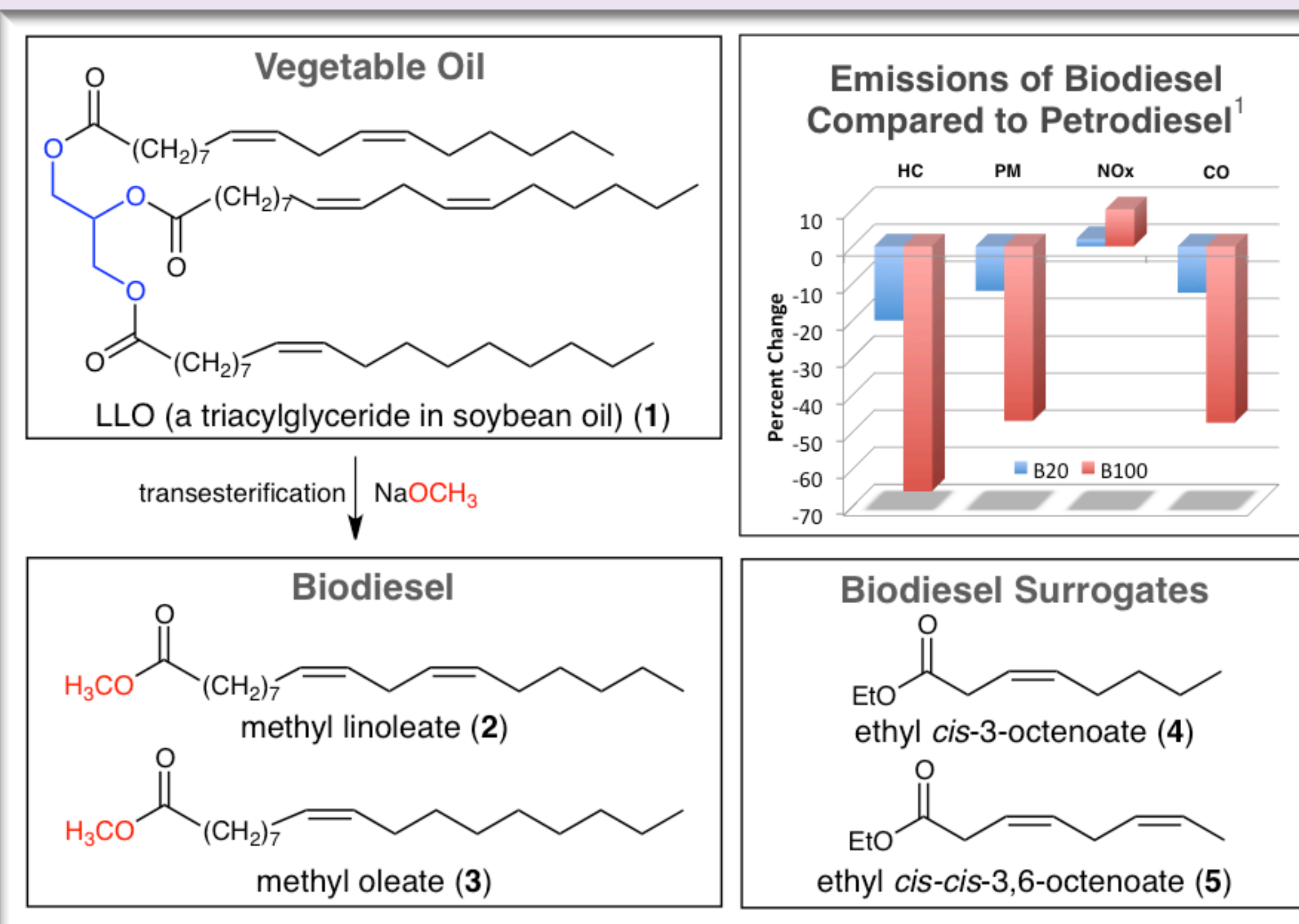


Preparation of a Biodiesel Surrogate by Stereoselective Hydrogenation of Ethyl-3-Octynoate

Min Ho Lee, Miae Lee, An Lam and Chad L. Landrie*

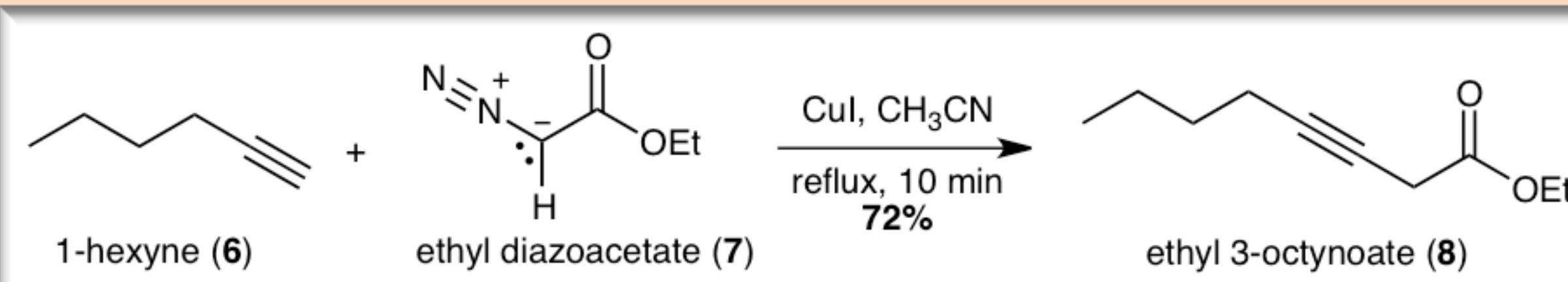


Introduction

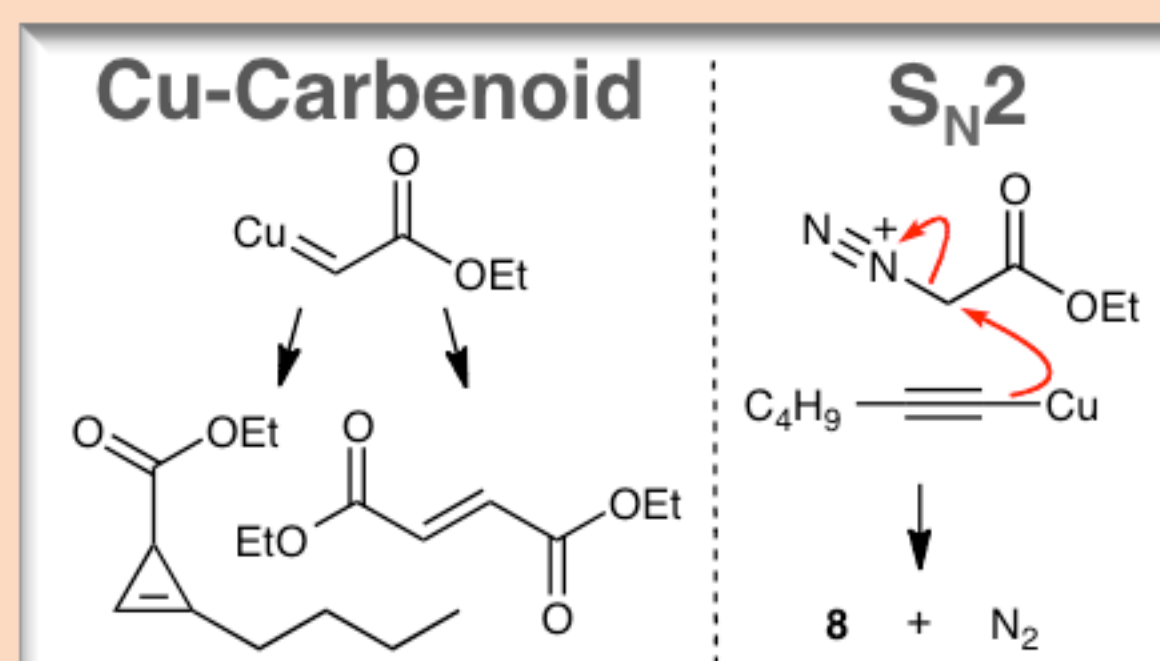


Biodiesel is a promising alternative fuel source that can be synthesized by transesterification of renewable resources such as vegetable oils (1) and animal fats. According to a 2002 EPA report, biodiesel emits less particulate matter (PM), carbon monoxide (CO), and unburned hydrocarbon (HC) pollutants, but 2% more nitrogen oxide (NO_x) pollutants compared to petroleum fuels.¹ It's been suggested that during combustion, the *cis*-alkene moieties in biodiesel methyl esters (2 and 3) produce alkynyl radicals that react with air to form NO_x. In order to test this hypothesis, saturated and unsaturated biodiesel surrogates (4 and 5) will undergo pyrolysis studies to establish a correlation between the degree of side-chain unsaturation and NO_x emissions. Since biodiesel surrogates are not commercially available, we aimed to develop a method to prepare *cis*-3-alkenoate alkyl esters such as 4 and 5.

Cu-Catalyzed Diazo Coupling



We envisioned that the *cis*-alkene could be obtained through stereoselective hydrogenation of an alkyne. Thus, we prepared ethyl 3-octynoate (8) through a diazo coupling between 1-hexyne (6) and ethyl diazoacetate (7).² The reaction is catalyzed by copper iodide (CuI) and provides high yields in short times. Other than small amounts of allene (< 5%), no other side-products were detected. Cyclopropanation and fumarate side-products typically complicate reactions involving carbenoid C-H insertion. Their absence may suggest that instead of a copper carbenoid, EDA (7) is first protonated to provide a diazonium ion which can then undergo S_N2 by a copper acetylide.³ Complexation of alkynes with Cu⁺ significantly increases their acidity, making this plausible.



Optimization & Characterization

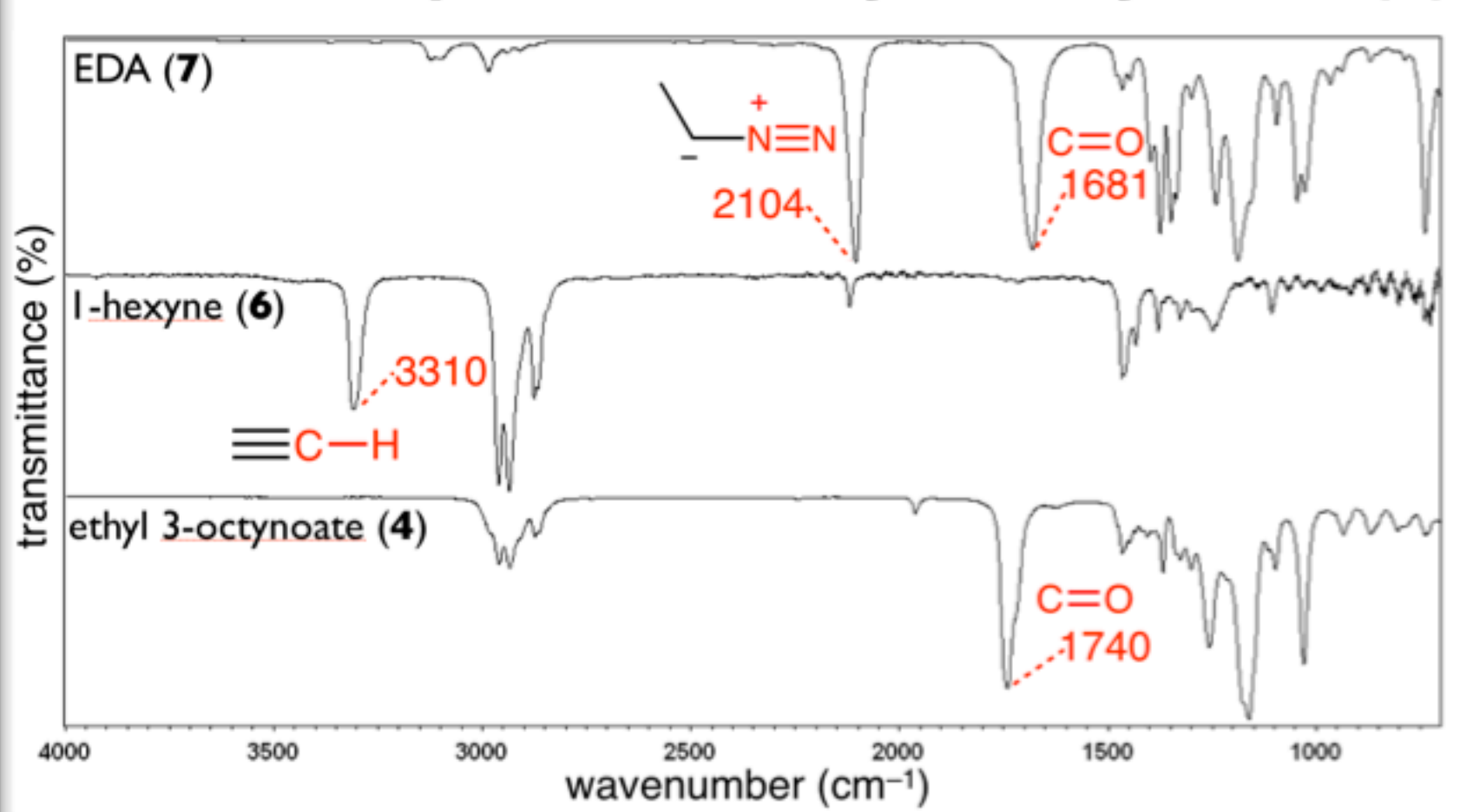
Conditions for Diazo Coupling

Solvent ^a	CuI	T (°C) ^b	Time (min)	Yield (8)
CH ₃ CN	10%	82	10	72%
CH ₃ CN	5%	82	45	70%
CH ₃ CN	1%	82	75	60%
Et ₂ O	5%	35	120	NR ^c
CH ₂ Cl ₂	5%	40	120	NR
THF	5%	66	120	NR

^a Solvents used without drying or degassing. ^b All reactions were held at reflux. ^c No reaction. No change in TLC observed.

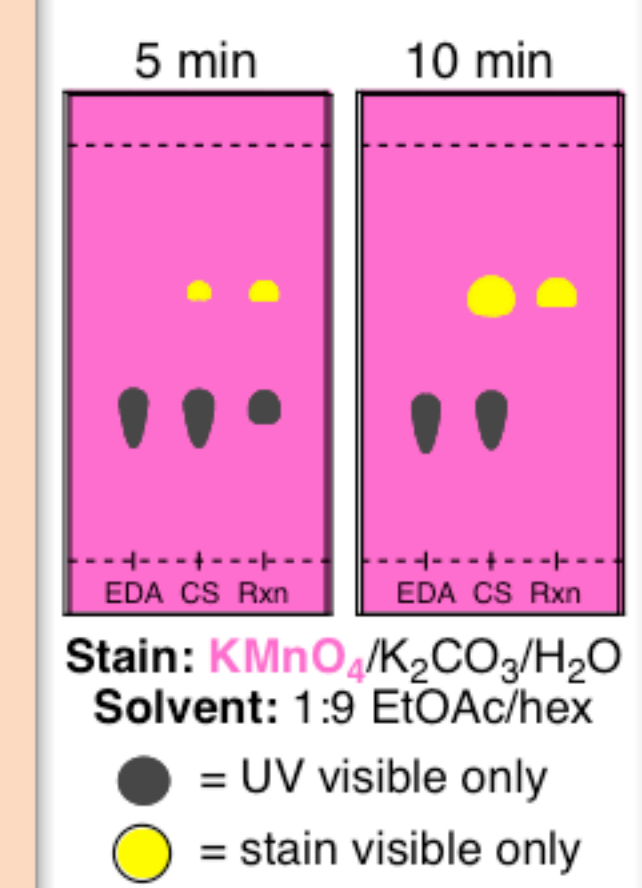
The diazo coupling was tested in three polar aprotic solvents and one non-polar solvent (Et₂O). No reaction was observed by TLC for Et₂O, CH₂Cl₂ or THF, most likely because CuI is insoluble in these solvents. In CH₃CN, however, 8 was obtained in good yields at catalyst loadings as low as 1 mol %. In all cases, EDA (7) was the limiting reagent and added in one portion, again suggesting an S_N2 mechanism since carbenoid insertion reactions generally require slow addition to prevent side-reactions (e.g. fumarate formation).

Infrared Spectra of ethyl 3-octynoate (8)

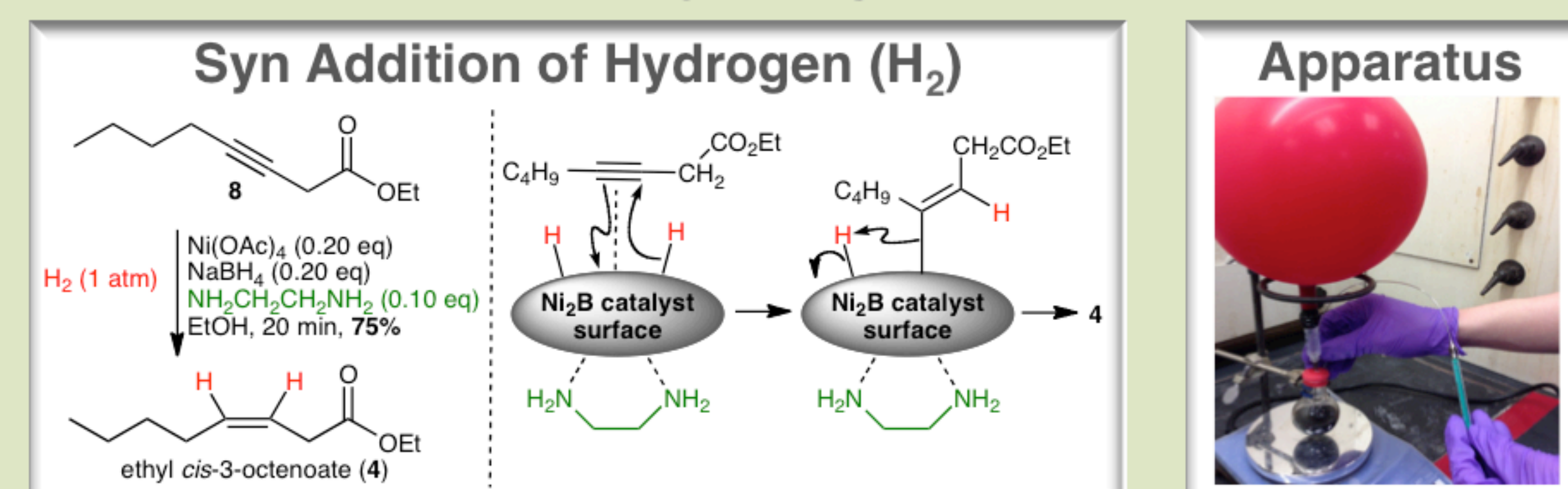


Infrared spectroscopy (IR) and nuclear magnetic resonance (NMR) (not shown) were used to deduce the identity of the product. The absence of the terminal alkyne C-H band (3310 cm⁻¹) and diazo band (2104 cm⁻¹) confirmed that the starting materials 6 and 7 were consumed. The band at 1740 cm⁻¹ is characteristic of the non-conjugated ester carbonyl (C=O) present in 8. Furthermore, the absence of alkene C=C and sp²-C-H bands around 1600 cm⁻¹ and 3100 cm⁻¹, respectively, precludes the formation of cyclopropene, fumarate and allene products.

Reaction Progress Monitored by TLC



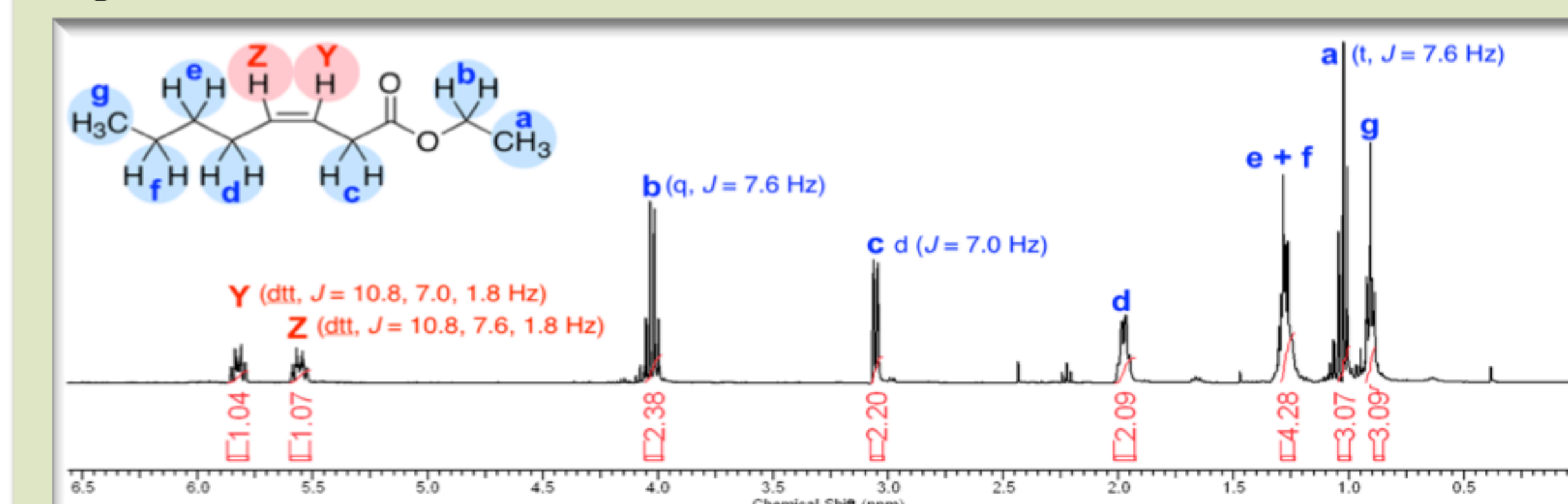
Stereoselective Hydrogenation



The *cis*-alkene 4 was prepared by Ni-catalyzed hydrogenation⁴ of 8. The active catalyst (Ni₂B) was formed by combining equimolar amounts of Ni(OAc)₄ and NaBH₄ in EtOH under an atmosphere of H₂ (established with a balloon fitted to a syringe and needle). Ethylenediamine was then added as a poison to reduce the activity of the catalyst and prevent hydrogenation of alkene 4 to the alkane. Hydrogen is first adsorbed by the catalyst surface which, after coordinating with the alkyne, delivers both H-atoms to the same face of the π-bond. Syn-addition of both H-atoms gives the *cis*-alkene stereoselectively over *trans*.

Determining the Structure of 4 by NMR

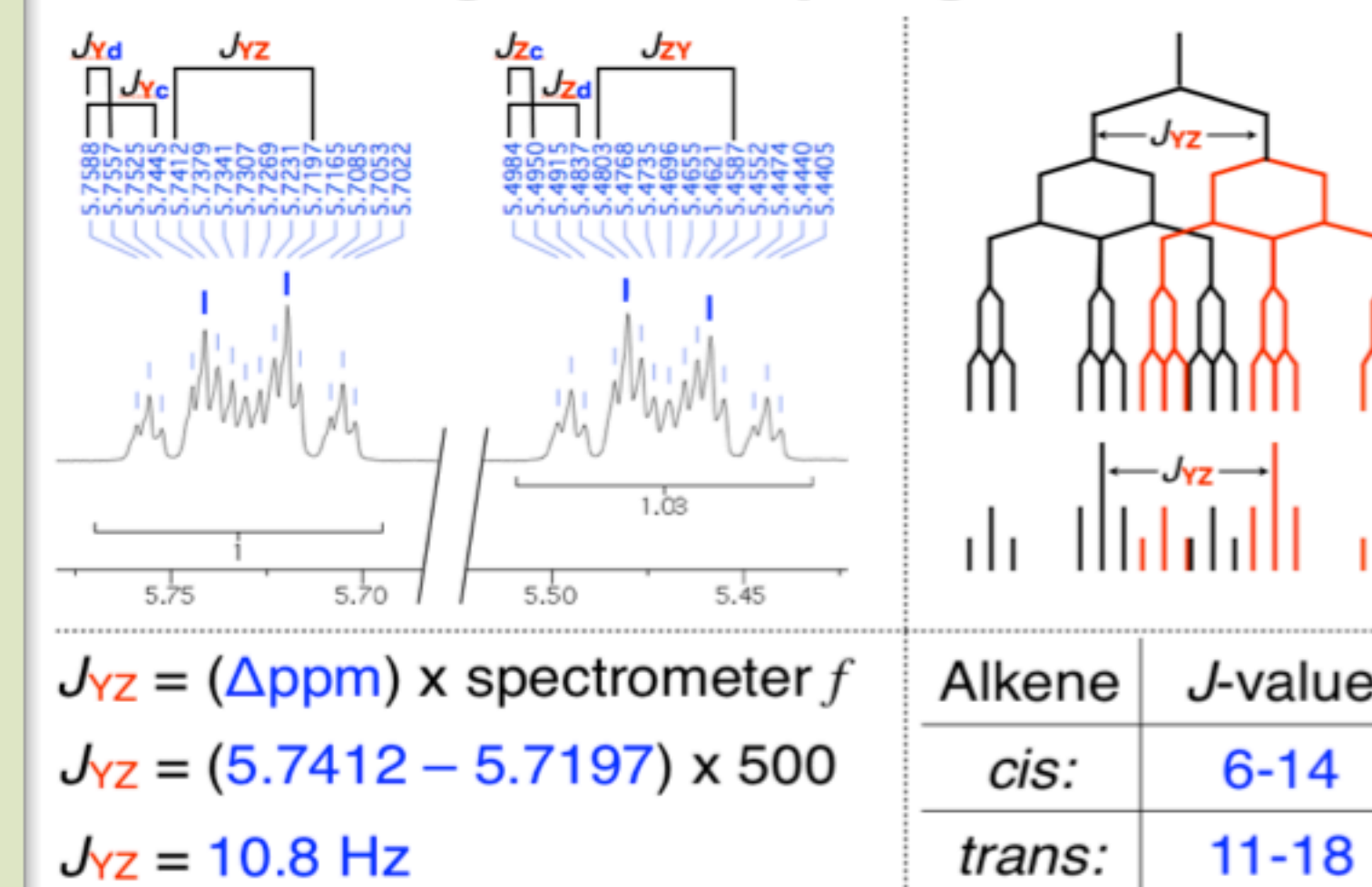
The ¹H-NMR spectrum of 4 clearly shows two new downfield signals at 5.73 and 5.47 ppm, which are characteristic of alkene H-atoms Y and Z. Additionally, CH₂ group c changed from a singlet in the NMR of alkyne 8 to a doublet (d) in 4 where it is adjacent to 1 alkene H-atom. Since Y and c are adjacent, and therefore should have a shared coupling constant (J = 7.0 Hz), the signal at 5.73 was assigned to H-atom Y. Since both Y and Z are adjacent (3-bond) to each other and a CH₂ group (Y to c; Z to d), we expected to observe a doublet-of-triplets (dt) for each signal. However, it is evident that each experiences a 4-bond coupling with another CH₂ group (Y to d; Z to c) giving rise to a doublet-of-triplet-of-triplets (dtt) for each signal.



J-Value Proves *cis*-Geometrical Isomer

The multiplicity of each alkene signal was determined to be a doublet-of-triplet-of-triplets (dtt). The large doublet represents the coupling between H-atoms Y and Z. That J-value was calculated to be 10.8 Hz, which confirms that a *cis*-alkene, not *trans*, was obtained. Interestingly, we were only able to obtain well-resolved alkene signals with discernible splitting in d₆-benzene. Chloroform-d gave only unresolved multiplets.

Calculating the Coupling Constants



Conclusion

We have developed an expeditious two-step method for preparing *cis*-3-alkenoate biodiesel surrogates. The structure of 4 was determined by NMR and its *cis*-stereochemistry confirmed by calculating the coupling constant for each alkene H-atom. Next, we plan to investigate transfer-hydrogenation conditions that eliminate the need for H₂ gas and begin our synthesis of biodiesel surrogates, such as 5, by coupling 1,4-diyne to EDA (7).

References

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