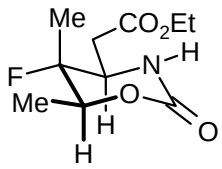
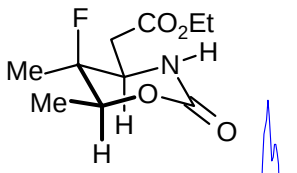
Problem R-13G ($C_{10}H_{16}FNO_4$)

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

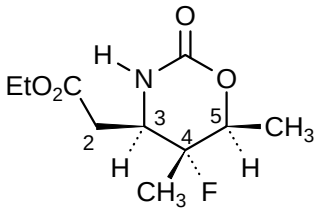
Source: *J. Org. Chem.* **1987**, *52*, 3218 (digitized hard copy)



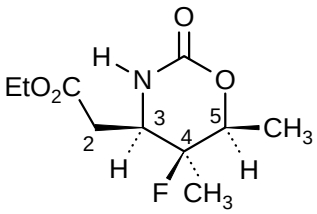


PLT ex-3-2013-14-gq.plt

Problem R-13G. This problem requires you to interpret the ^{1}H NMR spectrum of a pair of stereoisomeric carbamates (A and B below). The frequency scale for the expansions are the same in both spectra. Assign all the couplings using the format $^{n}J_{XY}$ = Z Hz.



A



B

(a) Give the chemical shifts and assign the coupling constants for the protons at C-2 for each isomer (first-order analysis is OK).

Spectrum 1 Spectrum 2

(b) Give the chemical shifts and assign the coupling constants for the protons at C-3 for each isomer (first-order analysis is OK).

Spectrum 1 Spectrum 2

(c) Give the chemical shifts and assign the coupling constants for the protons at C-5 for each isomer (first-order analysis is OK).

Spectrum 1 Spectrum 2

(d) Which spectrum corresponds to structure A?_____ Give your reasoning. **Use conformational drawings**.

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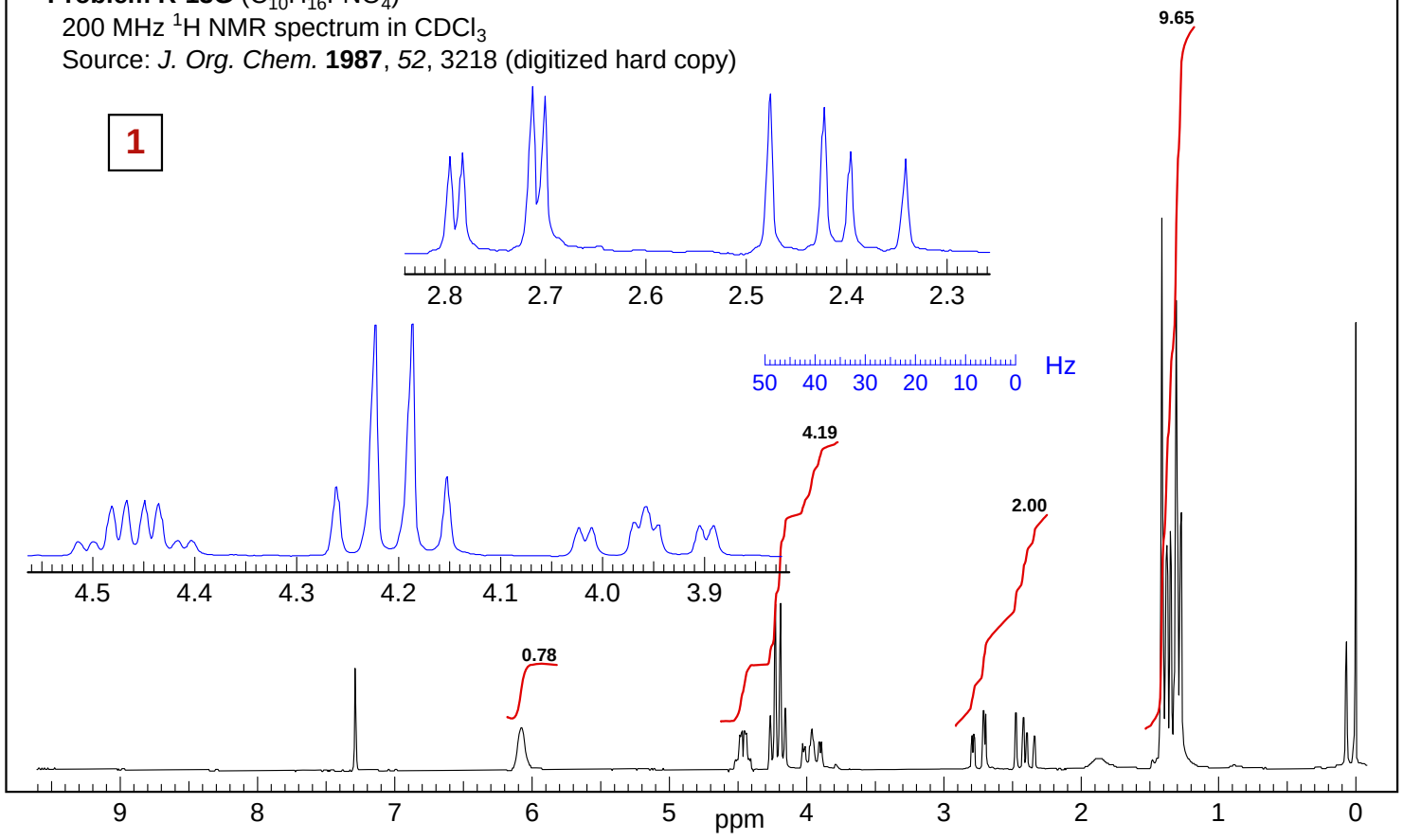

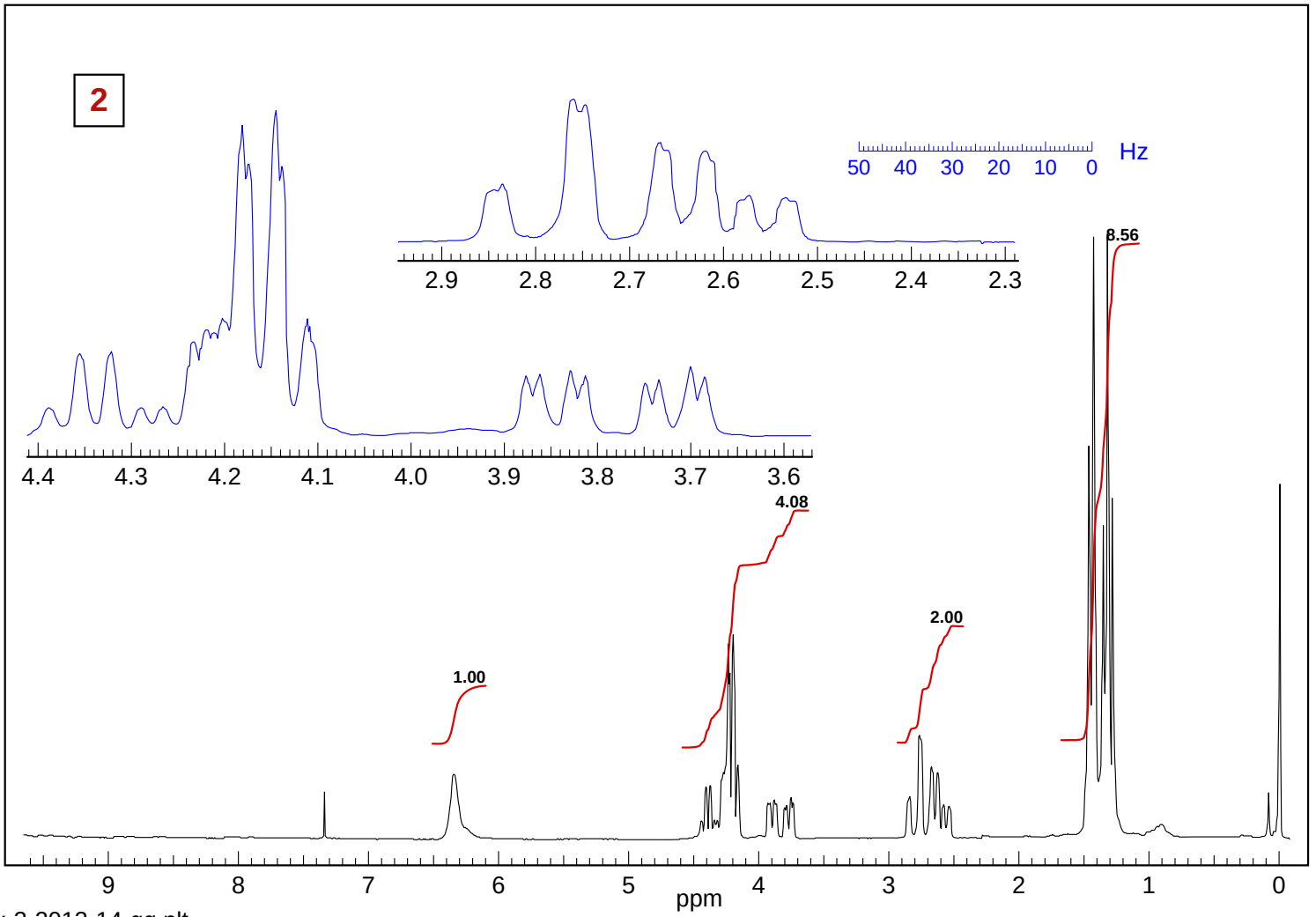

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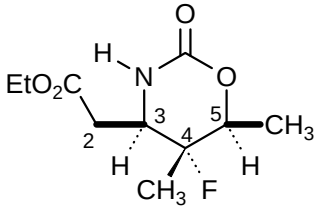
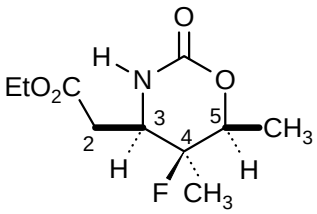
Problem R-13G. This problem requires you to interpret the ^{1}H NMR spectrum of a pair of stereoisomeric carbamates (A and B below). The frequency scale for the expansions are the same in both spectra. Assign all the couplings using the format $^{n}J_{XY}$ = Z Hz.



A



B

(a) Give the chemical shifts and assign the coupling constants for the protons at C-2 for each isomer (first-order analysis is OK).

Spectrum 1

ABX pattern

δ 2.4, dd, *J* = 16, 11 $^{3}J_{HH}$ = 11 Hz (to H_3)

δ 2.75, dd, *J* = 16, 3 $^{3}J_{HH}$ = 3 Hz (to H_3)

$^{2}J_{HH}$ = 16 Hz

4 2

Spectrum 2

ABXY pattern

δ 2.6, ddd, *J* = 17, 10, 2 $^{3}J_{HH}$ = 10 Hz (to H_3)

δ 2.8, dd, *J* = 17, 3 $^{3}J_{HH}$ = 3 Hz (to H_3)

$^{2}J_{HH}$ = 17 Hz 2 Hz: $^{4}J_{HF}$?

(b) Give the chemical shifts and assign the coupling constants for the protons at C-3 for each isomer (first-order analysis is OK).

Spectrum 1

δ 3.95 ddd, *J* = 13, 11, 3

$^{3}J_{HH}$ = 11 Hz (to H_2)

$^{3}J_{HH}$ = 3 Hz (to H_2)

$^{3}J_{HF}$ = 13 Hz

5

Spectrum 2

δ 3.8 ddd, *J* = 26,10, 3

$^{3}J_{HH}$ = 10 Hz (to H_2)

$^{3}J_{HH}$ = 3 Hz (to H_2)

$^{3}J_{HF}$ = 26 Hz

(c) Give the chemical shifts and assign the coupling constants for the protons at C-5 for each isomer (first-order analysis is OK).

Spectrum 1 2

δ 4.45 qd, *J* = 7, 4 Hz

$^{3}J_{HCH3}$ = 7 Hz

$^{3}J_{HF}$ = 4 Hz

5

Spectrum 2 3

δ 4.3 dq, *J* = 25, 7

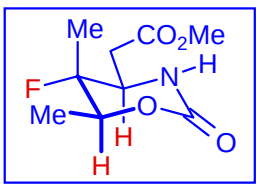
$^{3}J_{HCH3}$ = 7 Hz

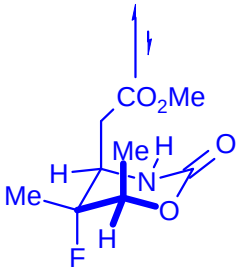
$^{3}J_{HF}$ = 25 Hz

Half of the quartet is partially hidden

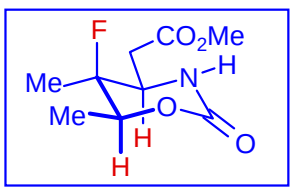
(d) Which spectrum corresponds to structure A? 1 3 Give your reasoning. Use conformational drawings.

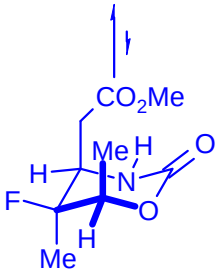
A = 1





B = 2





6

The favored conformation for each isomer places the two alkyl groups at C-3 and C-5 equatorial. In **B** one would expect two large H-F 3-bond axial-axial couplings, and that is what we see in isomer 2 (25 and 26 Hz). In isomer 1 the $^{3}J_{H\text{-}F}$ are 3 and 13, corresponding to axial-equatorial couplings.

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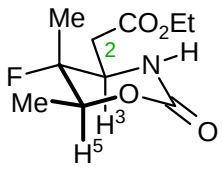


1

δ 2.75, dd, J=16, 3

H^2

δ 2.4, dd, J=16, 11

δ 4.45 qd, J = 7,4

H^5

H^3

δ 3.95 ddd, J = 13,11,3

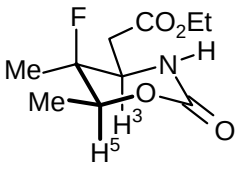
9.65

4.19

2.00

0.78

ppm



2

δ 4.3 dq, J = 25, 7

H^5

H^2

δ 2.8, dd, J=17, 3

δ 2.6, ddd, J=17, 10, 2

δ 3.8 ddd, J = 26,10, 3

H^3

This is only 1/2 proton

8.56

4.08

2.00

1.00

ppm

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