

Supporting Information

Solvent-Free Methallylboration of Ketones Accelerated by *tert*-Alcohols

Yongda Zhang,* Ning Li, Navneet Goyal, Guisheng Li, Heewon Lee, Bruce Z. Lu, Chris H. Senanayake

*Chemical Development, Boehringer Ingelheim Pharmaceutical, Inc.
900 Ridgebury Road, Ridgefield, CT 06877*

E-mail: yongda.zhang@boehringer-ingelheim.com

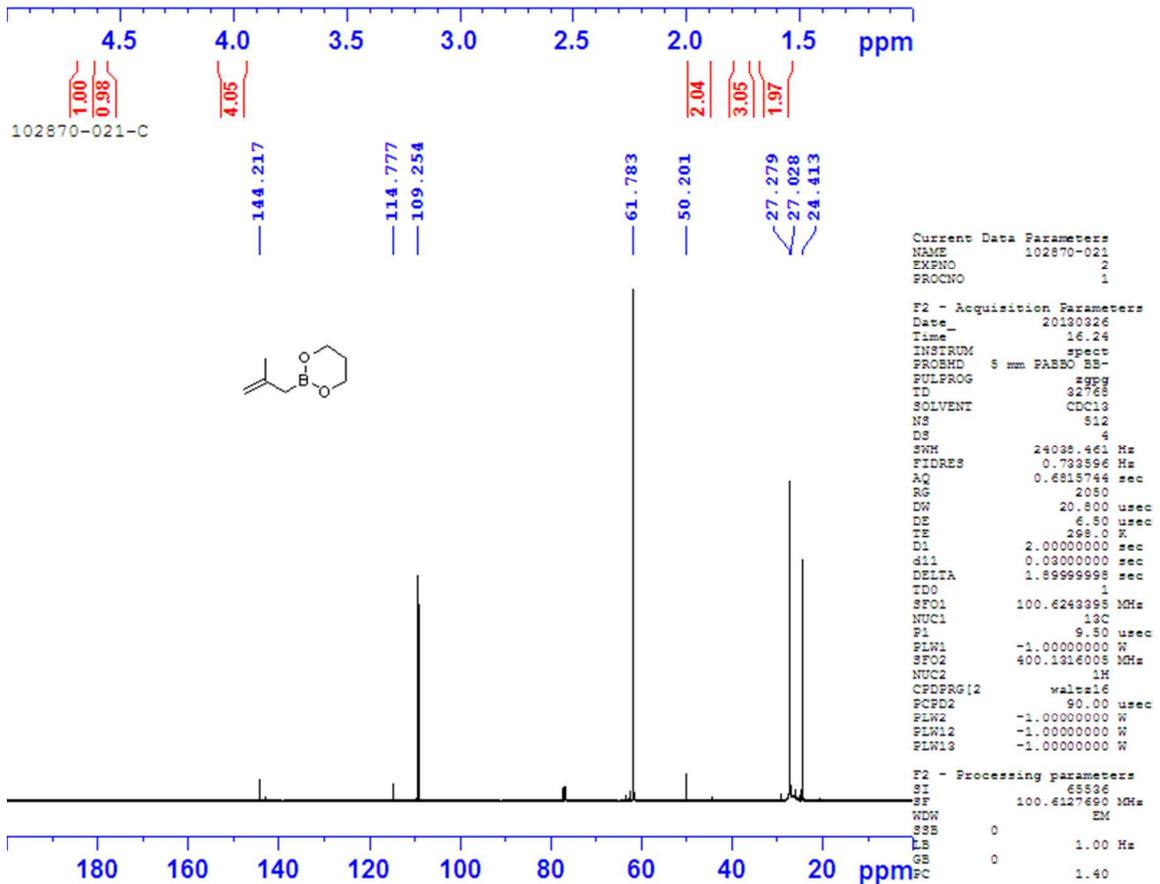
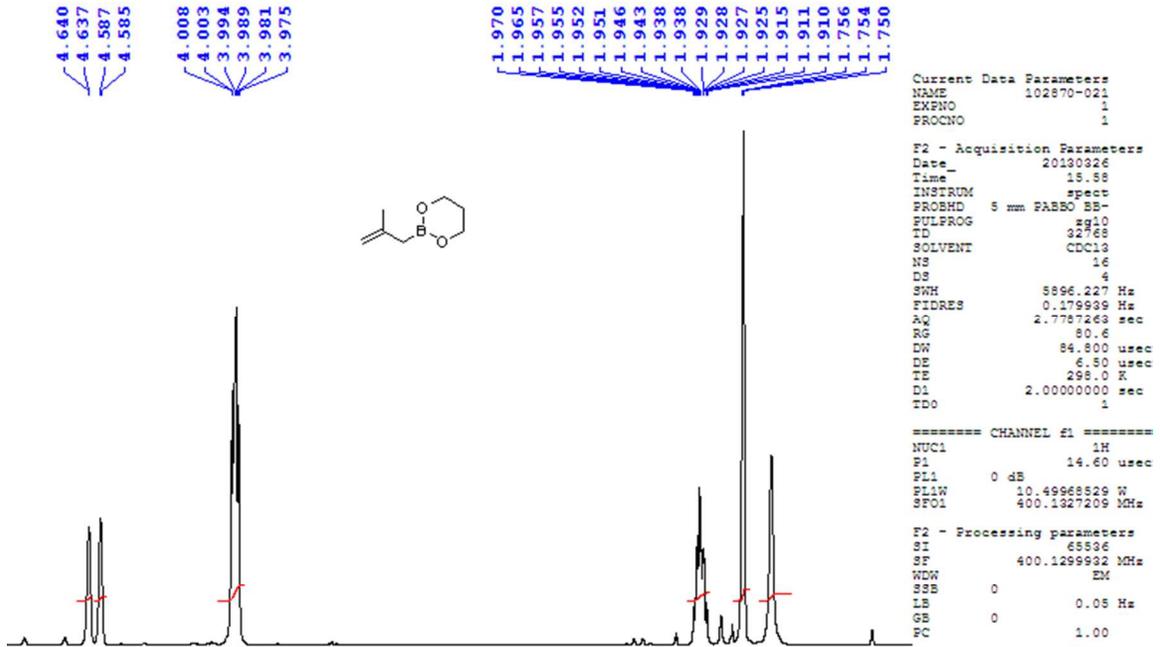
- I. General Methods (page SI-1)
- II. ¹H-NMR and ¹³C NMR of key new compounds (page SI-2)

General Methods. All reactions were carried out under an atmosphere of nitrogen in dry glassware with magnetic stirring. Commercially available Mg turning, ketones, anhydrous THF and alcohols are received and used without any further purification. Column chromatography was performed on silica gel 60 (230-400 mesh). Thin layer chromatography was performed on 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light, KMnO₄, aqueous ceric ammonium molybdate, or bromocresol green dips followed by heating.

¹H NMR and spectra were recorded at ambient temperature. Data are reported as follows: chemical shift in parts per million (δ , ppm) from an internal standard [tetramethylsilane (TMS) or deuterated chloroform (CDCl₃)], multiplicity (s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet), integration, and coupling constant (Hz). ¹³C NMR and spectra were recorded at ambient temperature. Chemical shifts are reported in ppm from CDCl₃ taken as 77.0 ppm.

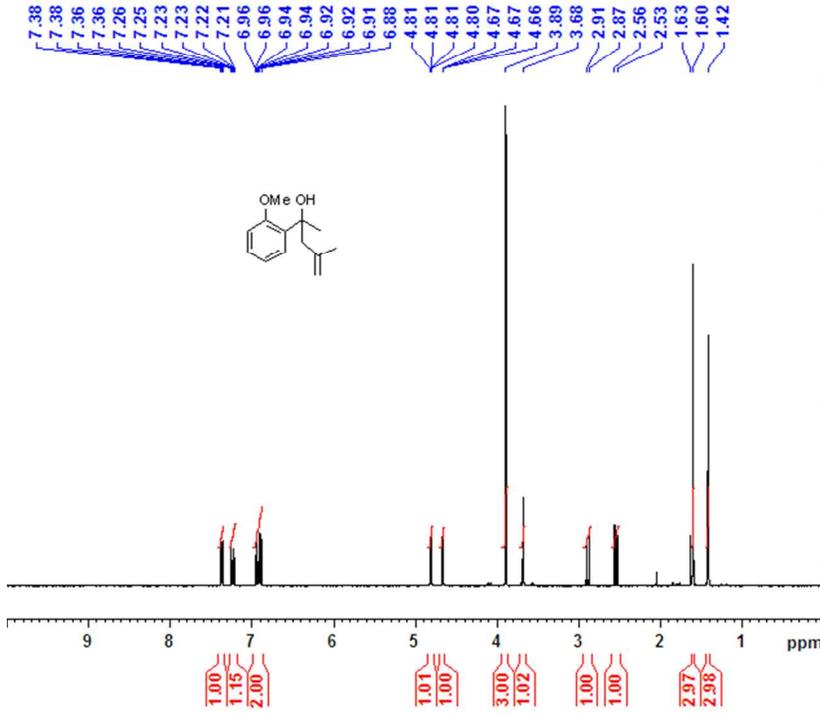
2-(2-Methylallyl)-1,3,2-dioxaborinane 1

102870-021



2-(2-Methoxyphenyl)-4-methylpent-4-en-2-ol 3

102478-043-H



```

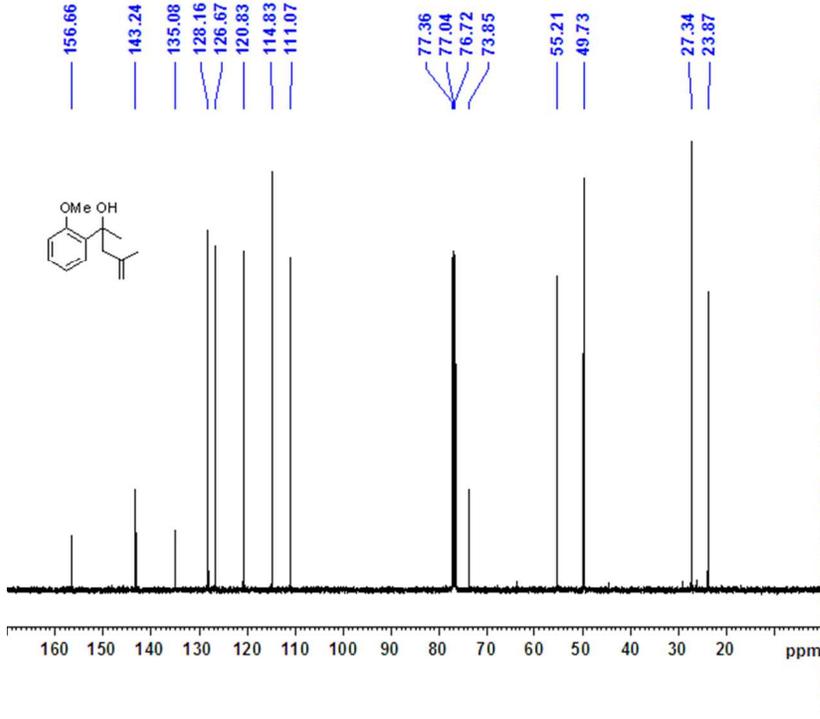
Current Data Parameters
NAME      102327-043
EXPNO    1
PROCNO   1

F2 - Acquisition Parameters
Date_    20111208
Time     18.37
INSTRUM  spect
PROBHD   5 mm PABBO BB-
PULPROG  zg30
TD        32768
SOLVENT  CDCl3
NS        16
DS        4
SWH       8896.227 Hz
FIDRES   0.178939 Hz
AQ        2.7787764 sec
RG        362
DW        84.800 usec
DE        6.50 usec
TE        298.0 K
D1        2.00000000 sec
TDO       1

===== CHANNEL f1 =====
NUC1      1H
P1        14.00 usec
PL1       0.00 dB
PL1W      10.49968829 W
SFO1      400.1327209 MHz

F2 - Processing parameters
SI        65536
SF        400.1300118 MHz
WDW       EM
SSB       0
LB        0.05 Hz
GB        0
FC        1.00
    
```

102327-043



```

Current Data Parameters
NAME      102327-043
EXPNO    2
PROCNO   1

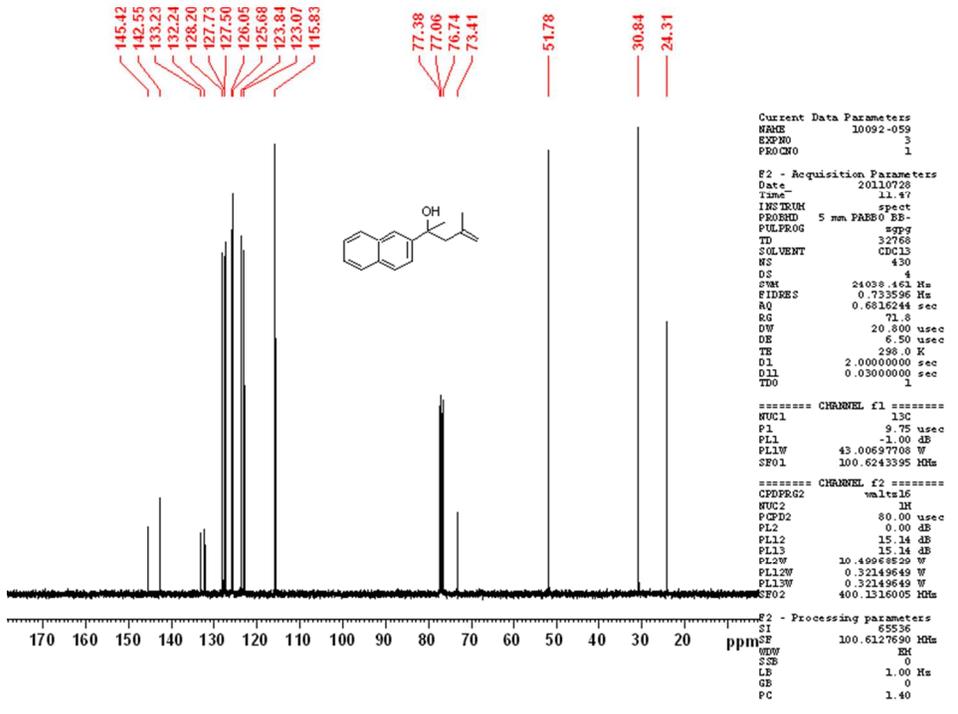
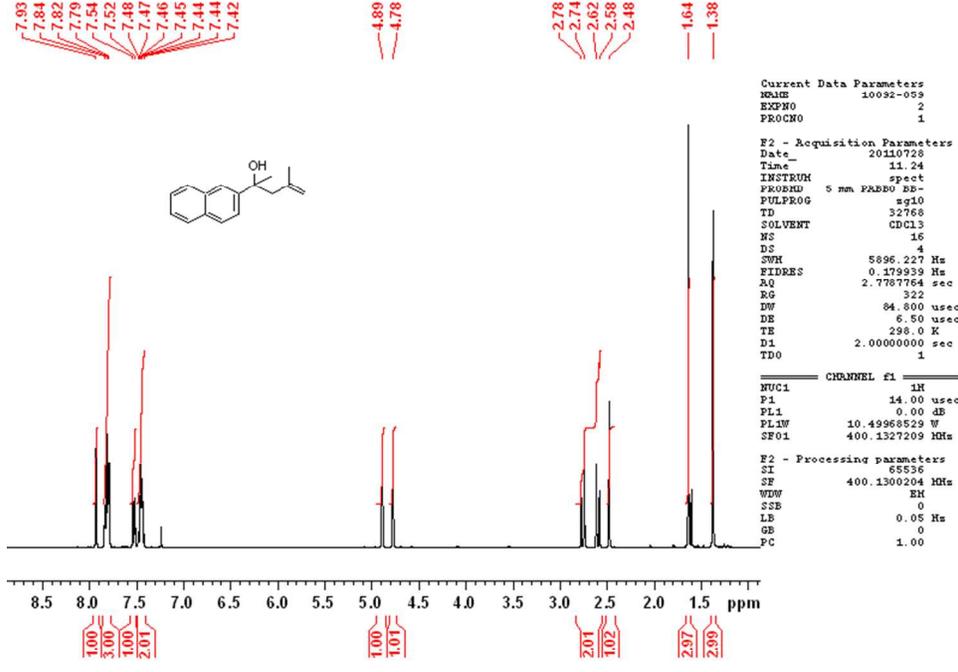
F2 - Acquisition Parameters
Date_    20111208
Time     18.48
INSTRUM  spect
PROBHD   5 mm PABBO BB-
PULPROG  zgpg3
TD        32768
SOLVENT  CDCl3
NS        1024
DS        4
SWH       24028.461 Hz
FIDRES   0.782896 Hz
AQ        0.6816244 sec
RG        1030
DW        20.800 usec
DE        6.50 usec
TE        298.0 K
D1        2.00000000 sec
D11       0.00000000 sec
TDO       1

===== CHANNEL f1 =====
NUC1      13C
P1        9.78 usec
PL1       -1.00 dB
PL1W      48.00697708 W
SFO1      100.6242285 MHz

===== CHANNEL f2 =====
CDEPRG2  waltz16
NUC2      1H
PCPD2    80.00 usec
PL2       0.00 dB
PL12     18.14 dB
PL13     18.14 dB
PL2W     10.49968829 W
PL12W    0.32149649 W
PL13W    0.32149649 W
SFO2     400.1316005 MHz

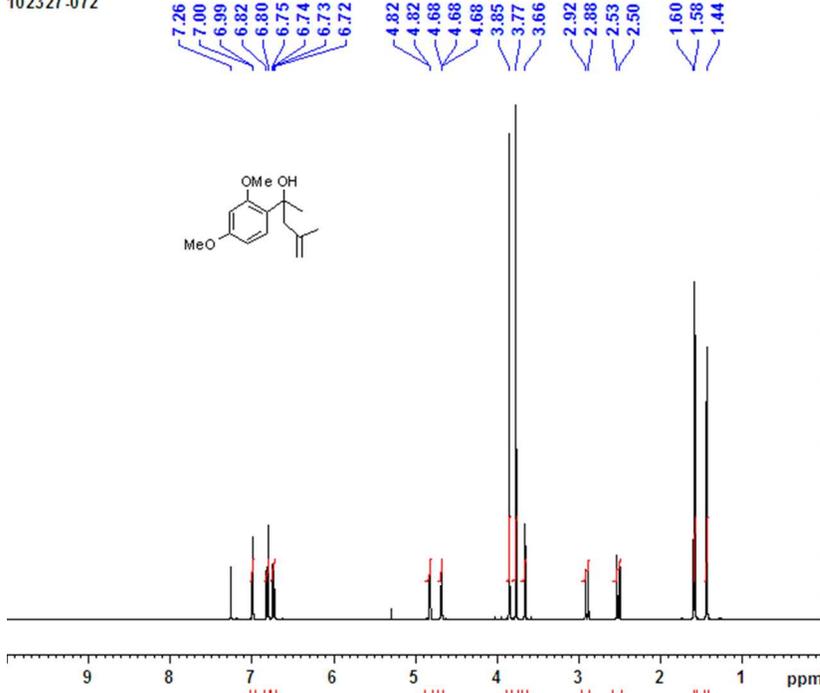
F2 - Processing parameters
SI        65536
SF        100.6127690 MHz
WDW       EM
SSB       0
LB        1.00 Hz
GB        0
FC        1.40
    
```

4-Methyl-2-(naphthalen-2-yl)pent-4-en-2-ol 5



2-(2,5-Dimethoxyphenyl)-4-methylpent-4-en-2-ol 7

102327-072



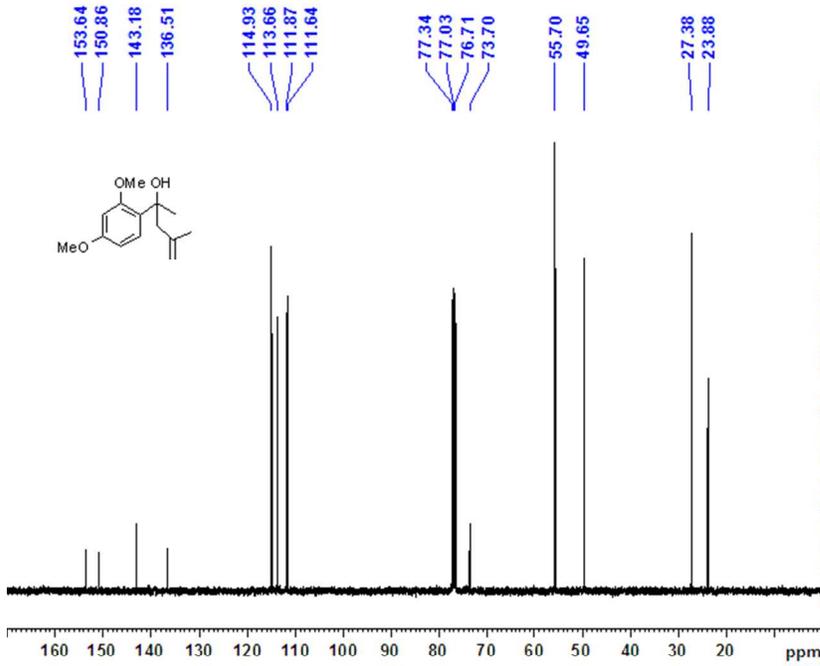
```
Current Data Parameters
NAME      102327-072
EXPNO    1
PROCNO   1

F2 - Acquisition Parameters
Date_    20111208
Time     19.34
INSTRUM  spect
PROBHD   5 mm PABBO BB-
PULPROG  zg10
TD        32768
SOLVENT  CDCl3
NS        16
DS        4
SWH       5896.227 Hz
FIDRES   0.179999 Hz
AQ        2.7787764 sec
RG        512
DM        84.800 usec
DE        6.50 usec
TE        298.0 K
D1        2.00000000 sec
TD0       1

===== CHANNEL f1 =====
NUC1      1H
P1        14.00 usec
PL1       0.00 dB
PL1W      10.49865329 W
SFO1      400.1327209 MHz

F2 - Processing parameters
SI        65536
SF        400.1300103 MHz
WDW       EM
SSB       0
LB        0.06 Hz
GB        0
PC        1.00
```

102327-072-product



```
Current Data Parameters
NAME      102327-072
EXPNO    2
PROCNO   1

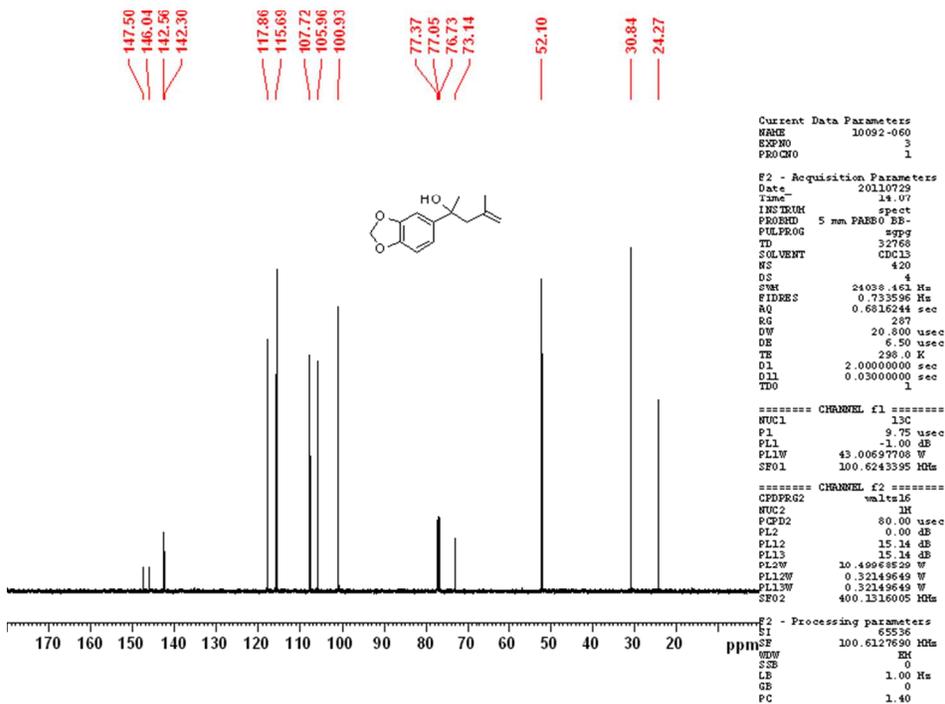
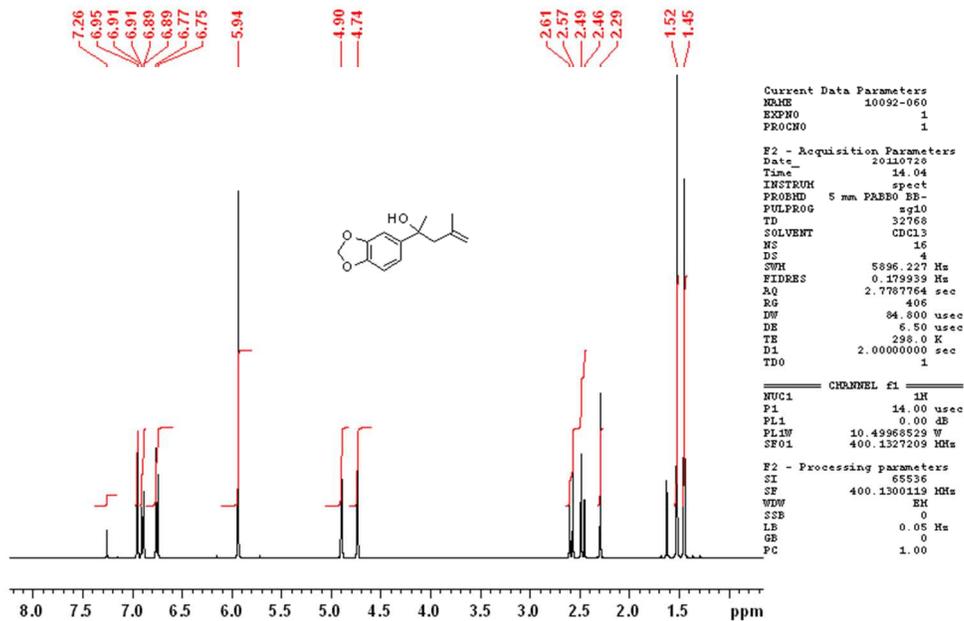
F2 - Acquisition Parameters
Date_    20111208
Time     20.22
INSTRUM  spect
PROBHD   5 mm PABBO BB-
PULPROG  zgpg
TD        32768
SOLVENT  CDCl3
NS        1024
DS        4
SWH       2408.461 Hz
FIDRES   0.732856 Hz
AQ        0.6816244 sec
RG        256
DM        20.500 usec
DE        6.50 usec
TE        298.0 K
D1        2.00000000 sec
D11       0.03000000 sec
TD0       1

===== CHANNEL f1 =====
NUC1      13C
P1        9.78 usec
PL1       -1.00 dB
PL1W      43.00697708 W
SFO1      100.6248888 MHz

===== CHANNEL f2 =====
CFDPRG2  waltz16
NUC2      1H
PCPD2     80.00 usec
PL2       0.00 dB
PL12      15.14 dB
PL13      15.14 dB
PL1W      10.49865329 W
PL12W     0.32149649 W
PL13W     0.32149649 W
SFO2      400.1316005 MHz

F2 - Processing parameters
SI        65536
SF        100.6127690 MHz
WDW       EM
SSB       0
LB        1.00 Hz
GB        0
PC        1.40
```

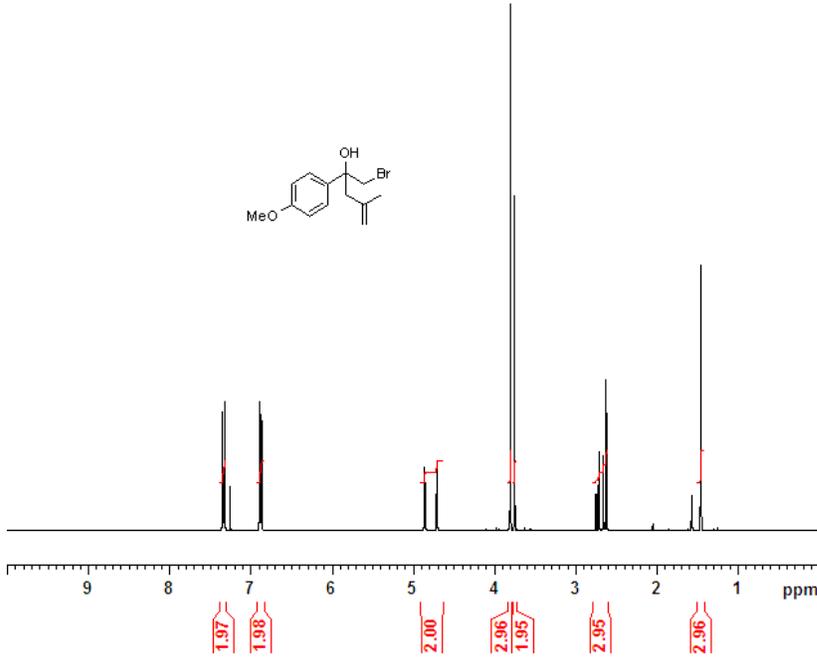
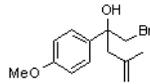
2-(Benzo[d][1,3]dioxol-5-yl)-4-methylpent-4-en-2-ol 9



1-Bromo-2-(4-methoxyphenyl)-4-methylpent-4-en-2-ol 11

102464-052

7.35
7.35
7.33
7.33
7.26
6.89
6.89
6.88
6.87
4.87
4.86
4.86
4.86
4.71
3.81
3.76
2.75
2.72
2.66
2.63
1.57
1.46



```
Current Data Parameters
NAME      102464-052
EXPNO     1
PROCNO    1

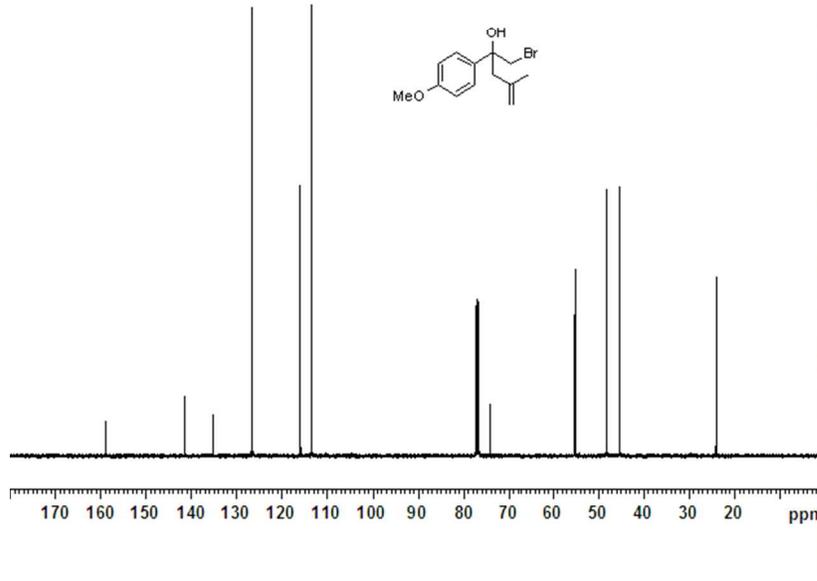
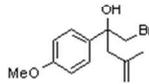
F2 - Acquisition Parameters
Date_     20111220
Time      14.27
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zg10
TD         32768
SOLVENT   CDCl3
NS         16
DS         4
SWH       5896.227 Hz
FIDRES    0.179939 Hz
AQ         2.7787764 sec
RG         406
RW         84.800 usec
DE         6.50 usec
TE         298.0 K
D1         2.0000000 sec
TD0        1

===== CHANNEL f1 =====
NUC1       1H
P1         14.00 usec
PL1        0.00 dB
PL1W       10.4996529 W
SFO1       400.1327209 MHz

F2 - Processing parameters
SI         65536
SF         400.1300110 MHz
WDW        EM
SSB        0
LB         0.05 Hz
GB         0
PC         1.00
```

102464-052

158.83
141.52
135.21
126.68
116.05
113.57
77.34
77.03
76.71
74.26
55.22
48.20
45.34
24.11



```
Current Data Parameters
NAME      102464-052
EXPNO     3
PROCNO    1

F2 - Acquisition Parameters
Date_     20111220
Time      22.17
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zgpg
TD         32768
SOLVENT   CDCl3
NS         2048
DS         4
SWH       24028.461 Hz
FIDRES    0.763596 Hz
AQ         0.6816244 sec
RG         256
RW         20.800 usec
DE         6.50 usec
TE         298.0 K
D1         2.0000000 sec
D11        0.0300000 sec
TD0        1

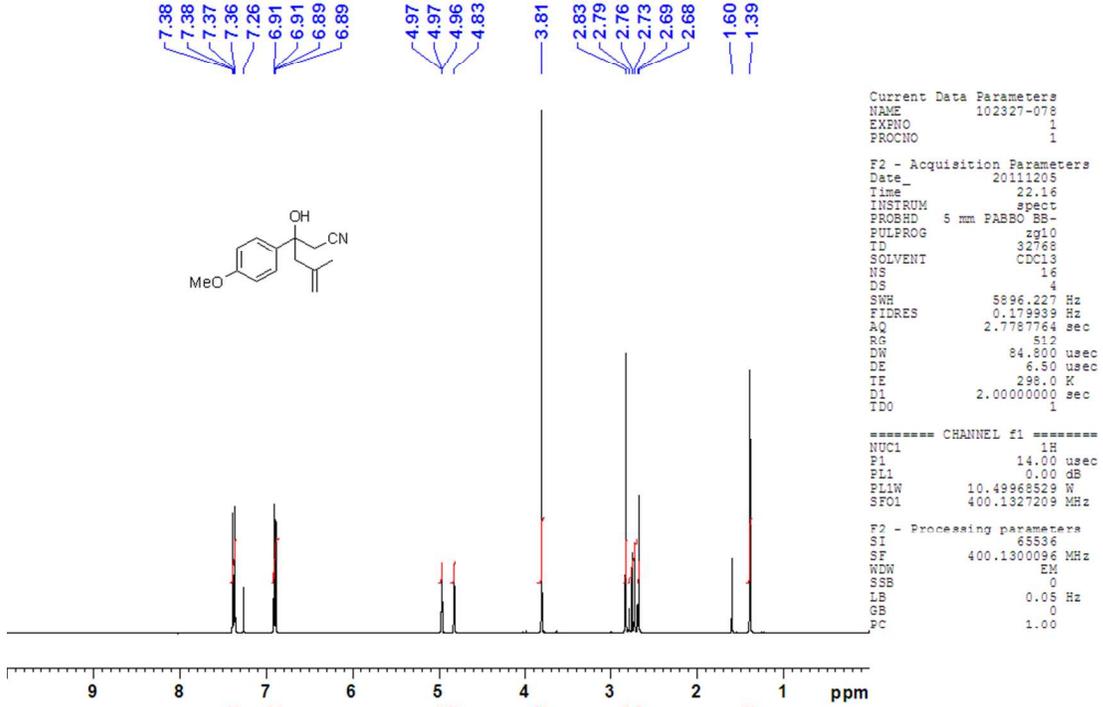
===== CHANNEL f1 =====
NUC1       13C
P1         9.75 usec
PL1        -1.00 dB
PL1W       42.00687708 W
SFO1       100.6242298 MHz

===== CHANNEL f2 =====
CQDPRG2    waltz16
NUC2       1H
PCPD2      80.00 usec
PL2        0.00 dB
PL12       18.14 dB
PL13       18.14 dB
PL2W       10.4996529 W
PL12W      0.32149649 W
PL13W      0.32149649 W
SFO2       400.1316008 MHz

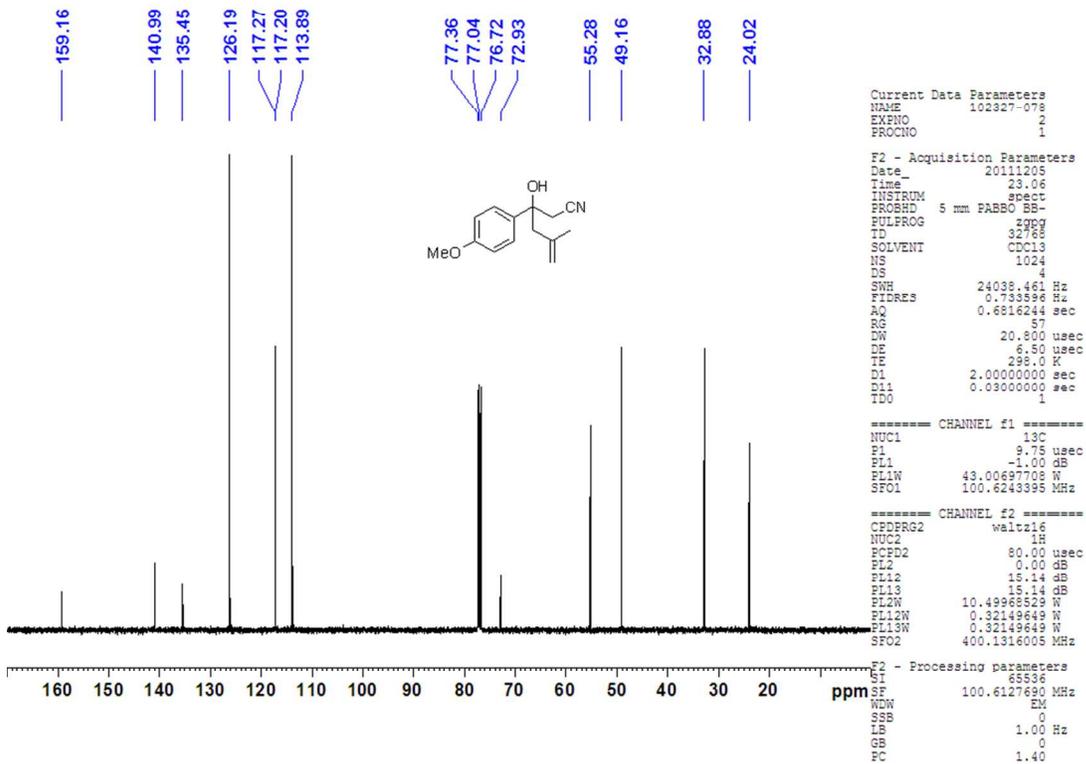
F2 - Processing parameters
SI         65536
SF         100.6127680 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
```

3-Hydroxy-3-(4-methoxyphenyl)-5-methylhex-5-enitrile13

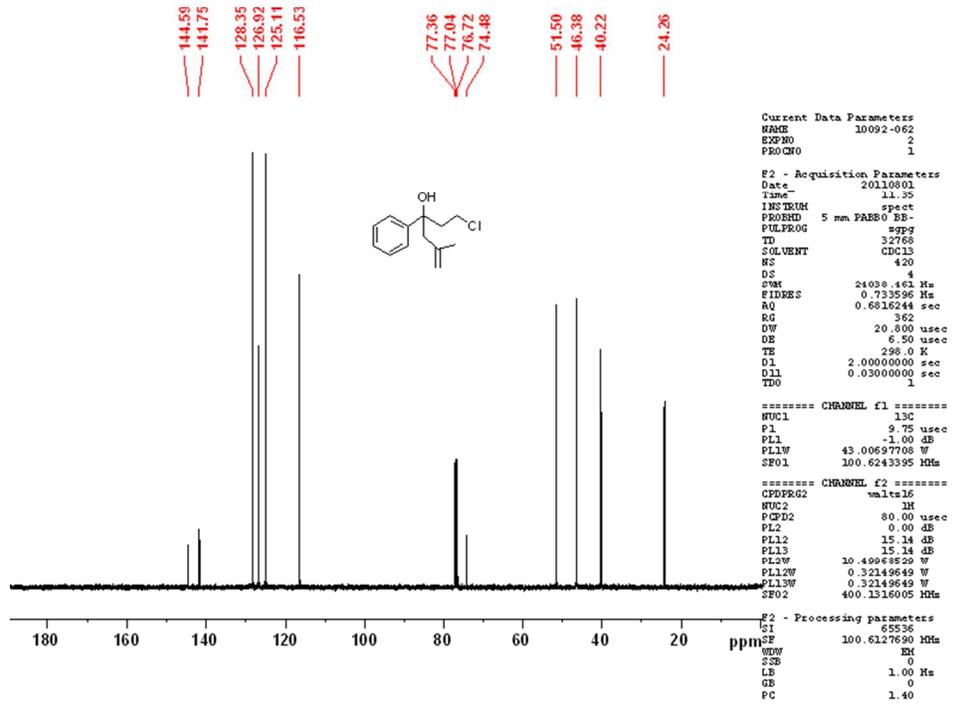
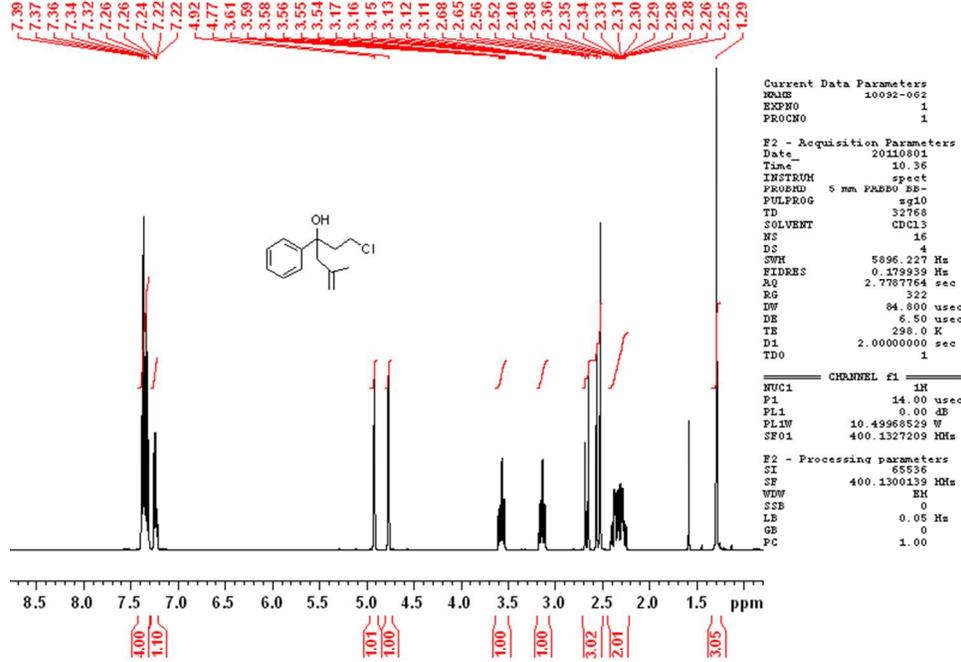
102327-078-product



102327-078-product

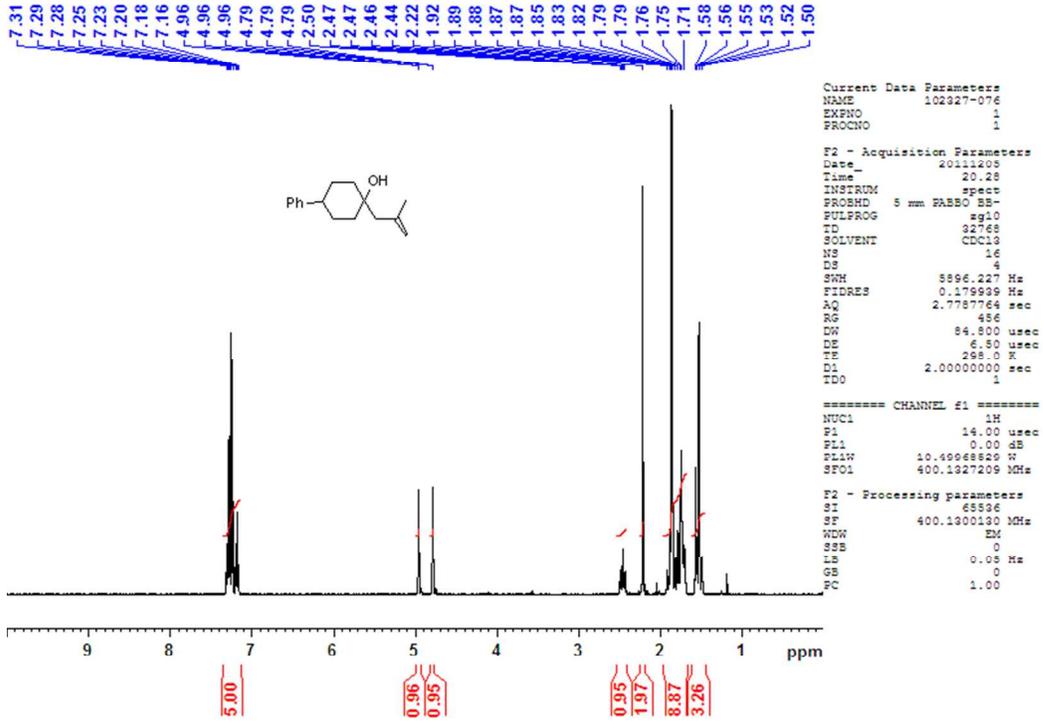


1-Chloro-5-methyl-3-phenylhex-5-en-3-ol 15

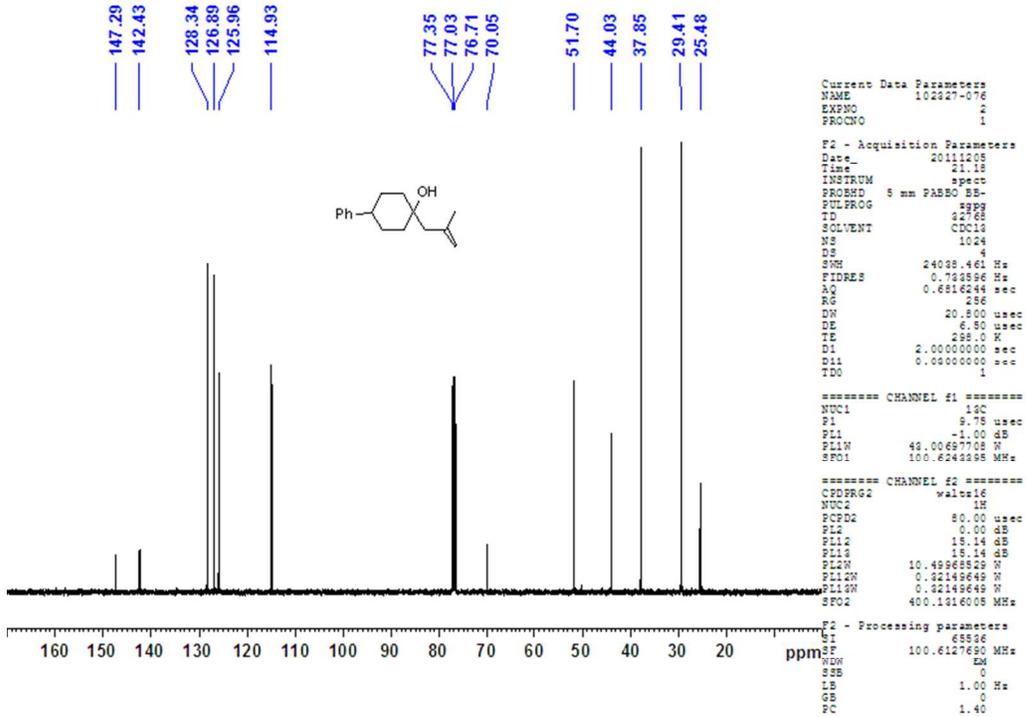


1-(2-Methylallyl)-4-phenylcyclohexanol 17

102327-076-product

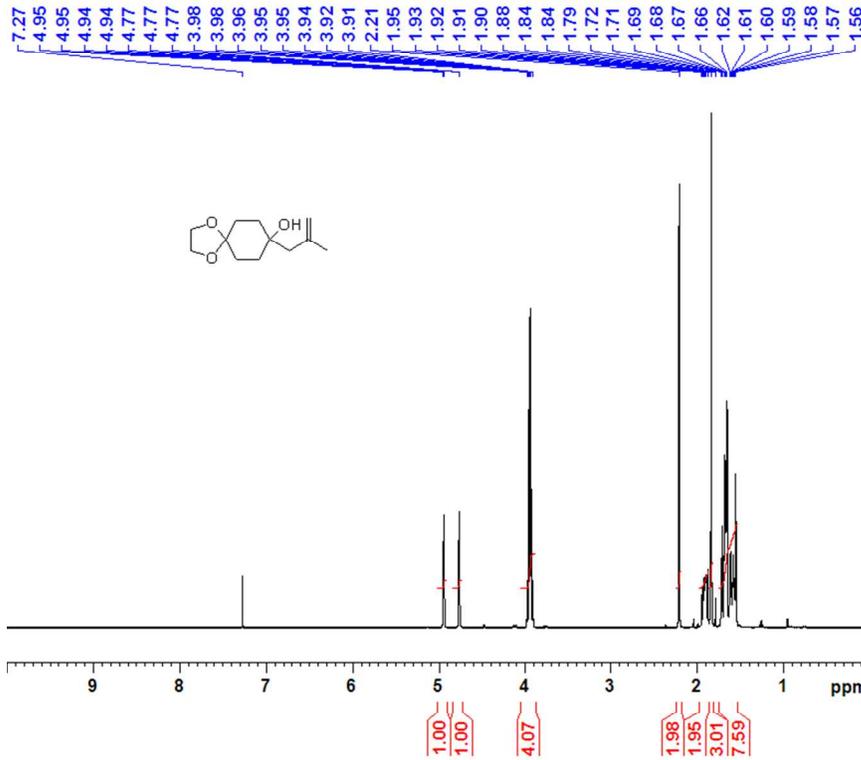


102727-076-product

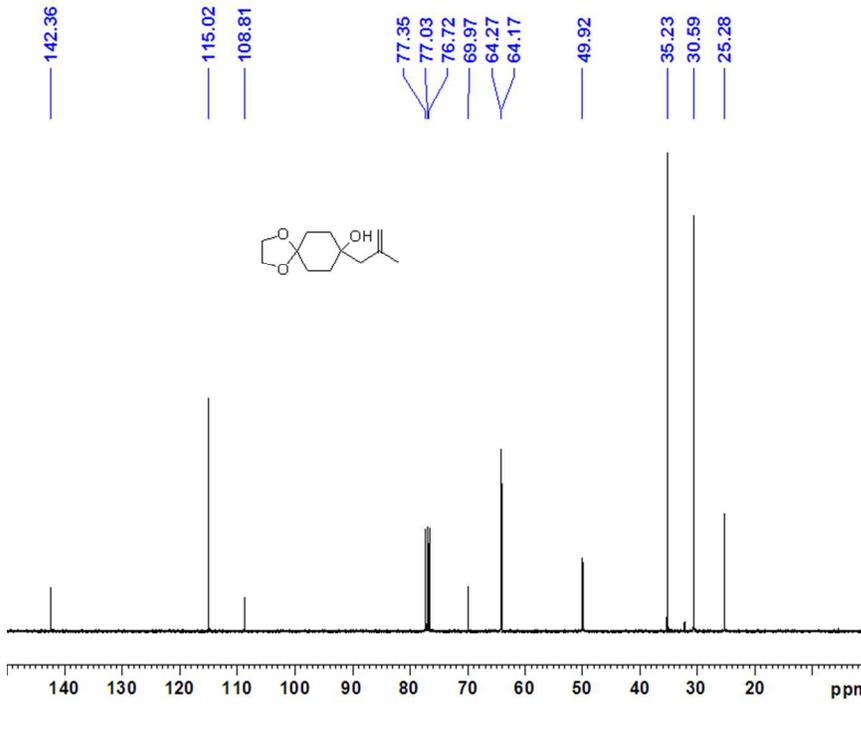


8-(2-Methylallyl)-1,4-dioxaspiro[4.5]decan-8-ol 19

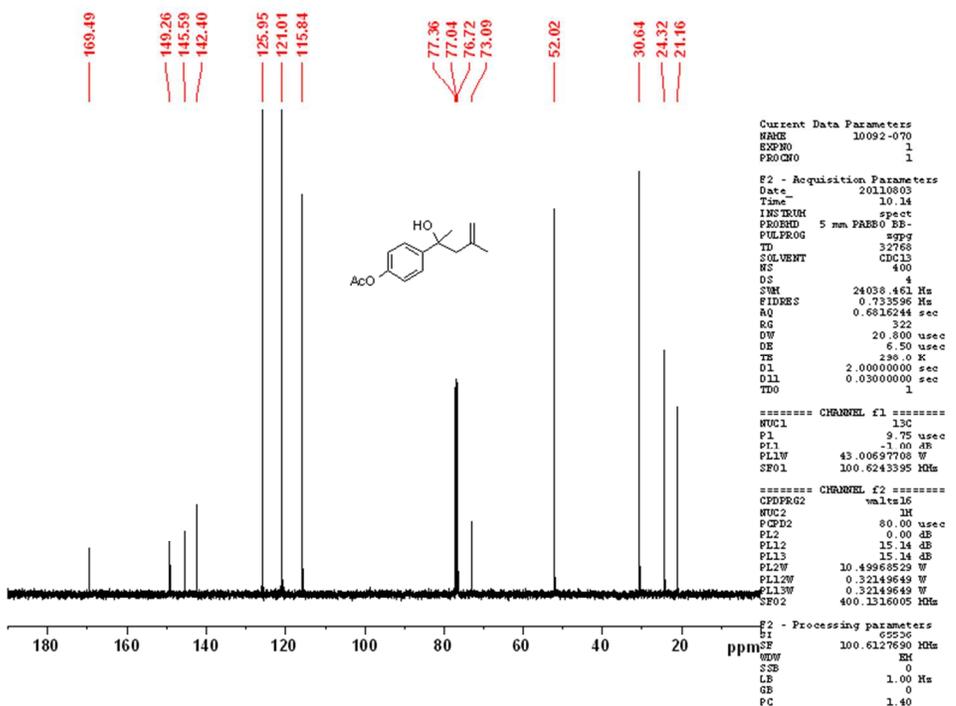
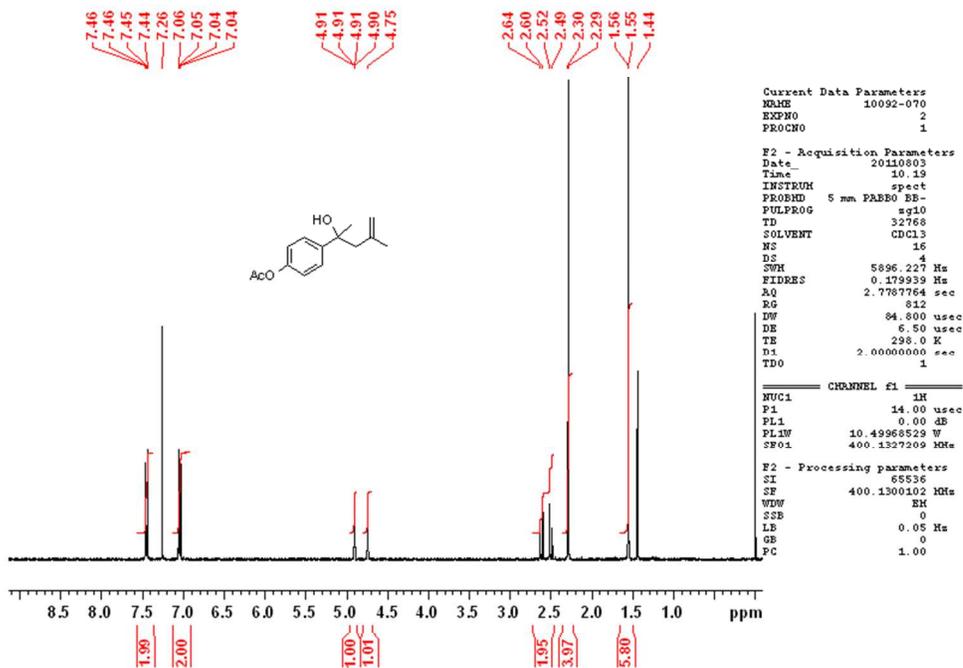
102327-077-product



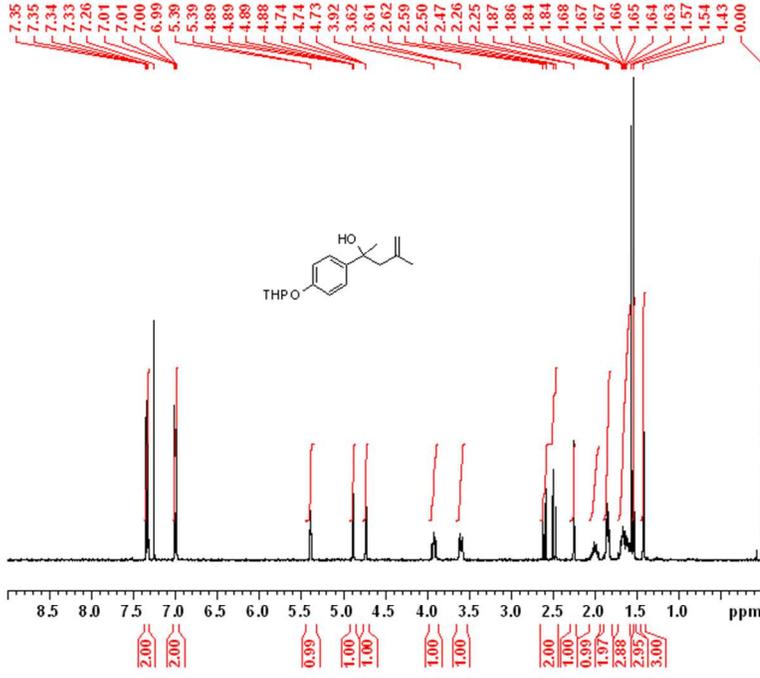
102327-077-product



4-(2-Hydroxy-4-methylpent-4-en-2-yl)phenyl acetate 21



4-Methyl-2-(4-(tetrahydro-2H-pyran-2-yloxy)phenyl)pent-4-en-2-ol 23



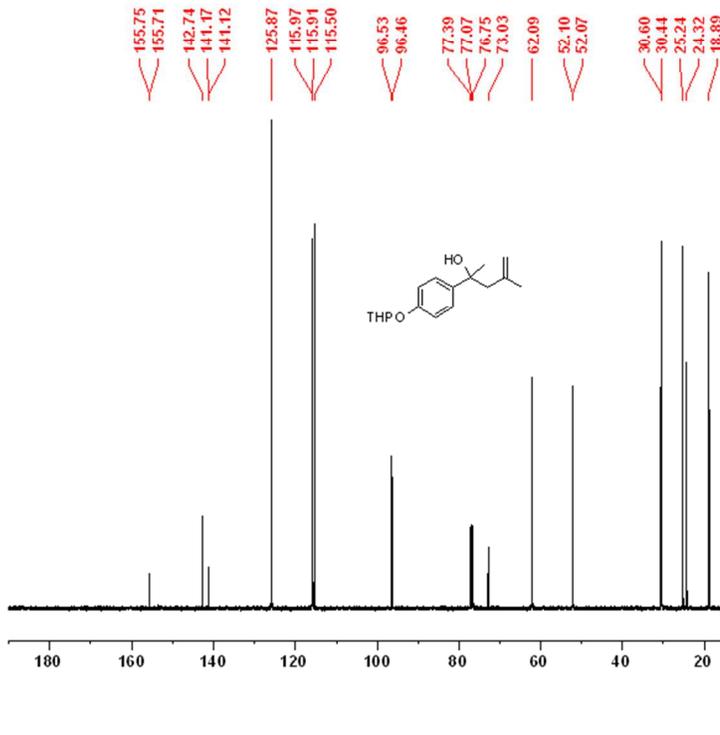
```

Current Data Parameters
NAME      10092-069
EXPNO     3
PROCNO    1

F2 - Acquisition Parameters
Date_     20110803
Time      11.08
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   sg10
TD         32768
SOLVENT   CDCl3
NS         16
DS         4
SWH        5896.227 Hz
FIDRES     0.179939 Hz
AQ         2.7767764 sec
RG         645
DW         84.800 usec
DE         6.50 usec
TE         298.0 K
D1         2.00000000 sec
TD0        1

===== CHANNEL f1 =====
NUC1       1H
P1         14.00 usec
PL1        0.00 dB
PL1W       10.49968529 W
SF01       400.1327209 MHz

F2 - Processing parameters
SI         65536
SF         400.1300103 MHz
WDW        EM
SSB        0
LB         0.05 Hz
GB         0
PC         1.00
    
```



```

Current Data Parameters
NAME      10092-069
EXPNO     4
PROCNO    1

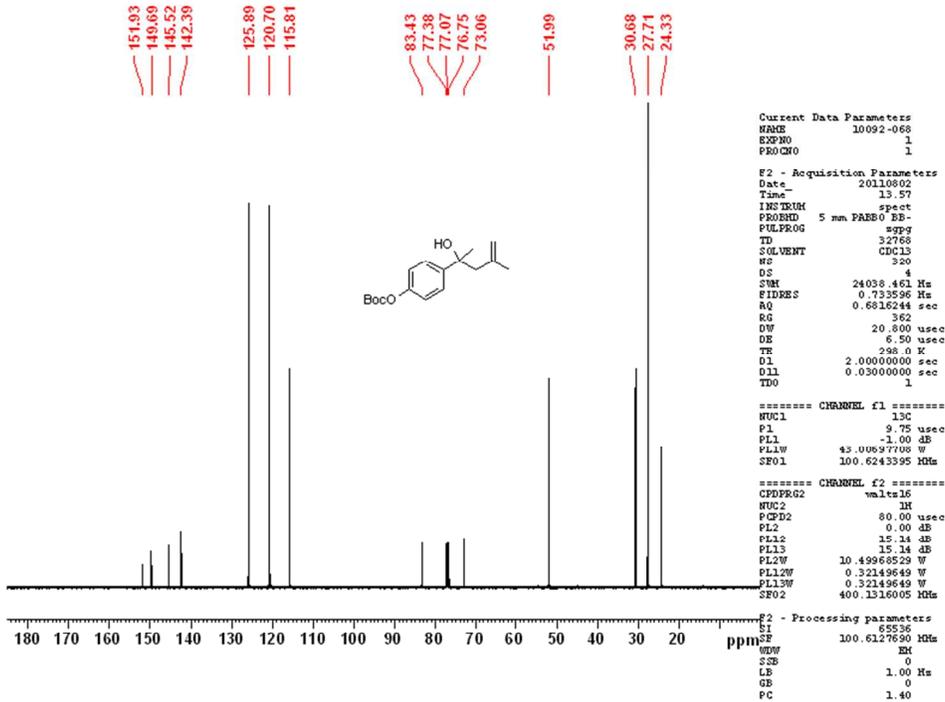
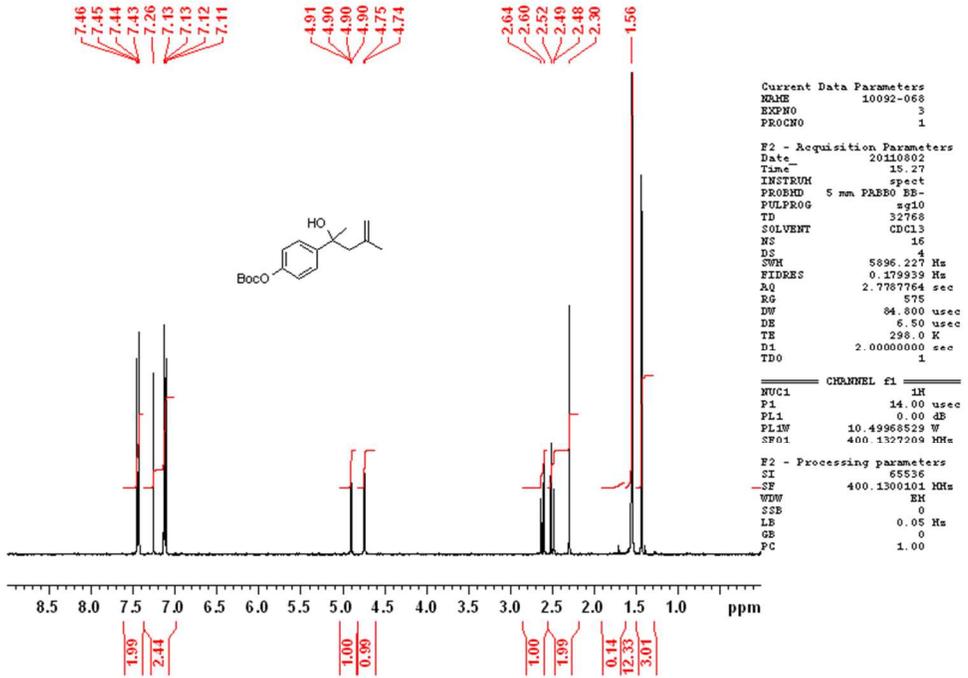
F2 - Acquisition Parameters
Date_     20110802
Time      17.24
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   sgpg
TD         32768
SOLVENT   CDCl3
NS         320
DS         4
SWH        24038.461 Hz
FIDRES     0.733596 Hz
AQ         0.6815244 sec
RG         322
DW         20.800 usec
DE         6.50 usec
TE         298.0 K
D1         2.00000000 sec
D11        0.03000000 sec
TD0        1

===== CHANNEL f1 =====
NUC1       13C
P1         9.75 usec
PL1        -1.00 dB
PL1W       43.00697708 W
SF01       100.6243395 MHz

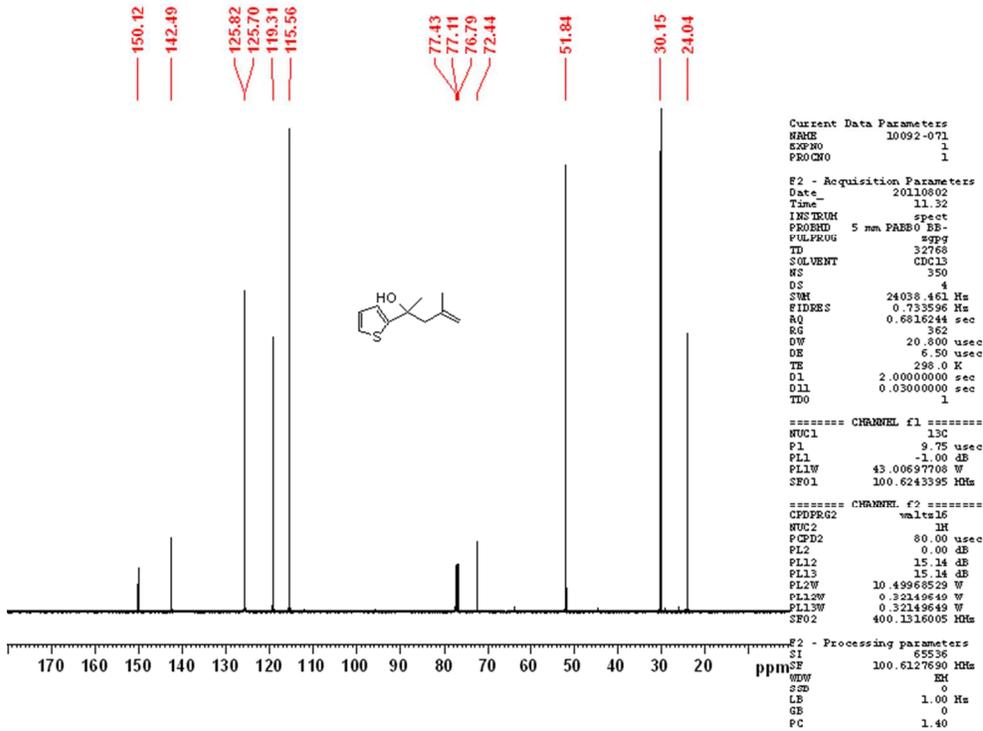
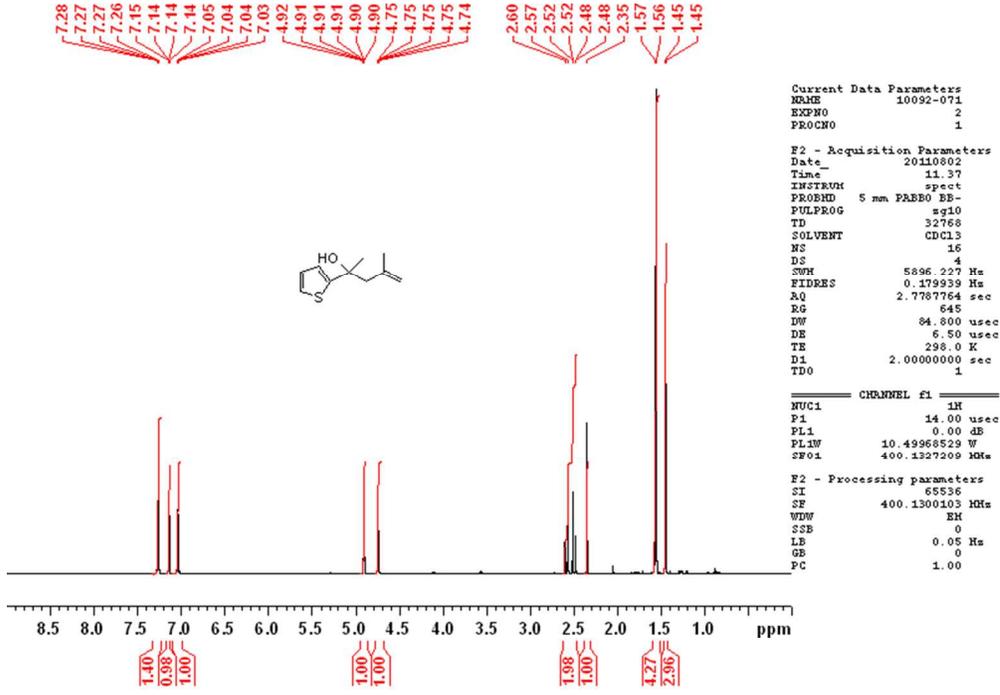
===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2       1H
PCPD2     80.00 usec
PL2        0.00 dB
PL12       15.14 dB
PL13       15.14 dB
PL2W       10.49968529 W
PL12W      0.32149649 W
PL13W      0.32149649 W
SF02       400.1316005 MHz

F2 - Processing parameters
SI         65536
SF         100.6127630 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
    
```

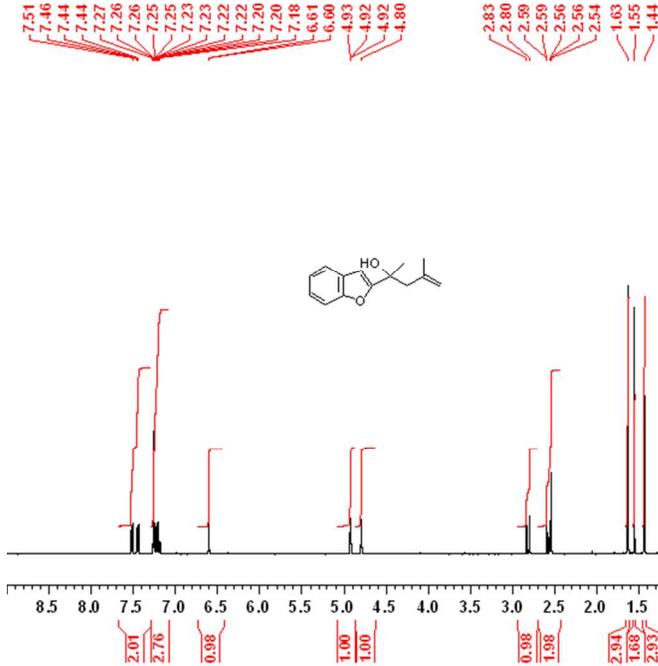
tert-Butyl 4-(2-hydroxy-4-methylpent-4-en-2-yl)phenyl carbonate 25



4-Methyl-2-(thiophen-2-yl)pent-4-en-2-ol 27



2-(Benzofuran-3-yl)-4-methylpent-4-en-2-ol 29



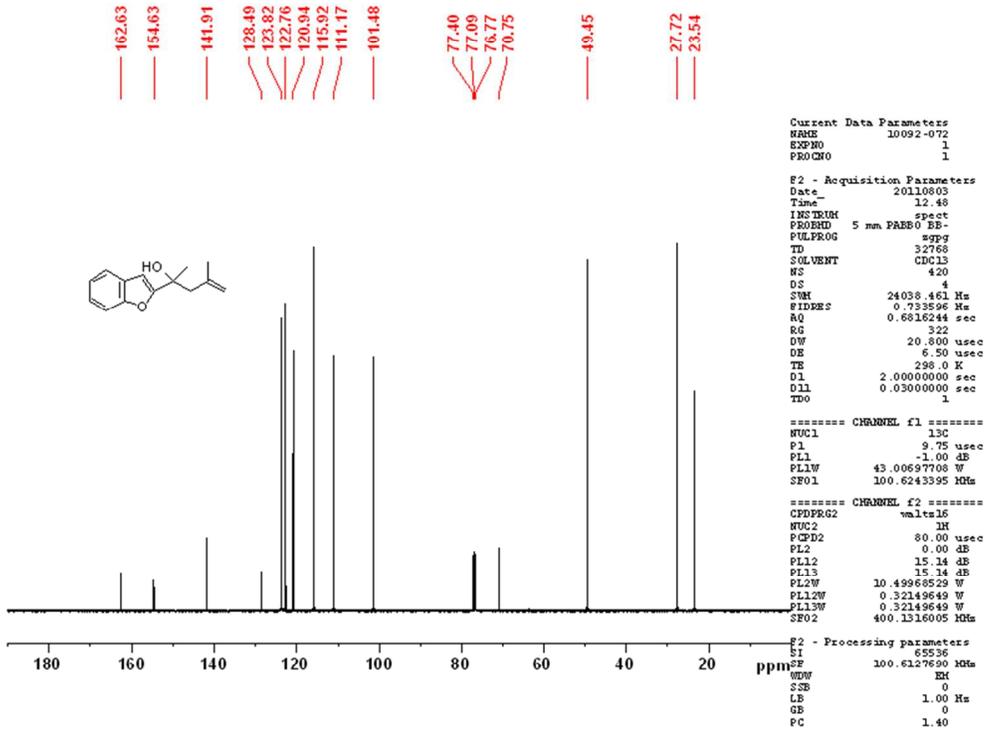
```

Current Data Parameters
NAME      10092-072
EXPNO     2
PROCNO    1

F2 - Acquisition Parameters
Date_     20110803
Time      12.54
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zg10
TD         32768
SOLVENT   CDCl3
NS         16
DS         4
SWH        5896.227 Hz
FIDRES     0.179939 Hz
AQ         2.7787764 sec
RG         312
DW          84.800 usec
DE          6.50 usec
TE          298.0 K
D1          2.00000000 sec
TDO        1

===== CHANNEL f1 =====
NUC1       1H
P1         14.00 usec
PL1        0.00 dB
PL1W       10.49968529 W
SF01       400.1327209 MHz

F2 - Processing parameters
SI         65536
SF         400.1300110 MHz
WDW        EM
SSB        0
LB         0.05 Hz
GB         0
PC         1.00
    
```



```

Current Data Parameters
NAME      10092-072
EXPNO     1
PROCNO    1

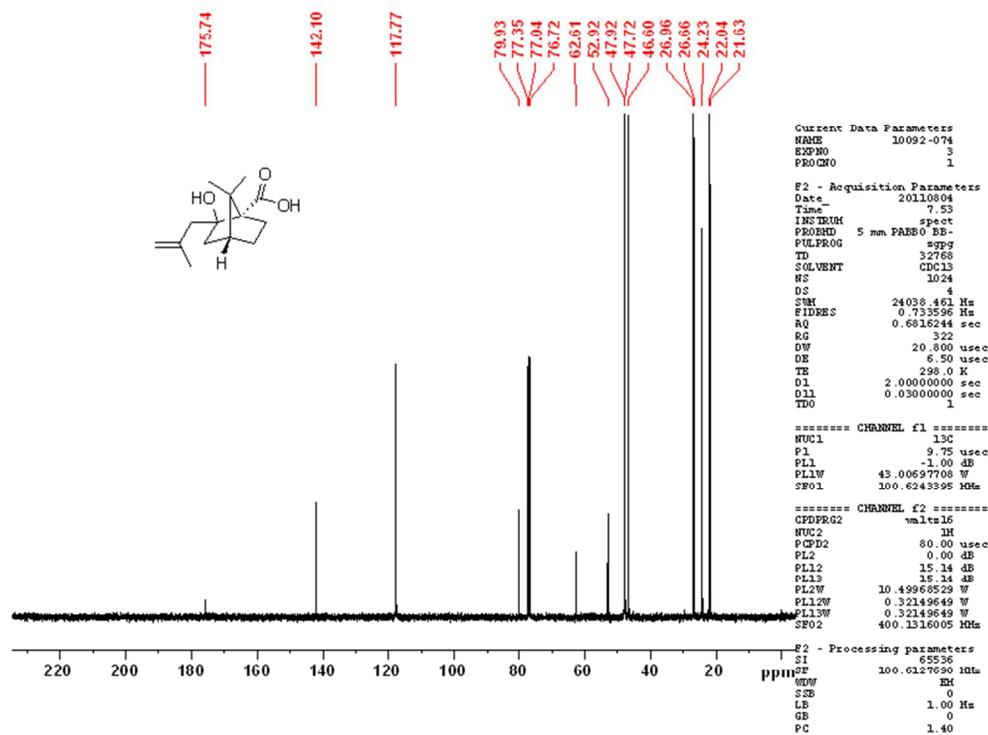
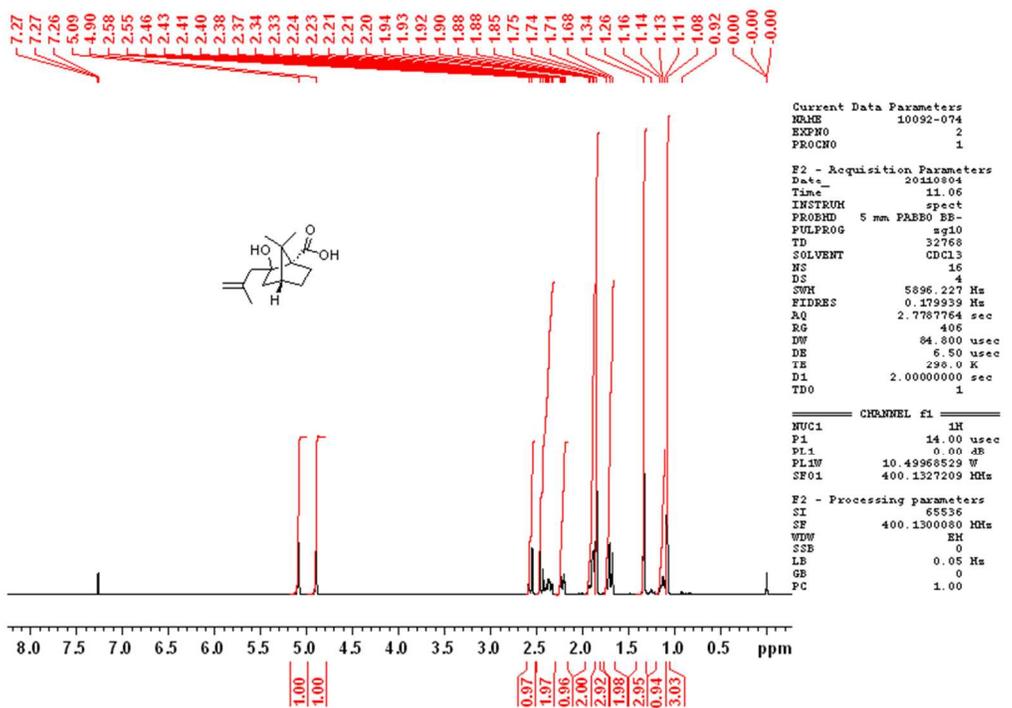
F2 - Acquisition Parameters
Date_     20110803
Time      12.48
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zgpg
TD         32768
SOLVENT   CDCl3
NS         420
DS         4
SWH        24038.461 Hz
FIDRES     0.733596 Hz
AQ         0.6816244 sec
RG         322
DW          20.800 usec
DE          6.50 usec
TE          298.0 K
D1          2.00000000 sec
D11        0.03000000 sec
TDO        1

===== CHANNEL f1 =====
NUC1       13C
P1         9.75 usec
PL1        -1.00 dB
PL1W       43.00697708 W
SF01       100.6243395 MHz

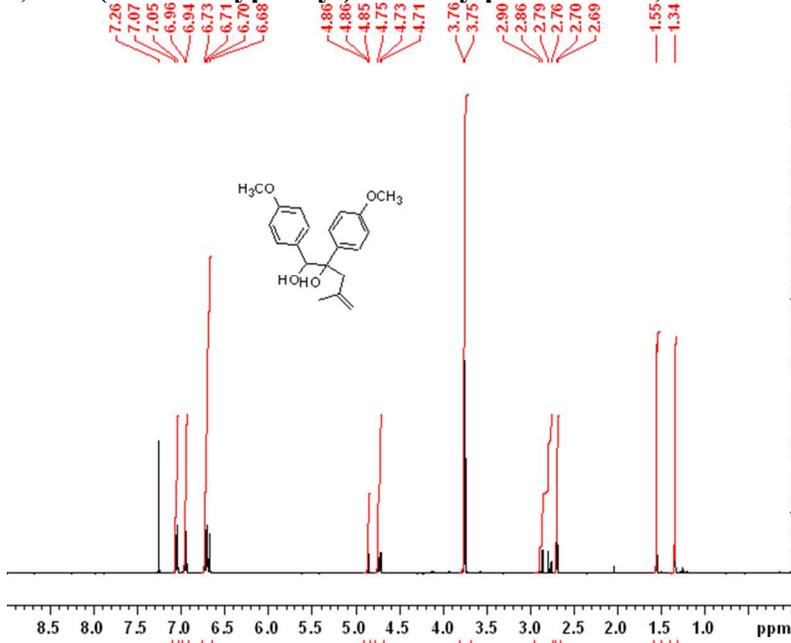
===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2       1H
PCPD2      80.00 usec
PL2        0.00 dB
PL12       15.14 dB
PL13       15.14 dB
PL2W       10.49968529 W
PL12W      0.32149649 W
PL13W      0.32149649 W
SF02       400.1316005 MHz

F2 - Processing parameters
SI         65536
SF         100.6127690 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
    
```

(1S,2S,4R)-2-Hydroxy-7,7-dimethyl-2-(2-methylallyl)bicyclo[2.2.1]heptane-1-carboxylic acid 31



1,2-Bis(4-methoxyphenyl)-4-methylpent-4-ene-1,2-diol 33



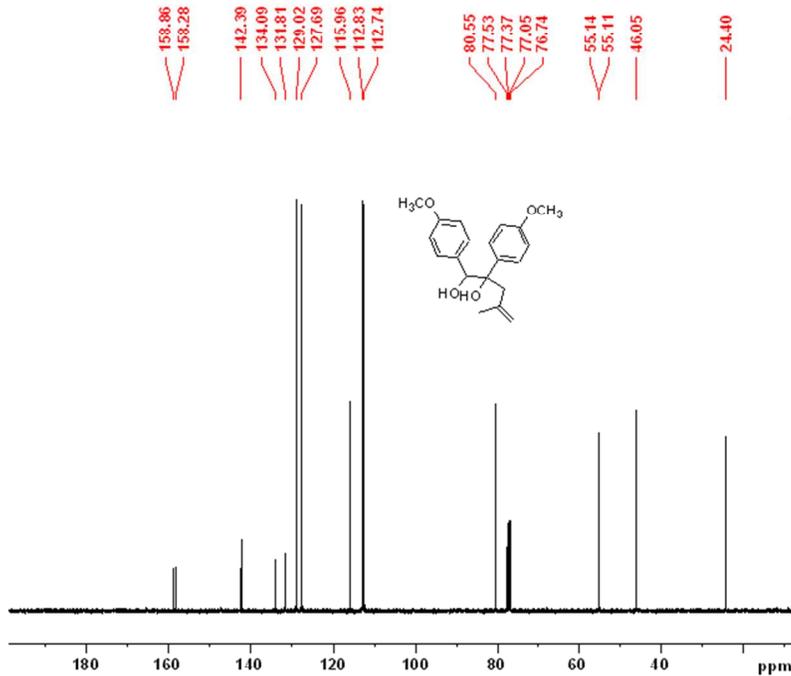
```

Current Data Parameters
NAME      10092-075
EXPNO     2
PROCNO    1

F2 - Acquisition Parameters
Date_     20110803
Time      16.27
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   sg10
TD         32768
SOLVENT   CDCl3
NS         16
DS         4
SWH        5886.277 Hz
FIDRES     0.179939 Hz
AQ         2.7787764 sec
RG         812
DW         84.800 usec
DE         6.50 usec
TE         298.0 K
D1         2.00000000 sec
TD0        1

===== CHANNEL f1 =====
NUC1       1H
P1         14.00 usec
PL1        0.00 dB
PL1W       10.49968529 W
SFO1       400.1327209 MHz

F2 - Processing parameters
SI         65536
SF         400.1300104 MHz
WDW        EM
SSB        0
LB         0.05 Hz
GB         0
PC         1.00
    
```



```

Current Data Parameters
NAME      10092-075
EXPNO     1
PROCNO    1

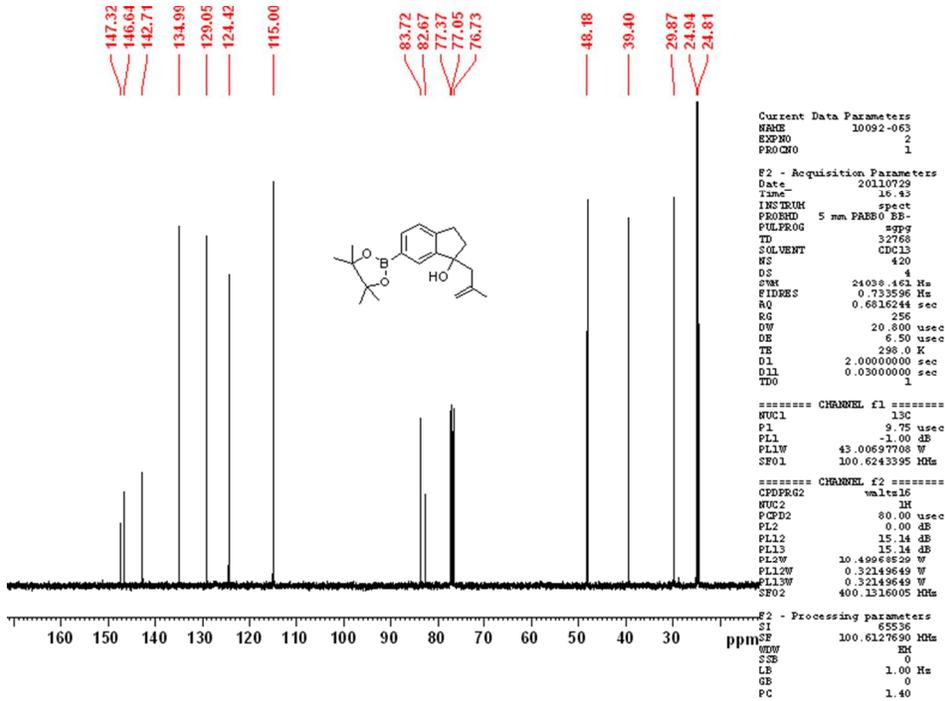
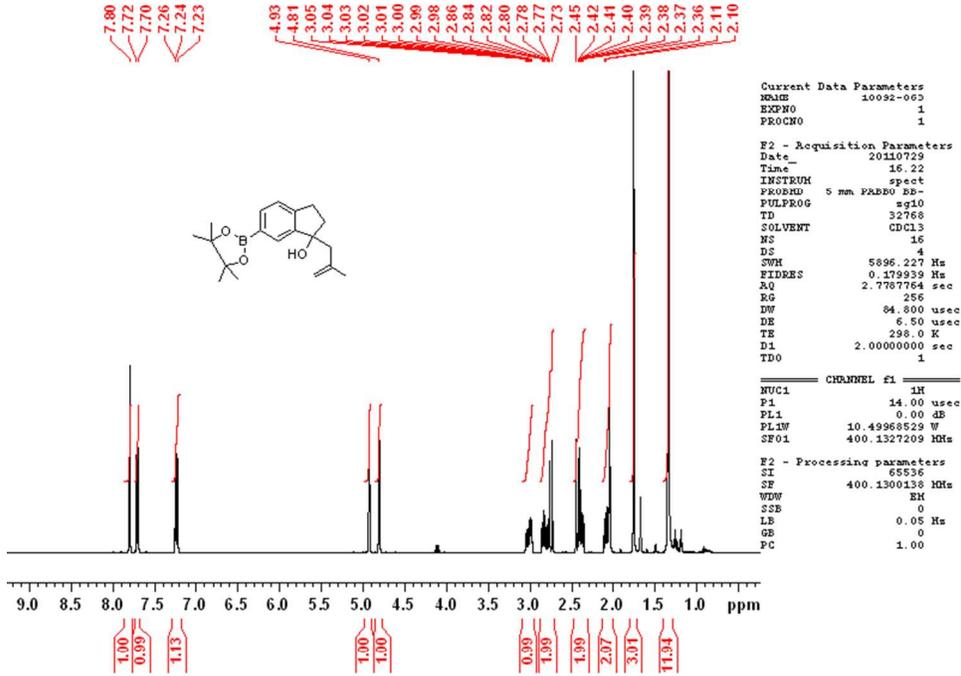
F2 - Acquisition Parameters
Date_     20110803
Time      16.22
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   sgpg
TD         32768
SOLVENT   CDCl3
NS         350
DS         4
SWH        24038.461 Hz
FIDRES     0.733596 Hz
AQ         0.6816244 sec
RG         322
DW         20.800 usec
DE         6.50 usec
TE         298.0 K
D1         2.00000000 sec
D11        0.03000000 sec
TD0        1

===== CHANNEL f1 =====
NUC1       13C
P1         9.75 usec
PL1        -1.00 dB
PL1W       43.00697708 W
SFO1       100.6243395 MHz

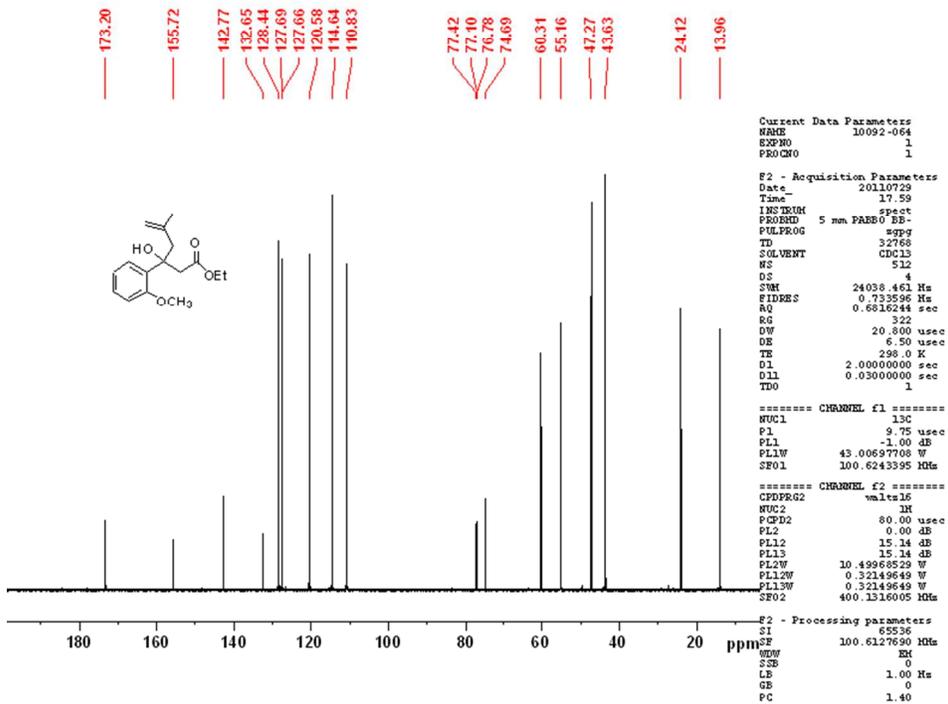
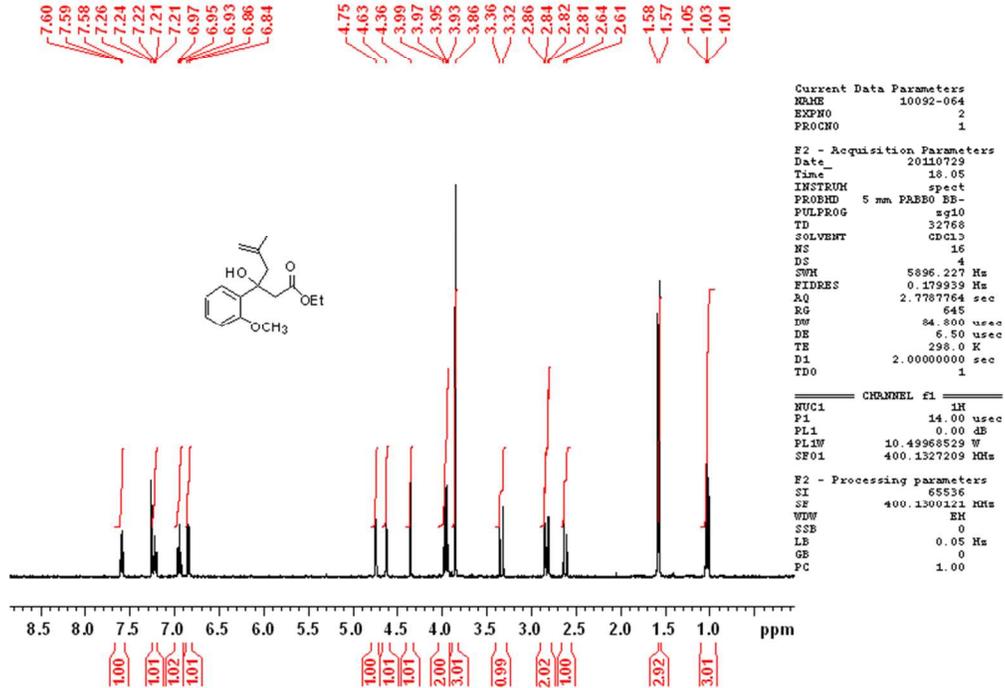
===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2       1H
PCPD2      80.00 usec
PL2        0.00 dB
PL12       15.14 dB
PL13       15.14 dB
PL2W       10.49968529 W
PL12W      0.32149649 W
PL13W      0.32149649 W
SFO2       400.1316005 MHz

F2 - Processing parameters
SI         65536
SF         100.6127690 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
    
```

1-(2-Methylallyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydro-1H-inden-1-ol 35



Ethyl 3-hydroxy-3-(2-methoxyphenyl)-5-methylhex-5-enoate 37



2-(2-Methylallyl)-1,2,3,4-tetrahydronaphthalene-2,6-diol 39

