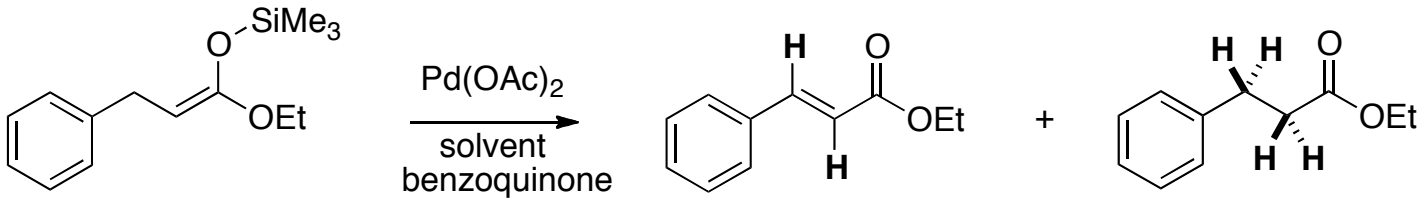
Saegusa-Ito Oxidation



Starting material (silyl enol ether)

Product A (target product)

Product B (by-product)

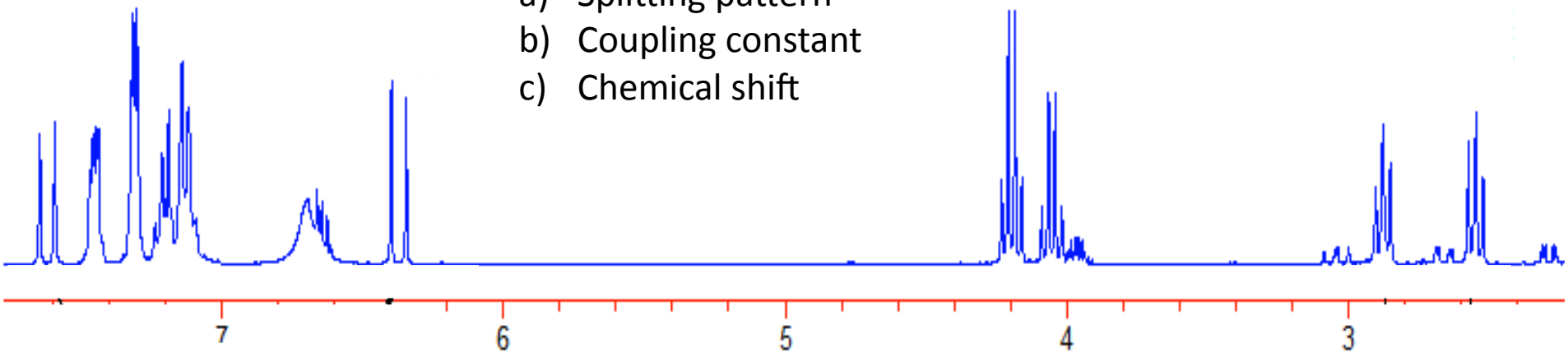
Assume that reaction went to 100% completion (i.e. no starting material remaining)

^{1}H-NMR spectrum of crude reaction mixture shown below

Need to determine product ratio in crude reaction mixture using integration values

Assign signals using:

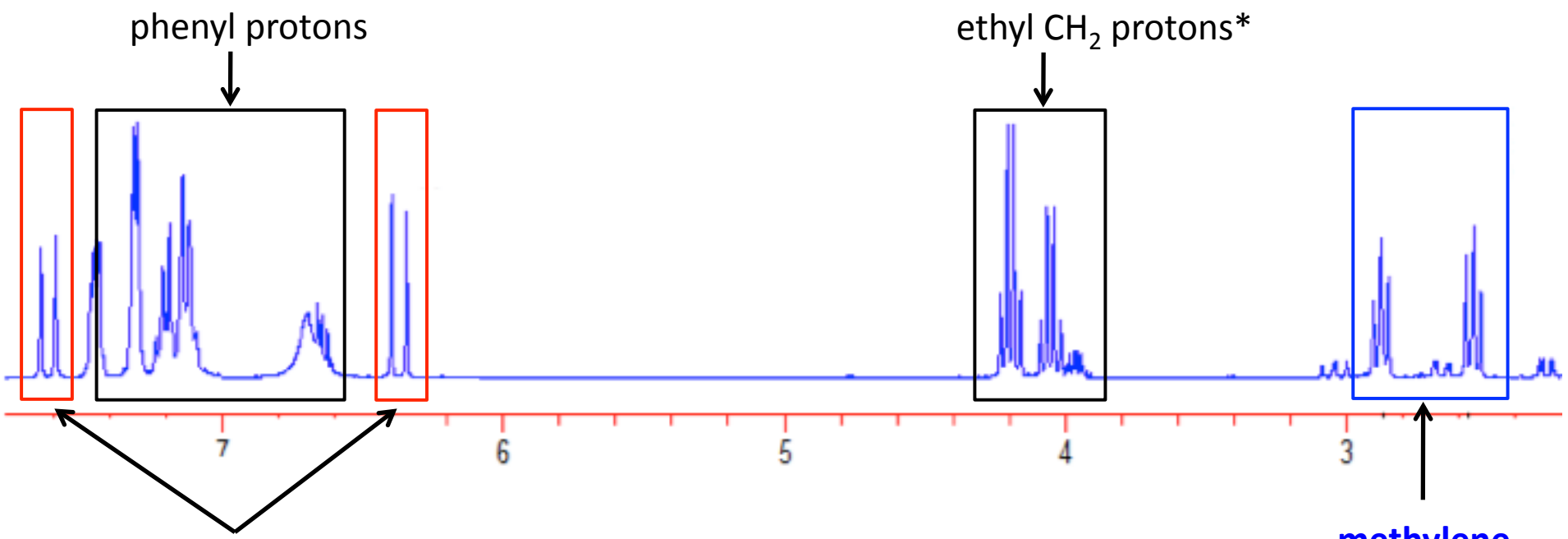
a) Splitting pattern
b) Coupling constant
c) Chemical shift



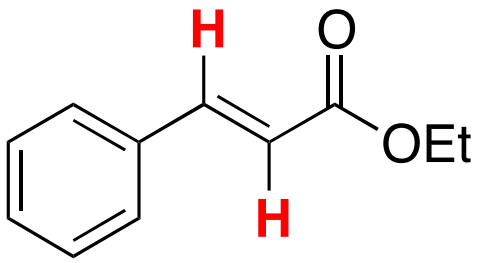
Which signals do we pick to integrate?

Ethyl **and** phenyl **group signals don't help because they are overlapped or not well resolved**

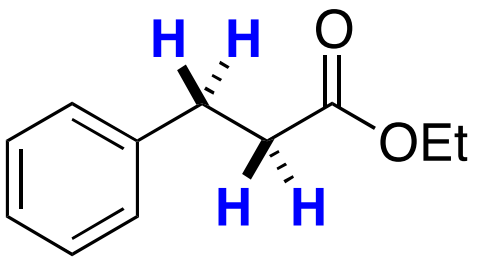
Vinyl and methylene signals are <u>well separated</u> and <u>clear of other signals</u>



So lets use their integration values……



Product A



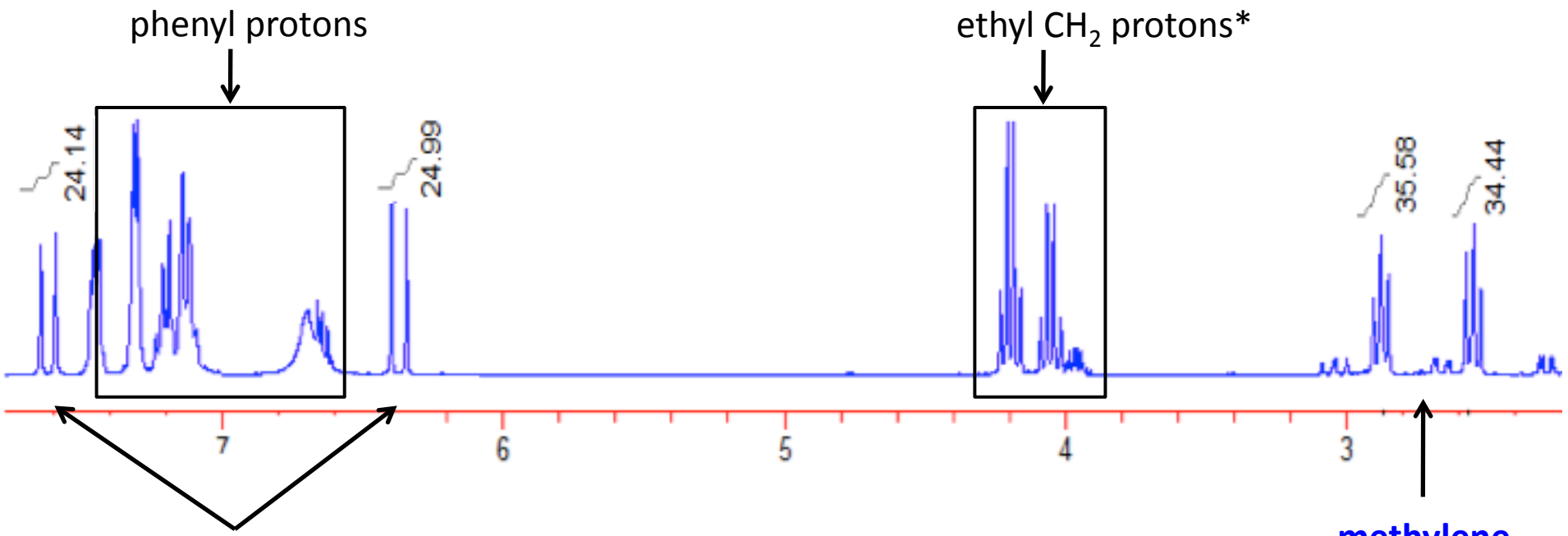
Product B

*ethyl CH_3 protons overlapped ~1.4 ppm

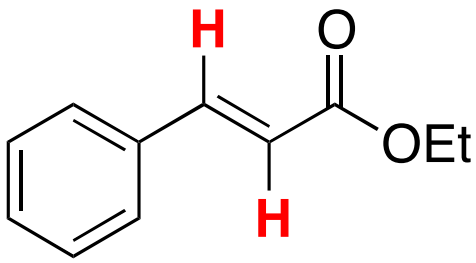
Vinyl proton integrations are 24.99 and 24.14 ("raw" or "absolute" values)

Methylene proton integrations are 35.58 and 34.44

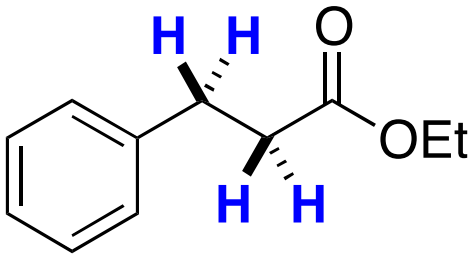
There are 2 methylene protons per vinyl proton



Calculate ratio of products in terms of x:1



Product A



Product B

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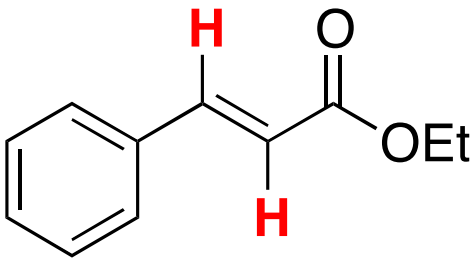
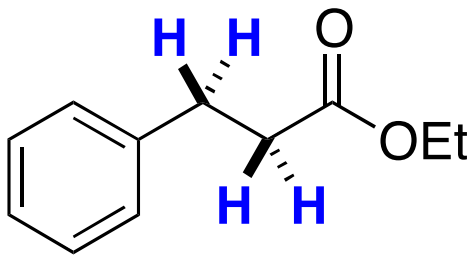


Product A



Product B

$$\text{Ratio products} = \frac{\text{Integration 1 vinyl proton}}{\text{Integration 1 methylene proton}} = \frac{24.99}{34.44 \div 2} = 1.45 : 1$$

Why ÷ 2 ?

because there are 2 methylene protons per vinyl proton

Could also use

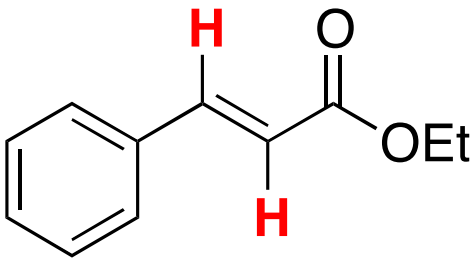
24.14/(35.58 ÷ 2) = 1.36 : 1

24.99/(35.58 ÷ 2) = 1.40 : 1

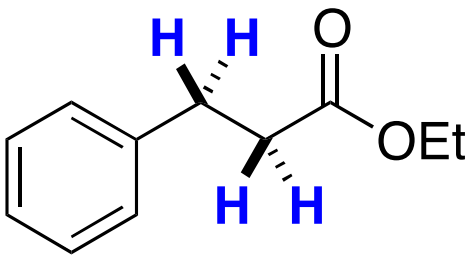
24.14/(34.44 ÷ 2) = 1.40 : 1

Any of the above product ratios are OK to use

What can be concluded about the reaction we performed?



Product A



Product B

Product ratios from ^{1}H-NMR signals

24.99/(34.44 ÷ 2) = 1.45 : 1
24.14/(35.58 ÷ 2) = 1.36 : 1
24.99/(35.58 ÷ 2) = 1.40 : 1
24.14/(34.44 ÷ 2) = 1.40 : 1

Ratio Product A : Product B = ~ 1.40 : 1

- **Reaction gave desired product (A) as major product**

- **Only slight excess of A thus <u>selectivity</u> of reaction is low**

Summary

1) Assign signals using splitting pattern, *J* value, and chemical shift

2) Look for signals that are well resolved and clear of other signals (i.e. not overlapped or cluttered)

3) Use the raw integration values of each signal that you pick

4) Account for the number of protons in the molecule that give each signal

5) Express ratio in terms of x:1 (x = major product)

Thanks to Jon Jaworski (Stahl group) for NMR data