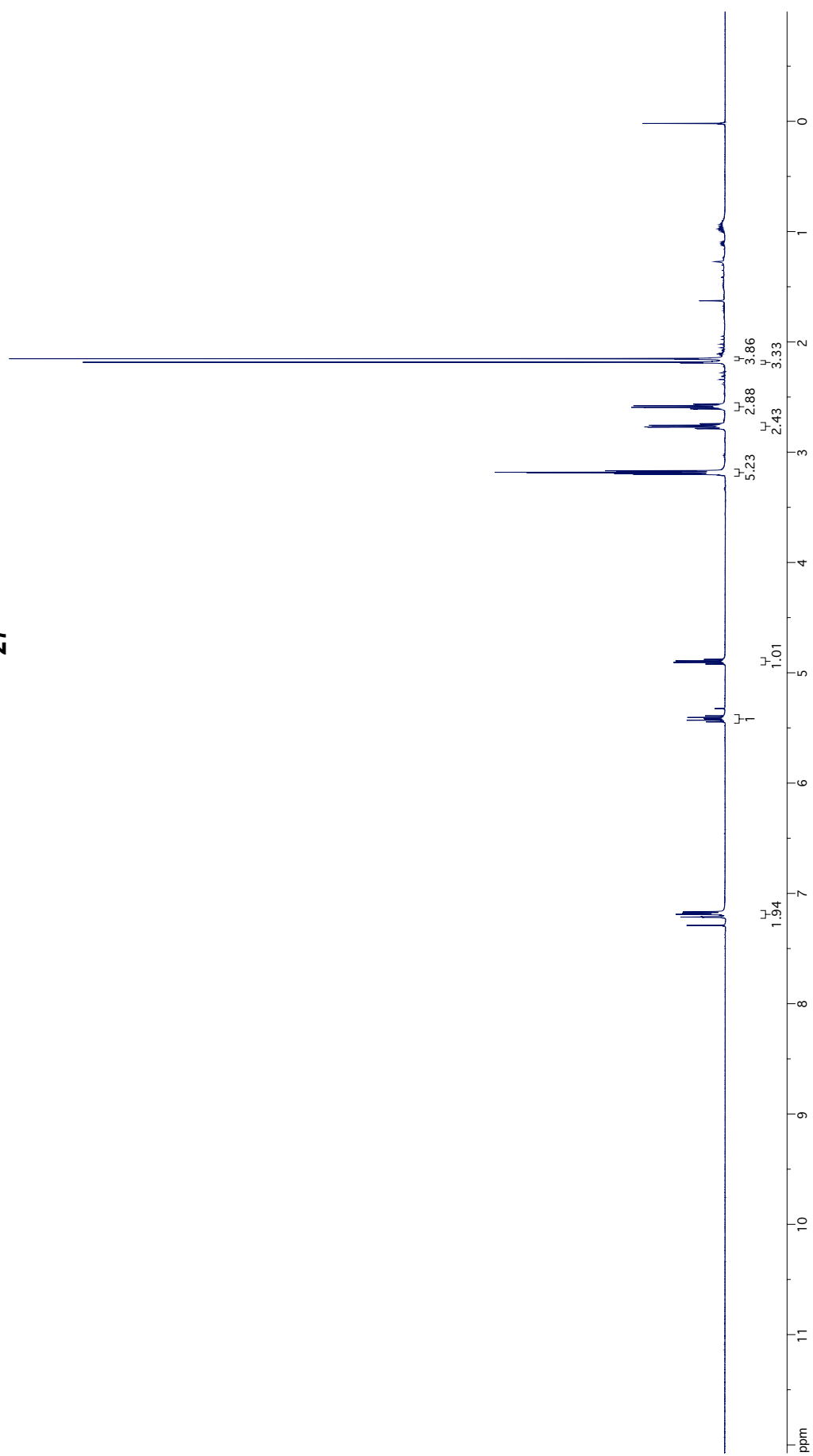
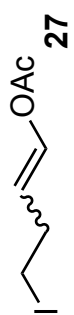


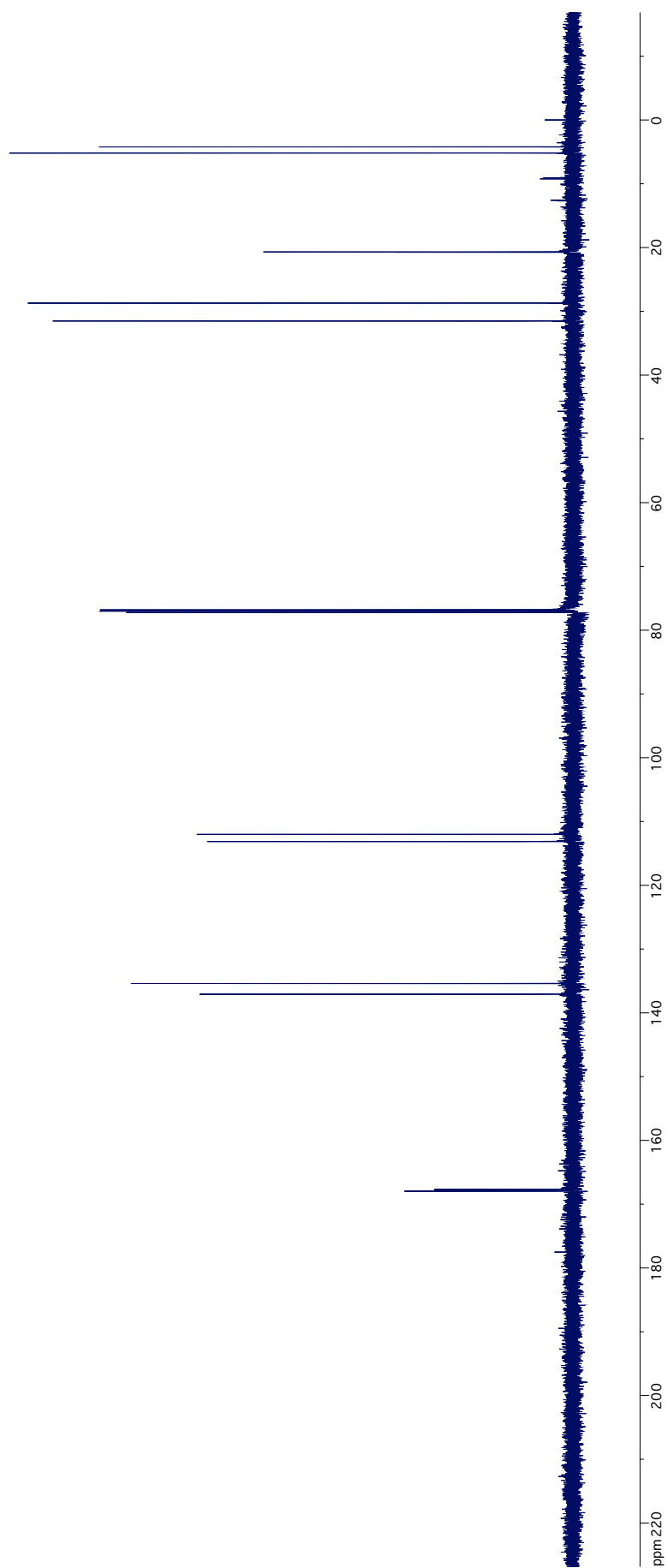
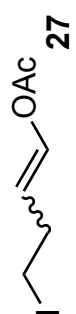


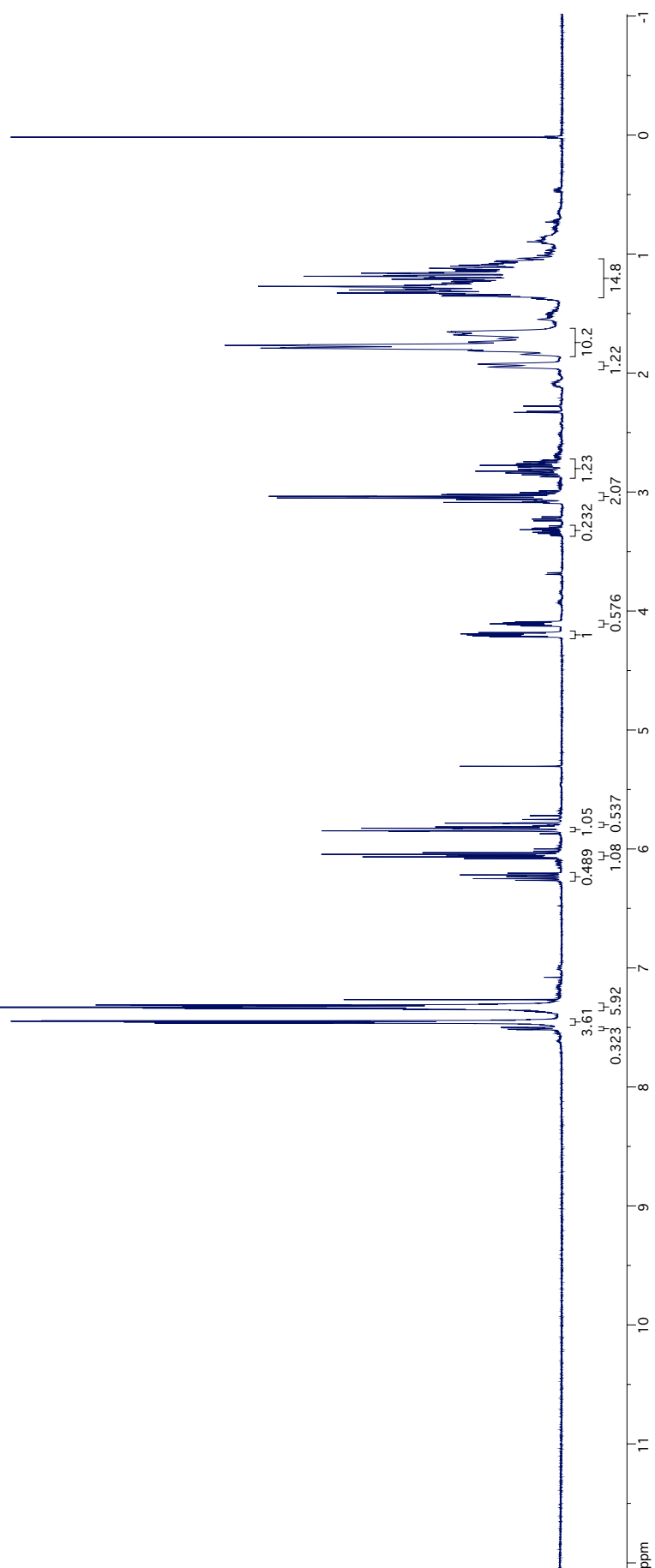
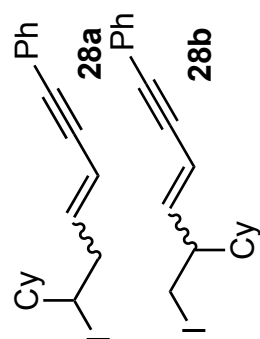


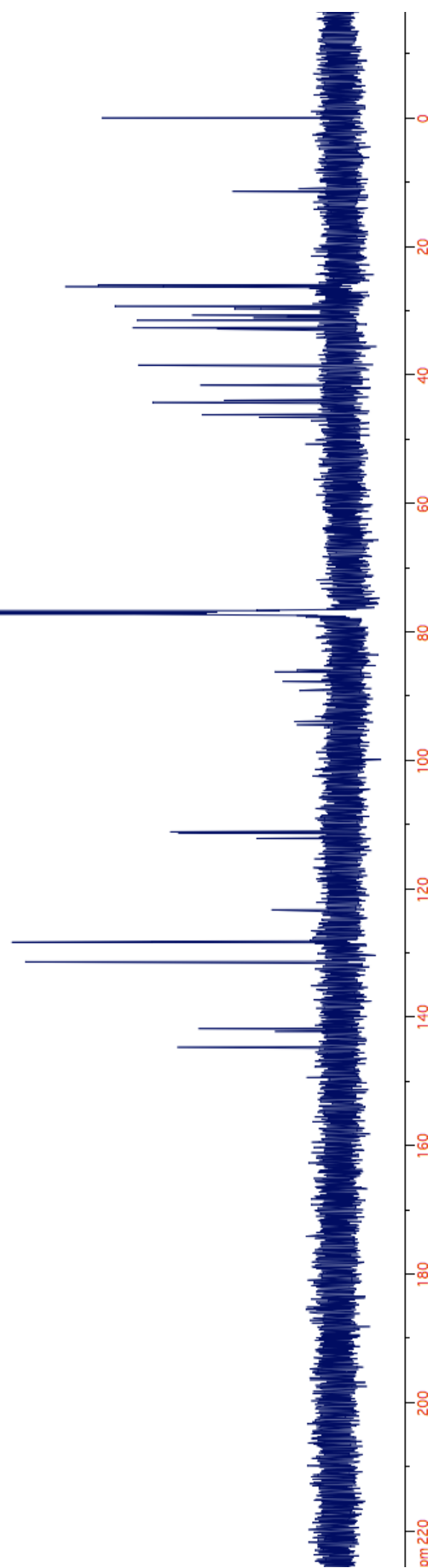
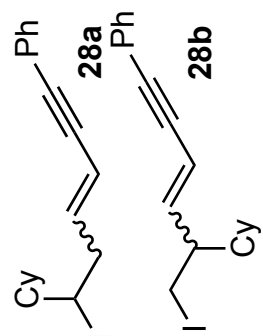
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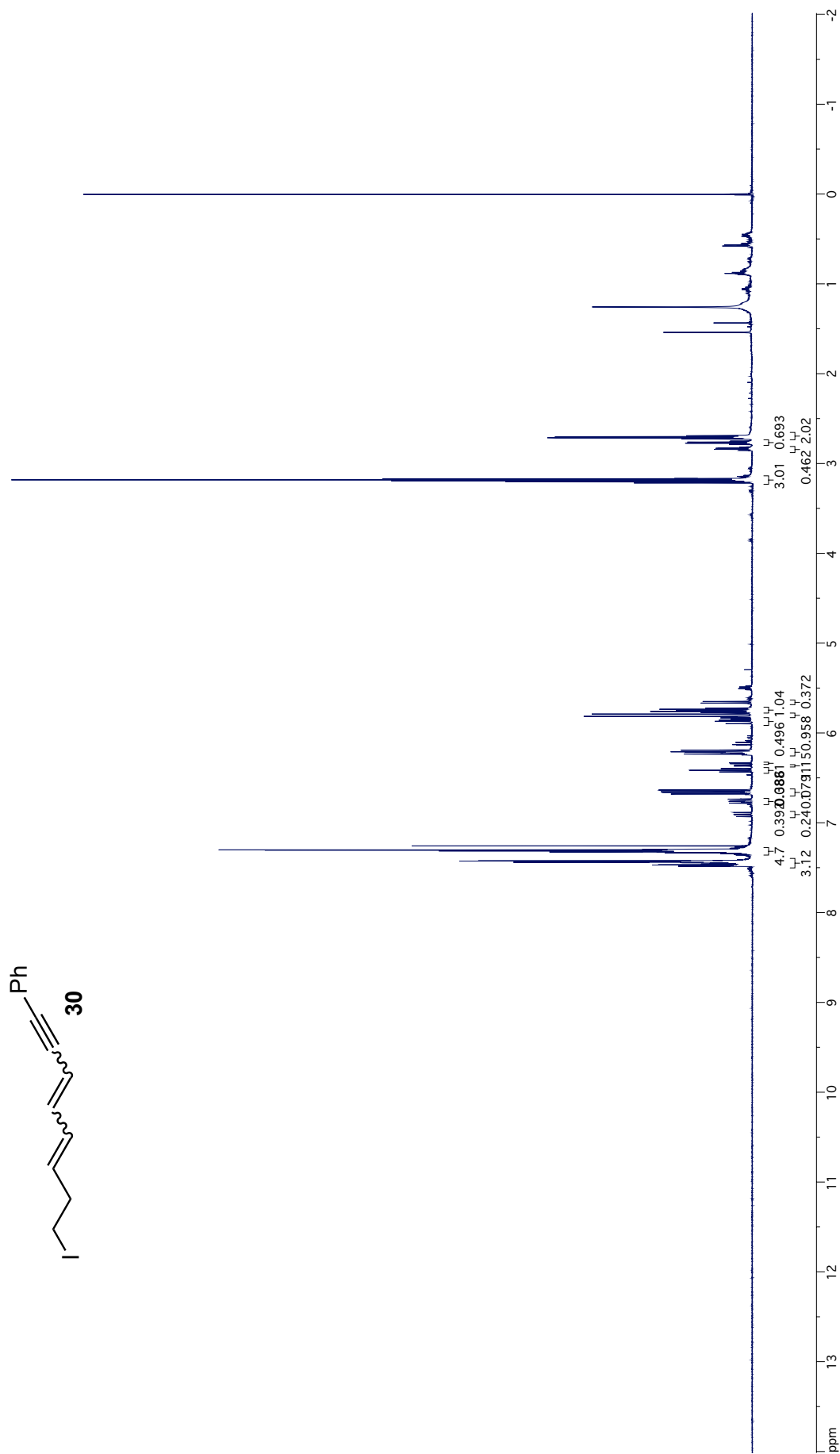


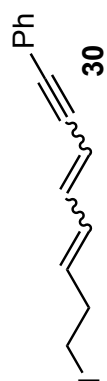












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