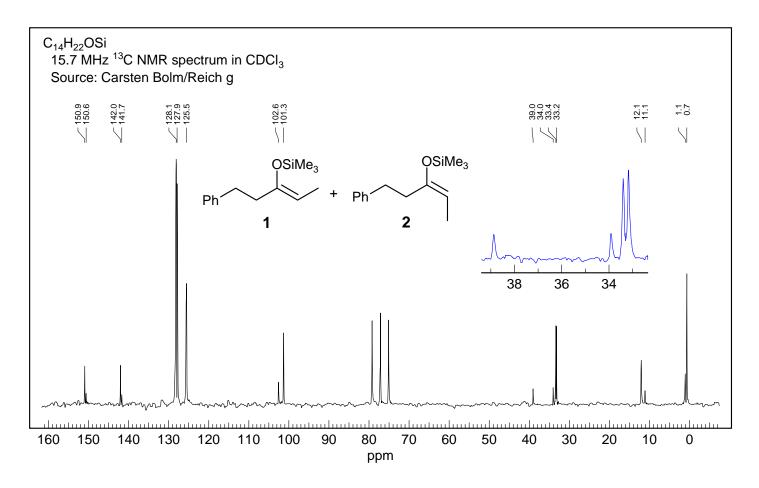
Exercise: The 15.7 MHz ¹³C NMR spectrum (CDCl₃) below is of an approximately 3:1 mixture of stereoisomers. Which is the major isomer? Explain.



Solution:

The chemical shifts of the major and minor isomers for all carbons except one differ by less than 1.4 ppm. The exception are of the CH_2 carbons. In the major isomers the two CH_2 are close together (33.2 and 33.4), whereas in the minor isomer one of them is downfield at 39.4, the other at 34.0. Thus one of the CH_2 , likely the one marked, differs by at least 5.4 ppm, a typical γ -shift for cis interaction across the double bond. Thus the major isomer is $\mathbf{2}$, the E-isomer, where the CH_3 and CH_2 are cis to each other. Note that the CH_3 group, which has a γ -interaction with the CH_2 in the E-isomer, and with the CH_3 group in the Z-isomer has a shift difference of only 1.0 ppm in the two isomers.

OSiMe₃ OSiMe₃ OSiMe₃
$$\frac{34.0 \text{ 150.6}}{102.6}$$
 $\frac{11.1}{102.6}$ $\frac{150.9}{102.6}$ $\frac{101.3}{101.3}$ CH₃ sees γ-effect in both isomers γ-effect here Minor Major