

Supporting Information for publication

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

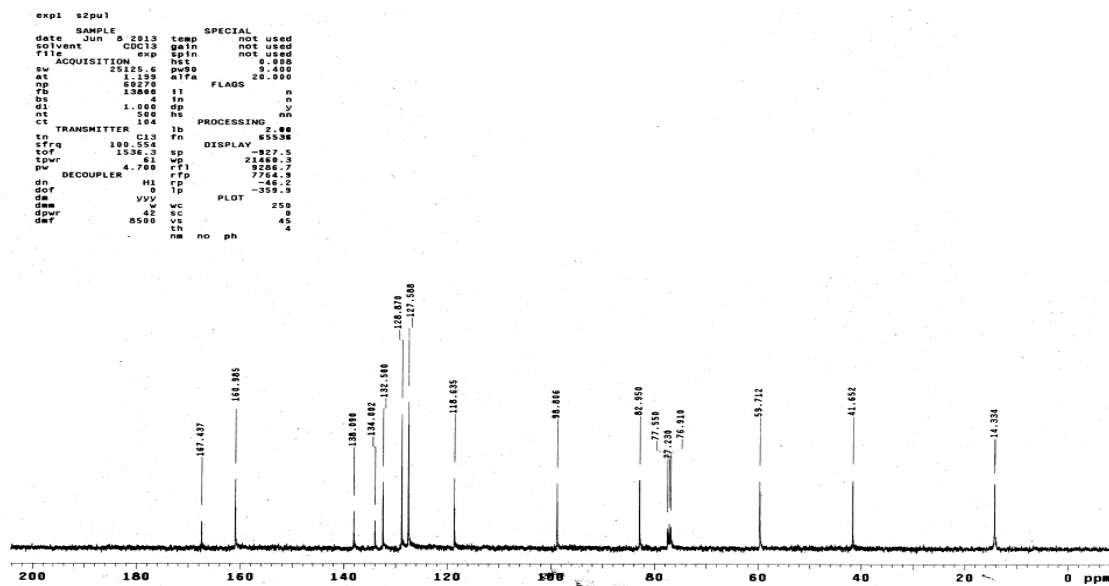
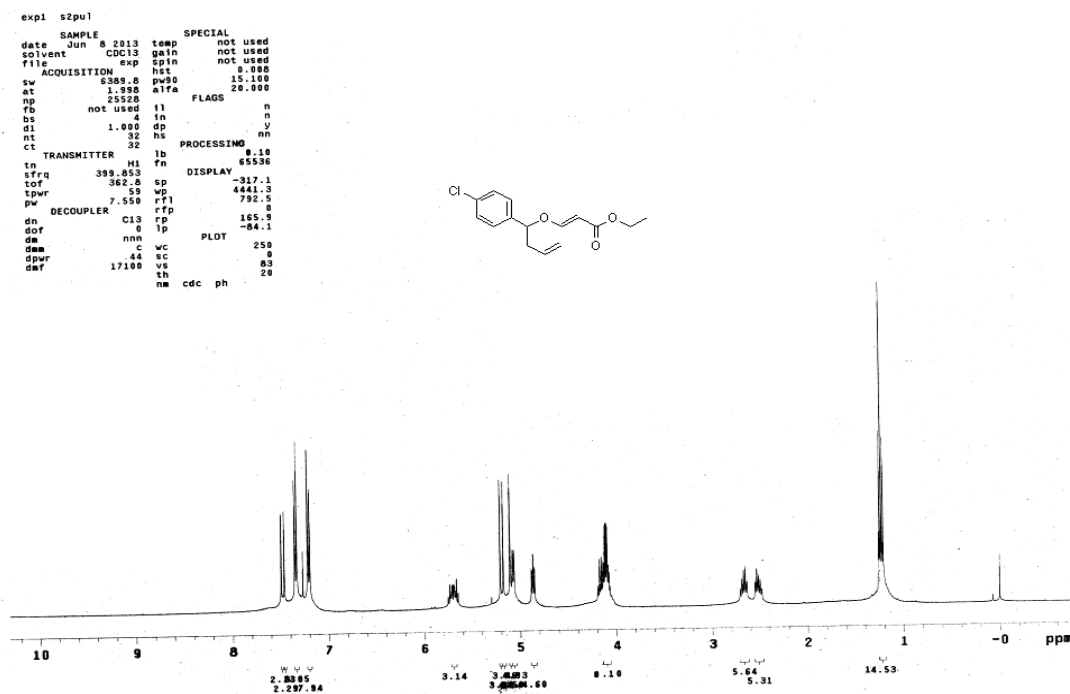
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Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati 781039, Assam, India, e-mail: asaikia@iitg.ernet.in

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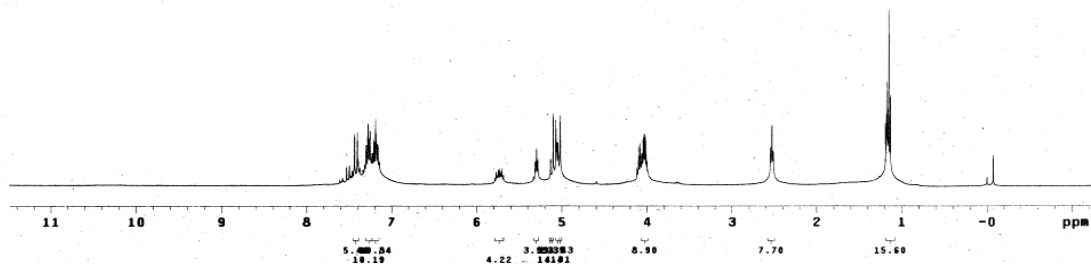
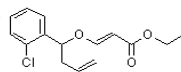
¹H and ¹³C NMR spectra of (E)-Ethyl 3-((1-(4-chlorophenyl)but-3-en-1-yl)oxy)acrylate, 1b



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

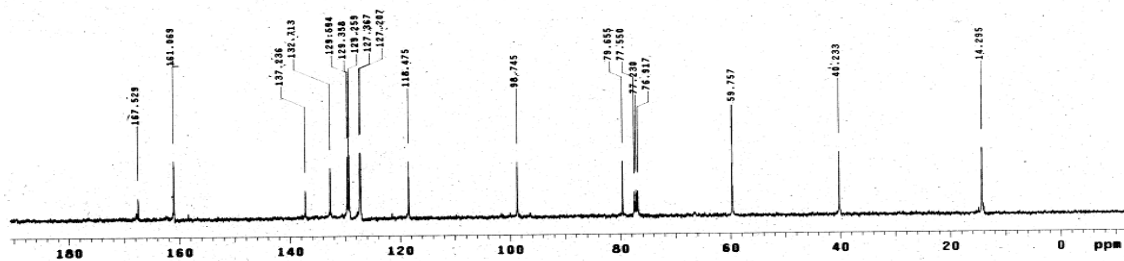
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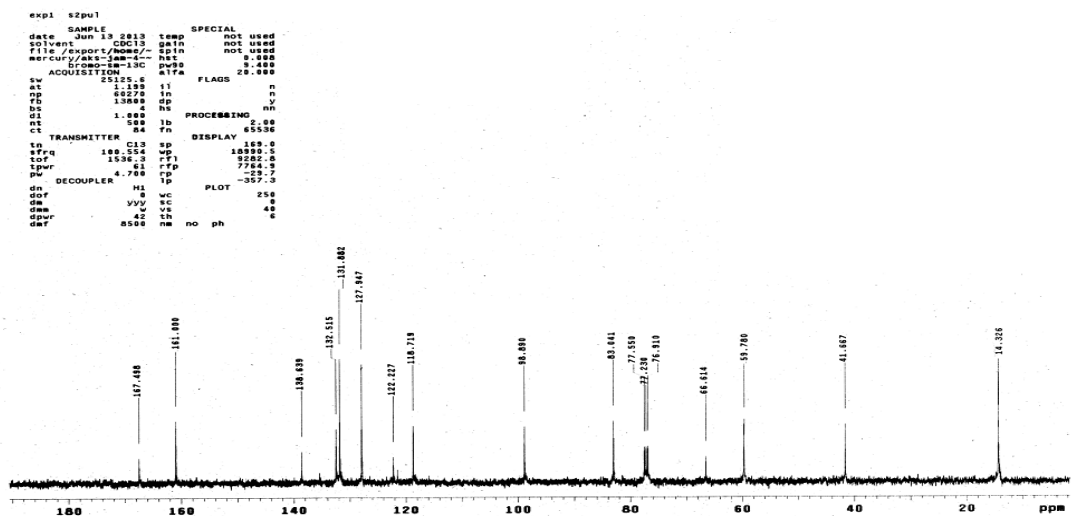
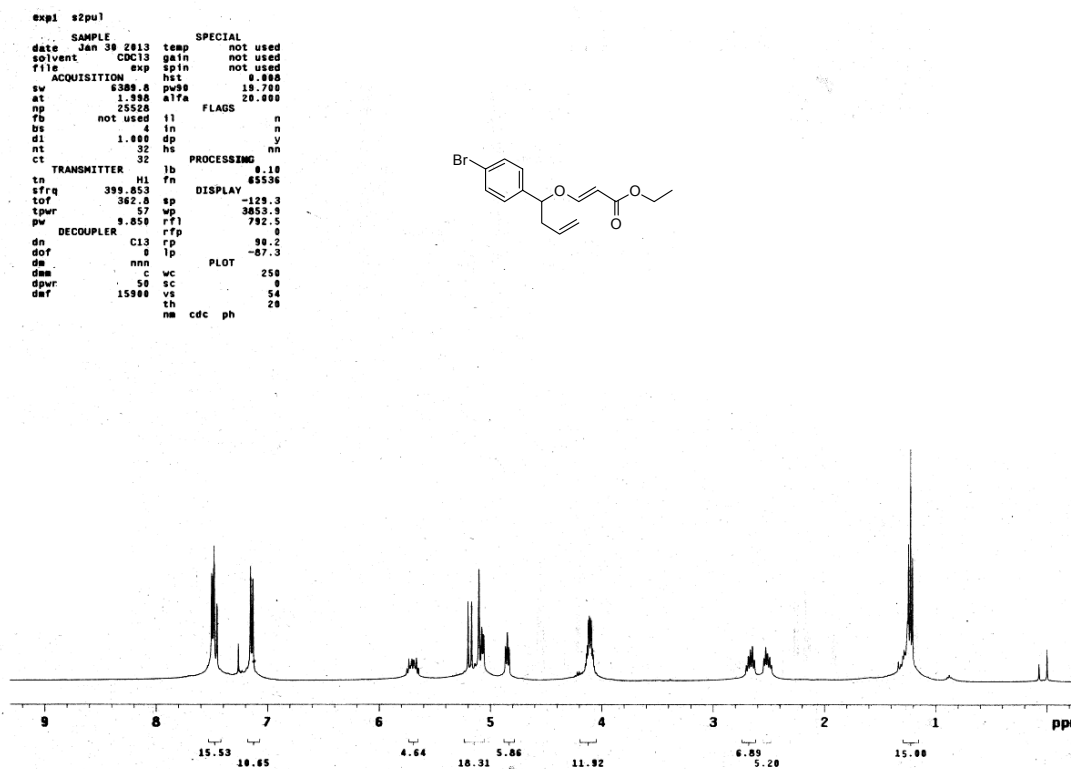


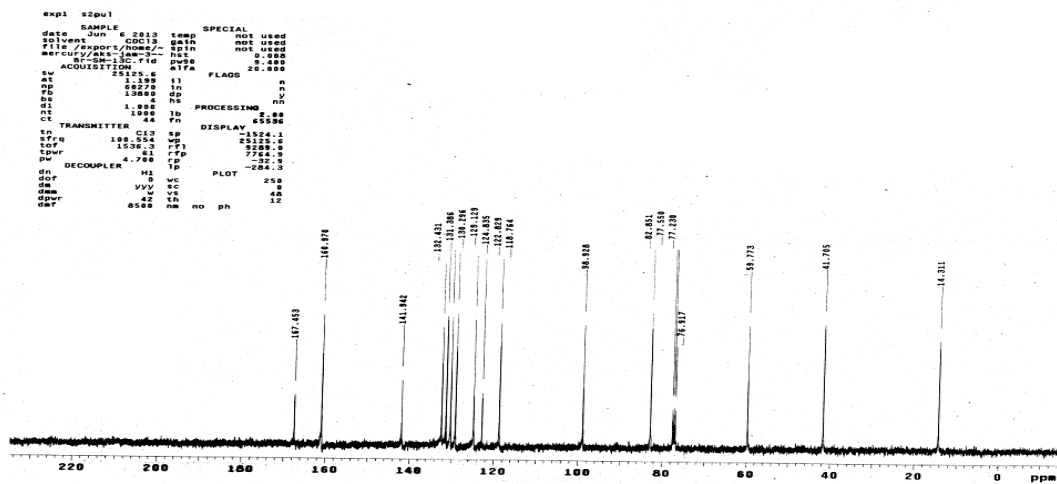
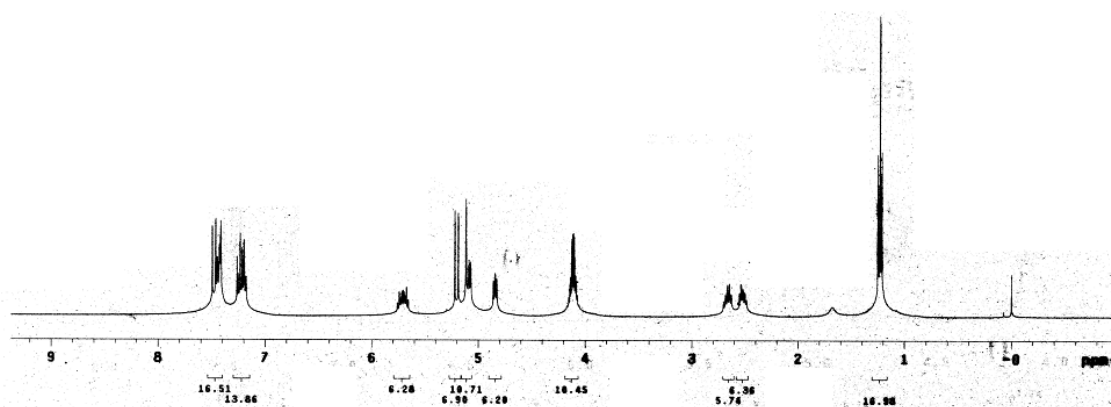
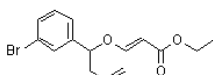
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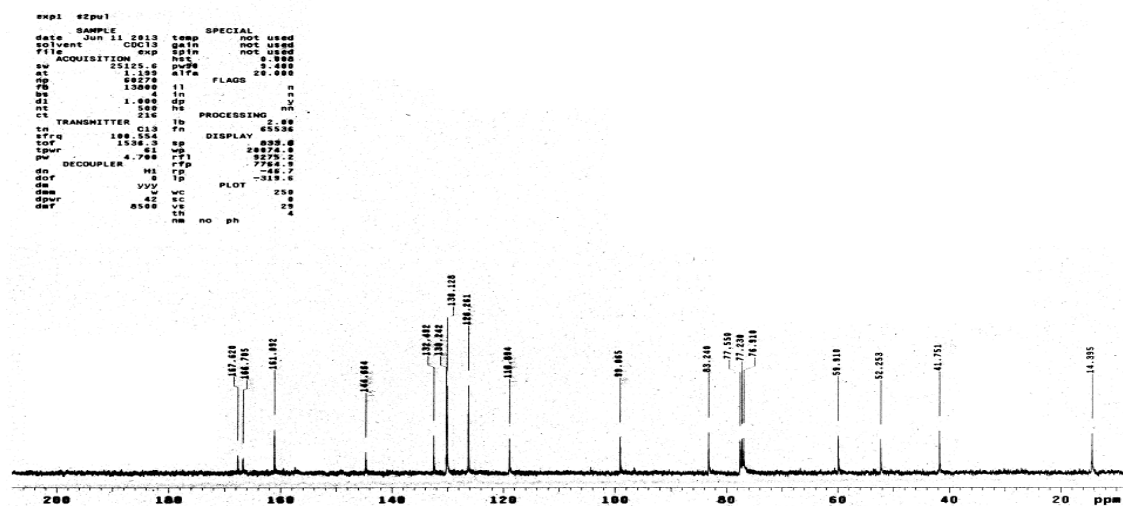
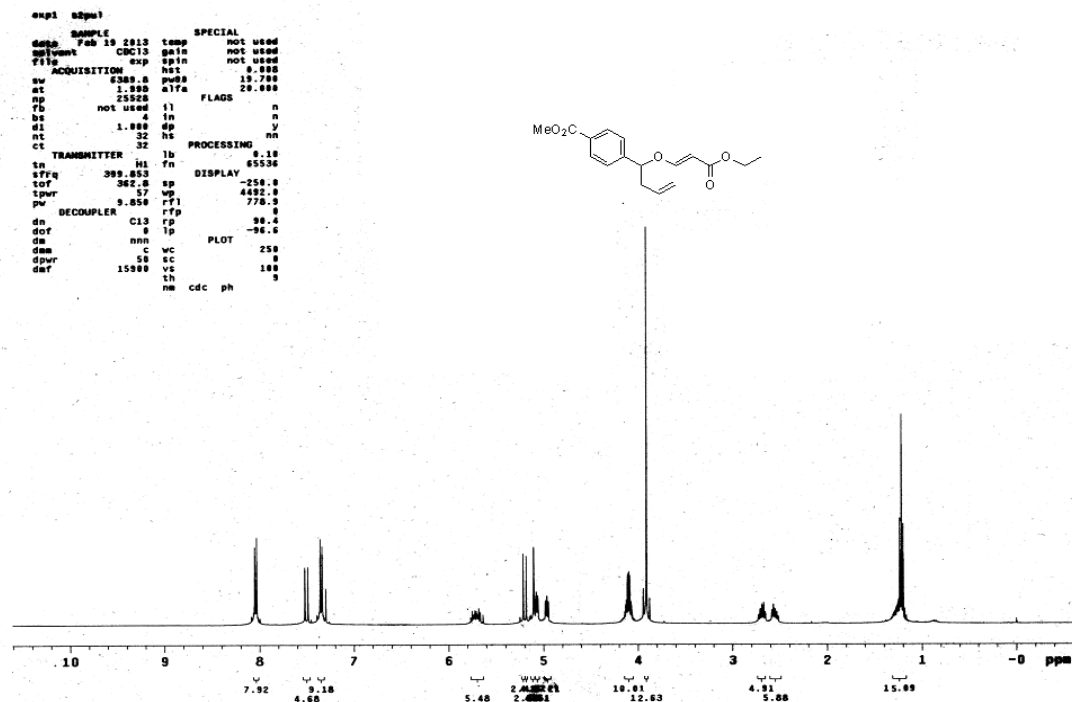


¹H and ¹³C NMR spectra of (*E*)-Ethyl 3-((1-(4-bromophenyl)but-3-en-1-yl)oxy)acrylate, 1d

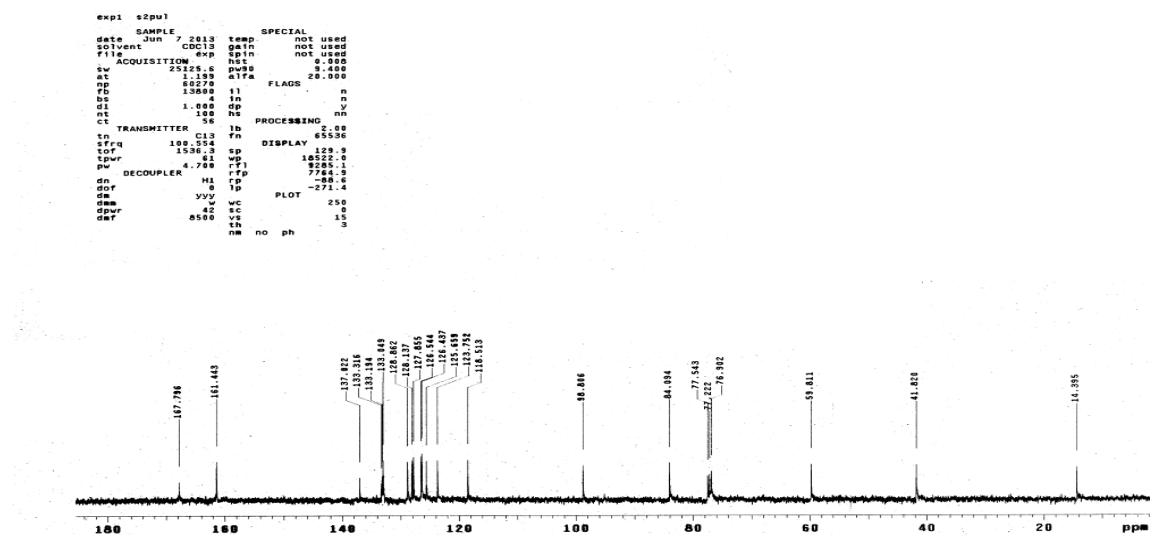
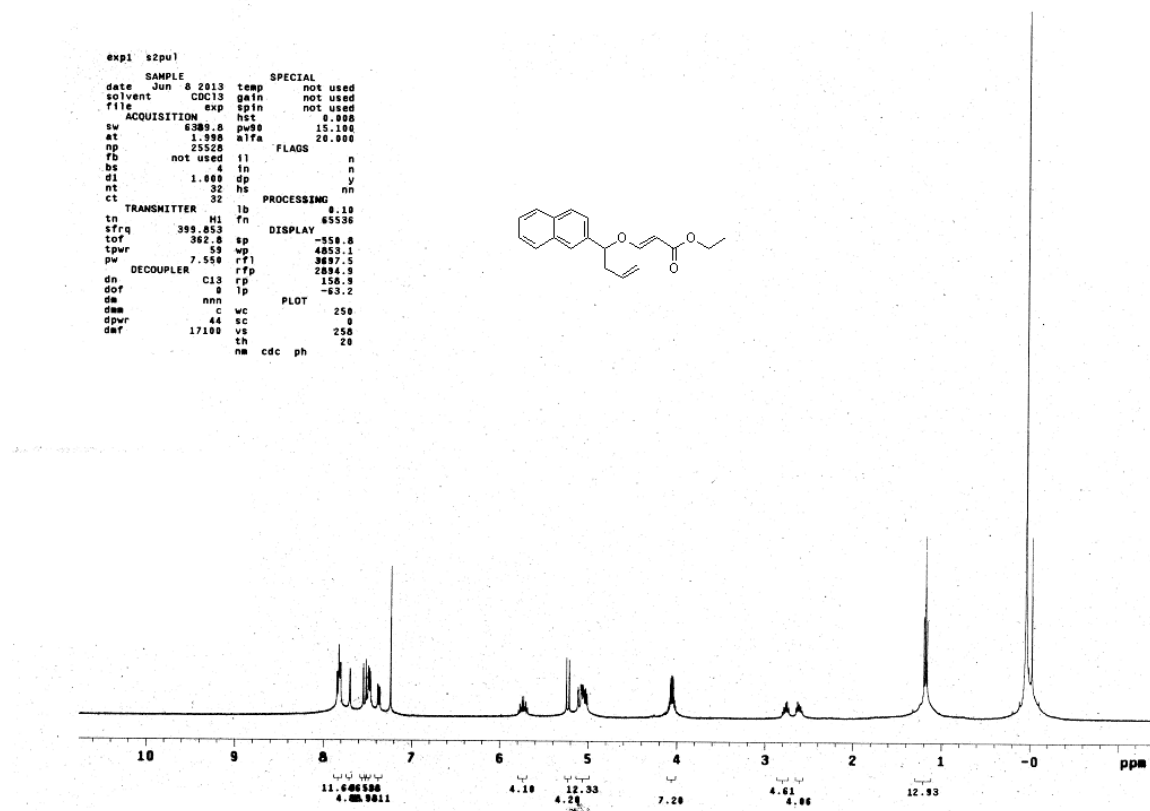




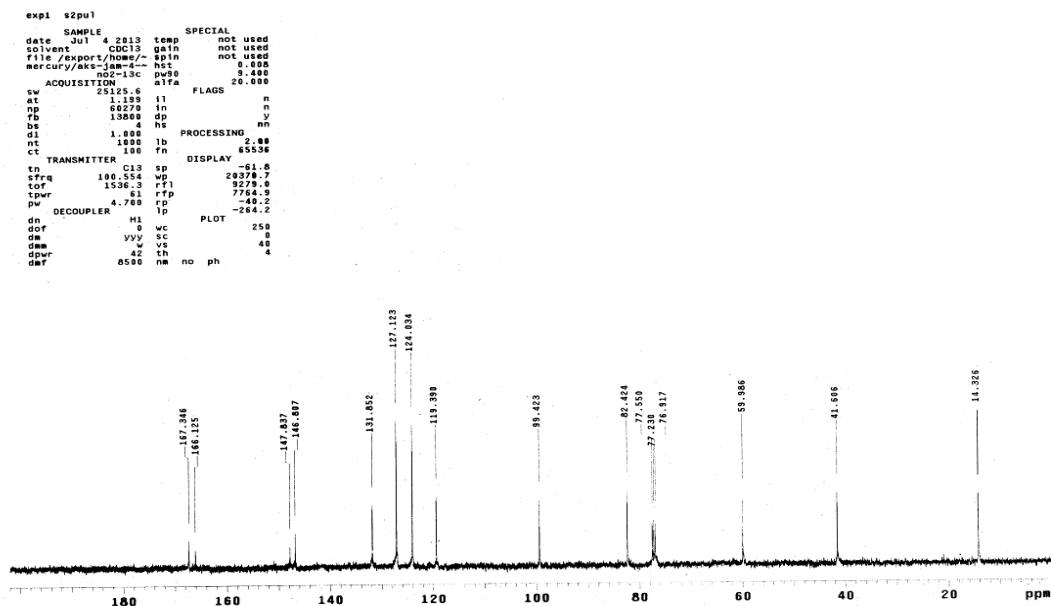
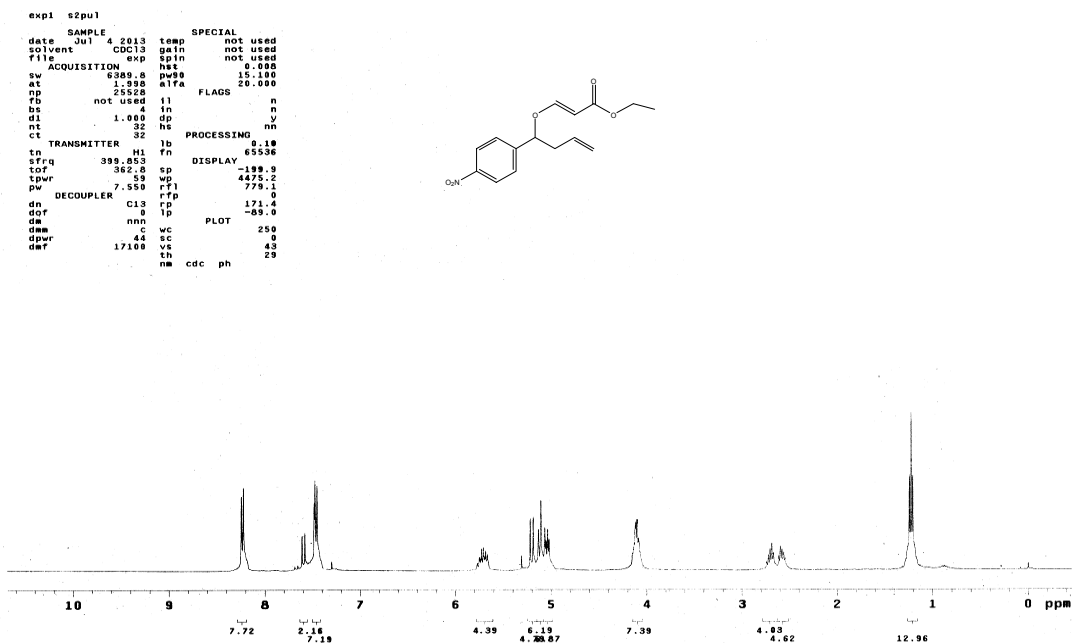
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¹H and ¹³C NMR spectra of (*E*)-Ethyl 3-((1-(naphthalen-2-yl)but-3-en-1-yl)oxy)acrylate, 1g



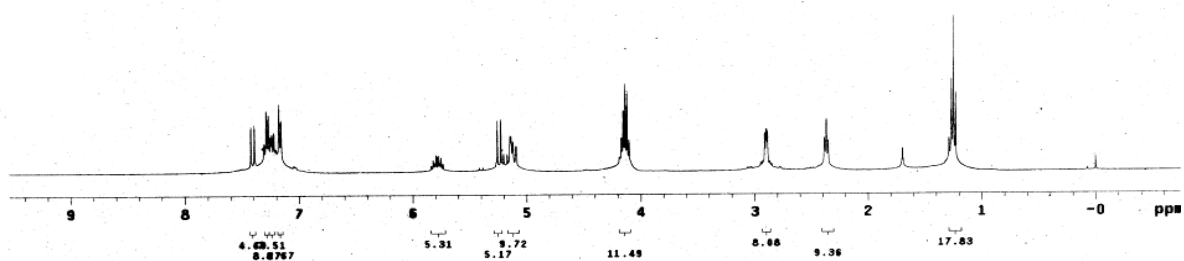
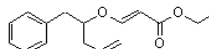
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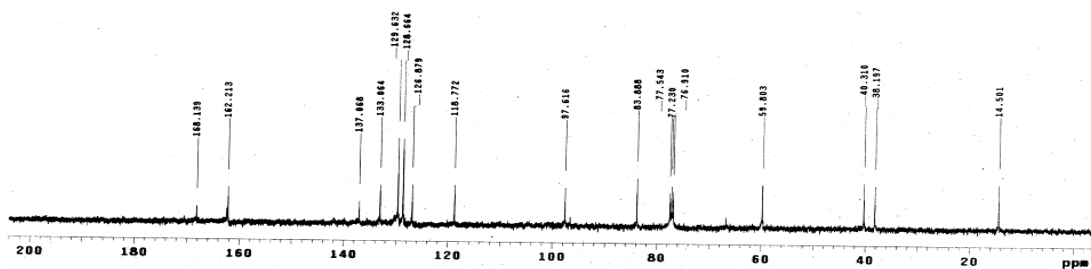
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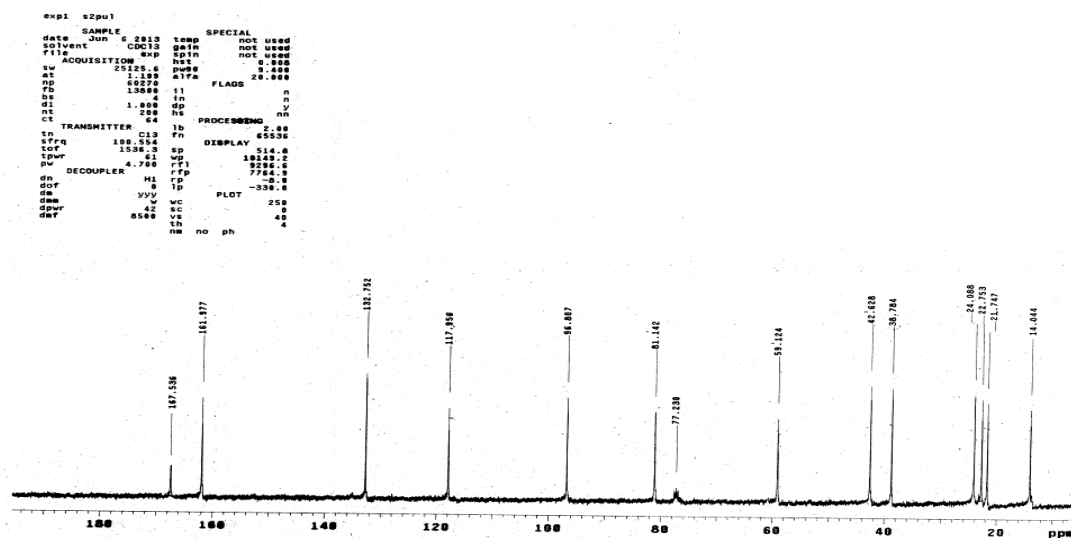
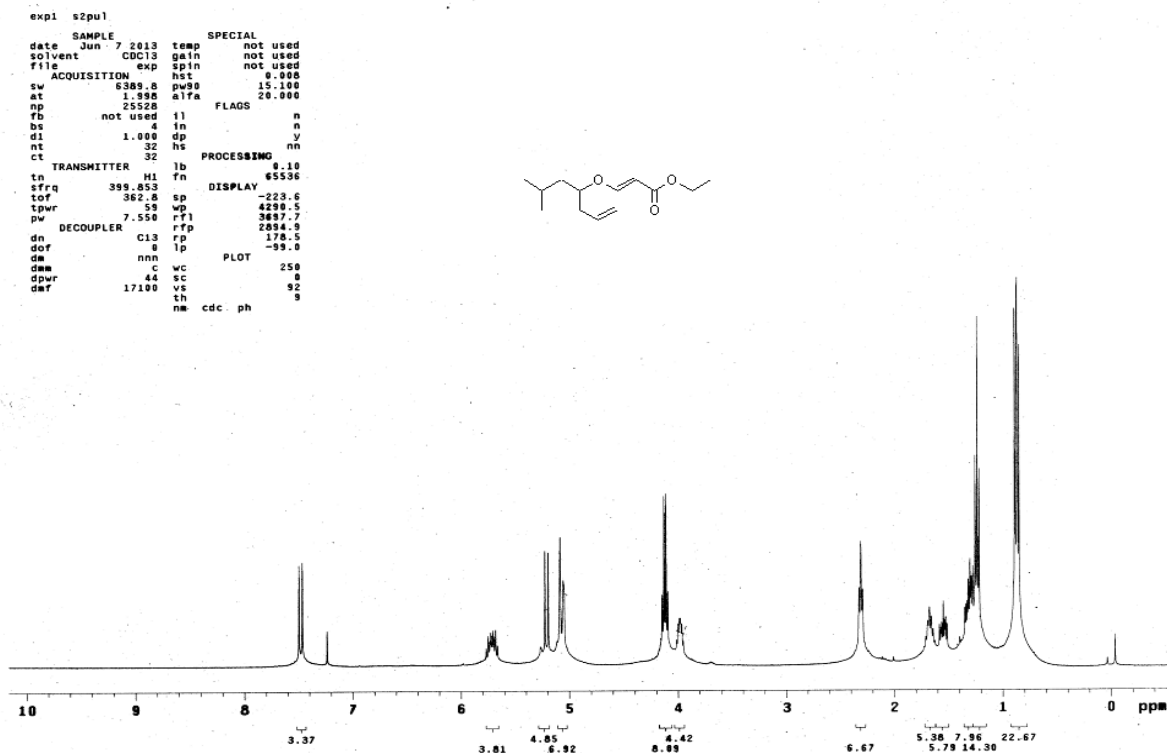


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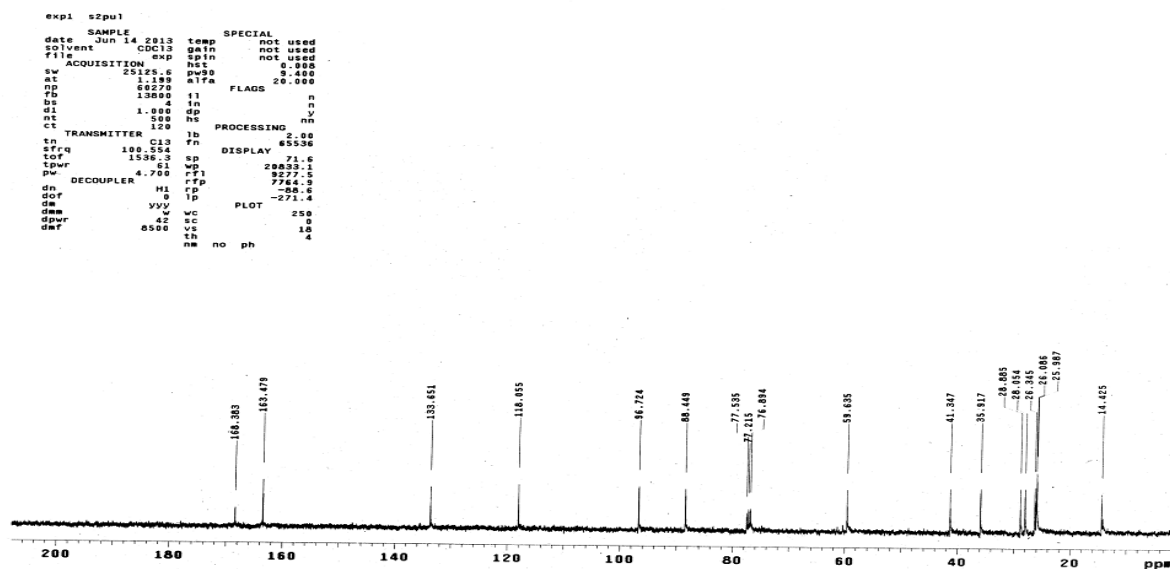
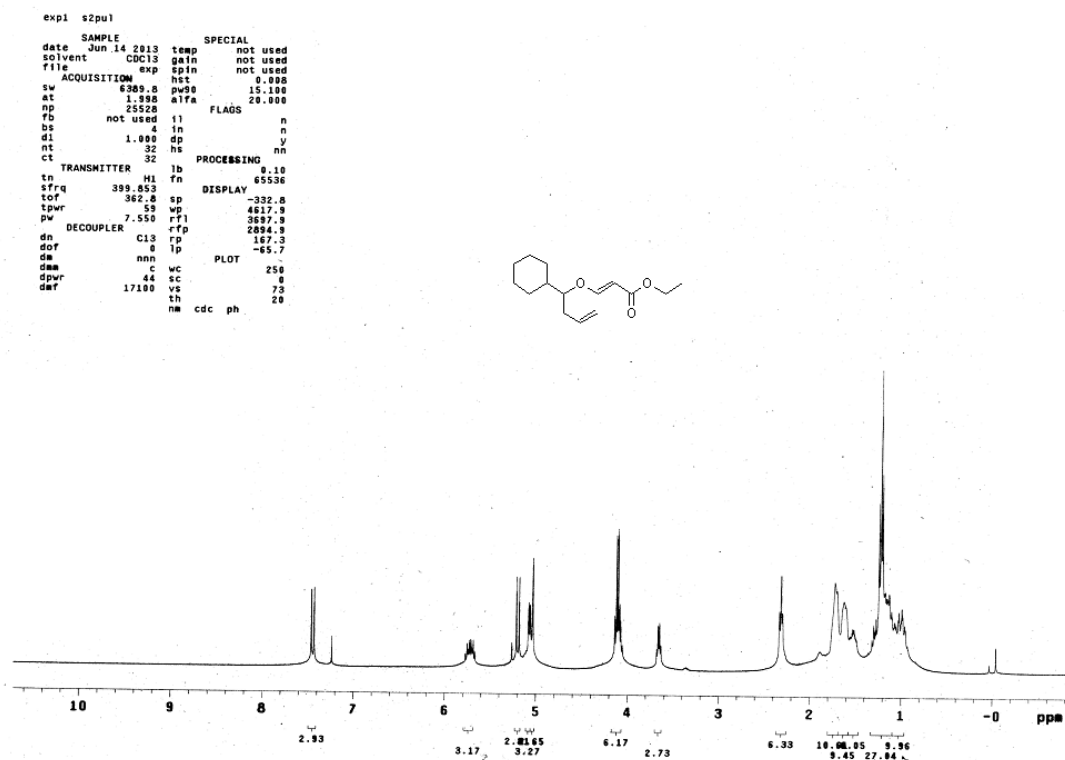
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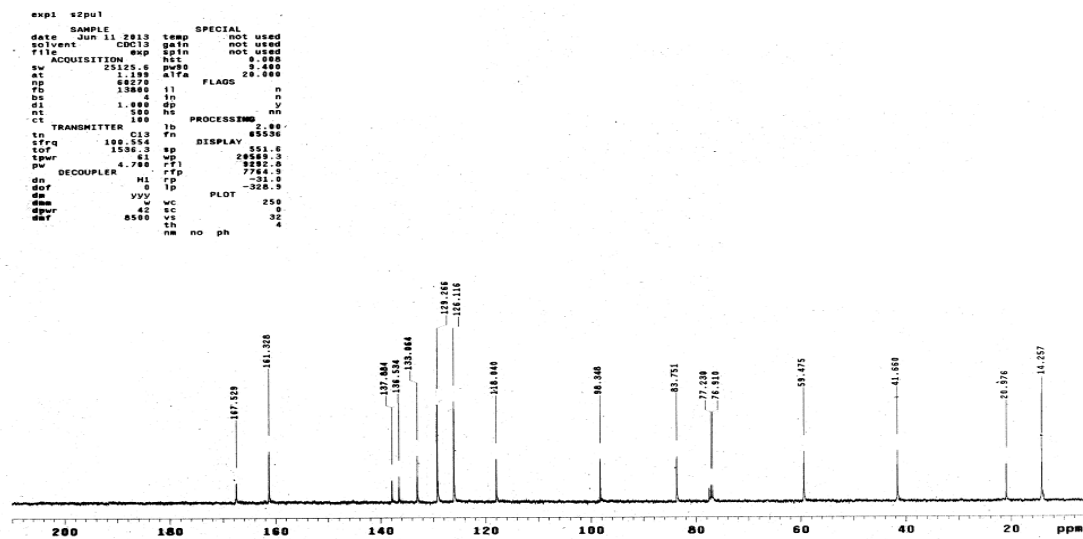
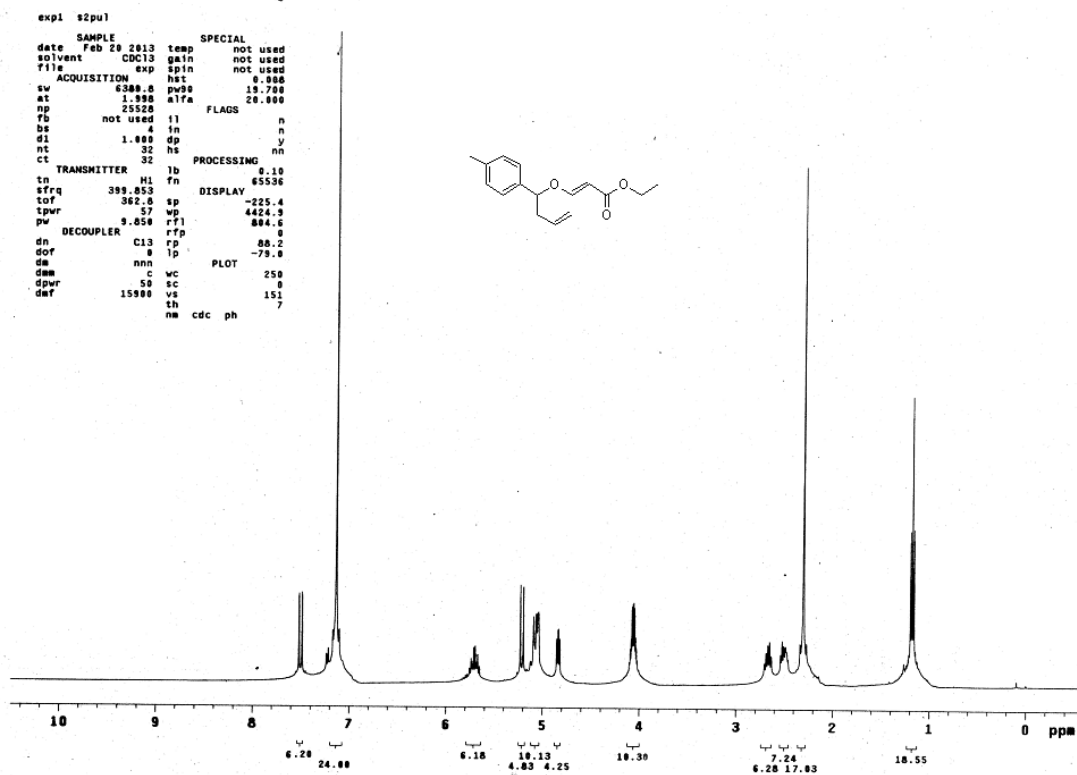
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¹H and ¹³C NMR spectra of (*E*)-Ethyl 3-((1-cyclohexylbut-3-en-1-yl)oxy)acrylate, 11



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

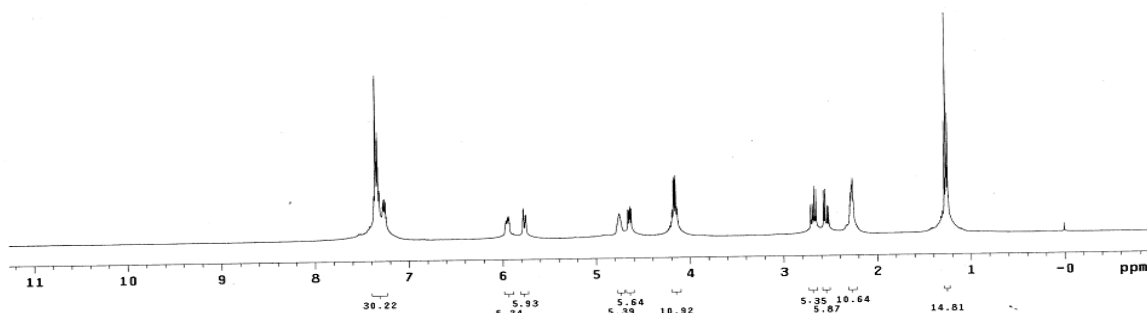
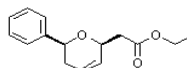


¹H and ¹³C NMR spectra of Ethyl-2-(6-phenyl-5,6-dihydro-2H-pyran-2-yl) acetate, 2a

aks-jam-9-u

expt s2pu1

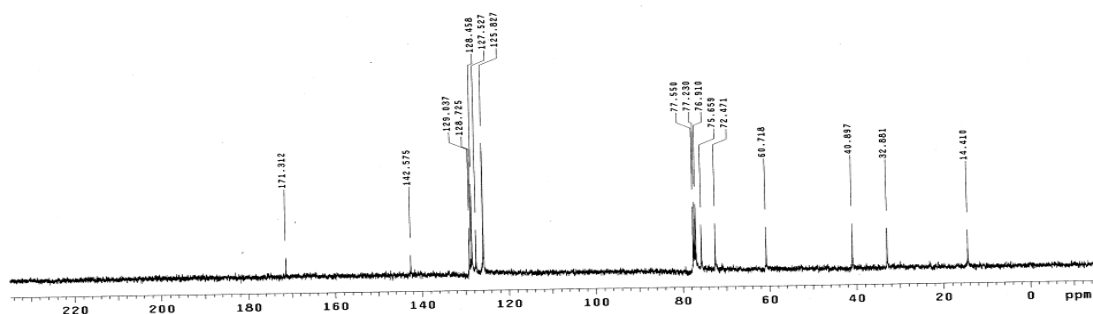
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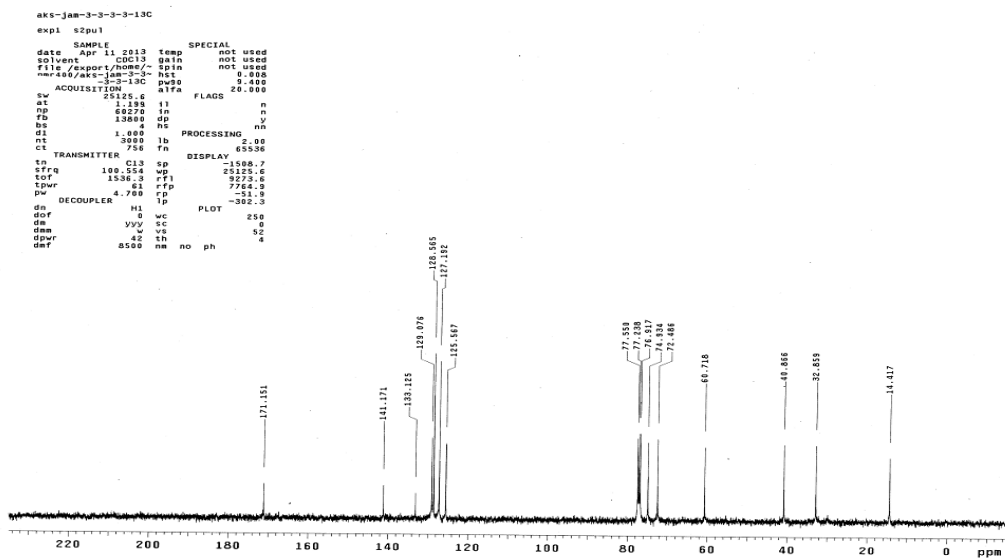
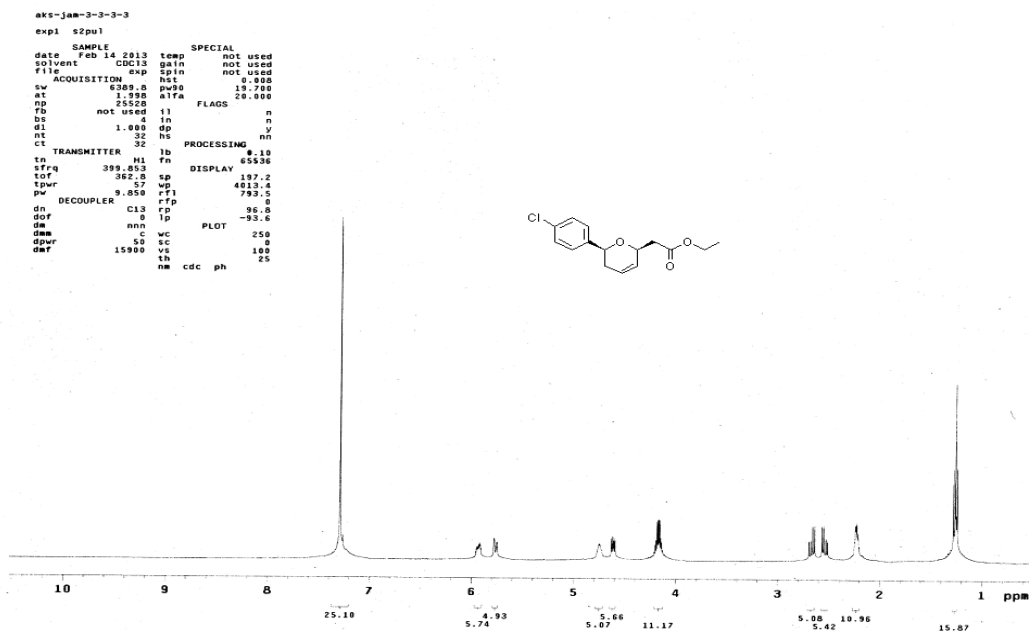
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^1H and ^{13}C NMR spectra of Ethyl-2-(6-(4-chlorophenyl)-5,6-dihydro-2H-pyran-2-yl)acetate, 2b



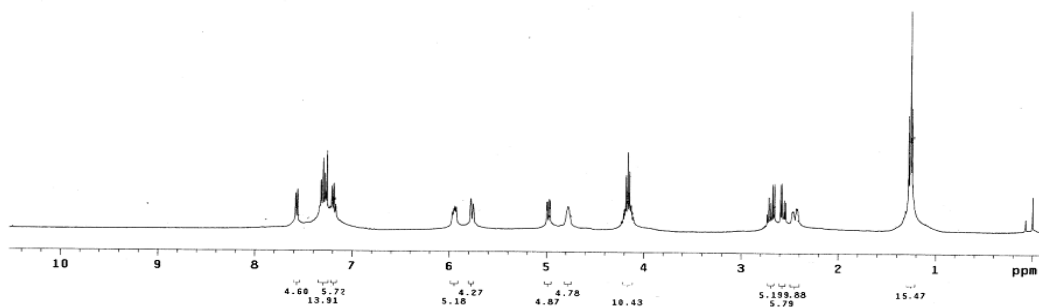
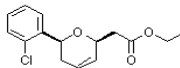
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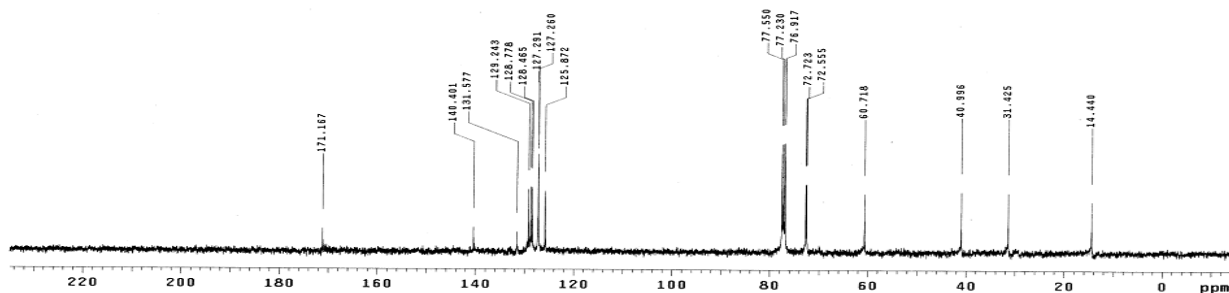
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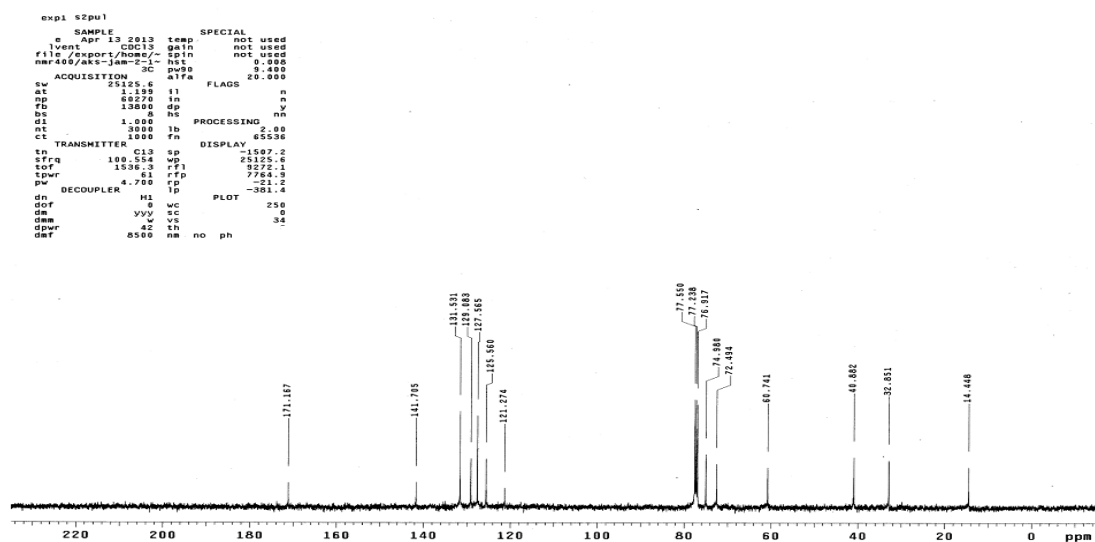
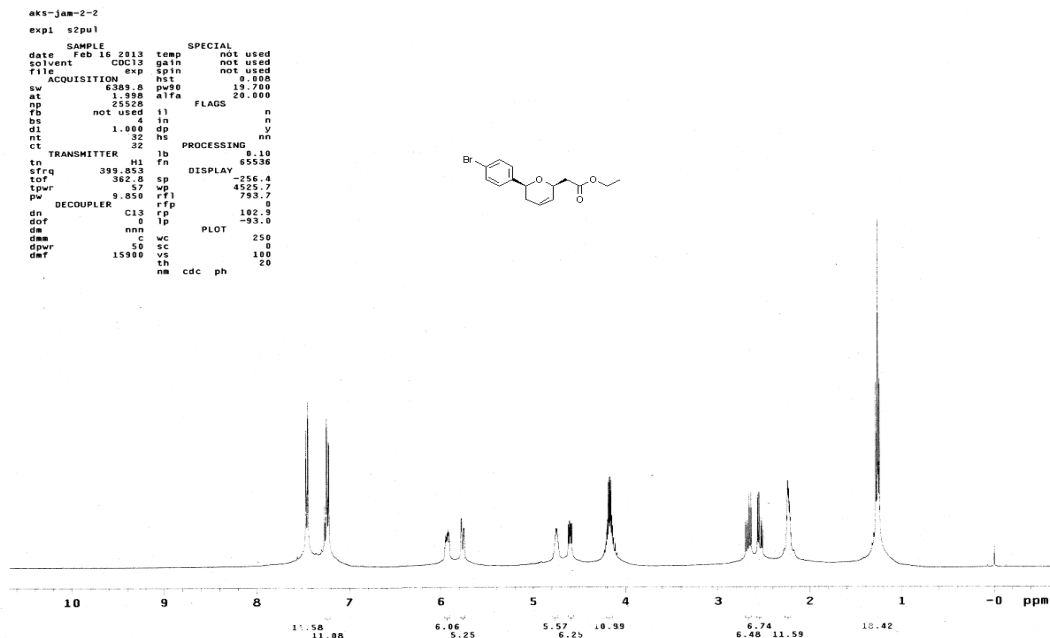
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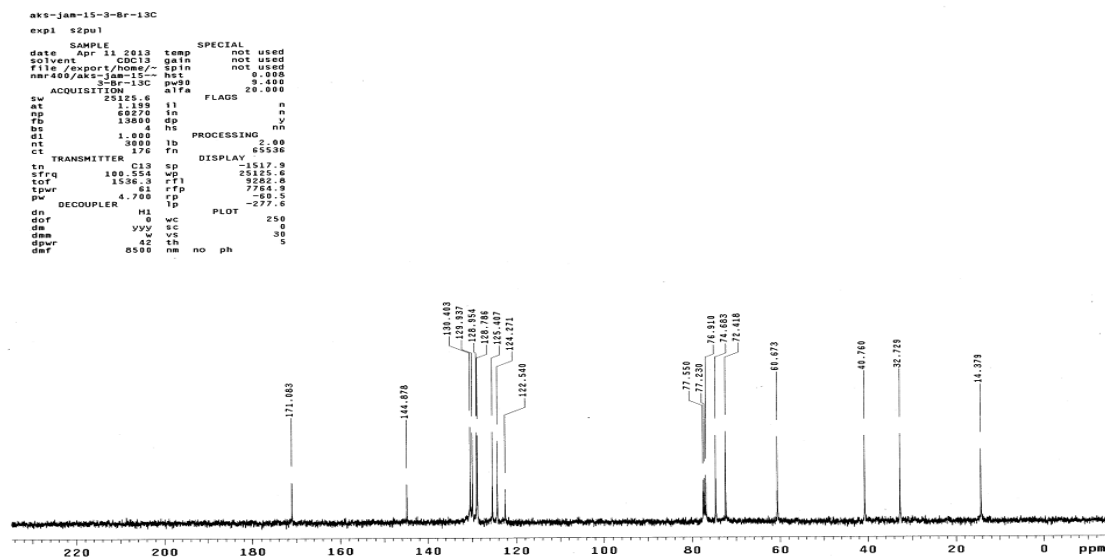
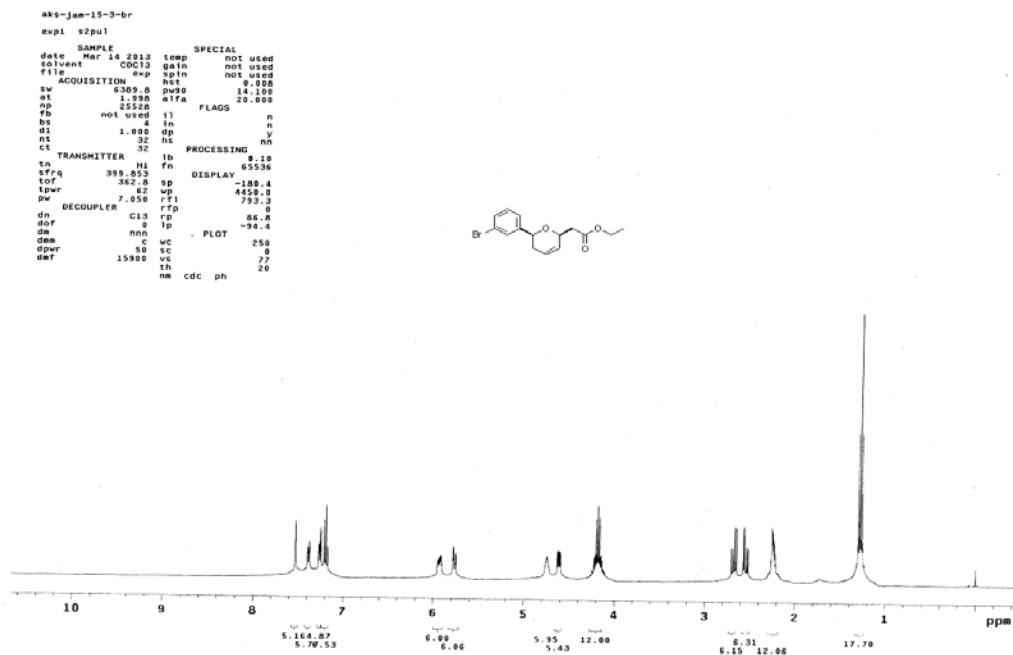
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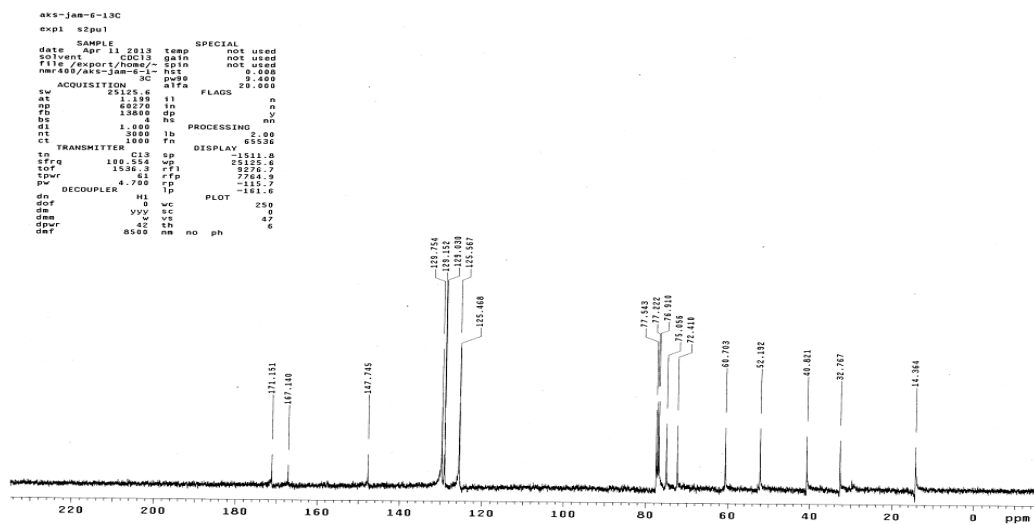
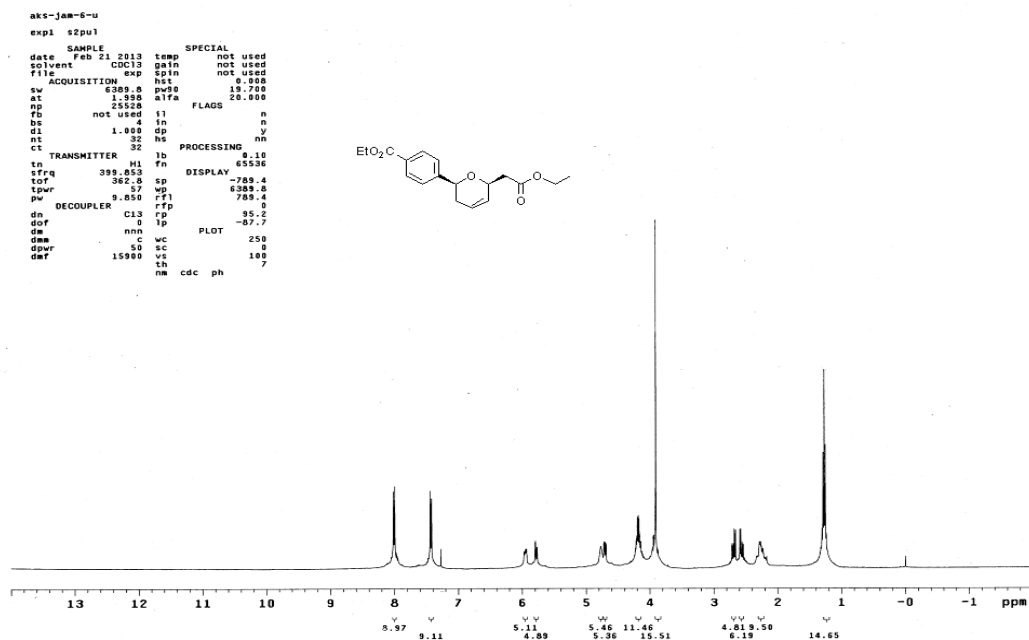
¹H and ¹³C NMR spectra of Ethyl-2-(6-(4-bromophenyl)-5,6-dihydro-2H-pyran-2-yl)acetate, 2d



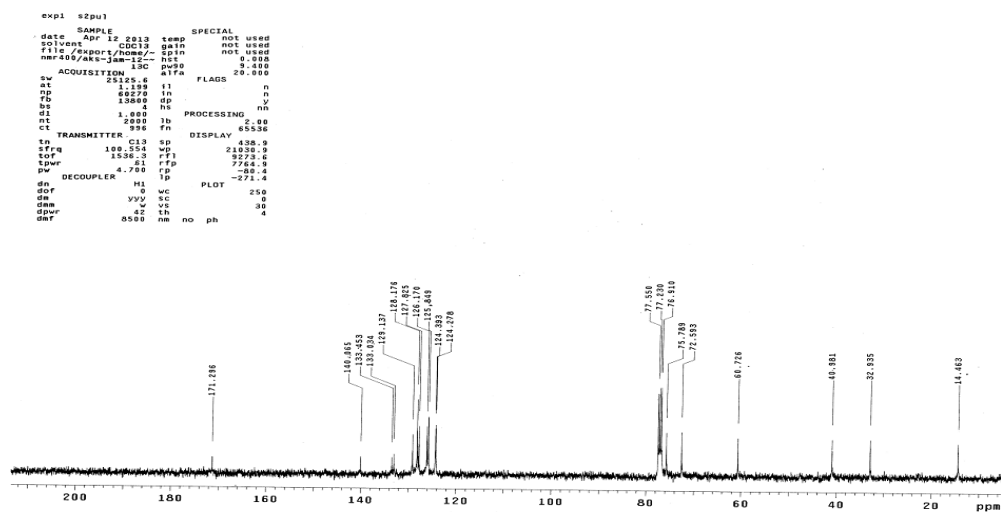
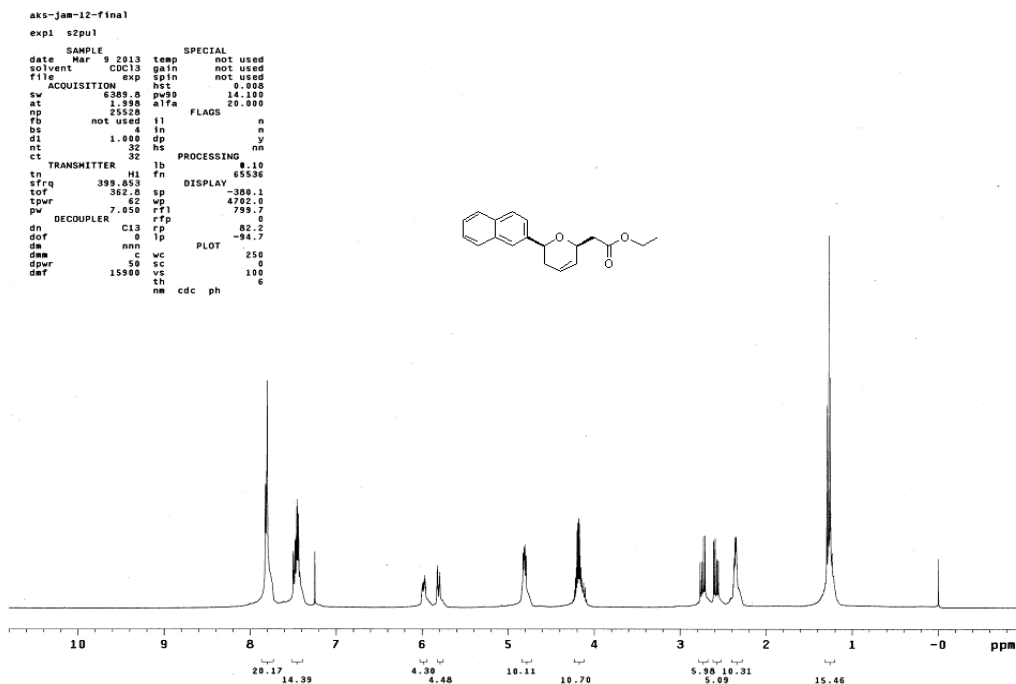
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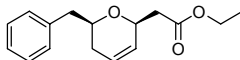
¹H and ¹³C NMR spectra of Methyl-4-(6-(2-ethoxy-2-oxoethyl)-3,6-dihydro-2H-pyran-2-yl)benzoate, 2f



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



^1H and ^{13}C NMR spectra of Ethyl-2-(6-benzyl-5,6-dihydro-2H-pyran-2-yl)acetate, 2i



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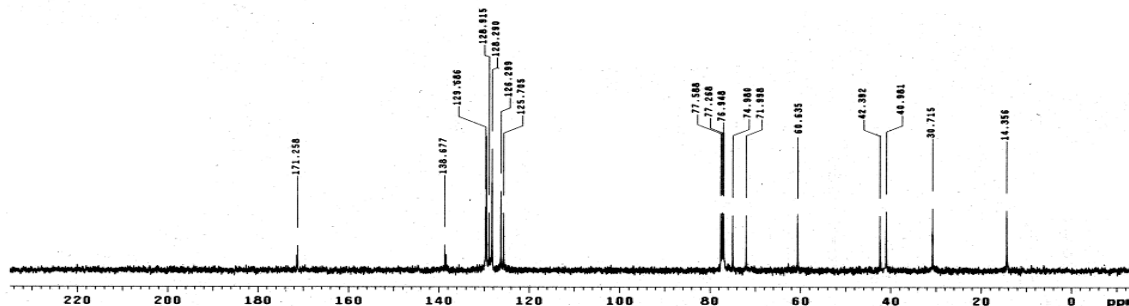
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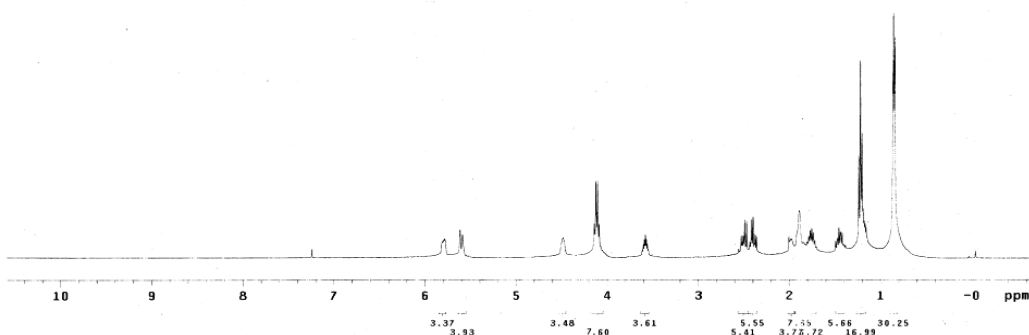
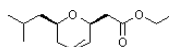


¹H and ¹³C NMR spectra of Ethyl 2-(6-isobutyl-5,6-dihydro-2H-pyran-2-yl)acetate, 2j

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aks-jam-18
expi s2pul

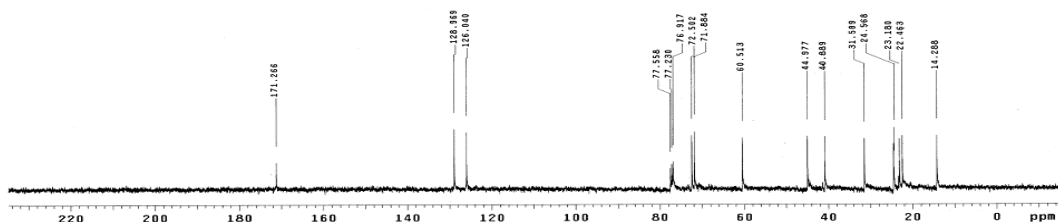
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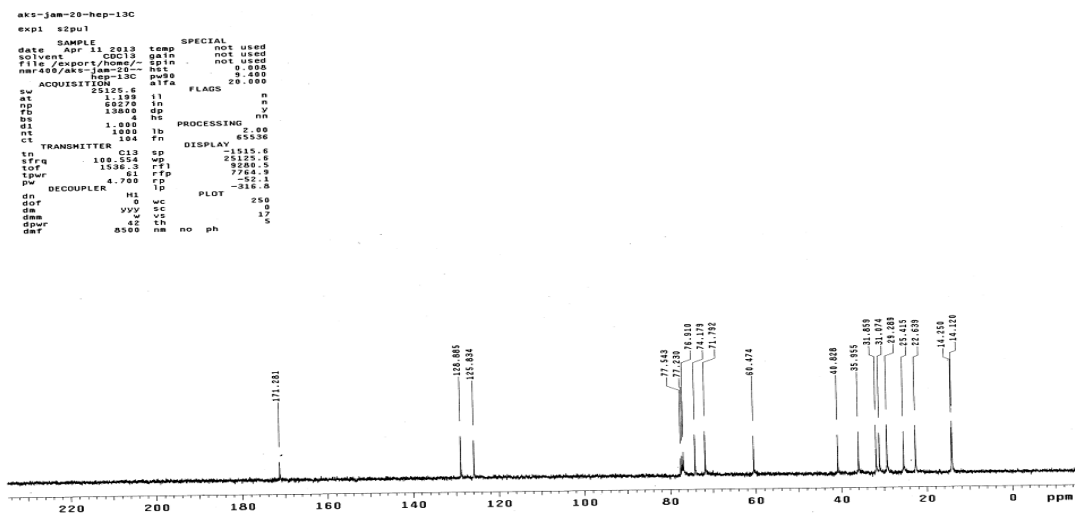
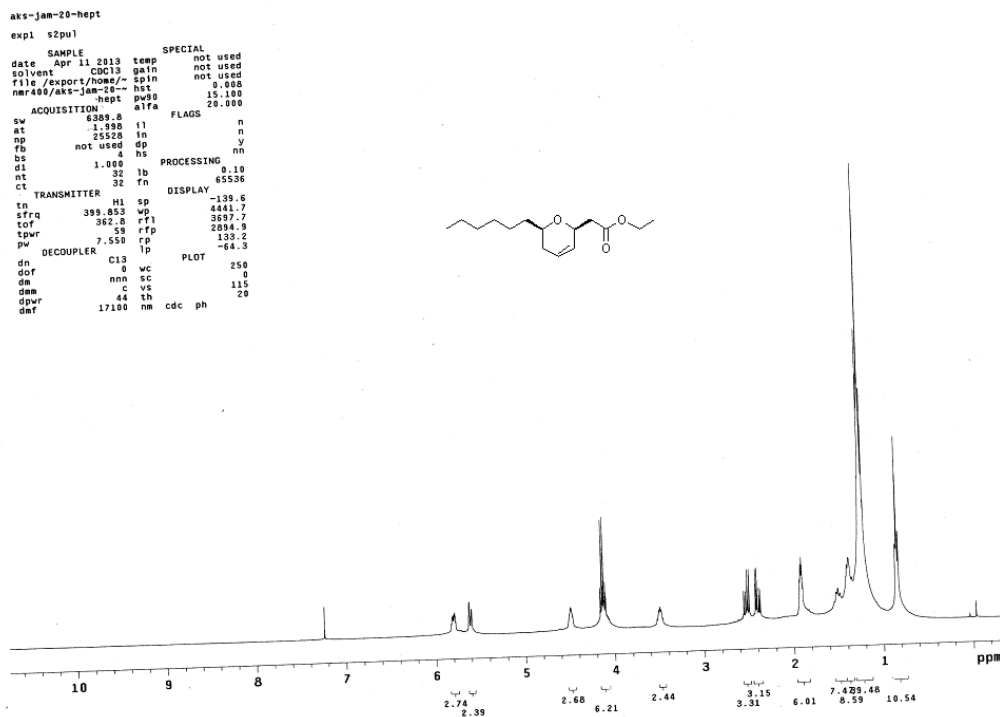
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aks-jam-18-13C
expi s2pul

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solvent CDCl3 gain not used
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bs 4 hs
di 1.000 lb PROCESSING 65536
nt 3000 fn DISPLAY
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tn C13 sp -1518.3
sfrq 100.624 wp 25125.6
tof 1536.3 rfp 9275.2
tpwr 61 rp 7768.9
pw 4.700 rp -98.6
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dm 50 vs 5
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¹H and ¹³C NMR spectra of Ethyl 2-(6-hexyl-5,6-dihydro-2H-pyran-2-yl)acetate, 2k^{14d}



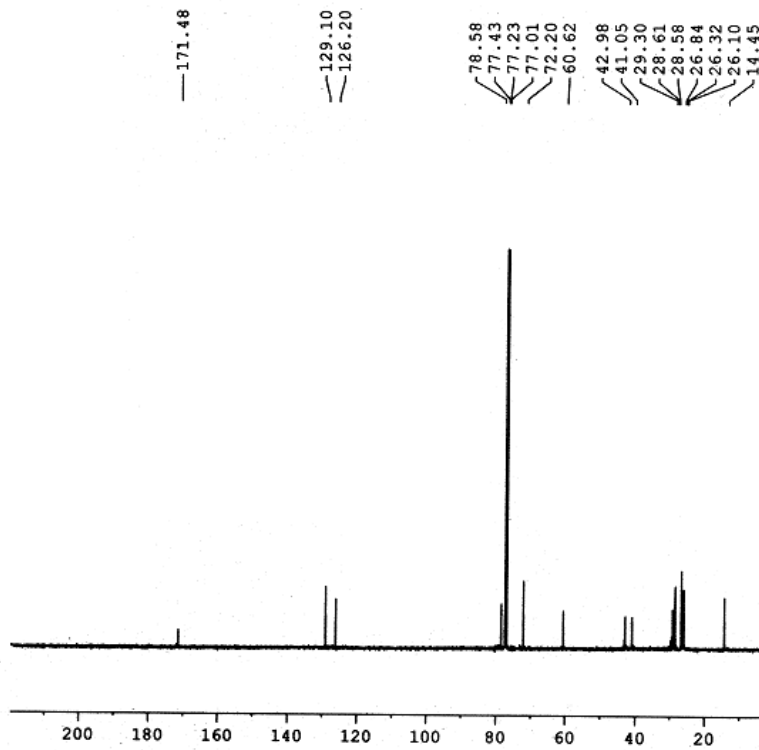
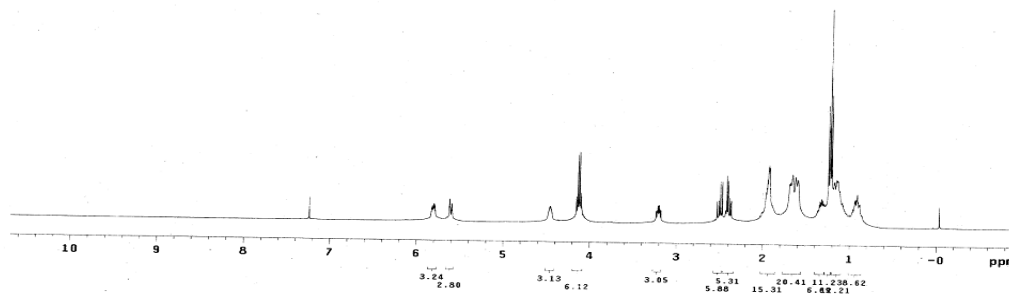
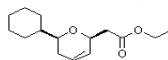
¹H and ¹³C NMR spectra of Ethyl 2-(6-cyclohexyl-5,6-dihydro-2H-pyran-2-yl)acetate, 2l

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pp 25520
fd not used
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d1 1.000 00 n
rt 32 hs PROCESSING nn
ct

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tof 398.053 sp DISPLAY -383.7
tpr 82 wp 4660.1
pw DECOUPLER 7.050 rf1 3690.3
dn C13 rfp 2834.9
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nm cdc ph 20
  
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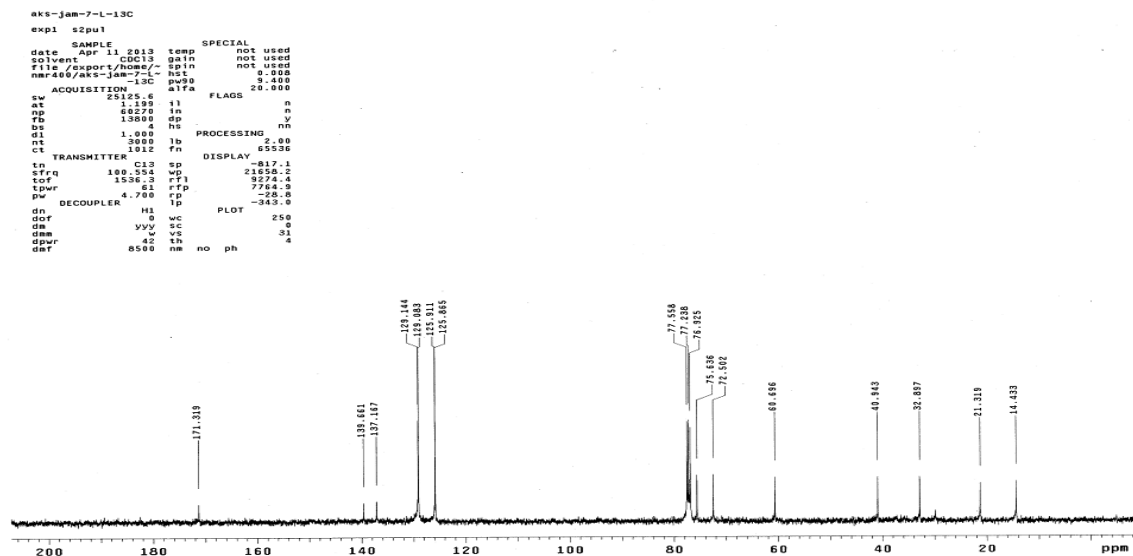
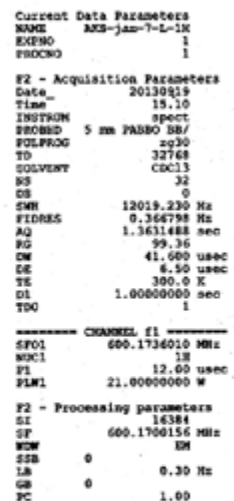
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PROCNO 1

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FIDRES 1.100393 Hz
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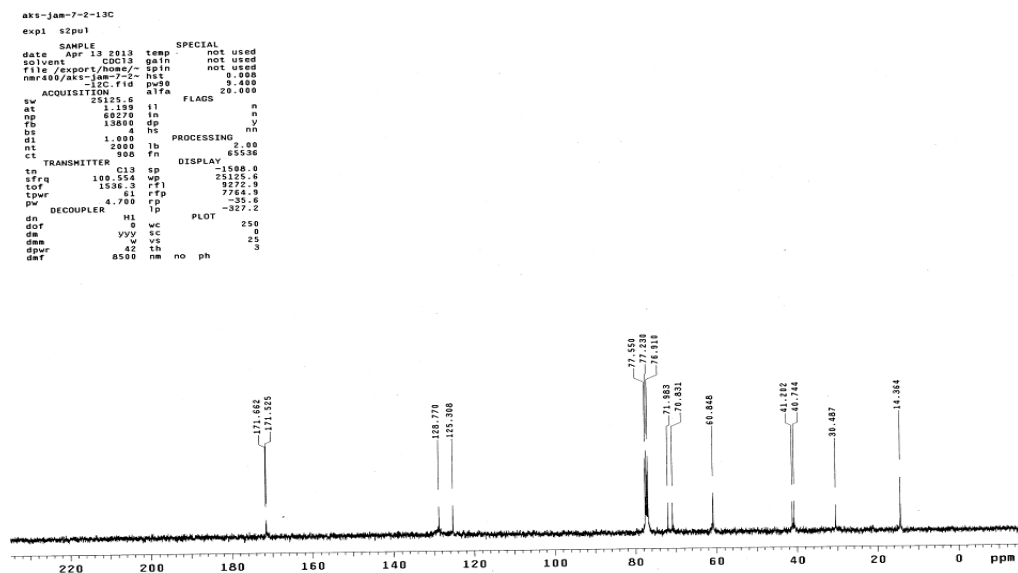
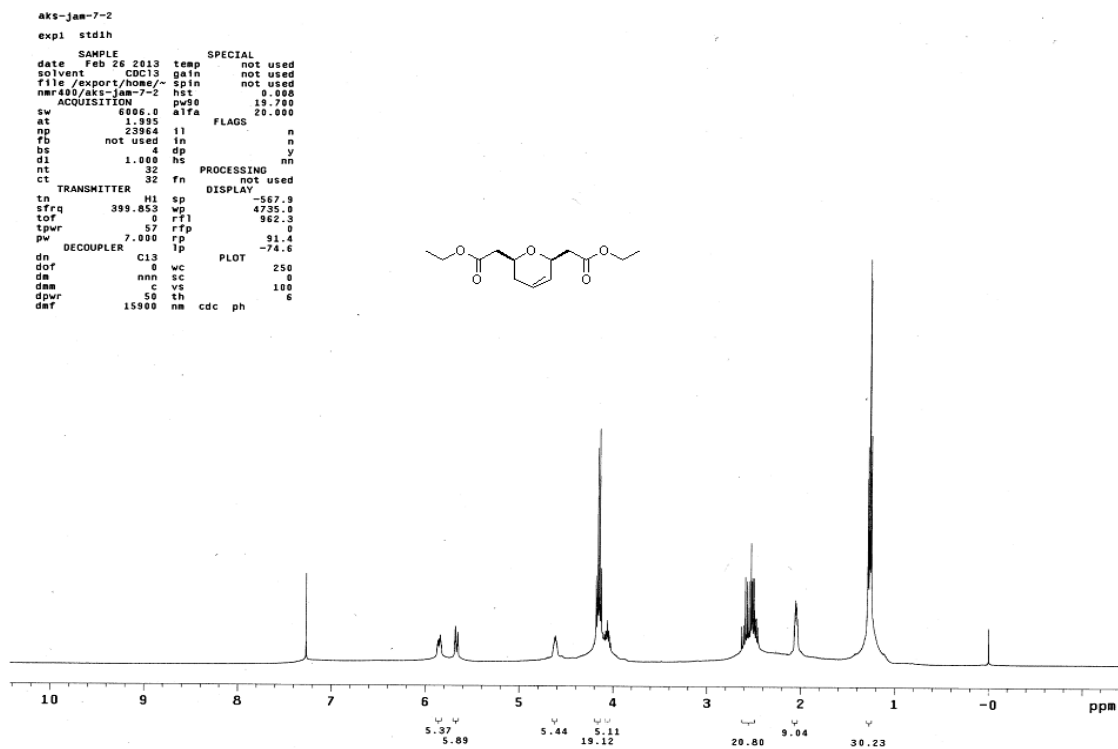
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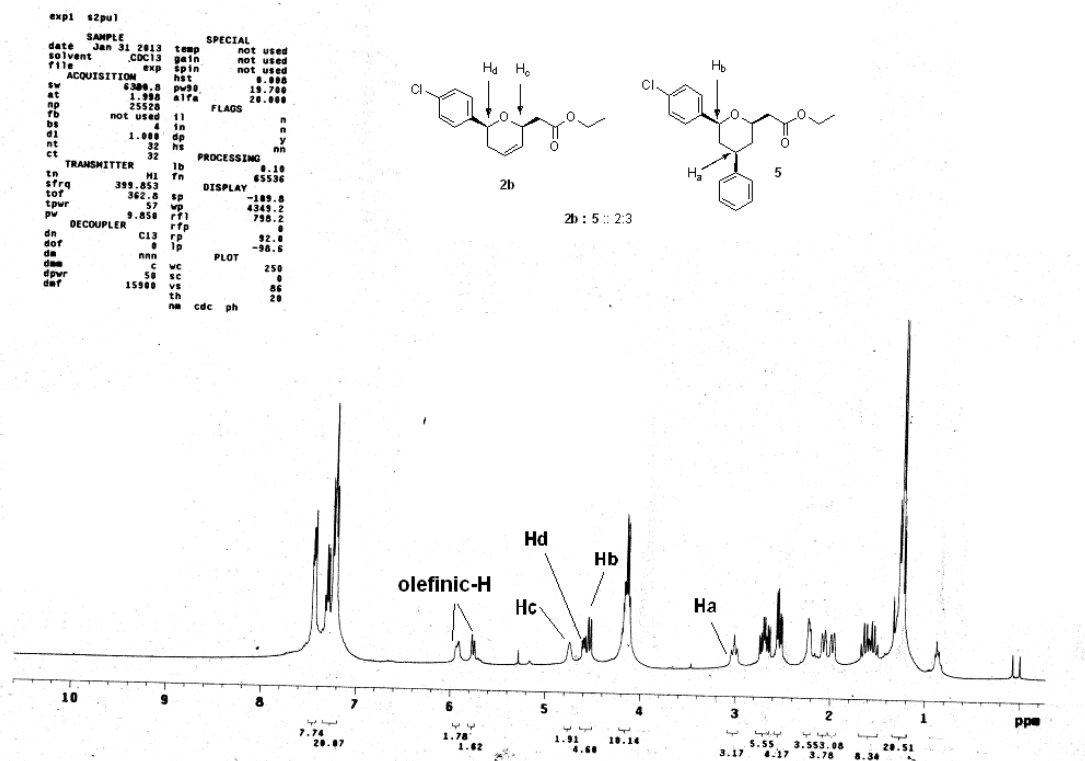
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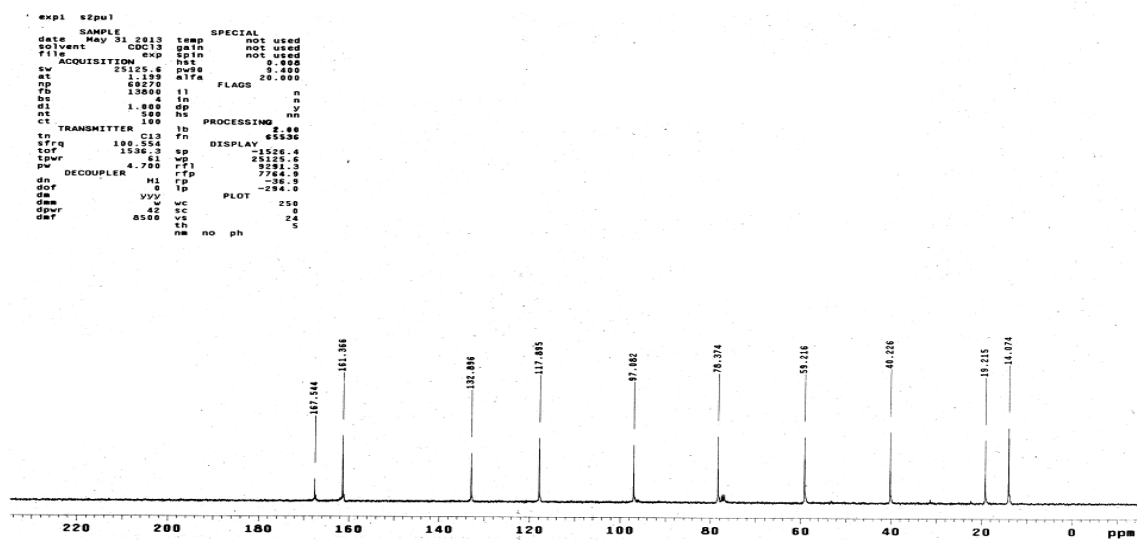
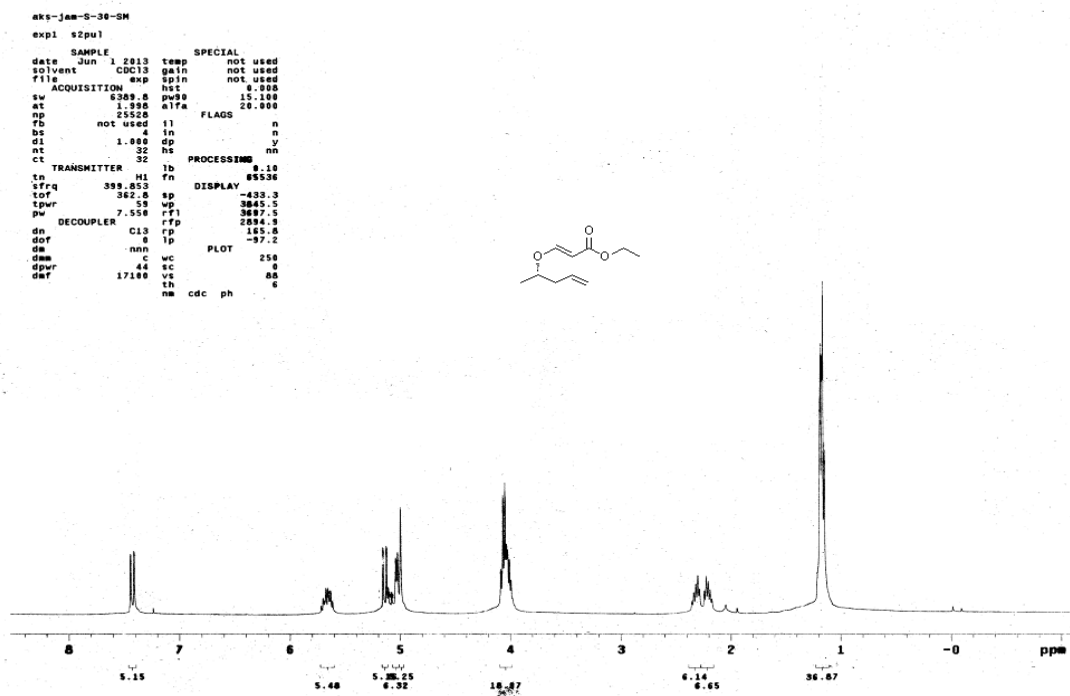
^1H and ^{13}C NMR spectra of Diethyl 2,2'-(3,6-dihydro-2H-pyran-2,6-diyl)diacetate, 2m'



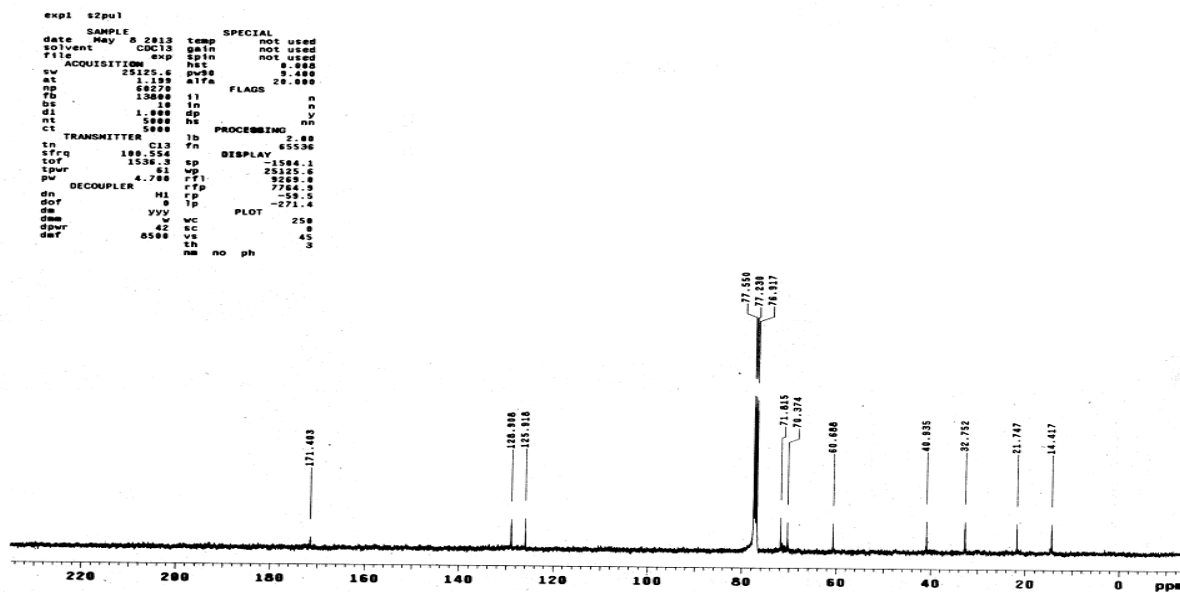
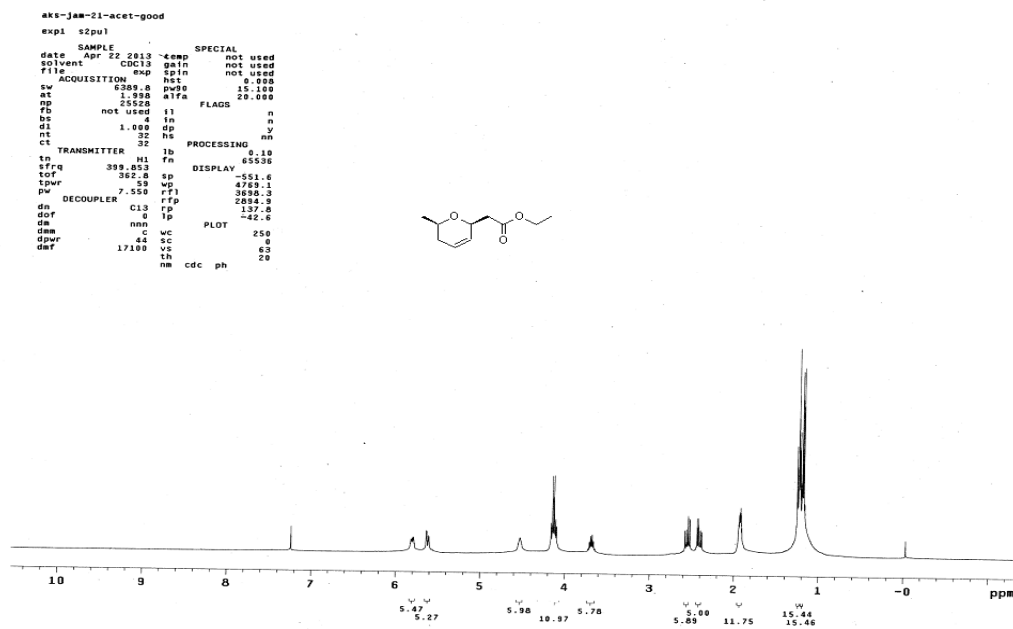
¹H spectra of Ethyl 2-(6-(4-chlorophenyl)-4-phenyltetrahydro-2H-pyran-2-yl)acetate, **5** and Ethyl-2-(6-(4-chlorophenyl)-5,6-dihydro-2H-pyran-2-yl)acetate, **2b**



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

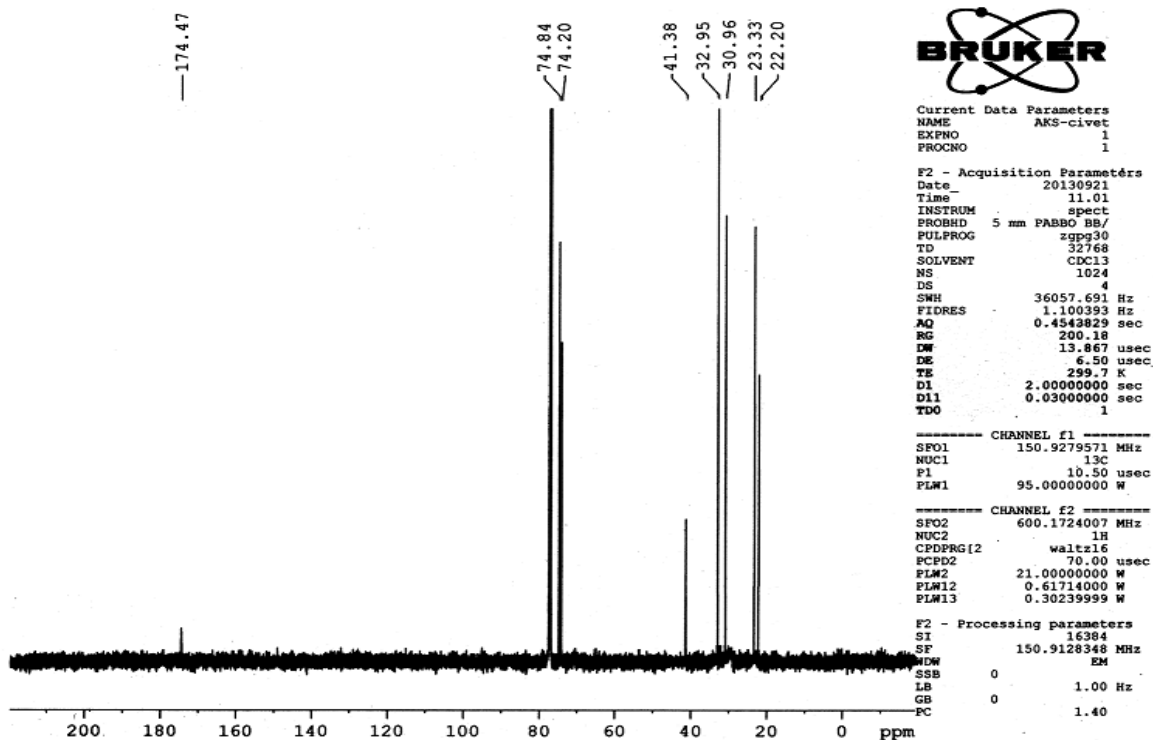
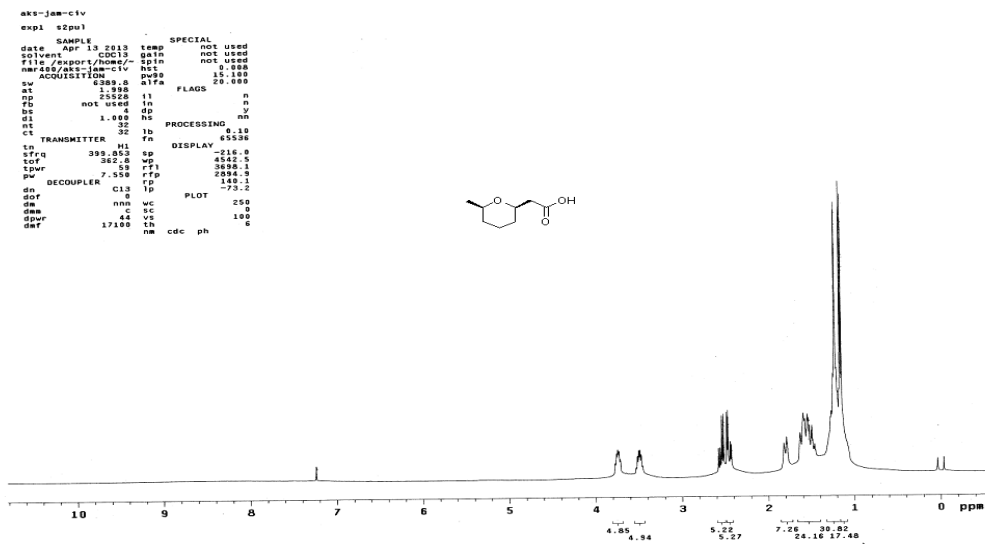


¹H and ¹³C NMR spectra of Ethyl 2-(2*R*,6*S*)-6-methyl-5,6-dihydro-2*H*-pyran-2-yl)acetate, 18

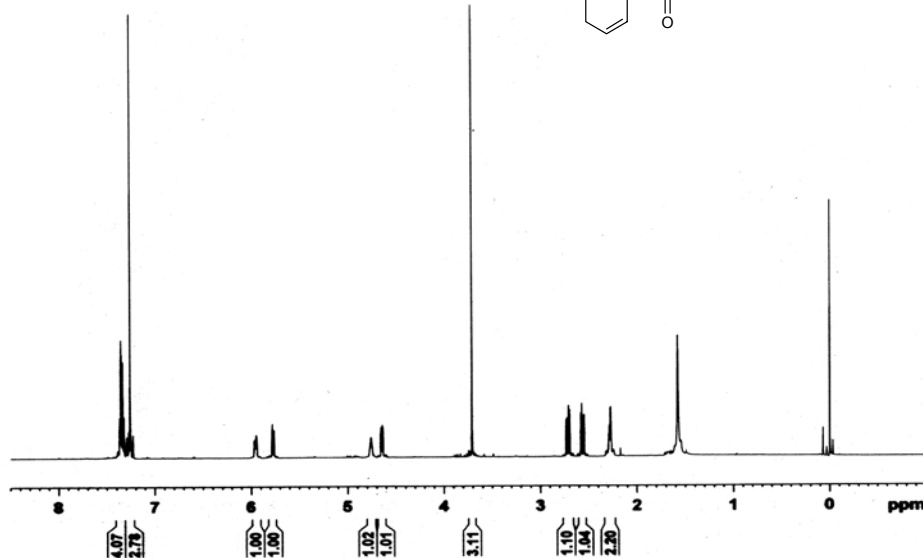
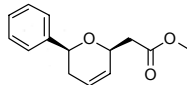




^1H and ^{13}C NMR spectra of 2-((2*S*,6*S*)-6-Methyltetrahydro-2*H*-pyran-2-yl)acetic acid, (+)-Civet, 20



Methyl 2-((2S,6S)-6-phenyl-5,6-dihydro-2H-pyran-2-yl)acetate, 2a¹⁶



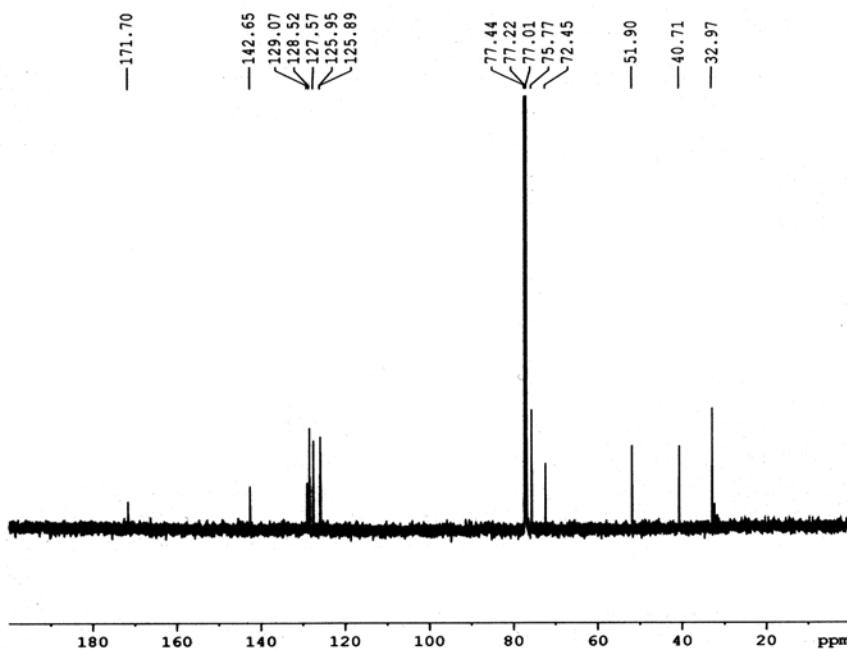
BRUKER

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PROCNO 1

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TE 299.3 K
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TDO 1

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NUC1 1H
P1 12.00 usec
PLW1 21.00000000 W

F2 - Processing parameters
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BRUKER

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PROCNO 1

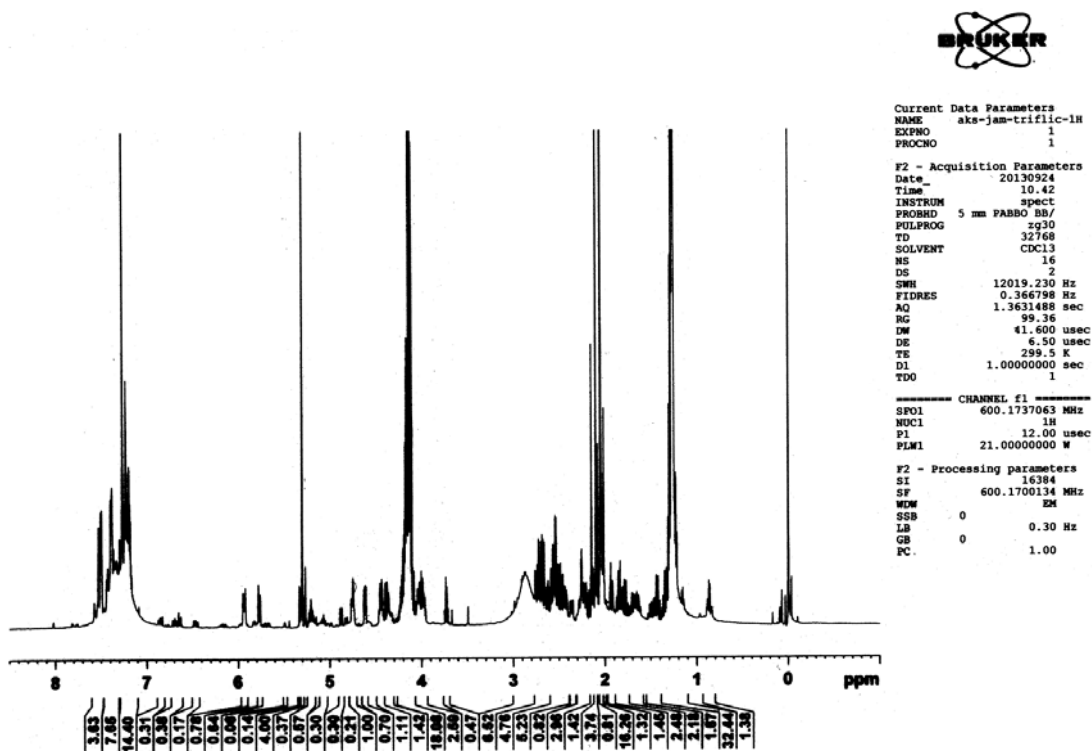
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PULPROG zgpg30
TD 32768
SOLVENT CDCl3
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DS 2
SWH 36057.691 Hz
FIDRES 1.100393 Hz
AQ 0.4543829 sec
RG 200.18
DW 13.867 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TDO 1

CHANNEL f1
SFO1 150.9279571 MHz
NUC1 13C
P1 10.50 usec
PLW1 95.00000000 W

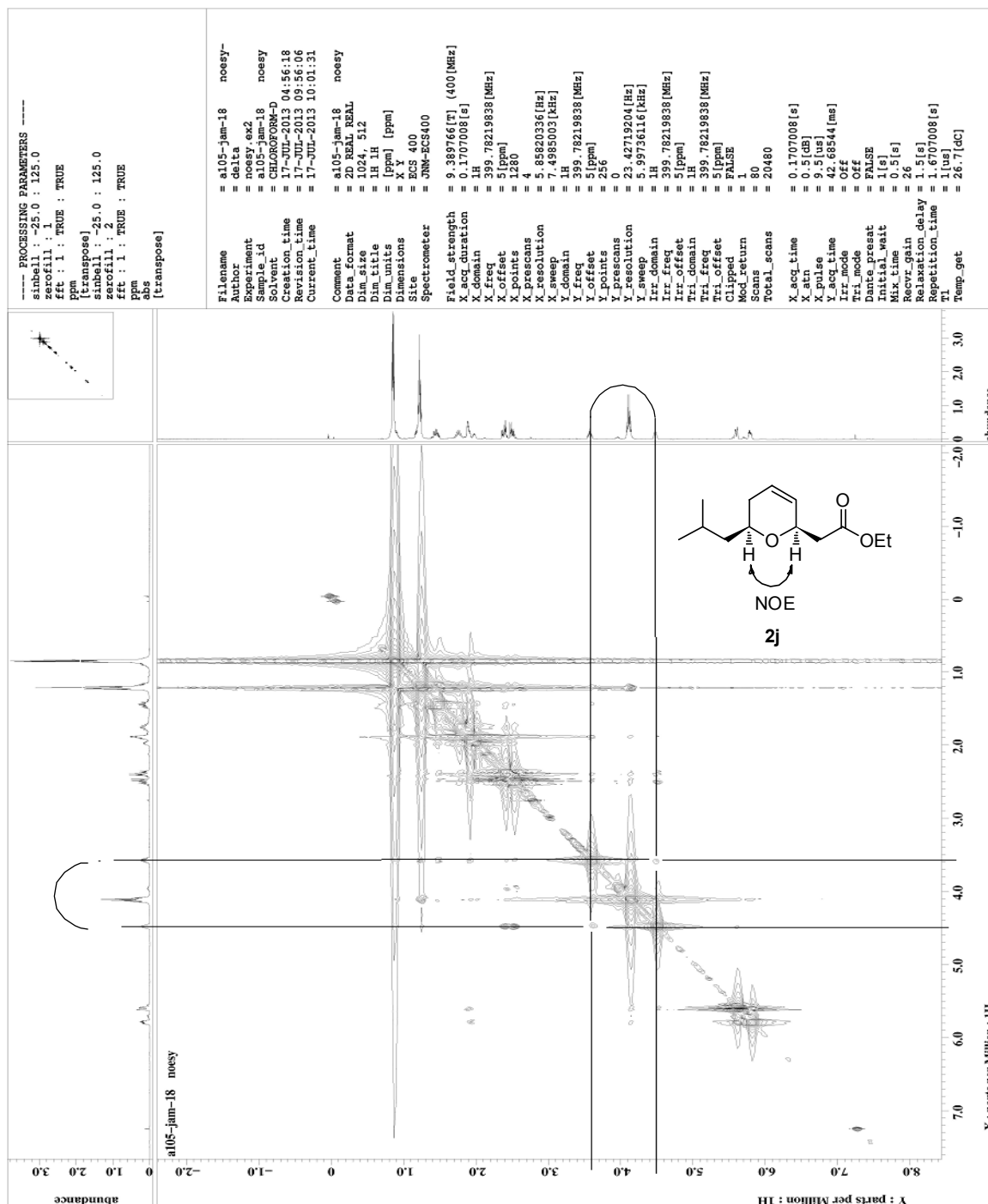
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NUC2 1H
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PCPD2 70.00 usec
PLW2 21.00000000 W
PLW12 0.61714000 W
PLW13 0.30239999 W

F2 - Processing parameters
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WDW EM
SSB 0
LB 1.00 Hz
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PC 1.40

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