

Supporting Information for publication

Diastereoselective Synthesis of Dihydropyrans via Prins Cyclization of Enol Ethers: Total Asymmetric Synthesis of (+)-Civet Cat Compound

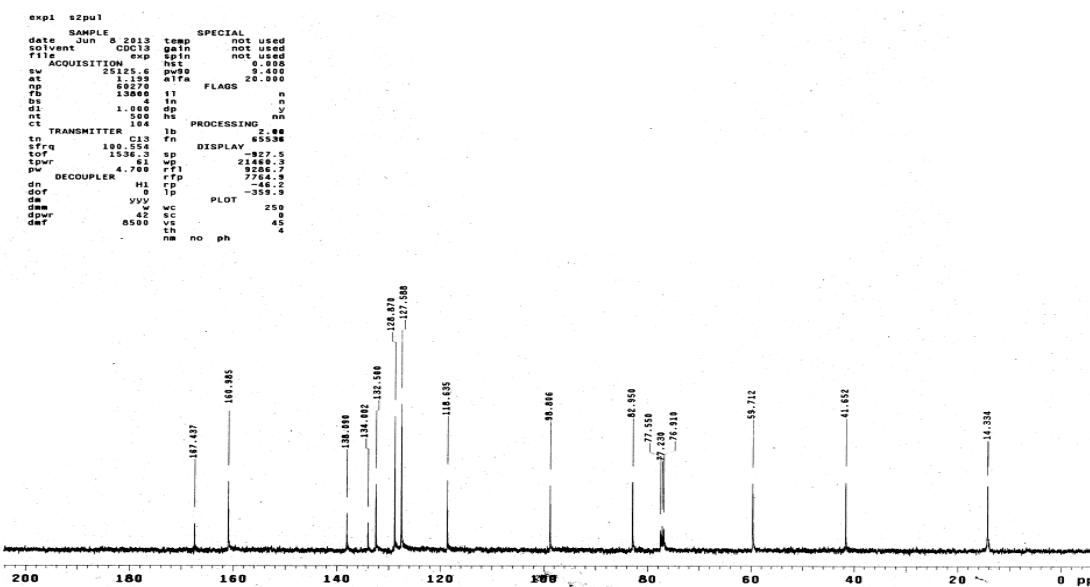
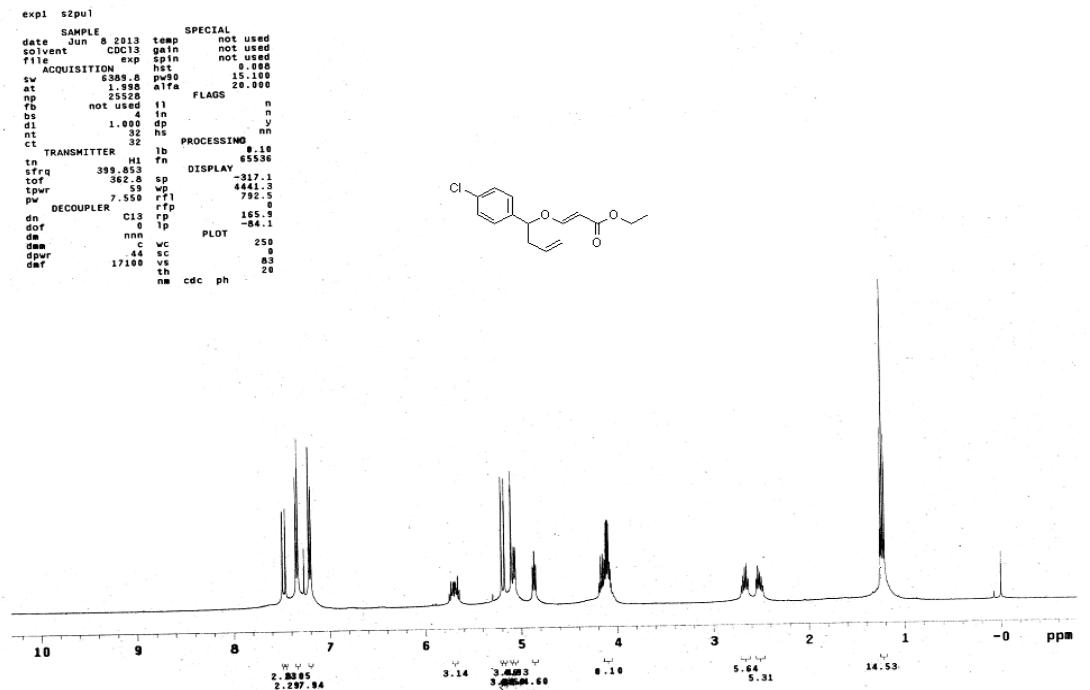
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Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati 781039, Assam,
India, e-mail: asaikia@iitg.ernet.in

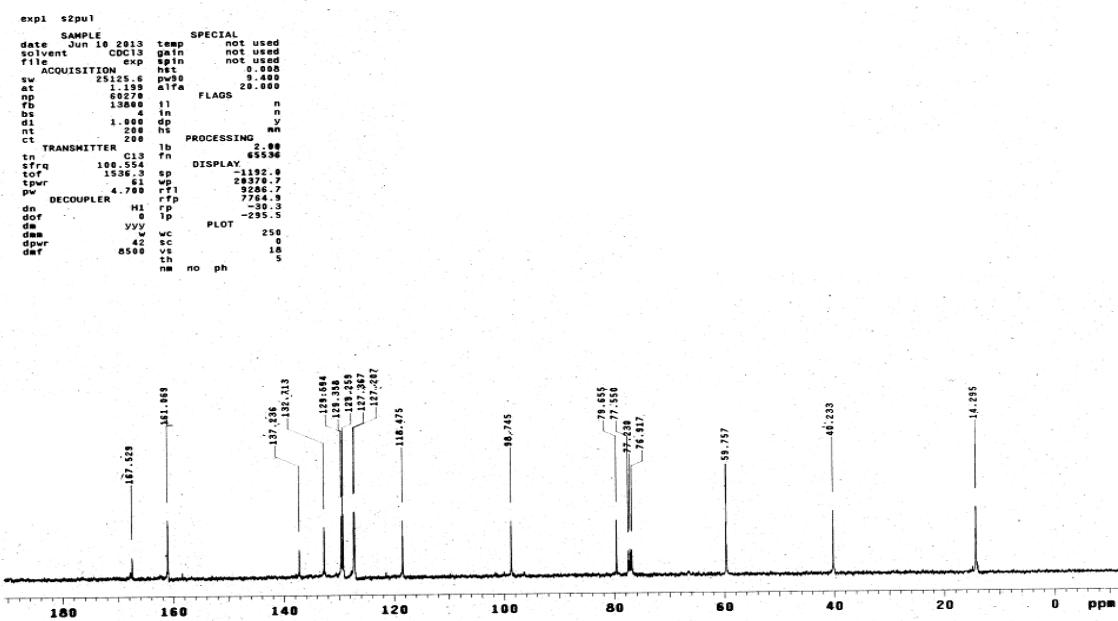
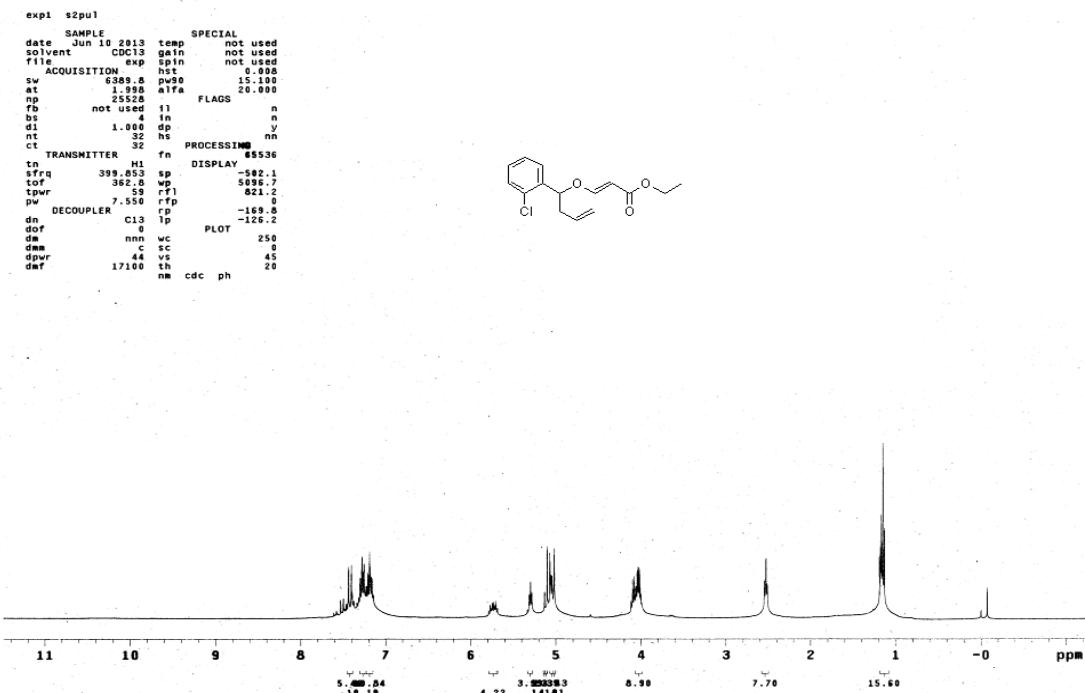
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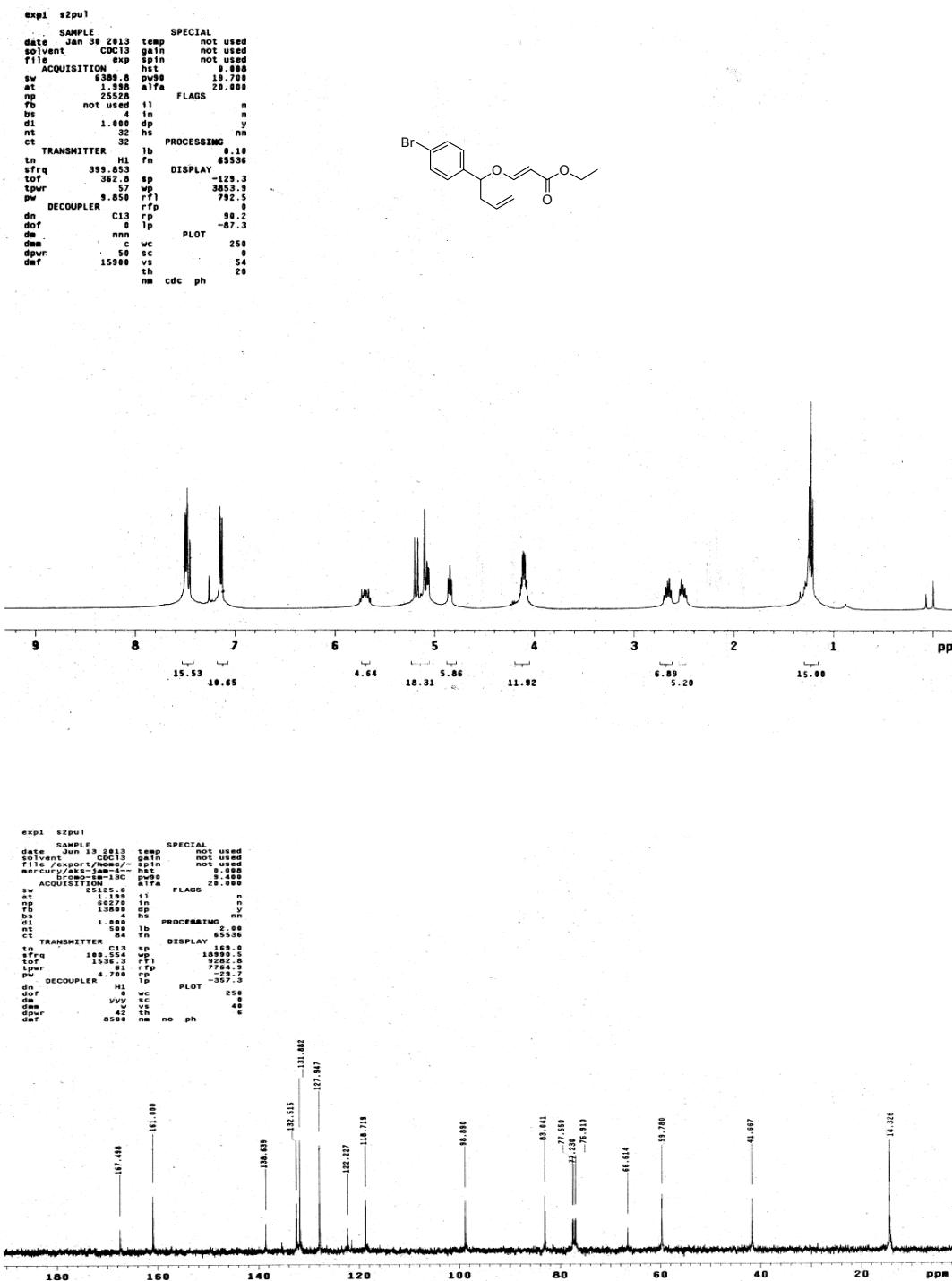
¹H and ¹³C NMR spectra of (E)-Ethyl 3-((1-(4-chlorophenyl)but-3-en-1-yl)oxy)acrylate, 1b



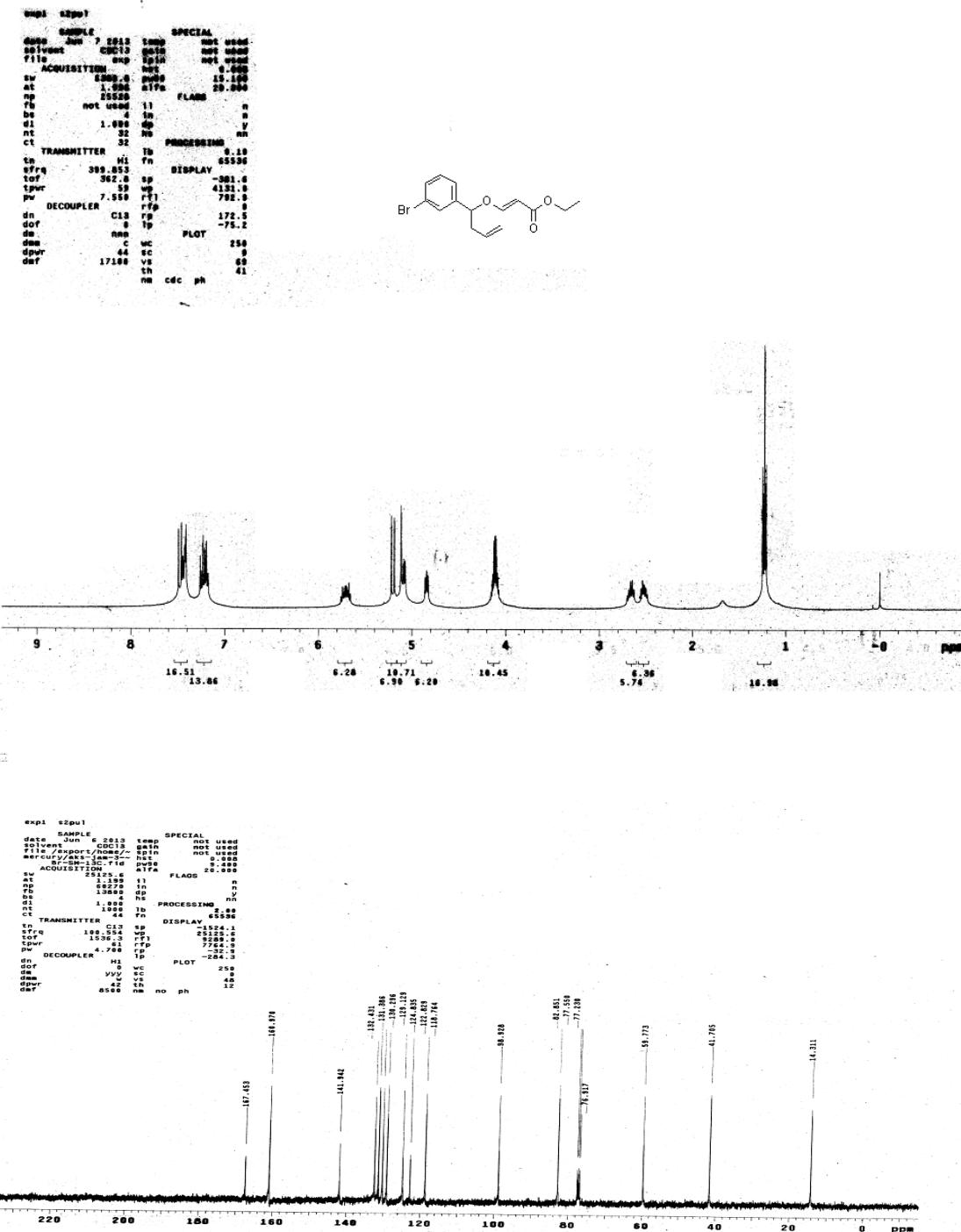
¹H and ¹³C NMR spectra of (E)-Ethyl 3-((1-(2-chlorophenyl)but-3-en-1-yl)oxy)acrylate, 1c



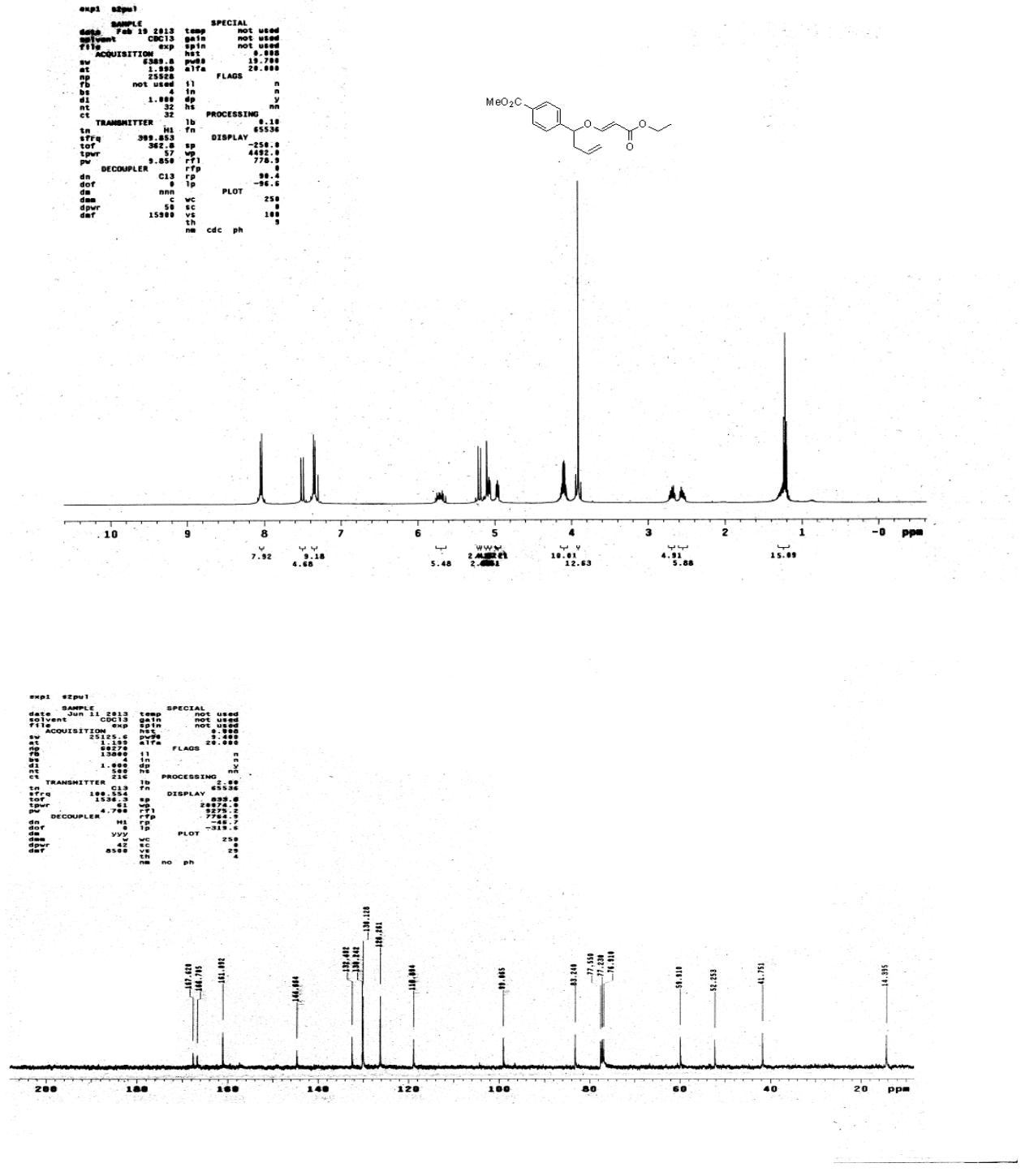
¹H and ¹³C NMR spectra of (E)-Ethyl 3-((1-(4-bromophenyl)but-3-en-1-yl)oxy)acrylate, 1d



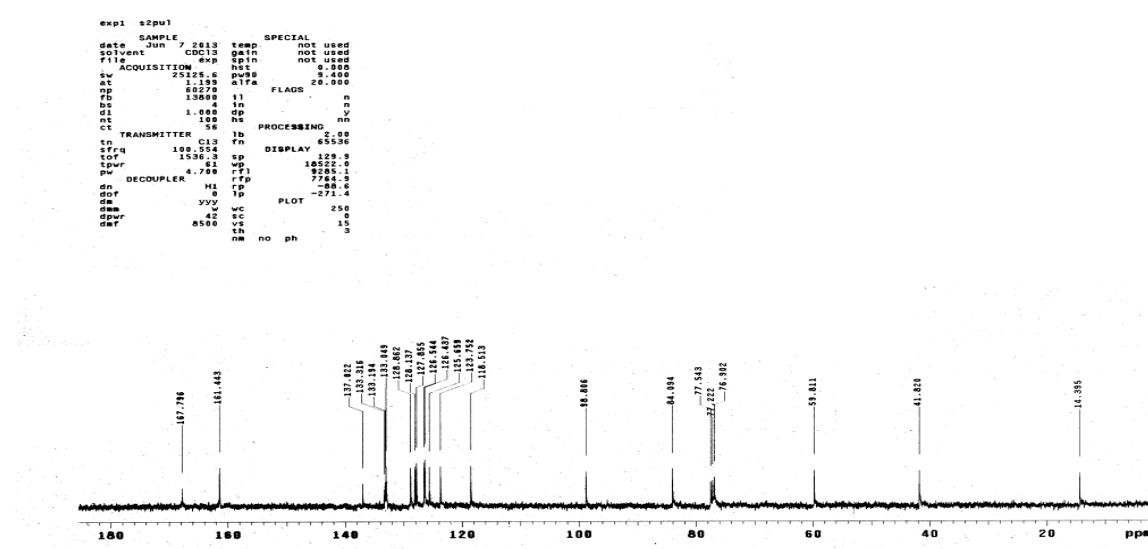
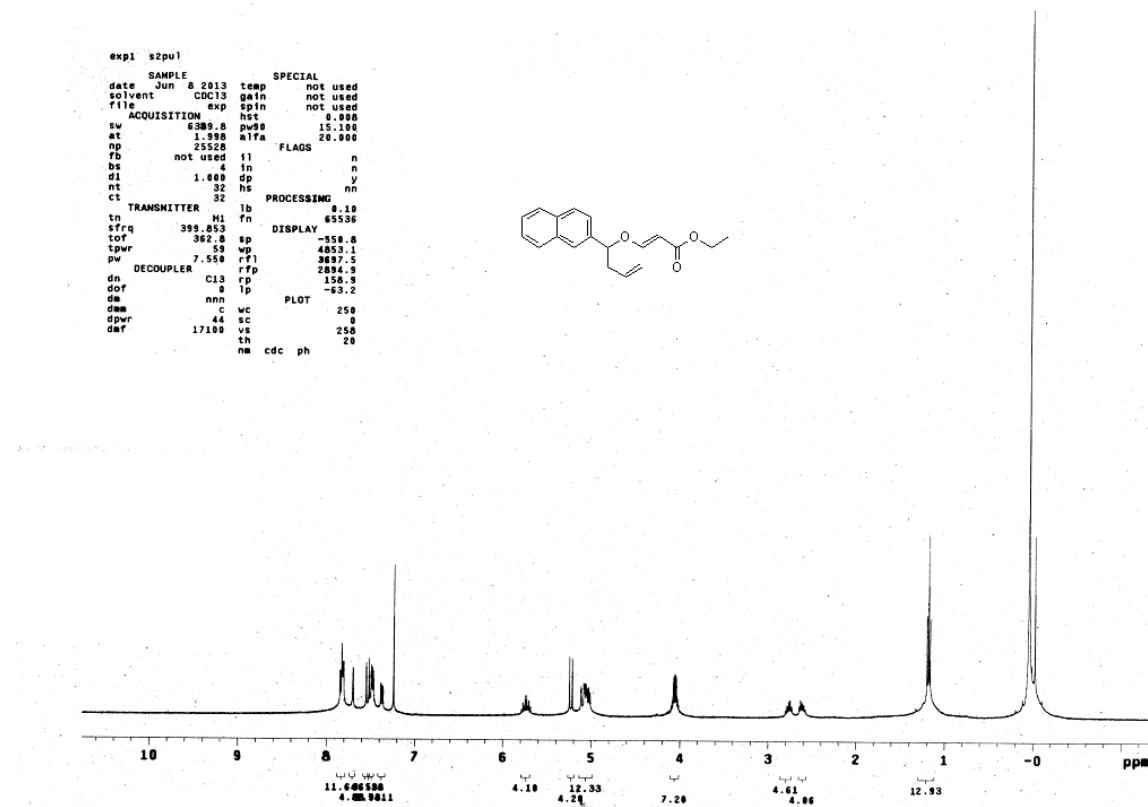
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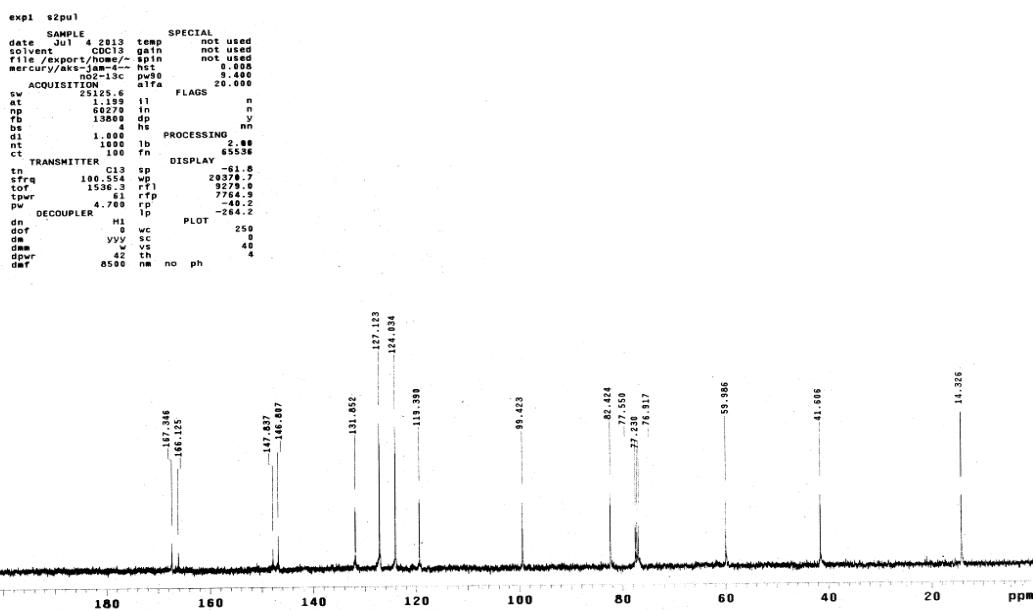
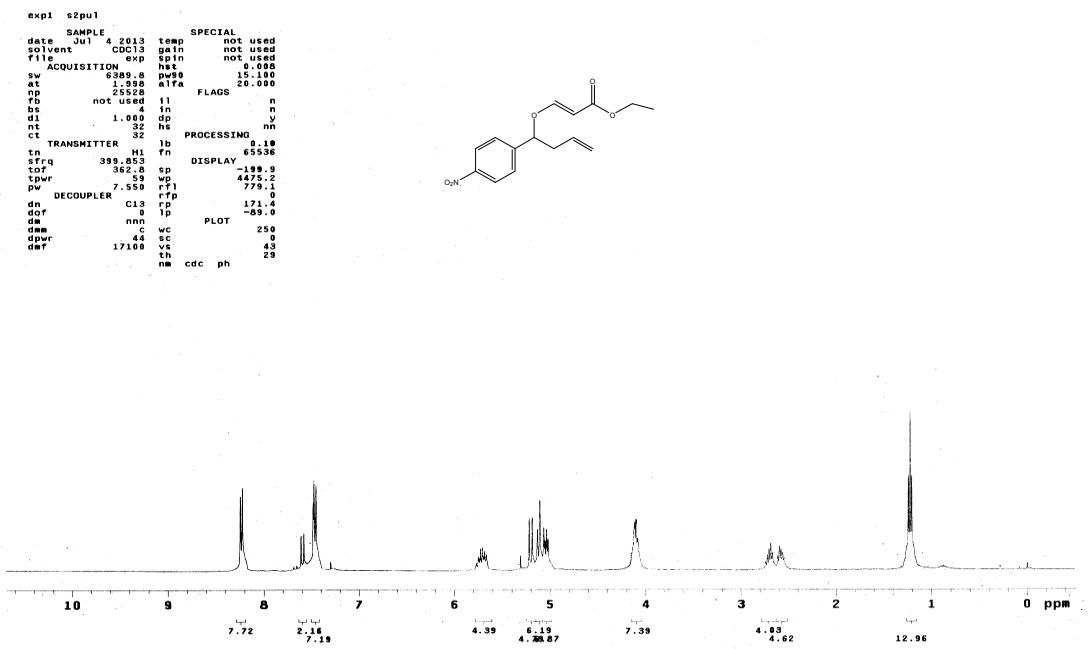
¹H and ¹³C NMR spectra of (E)-Methyl 4-((3-ethoxy-3-oxoprop-1-en-1-yl)oxy)but-3-en-1-yl)benzoate, **1f**



¹H and ¹³C NMR spectra of (E)-Ethyl 3-((1-(naphthalen-2-yl)but-3-en-1-yl)oxy)acrylate, 1g



¹H and ¹³C NMR spectra of (E)-Ethyl 3-((1-(4-nitrophenyl)but-3-en-1-yl)oxy)acrylate, 1h

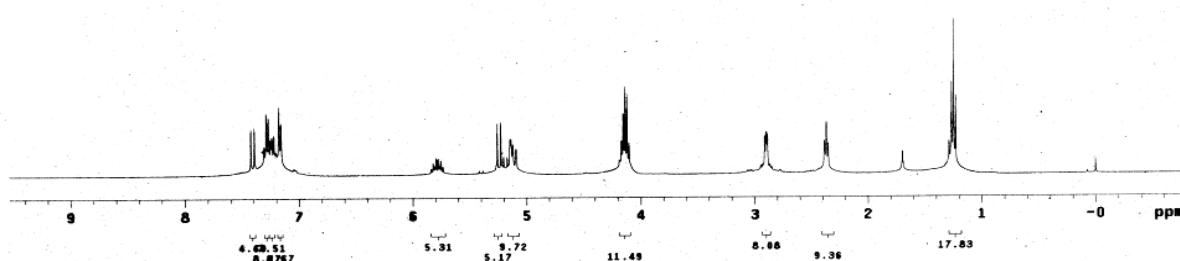
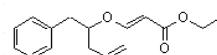


¹H and ¹³C NMR spectra of (*E*)-Ethyl 3-((1-phenylpent-4-en-2-yl)oxy)acrylate, 1i

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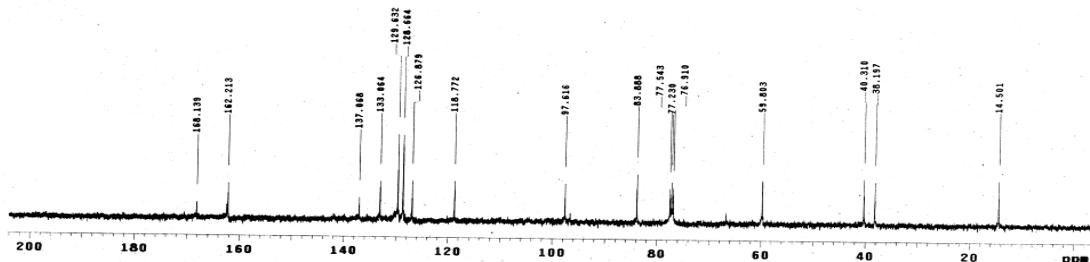
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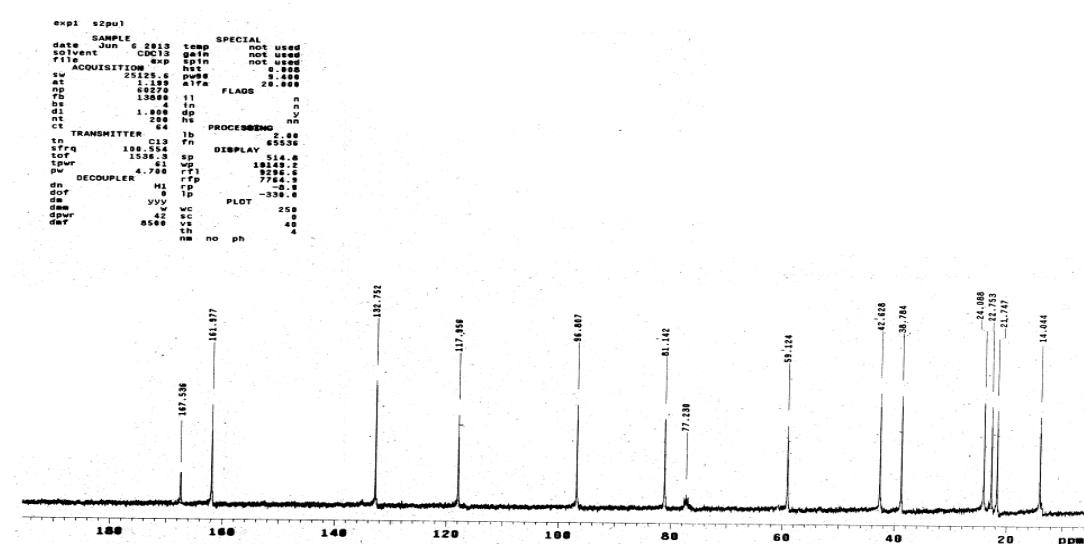
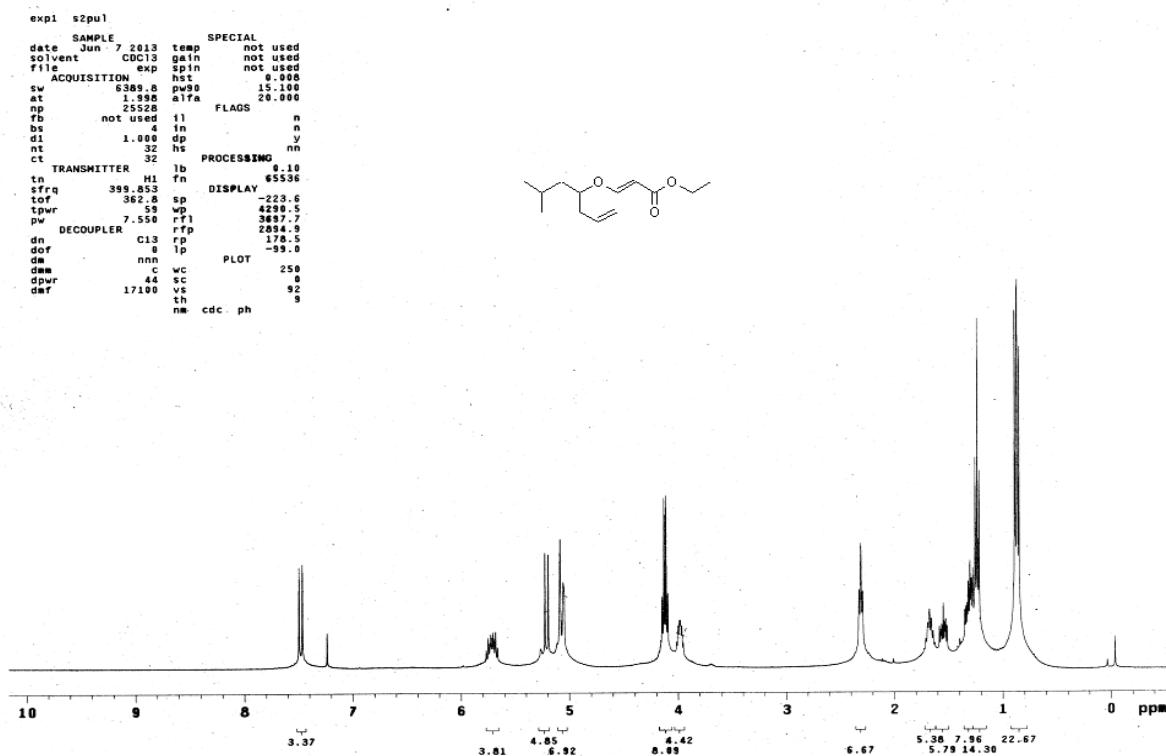
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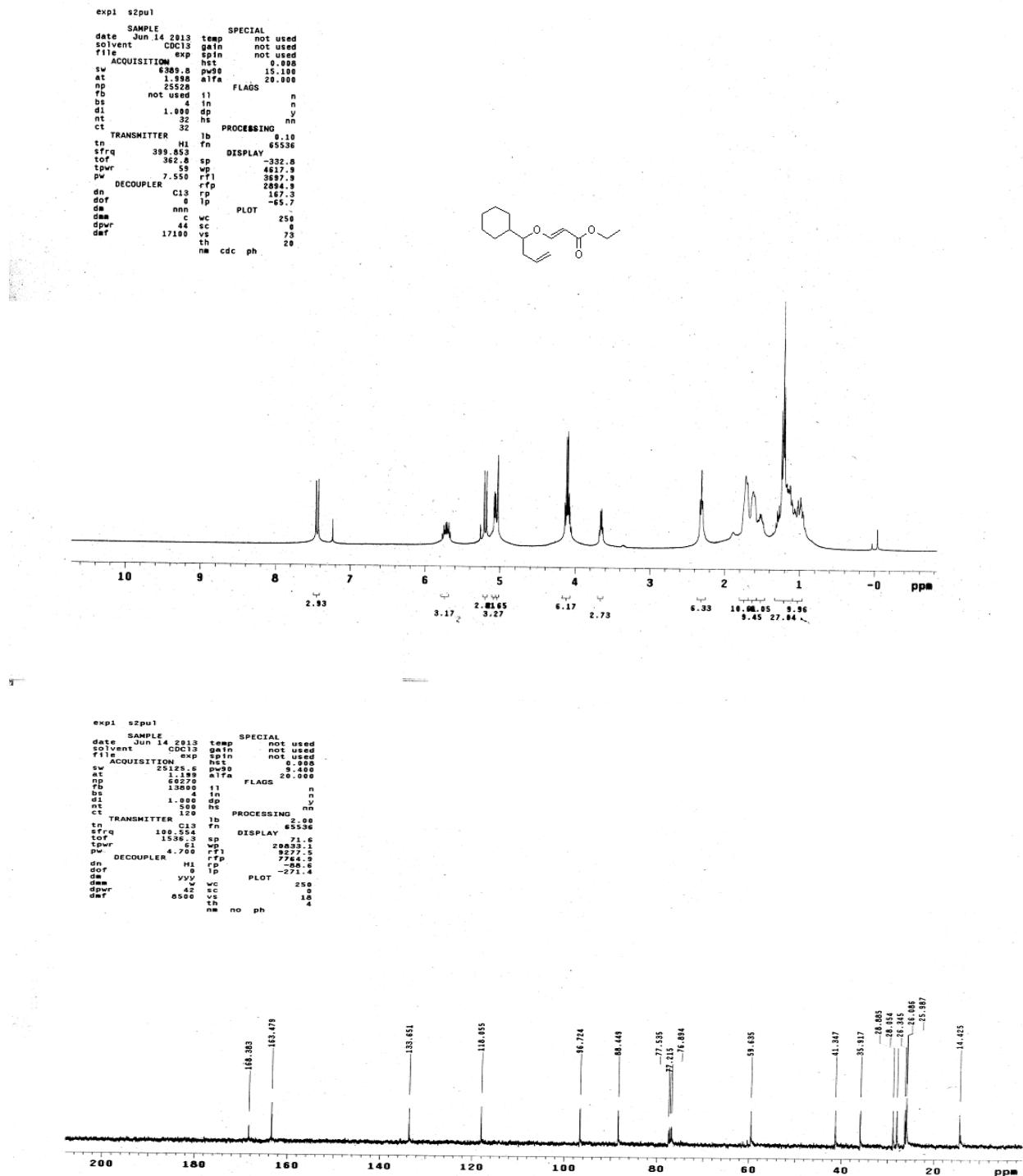
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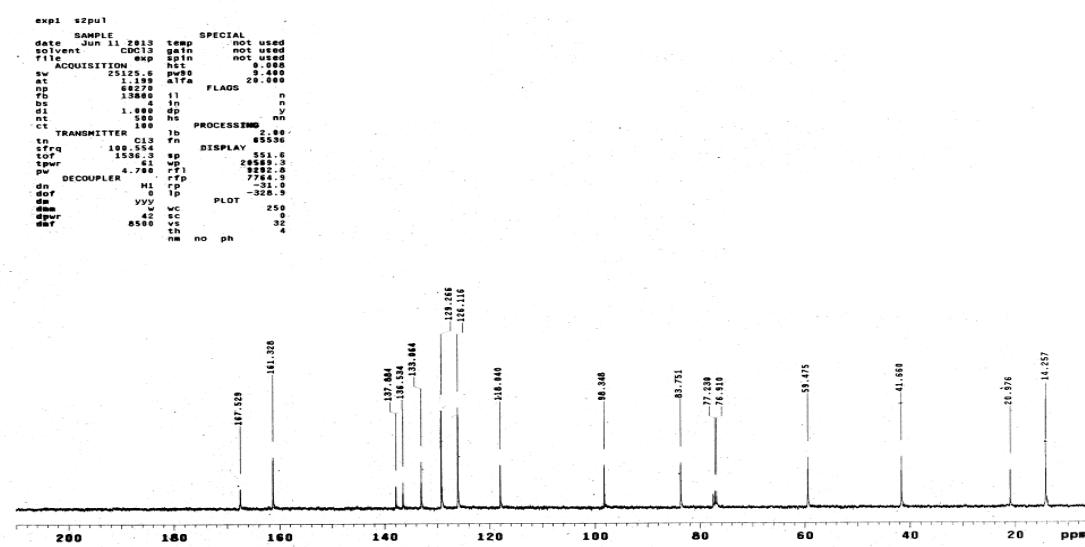
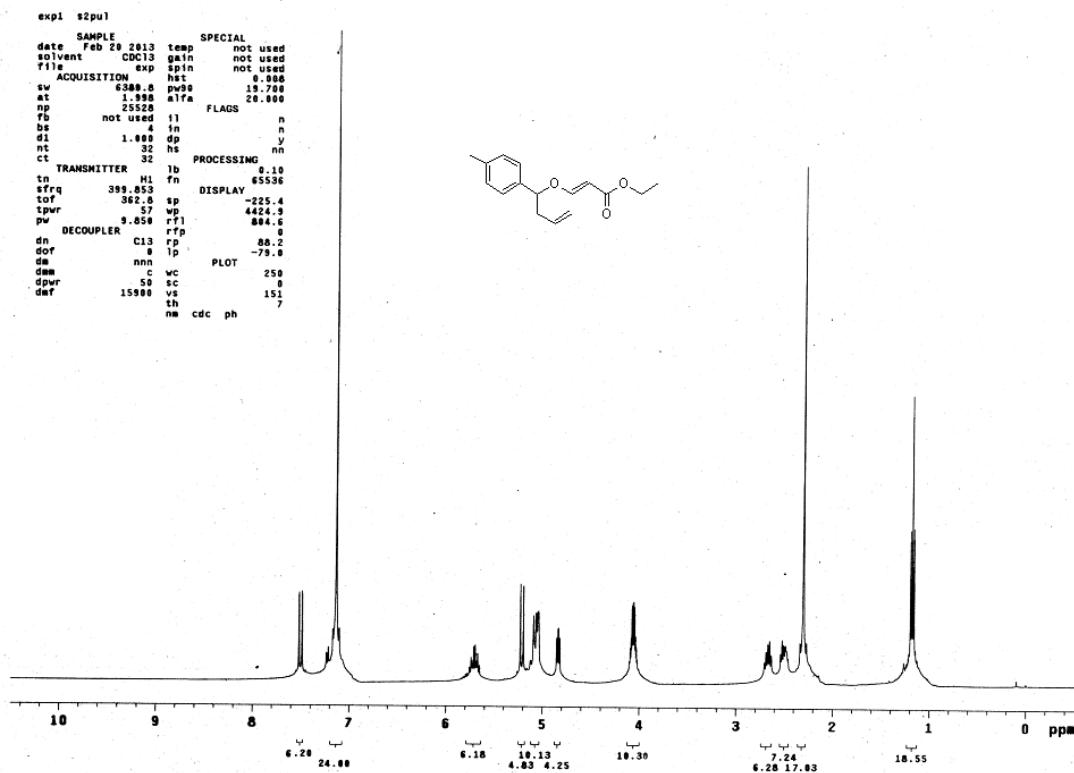
¹H and ¹³C NMR spectra of (*E*)-Ethyl 3-((6-methylhept-1-en-4-yl)oxy)acrylate, 1j



¹H and ¹³C NMR spectra of (E)-Ethyl 3-((1-cyclohexylbut-3-en-1-yl)oxy)acrylate, 11



¹H and ¹³C NMR spectra of (E)-Ethyl 3-((1-(*p*-tolyl)but-3-en-1-yl)oxy)acrylate, 1m

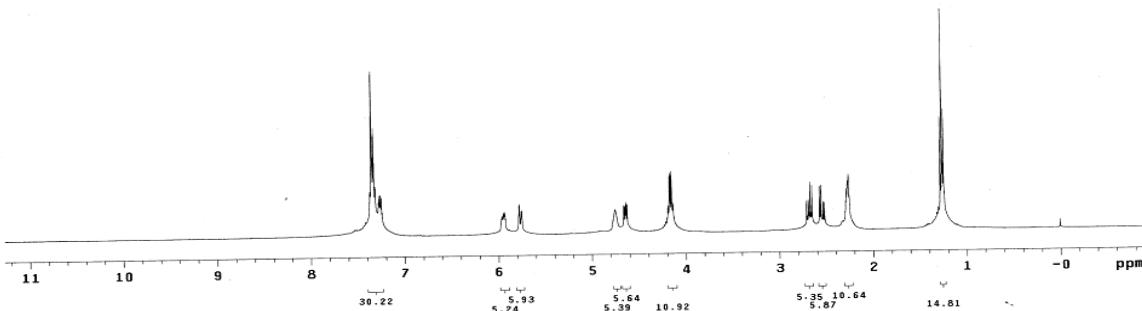
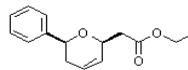


¹H and ¹³C NMR spectra of Ethyl-2-(6-phenyl-5,6-dihydro-2H-pyran-2-yl) acetate, 2a

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      ct     32      PROCESSING
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      tn      H1    fn      65536
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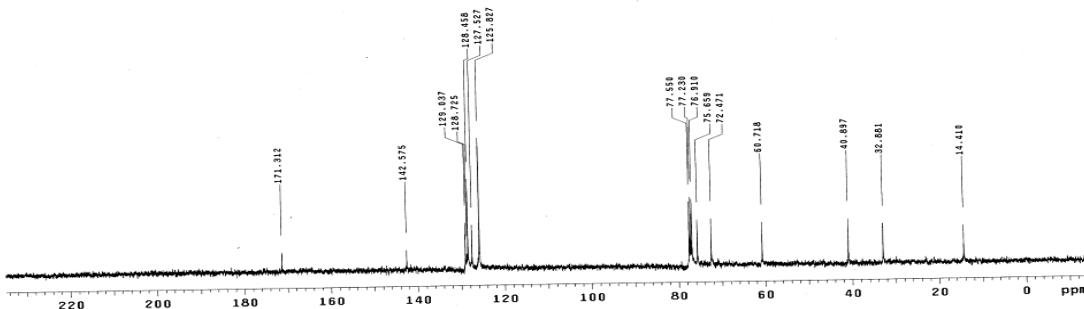
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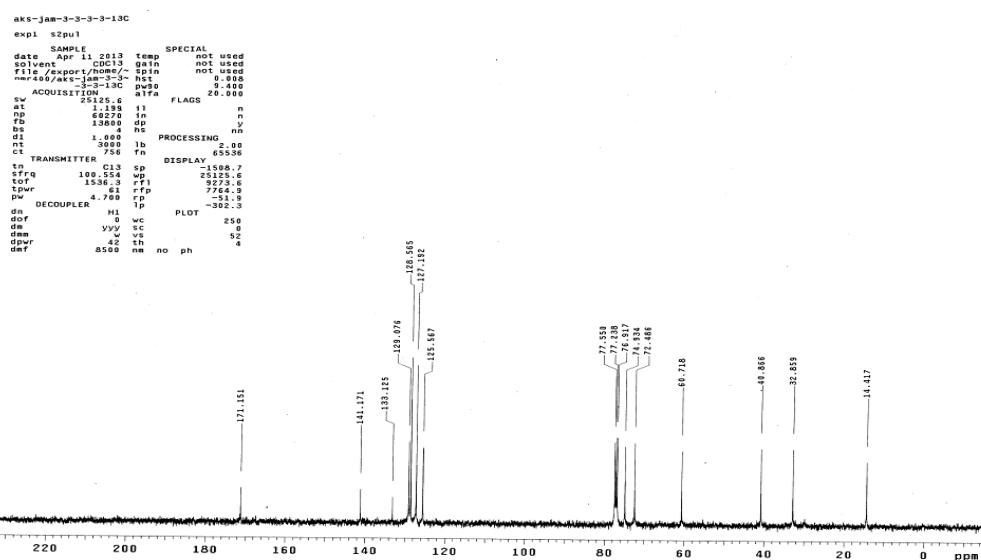
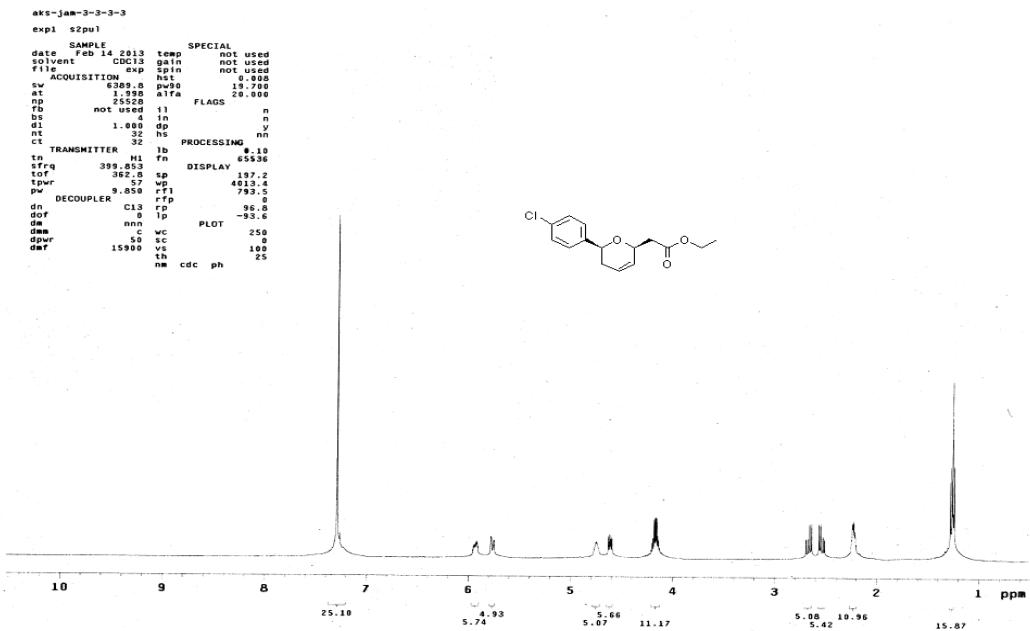
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      np     13890   dp      v
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      di     1.000   lb      2.00
      nt     32      ts      65536
      ct     616   tf      65536
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      tof     100.554  rfp    7764.9
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      pw     4.760   fp      -304.7
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¹H and ¹³C NMR spectra of Ethyl-2-(6-(4-chlorophenyl)-5,6-dihydro-2H-pyran-2-yl)acetate, 2b

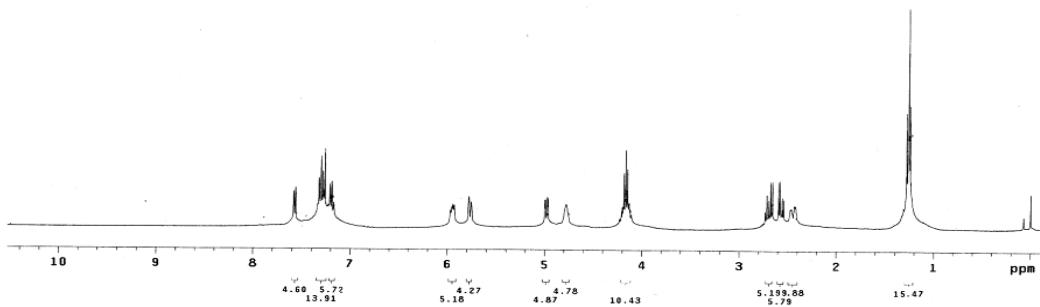
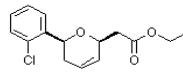


¹H and ¹³C NMR spectra of Ethyl-2-(6-(2-chlorophenyl)-5,6-dihydro-2H-pyran-2-yl)acetate, 2c

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bs 4 in n
dt 1.000 np y
nt 32 s m
ct 32 PROCESSING m
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nm cdc ph 6

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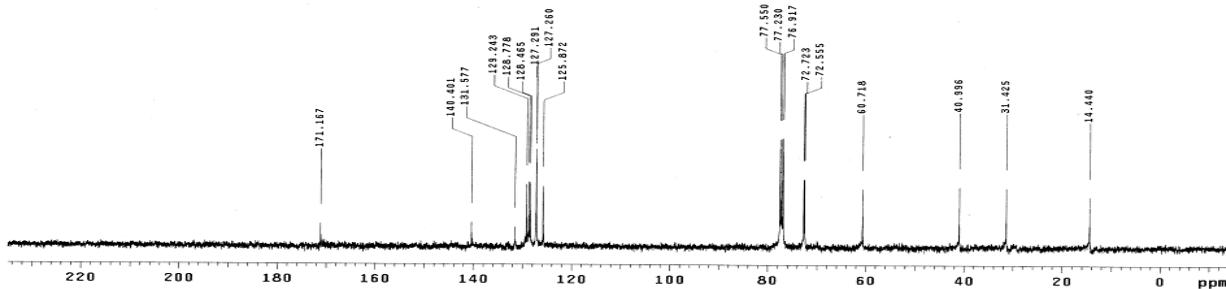


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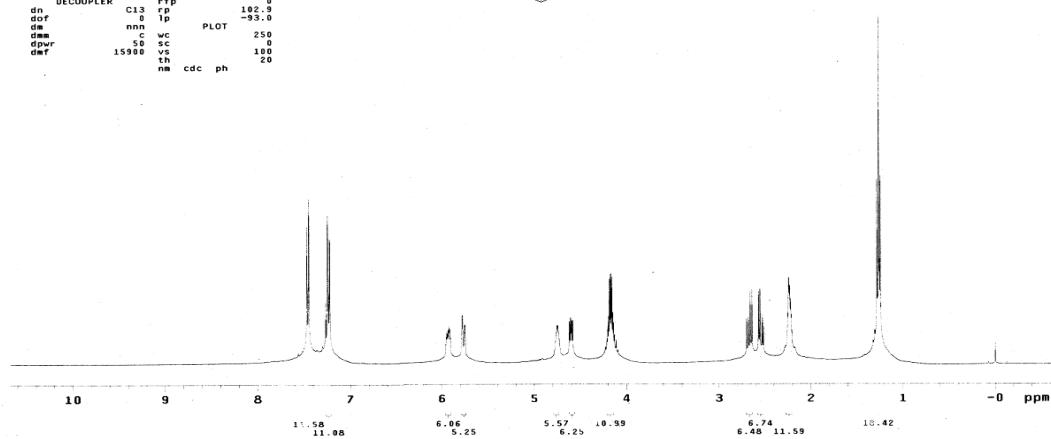


¹H and ¹³C NMR spectra of Ethyl-2-(6-(4-bromoophenyl)-5,6-dihydro-2H-pyran-2-yl)acetate, 2d

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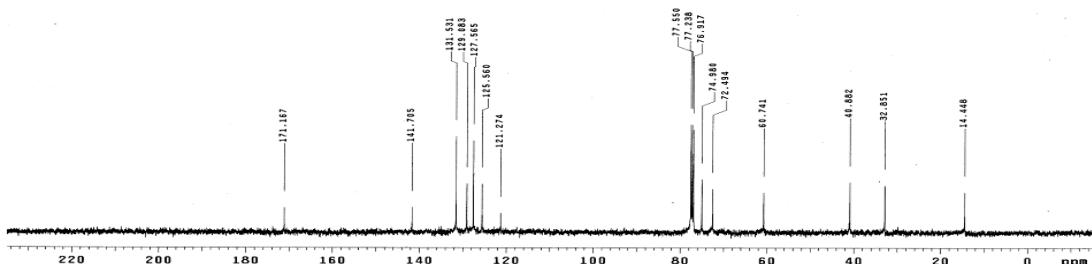
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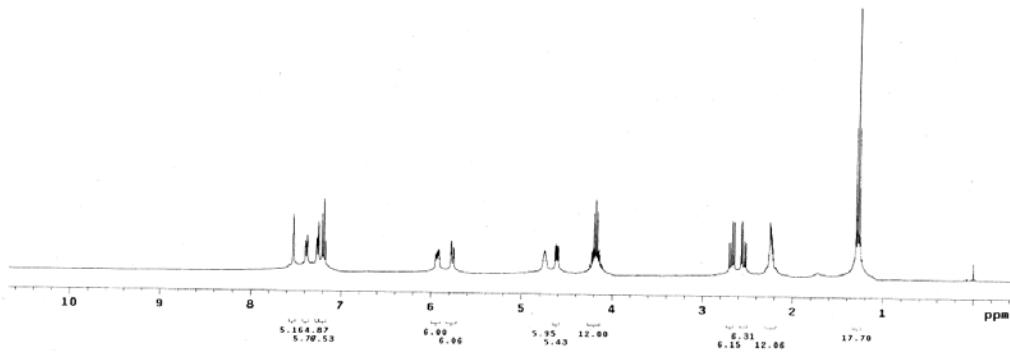
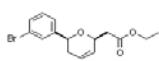


¹H and ¹³C NMR spectra of Ethyl-2-(6-(3-bromoophenyl)-5,6-dihydro-2H-pyran-2-yl)acetate, 2e

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ct 32 ph n
c1 32 processing n
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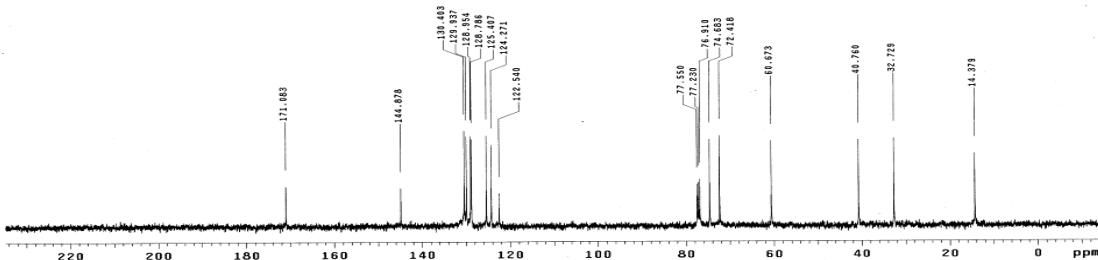


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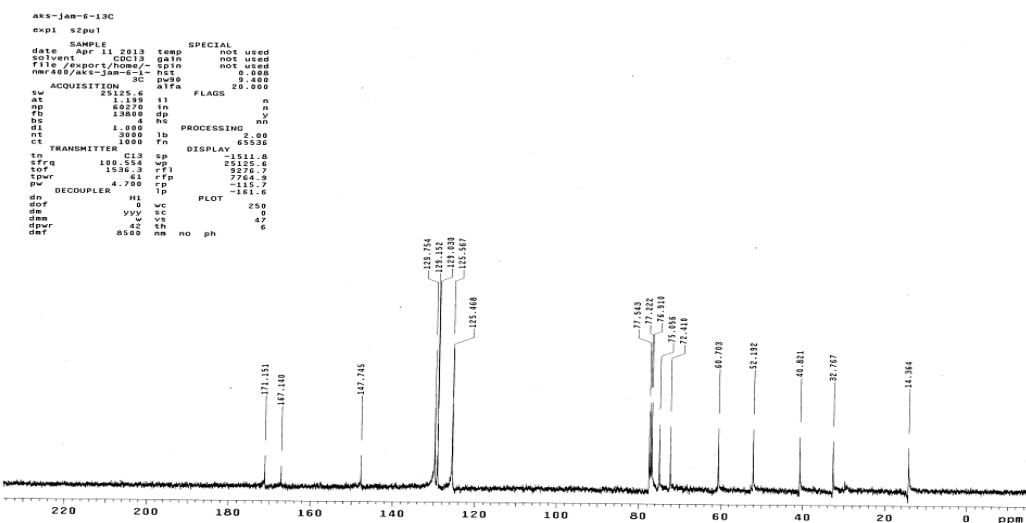
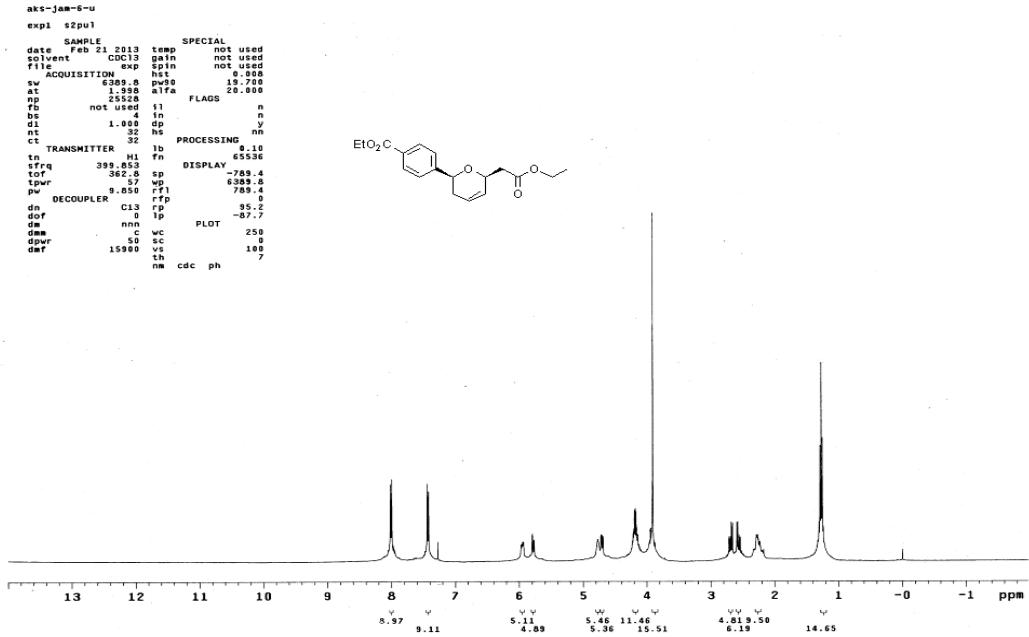
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¹H and ¹³C NMR spectra of Methyl-4-(6-(2-ethoxy-2-oxoethyl)-3,6-dihydro-2H-pyran-2-yl)benzoate, 2f



¹H and ¹³C NMR spectra of Ethyl 2-(6-(naphthalen-1-yl)-5,6-dihydro-2H-pyran-2-yl)acetate, 2g

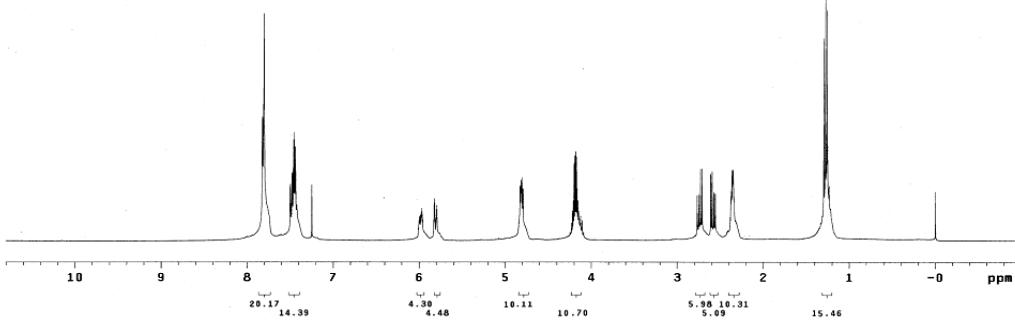
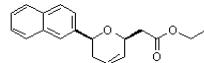
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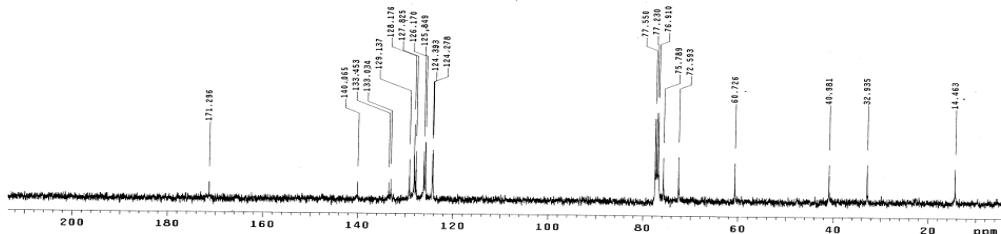


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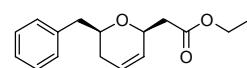
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DECOUPLER H1 sp -271.4
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dof   VVY sc 0
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¹H and ¹³C NMR spectra of Ethyl-2-(6-benzyl-5,6-dihydro-2H-pyran-2-yl)acetate, 2i



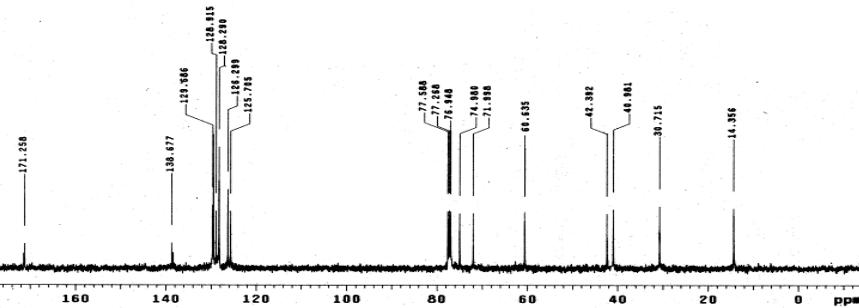
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 DS 2
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 AQ 1.3631488 sec
 RG 99.36
 DW 41.600 usec
 DE 6.50 usec
 TE 299.9 K
 D1 1.00000000 sec
 TDO 1

CHANNEL f1
 SP01 600.1737063 MHz
 NC1 1H
 PI 12.00 usec
 PLW1 21.00000000 W

F2 - Processing parameters
 SI 16384
 SF 600.1700152 MHz
 WDM EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



```
akr-jam-19-13C
Sample: 2i
Date: Apr 11 2013
Time: 10:26:26
INSTRUM: spect
PROBHD: 5 mm PABBO BB/
PULPROG: zg30
TD: 32768
SOLVENT: CDCl3
NS: 16
DS: 2
SWH: 12019.230 Hz
FIDRES: 0.366798 Hz
AQ: 1.3631488 sec
RG: 99.36
DW: 41.600 usec
DE: 6.50 usec
TE: 299.9 K
D1: 1.00000000 sec
TDO: 1
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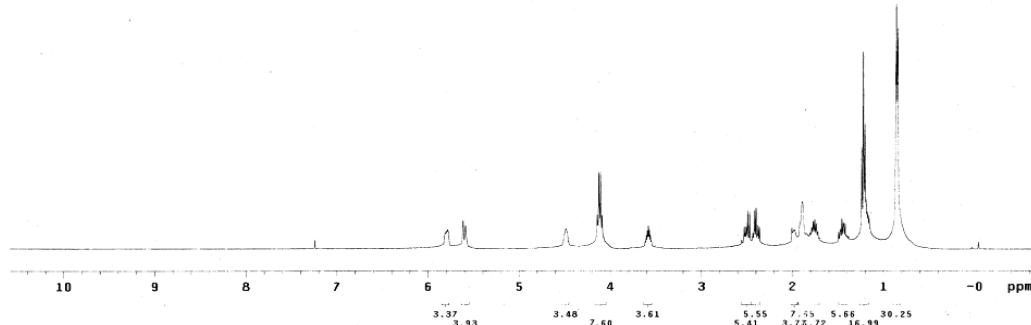
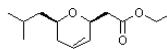


¹H and ¹³C NMR spectra of Ethyl 2-(6-isobutyl-5,6-dihydro-2H-pyran-2-yl)acetate, 2j

```

aks-jam-18
exp1 s2pul
      SAMPLE SPECIAL
date Mar 19 2013 temp not used
solvent CDCl3 gain 0.000
file /export/home/~/spin not used
ACQUISITION hst pw 0.000
sw 6389.8 pw0 14.100
at 1.998 g1 20.000
np 25528 flags 20.000
rb not used d1 n
bs 4 d1 n
d1 1.000 dp y
nt 32 nn
ct 32 PROCESSING
TRANSMITTER H1 fn 65536
srfq 399.853 DISPLAY
totf 362.8 sp -274.1
tpr 1536.3 rfp 454.9
pw 7.050 rfp 3697.9
DECOUPLER C13 rfp 2894.9
dn C13 ip 74.9
dof 0 1p -58.3
dmt nuc PLOT 250
dmc c wc 0
dpwr 50 sc 0
dmf 15900 vs 64
dmr 10 th 10
nm cdc ph

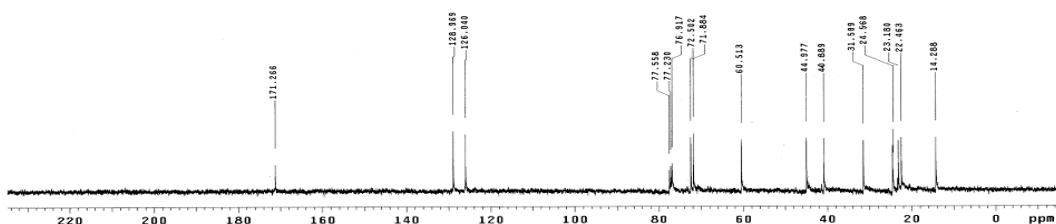
```



```

aks-jam-18-13C
exp1 s2pul
      SAMPLE SPECIAL
date Apr 11 2013 temp not used
solvent CDCl3 spin not used
file /export/home/~/spin not used
nmr400/aks-jam-18-13C he1 9.400
he2 9.400
alpha 20.000
ACQUISITION 25125.6 flags 65536
at 1.198 d1 n
np 25528 fn 0
rb 138600 dp 0
bs 16000 n
d1 1.000 lb 2.00
ct 160 fn 65536
TRANSMITTER C13 sp DISPLAY
srfq 138.963 pw -1510.3
totf 1536.3 rfp 9275.2
tpr 4.700 rfp 7768.5
pw 6.5 rfp 271.4
DECOUPLER H1 ip -271.4
dn C13 ip 250
dof 0 wc 250
dmc y sc 0
dmc c vs 18
dpwr 8500 nm th 5
dmr 8500 nm no ph

```



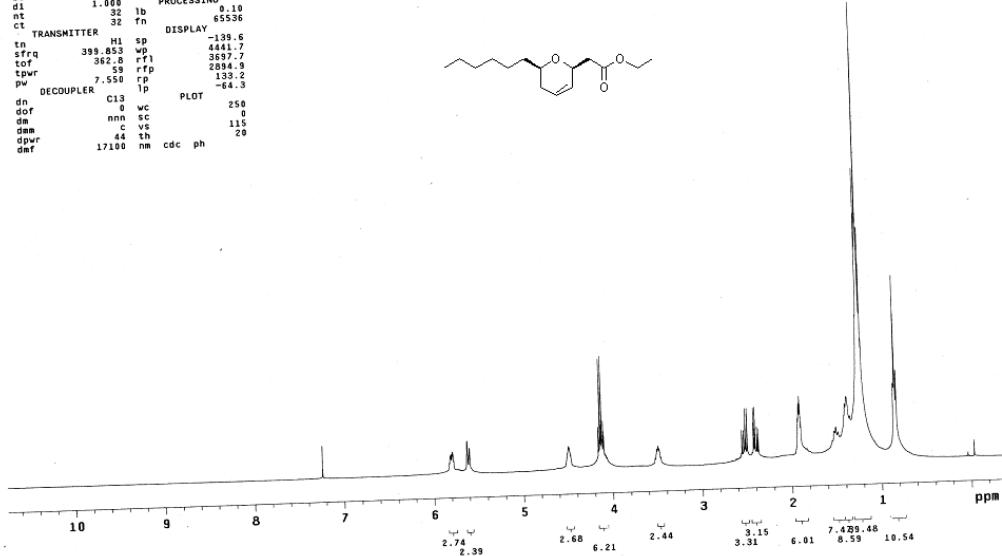
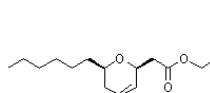
¹H and ¹³C NMR spectra of Ethyl 2-(6-hexyl-5,6-dihydro-2H-pyran-2-yl)acetate, 2k^{14d}

```

aks-jam-20-hept
exp1 szpul

SAMPLE          SPECIAL
date  Apr 11 2013 temp  not used
temp   200.00 gain  not used
t1file /export/home/-/spin  not used
t1file /export/home/-/hs  not used
nmr409/aks-jam-20-- hst  15.100
nmr409/aks-jam-20-- hept  15.100
ACQUISITION alfa  20.000
SW      6389.8   FLAGS
AT      1.000    1L  n
NP      25528   IN  n
RB      not used DP  V
BS      1.000    PROCESSING nn
TD      32    1B  0.10
NT      32    32  65536
CT      1.000    1B  65536
TRANSMITTER H1 SP  -138.6
TN      399.80   1P  4441.7
SFREQ  399.80   1P  3657.7
TCF     362.8   RF1  285.8
TPWR   7.550   RF1  133.2
PW      64.3    P1  -64.3
DECOUPLER C13 PLOT 54.3
DN      0        WC  250
DOR    0        MN  0
DE     0        SC  115
DMM    0        VS  20
DPWR   17100   NM  cdc ph
DMT

```

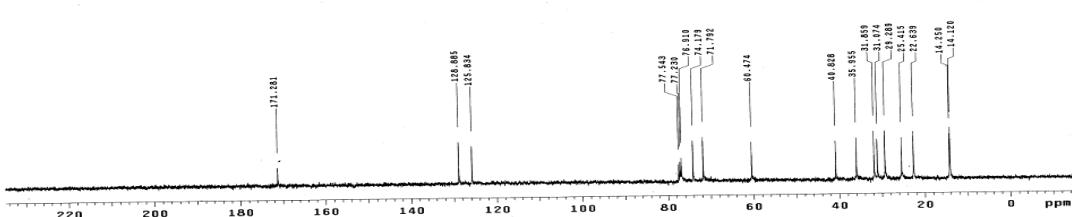


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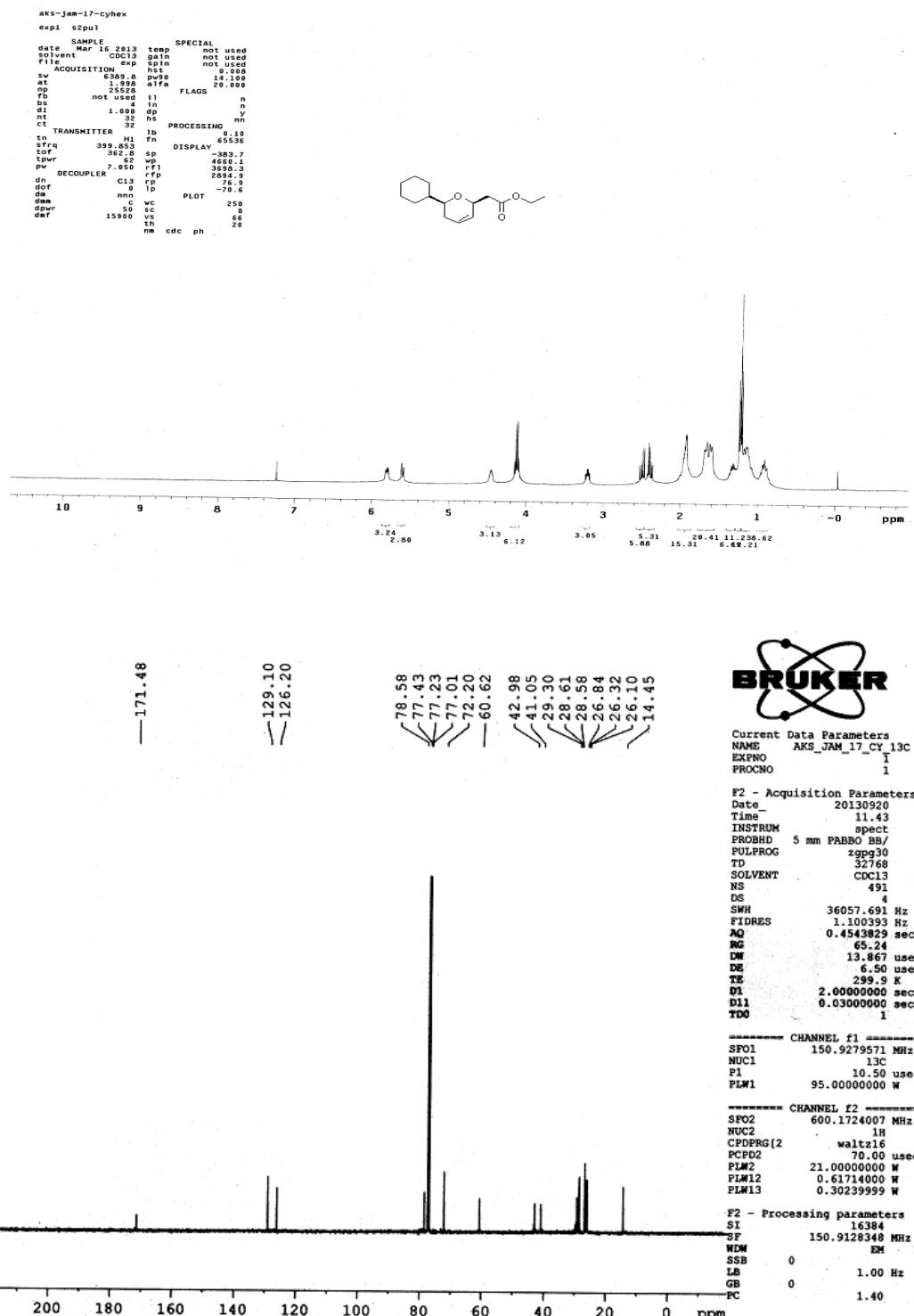
aks-jam-20-hept-13C
exp1 szpul

SAMPLE          SPECIAL
date  Apr 11 2013 temp  not used
temp   200.00 gain  not used
t1file /export/home/-/spin  not used
t1file /export/home/-/hs  not used
nmr409/aks-jam-20-- hsp90  3.400
nmr409/aks-jam-20-- hept  20.000
ACQUISITION alfa  20.000
SW      25125.6   FLAGS
AT      1.000    1L  n
NP      60278   IN  V
RB      130.4   NS  nn
BS      1.000    PROCESSING 2.00
TD      1000    1B  65536
NT      1000    1B  65536
CT      1.000    1B  65536
TRANSMITTER C13 SP  -115.6
TN      100.554   1P  25125.6
SFREQ  100.554   1P  115.6
TCF     61   RF1  7764.9
TPWR   4.750   RF1  121.3
PW      316.8    P1  -316.8
DECOUPLER H1 PLOT 250
DN      0        WC  250
DOR    0        MN  0
DE     0        SC  12
DMM    0        VS  5
DPWR   8500   NM  no ph
DMT

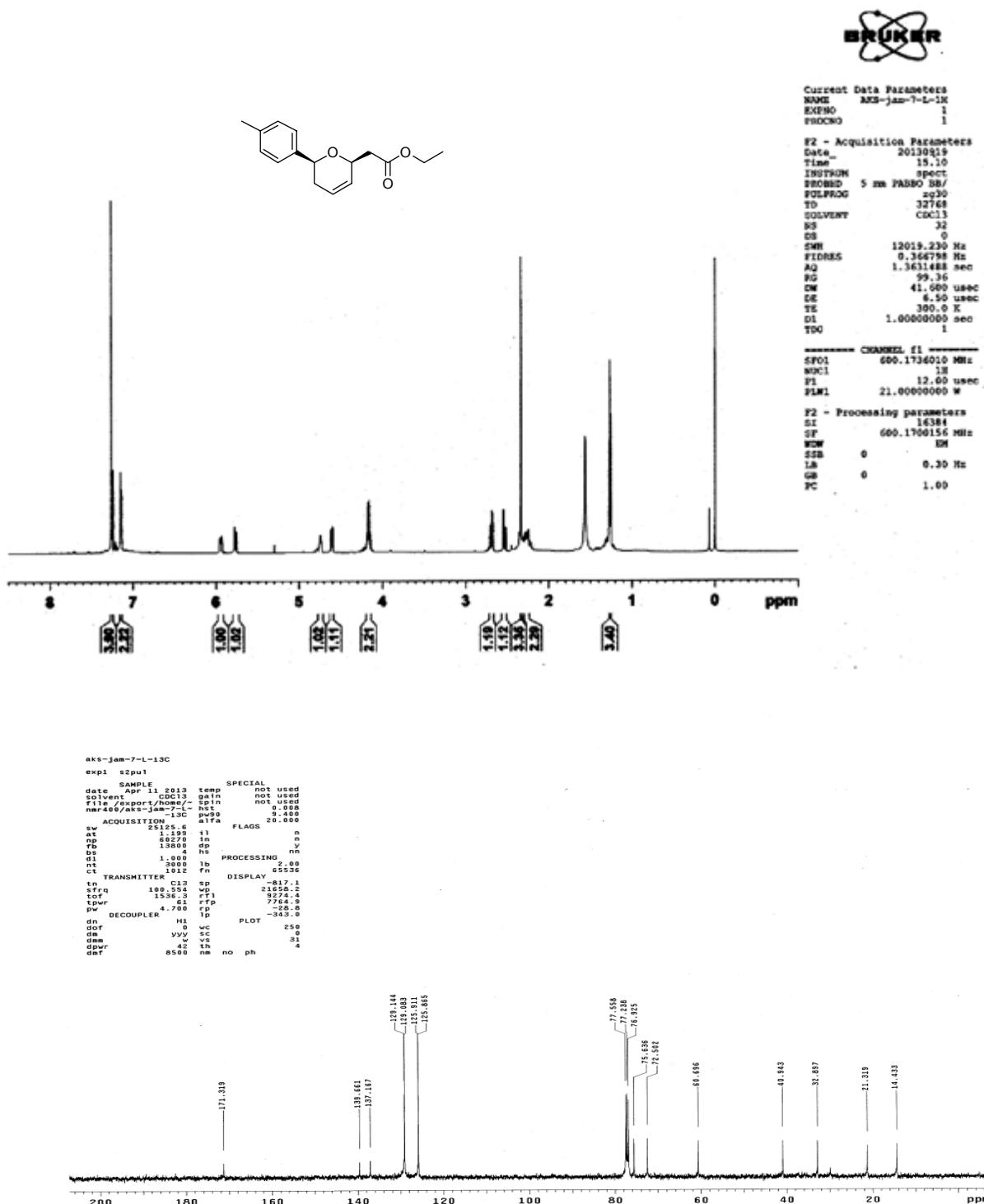
```



¹H and ¹³C NMR spectra of Ethyl 2-(6-cyclohexyl-5,6-dihydro-2H-pyran-2-yl)acetate, 2l



¹H and ¹³C NMR spectra of Ethyl 2-(6-(*p*-tolyl)-5,6-dihydro-2*H*-pyran-2-yl)acetate, 2m

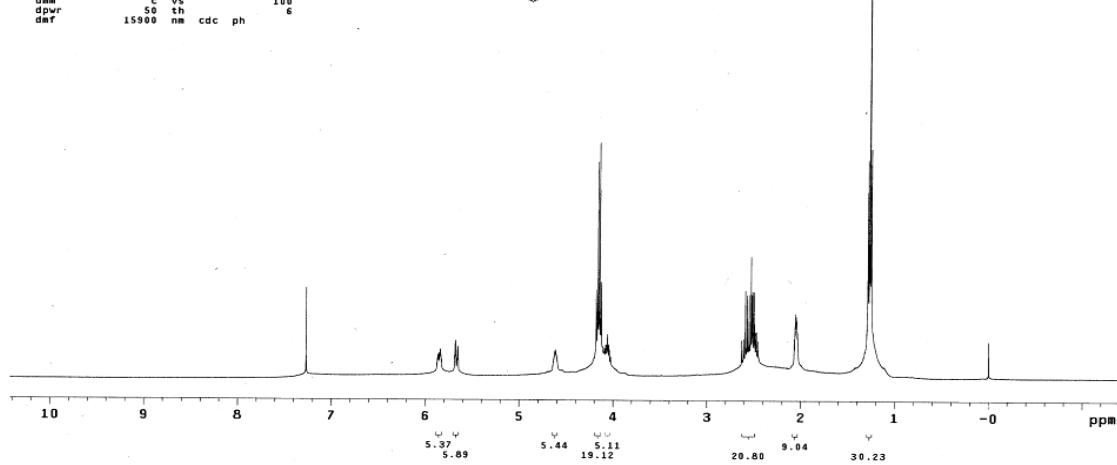
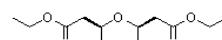


¹H and ¹³C NMR spectra of Diethyl 2,2'-(3,6-dihydro-2H-pyran-2,6-diyl)diacetate, 2m'

```

aks-jam-7-2
expt stdh
SAMPLE          SPECIAL
date  Feb 26 2013 temp  not used
solvent   CDCl3 gain  not used
file /export/home/~/spin  not used
nmridx/akr-jam-7-2 hst  0.008
acquisition 1000 1000
sw       6006.0 alfa  20.000
at        23954 il    n
sp        23954 il    n
fb      not used in    n
bs        4 dp    y
il      1.000 hs    nn
nt        32 fr    PROCESSING
ct        32 fr    not used
TRANSMITTER H1 sp  DISPLAY -567.9
tn      399.853 wp  4735.0
sfrq    399.853 r1  962.3
tpwr    57 rfp  0
pw      7.000 rp  91.4
-74.6
dnc     C13 PLOT
dof      0 wc  250
dme     nnn sc  0
dms     vvt tb  100
dpwr    50 th  6
dmf     15900 nm cdc ph

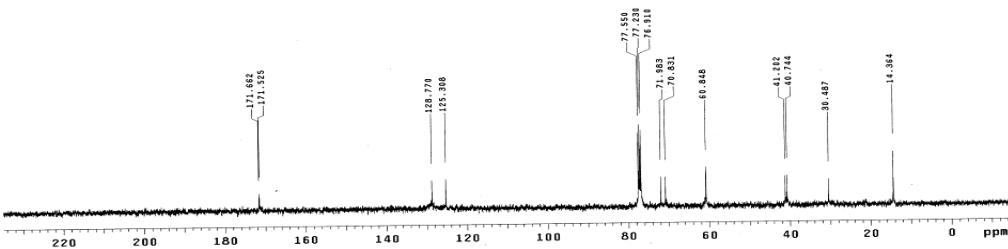
```



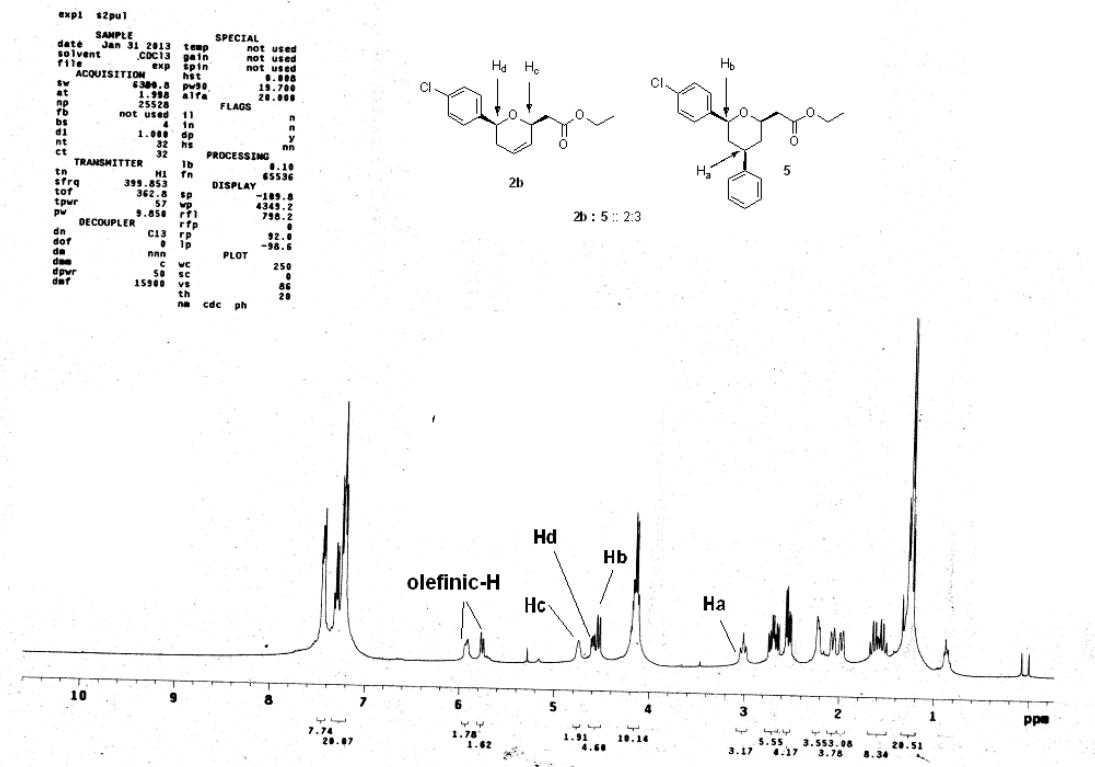
```

aks-jam-7-2-13C
expt s2pu1
SAMPLE          SPECIAL
date  Apr 13 2013 temp  not used
solvent   CDCl3 gain  not used
file /export/home/~/spin  not used
nmridx/akr-jam-7-2 hst  0.008
acquisition 1000 1000
sw       25125.6 alfa  20.000
at        60270 il    n
sp        60270 il    n
fb      13860 dp    y
bs      13860 dp    y
il      1.000 hs    nn
nt        2000 lb    2.00
ni      2000
sc      900 fn    655.36
ct        900 fn    DISPLAY 655.36
TRANSMITTER C13 sp  DISPLAY -1500.0
tn      1000.0 wp  2145.6
sfrq    1000.0 r1  9272.9
tot     1536.3 rfp  7255.8
tpwr    61 rfp  7255.8
pw      4.00 rfp  7255.8
-327.2
dnc     H1 PLOT
dof      0 wc  250
dme     vvt sc  0
dms     vvt tb  25
dpwr    0 th  3
dmf     8500 nm no ph

```

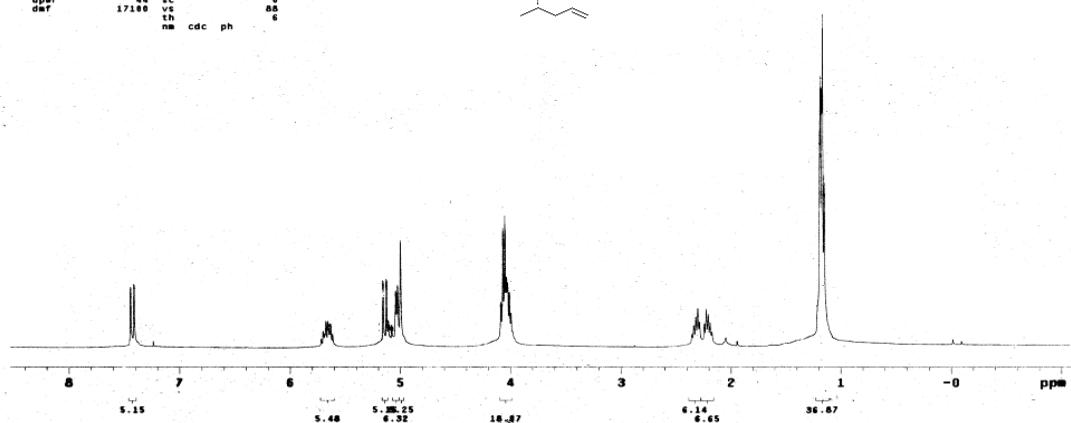
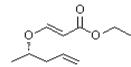


¹H spectra of Ethyl 2-(6-(4-chlorophenyl)-4-phenyltetrahydro-2H-pyran-2-yl)acetate, 5 and Ethyl-2-(6-(4-chlorophenyl)-5,6-dihydro-2H-pyran-2-yl)acetate, 2b

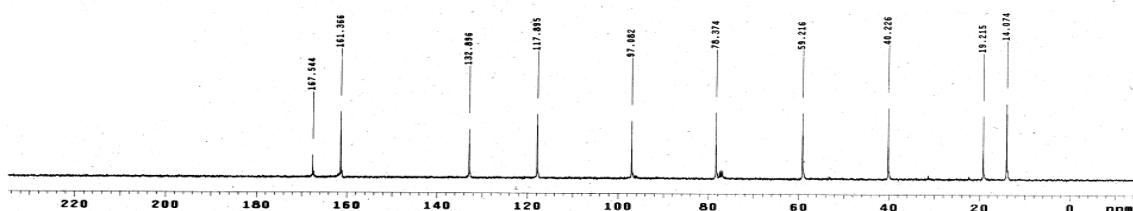


¹H and ¹³C NMR spectra of (S,E)-Ethyl 3-(pent-4-en-2-yloxy)acrylate, 17

```
aks-jam-S-30-SH
expi s2pul
SAMPLE          SPECIAL
date Jun 1 2013 temp not used
solvent CDCl3   gppm not used
file   exp spin not used
ACQUISITION hst   0.008
sw    1000.0   p17a 15.100
at    1.338   26.000
np    25528   FLAGS
fb    not used  n
bs    4        in
dt    1.066   dp  y
nt    32       mm
ct    32       PROCESSING
tn   TRANSMITTER H1 fn  6.13
      85536
sfreq 399.853   DISPLAY
t0f   362.0    sp -433.3
tpowr 7.550    wp 3845.5
pw    3687.5   rf1
      200.0
decoupler C13 rp  165.8
dn    C13      rp -97.2
dof   6        ip
dme   nm      PLOT
dme   c wc   250
dpowr 17100   sc  1
dmtf   17100   tc  6
      th  6
nm   cdc ph
```



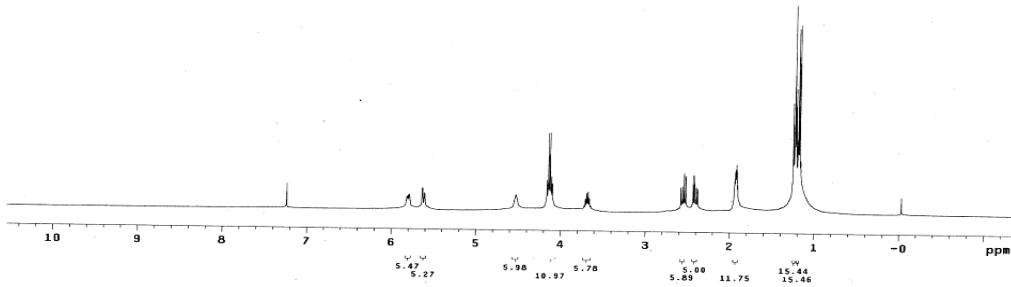
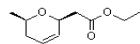
```
expi s2pul
SAMPLE          SPECIAL
date May 31 2013 temp not used
solvent CDCl3   gppm not used
file   exp spin not used
ACQUISITION hst   0.008
sw    25125.6   p17a 20.000
at    1.338   20.000
np    19232   FLAGS
bs    38800  in
dt    1.066   dp  y
nt    32       mm
ct    100      PROCESSING
tn   TRANSMITTER C13 fn  2.44
      65536
t0f   100.0    sp -1526.4
tpowr 4.700    rf1 29291.3
pw    4.700    rf1 -36.9
      294.0
decoupler H1 rp -36.9
dn    VVY      ip
dme   VVY    PLOT
dpowr 42      sc  250
dmtf   8500   tc  24
      th  no ph
```



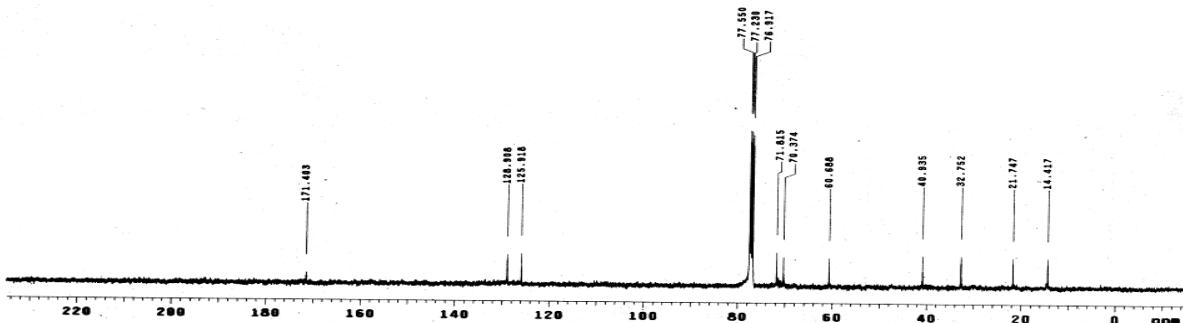
¹H and ¹³C NMR spectra of Ethyl 2-(2*R*,6*S*)-6-methyl-5,6-dihydro-2*H*-pyran-2-yl)acetate,

18

```
aks-jam-21-acet-good
exp1 s2pu1
SAMPLE . SPECIAL
date Apr 22 2013 temp not used
solvent CDCl3 spin not used
file exp spin not used
ACQUISITION
sw 6399.8 pwo 0.100
at 1.199 aita 20.080
np 25528 flags
tbo not used 11 n
bs 1.080 dp v
dt 1.080 sc v
nt 32 PROCESSING nm
ct 32
TRANSMITTER 1b
tn H1 fm 6550
sfrq 39.855 DISPLAY
tfrq 38.8 sp -551.6
tpwr 59 wpt 4789.1
pw 7.551 rfp 30.1
DECOUPLER C13 rfp 2884.3
dn C13 ip 137.8
dof 0 ip -145.8
dmn nnn PLOT
dmm 0 wc 250
dpwr 44 sc 0
dft 17100 v 62
th nm v 29
nm cdc ph
```



```
exp1 s2pu1
SAMPLE . SPECIAL
date May 8 2013 temp not used
solvent CDCl3 spin not used
file exp spin not used
ACQUISITION
sw 25125.6 het 0.000
at 1.199 aita 20.080
np 138000 flags
tbo 138000 11 n
bs 1.080 dp v
dt 1.080 sc v
nt 50000 nnn nm
ct 50000 PROCESSING nm
TRANSMITTER 1b
tn C13 fm 6550
sfrq 100.554 DISPLAY
tfrq 153.3 sp 1554.1
tpwr 59 wpt 2589.4
pw 4.700 rfp 5269.8
dn H1 ip 77.5
dof VVY ip -59.5
dm VVY PLOT
dmm 42 wc 250
dpwr 6500 vs 45
dft 6500 v 3
nm no ph
```

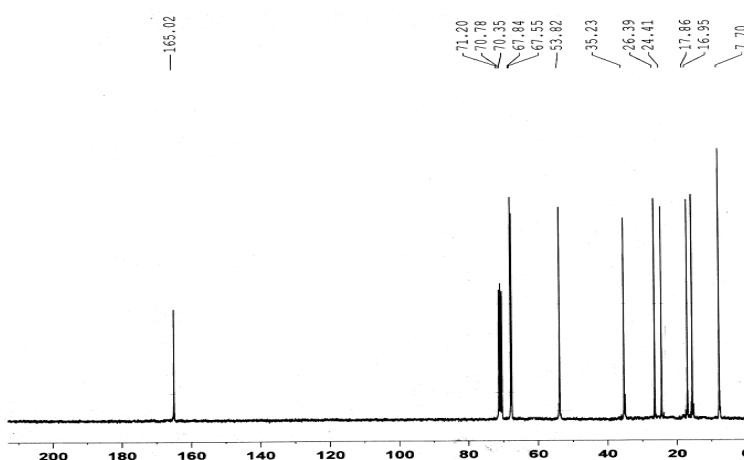
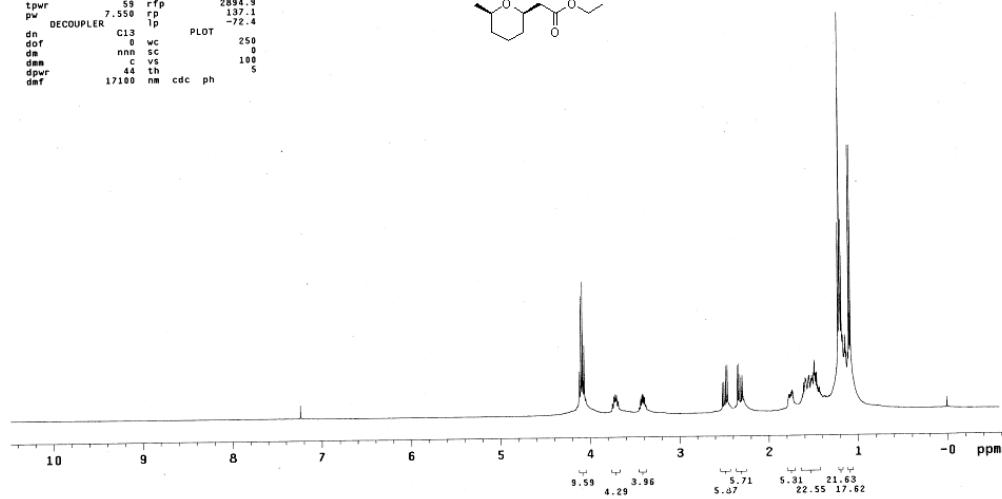
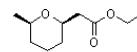


¹H and ¹³C NMR spectra of Ethyl 2-((2S,6S)-6-methyltetrahydro-2H-pyran-2-yl)acetate, 19

```

akis=jam-21-hyd
exptl s2pul
      SAMPLE          SPECIAL
date   Apr 12 2013 temp    not used
solvent   CDCl3 gain    not used
f1prf1  300.00 t1     not used
nmr400/akis=jam-21--> hst    0.008
nmr400/akis=jam-21--> hyd   15.100
nmr400/akis=jam-21--> pw90  20.000
      ACQUISITION alfa   20.000
sw      6389.8   FLAGS
at      1.998   t1    n
np      2592.0   in    n
dp      not used dp    y
bs      4 hs    processing nn
dd      1.000
nt      32 lb    processing 0.10
ct      32 fn    display 65536
      TRANSMITTER DISPLAY
tn      H1 sp    -257.4
sfrq   399.653  vp    4456.0
t0f    362.400  rfp   363.711
t0pw   5.19    rfp   2894.9
pw     7.550   rp    137.1
      DECOUPLER C13   PLOT
dn      0 wc    250
dof     nnn sc    8
dme    0 vc    100
dpwv   44 th    5
dmf    17100 nm cdc ph

```



```

NAME          2013-04-09-a
EXPTNO         1
PROCNO        1
Date        20130409
Time       14:10
INSTRUM  BRUKER DRX-300
PROBHD   5 mm BBO BB-1H
PULPROG  zg30
TD        65536
SOLVENT   CDCl3
NUC1      1H
DS        2000
SWH      18028.844 Hz
FIDRES   0.550197 Hz
AQ        0.908100 sec
RG        80.6
DW        27.00 usec
DE        6.50 usec
TE        2.0000000 sec
D1        0.03000000 sec
TODD
----- CHANNEL f1 -----
NUC1      13C
P1        9.00 usec
PL1     -0.50 dB
D1W     34.666100 MHz
SF01    75.4778101 MHz
----- CHANNEL f2 -----
CPDPRG2  waltz16
NUC2      1H
PCPD2    10.00 usec
P1        2.00 dB
PL2     19.20 dB
PL3     15.00 dB
PL2W    8.07971478 w
PL3W    0.07201053 w
SF02    300.147668 MHz
SF03    327.68 EM
SI        75.4707768 MHz
SWF        EM
SSB        0.00 Hz
SF        1.00 Hz
GB        0.00
PC        1.40

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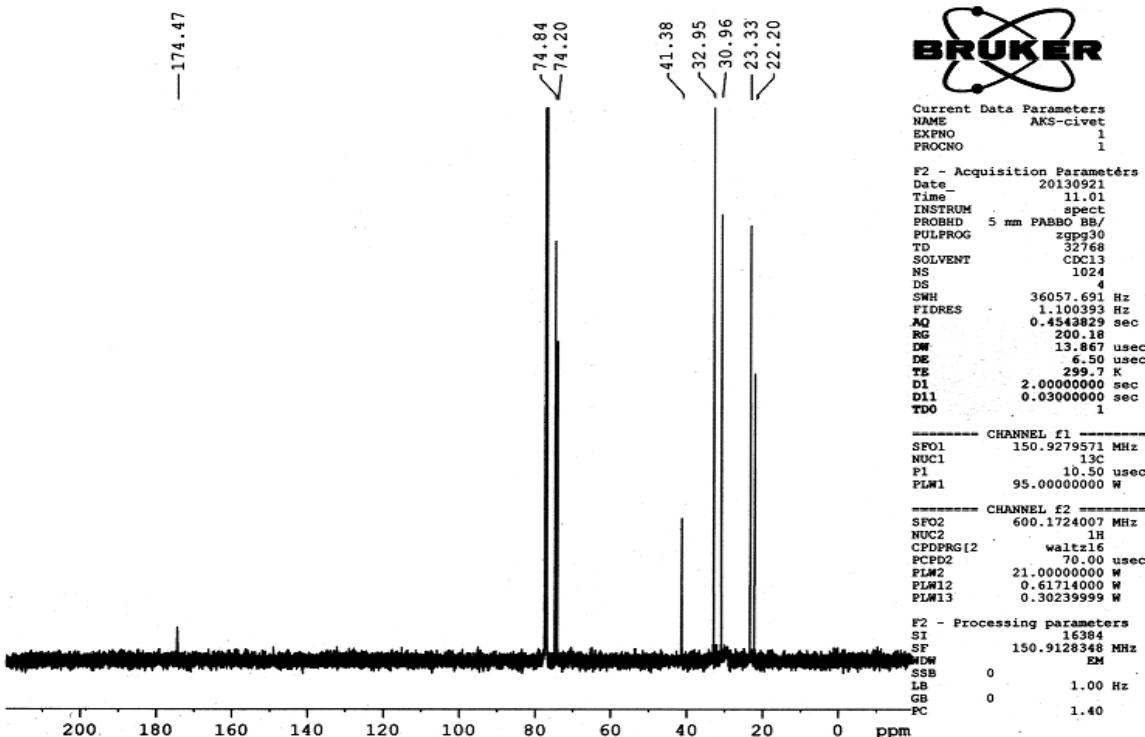
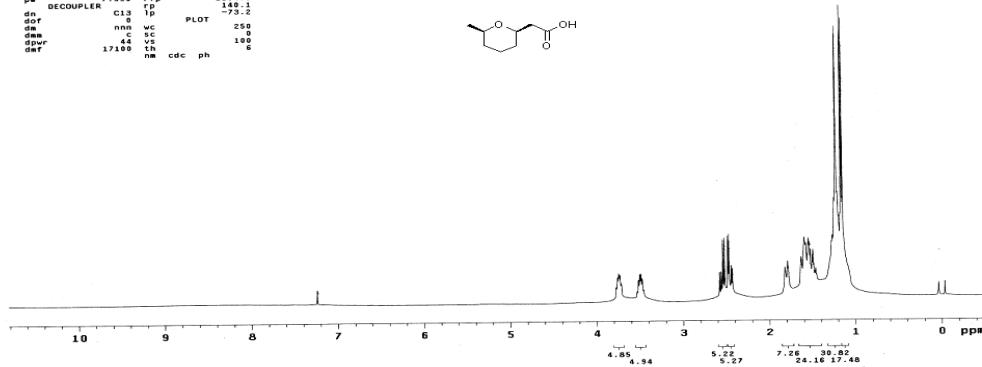
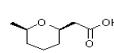
¹H and ¹³C NMR spectra of 2-((2S,6S)-6-Methyltetrahydro-2H-pyran-2-yl)acetic acid,

(+)-Civet, 20

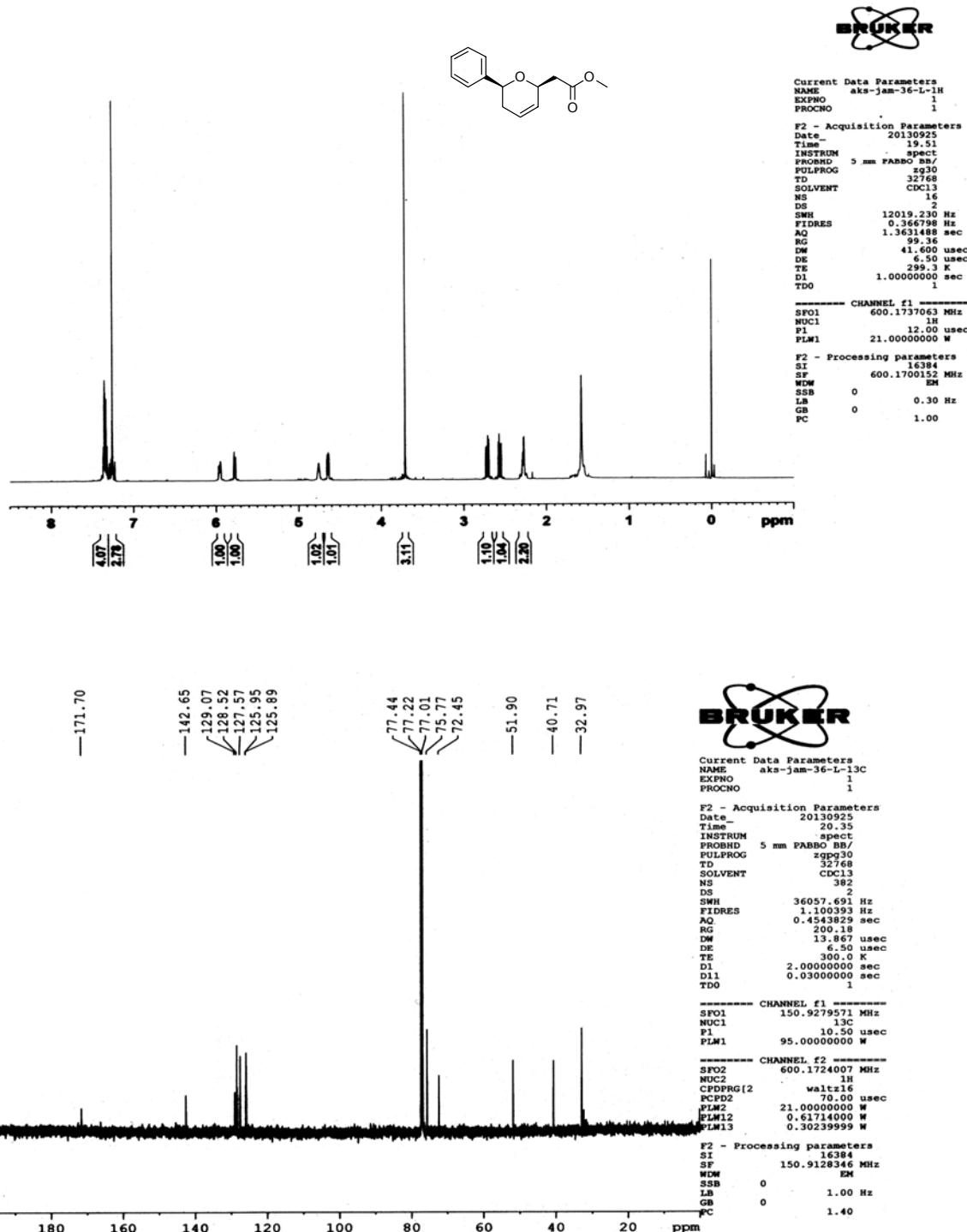
```

aks-jam-civet
expt1 s2p1
SAMPLE          SPECIAL
date Apr 13 2013 texp not used
solvent CDCl3 gain not used
f1file ./export/HOME/ spin 0.0000
recycle 1.0000 psw 15.0000
ACQUISITION psw 15.0000
sw 288.8 16.0000
at 1.998 11 FLAGS n
nd 1 11 n
not used in n
fb 1 11 v
bs 1 11 v
d1 1.000 ns nh
dt 32 16 32
ct 32 16 32
TRANSMITTER 65336
tn 399.053 sp DISPLAY 216.0
trfg 362.8 w1 4.5
tovr 362.8 w1 5.5
tovr 7.558 rfp 2688.1
pw 140.1
pw DECOPPLER 140.1
dnf C13 1P PLOT
dss nnn wc 250
dse c 100
dswr 171000 nm 100
def 171000 nm cdc ph

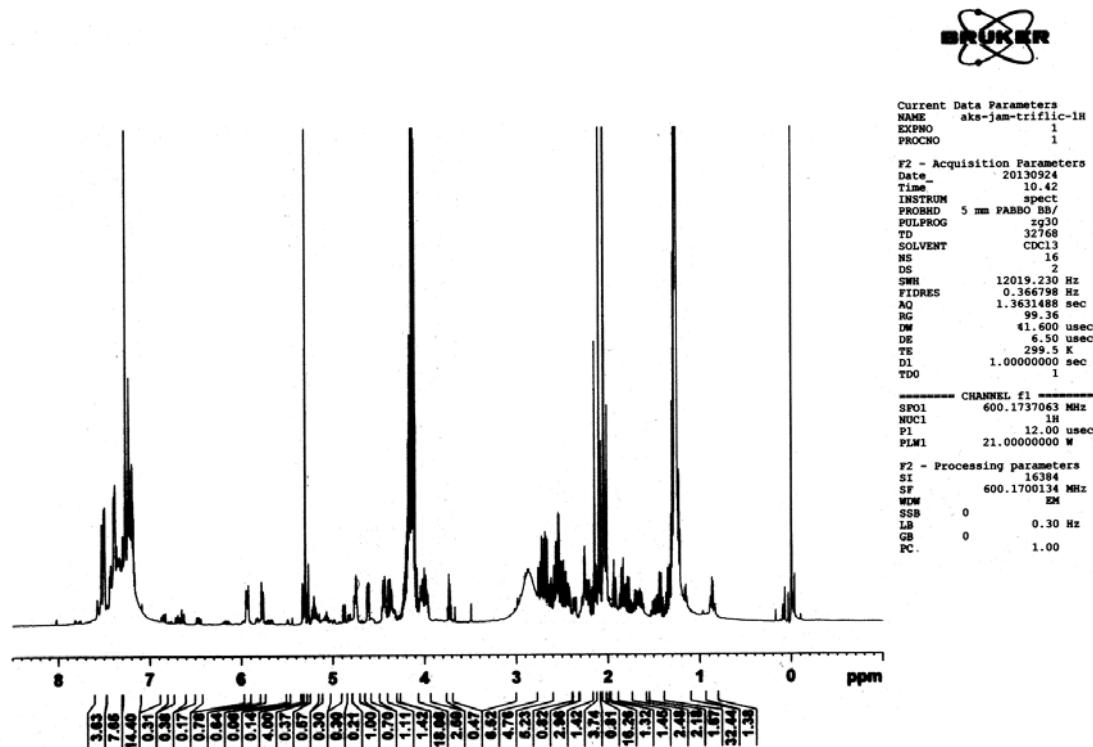
```



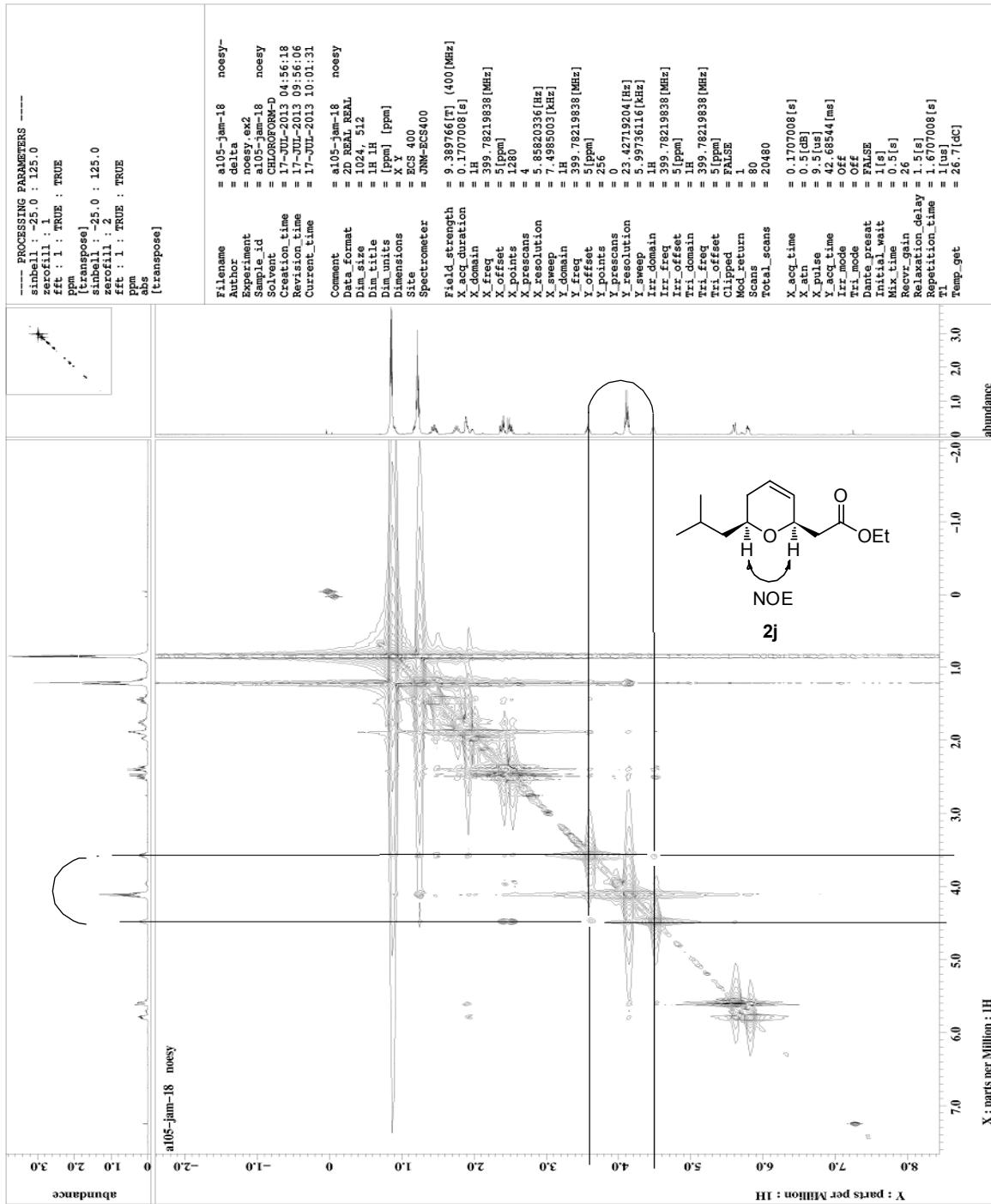
Methyl 2-((2S,6S)-6-phenyl-5,6-dihydro-2H-pyran-2-yl)acetate, 2a,¹⁶



**Reaction of (*E*)-Ethyl 3-((1-(4-bromophenyl)but-3-en-1-yl)oxy)acrylate with
Trifluoromethanesulfonic acid (TfOH)**



NOE spectra of spectra of Ethyl 2-(6-isobutyl-5,6-dihydro-2H-pyran-2-yl)acetate, 2j



Reference 14d: Hart, D. J.; Bennett, C. E. *Org. Lett.* **2003**, *5*, 1499-1502.

Reference 16: Kim, H.; Lee, C. *Angew. Chem. Int. Ed.* **2012**, *124*, 12469-12472