

## Supplementary Data

### Room Temperature Ionic Liquids: New Solvents for Schrock's Catalyst and Removal Using Polydimethylsiloxane Membranes

A. Lee Miller II and Ned B. Bowden

Department of Chemistry, University of Iowa, 423K Chemistry Building, Iowa City, Iowa 52242

#### Supporting Information.

- a. Materials
- b. NMR Instrumentation
- c. General Considerations
- d. Fabrication of PDMS Thimbles
- e. Spectroscopic Data for Olefin Ring-Closing and Cross Methathesis
- f. Spectroscopic Data for Small Molecules after Soxhlet Extraction
- g. References

#### a. Materials

The Schrock Catalyst **2** was purchased from Strem, placed in a Vacuum Atmospheres glove box under N<sub>2</sub> and stored at -30 °C. It was used as received. All solvents were purchased from Acros or Aldrich at their highest purities and were used as received. Geduran silica gel 60 was purchased from Fischer Scientific and used for all column chromatography. Uncross-linked PDMS (Sylgard 184) was purchased from Essex Brownell in its two component form.

#### b. NMR Instrumentation

A Bruker DPX 300 was used for recording all <sup>1</sup>H and <sup>13</sup>C NMR spectra. DCCl<sub>3</sub> was used as the solvent with TMS as an internal standard.

#### c. General Considerations

All metathesis reactions were carried out using standard Schlenk techniques under an N<sub>2</sub> atmosphere. The starting materials **5**, **17**, **18**, and **19** were commercially available from Aldrich. Compounds **7**<sup>1</sup>, **9**<sup>2</sup>, **11**<sup>3</sup>, **13**<sup>4</sup>, **15**<sup>1</sup>, and **20**<sup>5</sup> were synthesized based on literature precedents. The products **6**<sup>6</sup>, **8**<sup>6</sup>, **10**<sup>2</sup>, **12**<sup>7</sup>, **14**<sup>4</sup>, and **16**<sup>8</sup> have been characterized previously in the literature.

#### d. Fabrication of PDMS Thimbles:

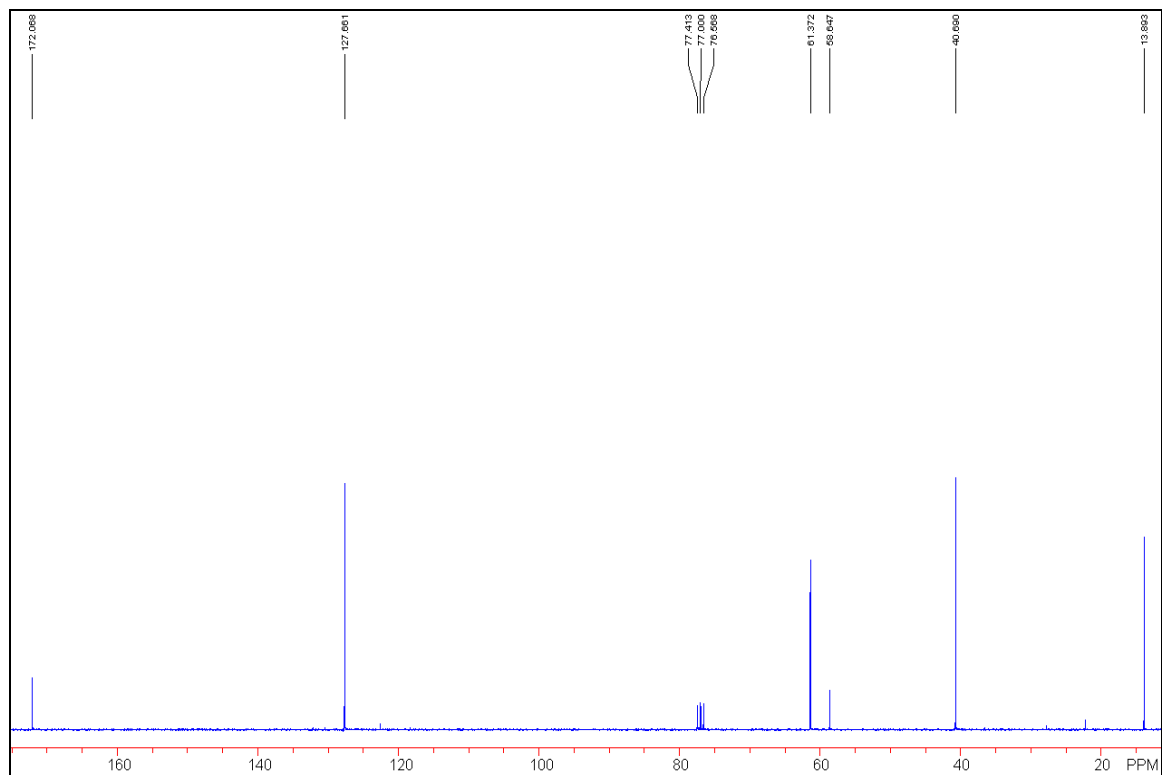
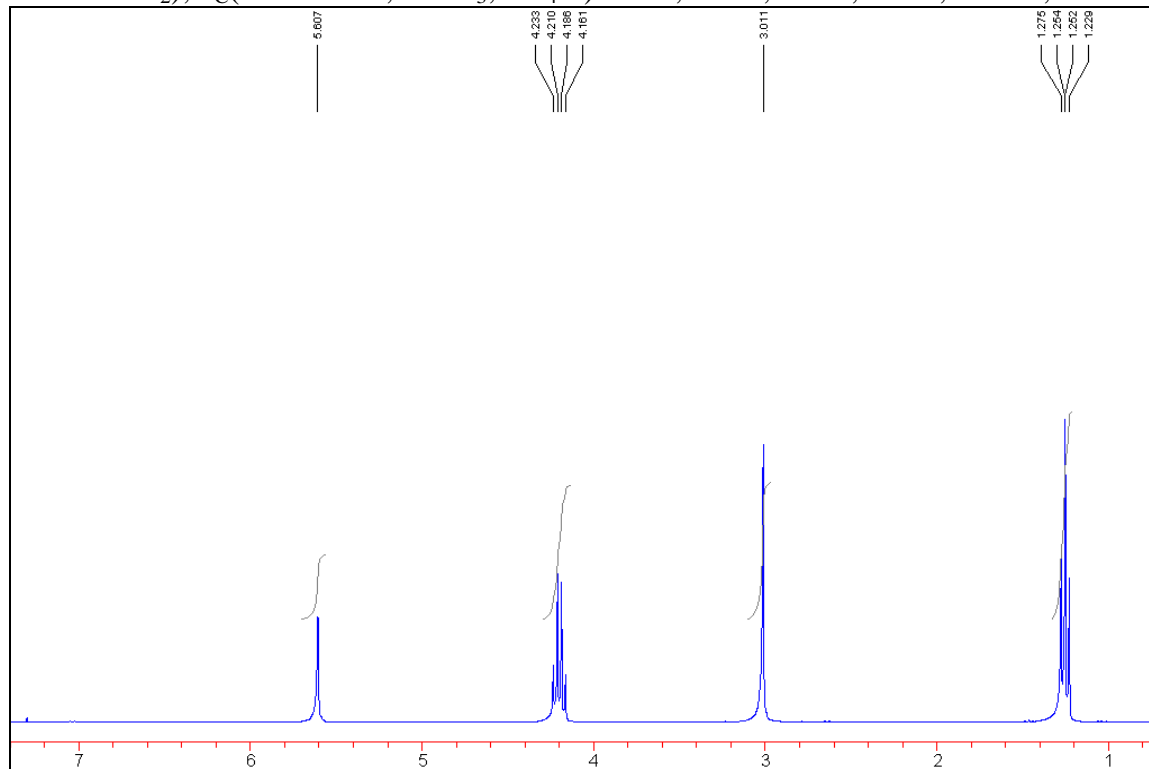
Commercially available PDMS (Sylgard 184) was purchased as two components and was mixed thoroughly in a 10/1 ratio (by mass) of PDMS/cross-linker and degassed for approximately 4

hours. A plastic drying tube (0.625 in. inside diameter) was capped on the bottom and clamped to a ring stand. A solid stainless steel rod (0.5 in. diameter) was clamped to the same ring stand and inserted into the drying tube approximately  $\frac{3}{4}$  of the way down to form the mold for thimble fabrication. The PDMS mixture was poured into the mold and allowed to sit at room temperature for 12 hours. The PDMS was then solid enough to move the entire mold apparatus to an oven and heated for at least 4 hours at 65 °C. The mold was then removed from the oven and the plastic drying tube was cut away and removed. The stainless steel rod was removed by swelling the cured PDMS in hexane for 10 minutes. The PDMS tube was then dried under vacuum and ready for use.

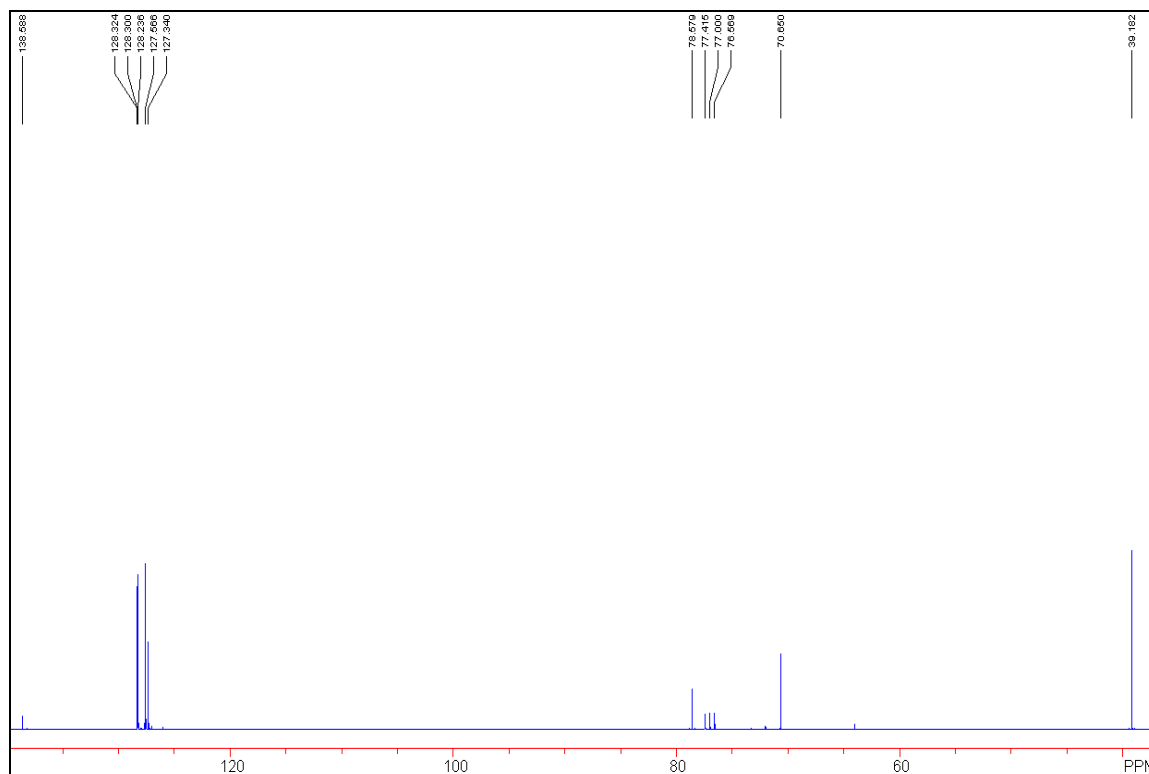
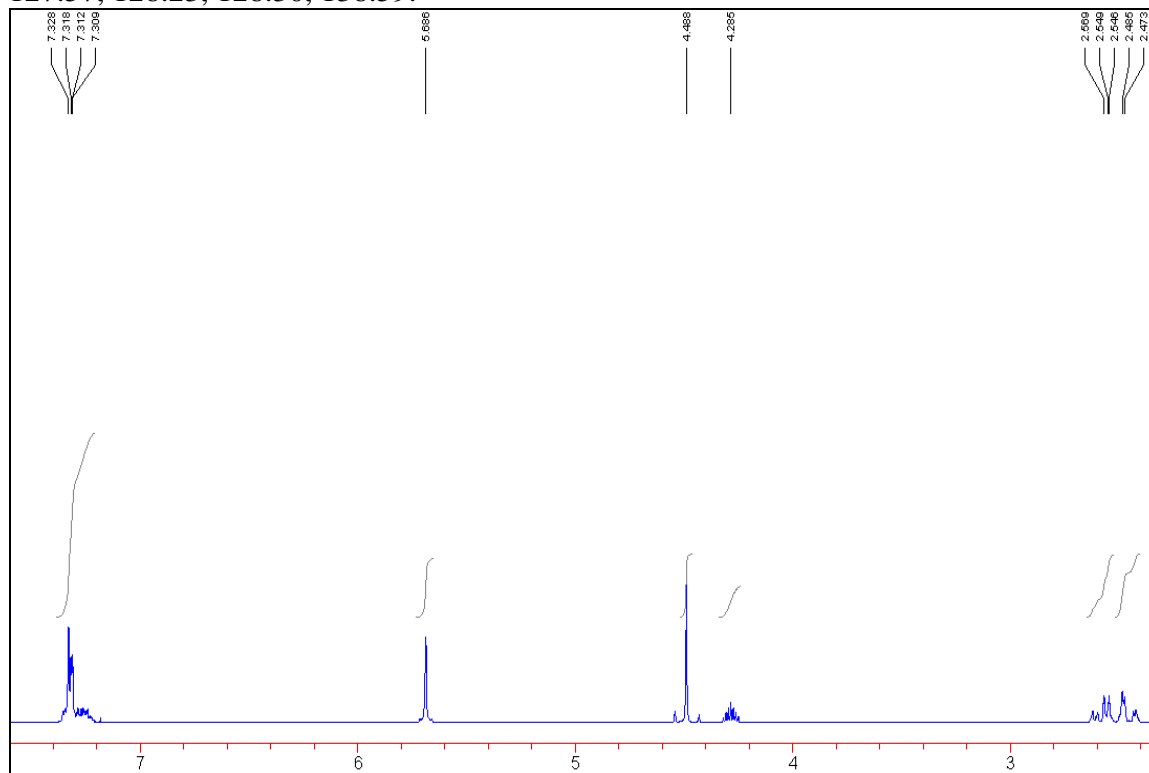
**e. Spectroscopic Data for Olefin Ring-Closing and Cross Methathesis:**

**2,2,2-trifluoro-1-(2H-pyrrol-1(5H)-yl)ethanone 14**  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 4.37 (2 H, m, CH=CHCH<sub>2</sub>), 4.47 (2 H, m, CH=CHCH<sub>2</sub>), 5.88 (2 H, m, CH=CHCH<sub>2</sub>);  $\delta_{\text{C}}$ (75.48 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 53.09 (q,  $J$  <sup>13</sup>C<sup>19</sup>F=3.7), 54.73, 116.34 (q,  $J$  <sup>13</sup>C<sup>19</sup>F=287.3), 124.72, 124.95 (q,  $J$  <sup>13</sup>C<sup>19</sup>F=1.5), 155.51 (q,  $J$  <sup>13</sup>C<sup>19</sup>F=37.1). This product was too volatile and evaporated at room temperature so no isolated yield was obtained.

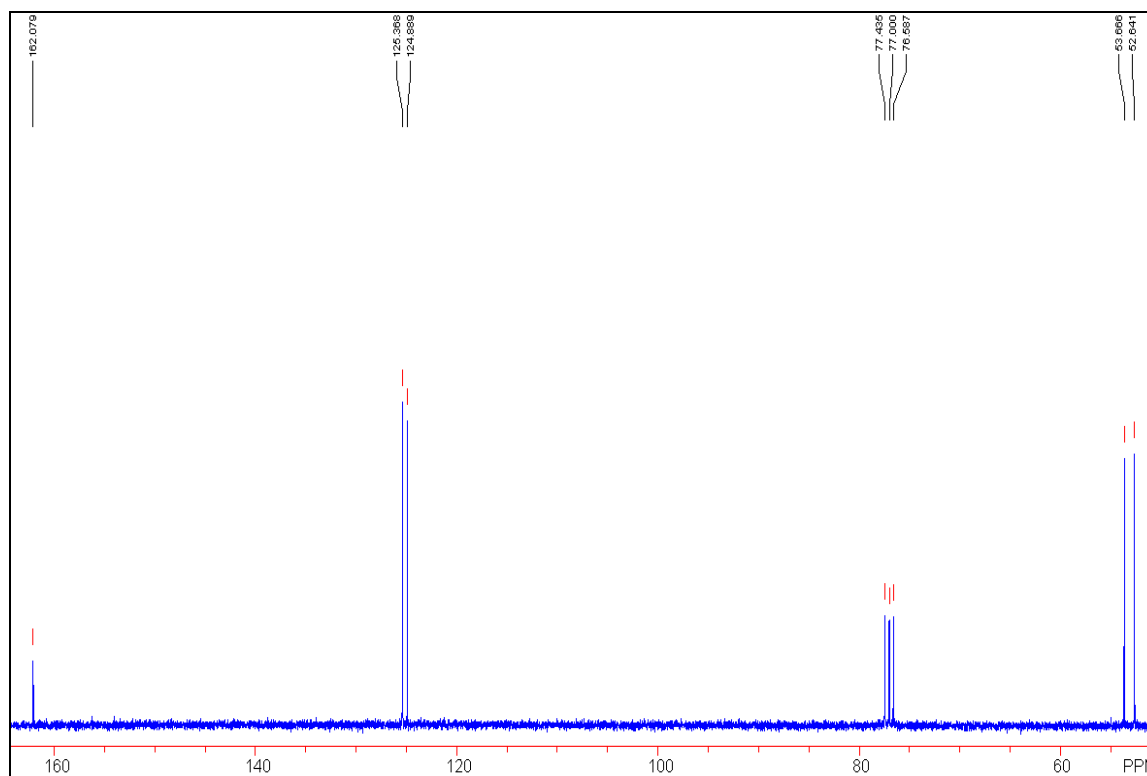
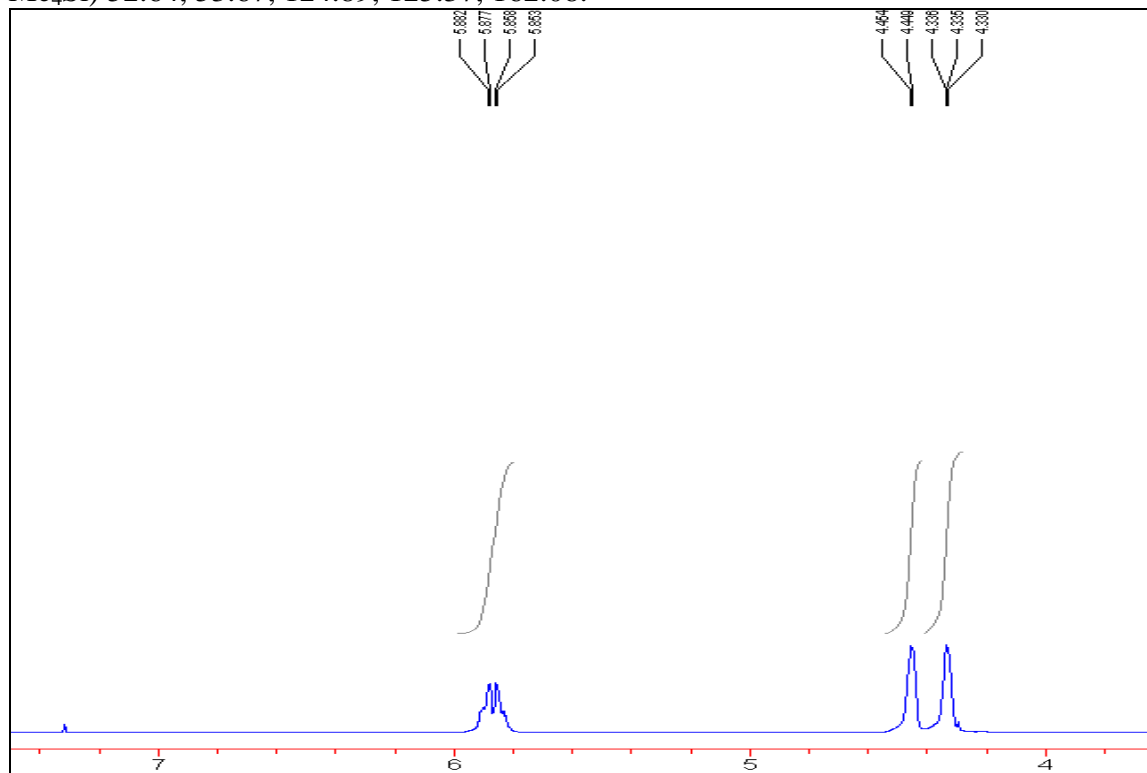
**Cyclopent-3-ene-1,1-dicarboxylic acid diethyl ester 6**  $\delta_{\text{H}}$ (300 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 1.25 (6 H, t,  $J$  7.1,  $\text{OCH}_2\text{CH}_3$ ), 3.01 (4 H, s,  $\text{CH}=\text{CHCH}_2$ ), 4.20 (4 H, q,  $J$  7.1,  $\text{OCH}_2\text{CH}_3$ ), 5.61 (2 H, s,  $\text{CH}=\text{CHCH}_2$ );  $\delta_{\text{C}}$ (75.48 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 13.89, 40.69, 58.65, 61.37, 127.66, 172.07.



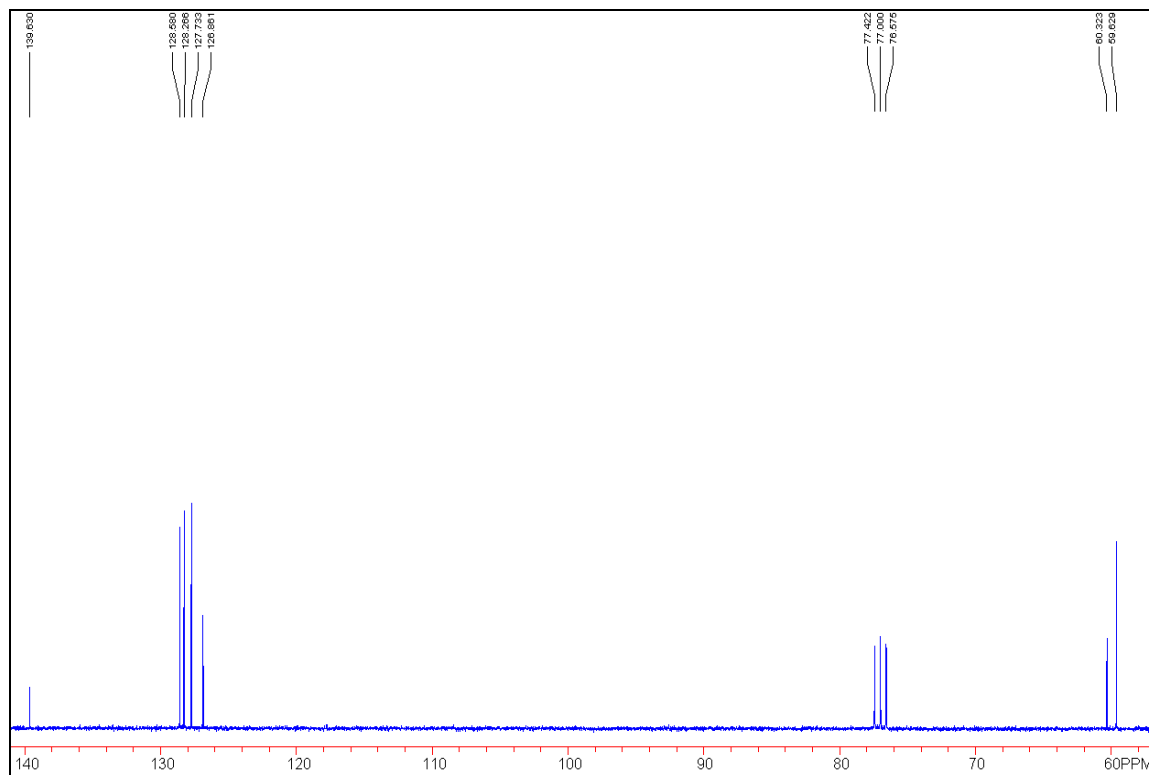
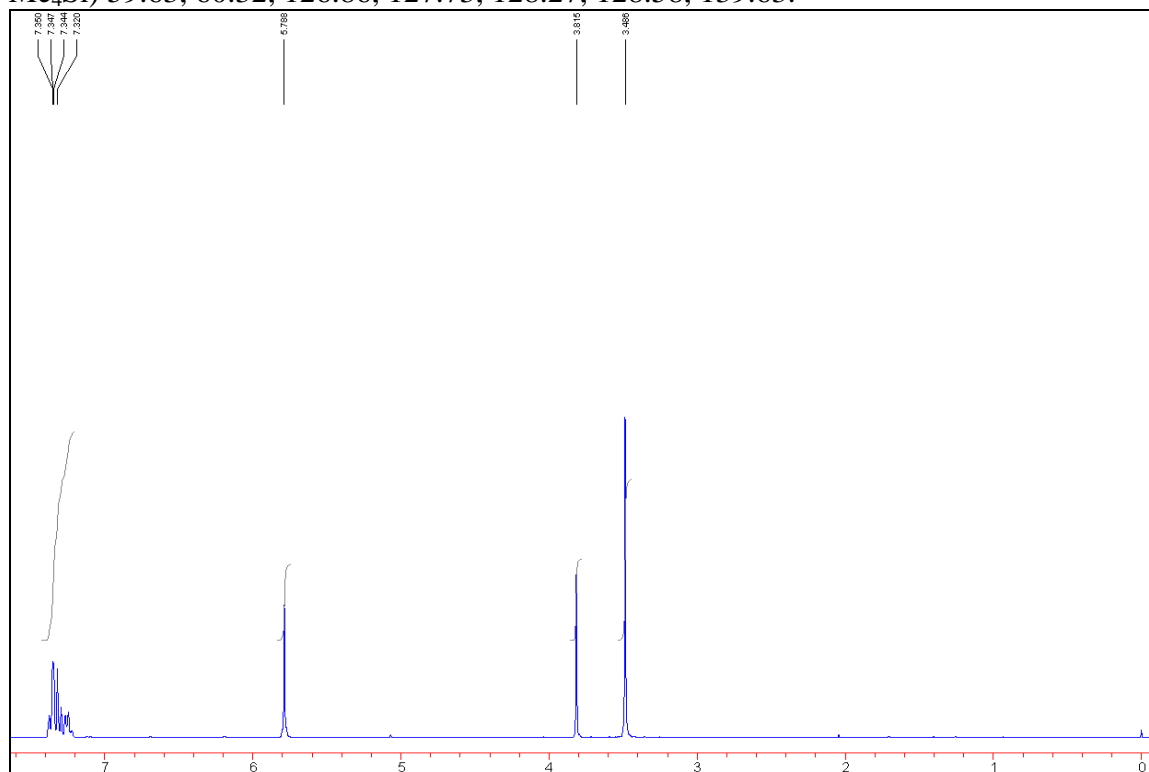
**1-((cyclopent-3-enyloxy)methyl)benzene 8**  $\delta_{\text{H}}$ (300 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 2.52 (4 H, m,  $\text{CH}=\text{CHCH}_2$ ), 4.29 (1 H, m,  $\text{CH}_2\text{CHOBn}$ ), 4.49 (2 H, s,  $\text{CHOCH}_2\text{Ph}$ ), 5.69 (2 H, s,  $\text{CH}=\text{CHCH}_2$ ), 7.32 (5 H, m, Ph);  $\delta_{\text{C}}$ (75.48 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 39.18, 70.65, 78.58, 127.34, 127.57, 128.23, 128.30, 138.59.



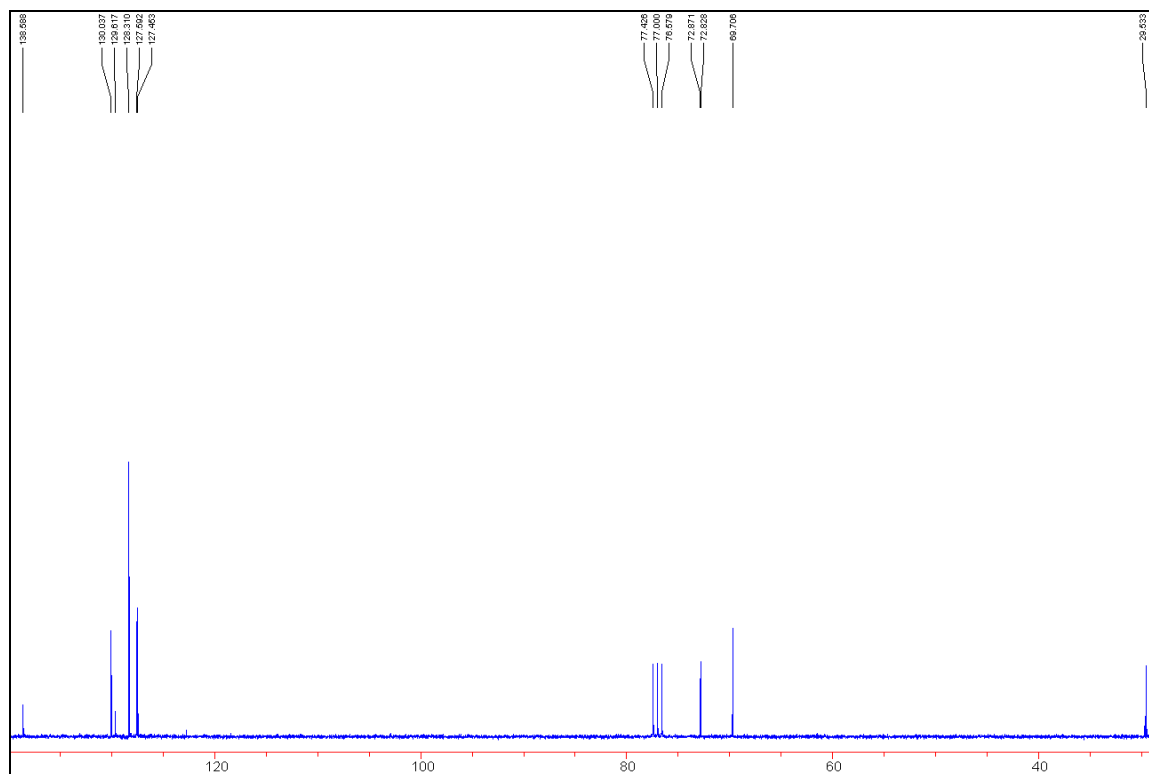
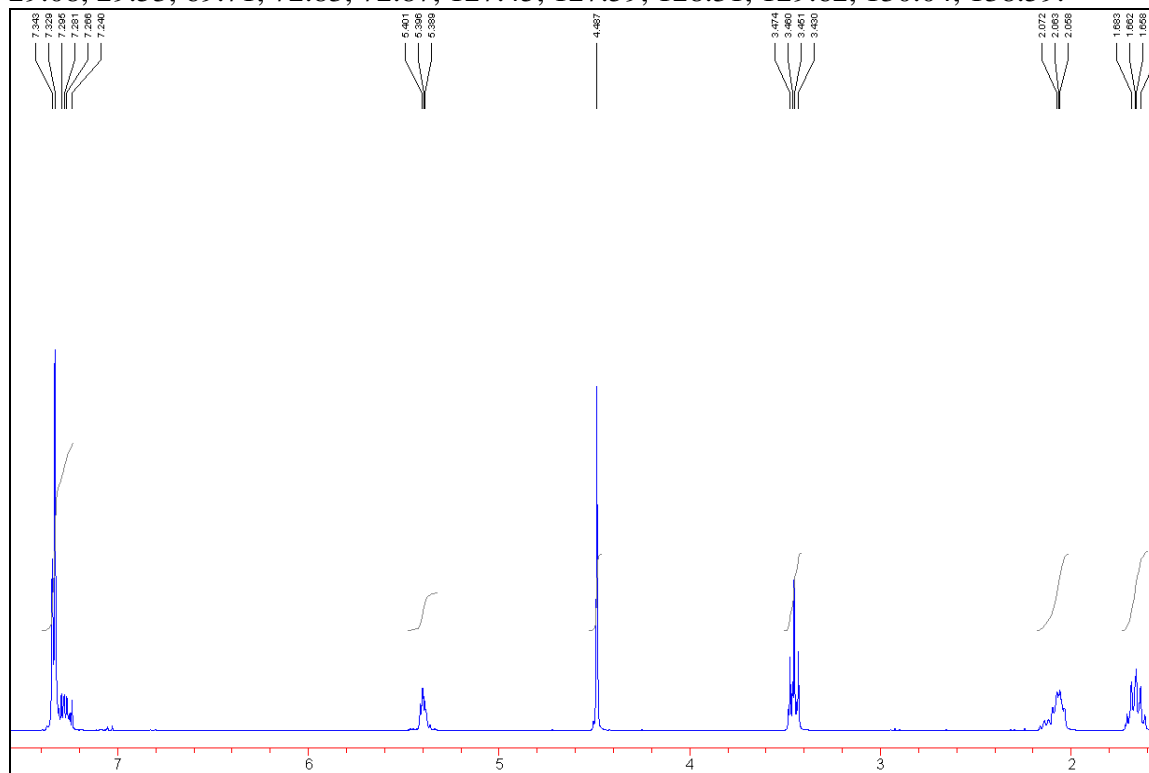
**1,2-di(2H-pyrrol-1(5H)-yl)ethane-1,2-dione 10**  $\delta_{\text{H}}$ (300 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 4.33 (4 H, m,  $\text{CH}=\text{CHCH}_2$ ), 4.45 (4 H, m,  $\text{CH}=\text{CHCH}_2$ ), 5.86 (4 H, m,  $\text{CH}=\text{CHCH}_2$ );  $\delta_{\text{C}}$ (75.48 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 52.64, 53.67, 124.89, 125.37, 162.08.



**1-benzyl-2,5-dihydro-1H-pyrrole 12**  $\delta_{\text{H}}$ (300 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 3.49 (4 H, s,  $\text{CH}=\text{CHCH}_2$ ), 3.82 (2 H, s,  $\text{NCH}_2\text{Ph}$ ), 5.79 (2 H, s,  $\text{CH}=\text{CHCH}_2$ ), 7.34 (5 H, m, Ph);  $\delta_{\text{C}}$ (75.48 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 59.63, 60.32, 126.86, 127.73, 128.27, 128.58, 139.63.

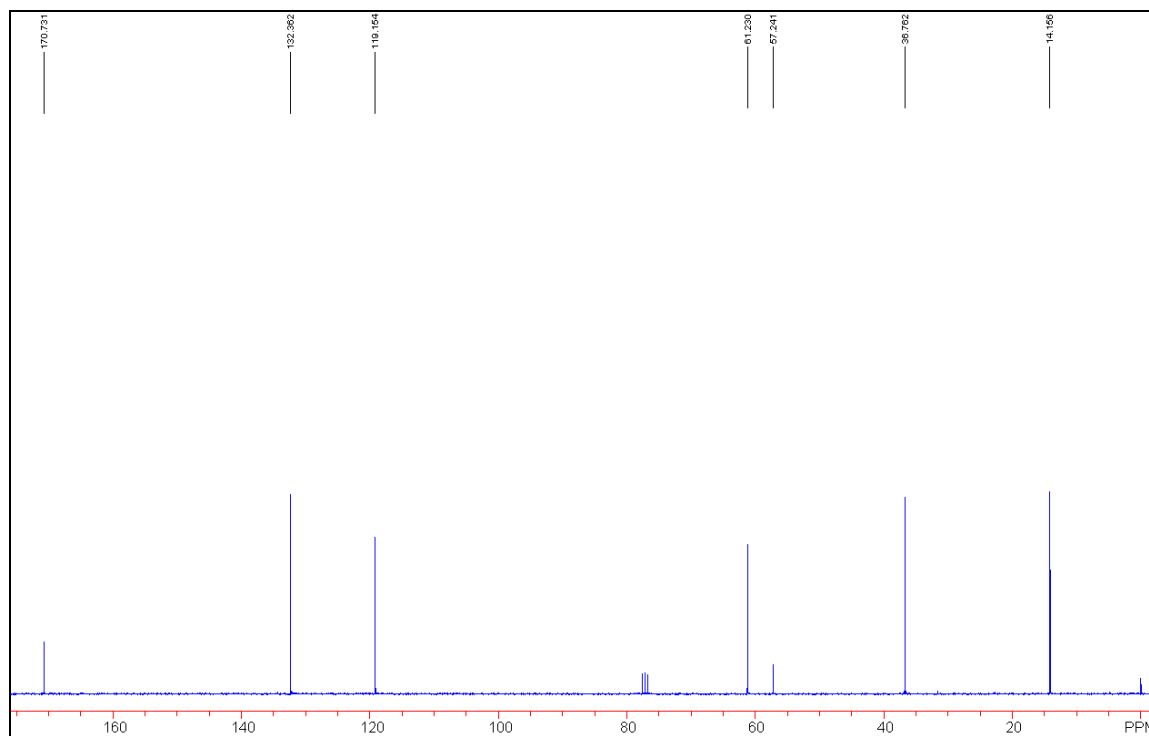
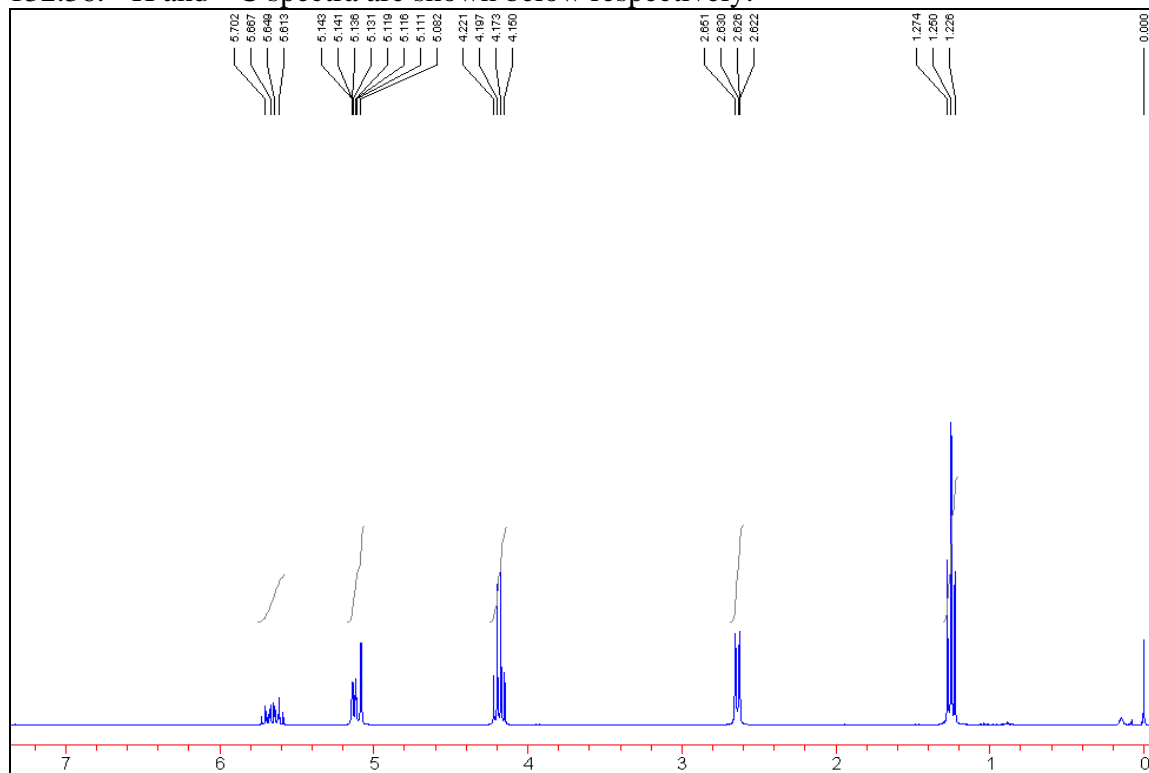


**1-((8-(benzyloxy)oct-4-enyloxy)methyl)benzene 16**  $\delta_{\text{H}}$ (300 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 1.66 (4 H, m,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 2.06 (4 H, m,  $\text{CH}=\text{CHCH}_2$ ), 3.46 (4 H, t,  $J$  6.6,  $\text{CH}_2\text{OCH}_2\text{Ph}$ ), 4.49 (4 H, s,  $\text{CH}_2\text{OCH}_2\text{Ph}$ ), 5.40 (2 H, m,  $\text{CH}=\text{CHCH}_2$ ), 7.33 (10 H, m, Ph);  $\delta_{\text{C}}$ (75.48 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 29.08, 29.53, 69.71, 72.83, 72.87, 127.45, 127.59, 128.31, 129.62, 130.04, 138.59.



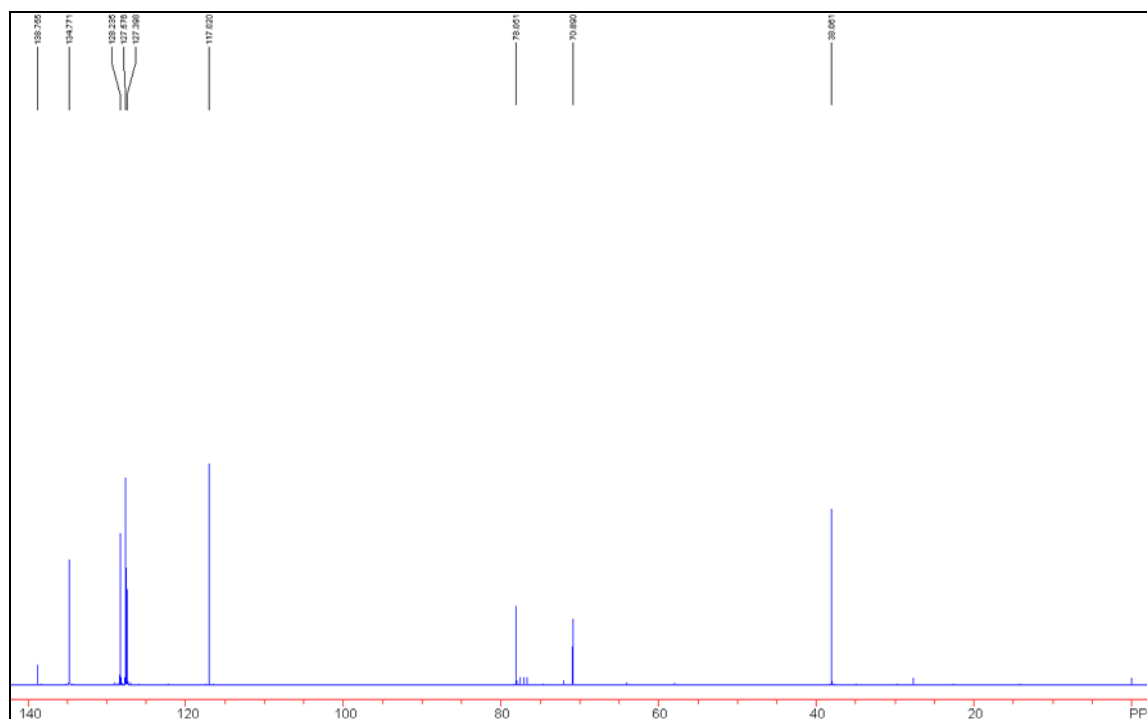
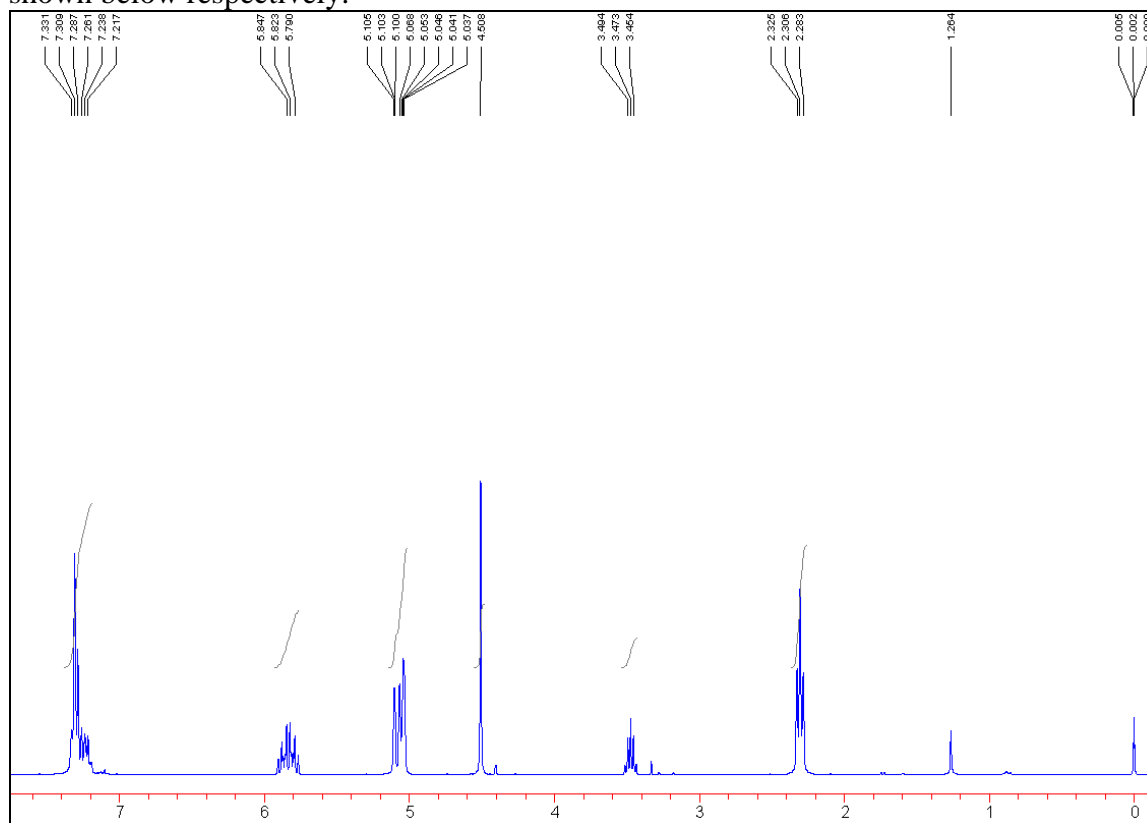
## f. Spectroscopic Data for Small Molecules after Soxhlet Extraction:

**diethyl 2,2-diallylmalonate 5**  $\delta_{\text{H}}$ (300 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 1.25 (6 H, t,  $J$  7.2,  $\text{OCH}_2\text{CH}_3$ ), 2.64 (4 H, d,  $J$  7.5,  $\text{CH}_2=\text{CHCH}_2$ ), 4.19 (4 H, q,  $J$  7.2,  $\text{OCH}_2\text{CH}_3$ ), 5.10 (4 H, m,  $\text{CH}_2=\text{CHCH}_2$ ) 5.66 (2 H, m,  $\text{CH}_2=\text{CHCH}_2$ );  $\delta_{\text{C}}$ (75.48 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 14.16, 36.76, 57.24, 61.23, 119.15, 132.36.  $^1\text{H}$  and  $^{13}\text{C}$  spectra are shown below respectively.





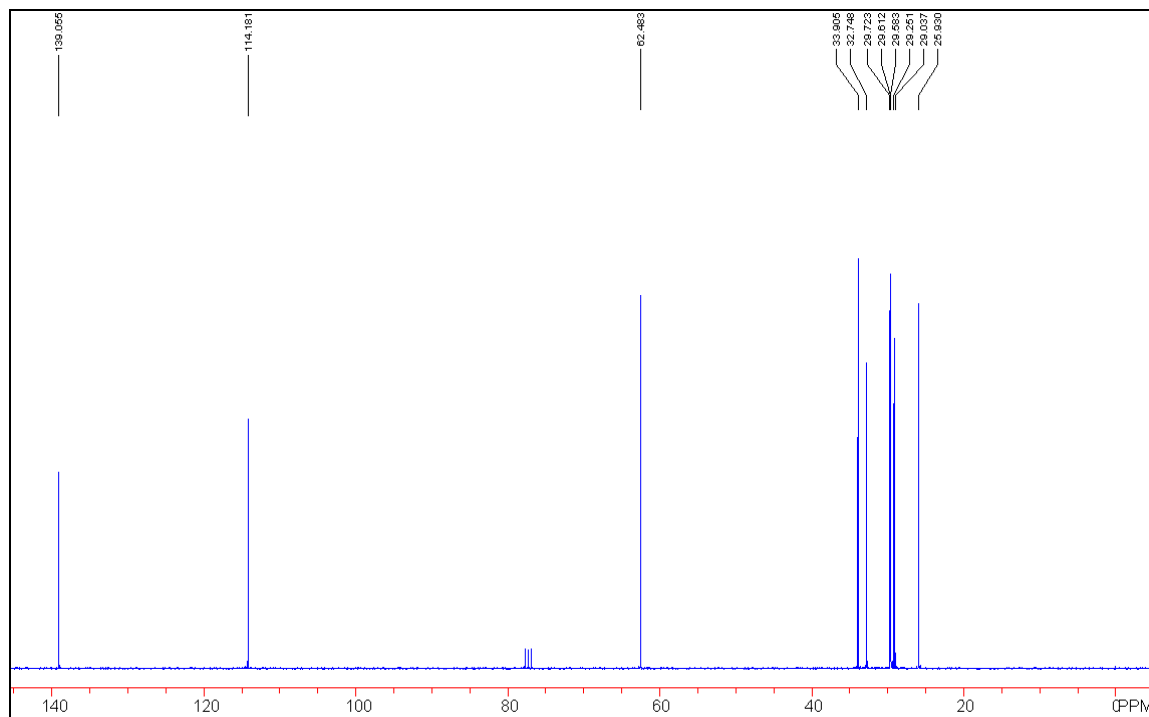
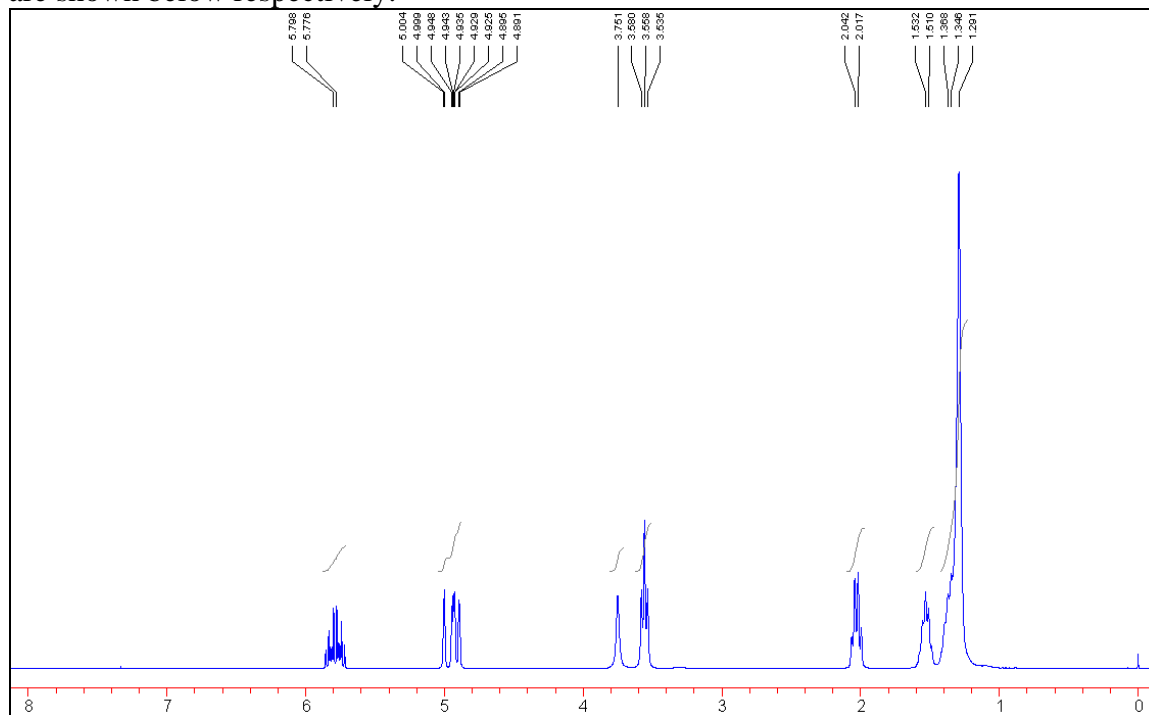
**1-((hepta-1,6-dien-4-yloxy)methyl)benzene 7**  $\delta_{\text{H}}$ (300 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 2.31 (4 H, m,  $\text{CH}_2=\text{CHCH}_2$ ), 3.47 (1 H, m,  $\text{CH}_2\text{CHOBN}$ ), 4.51 (2 H, s,  $\text{CHOCH}_2\text{Ph}$ ), 5.05 (4 H, m,  $\text{CH}_2=\text{CHCH}_2$ ), 5.82 (2 H, m,  $\text{CH}=\text{CHCH}_2$ ), 7.29 (5 H, m, Ph);  $\delta_{\text{C}}$ (75.48 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 38.06, 70.89, 78.05, 117.02, 127.40, 127.58, 128.24, 134.77, 138.76.  $^1\text{H}$  and  $^{13}\text{C}$  spectra are shown below respectively.







**10-undecen-1-ol 19**  $\delta_{\text{H}}$ (300 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 1.35 (12 H, m,  $\text{CH}_2=\text{CHCH}_2(\text{CH}_2)_6\text{CH}_2$ ), 1.52 (2 H, m,  $\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$ ), 2.03 (2 H, m,  $\text{CH}_2=\text{CHCH}_2$ ), 3.56 (2 H, t,  $J$  6.8,  $\text{CH}_2\text{OH}$ ), 3.75 (1 H, s, OH), 4.95 (2 H, m,  $\text{CH}_2=\text{CHCH}_2$ ), 5.78 (1 H, m,  $\text{CH}_2=\text{CHCH}_2$ );  $\delta_{\text{C}}$ (75.48 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 25.93, 29.04, 29.25, 29.58, 29.61, 29.72, 32.75, 33.91, 62.48, 114.18, 139.06.  $^1\text{H}$  and  $^{13}\text{C}$  spectra are shown below respectively.



**g. References**

- 1 T. W. Green and P. G. M. Wuts, in *Protective groups in organic synthesis*, John Wiley and Sons, Inc., New York, 2<sup>nd</sup> edn., 1991.
- 2 G. C. Fu and R. H. Grubbs, *J. Am. Chem. Soc.*, 1992, **114**, 7324-7325.
- 3 Y. Terada, M. Arisawa and A. Nishida, *Angew. Chem. Int. Ed.*, 2004, **43**, 4063-4067.
- 4 W. A. Nugent, J. Feldman and J. C. Calabrese, *J. Am. Chem. Soc.*, 1995, **117**, 8992-8998.
- 5 G. W. Oakley and K. B. Wagener, *Macromol. Chem. Phys.*, 2005, **206**, 15-24.
- 6 M. T. Mwangi, M. B. Runge and N. B. Bowden, *J. Am. Chem. Soc.*, 2006, **128**, 14434-14435.
- 7 M. M. Bowers Nemias, J. Lee and M. M. Joullie, *Synthetic Communications*, 1983, **13**, 1117-1123.
- 8 W. E. Crowe and Z. J. Zhang, *J. Am. Chem. Soc.*, 1993, **115**, 10998-10999.
- 9 *Fr. Pat.*, 2854400A1, 2004.