

## Electronic Supplementary Information (ESI)

### Amberlyst-15<sup>®</sup> catalyst for environmentally Benign syntheses of Hexahydro-cyclopenta(b)furan and of 2-oxabicyclo[3.2.1]octane derivatives

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## Experimental

### General

Commercial solvents were used with further purification by drying and distillation. The monitoring of reaction and checking of purity of the products were done using pre-coated silica gel plates (Merck) and visualization using anisaldehyde sulfuric acid reagent. FT-IR spectra were recorded on Perkin-Elmer Spectrum One spectrometer. <sup>1</sup>H NMR spectra were recorded on Varian spectrometers at 300, 400 and MHz and <sup>13</sup>C at 75 and 100 MHz. GC-MS analysis was carried on Agilent instrument, where GC-6890 was coupled with mass spectrometer MS-5973 N with quadrapole mass detector, using HP-5 (5% phenyl methyl siloxane) column. The compounds **13-20** showed the required m/z: (M<sup>+</sup>) values.

### Synthesis of 2-(2,2,3-trimethylcyclopent-3-enyl)ethanol derivatives (6-7)

A mixture of (1'S)-campholenic aldehyde **1** (32 mmol), activated vinyl compound namely ethyl acrylate or acrylonitrile (60 mmol) and DABCO (0.5 wt eqv) was stirred at room temperature for 4 d. The reaction mixture was diluted with dichloromethane (20 ml); the organic layer was washed with 2N HCl and water and was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Solvent was evaporated and the residue was purified by silica gel column chromatography, the elution with hexane-ethyl acetate (8:2) provided the corresponding Baylis–Hillman adducts **6-7** (Scheme 1).

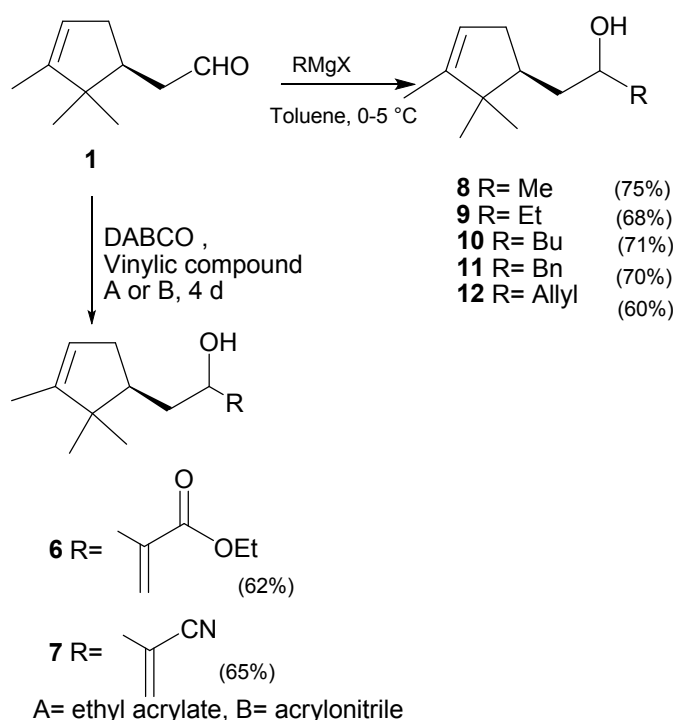
### General procedure for the synthesis of (1'S)-campholenic alcohols 8-12

To a stirred solution of freshly prepared Grignard reagent (80 mmol) in toluene (10 mL) cooled at 5°C under nitrogen atmosphere, was added dropwise (1'S)-campholenic aldehyde **1** (10 g, 64 mmol) in toluene (30 mL) in 30 min. Reaction mixture was further stirred at 5°C for 2-4 h. Reaction was monitored by TLC. The reaction was quenched with saturated aqueous NH<sub>4</sub>Cl solution (20 mL). The aqueous layer was extracted with toluene. The combined organic layer was washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Solvent was evaporated *in vacuo* and the residue was purified by silica gel column chromatography, the elution with hexane-ethyl acetate (8:2) provided the products **8-12** respectively (Scheme 1).<sup>10</sup>

### General procedure for the synthesis of 2-substituted 6,6,6a-trimethyl-hexahydrocyclopenta(b)furan derivatives 13-19

To a stirred solution of (1'S)-campholenic alcohols **6-12** (0.06 mol) in dry toluene (25 mL) Amberlyst-15<sup>®</sup> (1 g) was added and the reaction mixture was stirred at room temperature for 5-9 h. The reaction was monitored by TLC and was filtered. The filtrate was evaporated *in vacuo* and the residue was purified by silica gel column chromatography, the elution with hexane-ethyl acetate (8:2) provided the compounds **13-19** respectively (Table I).

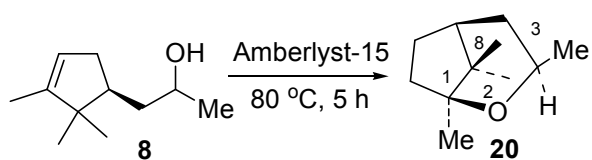
**Synthesis of 2,6,8,8-tetramethyl-1-oxabicyclo[3.2.1]octane (20).** To a stirred solution of **8** (0.063 mol) in dry toluene (25 mL) Amberlyst-15 (1 g) was added and reaction mixture was then stirred at 80 °C for 5 h. Reaction mixture was filtered and solvent was removed *in vacuo* and the residue was subjected to column chromatography (25 g silica gel; 100-200 mesh), the elution with EtOAc-Hexane (1:9) gave 1,3,8,8-tetramethyl-2-oxabicyclo[3.2.1]octane **20** (Scheme 3).



**Scheme 1 Synthesis of (1'S)-campholenic alcohols**



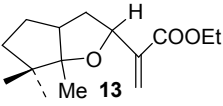
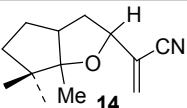
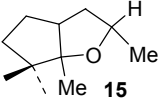
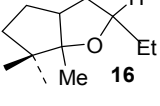
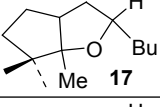
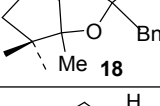
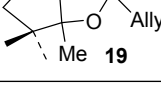
**Scheme 2 Synthesis of 2-substituted 6,6,6a-trimethylhexahydrocyclopenta(b)furan derivatives**



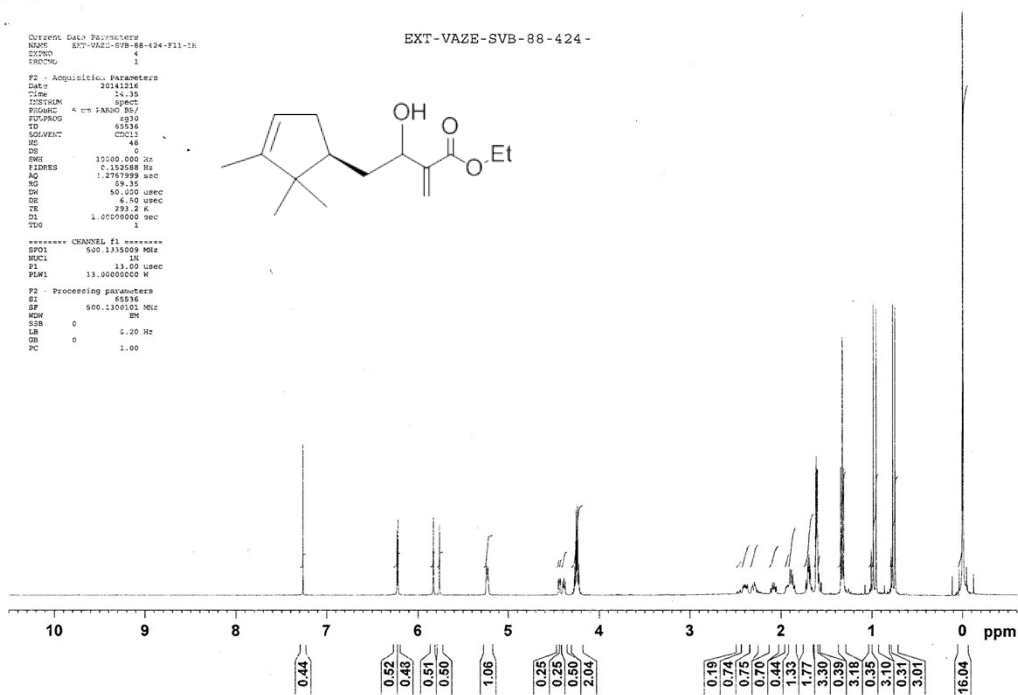
**Scheme 3 Synthesis of 2,6,8,8-tetramethyl-1-oxabicyclo[3.2.1]octane**

**Table 1 Synthesis of 2-substituted 6,6,6a-trimethyl-2-oxabicyclo[3.3.0]octane derivatives.**

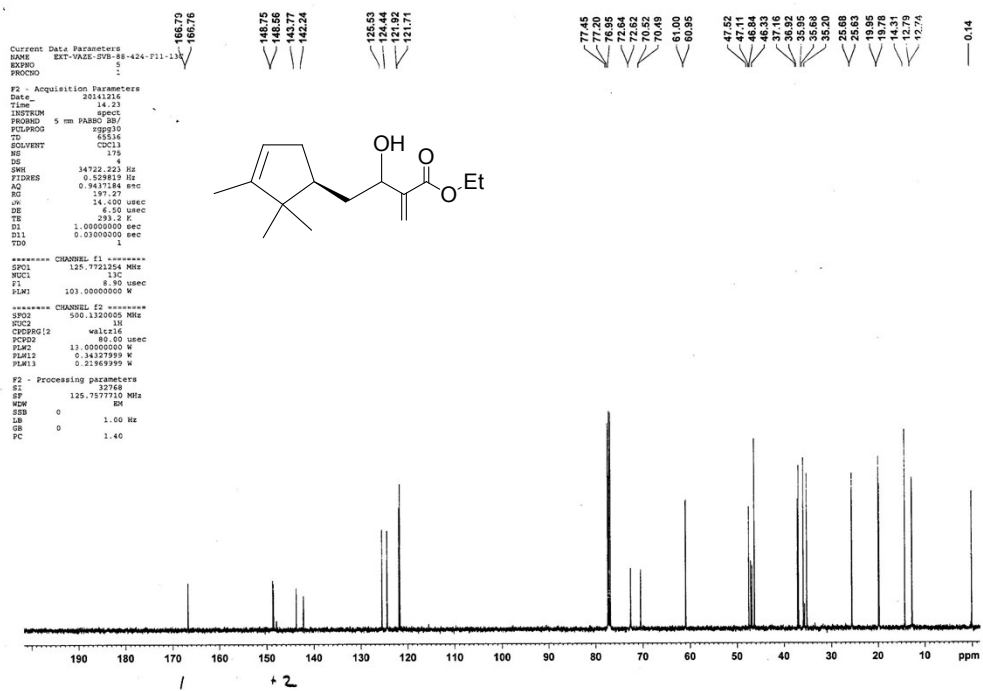
**Reaction time and yields**

Entry	Sub.	Product*	Time h	Yield (%)
1	6	 <b>13</b>	5	77
2	7	 <b>14</b>	5	72
3	8	 <b>15</b>	6	75
4	9	 <b>16</b>	6	68
5	10	 <b>17</b>	6	67
6	11	 <b>18</b>	9	60
7	12	 <b>19</b>	5	64

\* Minor amount of formation of 3-substituted-1,8,8-trimethyl-2-oxabicyclo[3.2.1]octane (<10%) has been observed

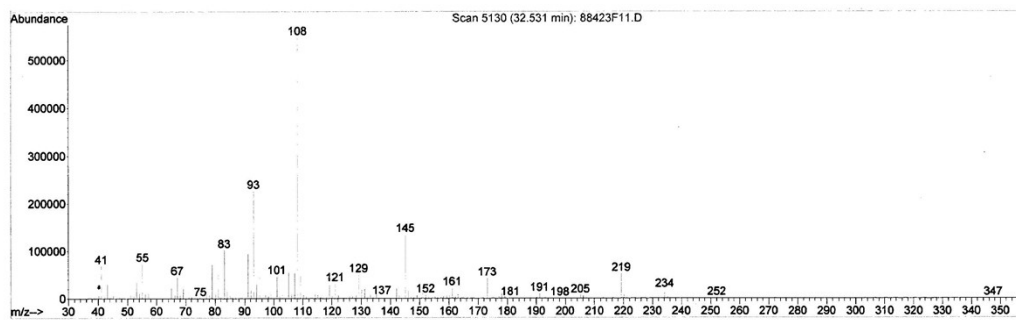
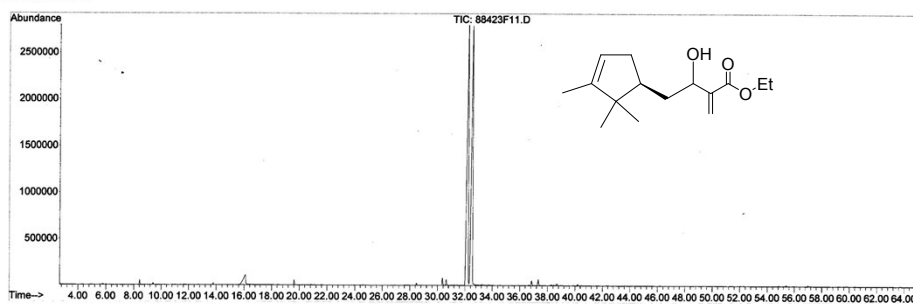


S Fig. 1 <sup>1</sup>H NMR spectrum (500 MHz) of compound 6



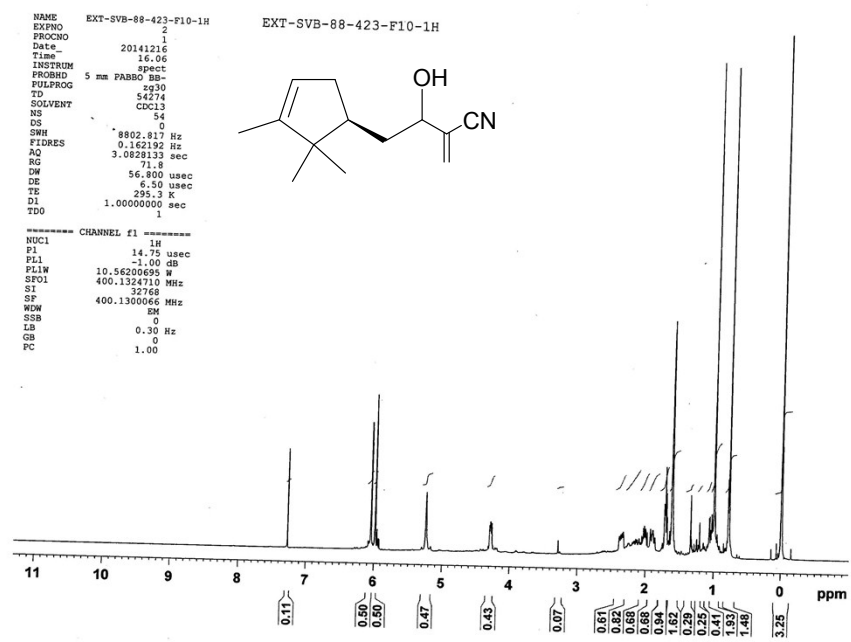
S Fig. 2 <sup>13</sup>C NMR spectrum (125 MHz) of compound 6

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Misc Info : R&D.09/01/15  
Vial Number : 4

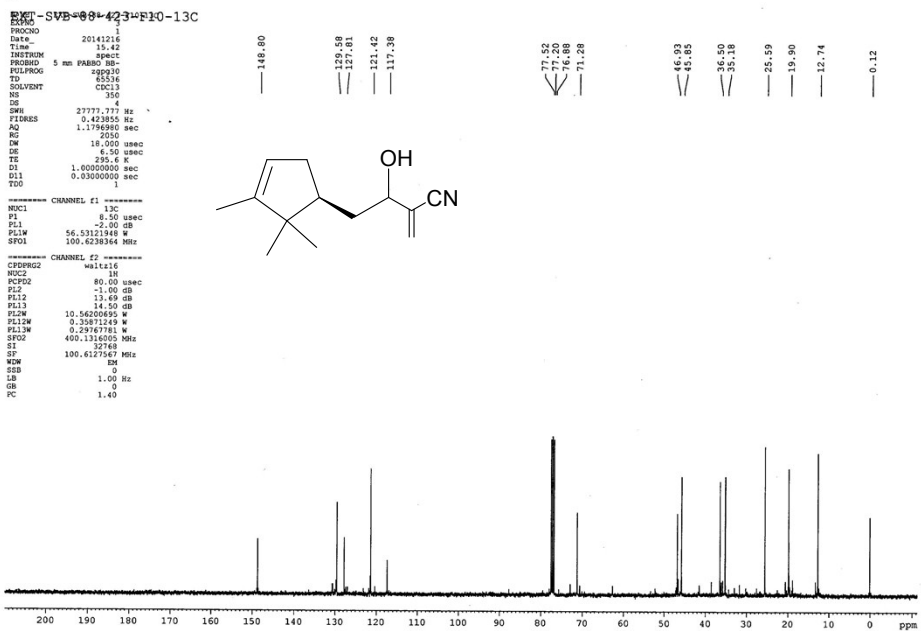


S Fig. 3 GC-MS spectrum of compound 6



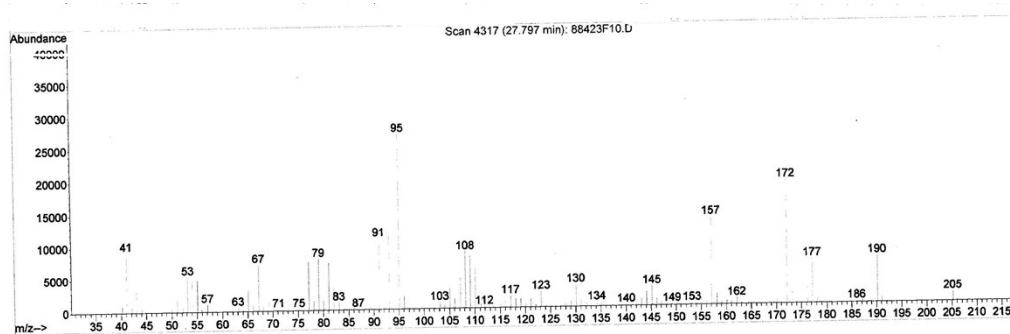
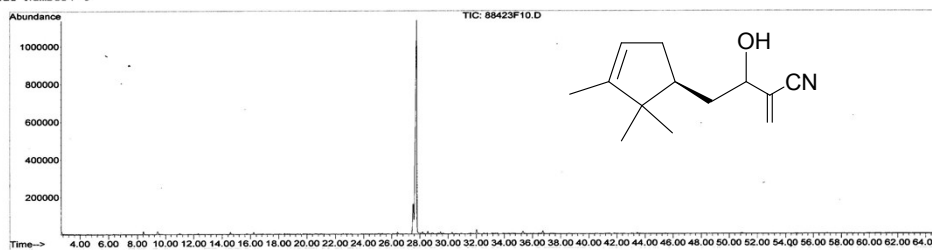


S Fig. 4 <sup>1</sup>H NMR spectrum (500 MHz) of compound 7

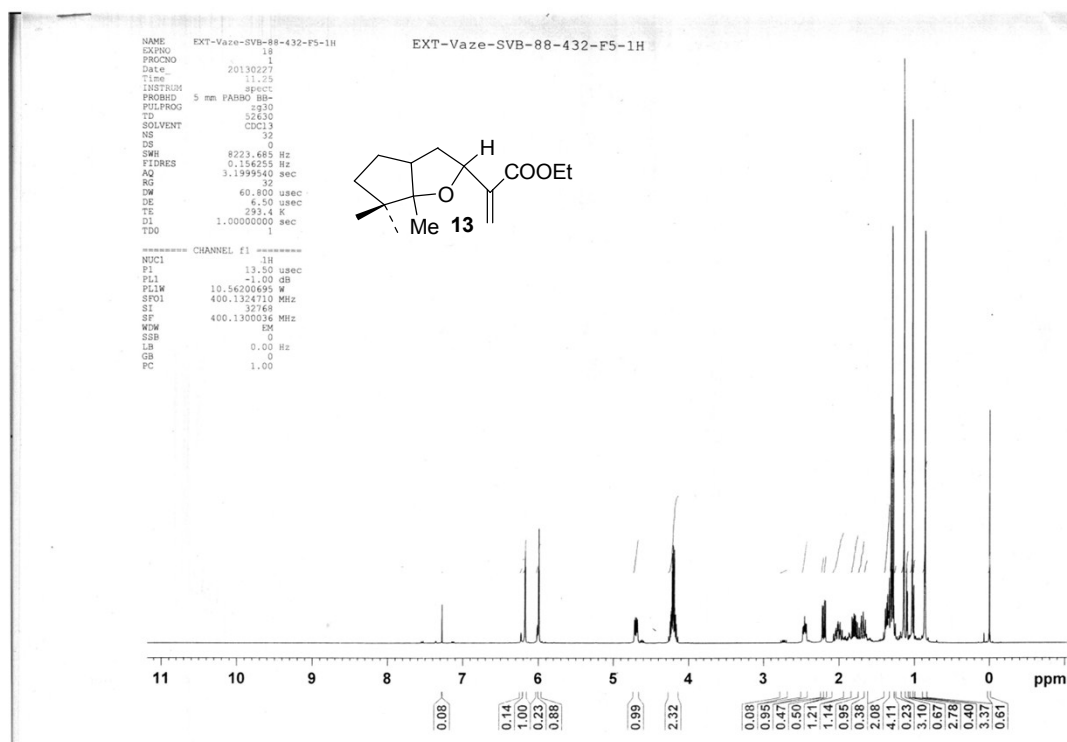


S Fig. 5 <sup>13</sup>C NMR spectrum (125 MHz) of compound 7

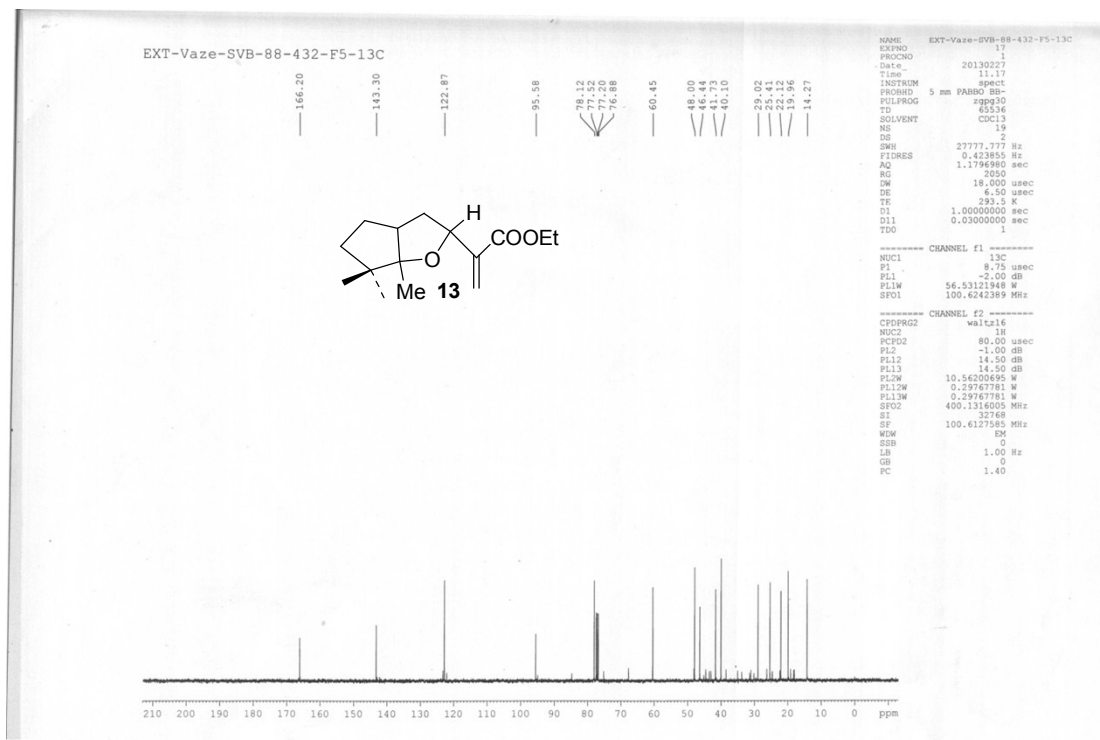
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Misc Info : R&D.09/01/15  
Vial Number : 3



S Fig. 6 GC-MS spectrum of compound 7

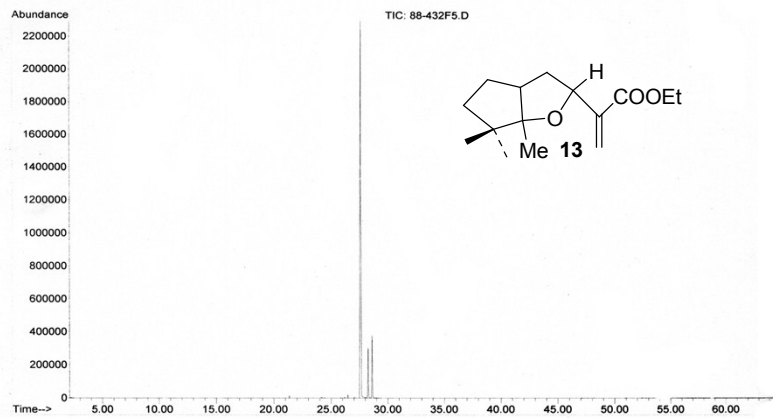


**S Fig. 7**  $^1\text{H}$  NMR spectrum (400 MHz) of compound **13**

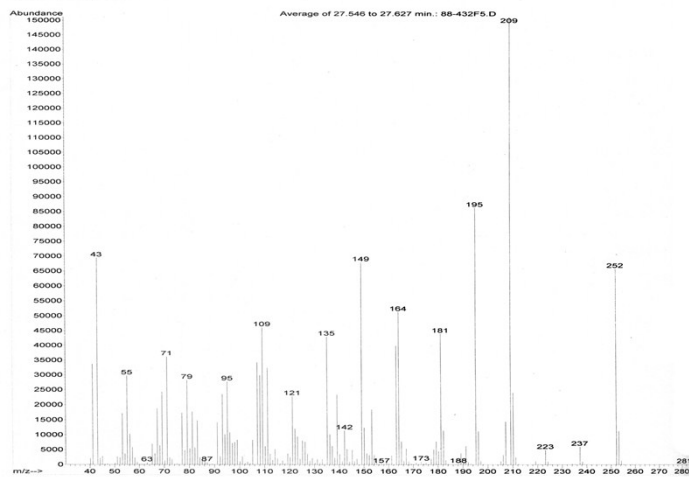


S Fig. 8  $^{13}\text{C}$  NMR spectrum (100 MHz) of compound 13

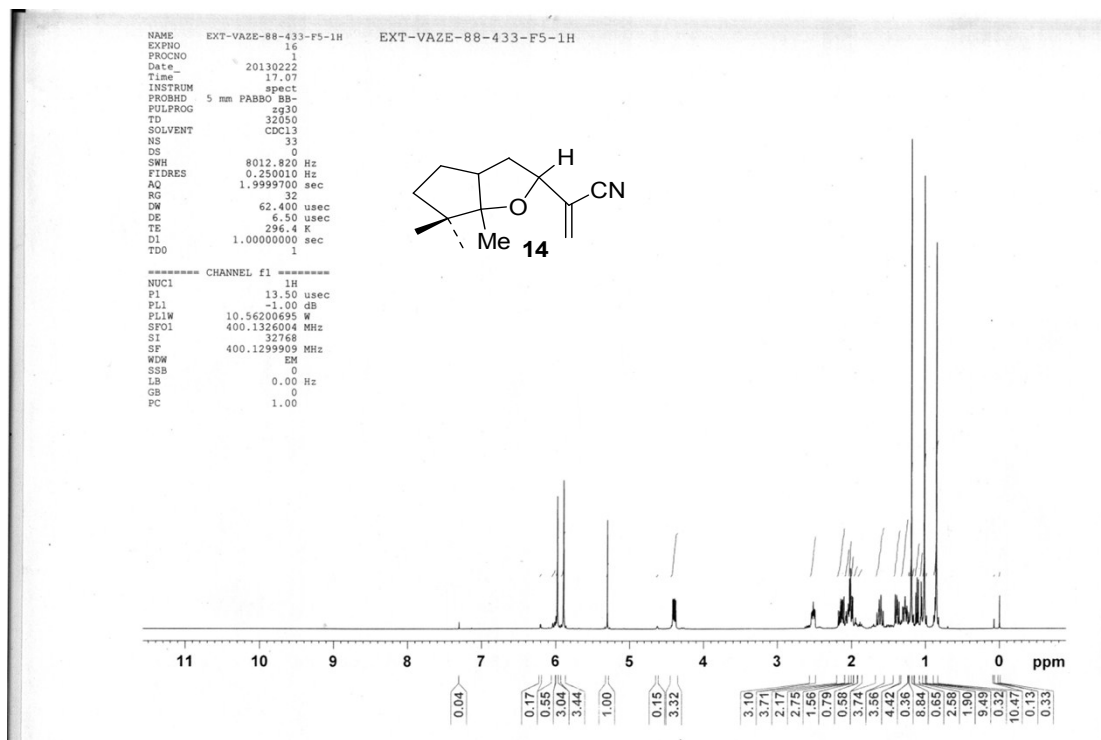
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Misc Info : FROM R&D, 4/2/2013  
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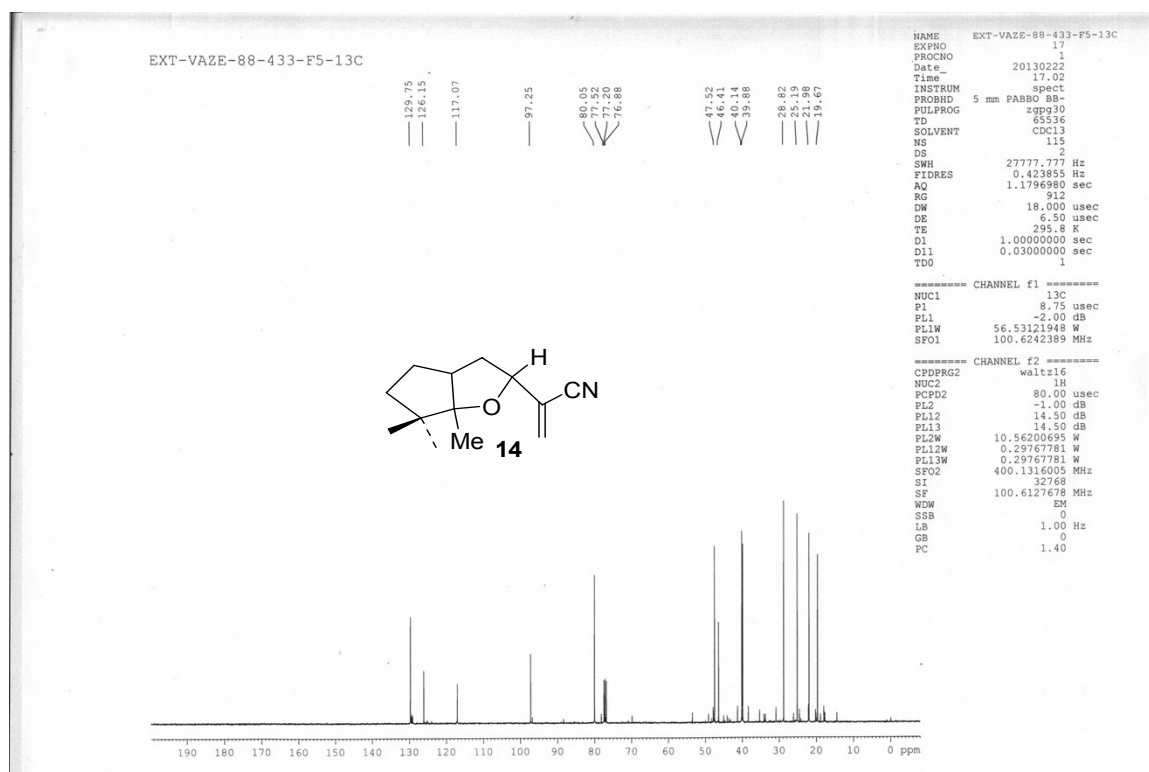
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Misc Info : FROM R&D, 4-2-2013  
Vial Number : 80



**S Fig. 9** GC-MS spectrum of compound 13



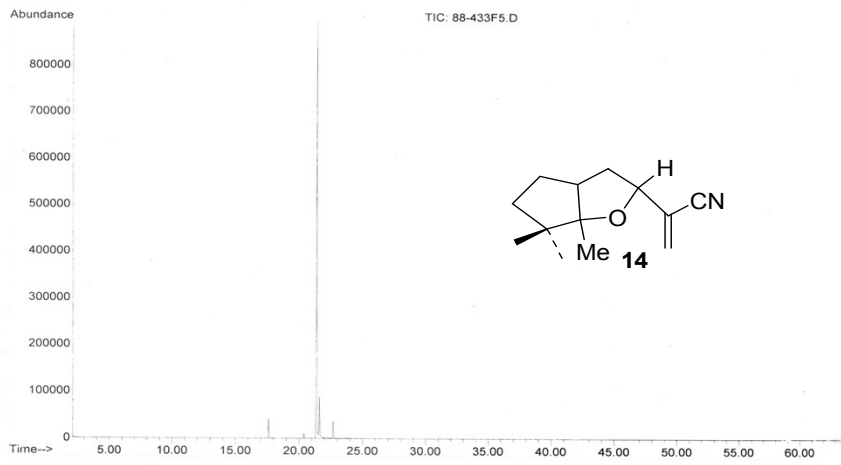
S Fig. 10  $^1\text{H}$  NMR (400 MHz) spectrum of compound 14



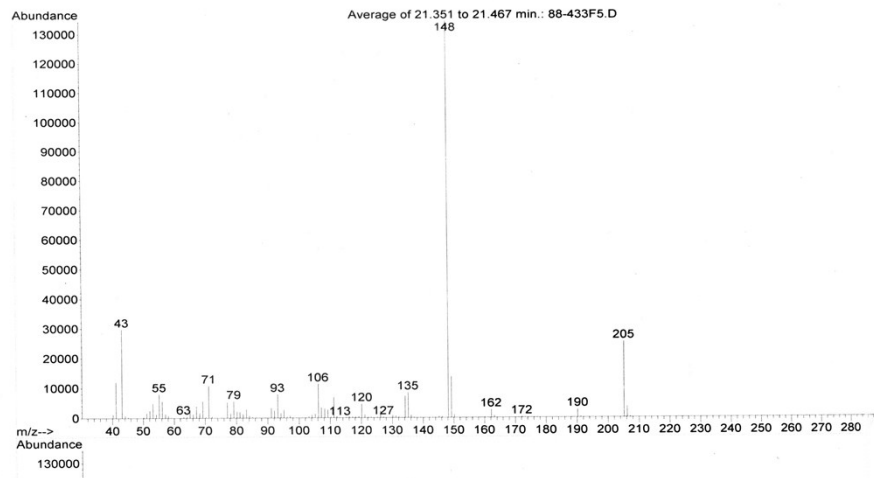
S Fig. 11  $^{13}\text{C}$  NMR spectrum (100 MHz) of compound 14



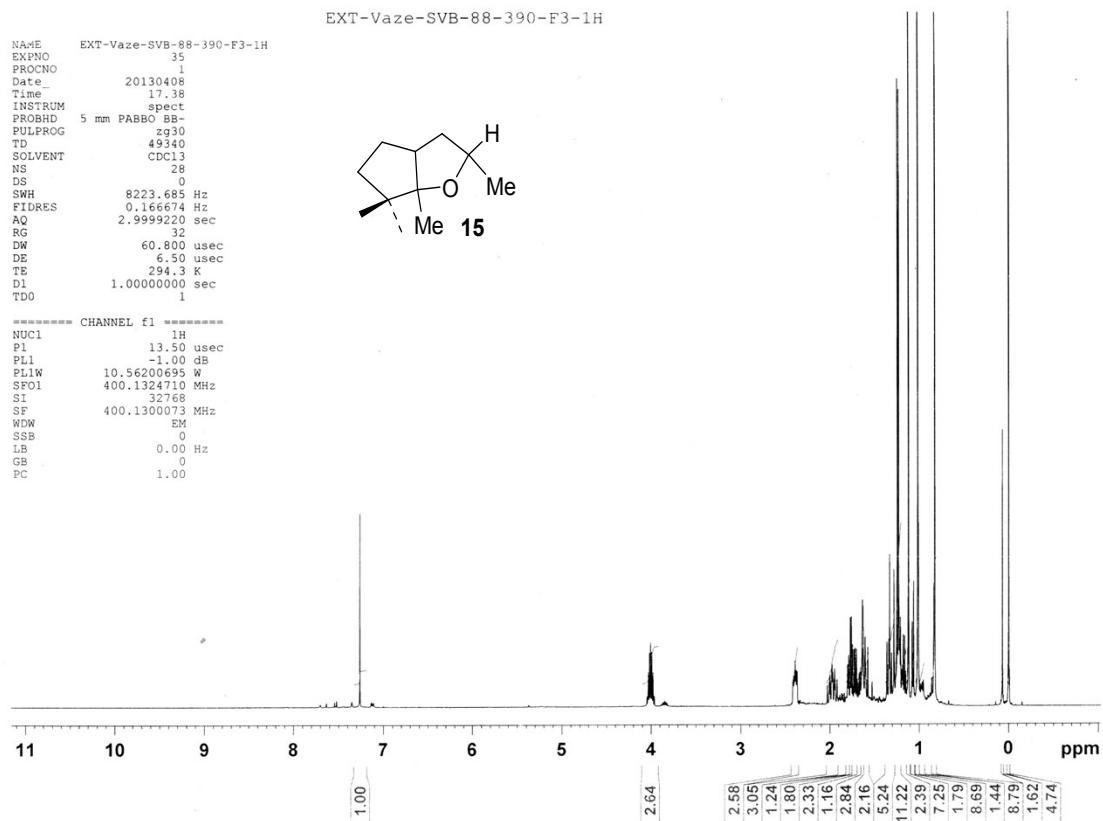
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Misc Info : FROM R&D, 4/2/2013  
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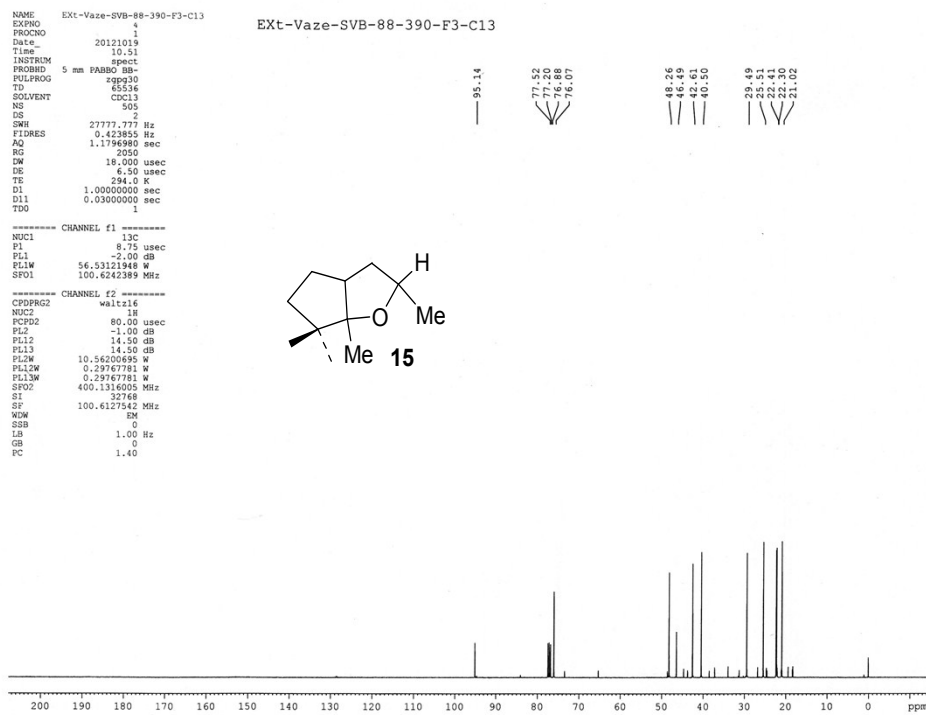
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Misc Info : FROM R&D, 4/2/2013  
Vial Number : 81



**S Fig. 12** GC-MS spectrum of compound **14**

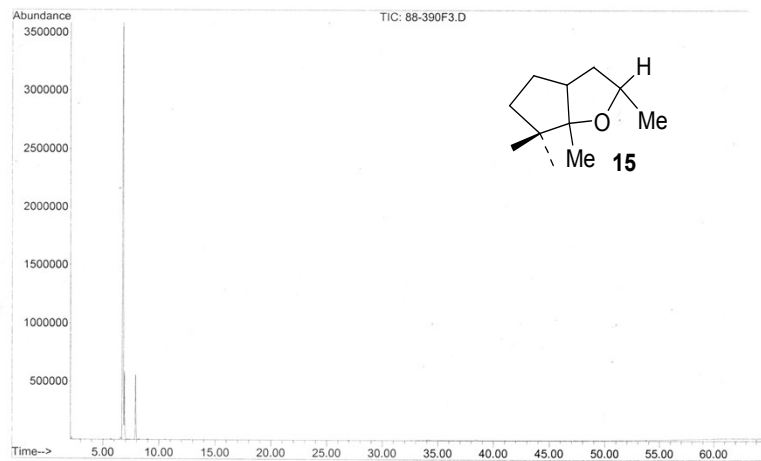


**S Fig. 13** <sup>1</sup>H NMR spectrum (400 MHz) of compound **15**

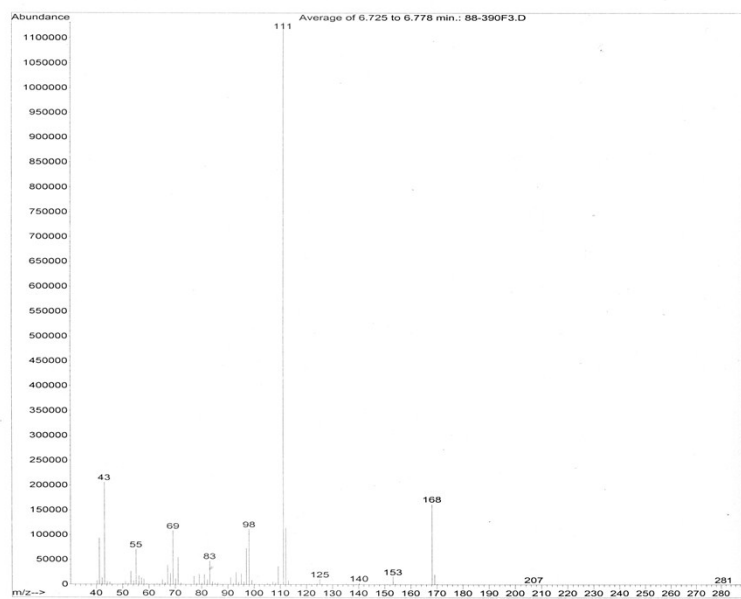


**S Fig. 14**  $^{13}\text{C}$  NMR spectrum (100 MHz) of compound **15**

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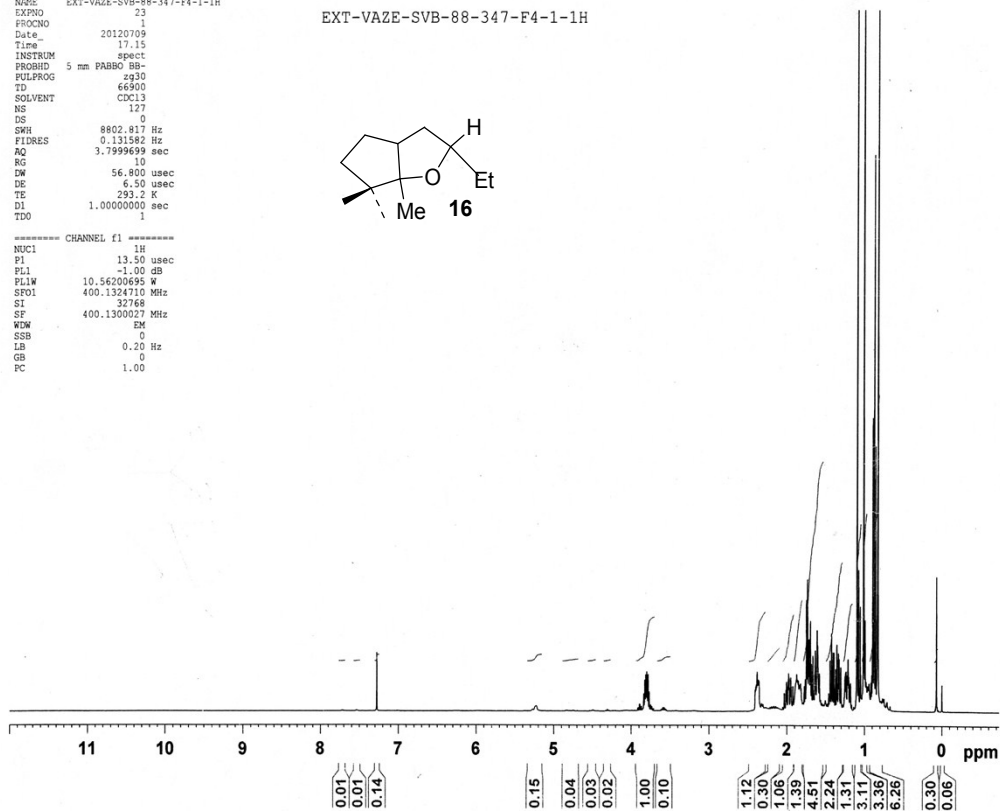
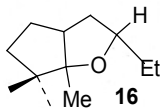
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Sample Name: 88-390-F3, PDCT MOL WT-168  
Misc Info : FROM R&D, 11/10/2012  
Vial Number: 36



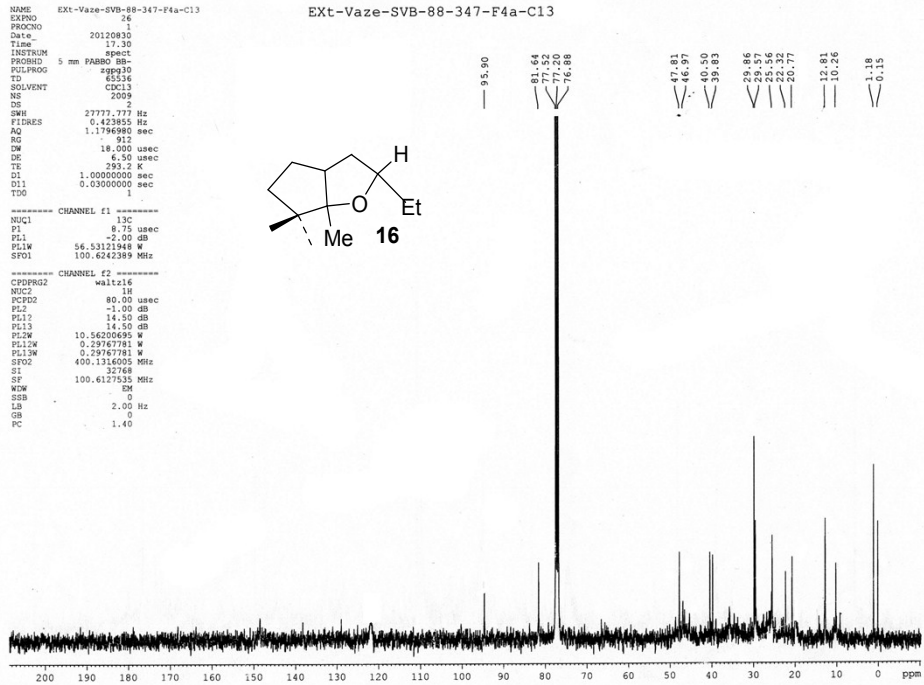
S Fig. 15 GC-MS spectrum of compound 15

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 EXPNO 23  
 FPRONO 1  
 Date\_ 20120709  
 Time 17:15  
 INSTRUM spect  
 PROBHD 5 mm PABBO BB-  
 PULPROG zg30  
 TD 66900  
 SOLVENT CDCl3  
 NS 127  
 DS 0  
 SWH 8802.817 Hz  
 FIDRES 0.131582 Hz  
 AQ 3.7999699 sec  
 RG 10  
 DW 56.800 usec  
 DE 6.50 usec  
 TE 293.2 K  
 D1 1.0000000 sec  
 TDO 1

EXT-VAZE-SVB-88-347-F4-1-1H

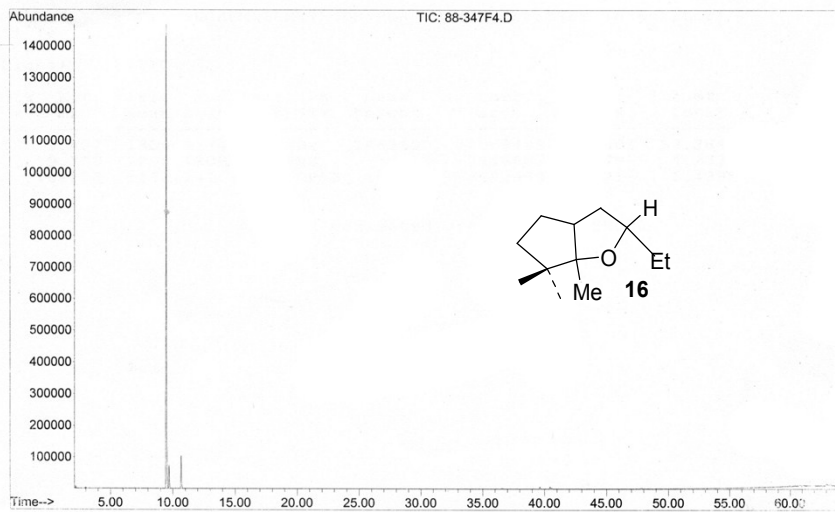


**S Fig. 16** <sup>1</sup>H NMR spectrum (400 MHz) of compound **16**

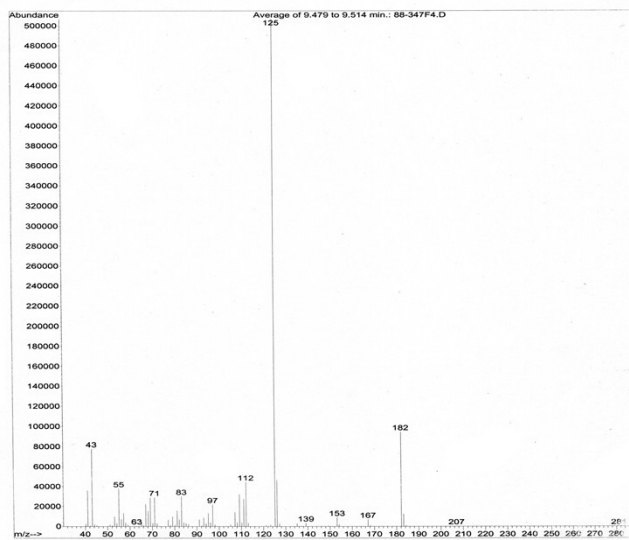


S Fig. 17  $^{13}\text{C}$  NMR spectrum (100 MHz) of compound 16

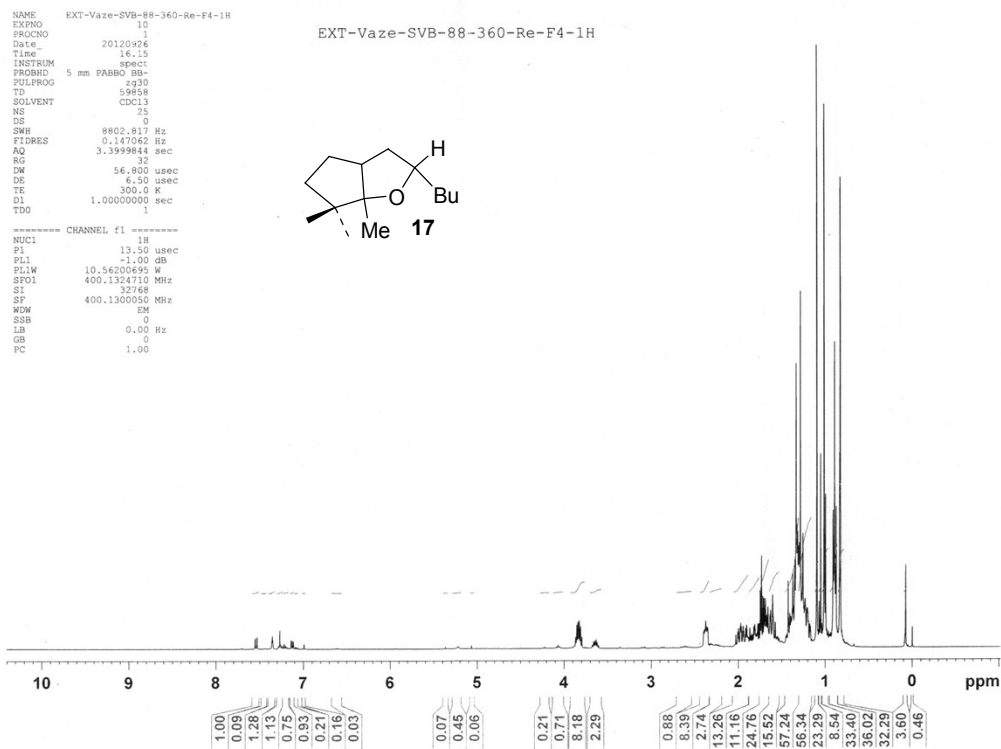
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Vial Number: 7



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Sample Name: 88-347F4(1), PDCT MOL WT-182  
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Vial Number: 7

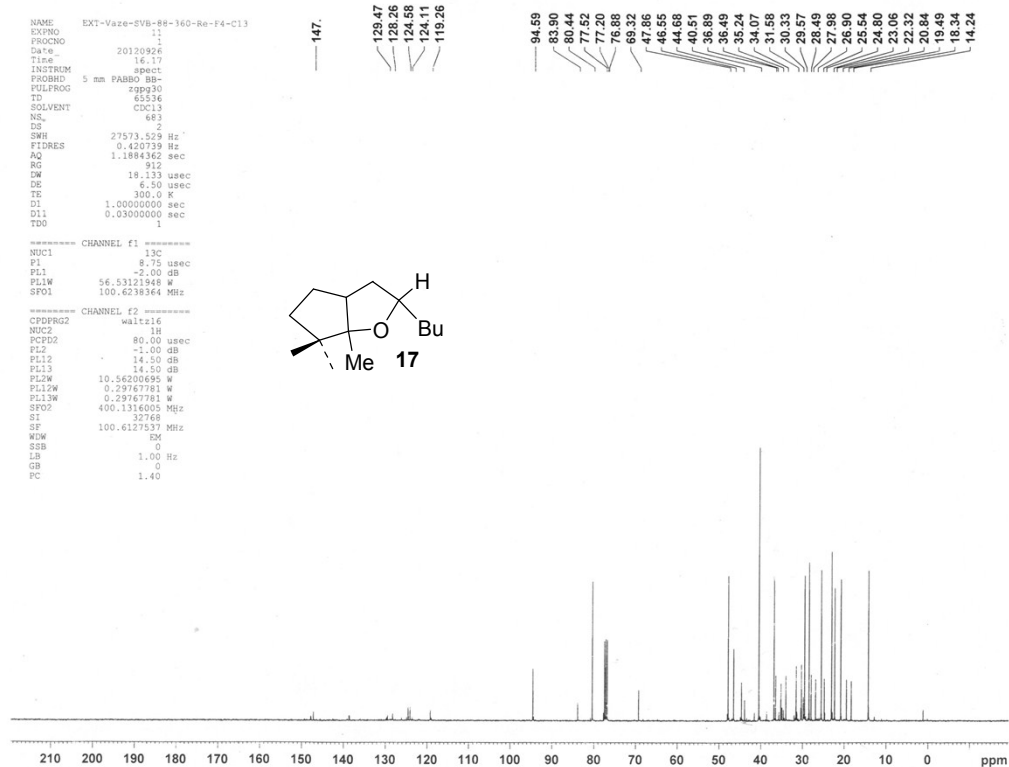


**S Fig. 18** GC-MS spectrum of compound 16



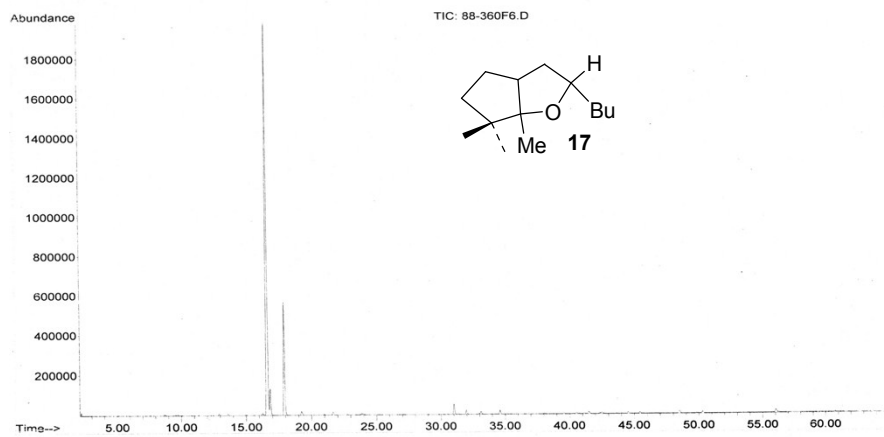
**S Fig 19**  $^1\text{H}$  NMR spectrum (400 MHz) of compound **17**



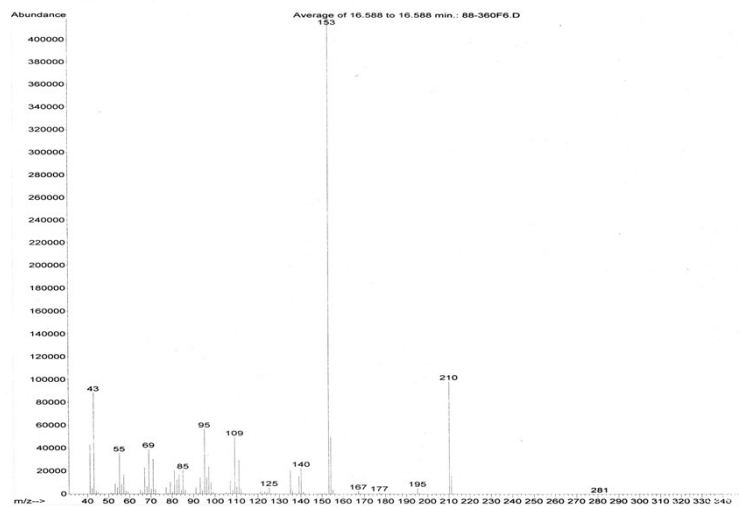


**S Fig. 20**  $^{13}\text{C}$  NMR spectrum (100 MHz) of compound **17**

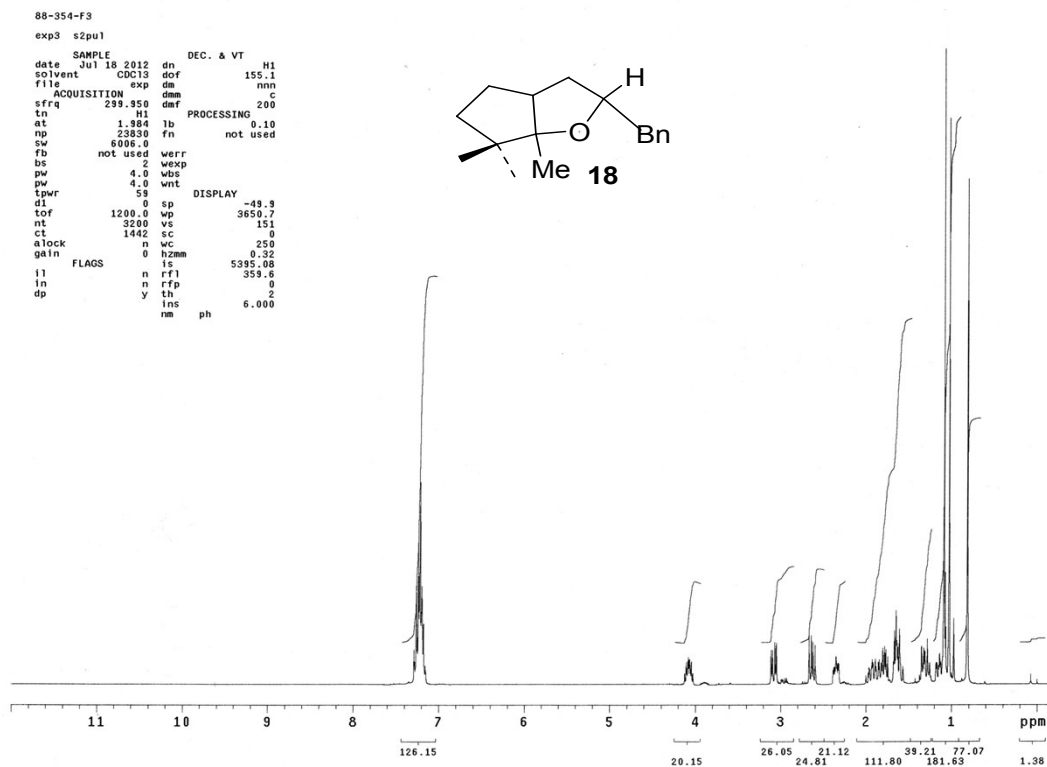
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Misc Info : FROM R&D, 8/8/2012  
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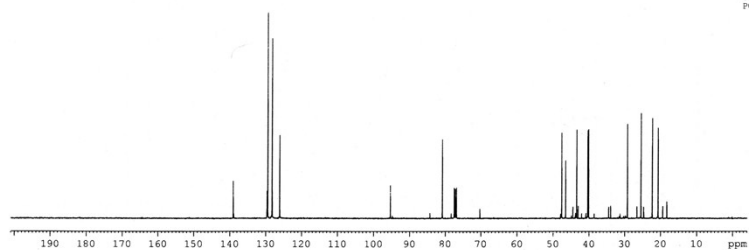
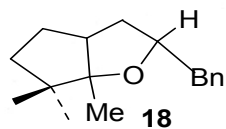


S Fig. 21 GC-MS spectrum of compound 17



S Fig. 22  $^1\text{H}$  NMR spectrum (300 MHz) of compound 18

Ext-Vaze-SVB-88-354-F3-C13



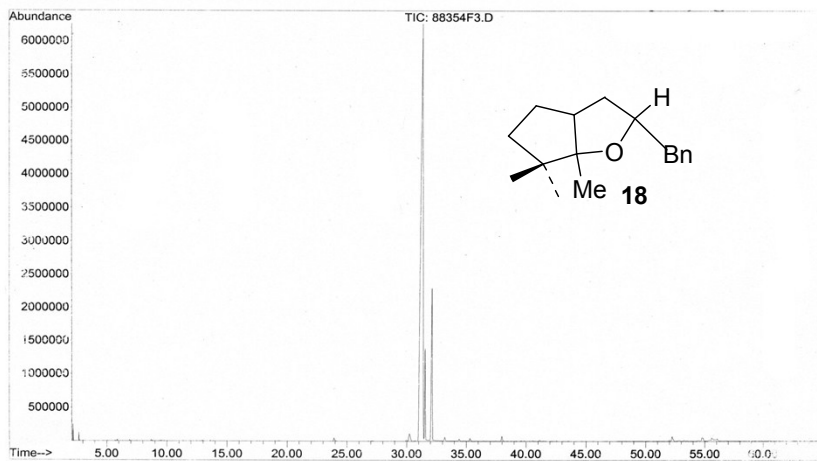
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PROCNO 1
Date_ 20120830
Time 17:10
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 128
DS 2
SWH 27777.777 Hz
FIDRES 0.423855 Hz
AQ 1.1796980 sec
RG 912
DM 18.000 usec
DE 6.50 usec
TE 293.0 K
D1 1.0000000 sec
D11 0.0300000 sec
TDO 1

===== CHANNEL f1 =====
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P1 8.75 usec
PL1 -2.00 dB
PL1W 56.53121948 W
SFO1 100.624389 MHz

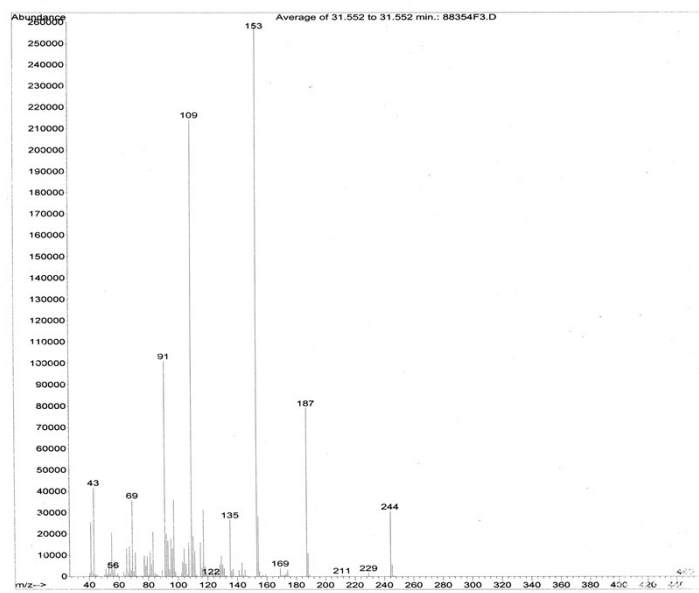
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CHOPRG2 waltz16
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PL2 -1.00 dB
PL12 14.50 dB
PL13 14.50 dB
PL2W 10.56200495 W
PL12W 0.28767781 W
PL13W 0.28767781 W
SFO2 400.1314005 MHz
SI 32768
SF 100.6127652 MHz
MDW 0
SSB 0
LB 1.00 Hz
GB 0
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S Fig. 23  $^{13}\text{C}$  NMR spectrum (75 MHz) of compound 18

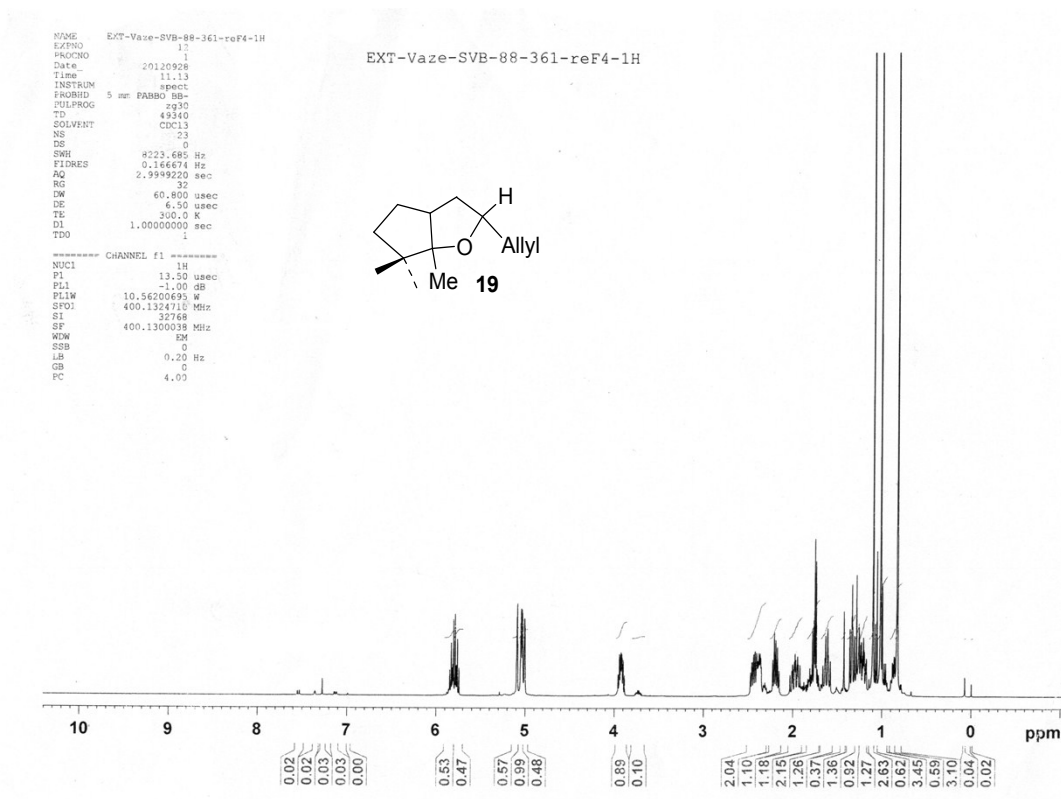
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Vial Number : 4



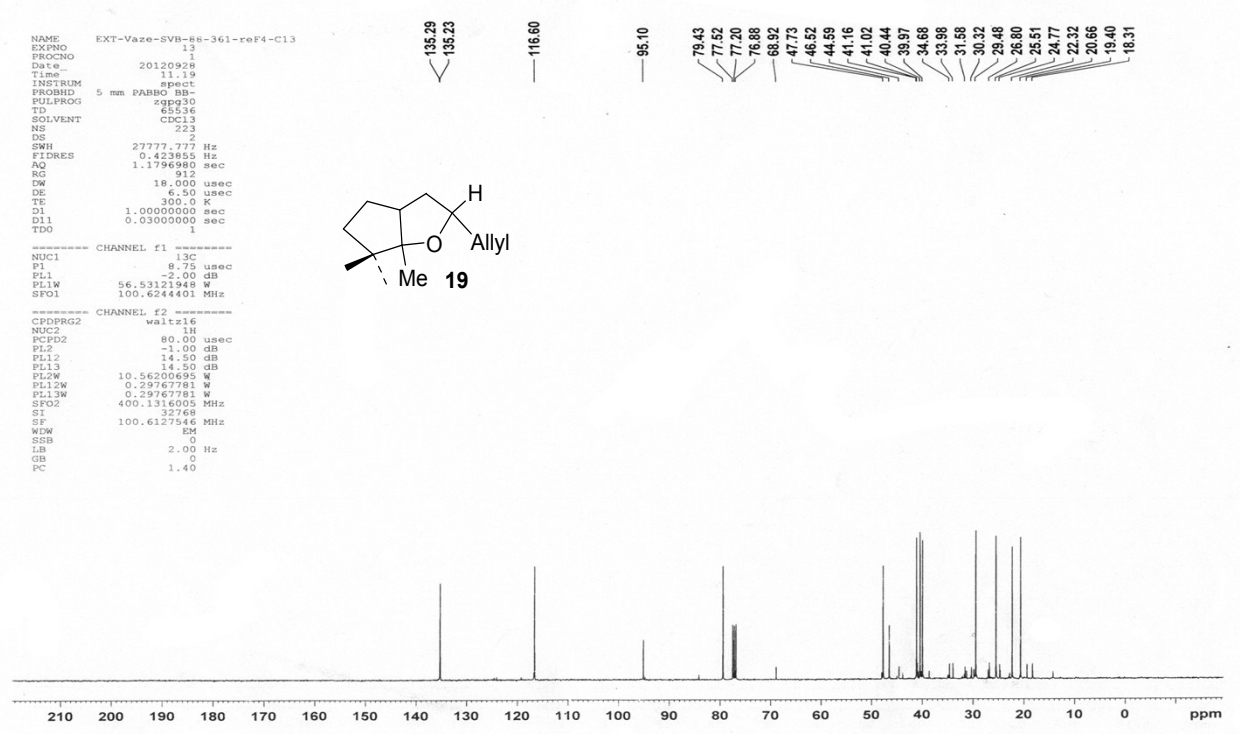
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Instrument : MS5973N  
Sample Name : 88-354F3 F12, PDCT MOL WT-244  
Misc Info : FROM R&D, 9/07/2012  
Vial Number : 4



**S Fig. 24** GC-MS spectrum of compound 18

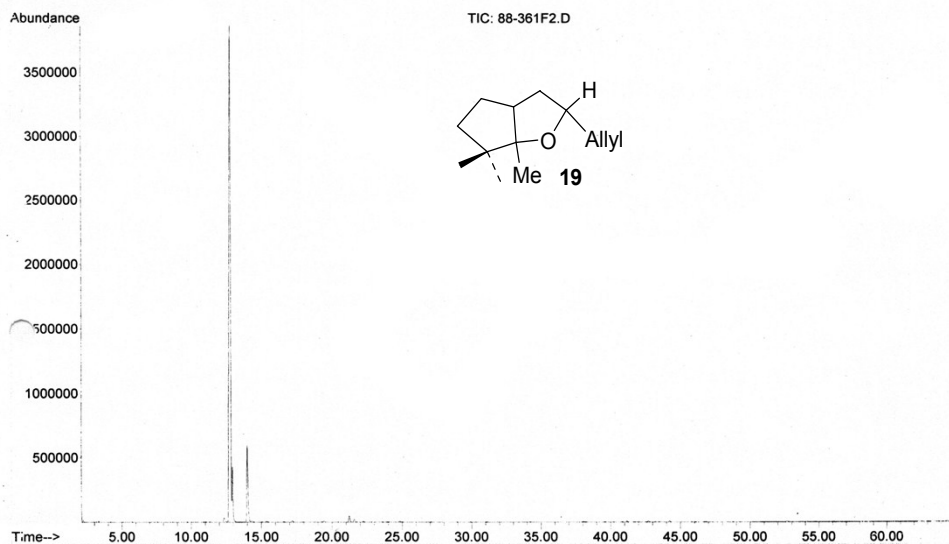


S Fig. 25 <sup>1</sup>H NMR spectrum (400 MHz) of compound 19

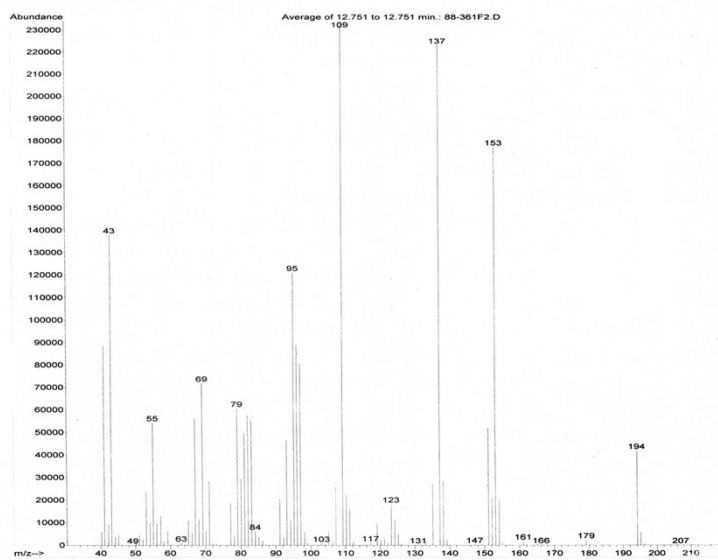


**S Fig. 26** <sup>13</sup>C NMR spectrum (100 MHz) of compound **19**

File : C:\MSDCHEM\1\DATA\88-361F2.D  
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 Instrument : MS5973N  
 Sample Name : 88-361-F2, PDCT MOL WT-194  
 Misc Info : FROM R&D, 8/8/2012  
 Vial Number : 36

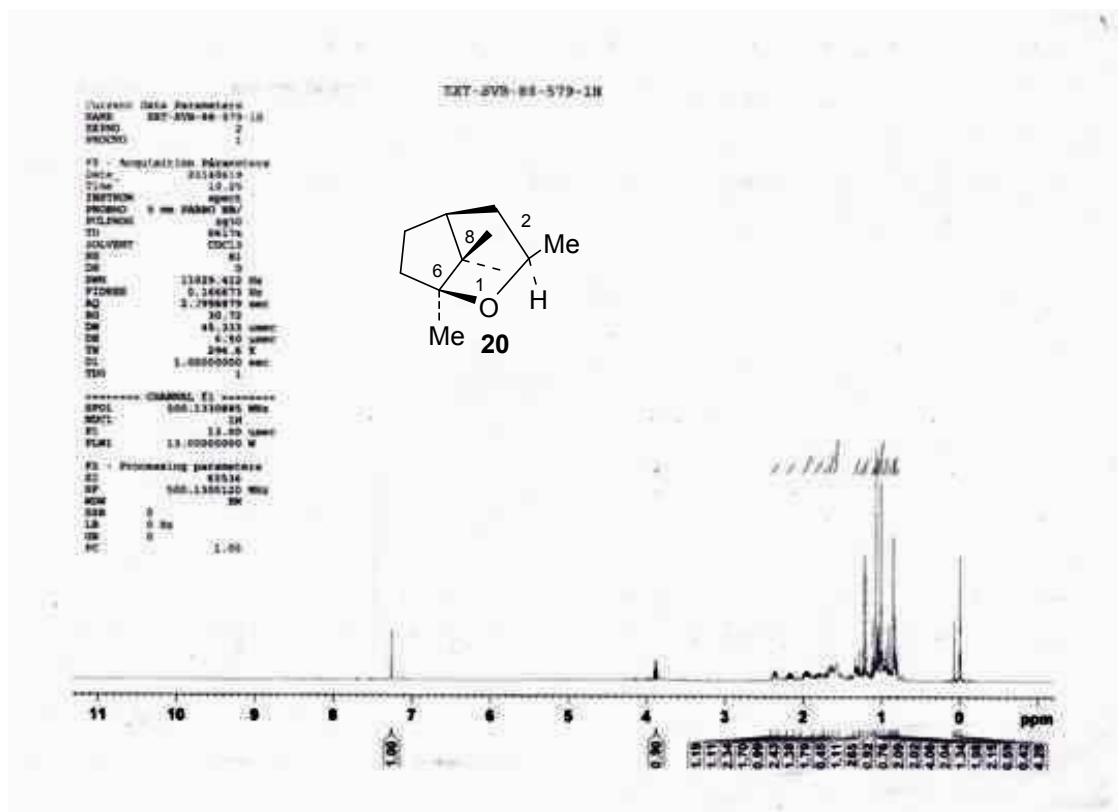


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 Operator :  
 Acquired : 8 Aug 2012 17:50 using AcqMethod PERF  
 Instrument : MS5973N  
 Sample Name : 88-361-F2, PDCT MOL WT-194  
 Misc Info : FROM R&D, 8/8/2012  
 Vial Number : 36



**S Fig. 27** GC-MS spectrum of compound 19



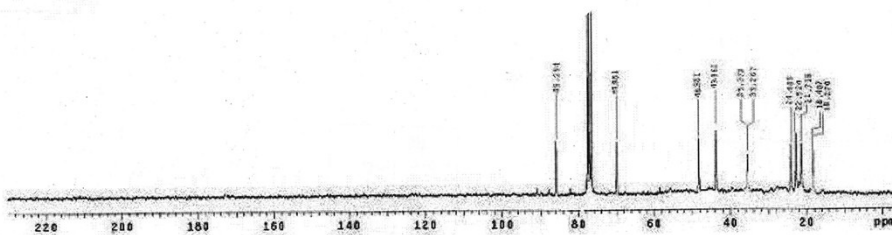
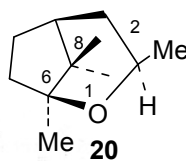


S Fig. 28 <sup>1</sup>H NMR spectrum (400 MHz) of compound 20

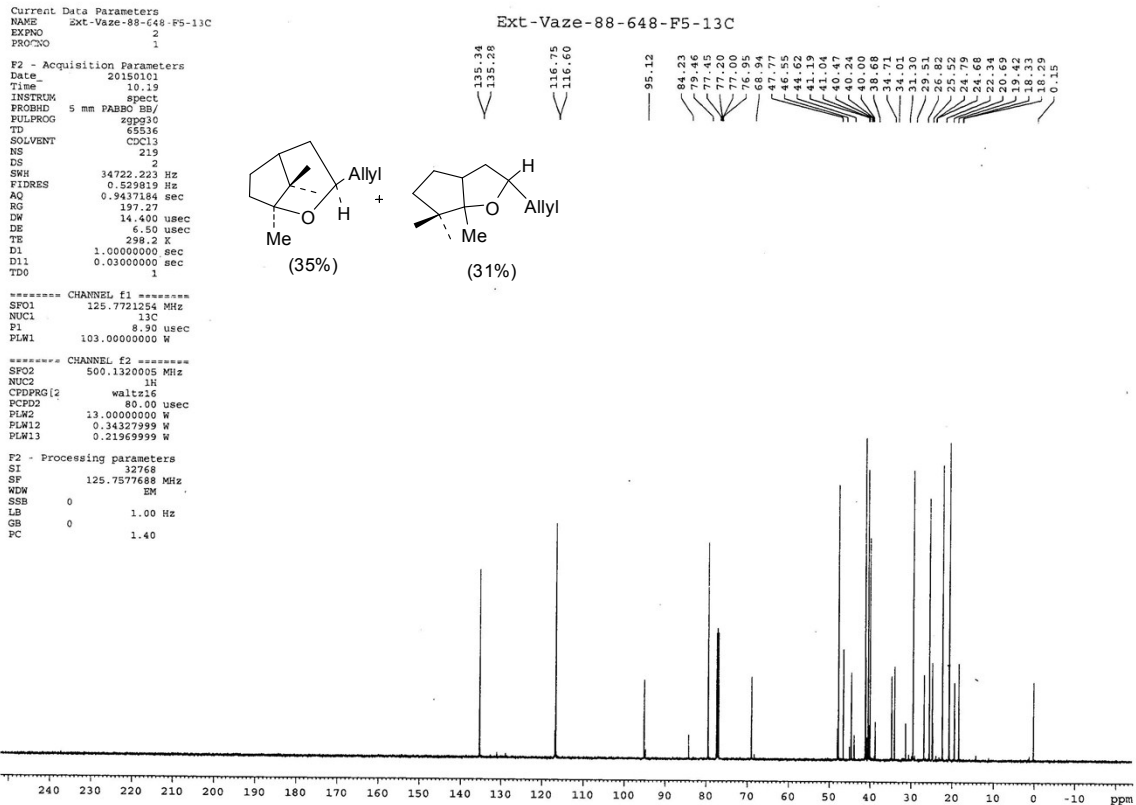
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  dsf  11390  mw  0h

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S Fig. 29 <sup>13</sup>C NMR spectrum (100 MHz) of compound 20



**S Fig. 30**  $^{13}\text{C}$  NMR spectrum (125 MHz) of mixture of 2-Allyl-6,6,6a-trimethyl-hexahydrocyclopenta(b)furan **19** and 2-Allyl-6,8,8-trimethyl-1-oxabicyclo[3.2.1]octane, (3:1 mixture)







