

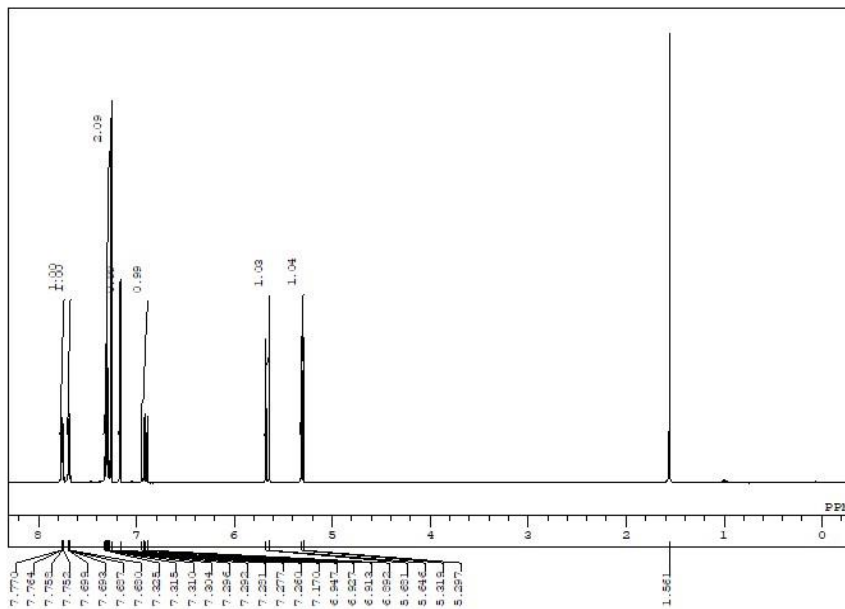
Supporting Information

The Use of Formaldehyde in the Rhodium-Catalyzed *Linear*-Selective Hydroformylation of Vinylheteroarenes

**Jian Pan, Tsumoru Morimoto,* Hideyuki Kobayashi, Hiroki Tanimoto,
and Kiyomi Kakiuchi**

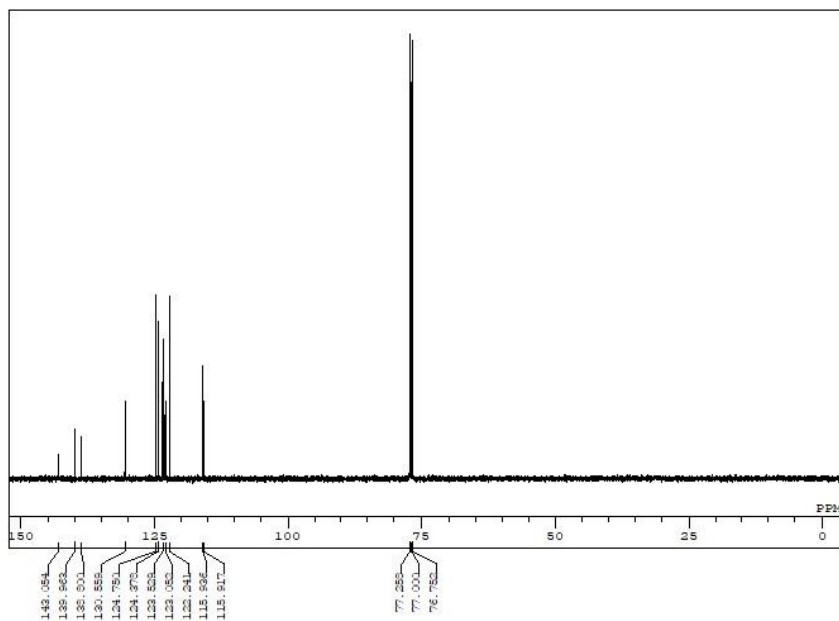
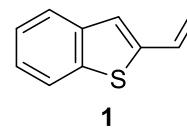
Division of Materials Science, Nara Institute of Science and Technology
(NAIST), Ikoma, Nara 630-0192, Japan E-mail: morimoto@ms.naist.jp.

^1H & ^{13}C NMR spectra



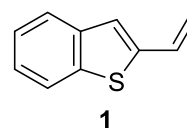
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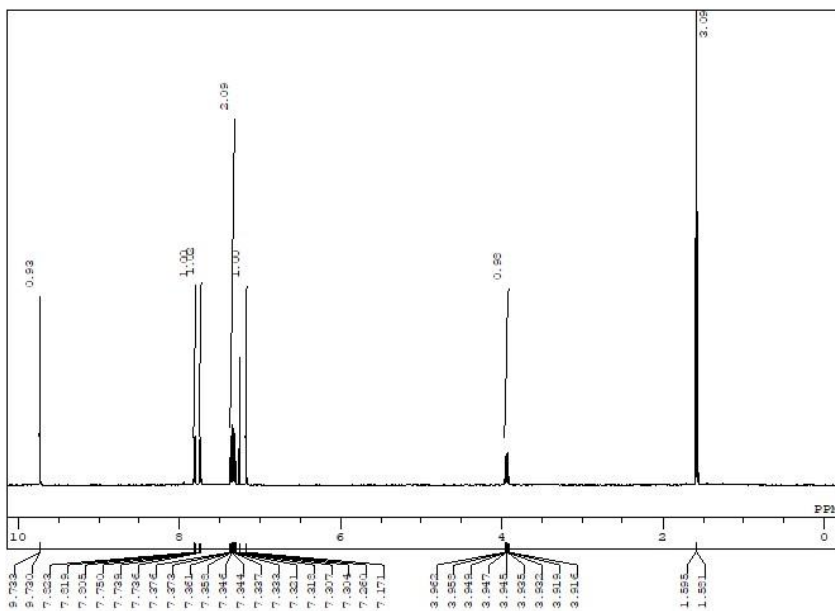
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DATIM 2016-05-06 16:12:48
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EXMOD proton_jump
OBFRQ 500.16 MHz
OBSETE 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.51 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
FWL 6.22 usec
IRNUC 1H
CTEMP 17.2 c
SIVNT CDCL3
EXREF 7.26 ppm
BF 0.10 Hz
RGAIN 48
    
```



```

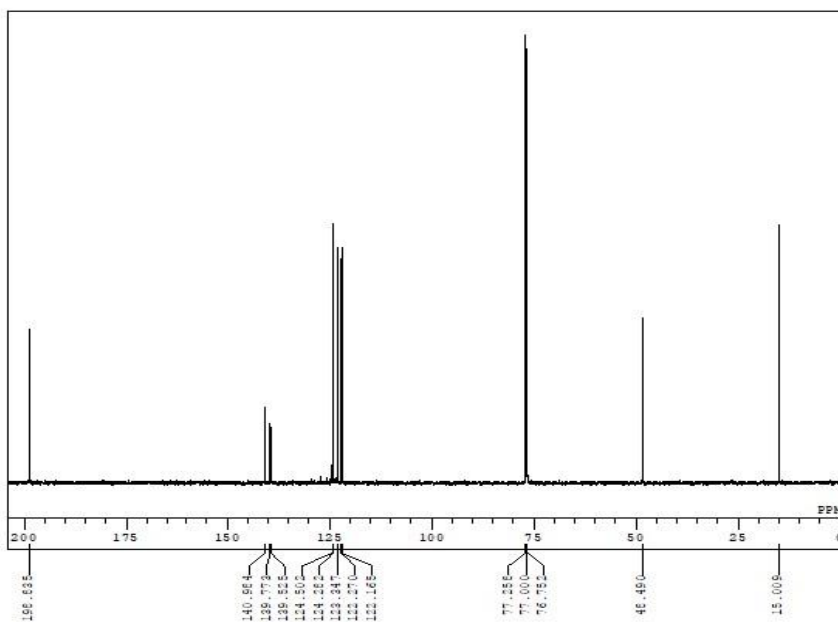
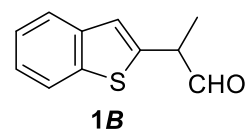
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COMNT single_pulse_decoupled_gated_NC
DATIM 2016-05-06 16:41:59
OBNUC 13C
EXMOD carbon_jump
OBFRQ 125.77 MHz
OBSETE 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.54 Hz
SCANS 1024
ACQTM 0.8226 sec
PD 2.0000 sec
FWL 3.12 usec
IRNUC 1H
CTEMP 17.9 c
SIVNT CDCL3
EXREF 77.00 ppm
BF 0.10 Hz
RGAIN 60
    
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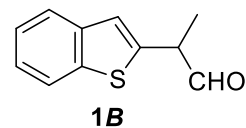
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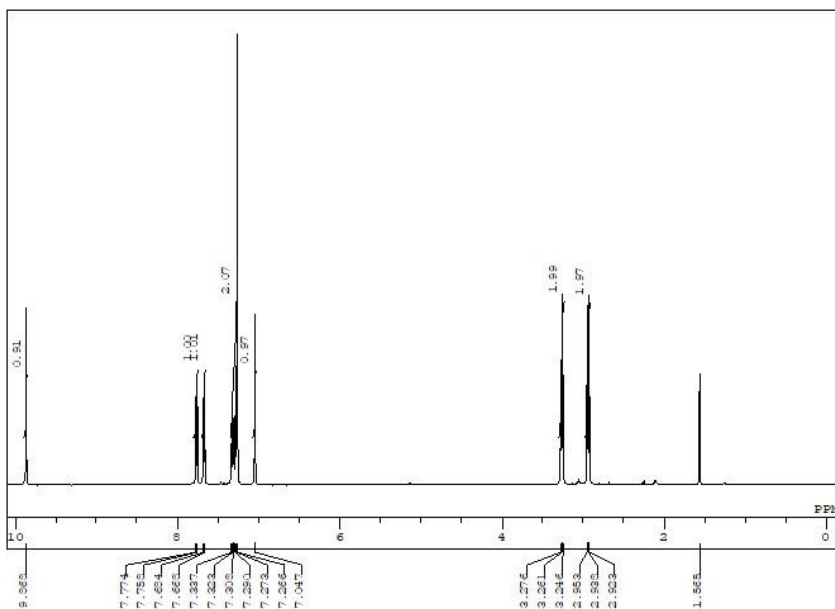
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EXMOD proton.jsp
OBFRO 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.51 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PWL 6.85 usec
IRNUC 1H
CTEMP 17.7 c
SIVM CDCL3
EXREF 7.26 ppm
BF 0.10 Hz
RGAIN 42
  
```



```

DFFILE 2-S-B-aldehyde_carbon-1-1.als
COMNT single_pulse decoupled gated MG
DATIM 2017-11-15 22:28:42
OBNUC 13C
EXMOD carbon.jsp
OBFRO 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.54 Hz
SCANS 1024
ACQTM 0.8236 sec
PD 2.0000 sec
PWL 3.12 usec
IRNUC 1H
CTEMP 18.5 c
SIVM CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 60
  
```

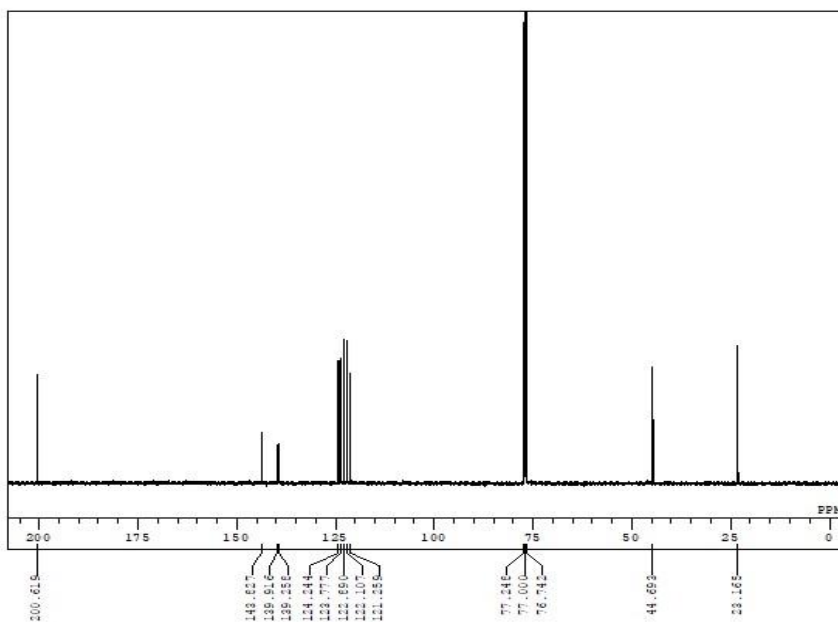
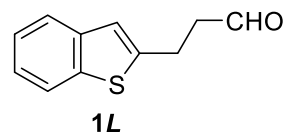




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DFFILE 2-S-L-aldehyde_proton-1-1.als
COMNT single_pulse
DATIM 2017-11-30 17:56:06
OBNUC 1H
EXMOD proton.jsp
OBFRO 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.51 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
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IRNUC 1H
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SVM CDCL3
EXREF 7.26 ppm
BF 1.20 Hz
RGAIN 46

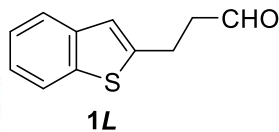
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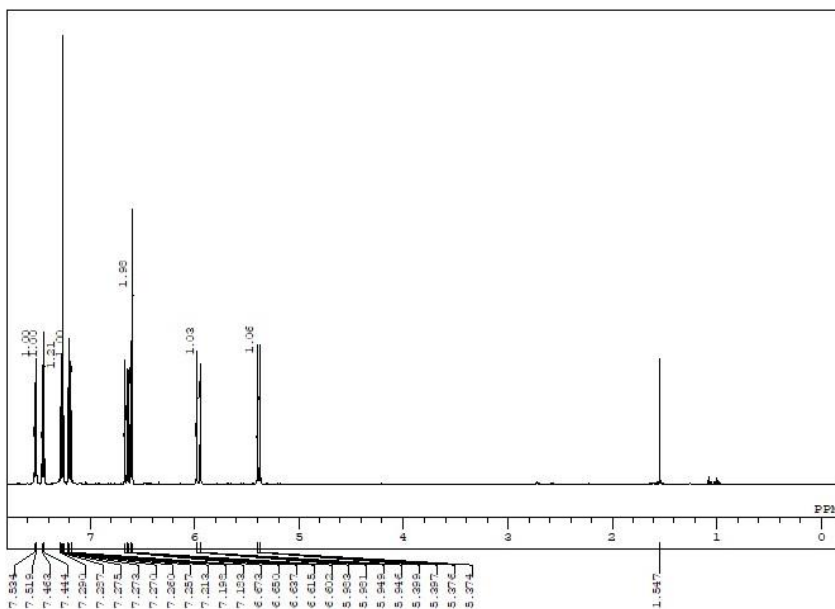


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COMNT single_pulse decoupled gated MG
DATIM 2017-11-30 20:26:24
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EXMOD carbon.jsp
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OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.54 Hz
SCANS 1024
ACQTM 0.8236 sec
PD 2.0000 sec
PWL 3.12 usec
IRNUC 1H
CTEMP 15.6 c
SVM CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 60

```

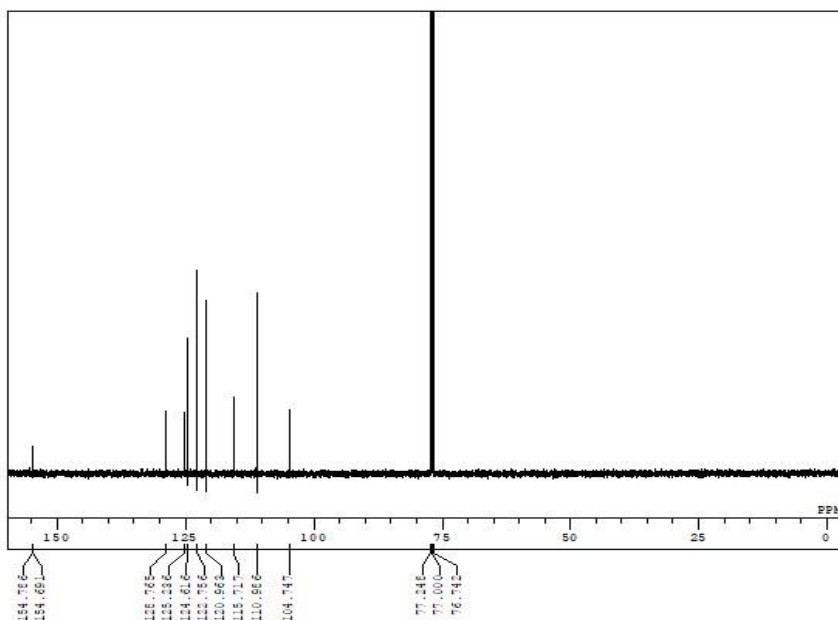
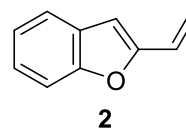




```

DFFILE 2-O-olefin_proton-1-1.als
COMNT single_pulse
DATIM 2017-11-13 14:45:58
OBNUC 1H
EXMOD proton.jsp
OBFRO 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.51 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
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IRNUC 1H
CTEMP 17.7 c
SVM CDCL3
EXREF 7.26 ppm
BF 0.10 Hz
RGAIN 44

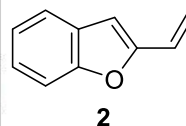
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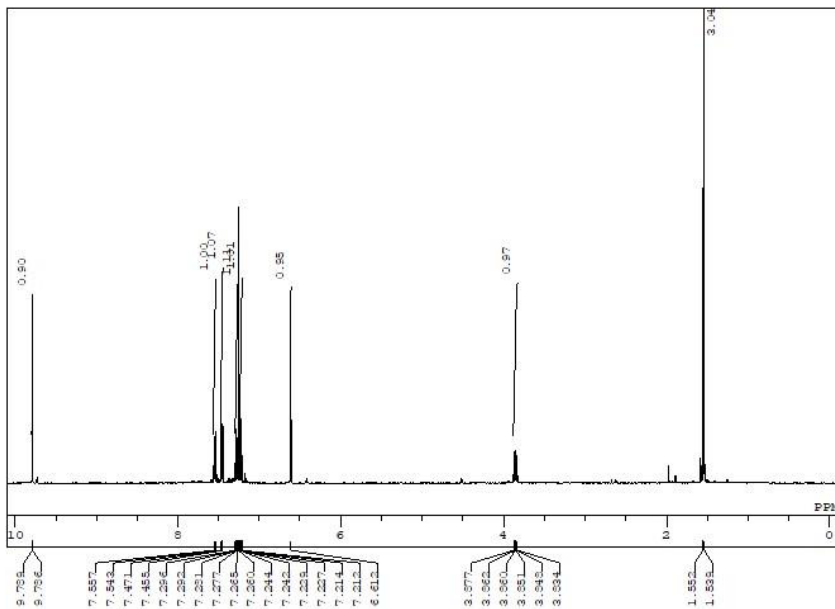


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COMNT single_pulse_decoupled_gated_NC
DATIM 2017-11-13 16:19:16
OBNUC 13C
EXMOD carbon.jsp
OBFRO 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.54 Hz
SCANS 1024
ACQTM 0.8236 sec
PD 2.0000 sec
PWL 3.12 usec
IRNUC 1H
CTEMP 17.1 c
SVM CDCL3
EXREF 77.00 ppm
BF 0.10 Hz
RGAIN 60

```

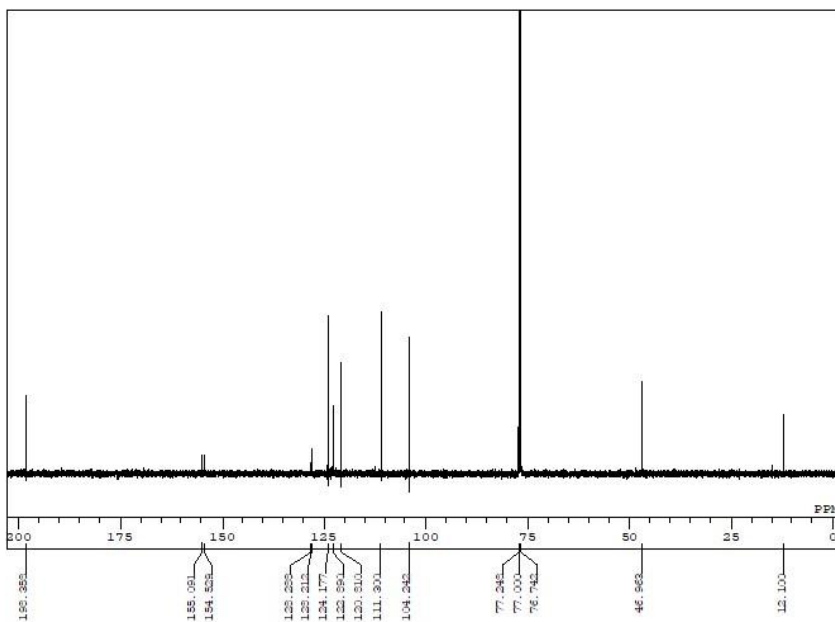
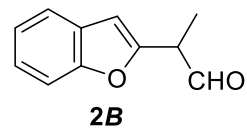




```

DFFILE 2-O-B-aldehyde_proton-1-1.als
COMNT single_pulse
DATIM 2017-11-13 20:52:54
OBNUC 1H
EXMOD proton.jsp
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.51 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
FWL 6.85 usec
IRNUC 1H
CTEMP 17.0 c
SUNT CDCL3
EXREF 7.26 ppm
BF 0.10 Hz
RGAIN 44

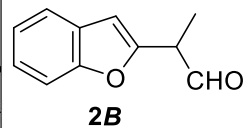
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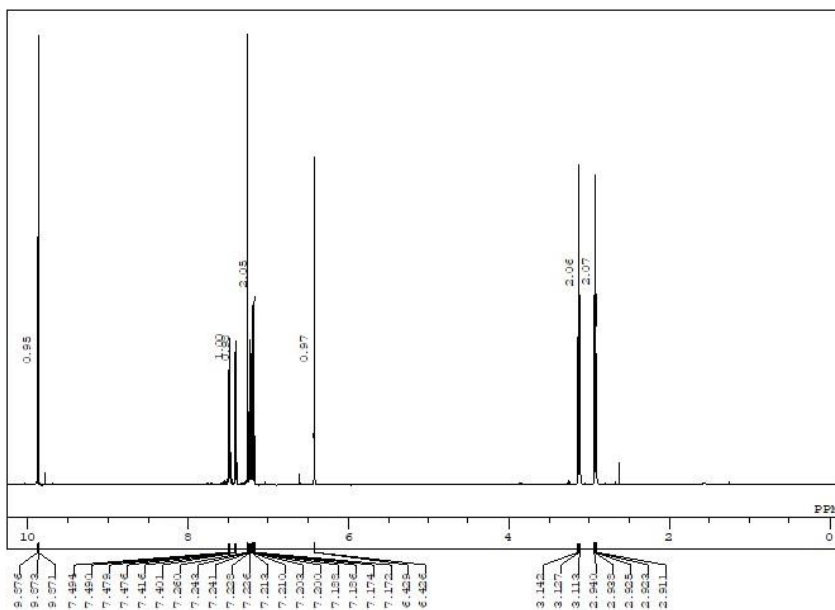


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COMNT single_pulse decoupled gated NC
DATIM 2017-11-14 22:17:33
OBNUC 13C
EXMOD carbon.jsp
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.54 Hz
SCANS 1024
ACQTM 0.8226 sec
PD 2.0000 sec
FWL 3.12 usec
IRNUC 1H
CTEMP 19.7 c
SUNT CDCL3
EXREF 77.00 ppm
BF 0.10 Hz
RGAIN 60

```

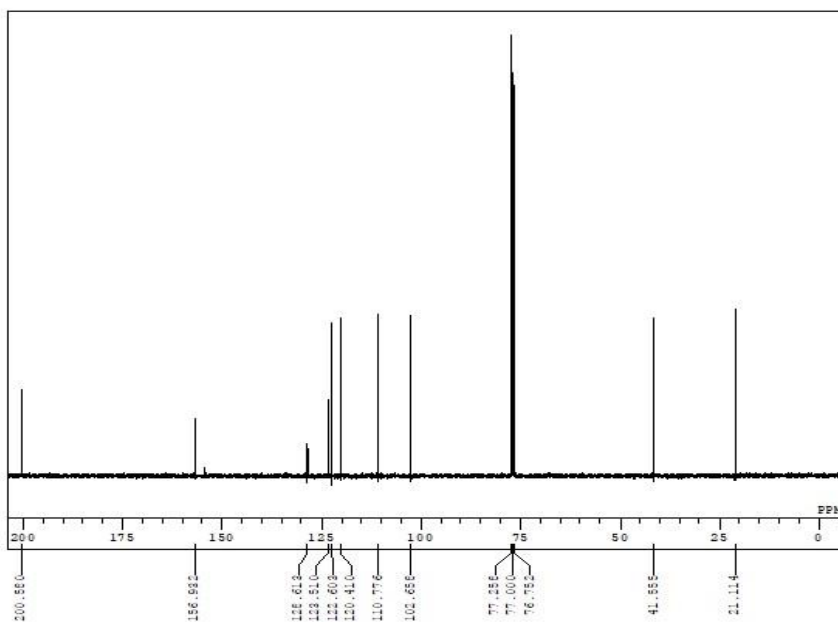
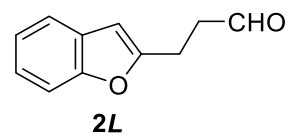




```

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COMNT single_pulse
DATIM 2017-11-10 14:48:06
OBNUC 1H
EXMOD proton.jsp
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.51 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PWL 6.85 usec
IRNUC 1H
CTEMP 16.8 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.10 Hz
RGAIN 42

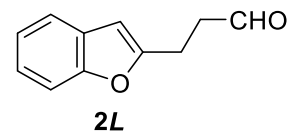
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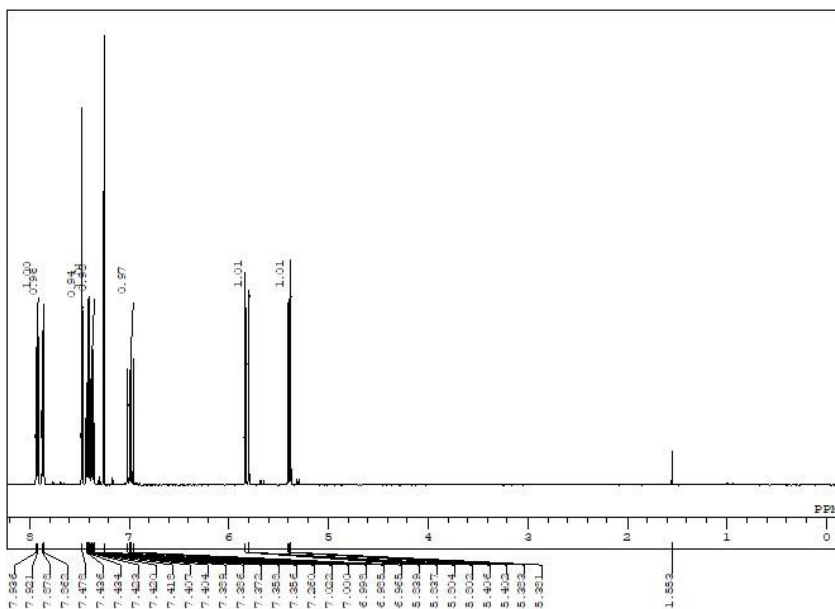


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COMNT single_pulse decoupled gated NC
DATIM 2017-11-10 14:56:10
OBNUC 13C
EXMOD carbon.jsp
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.54 Hz
SCANS 1024
ACQTM 0.8236 sec
PD 2.0000 sec
PWL 3.12 usec
IRNUC 1H
CTEMP 16.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.10 Hz
RGAIN 60

```

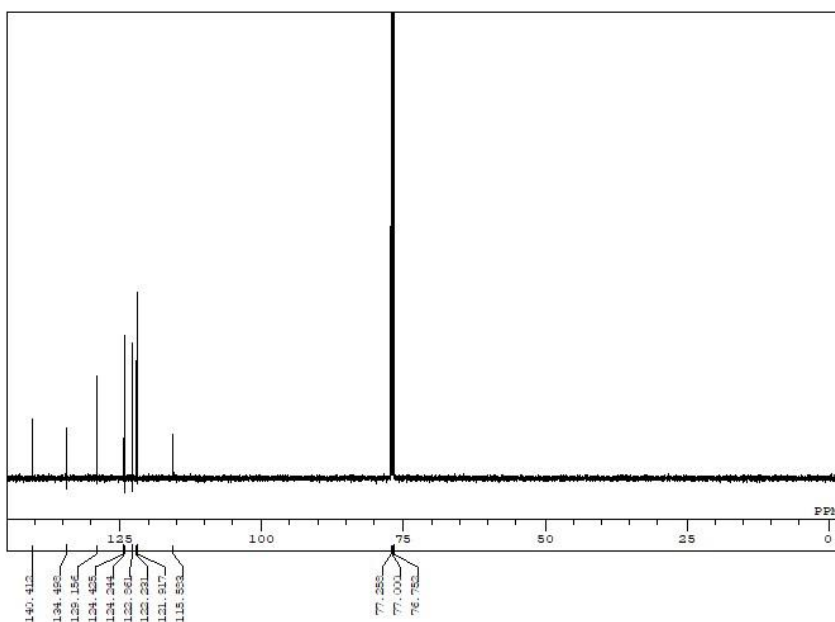
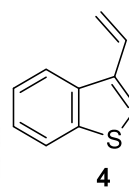




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DFFILE 3-S-olefin_proton-1-1.als
COMNT single_pulse
DATIM 2018-02-24 16:02:21
OBNUC 1H
EXMOD proton.jsp
OBFRO 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.51 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
FWL 6.85 usec
IRNUC 1H
CTEMP 14.0 c
SUNT CDCL3
EXREF 7.26 ppm
BF 0.10 Hz
RGAIN 42

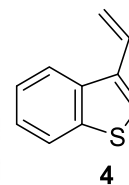
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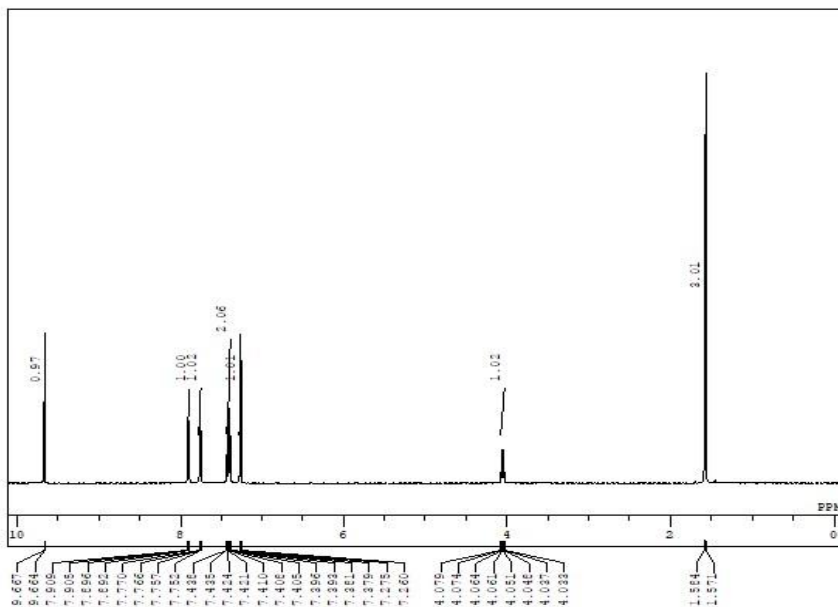


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DFFILE 3-S-olefin_carbon-1-1.als
COMNT single_pulse_decoupled_gated_NC
DATIM 2018-02-24 16:10:01
OBNUC 13C
EXMOD carbon.jsp
OBFRO 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.54 Hz
SCANS 1024
ACQTM 0.8226 sec
PD 2.0000 sec
FWL 3.12 usec
IRNUC 13C
CTEMP 13.6 c
SUNT CDCL3
EXREF 77.00 ppm
BF 0.10 Hz
RGAIN 56

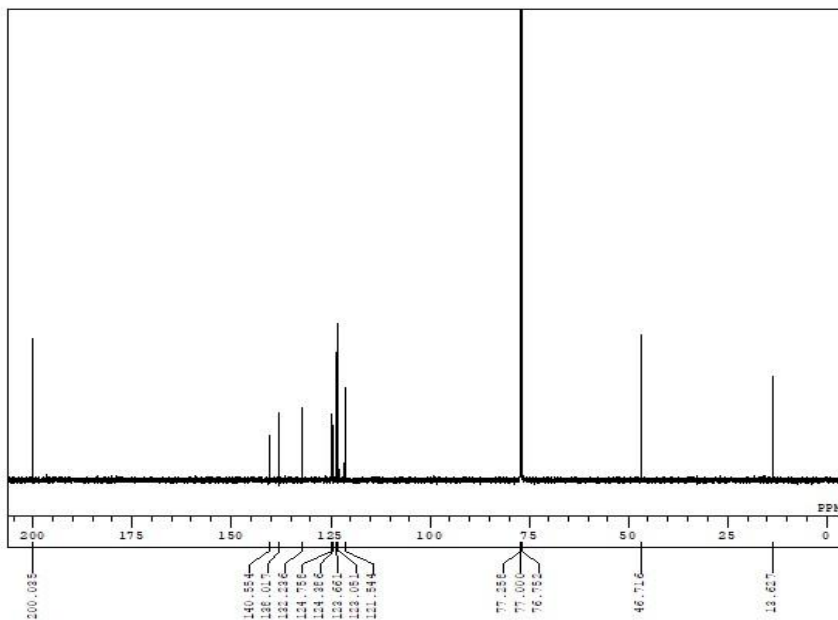
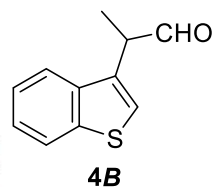
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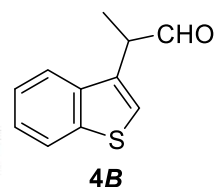
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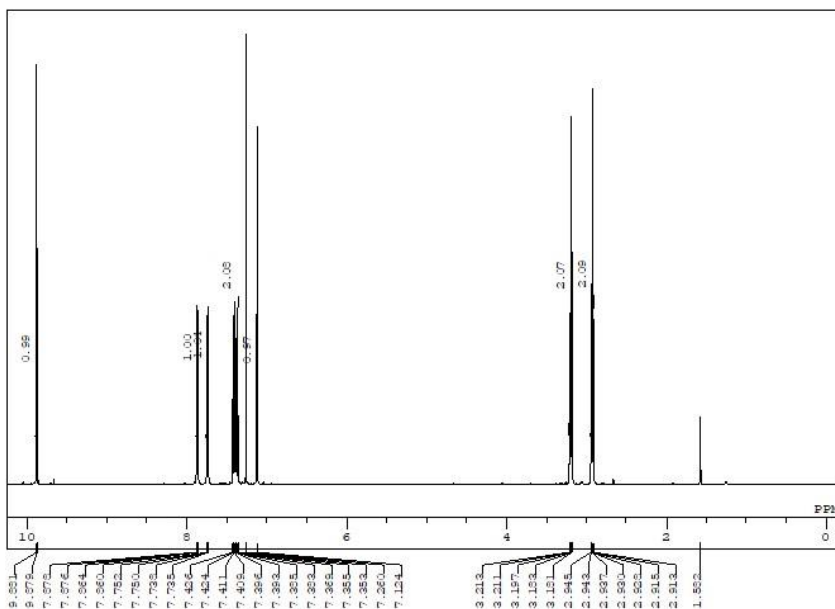
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COMNT single_pulse
DATIM 2018-02-27 15:25:26
OBNUC 1H
EXMOD proton.jsp
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 16384
FREQU 9384.38 Hz
SCANS 2
ACQTM 1.7455 sec
PD 5.0000 sec
PWL 6.85 usec
IRNUC 1H
CTEMP 12.9 c
SLVM CDCL3
EXREP 7.26 ppm
BF 0.10 Hz
RGAIN 40
  
```



```

DFFILE 3-5-B-aldehyde_carbon-1-1.als
COMNT single pulse decoupled gated MC
DATIM 2018-02-27 16:48:34
OBNUC 13C
EXMOD carbon.jsp
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 32767
FREQU 39308.18 Hz
SCANS 1024
ACQTM 0.8236 sec
PD 2.0000 sec
PWL 3.12 usec
IRNUC 1H
CTEMP 12.2 c
SLVM CDCL3
EXREP 77.00 ppm
BF 0.10 Hz
RGAIN 54
  
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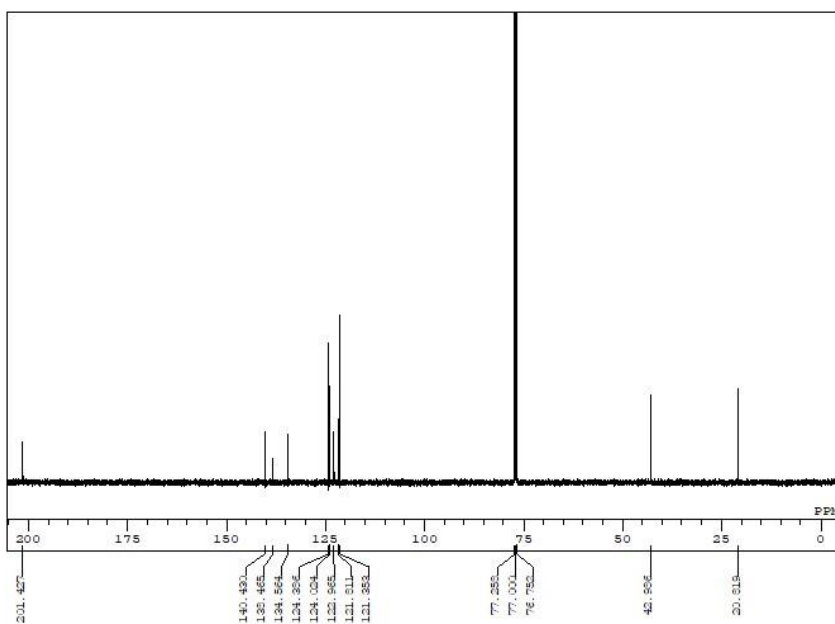
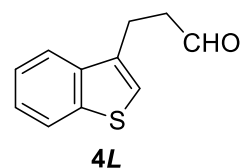




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D1FILE 3-S-L-aldehyde_proton-1-1.als
COMNT single_pulse
DATIM 2018-02-28 19:53:09
OBNUC 1H
EXMOD proton.jsp
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.51 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
FWL 6.85 usec
IRNUC 1H
CTEMP 12.4 c
SUNT CDCL3
EXREF 7.26 ppm
BF 0.10 Hz
RGAIN 42

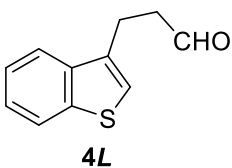
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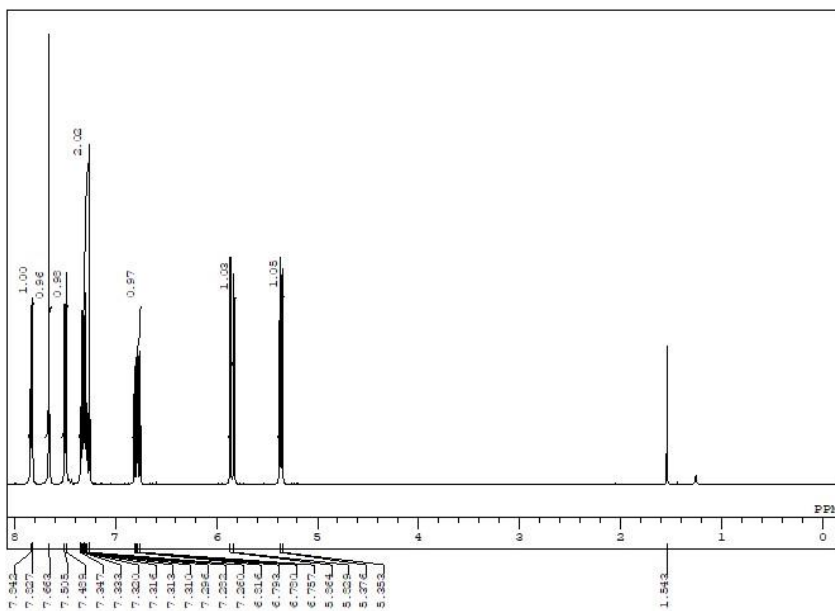


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D1FILE 3-S-L-aldehyde_carbon-1-1.als
COMNT single_pulse decoupled gated NC
DATIM 2018-02-28 21:18:54
OBNUC 13C
EXMOD carbon.jsp
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 32767
FREQU 39305.18 Hz
SCANS 1024
ACQTM 0.8226 sec
PD 2.0000 sec
FWL 3.12 usec
IRNUC 1H
CTEMP 12.8 c
SUNT CDCL3
EXREF 77.00 ppm
BF 0.10 Hz
RGAIN 56

```

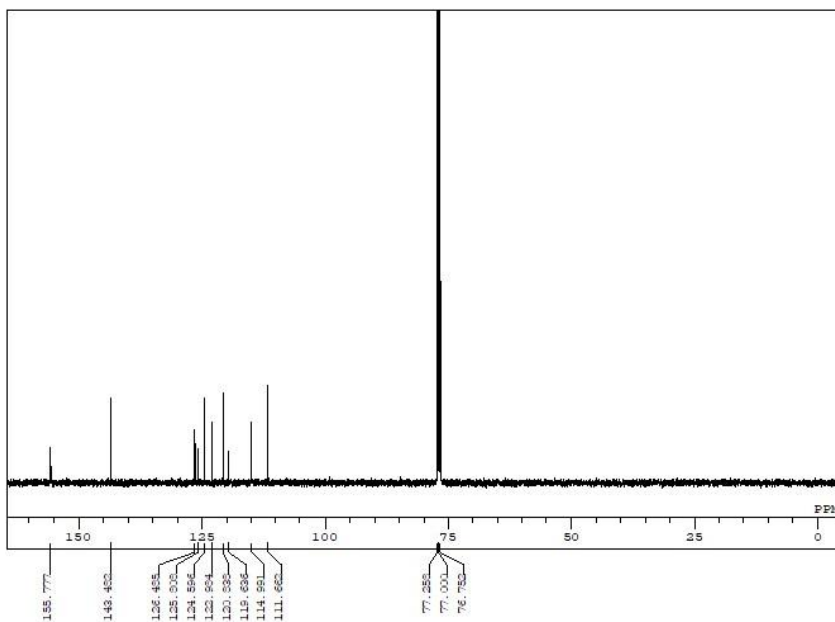
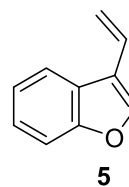




```

DFFILE 3-O-olefin_proton-1-1.als
COMNT single_pulse
DATIM 2018-07-26 16:44:10
OBNUC 1H
EXMOD proton.jsp
OBFRO 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 16394
FREQU 9384.38 Hz
SCANS 3
ACQTM 1.7459 sec
PD 5.0000 sec
FWL 6.85 usec
IRNUC 1H
CTEMP 19.9 c
SUNT CDCL3
EXREF 7.26 ppm
BF 1.20 Hz
RGAIN 46

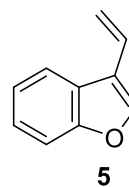
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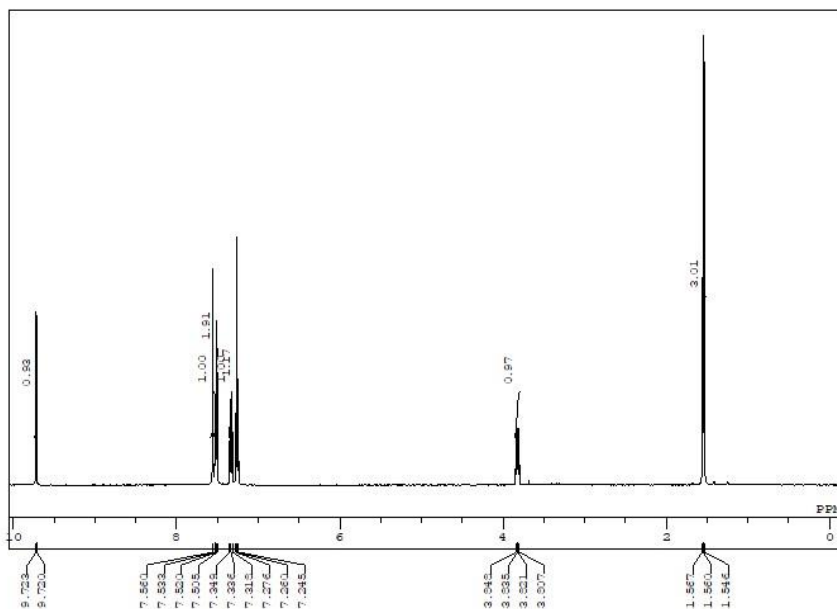


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DFFILE 3-O-olefin_carbon-1-1.als
COMNT single_pulse decoupled gated NC
DATIM 2018-07-26 16:46:15
OBNUC 13C
EXMOD carbon.jsp
OBFRO 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 32767
FREQU 39305.18 Hz
SCANS 1024
ACQTM 0.8236 sec
PD 2.0000 sec
FWL 3.12 usec
IRNUC 13C
CTEMP 20.2 c
SUNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 58

```

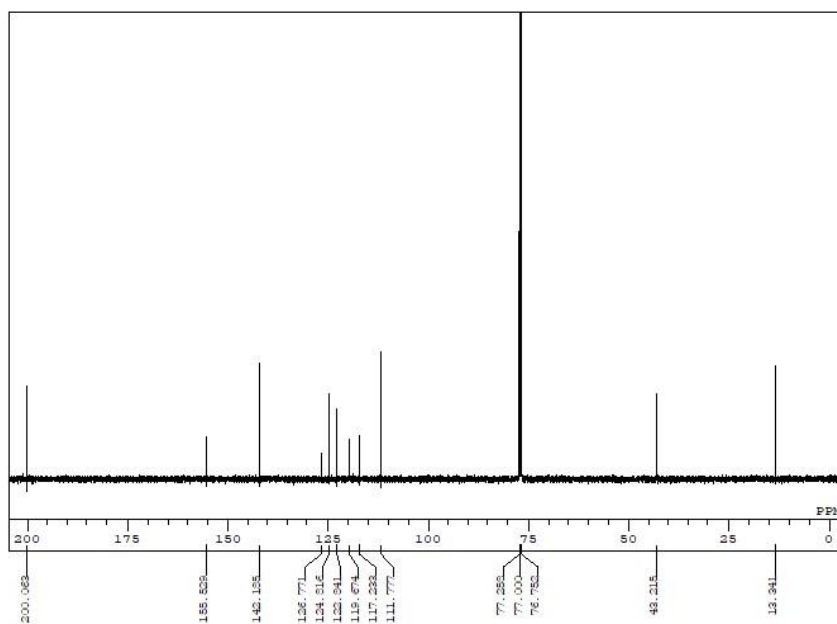
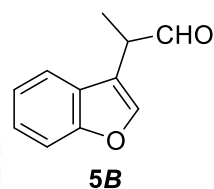




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D1FILE 3-O-B-aldehyde_proton-1-1.als
COMNT single_pulse
DATIM 2018-07-31 20:34:20
OBNUC 1H
EXMOD proton.jmp
OBFRO 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 16394
FREQU 9384.38 Hz
SCANS 3
ACQTM 1.7459 sec
PD 5.0000 sec
FWL 6.85 usec
IRNUC 1H
CTEMP 18.4 c
S1NT CDCL3
EXREF 7.26 ppm
BF 1.20 Hz
RGAIN 44

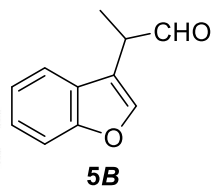
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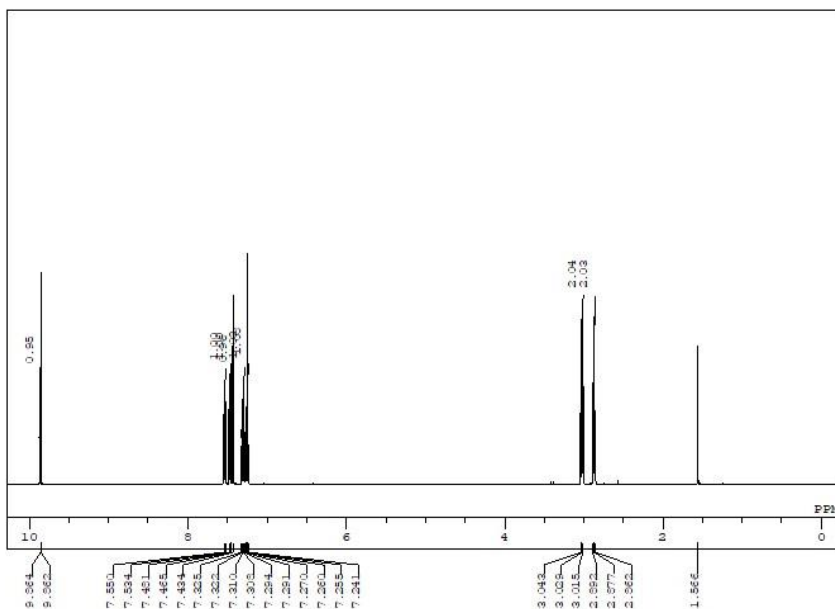


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D1FILE 3-O-B-aldehyde_carbon-1-1.als
COMNT single_pulse decoupled gated NC
DATIM 2018-07-31 22:23:46
OBNUC 13C
EXMOD carbon.jmp
OBFRO 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 32767
FREQU 39305.18 Hz
SCANS 1024
ACQTM 0.8236 sec
PD 2.0000 sec
FWL 3.12 usec
IRNUC 13C
CTEMP 18.7 c
S1NT CDCL3
EXREF 77.00 ppm
BF 0.10 Hz
RGAIN 58

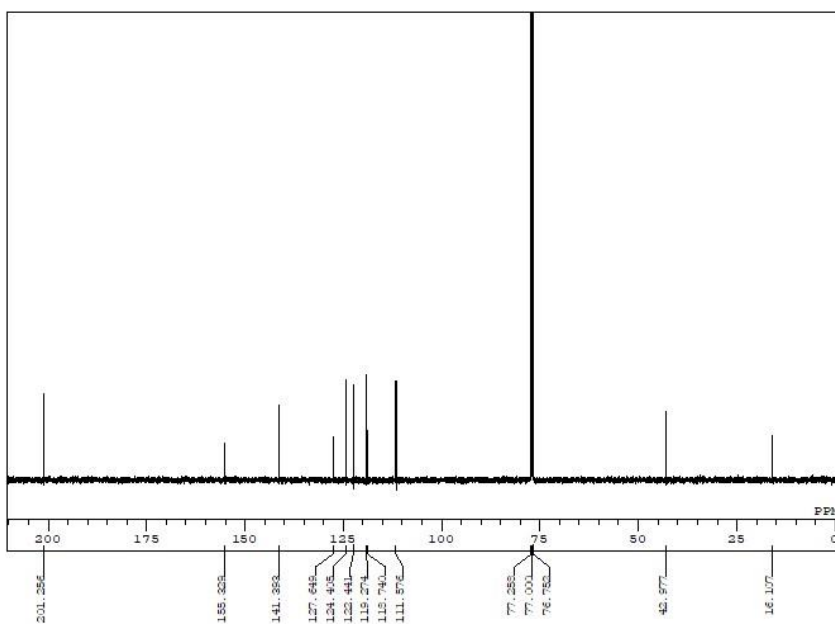
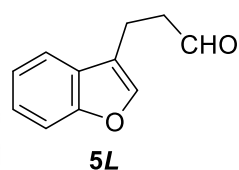
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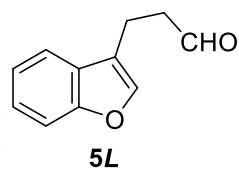
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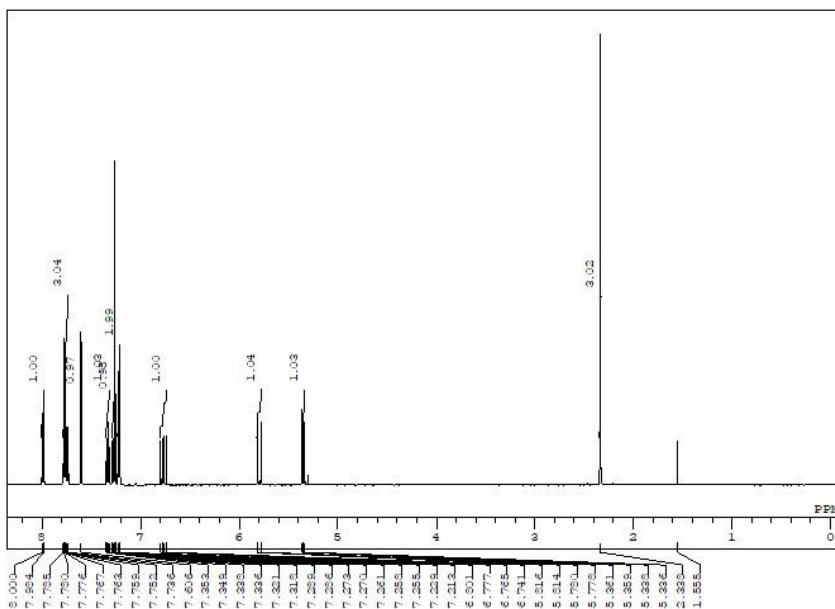
DFFILE 3-O-L-aldehyde_proton-1-1.als
COMNT single_pulse
DATIM 2018-08-01 16:18:12
OBNUC 1H
EXMOD proton.jsp
OBFRO 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 16384
FREQU 9384.38 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
FWL 6.85 usec
IRNUC 1H
CTEMP 19.1 c
SUNT CDCL3
EXREF 7.26 ppm
BF 0.10 Hz
RGAIN 44
  
```



```

DFFILE 3-O-L-aldehyde_carbon-1-1.als
COMNT single_pulse decoupled gated NC
DATIM 2018-08-01 16:20:52
OBNUC 13C
EXMOD carbon.jsp
OBFRO 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 32767
FREQU 39305.18 Hz
SCANS 1024
ACQTM 0.8226 sec
PD 2.0000 sec
FWL 3.12 usec
IRNUC 1H
CTEMP 19.4 c
SUNT CDCL3
EXREF 77.00 ppm
BF 0.10 Hz
RGAIN 56
  
```

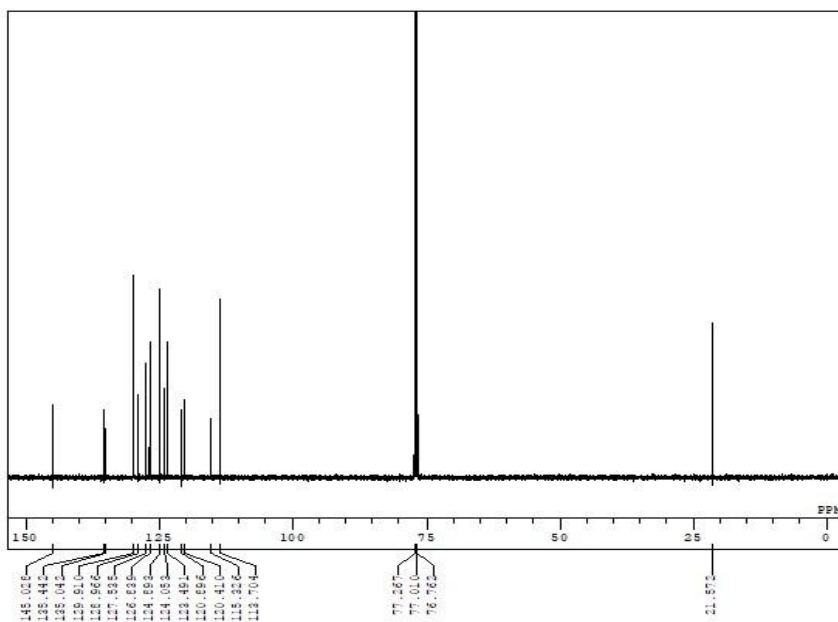
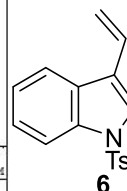




```

D1FILE 3-NtS-olefin_proton-1-1.als
COMNT single_pulse
DATIM 2017-11-15 20:27:31
OBNUC 1H
EXMOD proton.jsp
OBFRO 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.51 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PWL 6.85 usec
IRNUC 1H
CTEMP 17.3 c
S1VNT CDCL3
EXREF 7.26 ppm
BF 0.10 Hz
RGAIN 44

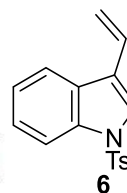
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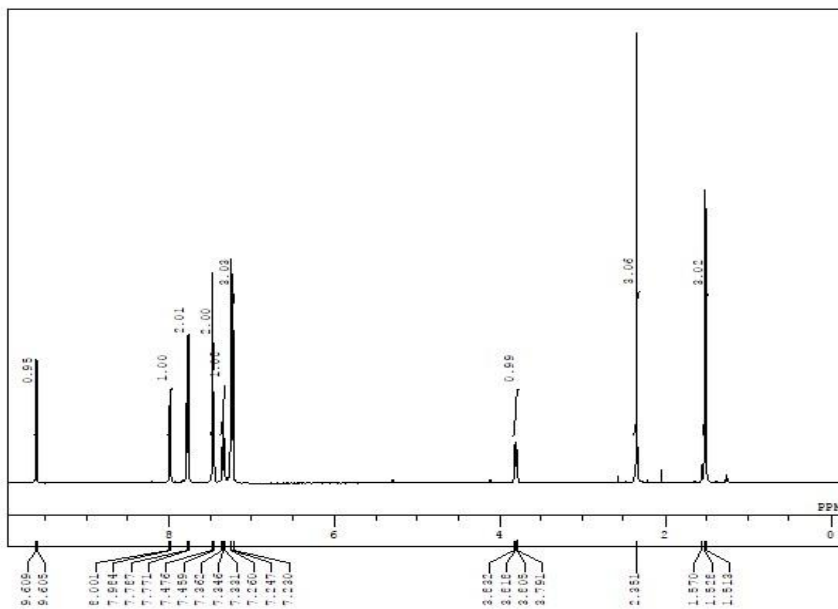


```

D1FILE 3-NtS-olefin_carbon-1-1.als
COMNT single_pulse decoupled gated MC
DATIM 2017-11-15 20:27:46
OBNUC 13C
EXMOD carbon.jsp
OBFRO 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.54 Hz
SCANS 1024
ACQTM 0.8236 sec
PD 2.0000 sec
PWL 3.12 usec
IRNUC 1H
CTEMP 18.0 c
S1VNT CDCL3
EXREF 77.00 ppm
BF 0.10 Hz
RGAIN 60

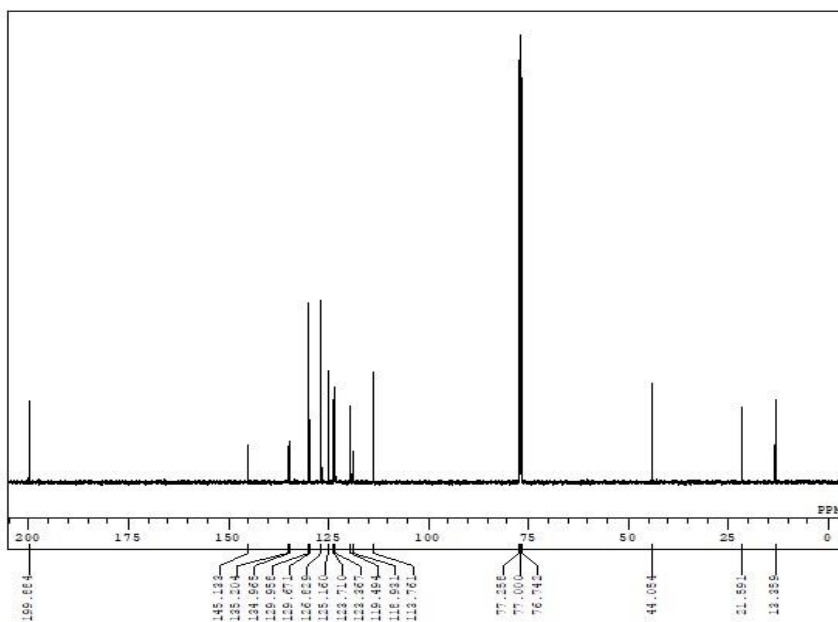
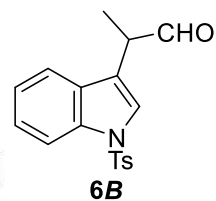
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```

D1FILE 3-NTs-B-aldehyde_proton-1-1.sls
COMNT single_pulse
DATIM 2017-11-27 11:57:53
OBNUC 1H
EXMOD proton.jsp
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 16384
FREQU 9384.38 Hz
SCANS 2
ACQTM 1.7455 sec
PD 5.0000 sec
PWL 6.85 usec
IRNUC 1H
CTEMP 16.9 c
S1VFI CDCL3
EXREP 7.26 ppm
BF 1.20 Hz
RGAIN 44
  
```



```

D1FILE 3-NTs-B-aldehyde_carbon-1-1.sls
COMNT single_pulse decoupled gated NC
DATIM 2017-11-27 16:47:43
OBNUC 13C
EXMOD carbon.jsp
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.54 Hz
SCANS 1024
ACQTM 0.8236 sec
PD 2.0000 sec
PWL 3.12 usec
IRNUC 1H
CTEMP 14.7 c
S1VFI CDCL3
EXREP 77.00 ppm
BF 1.20 Hz
RGAIN 60
  
```

