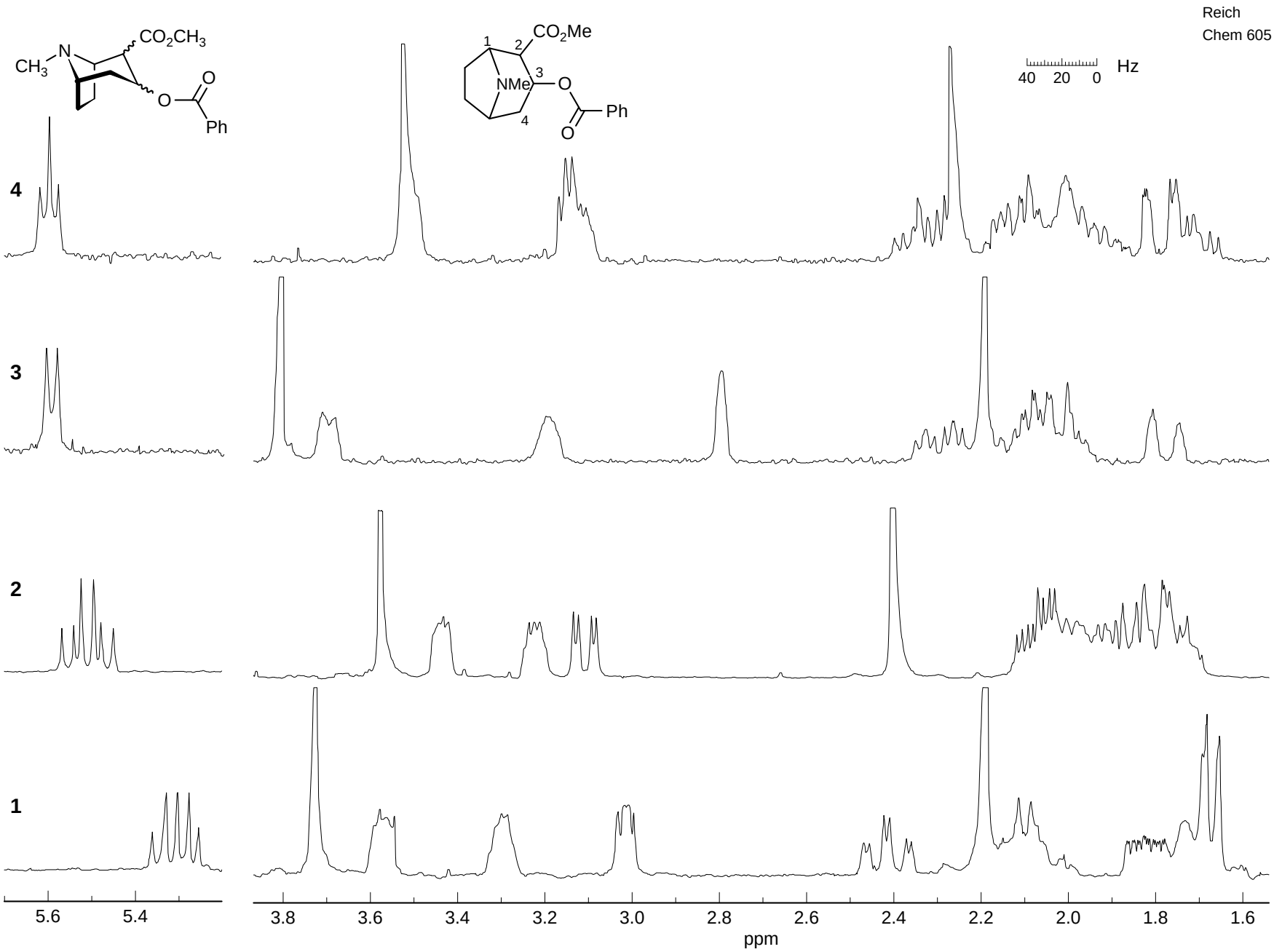
Problem N-302 ($C_{17}H_{19}NO_4$): 250 MHz ^{1}H NMR spectra of the four isomers of cocaine are shown below. Which proton appears at δ 5.3-5.6? **Assign relative stereochemistry to the four isomers. Assign the protons at δ 1.8 and 2.5 for 1** and 2.1 for **2** (*JOC* **1982**, *47*, 13).



PLT pn-080-to-373.plt

XLS

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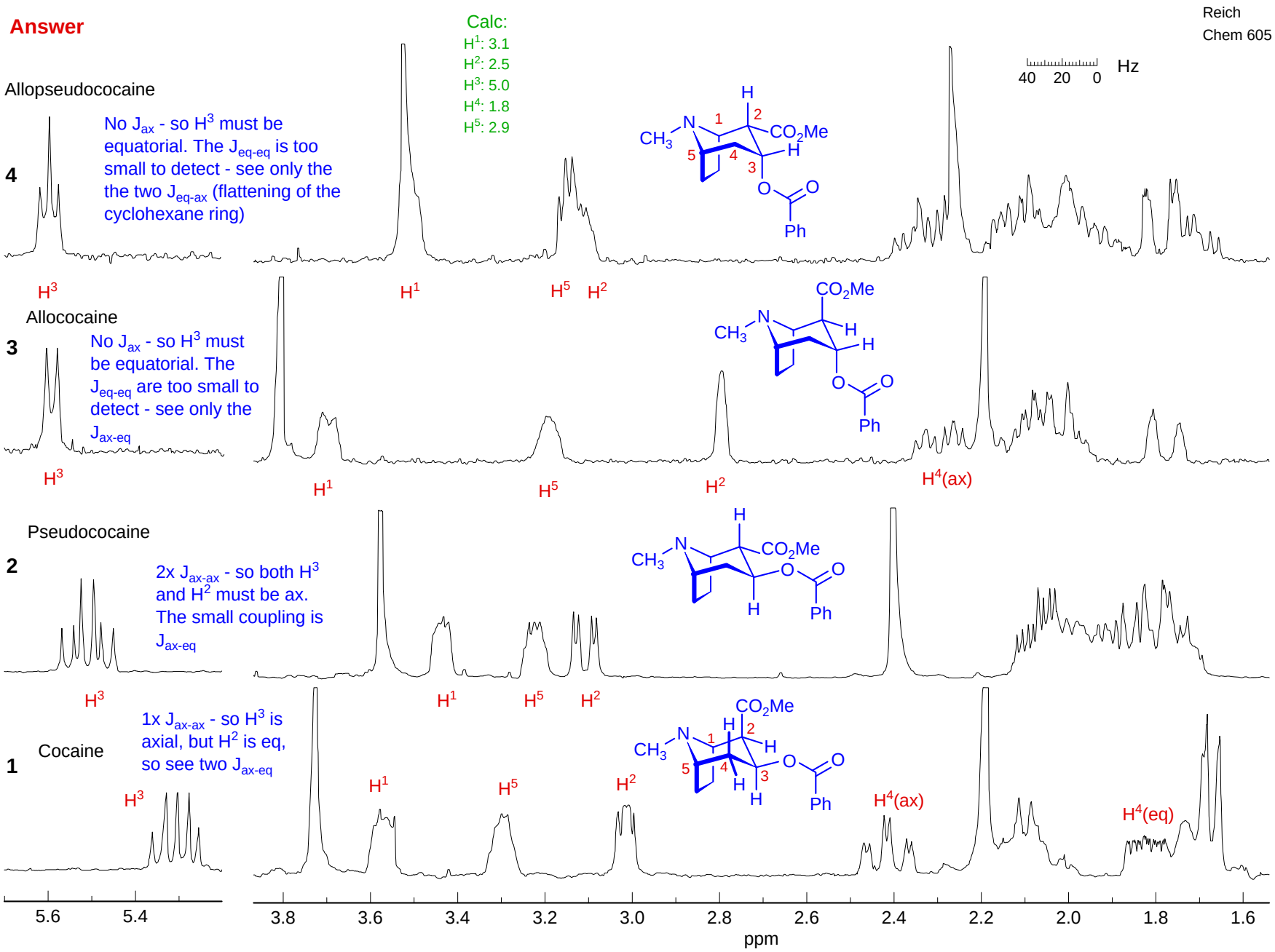
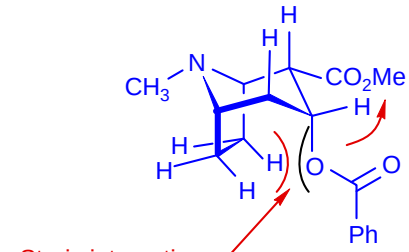


PLT pn-080-to-373.plt

In Bicyclo[3.3.1]nonanes and bicyclo[3.2.1]octanes (as in these examples) the cyclohexane ring is flattened due to repulsion between the two larger bridges, so the eq-eq dihedral angle approaches 90 degrees, and the $J_{eq\text{-}eq}$ coupling can be too small to resolve. The ring flattening has the effect of making $^3J_{ax\text{-}eq}$ unusually large, 5.4 Hz for Allopseudococaine, 6.2 Hz for Allococaine.



Allopseudococaine

Steric interaction causes ring flattening