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Configurational Correlations of Some Secondary Alcohols by ^{1}H NMR Spectroscopy

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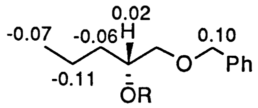
Examination of ^{1}H NMR of the MTPA esters of 21 examples of secondary alcohols allows facile correlations of the absolute configuration of the substrates without exception.

The determination of the absolute configuration of chiral alcohols by the correlations of their α-methoxy-α-trifluoromethylphenylacetates (MTPA esters) by means of ^{1}H as well as ^{13}C NMR spectroscopies (Mosher method) is one of the most reliable methods.[1-3] However, most of the correlations so far made by ^{1}H NMR have been limited to the signals of the proton(s) on the β- and β'-carbons from the carbinyl oxygen. In relation to our ongoing study using chiral glycols,[4] we measured ^{1}H NMR spectra of both enantiomeric MTPA esters of 21 chiral secondary alcohols using a 500 MHz NMR spectrometer. As appeared in Fig. 1 anisotropic effect exerted by the phenyl group of the MTPA moiety to the remote protons exerted in the same direction that to the protons on the β- and β'-carbons without exception. The protons directly attached to the carbinyl carbon were, however, not applicable since the difference of the chemical shifts between both the diastereomeric esters was irregularly ranged from positive to negative region. The present method may be particularly useful for the determination of the absolute structure of various natural products containing secondary hydroxyl group.



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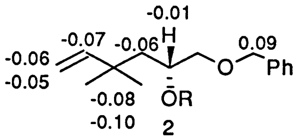

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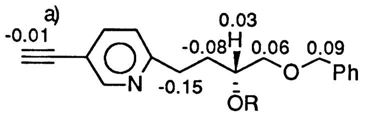

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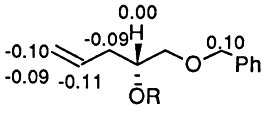

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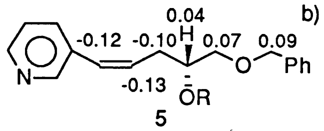

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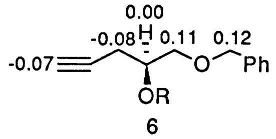

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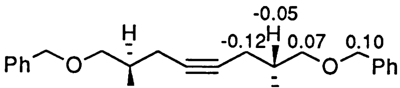

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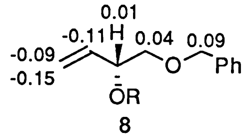

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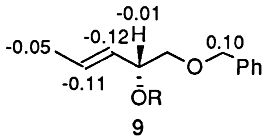

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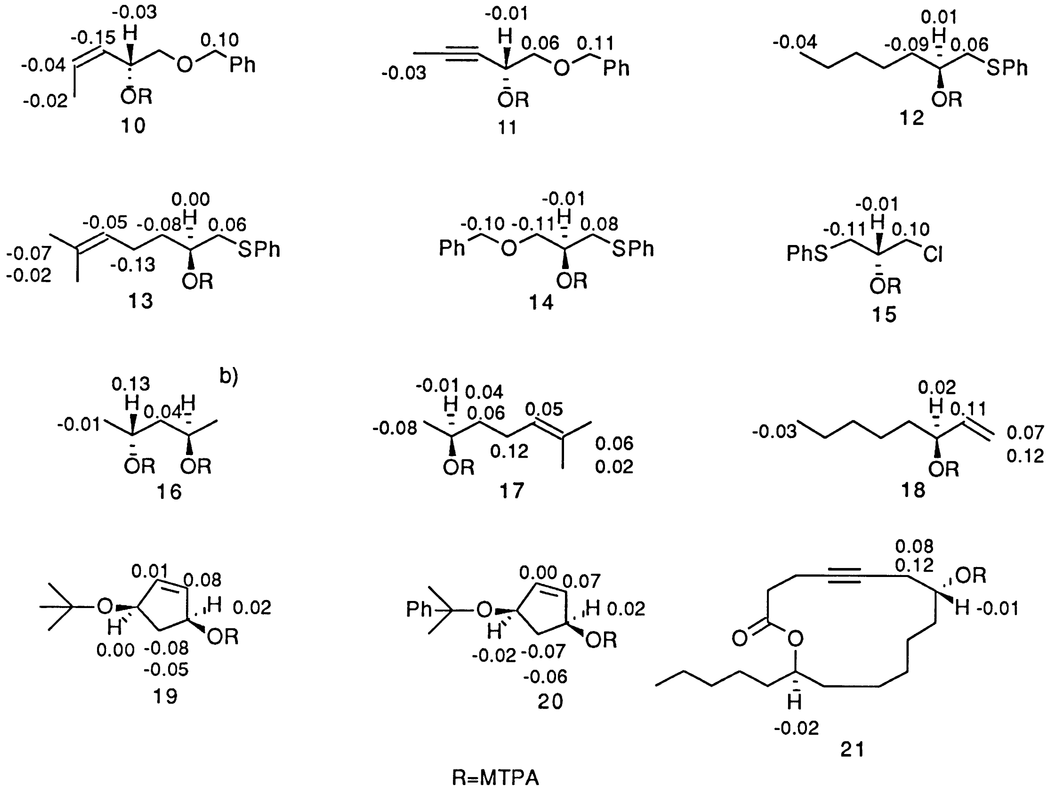

Fig. 1. ^{1}H NMR Chemical shift differences for MTPA derivatives: $\Delta\delta$ (ppm) = δ(R/R)(or S/S) - δ(R/S)(or S/R).
a) 0.01 ±0.001 ppm.
b) Measured by a 90 MHz spectrometer.

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References

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