Electronic Supplementary Information (ESI)

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

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30	**19**	^{1}H NMR
31	**19**	^{13}C NMR
32	**19**	GC-MS
33	**20**	^{1}H NMR
34	**20**	^{13}C NMR
35	**19** and **21** Inseparable mixture	^{13}C NMR

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. ^{1}H NMR spectra were recorded on Varian spectrometers at 300, 400 and MHz and ^{13}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^{+}) 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_2SO_4. 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).

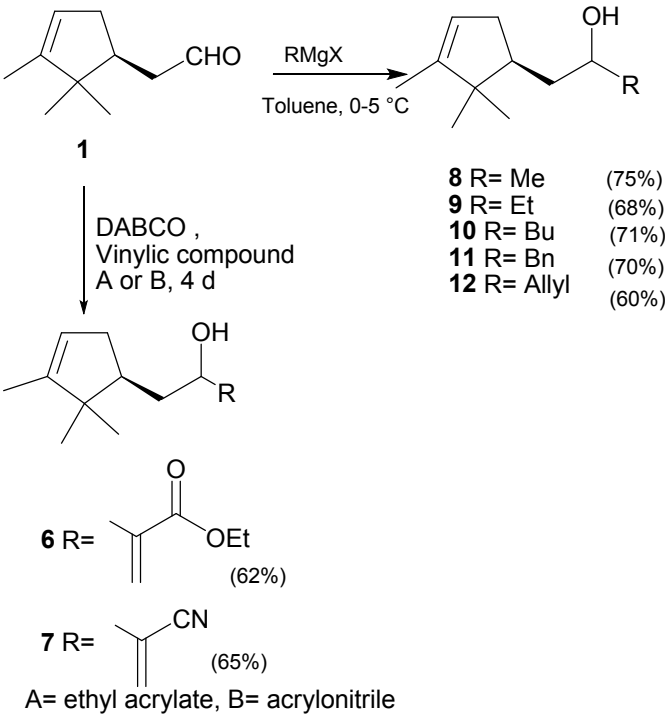
General procedure for the synthesis of (1'*S*)-campholenic alcohols 8-12

To a stirred solution of freshly prepared Grignard reagent (80 mmol) in toluene (10 mL) cooled at 5^{o}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^{o}C for 2-4 h. Reaction was monitored by TLC. The reaction was quenched with saturated aqueous NH_4Cl solution (20 mL). The aqueous layer was extracted with toluene. The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. 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).[10]

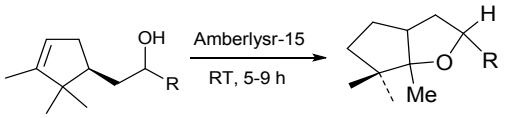
General procedure for the synthesis of 2-substituted 6,6,6a-trimethyl-hexahydrocyclopenta(b)furan derivatives 13-19

To a stirred solution of (1'*S*)-campholenic alcohols **6-12** (0.06 mol) in dry toluene (25 mL) Amberlyst-15® (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-oxabiclo[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-oxabiclo[3.2.1]octane **20** (Scheme 3 **)**.

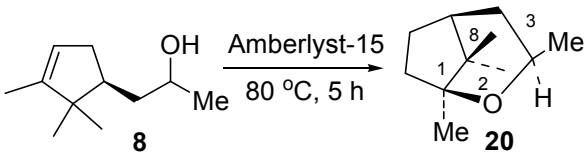


Scheme 1 Synthesis of (1'*S*)-campholenic alcohols



6-12 **13-19**

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

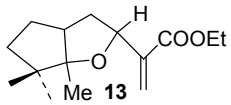
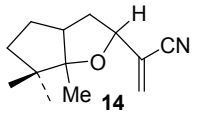
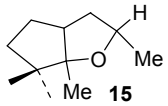
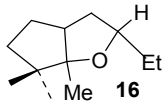
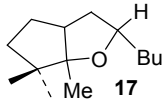
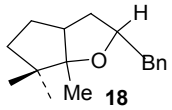
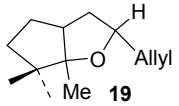


8 **20**

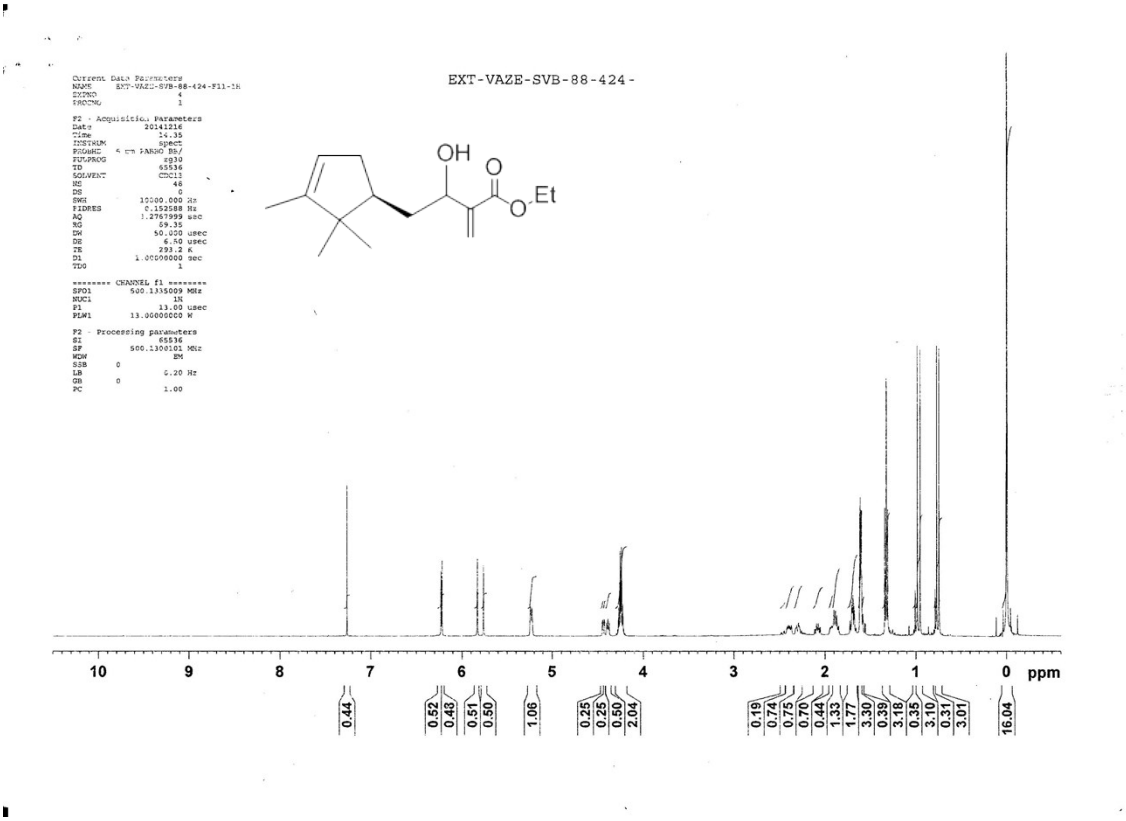
Scheme 3 Synthesis of 2,6,8,8-tetramethyl-1-oxabicyclo[3.2.1]octane

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

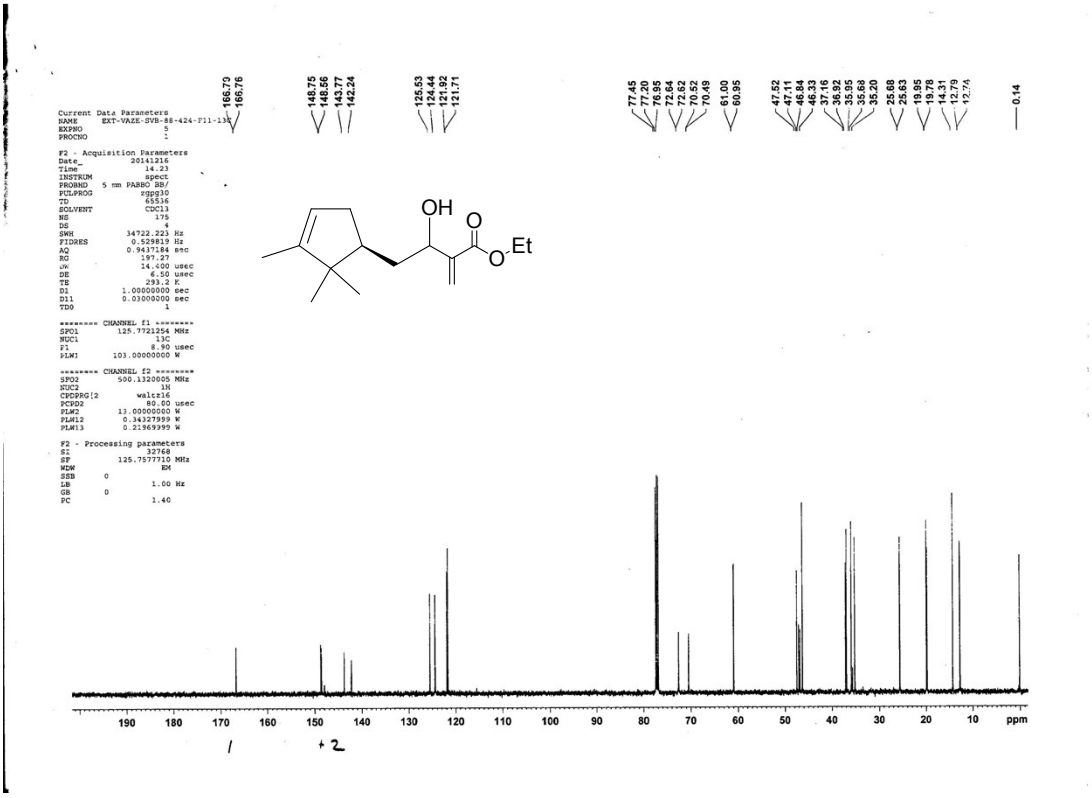
Reaction time and yields

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

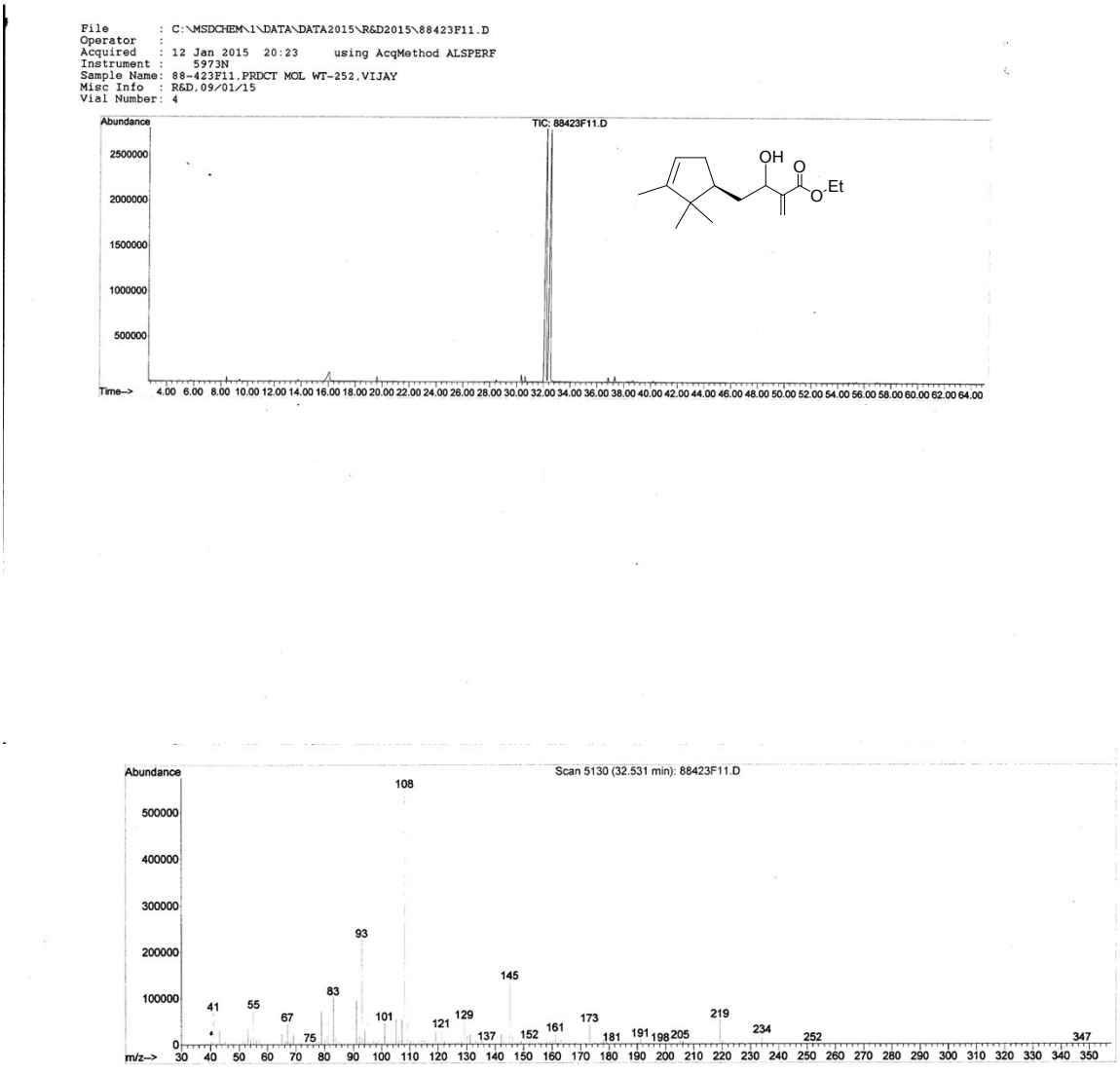
* Minor amount of formation of 3-substituted-1,8,8-trimethyl-2-oxabicyclo[3.2.1]octane (<10%) has been observed



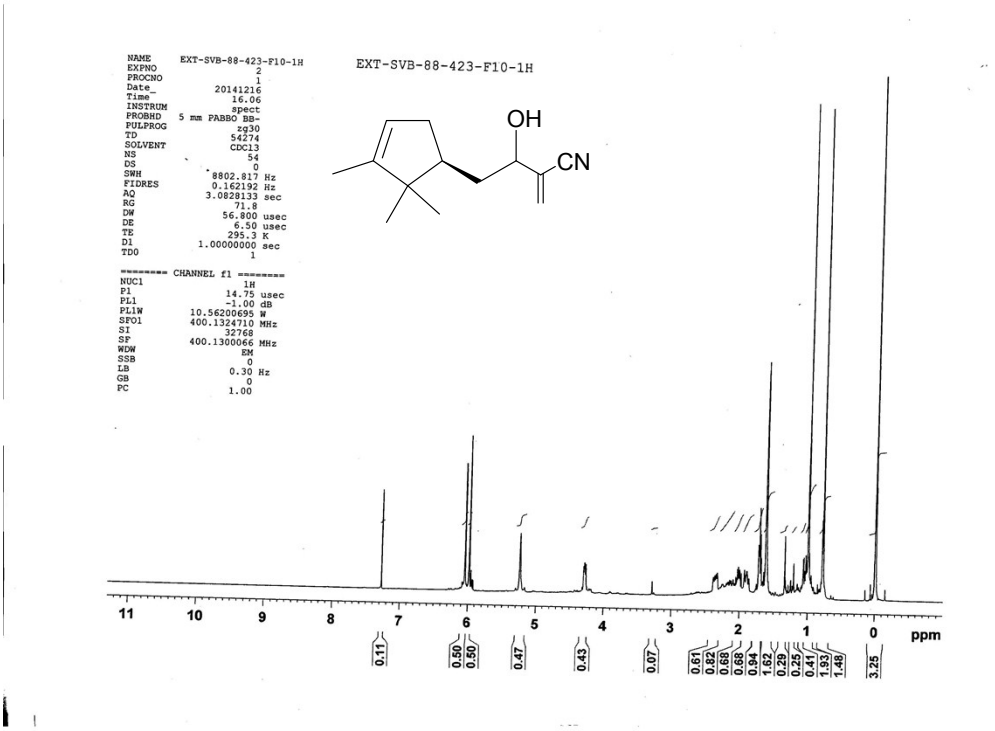
S Fig. 1 ^{1}H NMR spectrum (500 MHz) of compound **6**



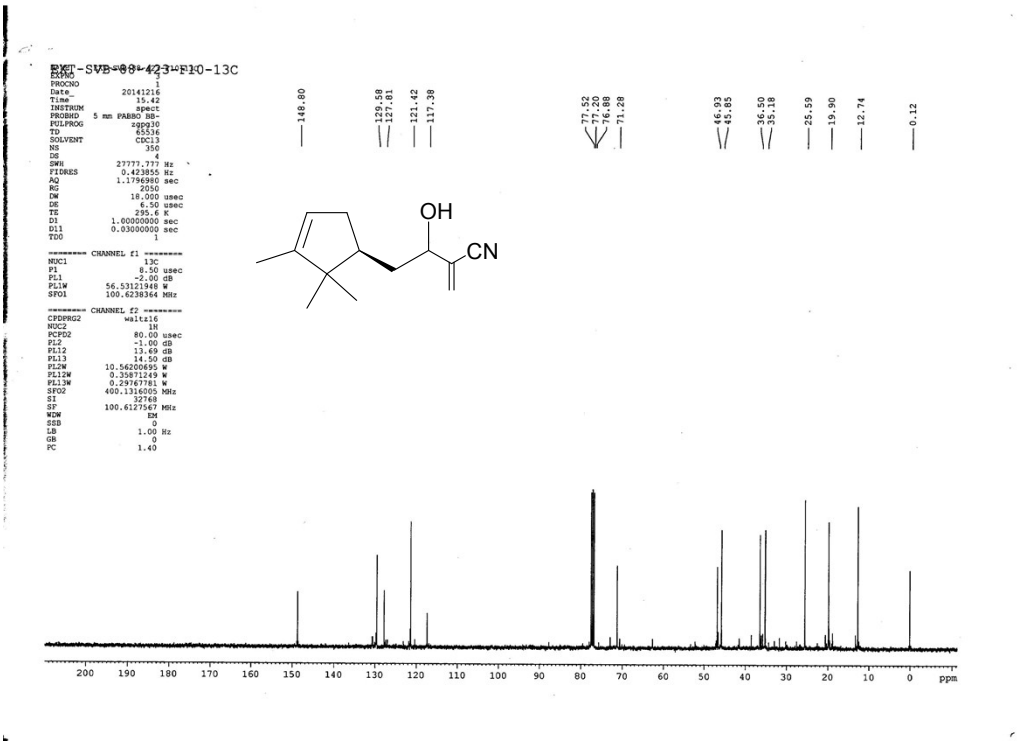
S Fig. 2 ^{13}C NMR spectrum (125 MHz) of compound **6**



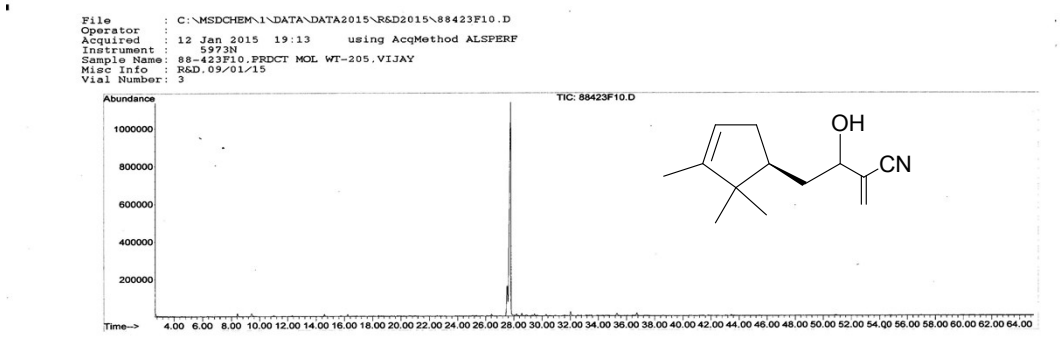
S Fig. 3 GC-MS spectrum of compound **6**

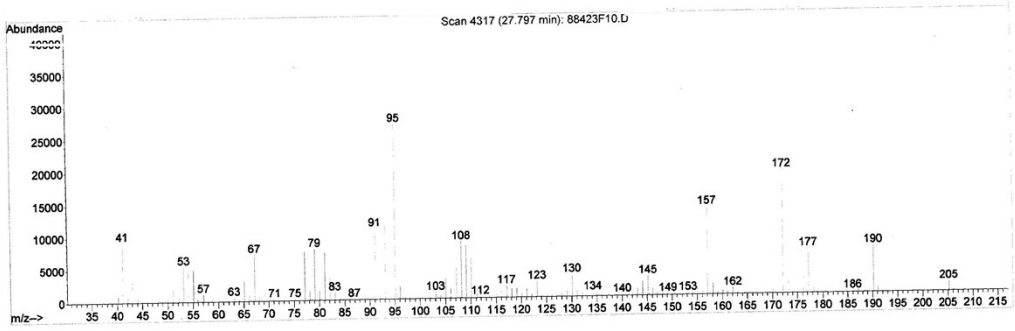


S Fig. 4 ^{1}H NMR spectrum (500 MHz) of compound **7**

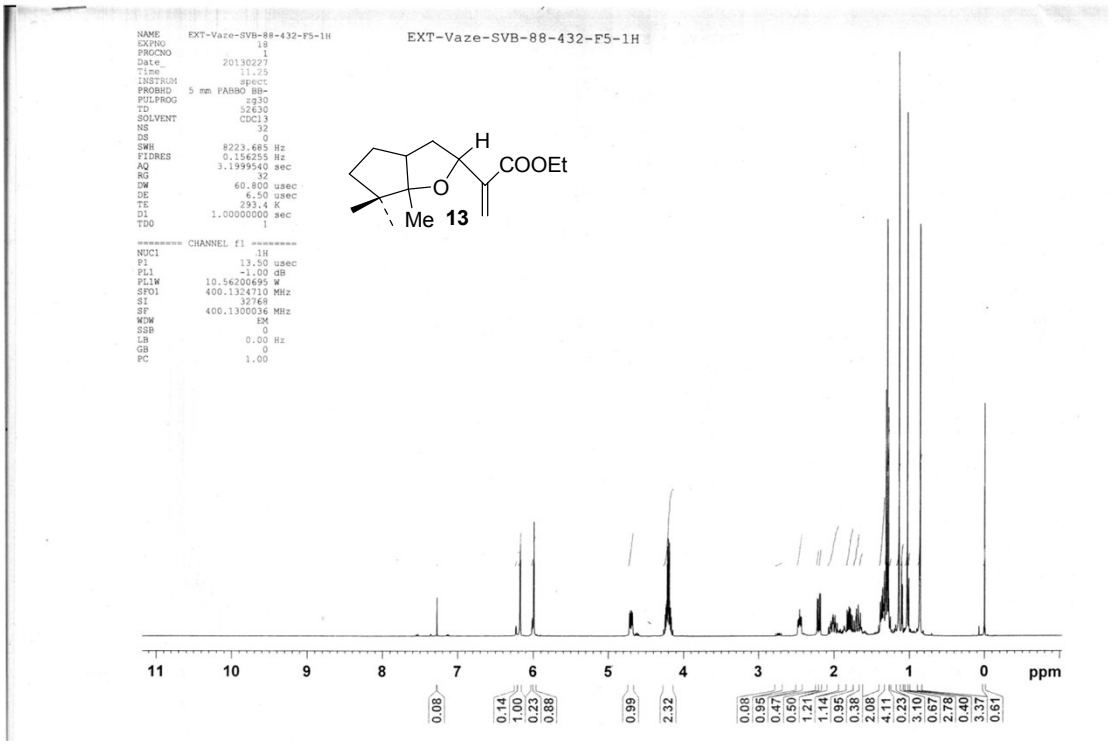


S Fig. 5 ^{13}C NMR spectrum (125 MHz) of compound **7**

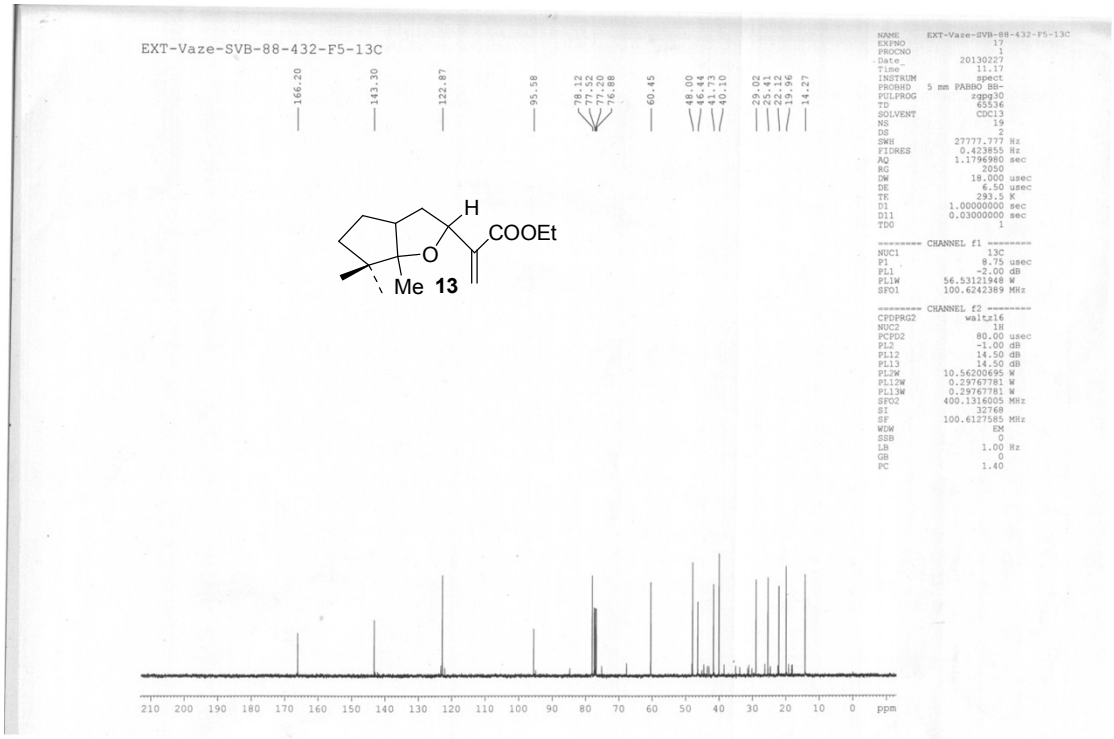




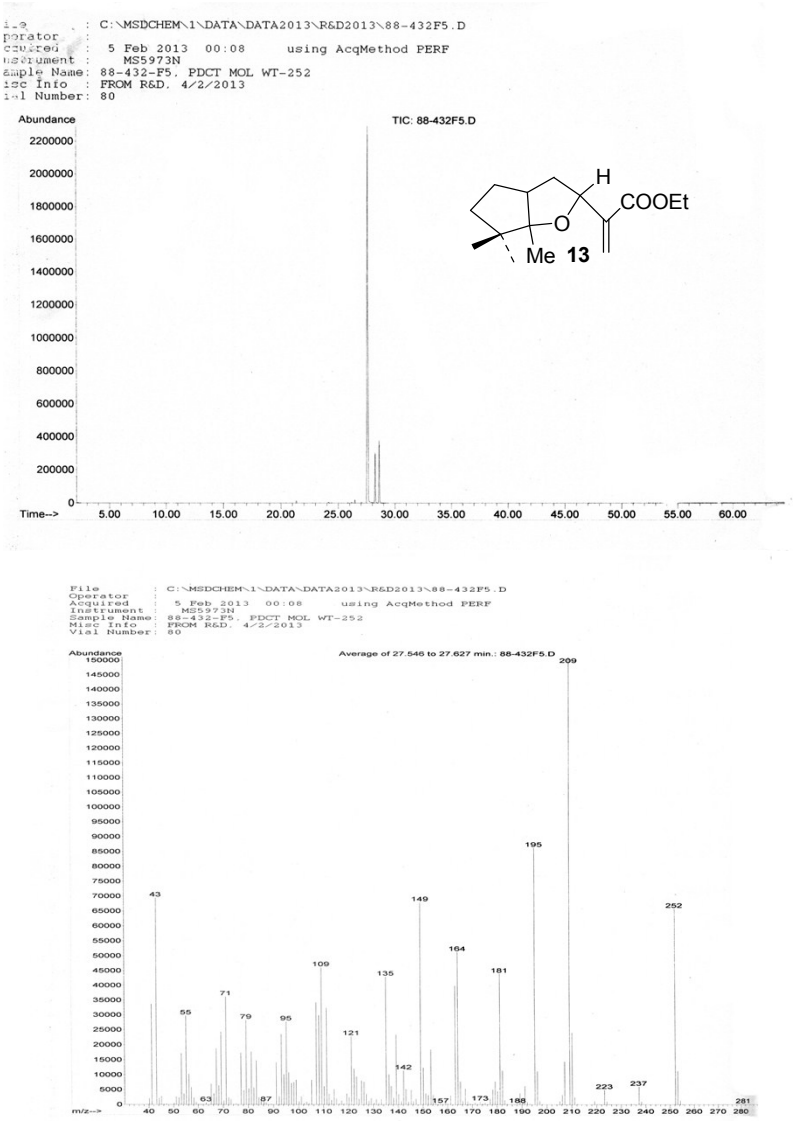
S Fig. 6 GC-MS spectrum of compound **7**



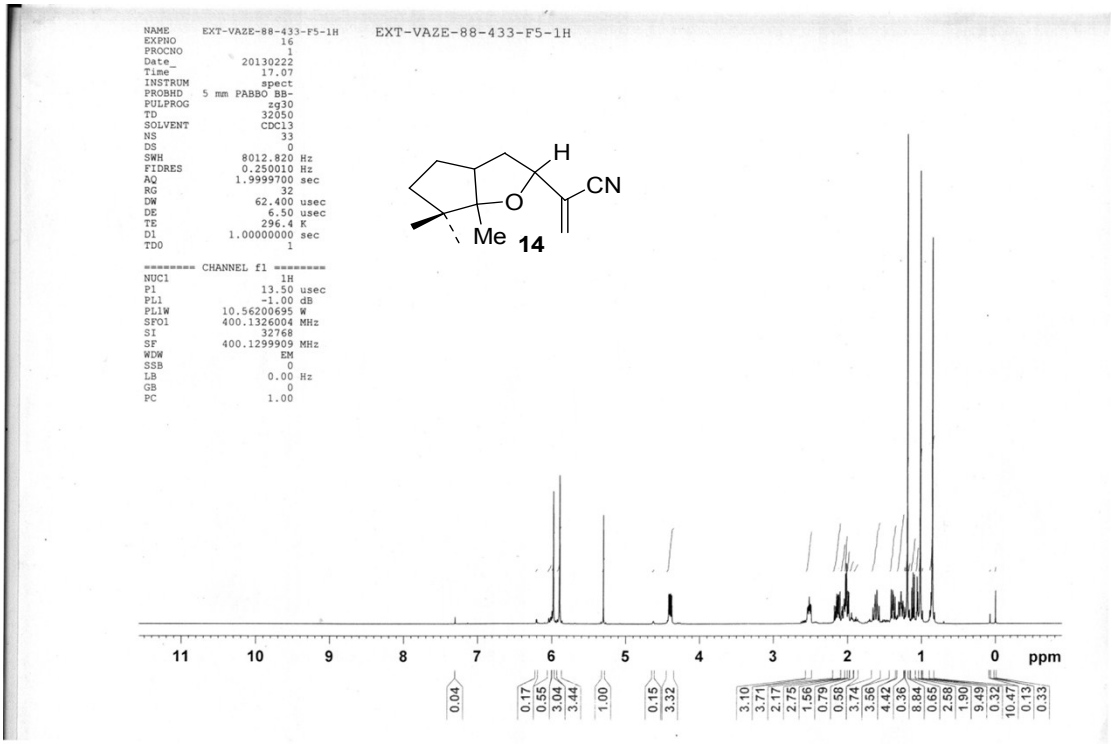
S Fig. 7 ^{1}H NMR spectrum (400 MHz) of compound **13**



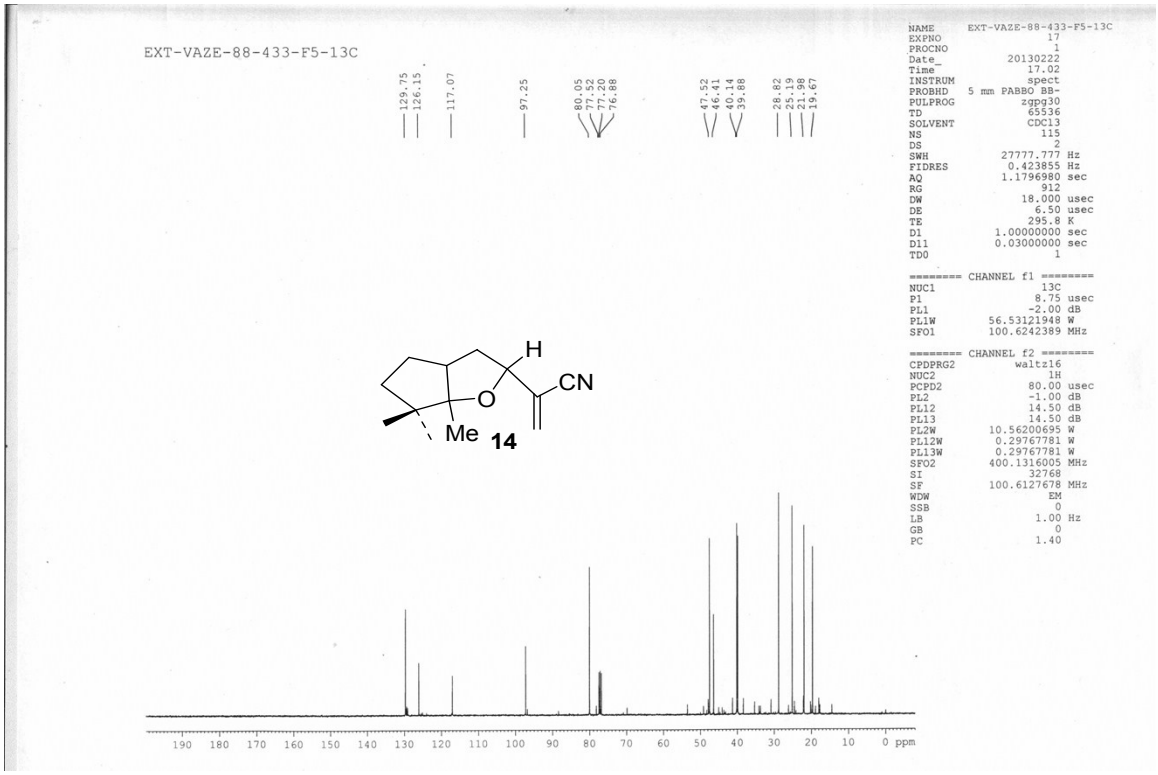
S Fig. 8 ^{13}C NMR spectrum (100 MHz) of compound **13**



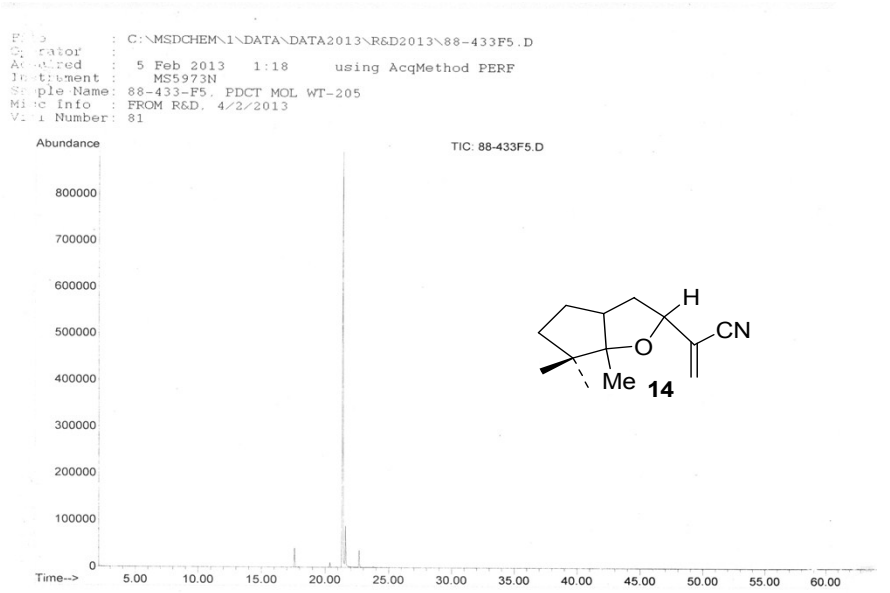
S Fig. 9 GC-MS spectrum of compound **13**

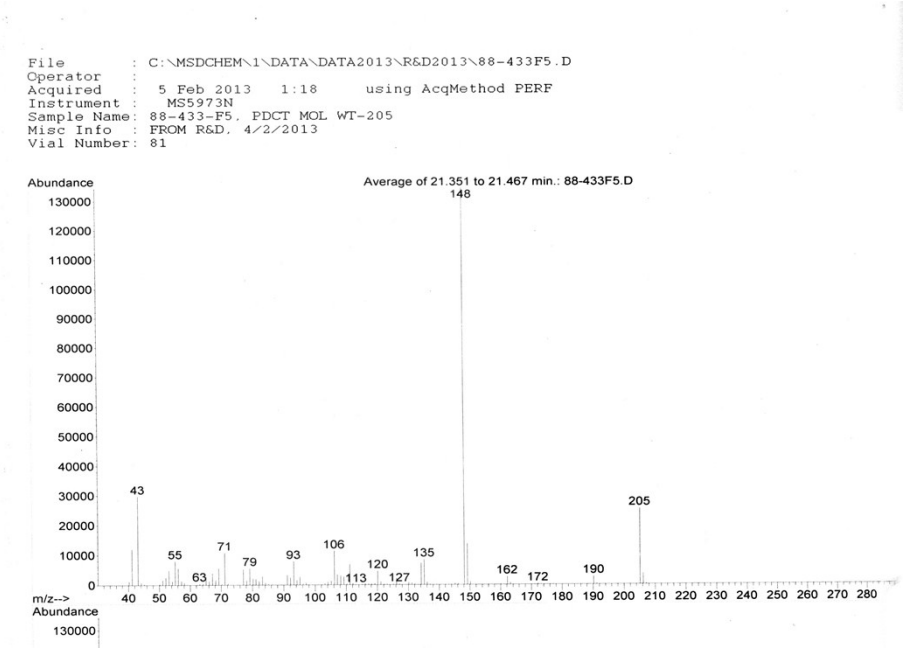


S Fig. 10 ^{1}H NMR (400 MHz) spectrum of compound **14**

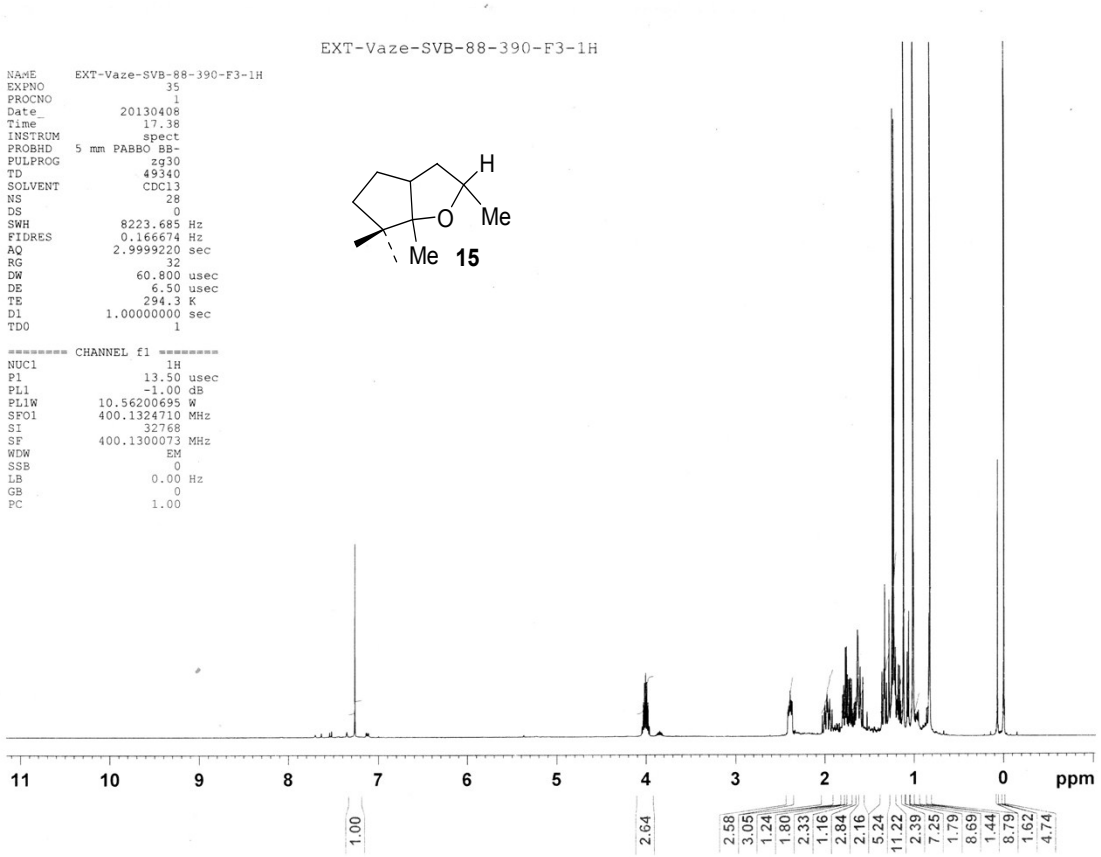


S Fig. 11 ^{13}C NMR spectrum (100 MHz) of compound **14**

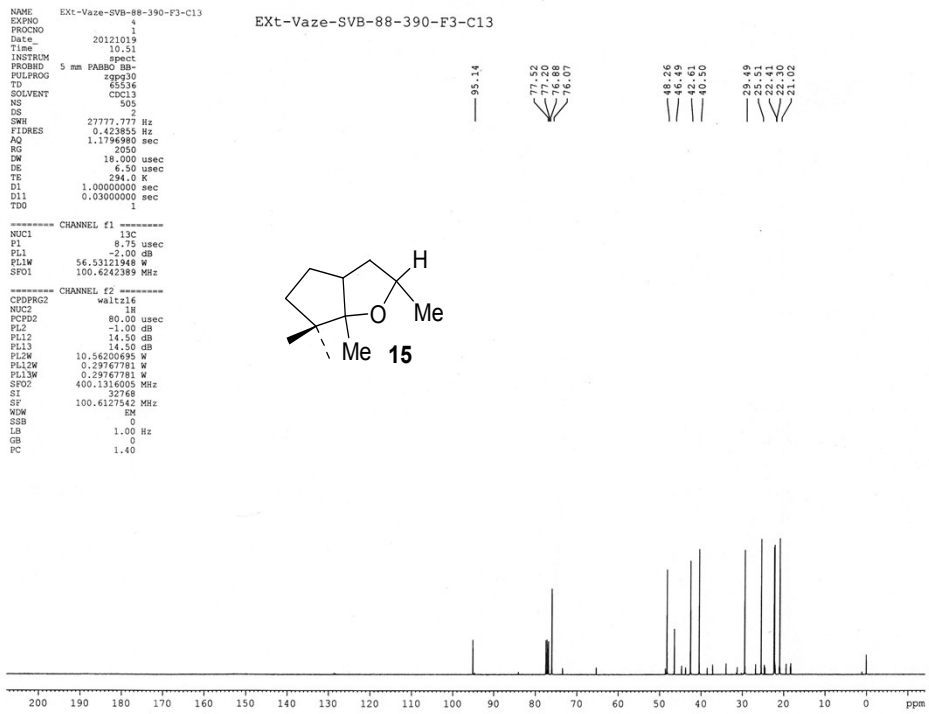




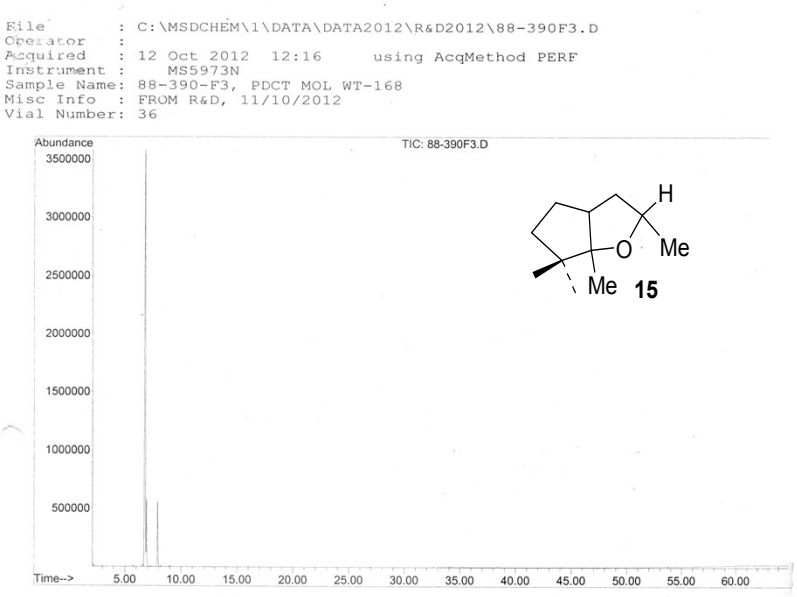
S Fig. 12 GC-MS spectrum of compound **14**

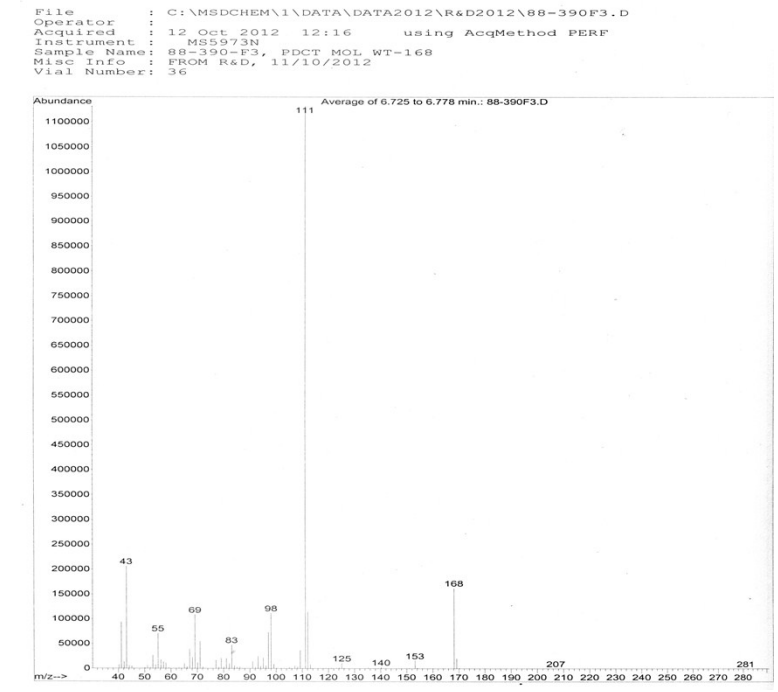


S Fig. 13 ^{1}H NMR spectrum (400 MHz) of compound **15**

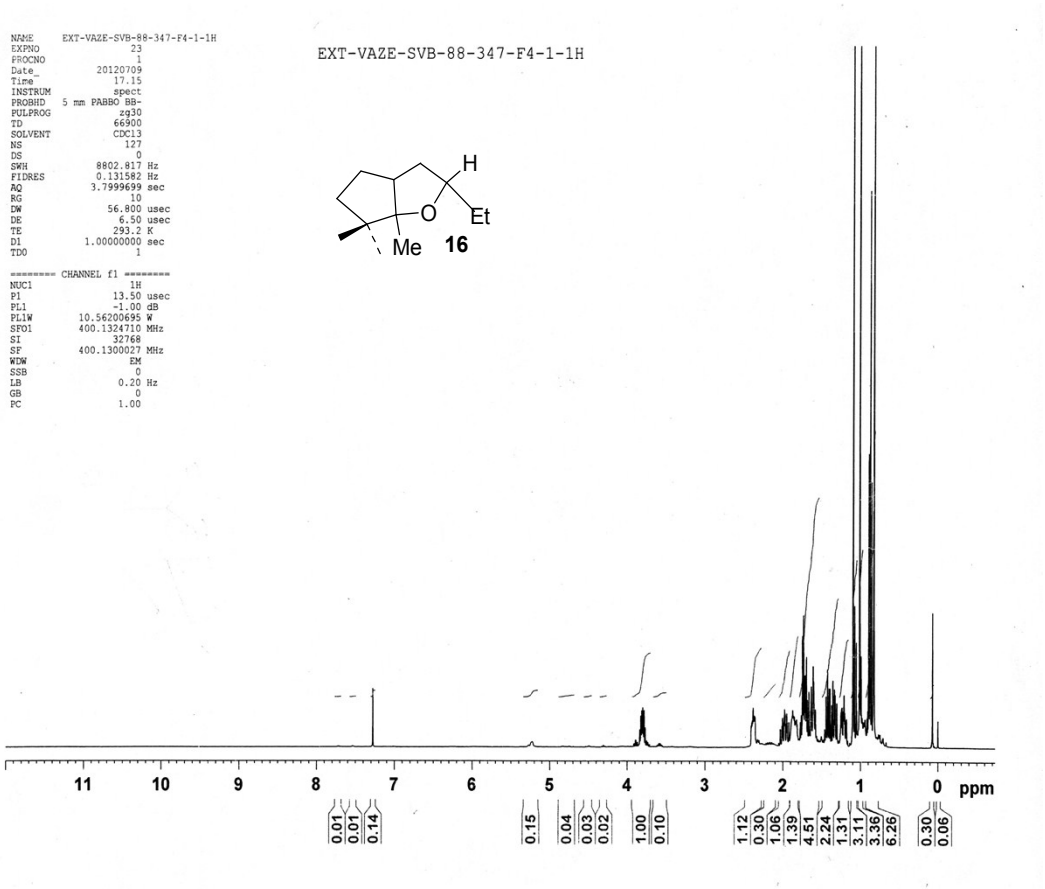


S Fig. 14 ^{13}C NMR spectrum (100 MHz) of compound **15**

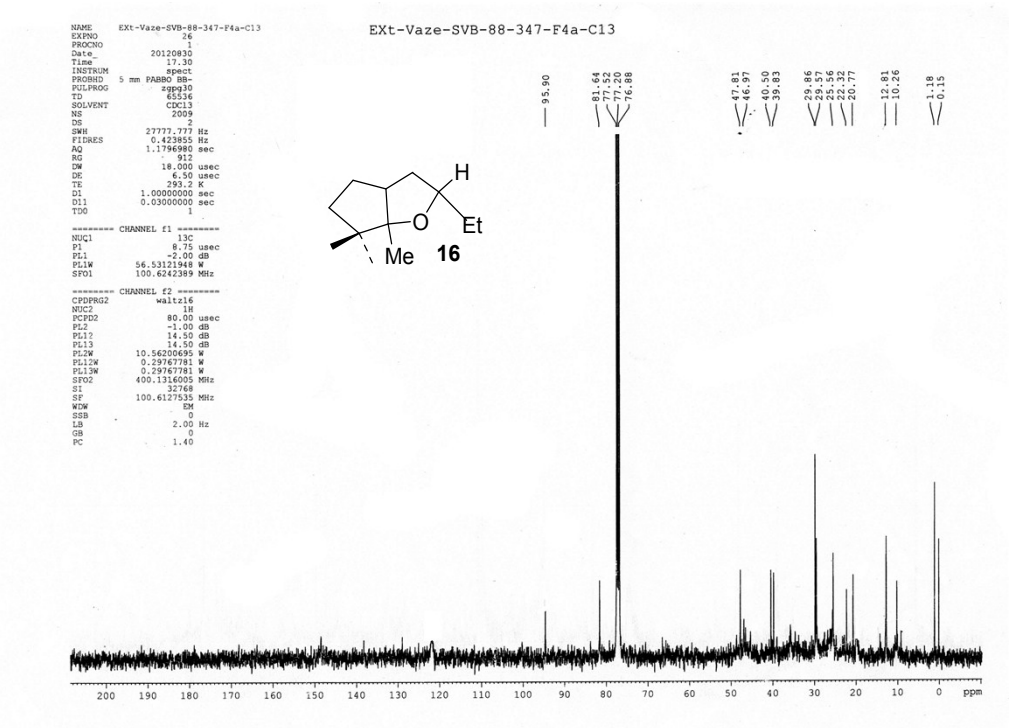




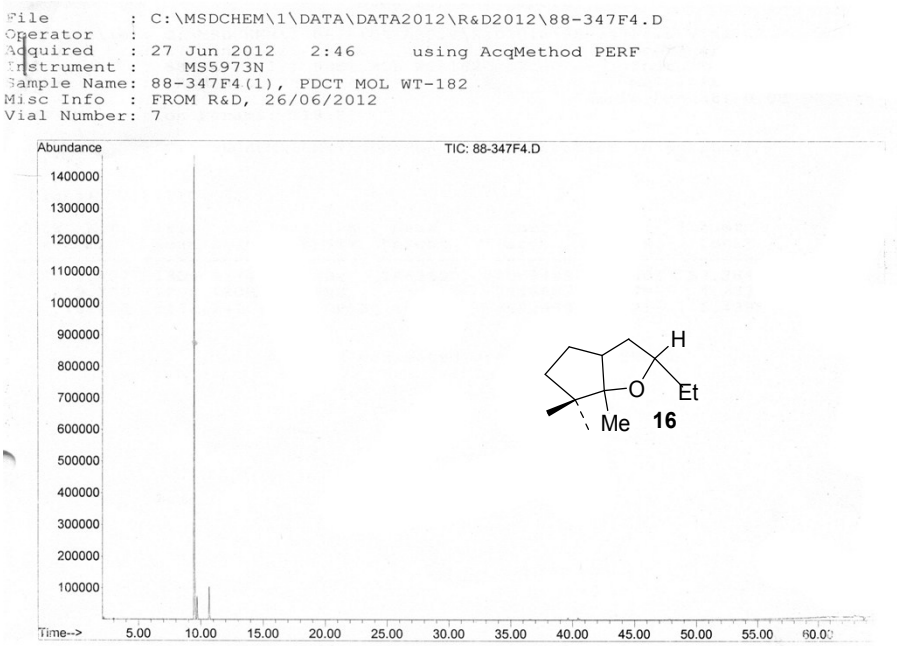
S Fig. 15 GC-MS spectrum of compound **15**

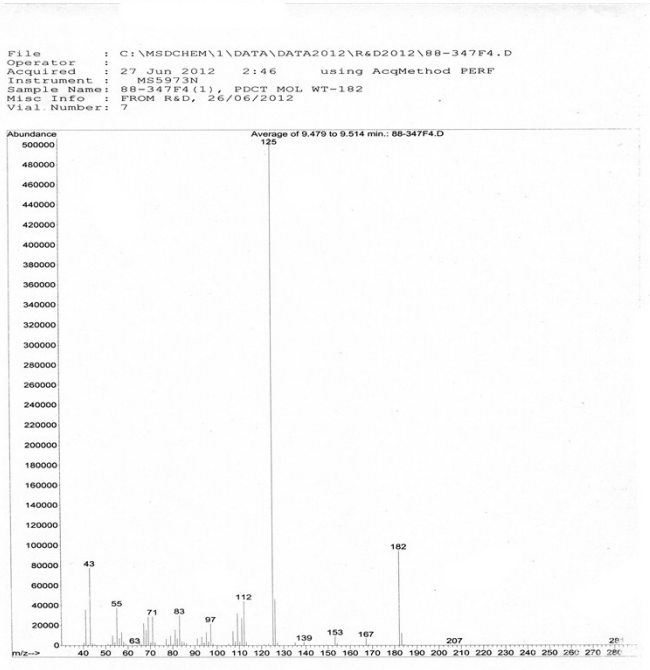


S Fig. 16 ^{1}H NMR spectrum (400 MHz) of compound **16**

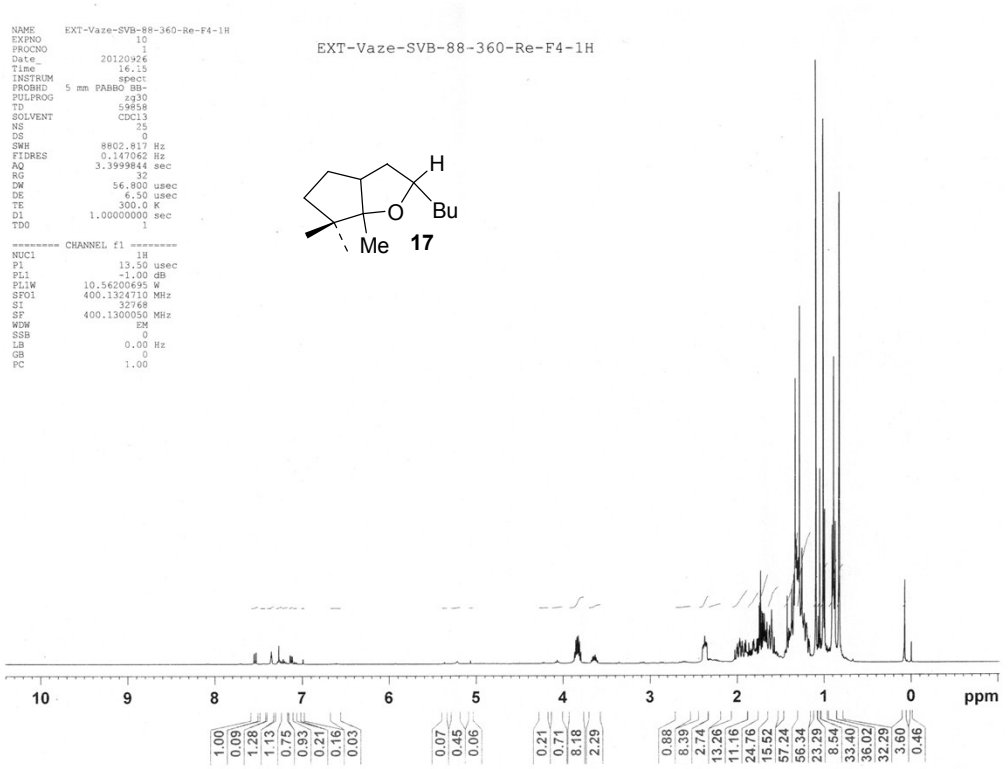


S Fig. 17 ^{13}C NMR spectrum (100 MHz) of compound **16**

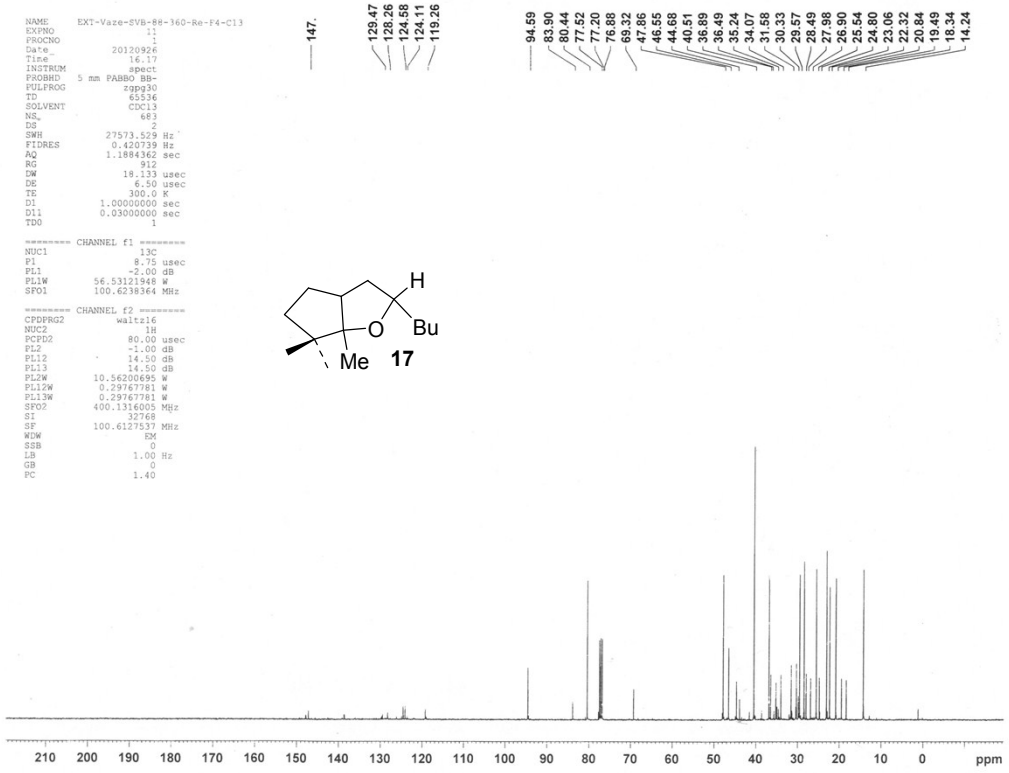




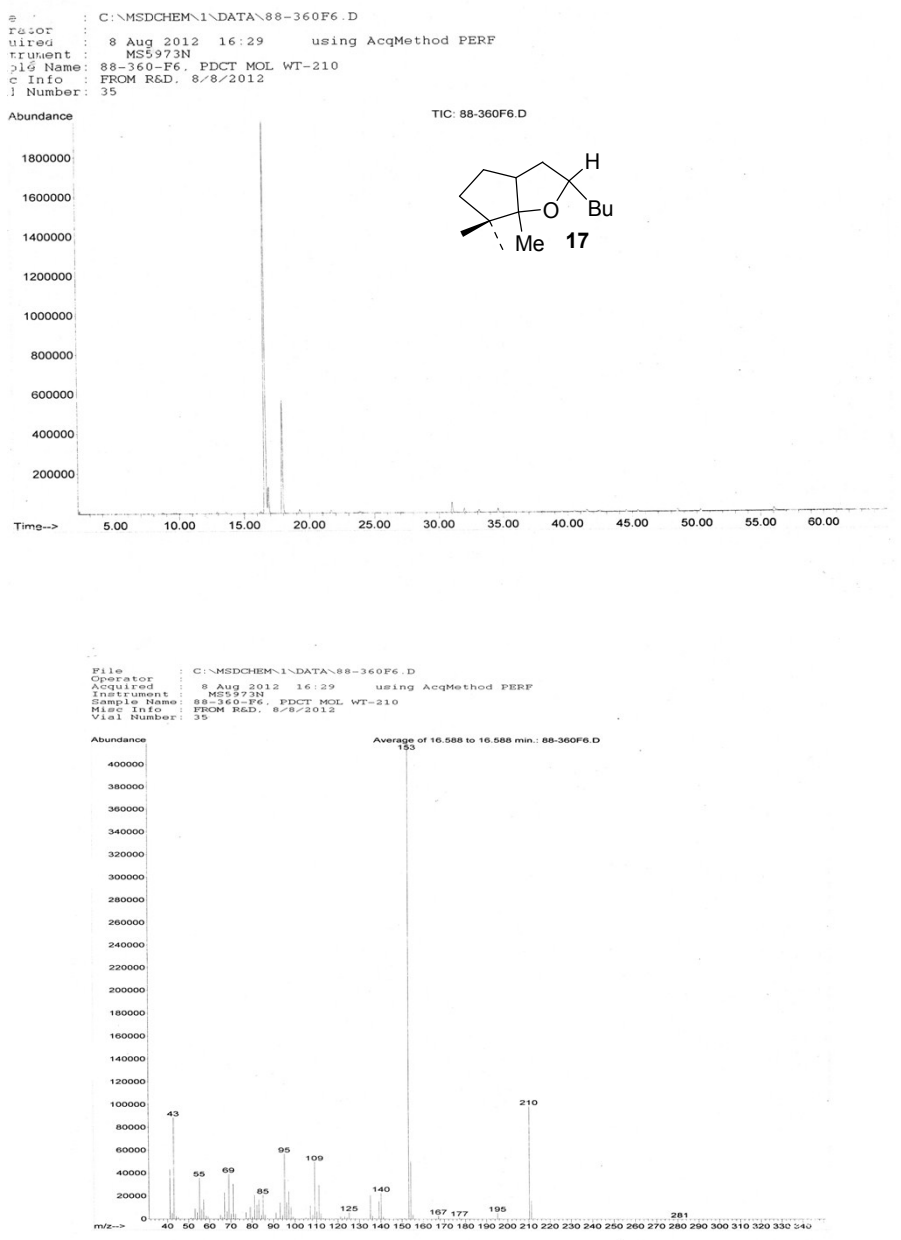
S Fig. 18 GC-MS spectrum of compound **16**



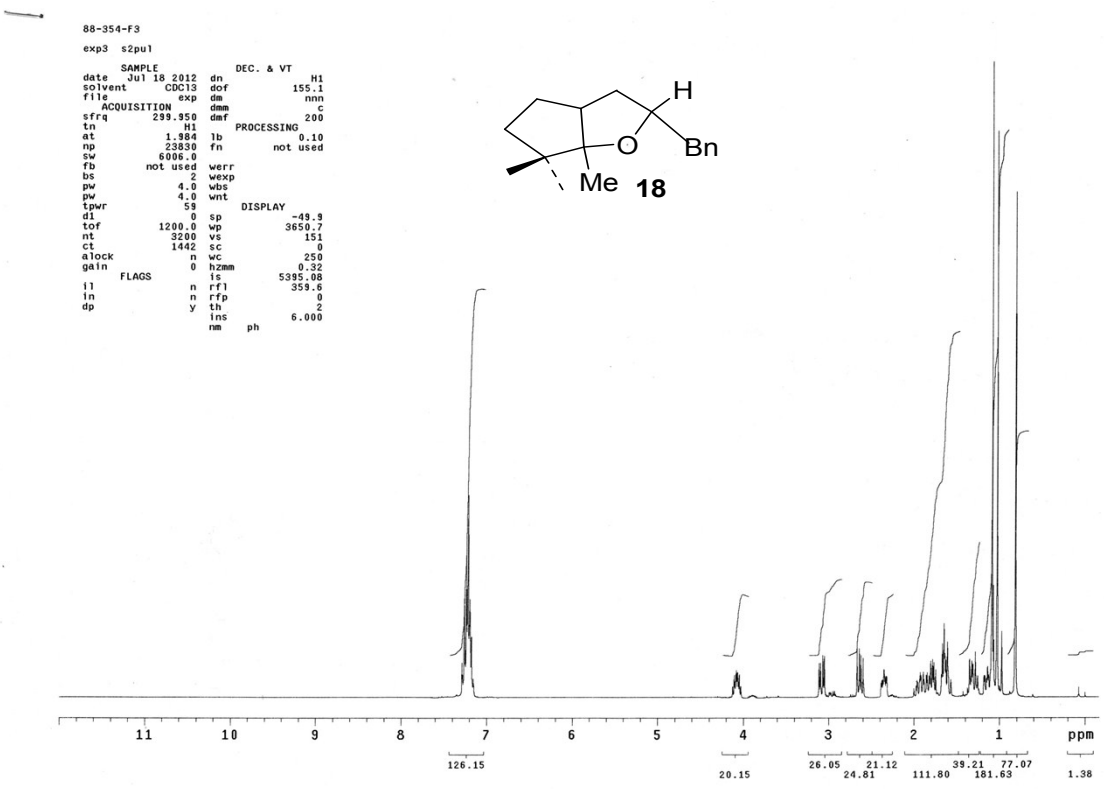
S Fig 19 ^{1}H NMR spectrum (400 MHz) of compound **17**



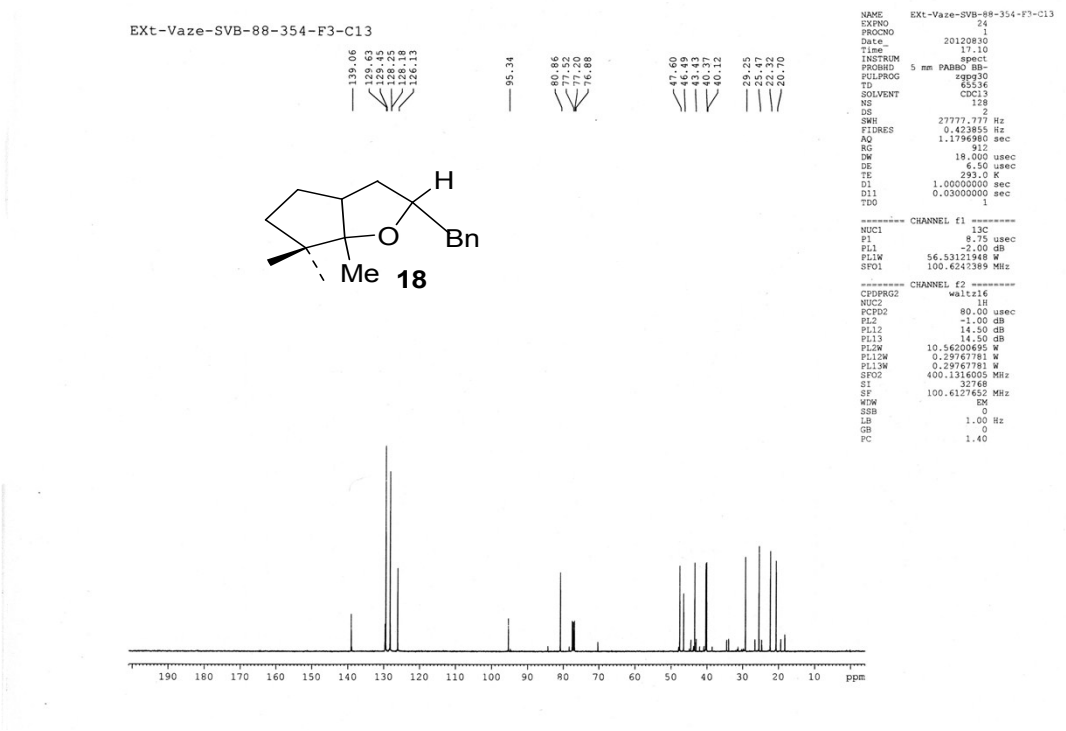
S Fig. 20^{13}C NMR spectrum (100 MHz) of compound **17**



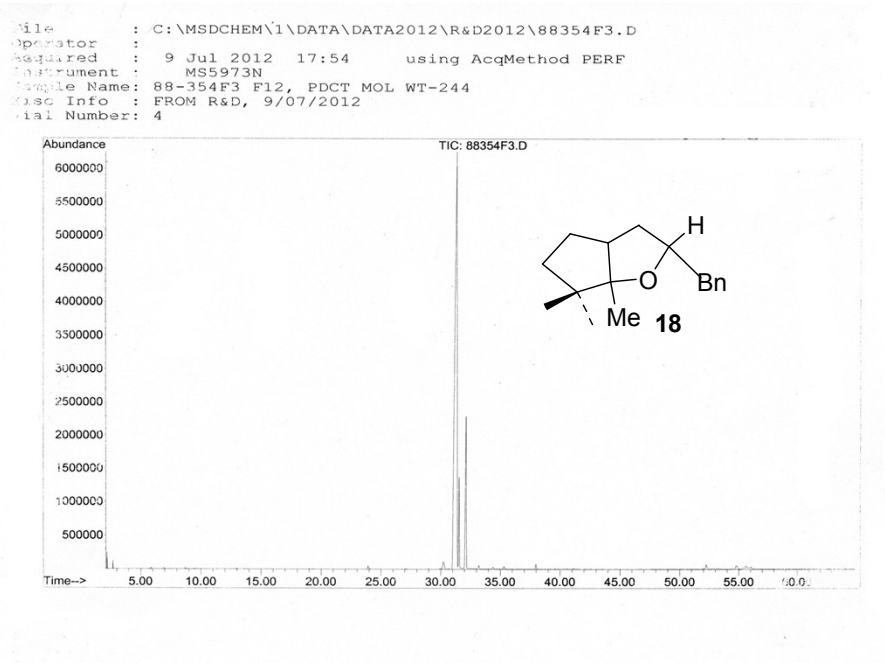
S Fig. 21 GC-MS spectrum of compound **17**

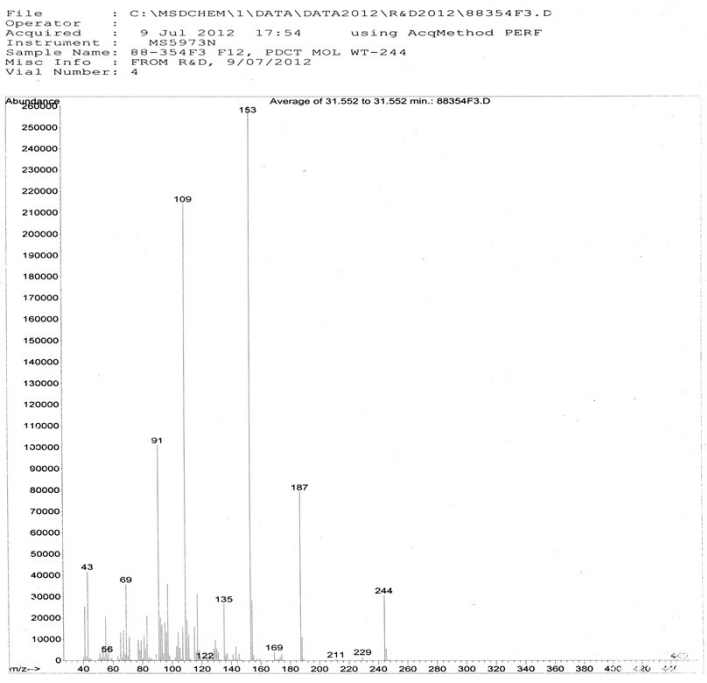


S Fig. 22 ^{1}H NMR spectrum (300 MHz) of compound **18**

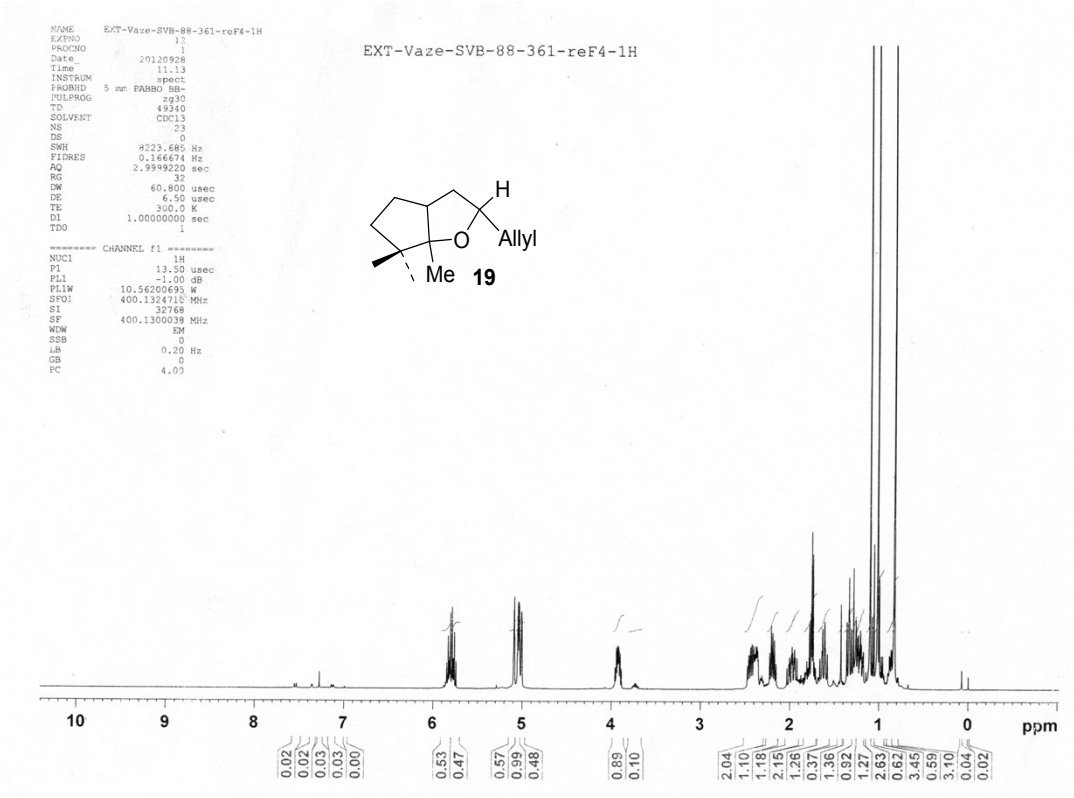


S Fig. 23 ^{13}C NMR spectrum (75 MHz) of compound **18**

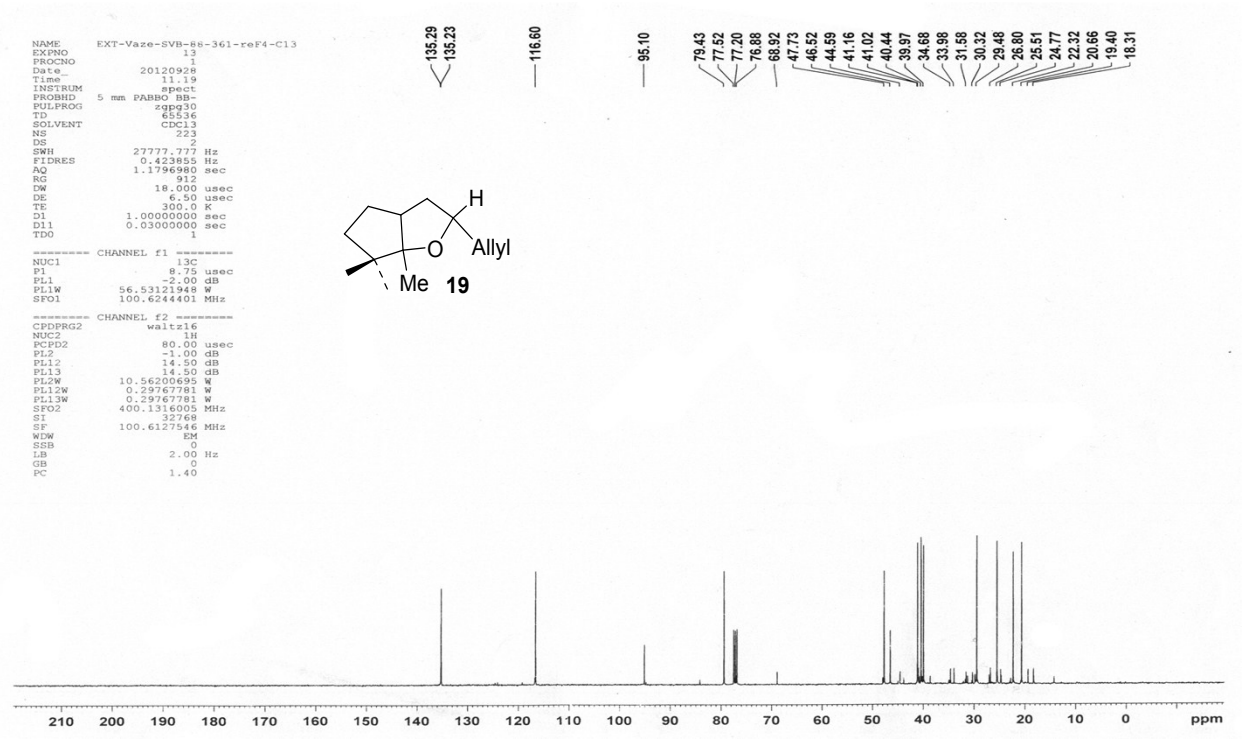




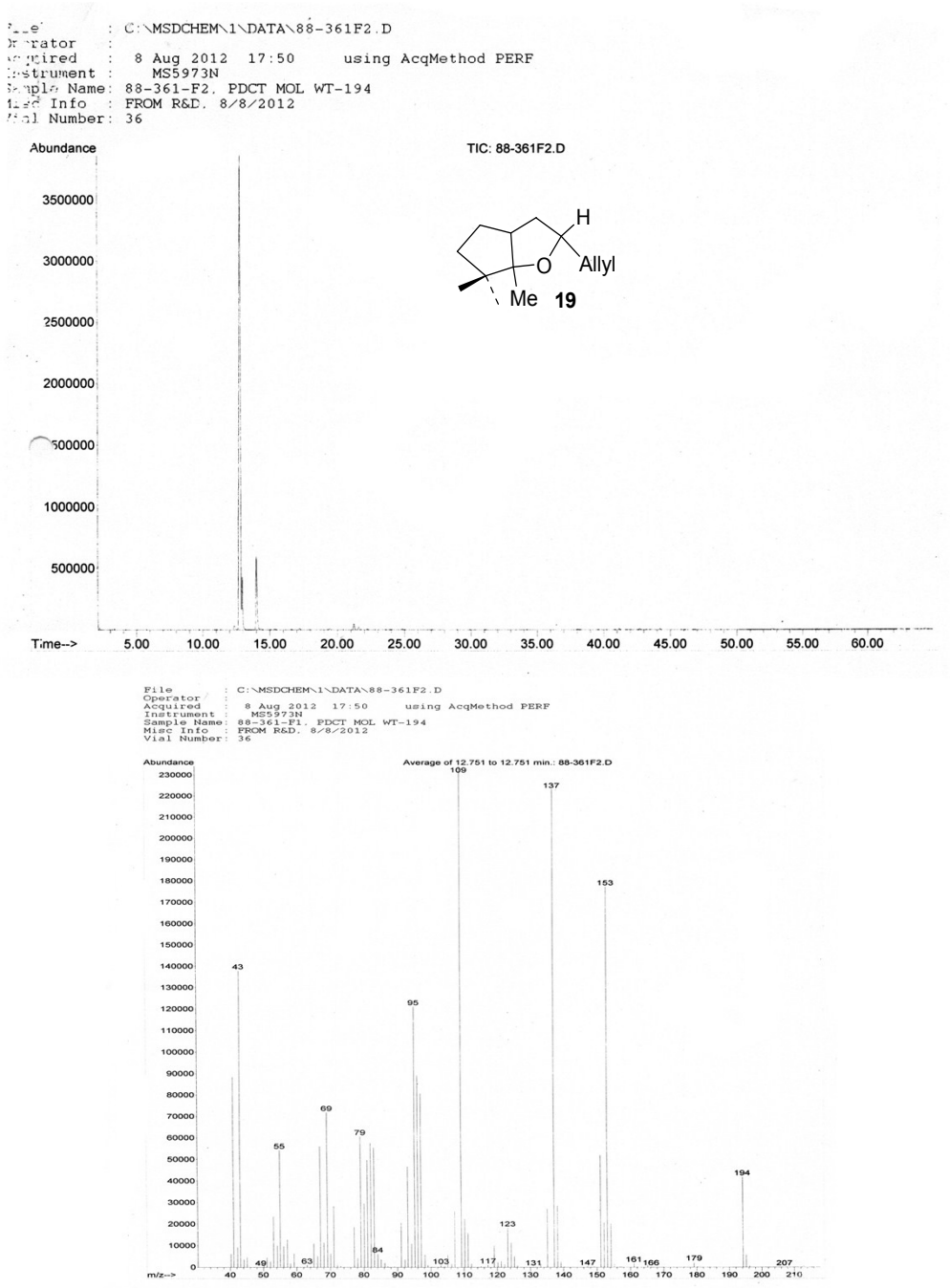
S Fig. 24 GC-MS spectrum of compound **18**



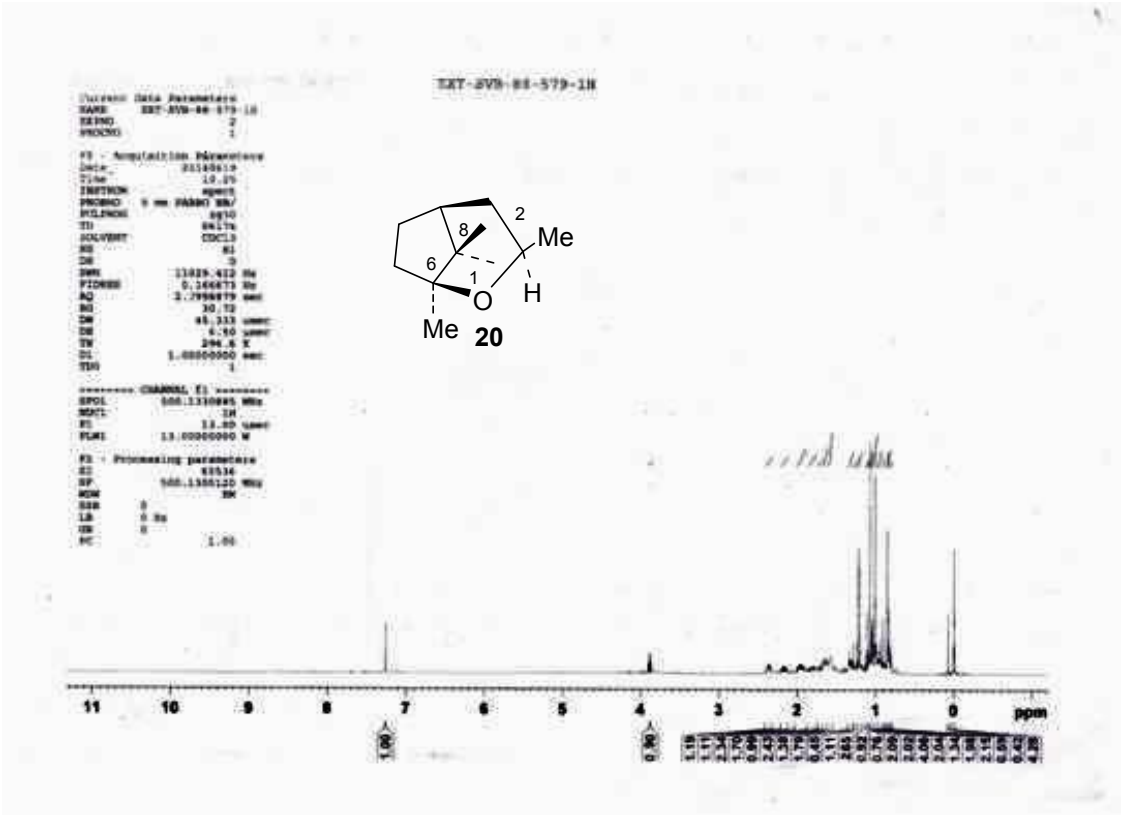
S Fig. 25 ^{1}H NMR spectrum (400 MHz) of compound **19**



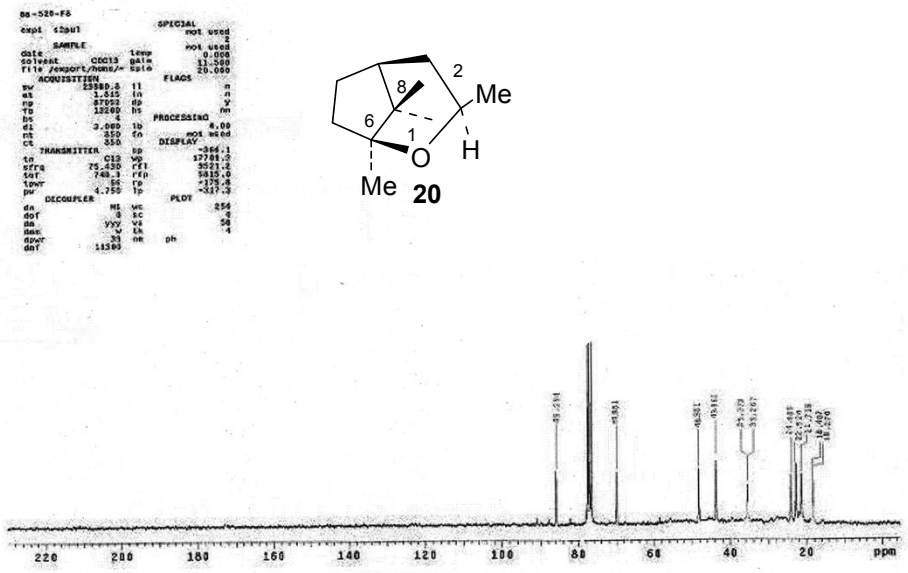
S Fig. 26 ^{13}C NMR spectrum (100 MHz) of compound **19**



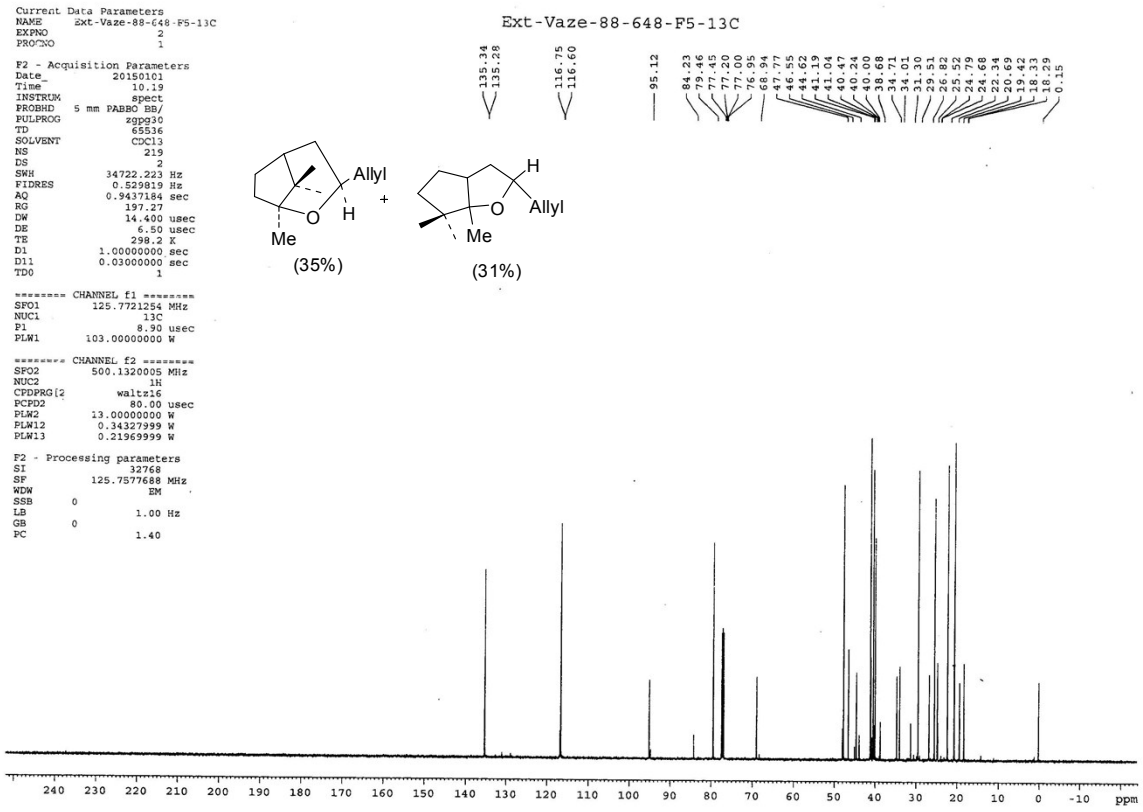
S Fig. 27 GC-MS spectrum of compound **19**



S Fig. 28 ^{1}H NMR spectrum (400 MHz) of compound **20**



S Fig. 29 ^{13}C NMR spectrum (100 MHz) of compound **20**



S Fig. 30 ^{13}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)