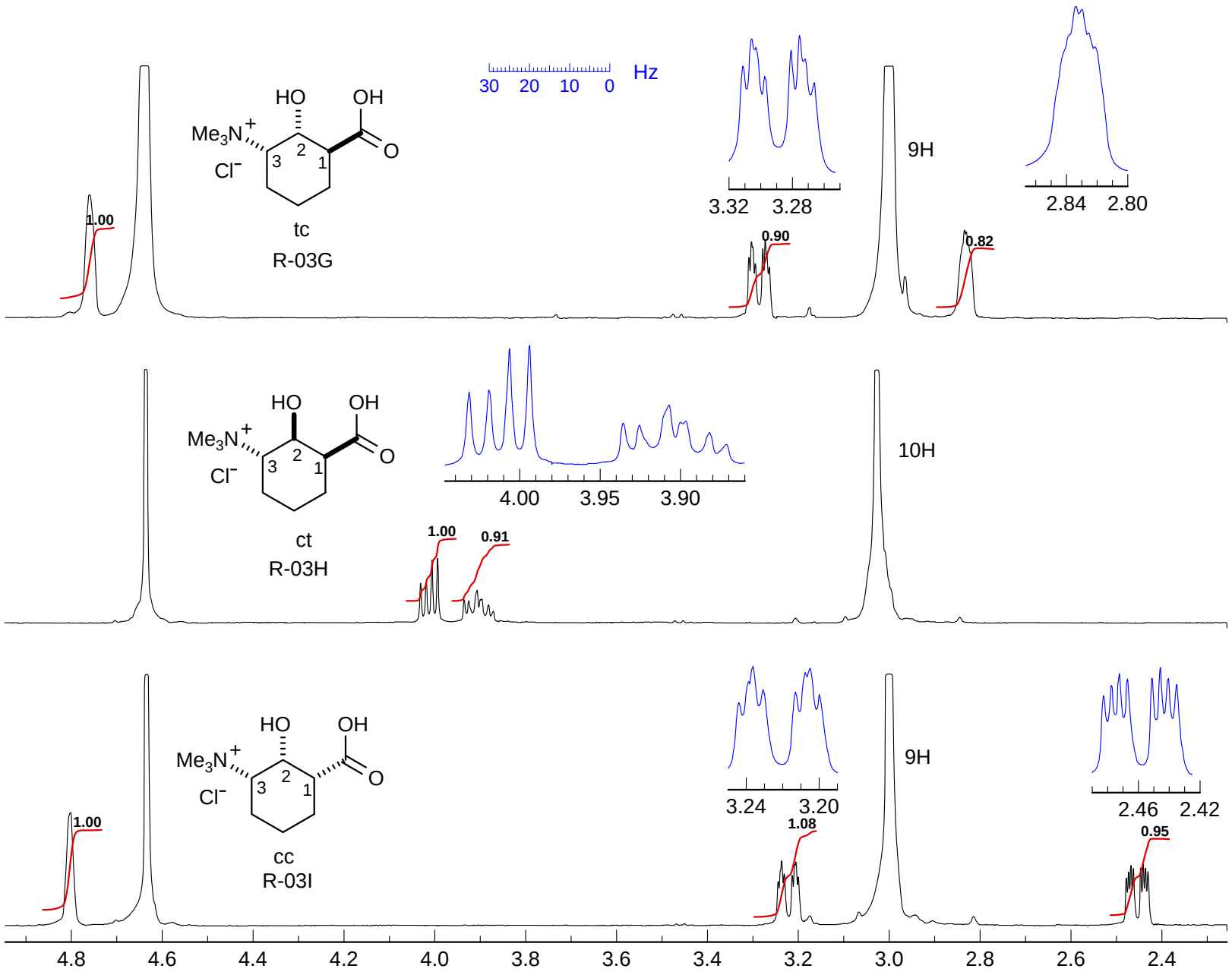
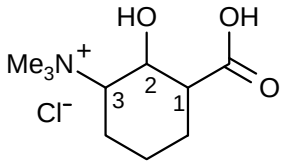
Problem R-03GHI ($C_{10}H_{20}ClNO_3$)
400 MHz ^{1}H NMR Spectra in D_2O
Source: Brouillette *J. Org. Chem.* **1994**, *59*, 4297 11/26 g



PLT ex-2-2003-g.plt

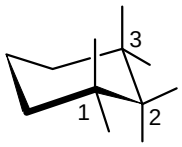
Problem R-03GHI. Determine the structure of three stereoisomeric 2-hydroxy-3-trimethylammoniocyclohexanecarboxylic acids from the partial 400 MHz ^{1}H NMR spectra provided (Brouillette *J. Org. Chem.* **1994**, *59*, 4297). You may find it useful to do part (c) first to aid in the assignments.



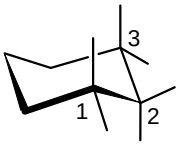
(a) For each isomer, identify the signals which are shown in the spectrum. Give coupling constants, multiplicities and chemical shifts.

	H^1	H^2	H^3
R-03G δ, *J*:	_____	_____	_____
R-03H δ, *J*:	_____	_____	_____
R-03I δ, *J*:	_____	_____	_____

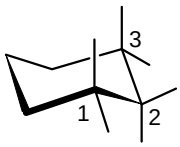
(b) Assign the stereochemistry and conformation of the three isomers by placing the proper substituents on the structures below. For each one, briefly give your reasoning.



R-03G



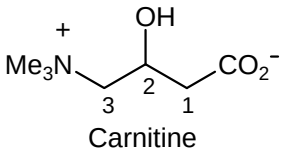
R-03H



R-03I

(c) The compounds **R-03GHI** are conformational models for carnitine. A spectrum of carnitine is shown below to aid in your analysis.

300 MHz ^{1}H NMR Spectrum in D_2O
Source: Aldrich Spectra Collection/Reich 11/33



Carnitine

Assign each of the four sets of peaks in the NMR spectrum, and identify each pattern (e.g., AA' part of an AA'XX' pattern). Do not attempt to extract coupling constants.

δ 2.4

δ 3.2

δ 3.4

δ 4.6

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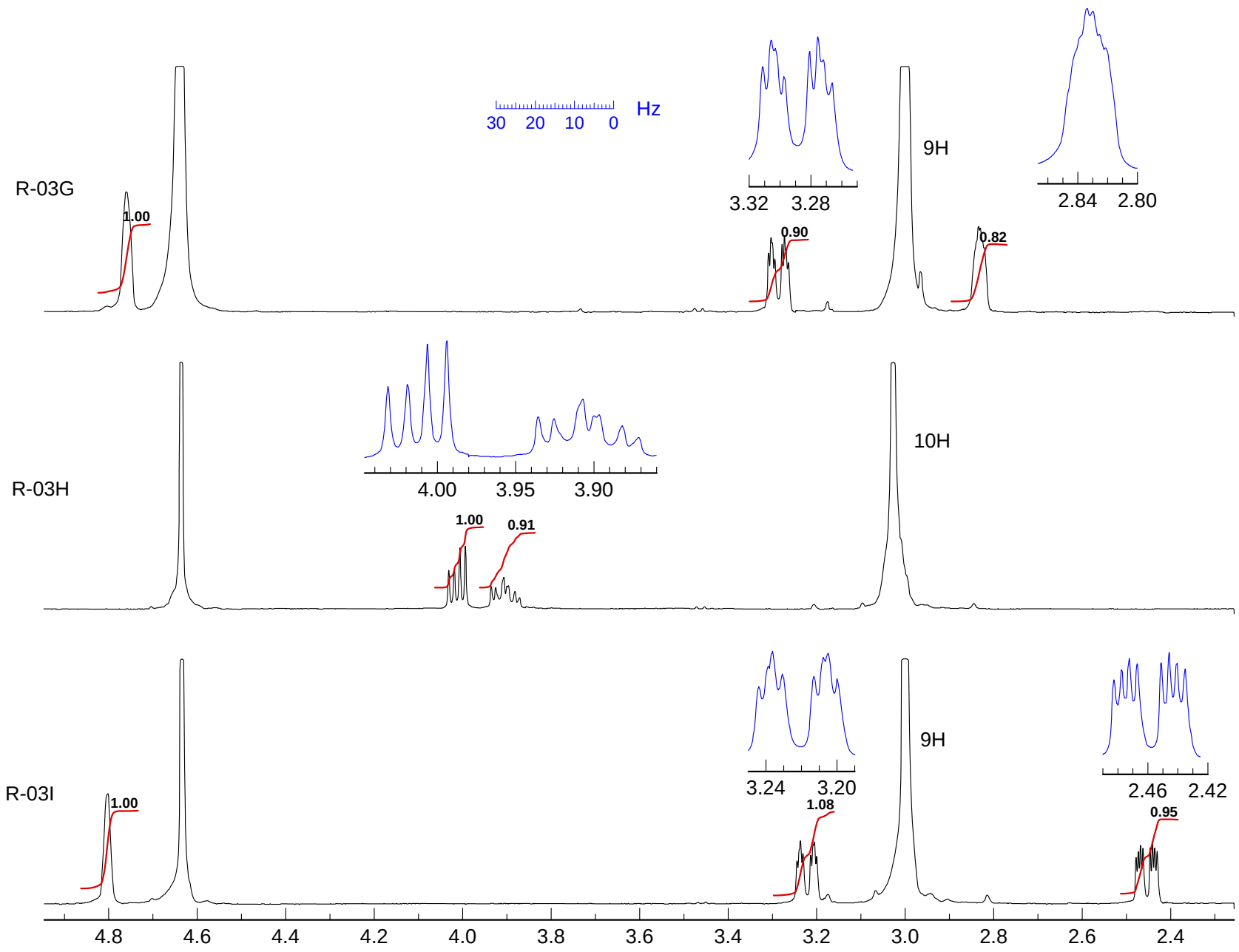
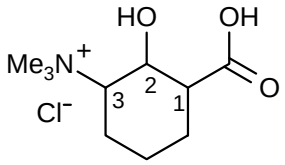
Problem R-03GHI. ($C_{10}H_{20}ClNO_3$)
400 MHz ^{1}H NMR Spectra in D_2O
(Source: Brouillette *J. Org. Chem.* **1994**, *59*, 4297 11/26)



PLT ex-2-2003-g.plt

Problem R-03GHI. Determine the structure of three stereoisomeric 2-hydroxy-3-trimethylammoniocyclohexanecarboxylic acids from the partial 400 MHz ^{1}H NMR spectra provided (Brouillette *J. Org. Chem.* **1994**, *59*, 4297). You may find it useful to do part (c) first to aid in the assignments.

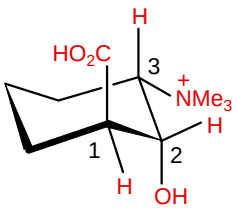


(a) For each isomer, identify the signals which are shown in the spectrum. Give coupling constants, multiplicities and chemical shifts.

	H^1	H^2	H^3 (always ax)
R-03G δ, *J*:	2.84, td, *J* = 4, 2 Hz	4.75, ≈s?	3.29, ddd, *J* = 12, 4, 3 Hz
8 R-03H δ, *J*:	3.05 hidden under $Me_3\overset{+}{N}$ peak	4.01, dd, *J* = 10, 5 Hz	3.91, td, *J* = 11, 5 Hz
R-03I δ, *J*:	2.46, ddd, *J* = 12, 5, 2 Hz	4.8, ≈s?	3.22, ddd, *J* = 12, 4, 3 Hz

Expect H^1 to be most upfield of the three protons, H^2 to be most downfield:
Curphy-Morrison Δδ: 2° α $\overset{+}{N}Me_3$: 2.06, α OH: 2.30; α CO_2H: 1.00

(b) Assign the stereochemistry and conformation of the three isomers by placing the proper substituents on the structures below. For each one, briefly give your reasoning.

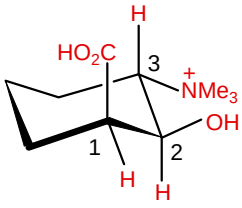


R-03G

For each compound, the $\overset{+}{N}Me_3$ should be the "anchor" - it is as large as a ^{t}Bu group - and should always be equatorial. This what we see: H^3 always has at least one large (ax-ax) coupling.

H^3 must be axial, since is shows one large coupling (12 Hz).

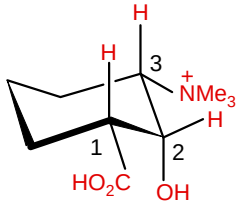
H^1 and H^2 must both be equatorial, since neither shows a large coupling



12 **R-03H**

H^3 shows two large couplings (3.91, td, *J* = 11, 5 Hz) so must be axial and have axial protons on both sides, so H^2 must also be axial

H^2 has only one ax-ax proton coupling (4.01, dd, *J* = 10, 5 Hz) so H^1 must be equatorial (even though we cannot see it well).



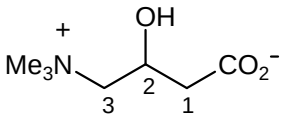
R-03I

H^3 has only one ax-ax coupling (3.22, ddd, *J* = 12, 4, 3 Hz) so it is axial, but H^2 must be equatorial

H^1 has one ax-ax coupling (2.46, ddd, *J* = 12, 5, 2 Hz), so it must be axial

(c) The compounds **R-03GHI** are conformational models for carnitine. A spectrum of carnitine is shown below to aid in your analysis.

300 MHz ^{1}H NMR Spectrum in D_2O
Source: Aldrich Spectra Collection/Reich 11/33



Carnitine

Assign each of the four sets of peaks in the NMR spectrum, and identify each pattern (e.g., AA' part of an AA'XX' pattern). Do not attempt to extract coupling constants.

δ 2.4 CH_2 at C^1: AB of ABMXY pattern

Calc δ: Base: 1.2
α CO_2H: 1.0
β OH: 0.2
Calc: 2.4

δ 3.2 $-\overset{+}{N}Me_3$ singlet

5

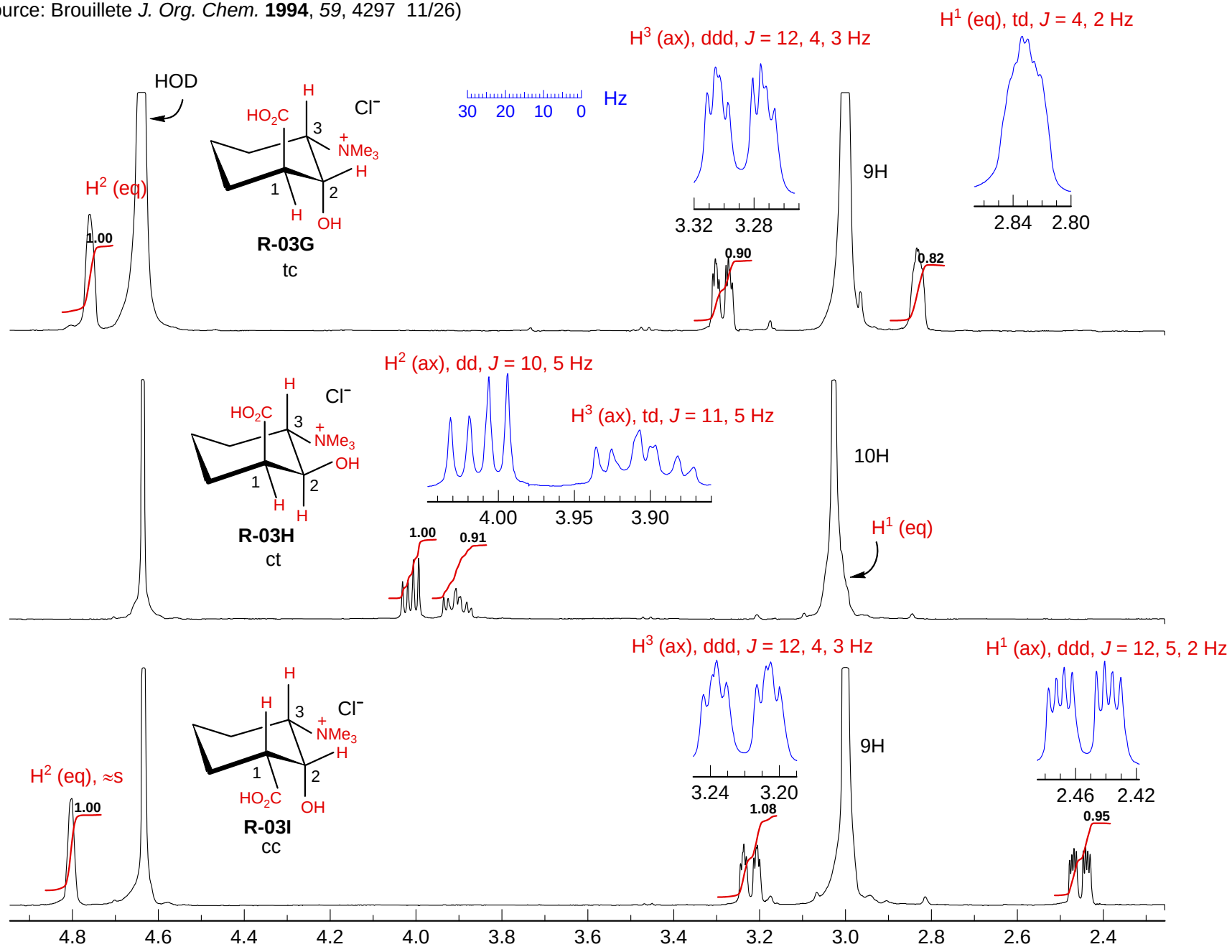
δ 3.4 CH_2 at C_3: XY of ABMXY

(ABX-type pattern with one ab quartet collapsed to singlet - 5-line ABX)

Calc δ: Base: 1.2
α $\overset{+}{N}Me_3$: 2.1
β OH: 0.2
Calc: 3.5

δ 4.6 CH at C^2: apparent quintet, probably a doublet of quartets

Problem R-03GHI. ($C_{10}H_{20}ClNO_3$)
400 MHz ^{1}H NMR Spectra in D_2O
(Source: Brouillette *J. Org. Chem.* **1994**, *59*, 4297 11/26)



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