

# The Regio- and Stereochemical Course of Reductive Cross-Coupling Reactions between 1,3-disubstituted Allenes and Vinylsilanes: Synthesis of Z-dienes

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## SUPPORTING INFORMATION:

**General.** All reactions were conducted in flame-dried glassware under nitrogen or argon using anhydrous solvents. Toluene, tetrahydrofuran, and diethyl ether were used after passing through an activated alumina column.  $\text{Ti}(\text{O}i\text{-Pr})_4$  was used after distillation of the commercially available reagent. All other commercially available reagents were used as received (Aldrich).

$^1\text{H}$  NMR data were recorded at 400 MHz on a Bruker AM-400 in  $\text{CDCl}_3$ .  $^{13}\text{C}$  NMR data were recorded at 100 MHz on a Bruker AM-400. Infrared spectra were recorded on a PerkinElmer SpectrumOne FT-IR instrument. Low resolution mass spectra were acquired on a Varian 500-MS mass spectrometer under soft ionization mode. HRMS data (ESITOF-MS) were obtained by the University of Florida Mass Spectrometry lab.  $^1\text{H}$  NMR chemical shifts are reported relative to residual  $\text{CHCl}_3$  (7.26 ppm).  $^{13}\text{C}$  chemical shifts are reported relative to the central line of  $\text{CDCl}_3$  (77.16 ppm). Chromatographic purification was performed using 60 Å, 35-75 μ particle size silica gel from Silicycle. All compounds purified by chromatography were sufficiently pure for use in further experiments, unless indicated otherwise. Semi-preparative HPLC normal phase separations were performed using an HPLC system composed of two Dynamax SD-1 pumps, a Rheodyne injector and a Dynamax UV-1 absorbance detector.

All allenes are known compounds or are prepared according to the published procedures:

**20:** Trost, B. M.; Fandrick, D. R.; Dinh, D. C. *J. Am. Chem. Soc.* **2005**, *127*, 14186-14187.

**27:** Imada, Y.; Nishida, M.; Kutsuwa, K.; Murahashi, S.; Naota, T. *Org. Lett.* **2005**, *7*, 5837-5839.

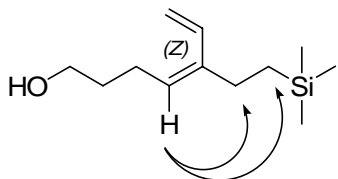
**30, 32:** Kang, S-K.; Kim, S-G.; and Cho, D-G. *Tetrahedron: Asymmetry* **1992**, *3*, 1509-1510.

**14:** Tarselli, M. A.; Micalizio, G. C. *Org. Lett.* **2009**, *11*, 4596-4599.

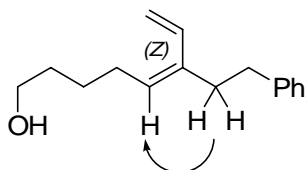
**16:** Meyers, A.G.; Zheng, B. *J. Am. Chem. Soc.* **1996**, *118*, 4492-4493.

**10, 12, 18:** Shimp, H. L.; Hare, A.; McLaughlin, M.; Micalizio, G. C. *Tetrahedron* **2008** *64*, 3437-3445.

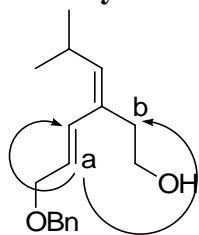
**nOe 17**



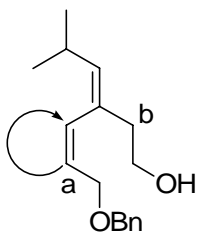
**nOe 23**



**nOe Analysis**



**33**

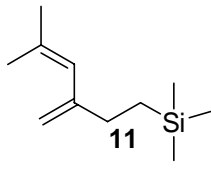


**34**

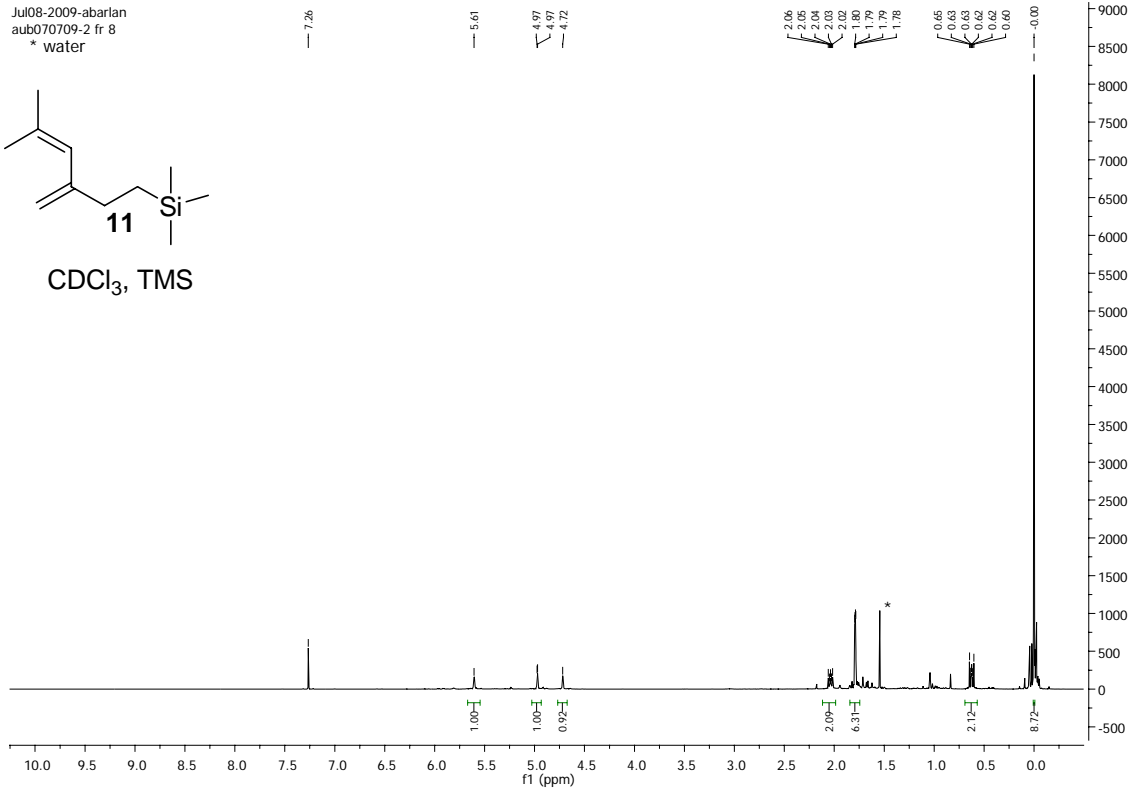
**33** (nOe was observed between protons a and b)

**34** (no nOe was observed between protons a and b)

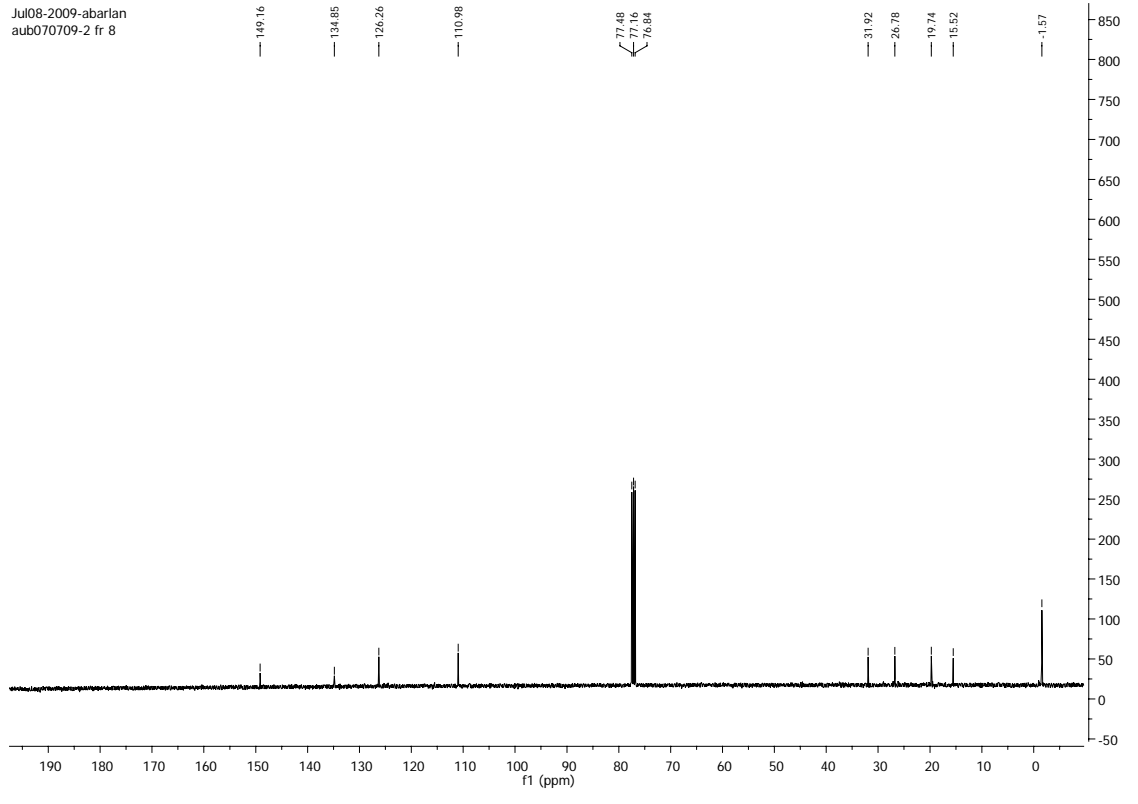
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\* water



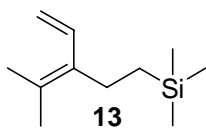
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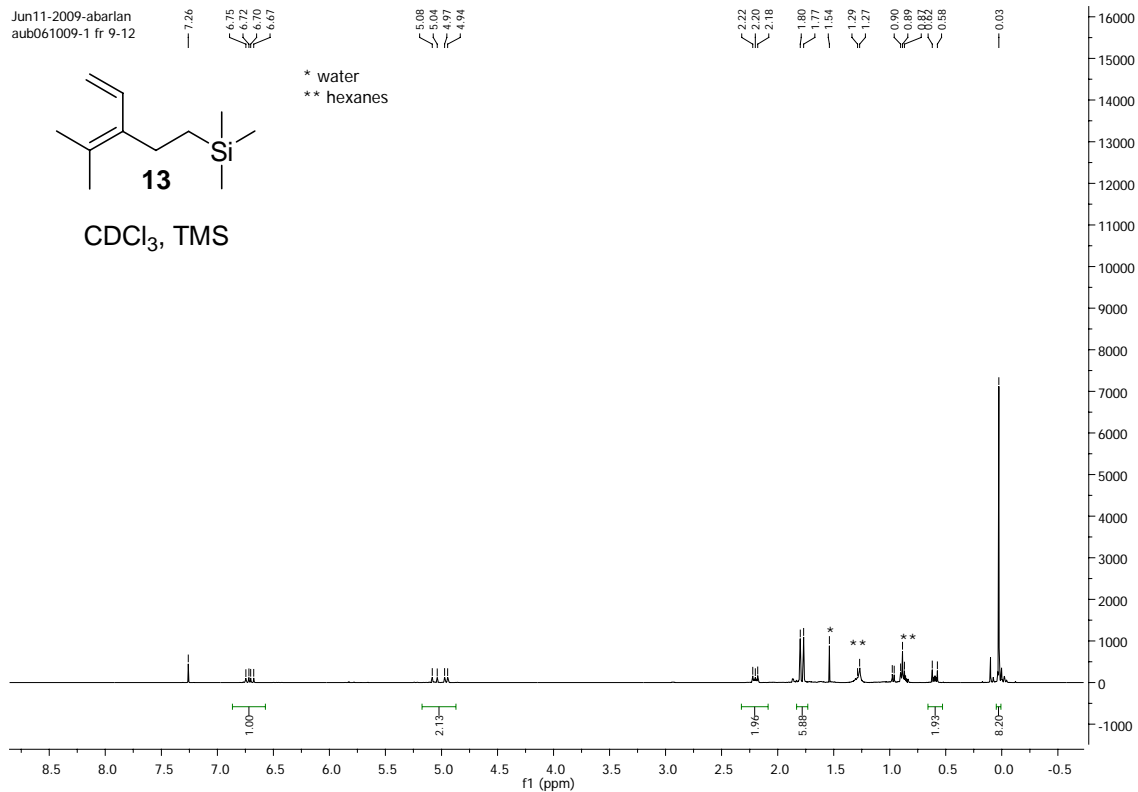


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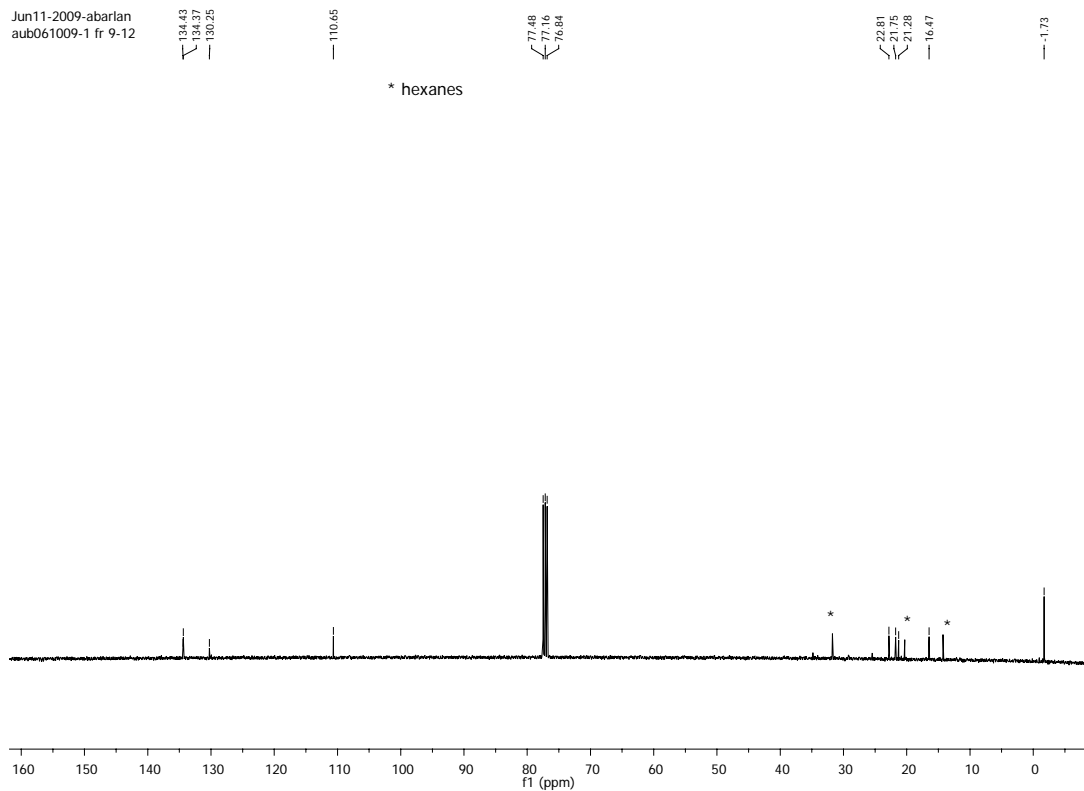


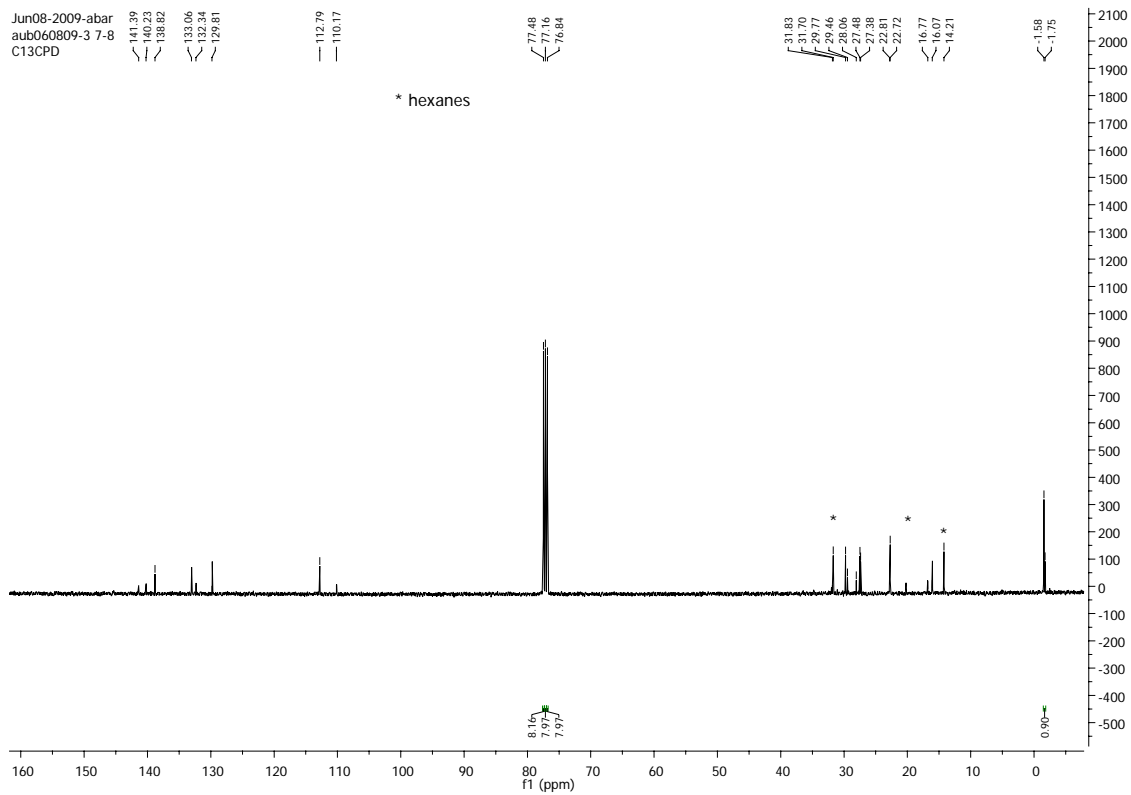
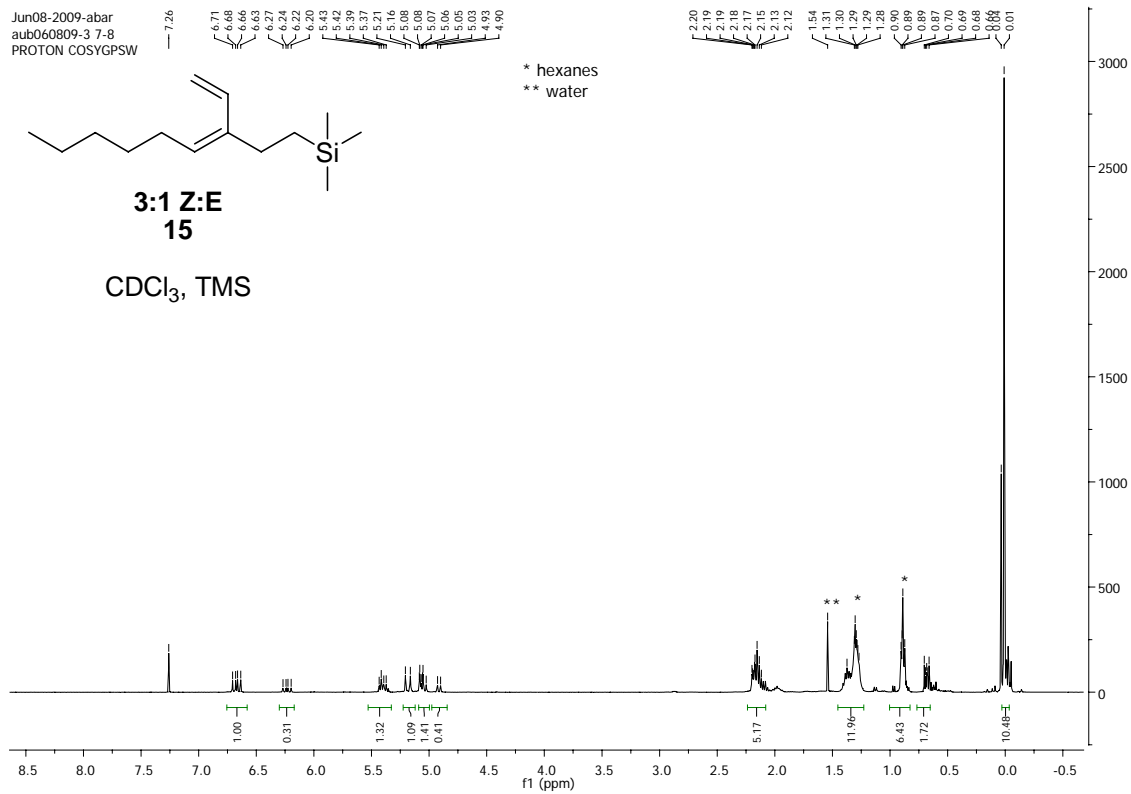
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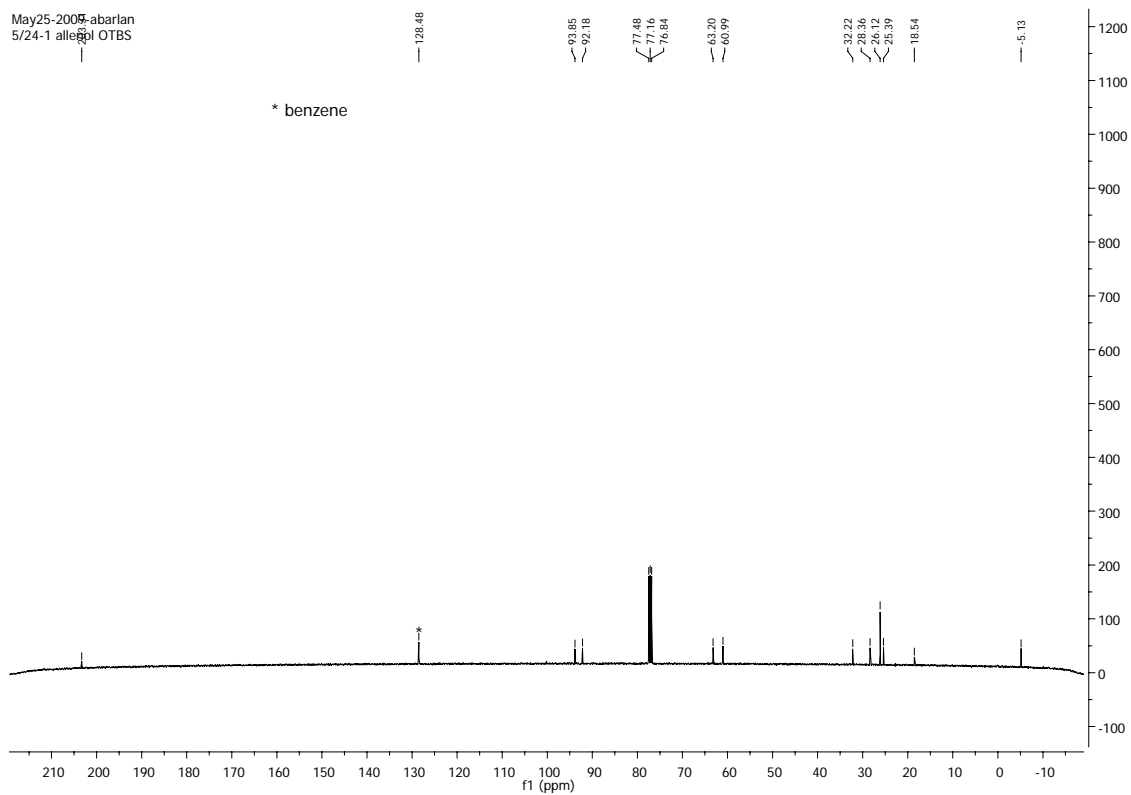
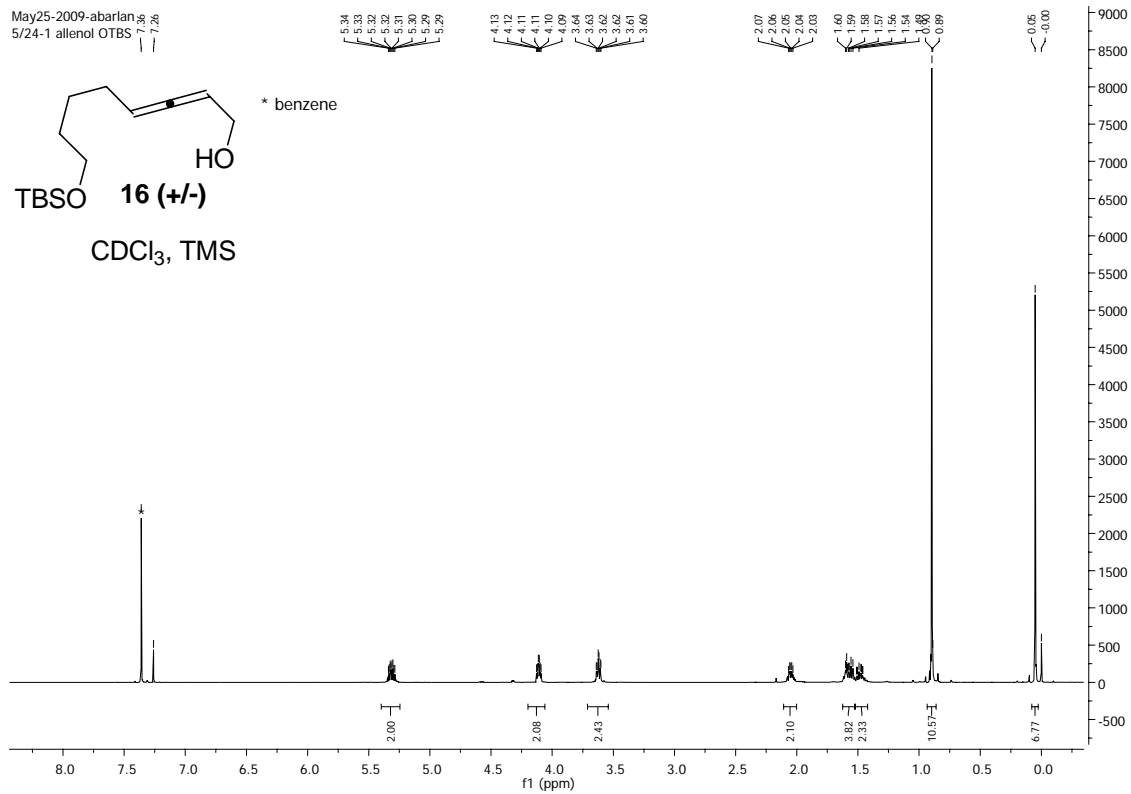
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\*\* hexanes



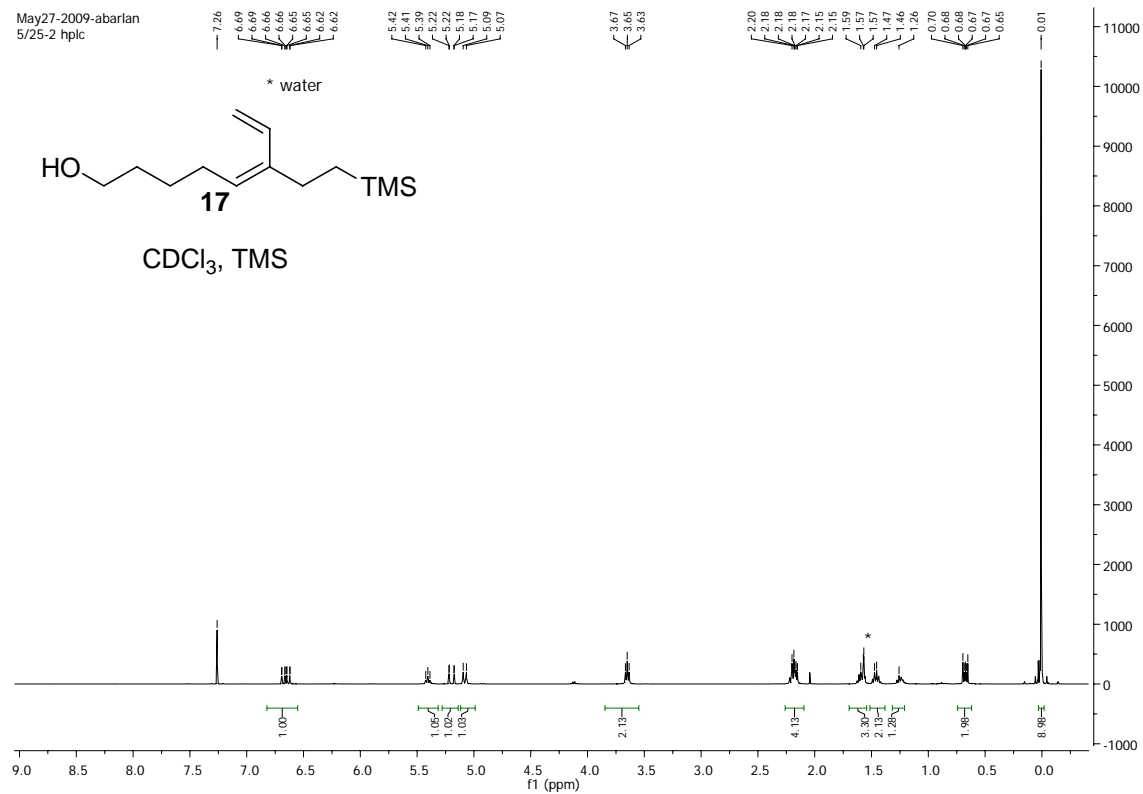
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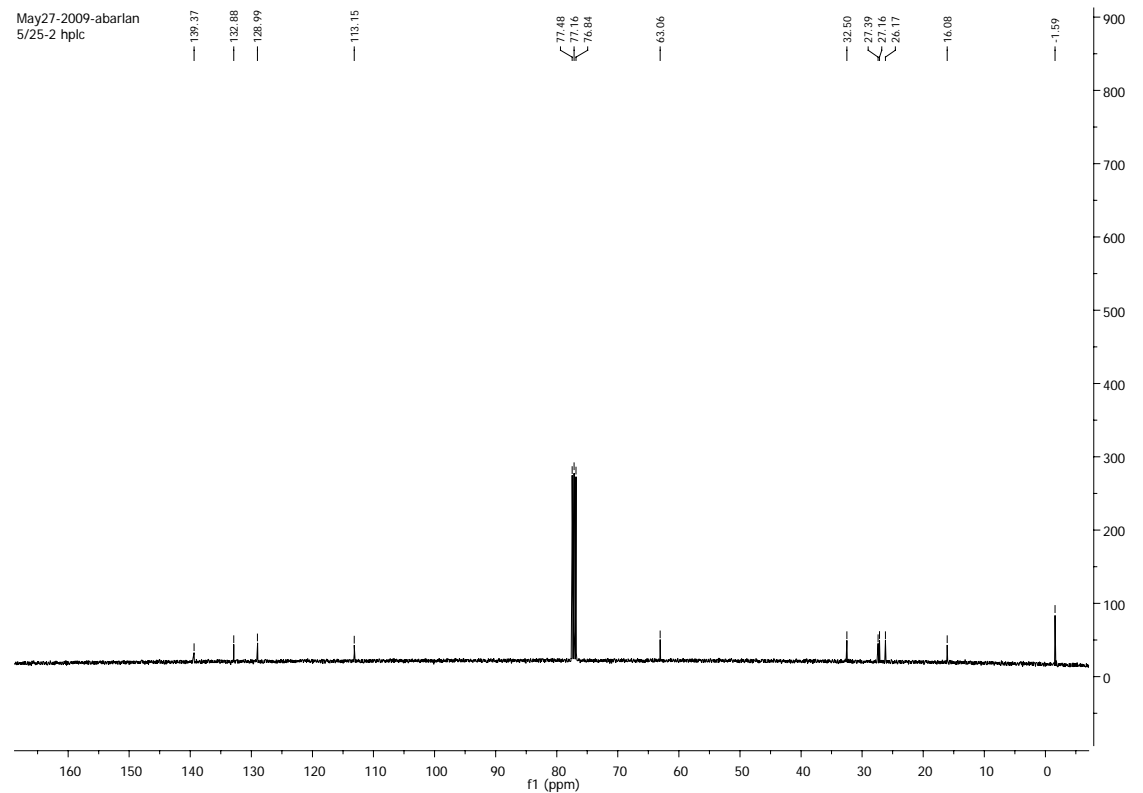




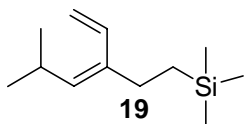
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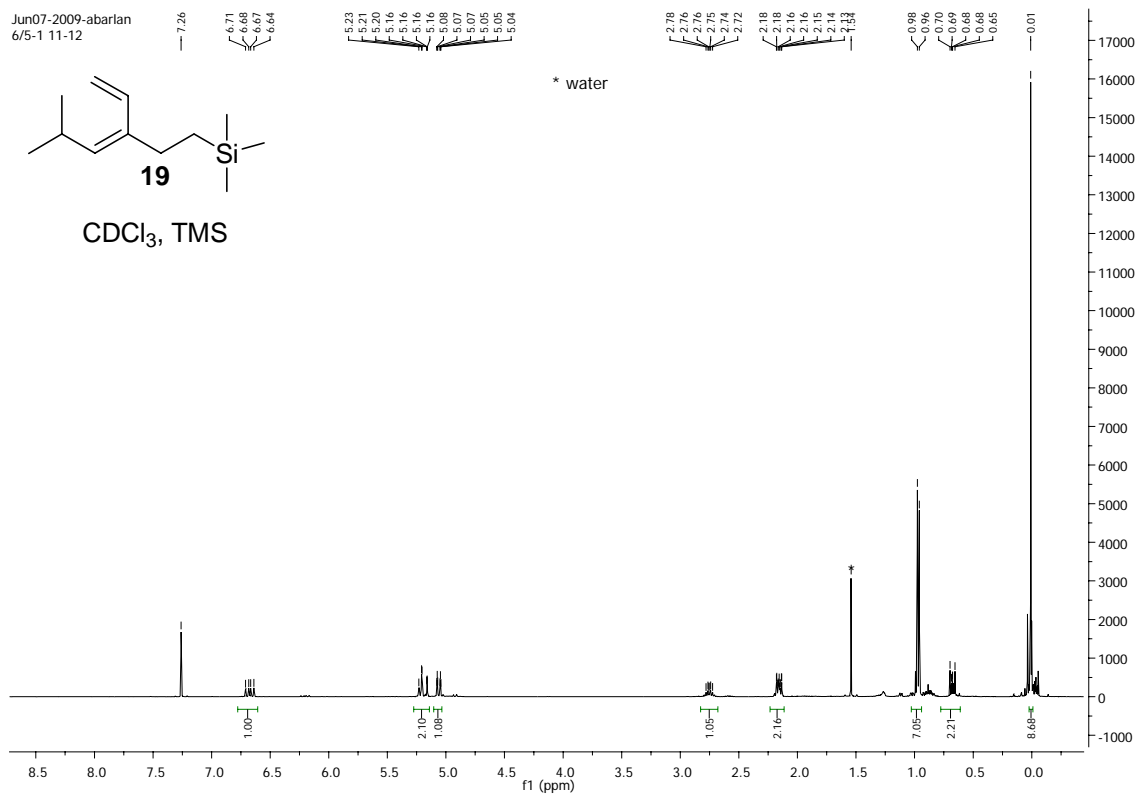
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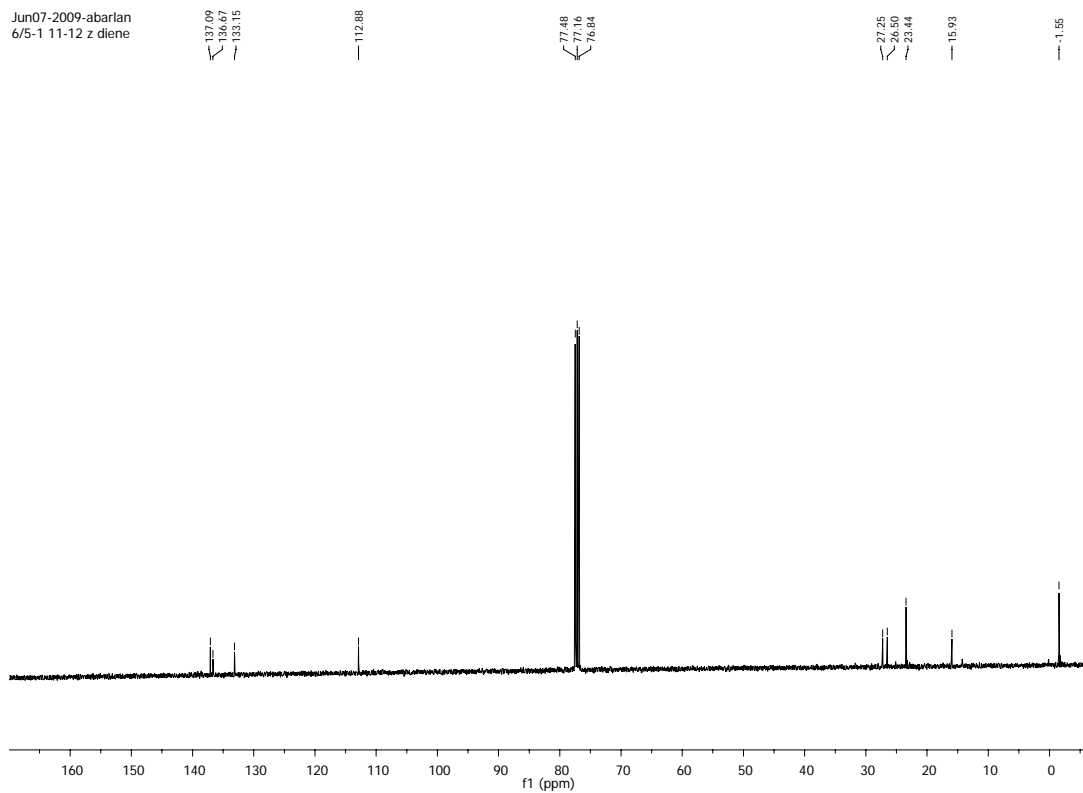
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CDCl<sub>3</sub>, TMS

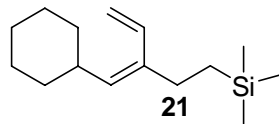


Jun07-2009-abarlan  
6/5-1 11-12 z diene



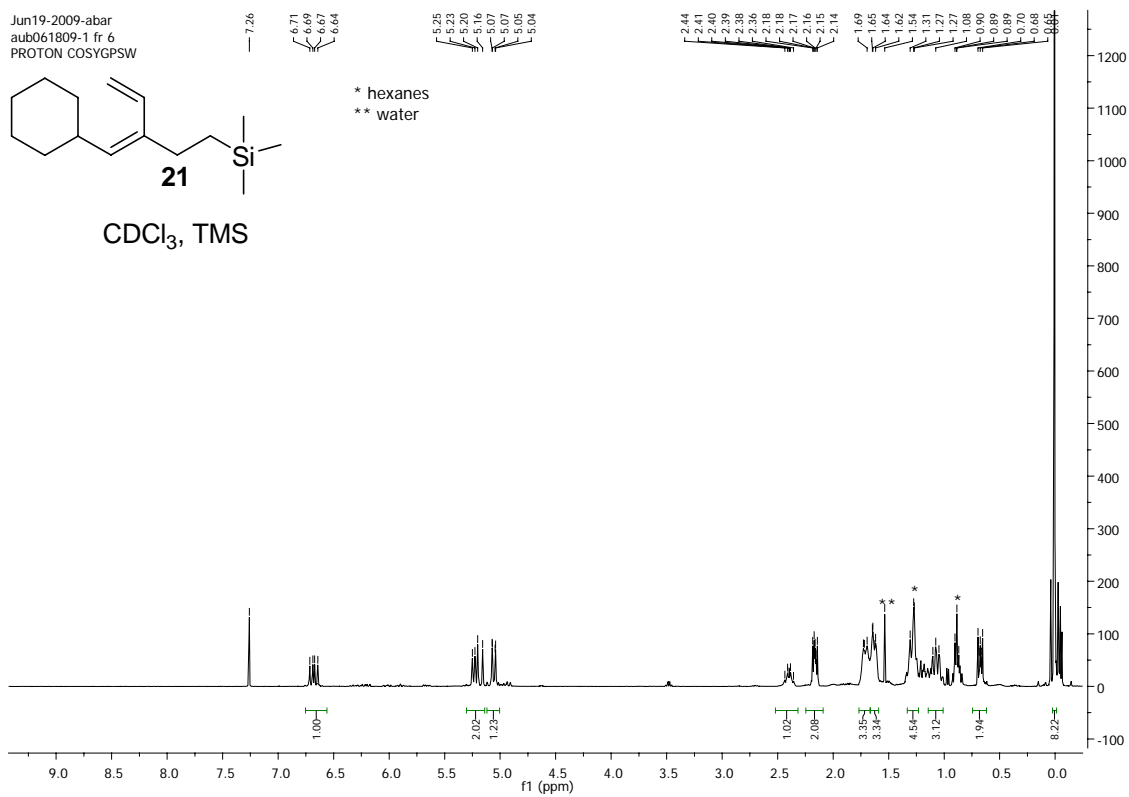


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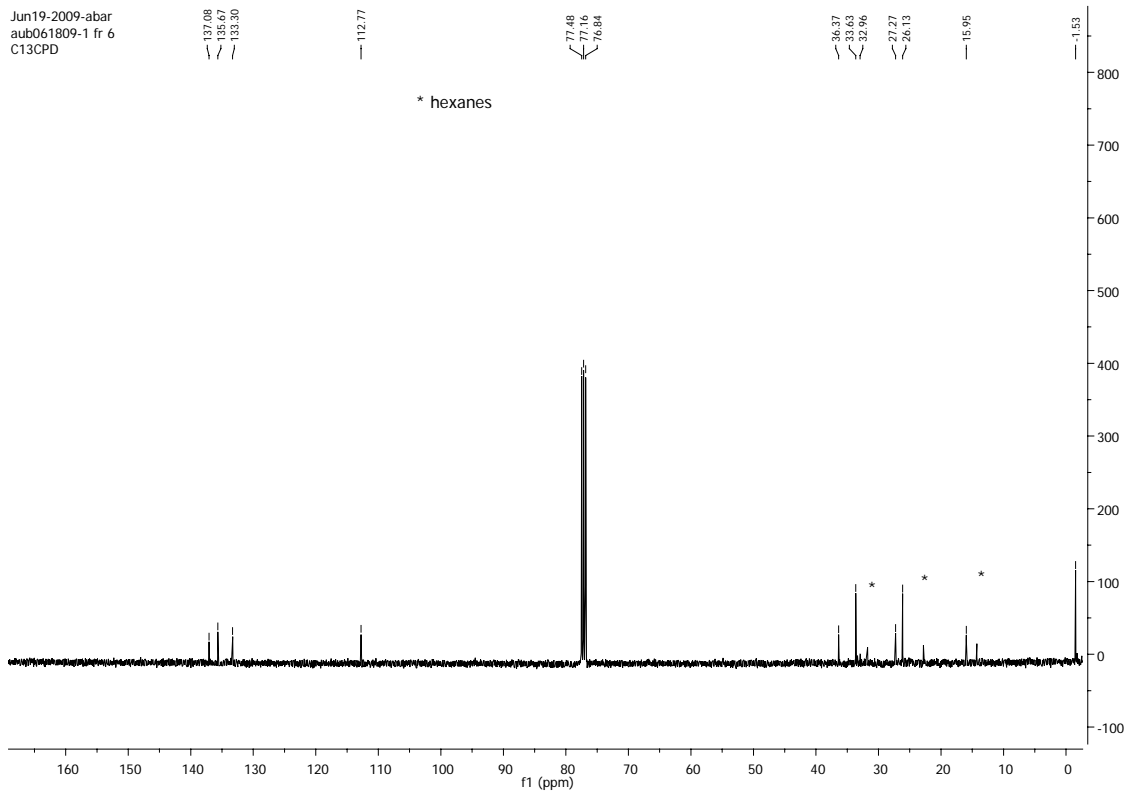


CDCl<sub>3</sub>, TMS

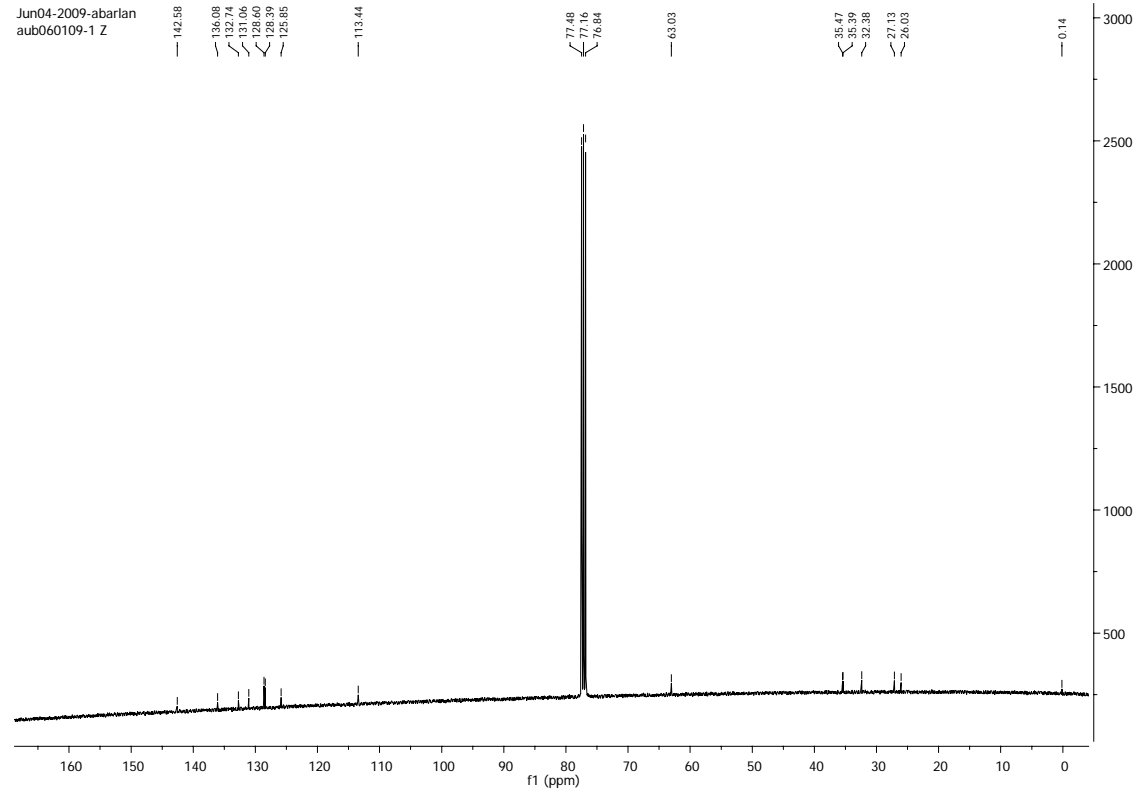
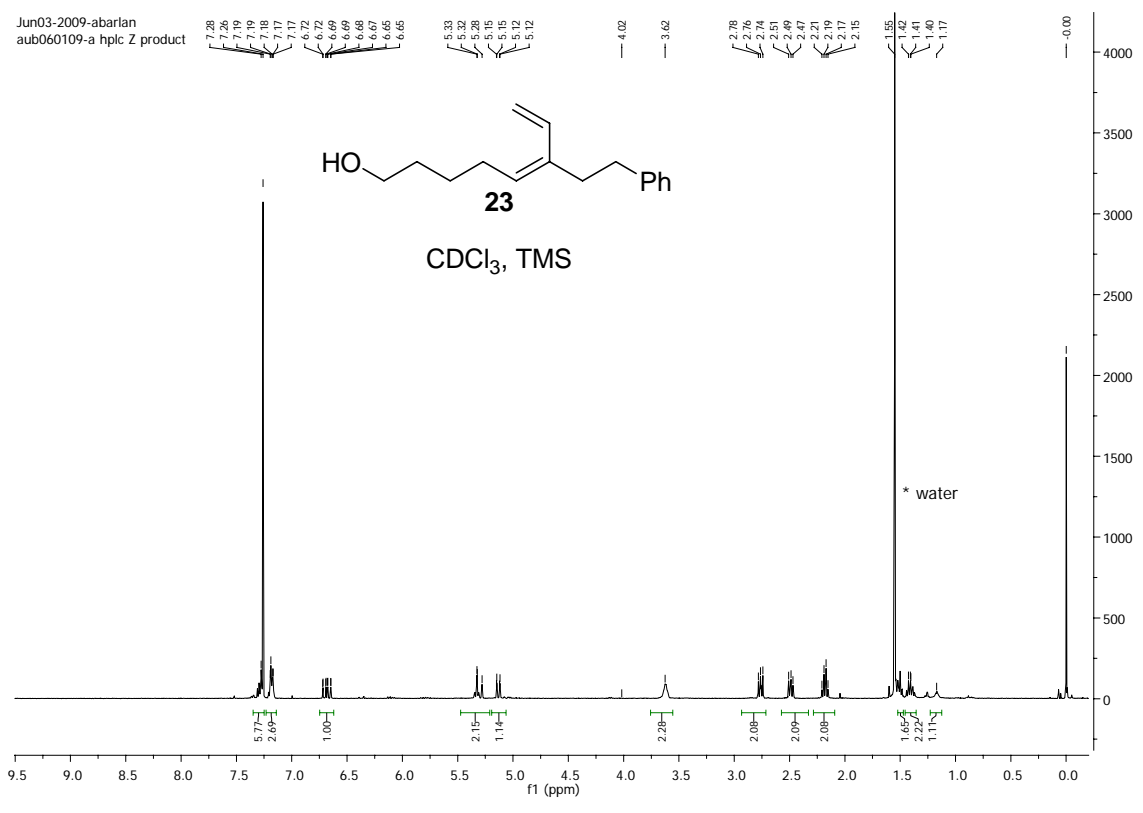
\* hexanes  
\*\* water



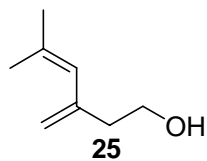
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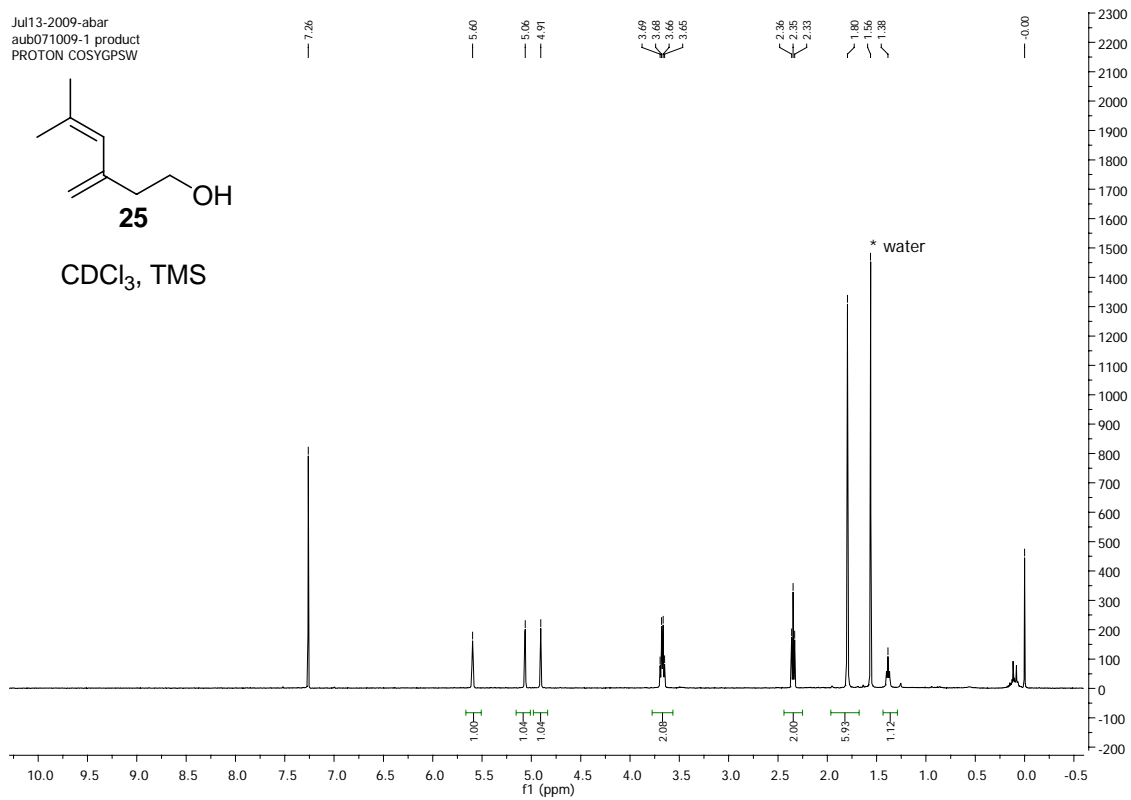
\* hexanes



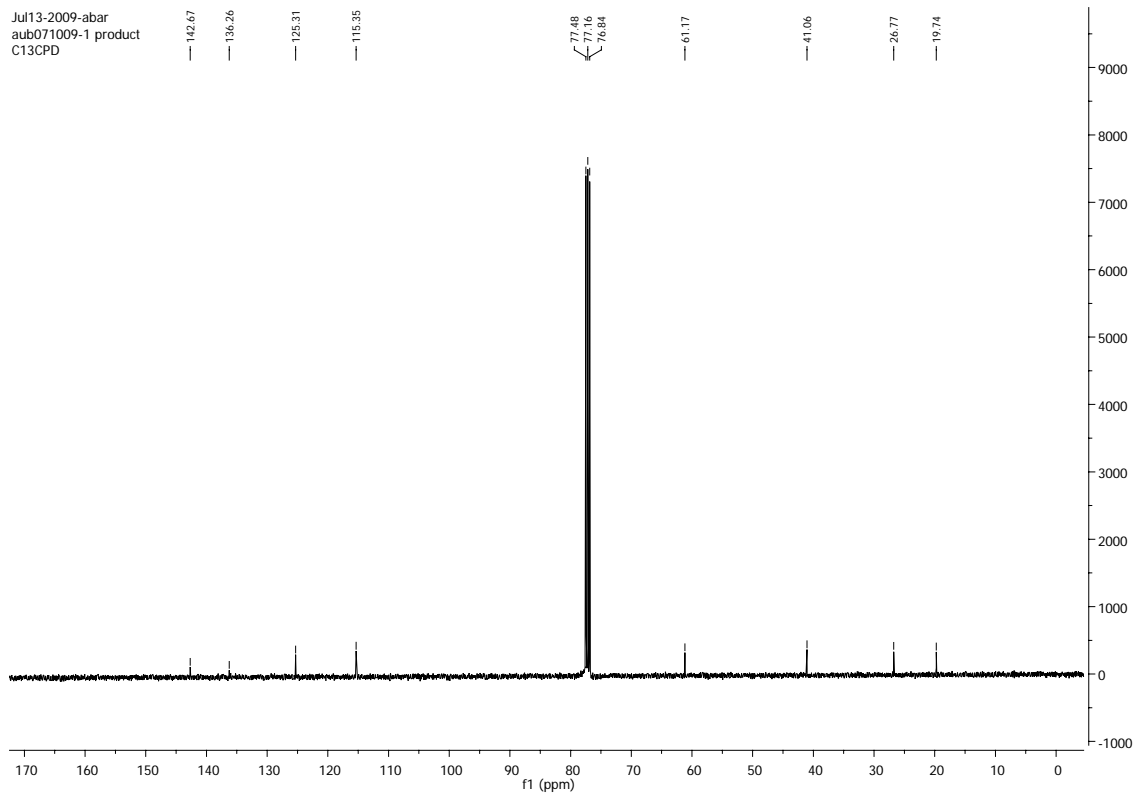
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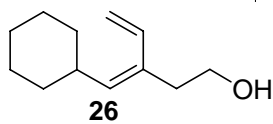
CDCl<sub>3</sub>, TMS



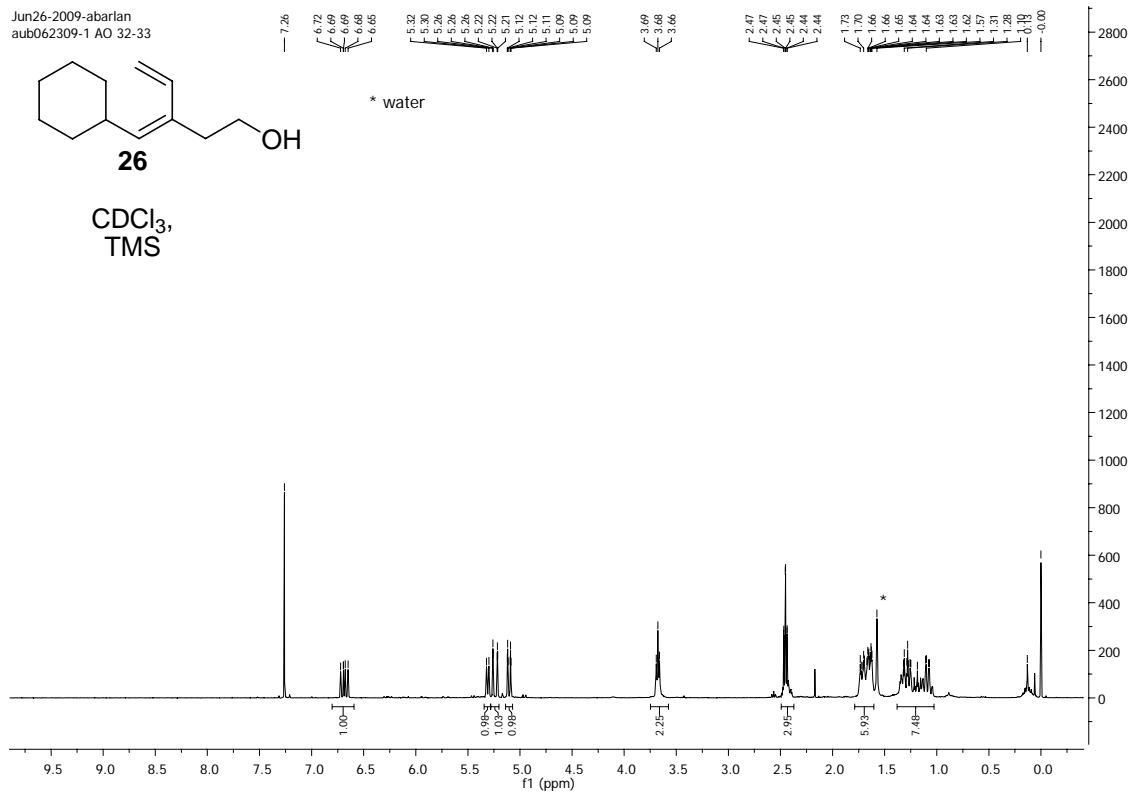
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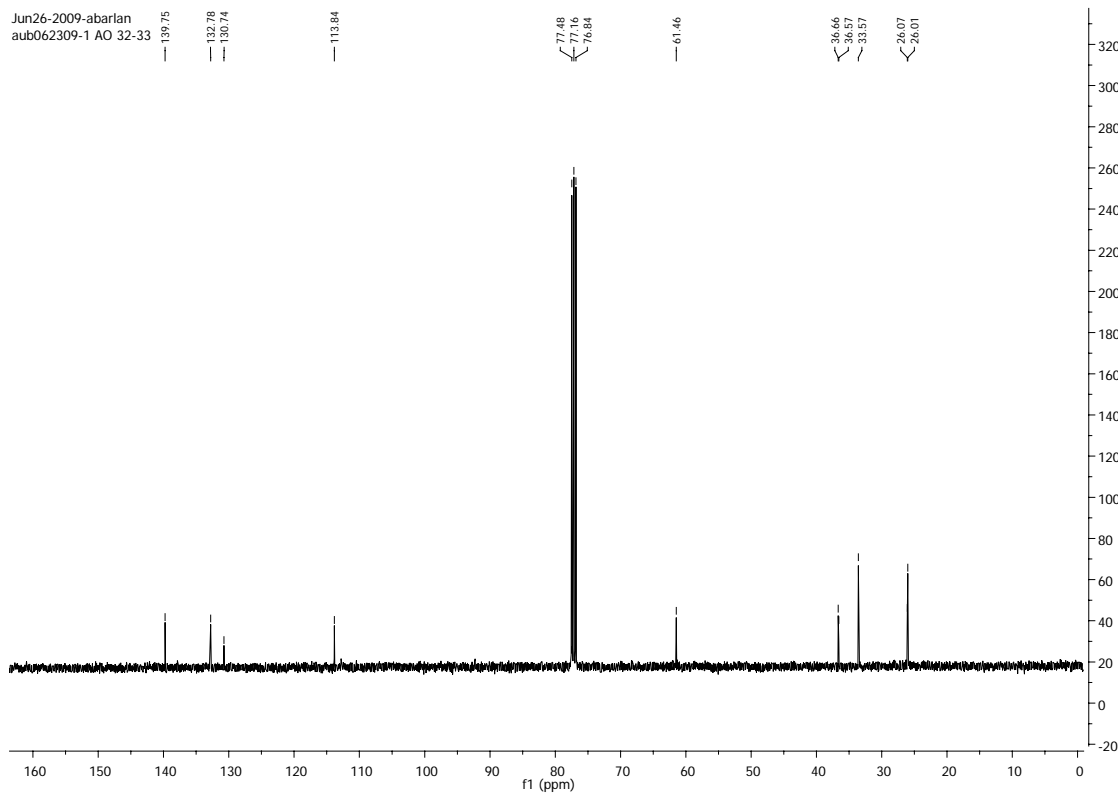
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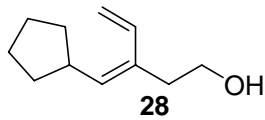
CDCl<sub>3</sub>,  
TMS



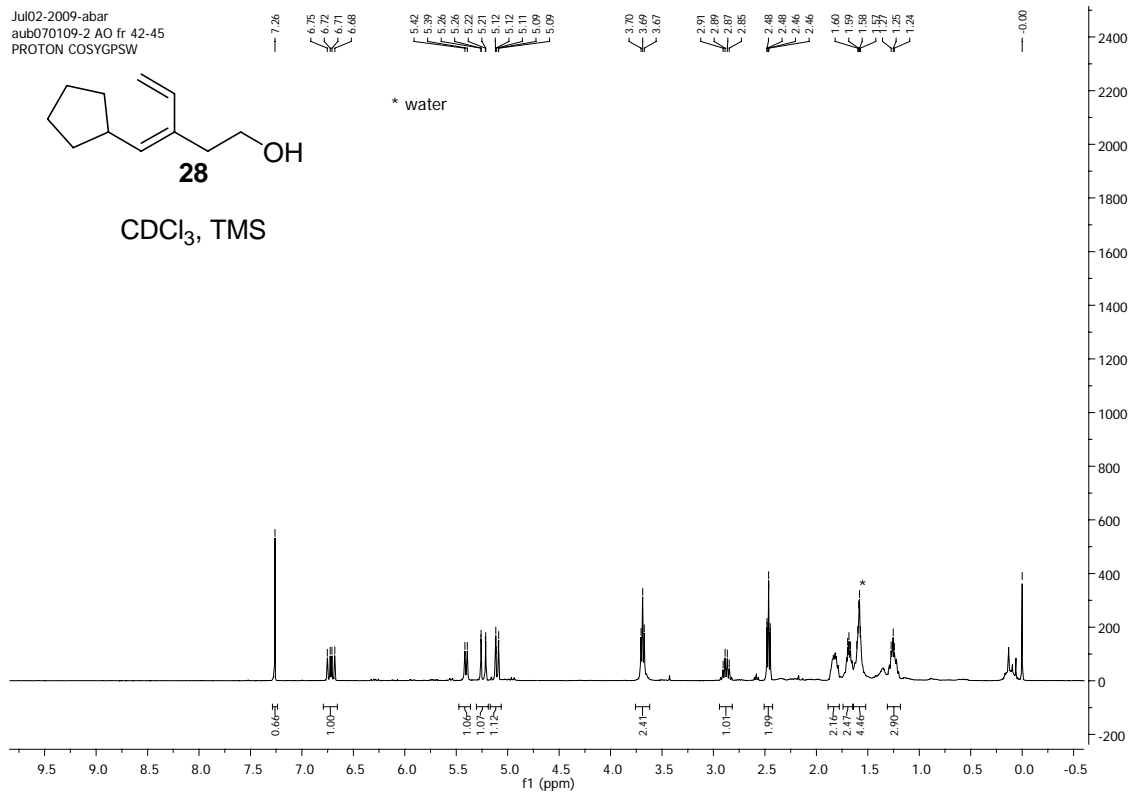
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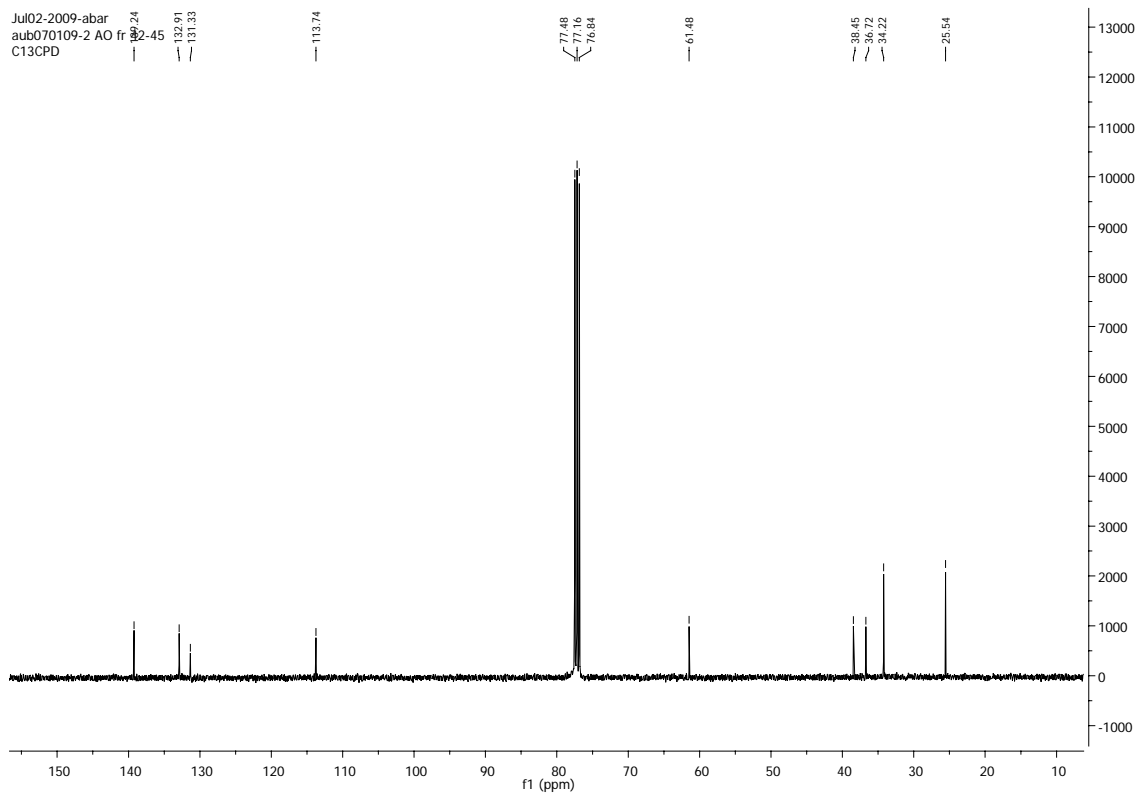
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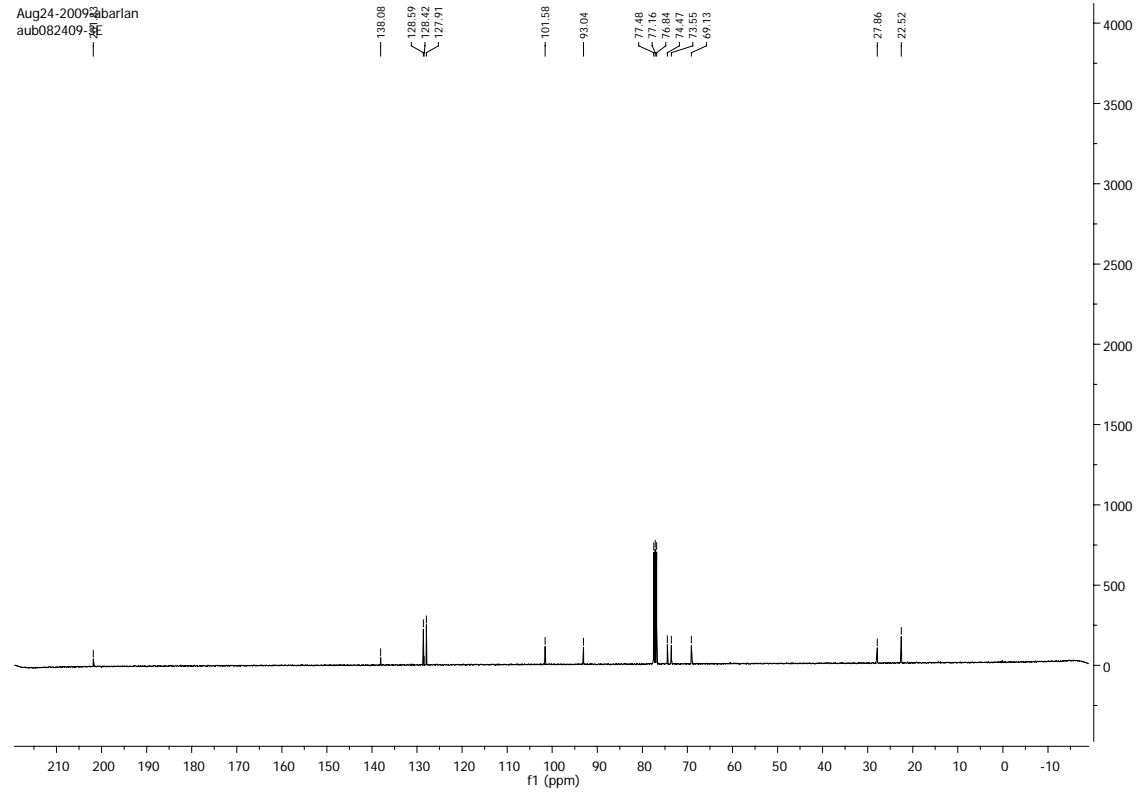
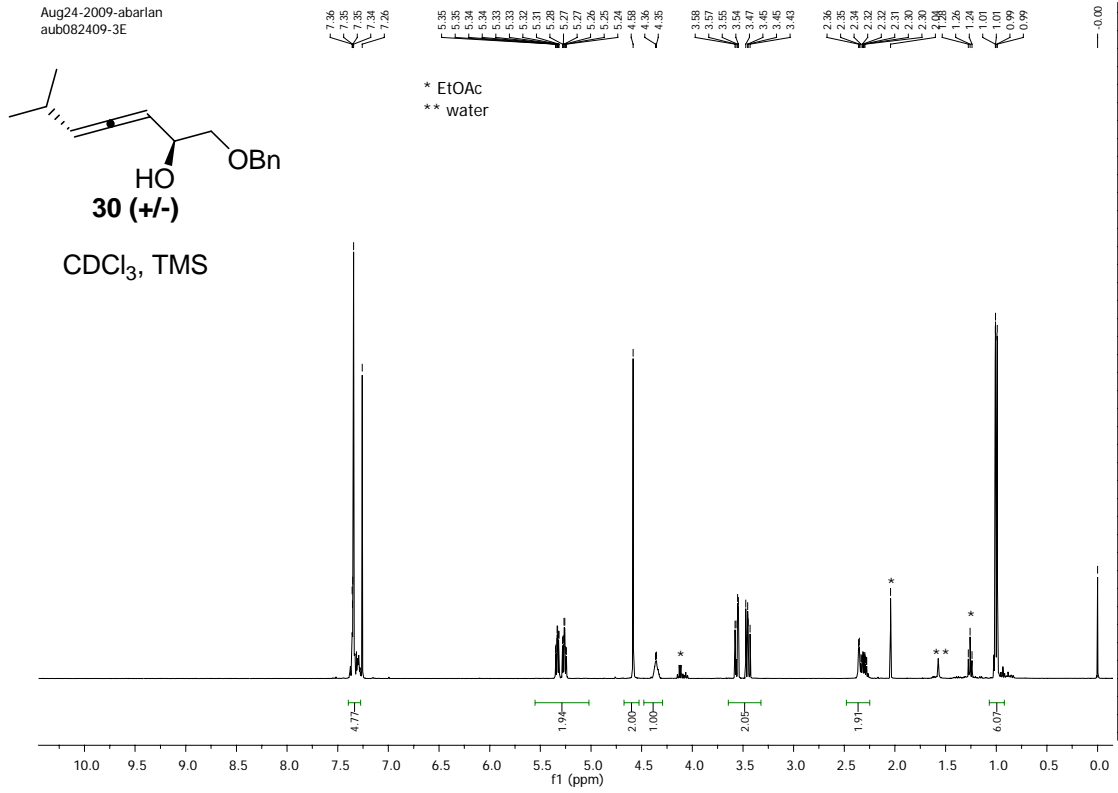


CDCl<sub>3</sub>, TMS

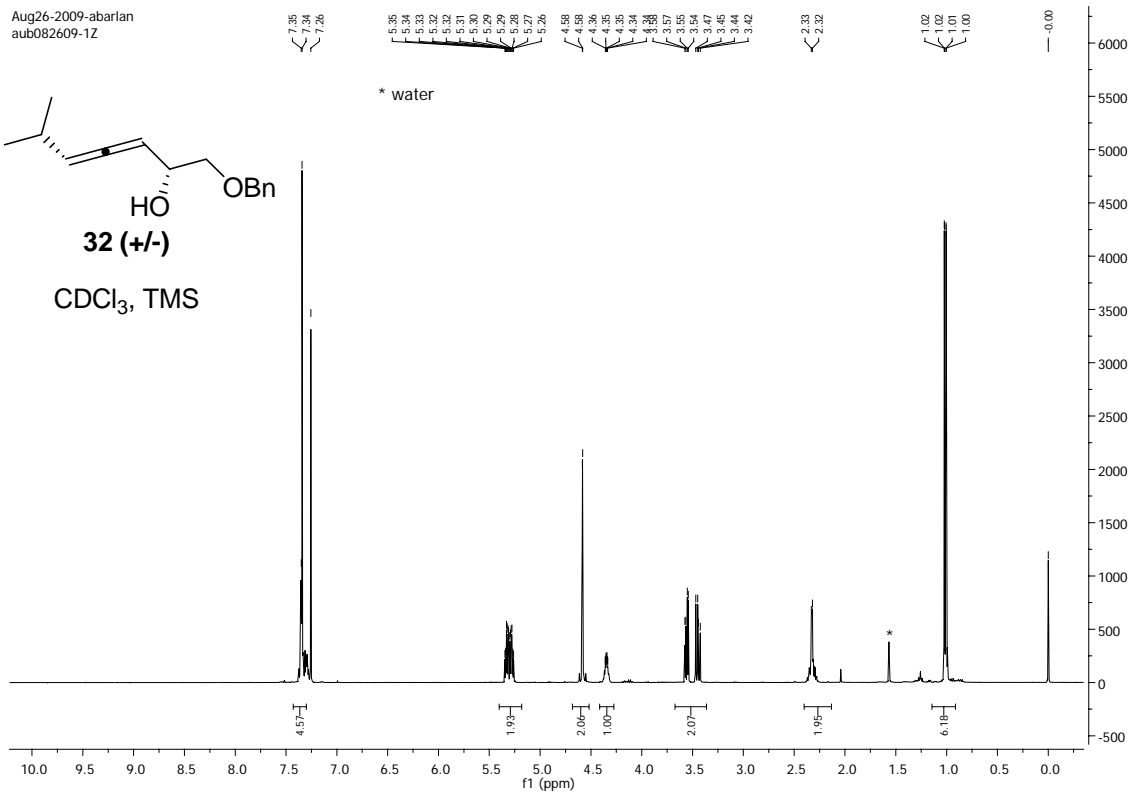
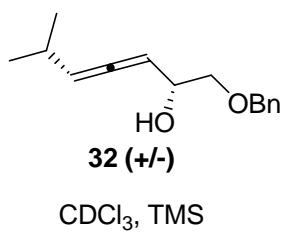


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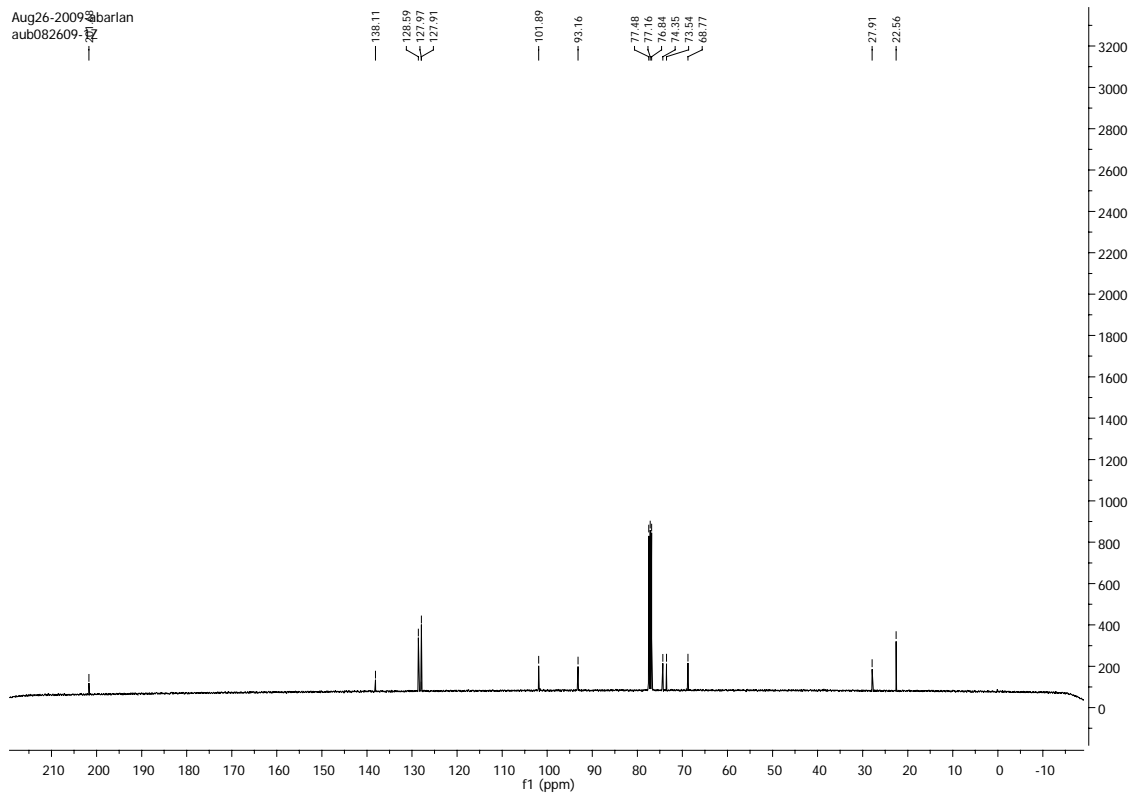




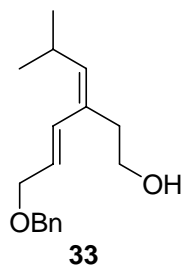
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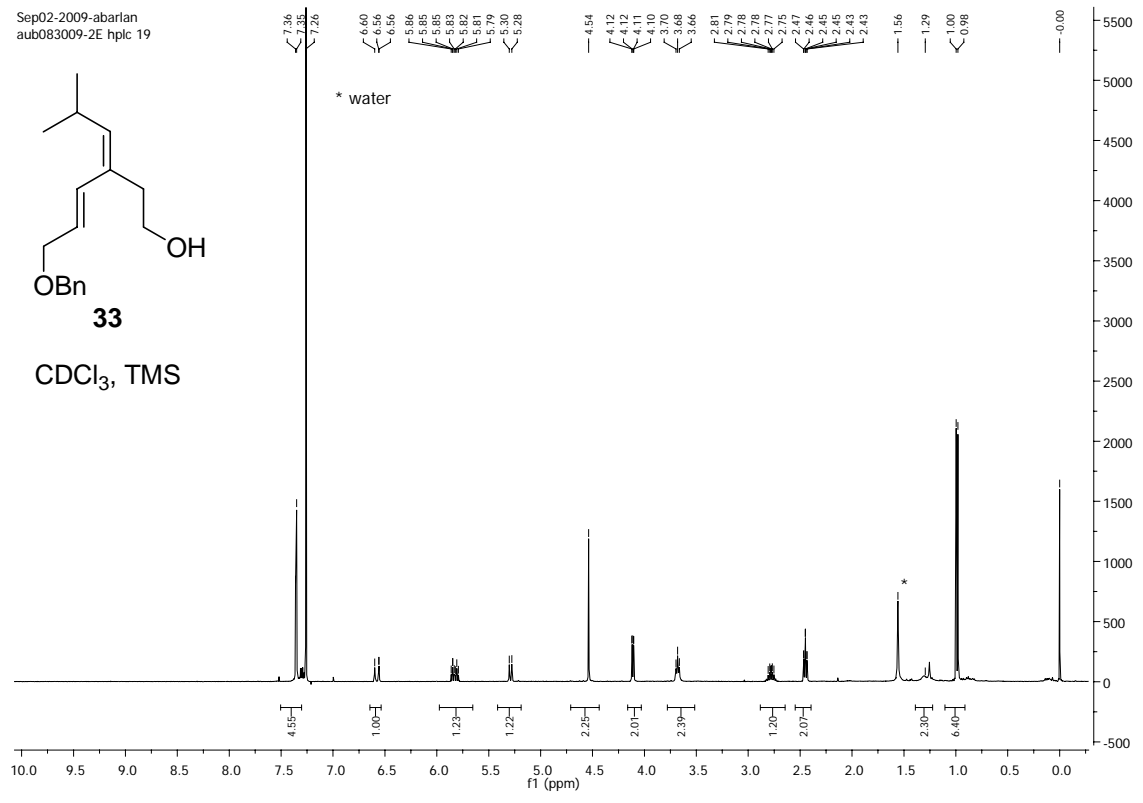
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Sep02-2009-abarlan  
aub083009-2E hplc 19



CDCl<sub>3</sub>, TMS



Sep02-2009-abar  
aub083009-2E hplc 19  
C13CPD

