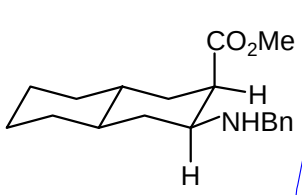
Problem R-02N-1. Decalin

300 MHz ^{1}H NMR spectrum in $CDCl_3$

Source: Tim Peelen/Gellman



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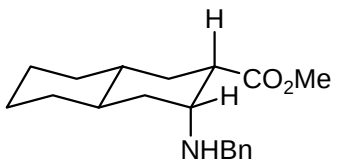
Problem R-02N-2. Decalin

300 MHz ^{1}H NMR spectrum in $CDCl_3$

Source: Tim Peelen/Gellman



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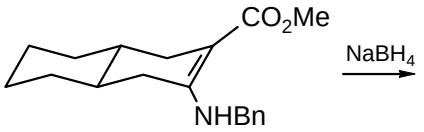
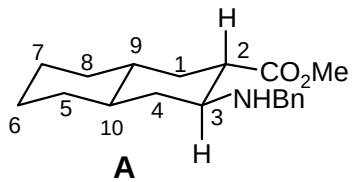
Problem R-02N. In this problem you are asked to determine which two isomers are formed in the reduction of an olefin by analyzing the ^{1}H NMR spectra.

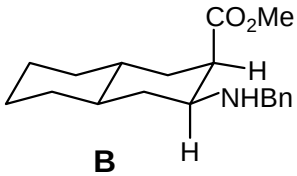


R-02N-1 + **R-0N-2** (1:4) Bn = CH_2-Ph

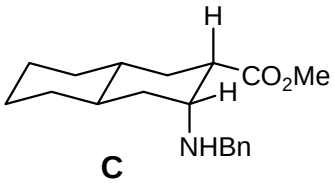
Four diastereomers could be formed. In your answers use the numbering system of structure **A** (e.g. H_{1a} or H_{1e}).



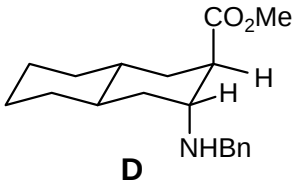
A



B



C



D

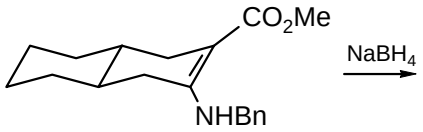
(a) Analyze key signals in the NMR spectrum of **R-02N-1**. Identify the signals below, report chemical shifts and couplings and report them in the standard format. Assign the signals. Compound **R-02N-1** is structure _____. Briefly explain.

(b) Analyze key signals in the NMR spectrum of **R-02N-2**. Identify the signals below, report chemical shifts and couplings and report them in the standard format. Assign the signals. Compound **R-02N-2** is structure _____. Briefly explain.

(c) Analyze the signals at δ 1.5 in **R-02N-1**, and identify which proton corresponds to this multiplet.

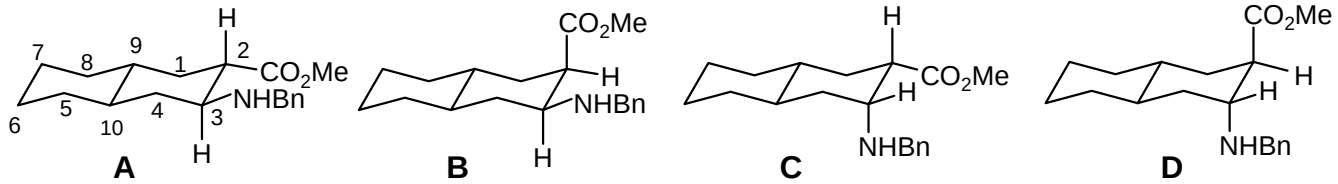
(d) Can you rationalize the different appearance of the signals near δ 3.8 in the two isomers?

Problem R-02N. In this problem you are asked to determine which two isomers are formed in the reduction of an olefin by analyzing the ^{1}H NMR spectra.



R-02N-1 + **R-0N-2** (1:4) Bn = CH_2-Ph

Four diastereomers could be formed. In your answers use the numbering system of structure **A** (e.g. H_{1a} or H_{1e}).



(a) Analyze key signals in the NMR spectrum of **R-02N-1**. Identify the signals below, report chemical shifts and couplings and report them in the standard format. Assign the signals. Compound **R-02N-1** is structure _____. B
Briefly explain.

The downfield protons (in addition to the OMe and the NH) will be C**H**-CO_2Me (H^2), C**H**-NHBn (H^3), and NH-C**H**$_2$P.

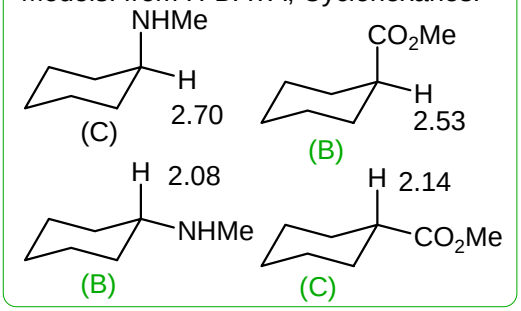
H^2: δ 3.03 narrow multiplet, possible tm, must be eq proton

H^3: δ 2.66, dt, J =12, 4.5 Hz, ax proton, with eq neighbors
From the models at the right, expect ax CH-N (H^3) to be upfield of eq CH-CO_2Me (H^2), by 0.45 ppm, and that is what we see here (0.63 ppm).

N-CH_2-Ph: 3.83, s, 2H

Can also assign H^4(ax) and H^4(eq): expect 3 large *J* for H^4(ax) proton, see a q, J = 12 Hz at δ 1.49), and one large two small coupling for H^4(eq), see dt, J = 12, 2 Hz at δ 1.92.

Models: from H-DATA, Cyclohexanes:



(b) Analyze key signals in the NMR spectrum of **R-02N-2**. Identify the signals below, report chemical shifts and couplings and report them in the standard format. Assign the signals. Compound **R-02N-2** is structure _____. C
Briefly explain.

H^2: δ 2.52, dt, *J* = 13, 4.5 Hz, must be ax proton

H^3: δ 3.26, q, J =3 Hz, eq proton

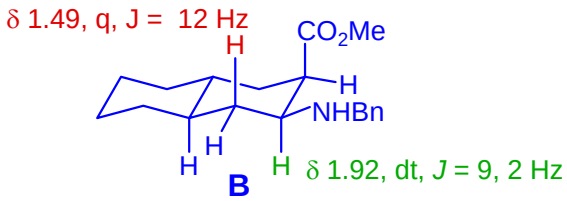
From the models expect ax CH-N (H^3) to be well downfield of eq CH-CO_2Me (H^2), by 0.56 ppm, and that is what we see here (0.74 ppm).

The coupling informations rules out assigmnet of A and D to either R-02N-1 or R-02N-2. However, the coupling is consistent with either B and C be assigned to either R-02N-1 or R-02N-2. However, the chemical shifts allow a clear distinction to be made.

The NH-CH_2-Ph protons are diastereotopic in this isomer, δ 3.63, d, *J* = 13.4 Hz and δ 3.84, d *J* = 13.4 Hz

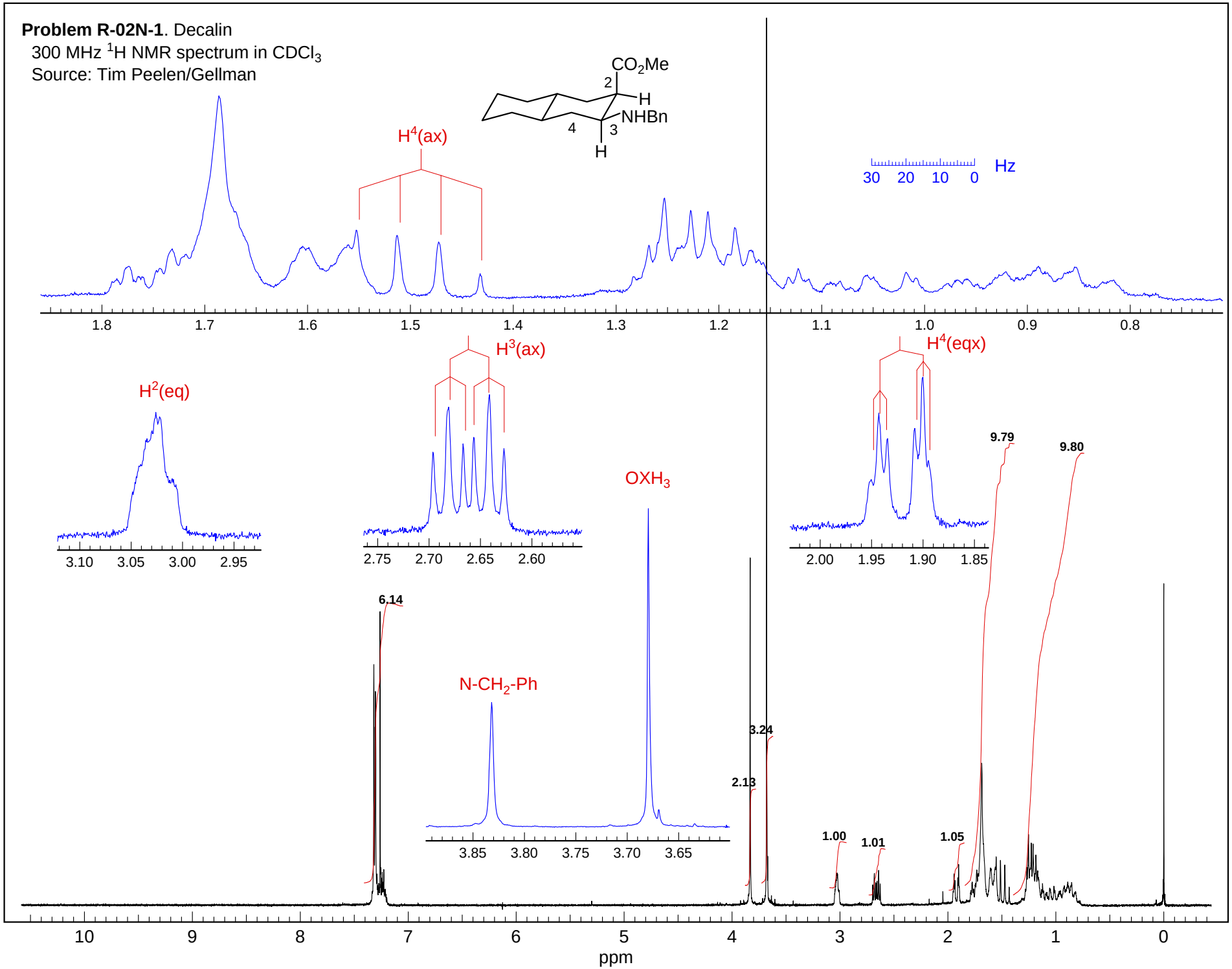
Can also assign H^1(ax) and H^1(eq): see a q, J = 13 Hz at δ 1.52 for H^1(ax), and a dt, J = 13, 3 Hz at δ 1.84 for H^1(eq).

(c) Analyze the signals at δ 1.5 in **R-02N-1**, and identify which proton corresponds to this multiplet.



(d) Can you rationalize the different appearance of the signals near δ 3.8 in the two isomers?

It seems likely that in C the axially oriented -NH-CH_2-Ph is more conformationally constrained, leading to the much larger diastereotopic effect than in B where the -NH-CH_2-Ph group is equatorial and there is no detectable diastereotopic shift.



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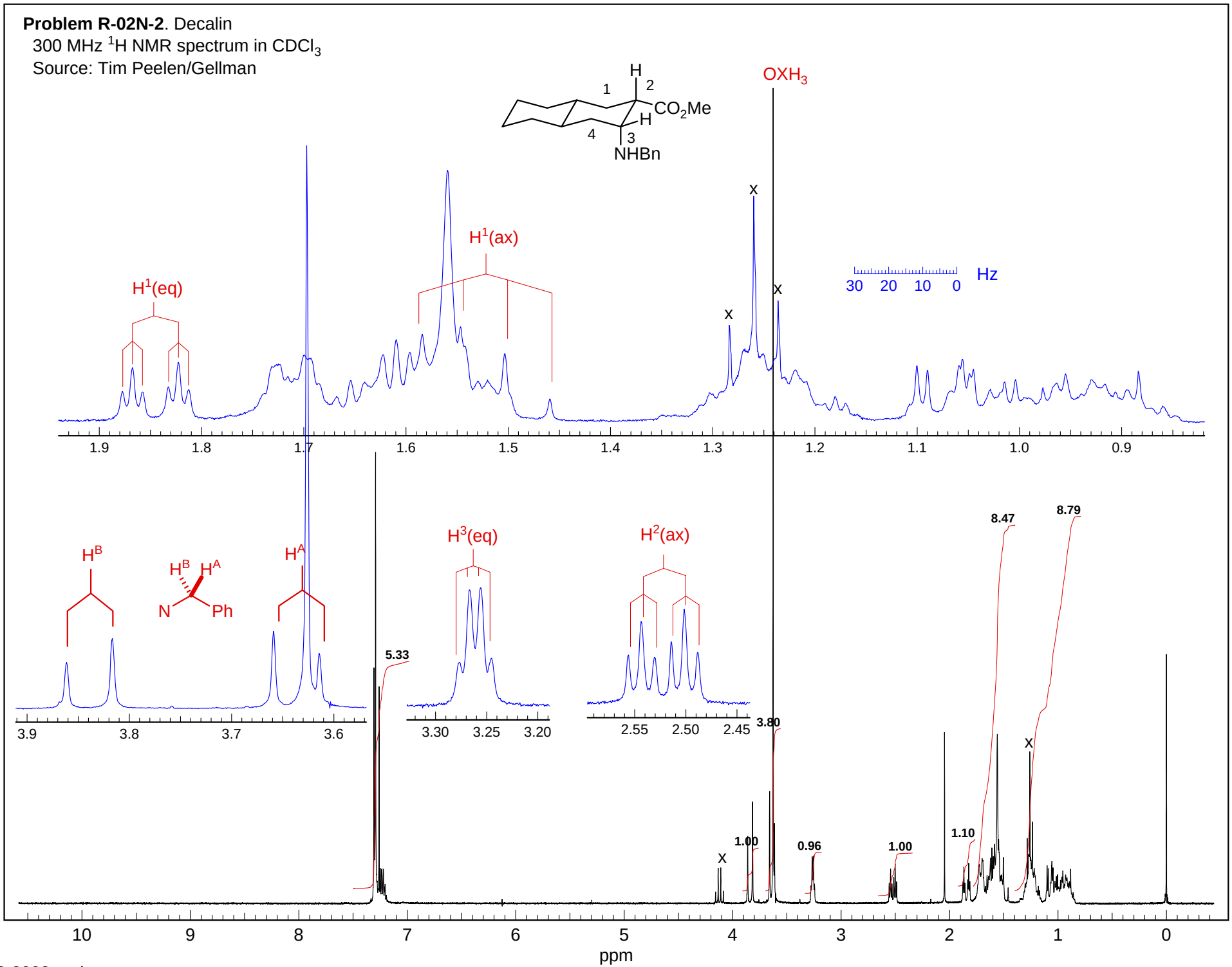

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