

FUNCTIONALIZED CONJUGATED DIENES FROM VEGETABLE OILS

VIA

CROSS ENE-YNE METATHESIS

Christian BRUNEAU

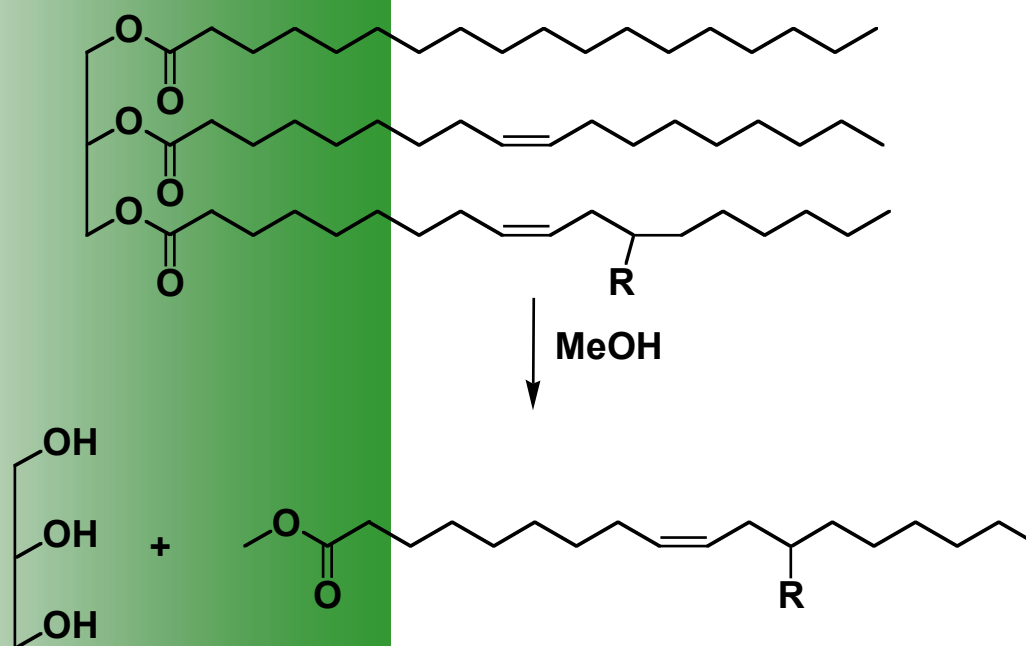
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UMR 6226 : CNRS – Université de Rennes 1

Sciences Chimiques de Rennes - Catalyse et Organométalliques

France

Transesterification or hydrolysis of triglycerides

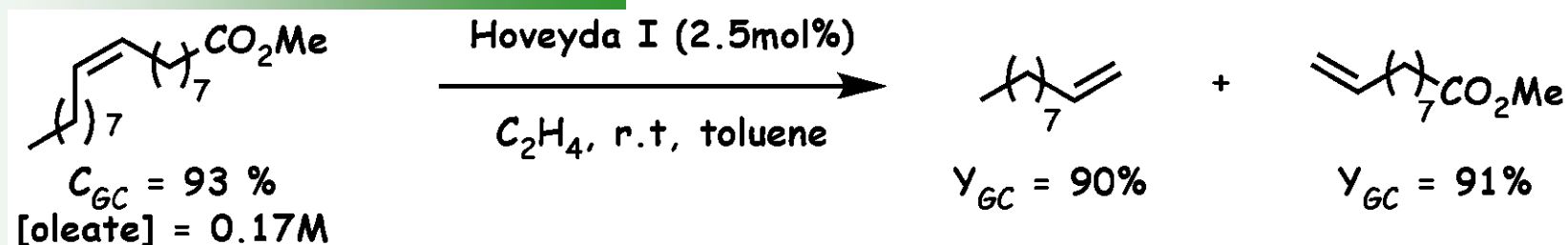


R= H : oleic acid (ester) from Sunflower
R= OH : ricinoleic acid (ester) from Castor oil

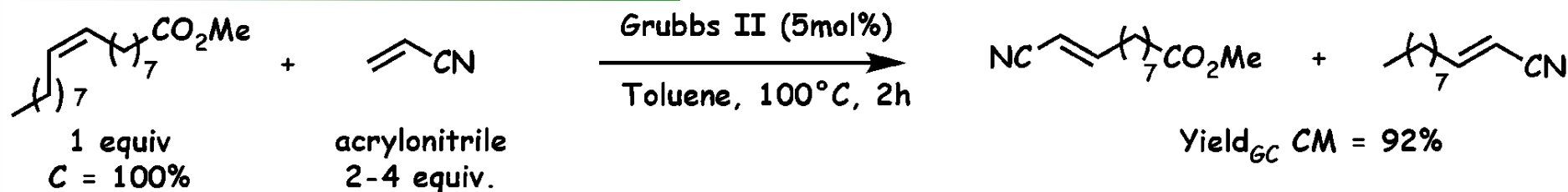
Cross metathesis with ethylene and acrylonitrile

Metathesis reactions from unsaturated fatty ester (from methyl oleate)

- Ethenolysis¹



- Cross metathesis with acrylonitrile²



¹ *ChemSusChem* **2008**, *1*, 118

² *Green Chem.* **2009**, *11*, 152



UNDECYLENIC ACID AND ALDEHYDE FROM CASTOR OIL

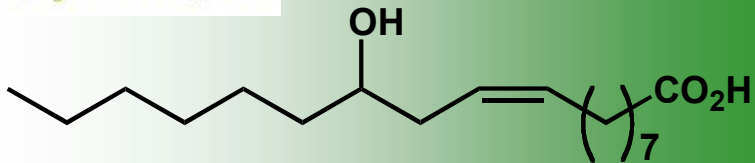


Castor oil

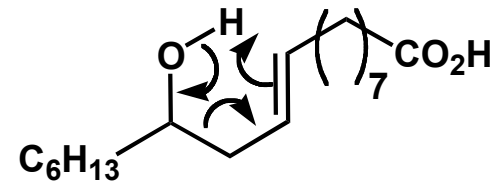


acids

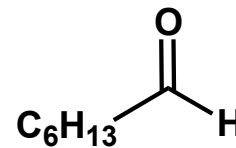
90 % ricinoleic acid



300 °C
≡

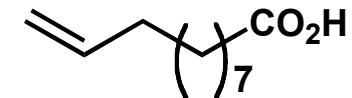


pyrolysis



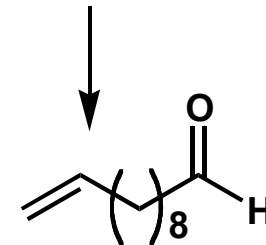
heptaldehyde

+



undecylenic acid

C11



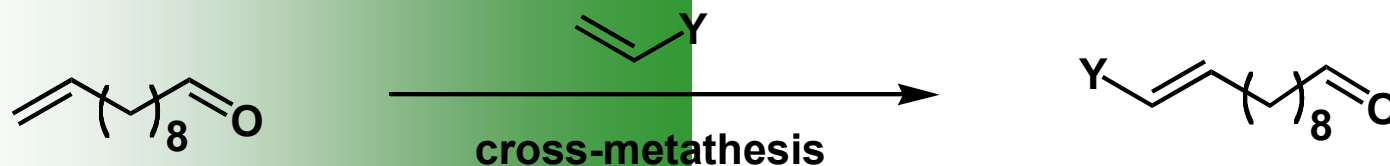
undecylenic aldehyde

C11



Metathesis reactions from unsaturated fatty derivatives (undecylenic aldehyde)

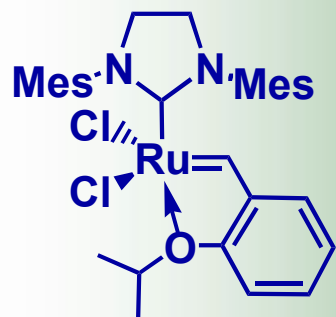
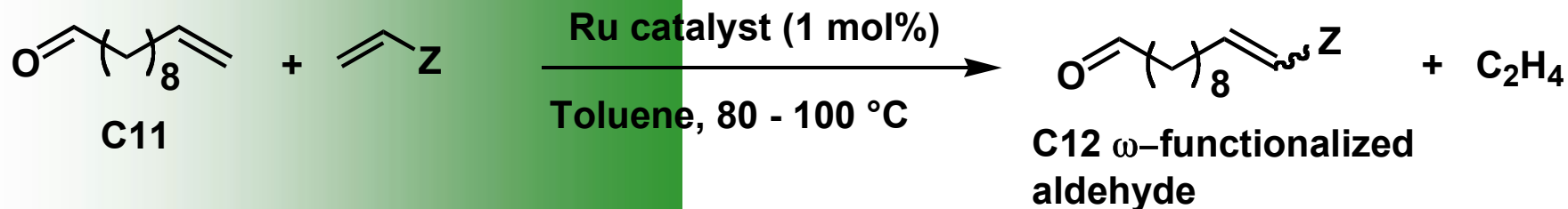
- Cross metathesis with electron deficient olefins



Y= CN : nitrile-aldehyde
Y= CO₂Me : ester-aldehyde
Y= CO₂H : acid-aldehyde
Y= CHO : dialdehyde

ChemSusChem 2009, 2, 542

Cross-metathesis of undecylenic aldehyde with electron-deficient olefins



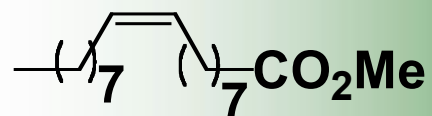
Z	Conversion	Isol. yield (Z/E)
CO ₂ H	99%	84% (<i>E</i> only)
CO ₂ Me	100%	92% (<i>E</i> only)
CHO	92%	78% (<i>E</i> only)
CN	98%	94% (2.4/1)

Efficient cross metathesis reaction with electron deficient olefins

Selective reaction : no isomerization of the C11-aldehyde

Ene-yne cross metathesis

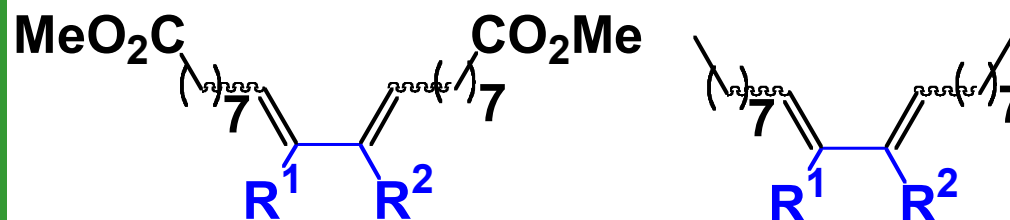
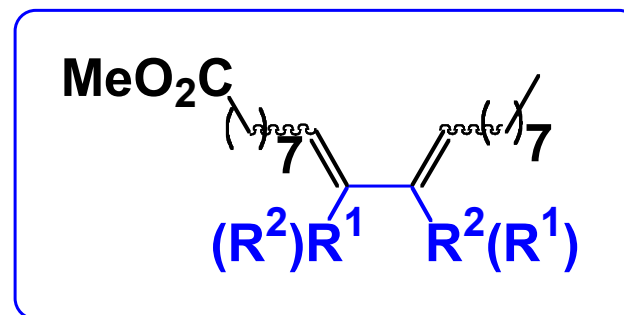
Objective : produce long hydrocarbon chains with a conjugated diene at internal position



+

[Ru]

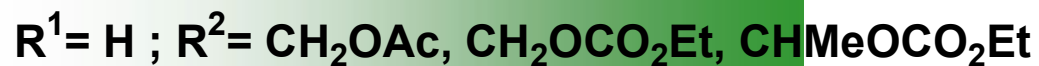
X



Internal alkyne:

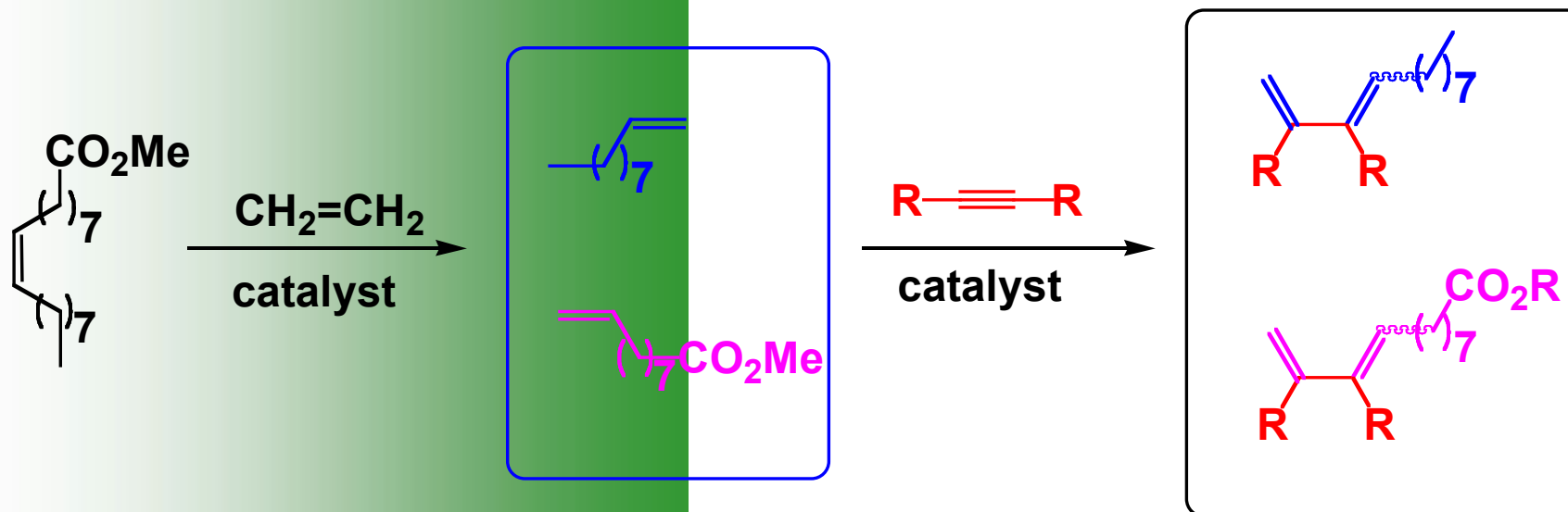


Terminal alkyne:



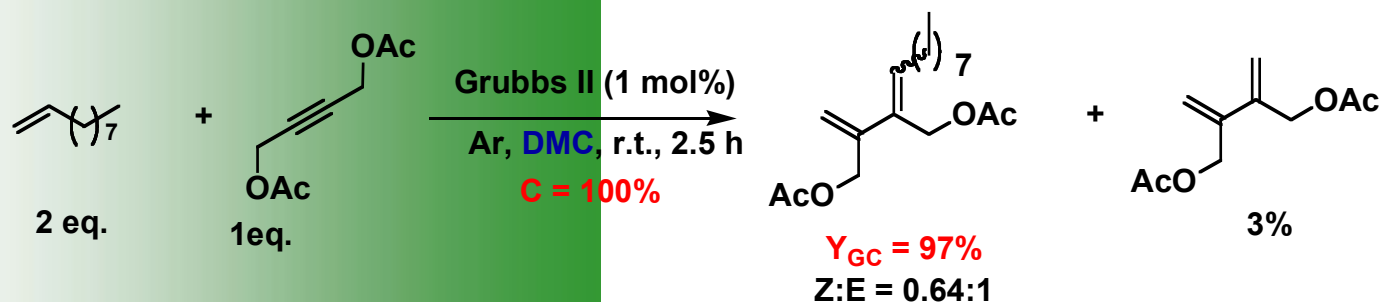
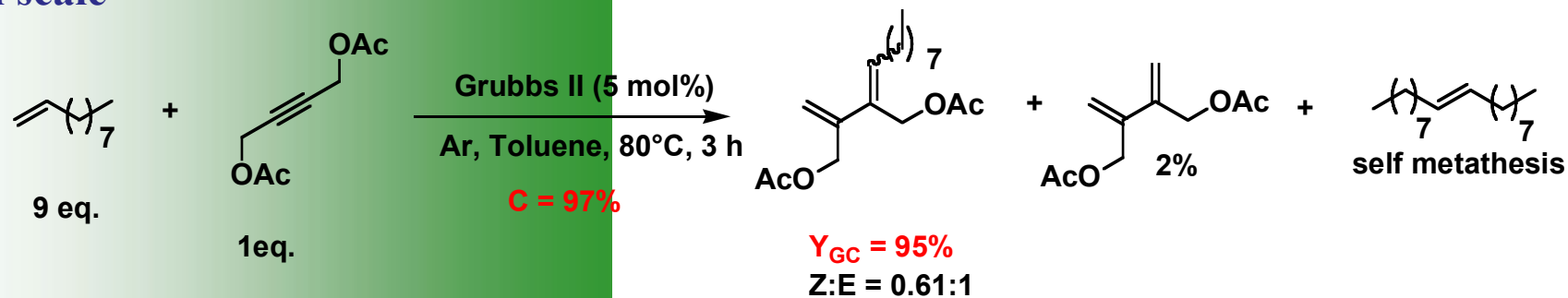
Other strategy : Ethenolysis + Ene-yne cross metathesis

Objective : produce long hydrocarbon chains with a functional group at each end

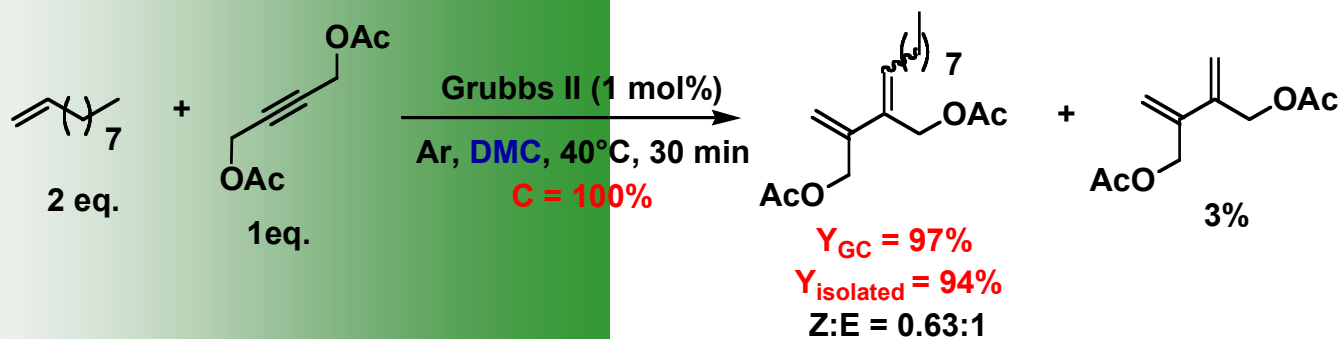


Optimization of ene-yne cross metathesis with 1-decene

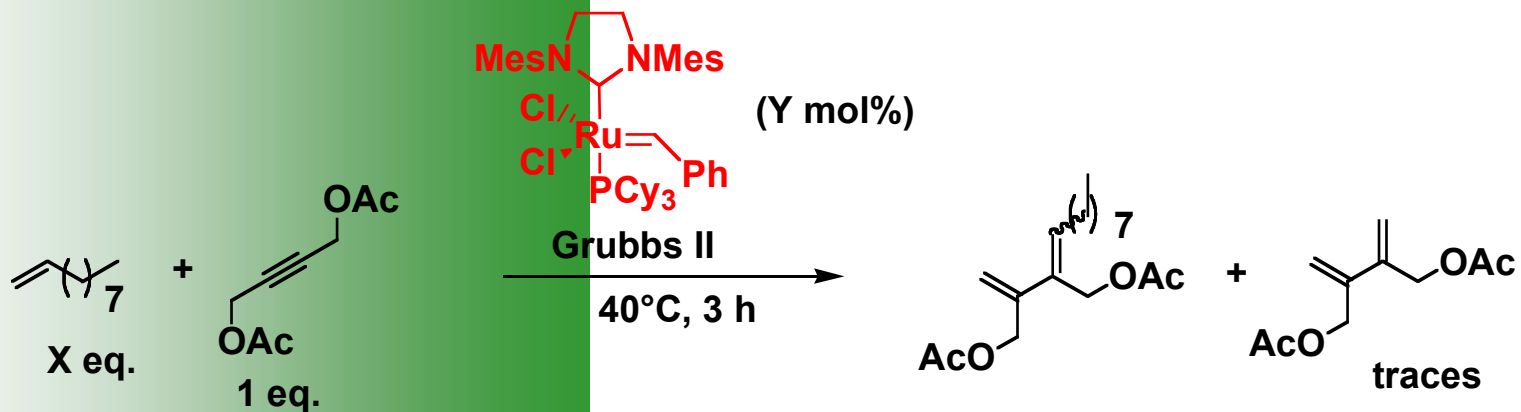
mmol scale



or



Optimization of ene-yne cross metathesis with 1-decene

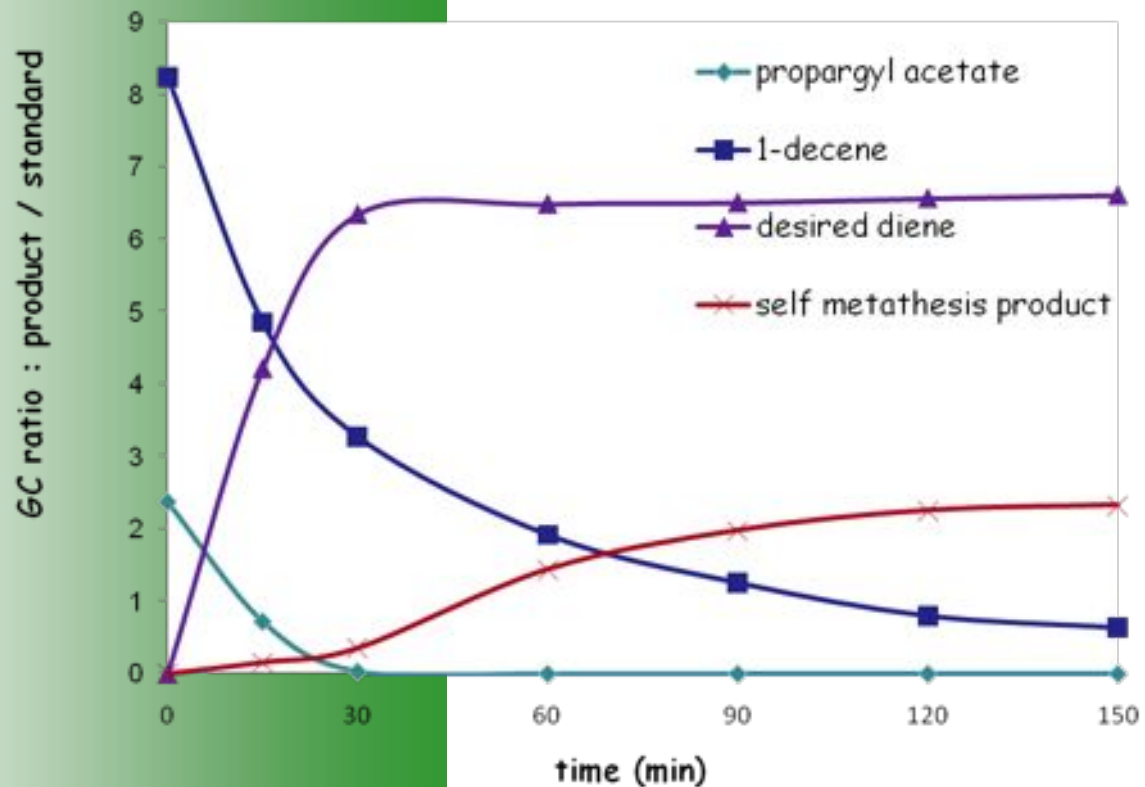
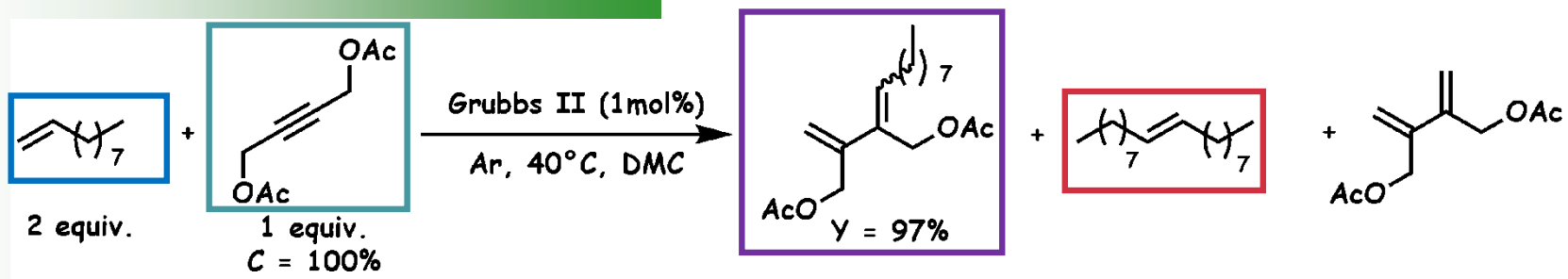


Catalyst (Y %)	Olefin (X equiv.)	Conversion (based on the alkyne)	GC yield
0.5 mol%	2 equiv	47%	44%
1 mol%	1 equiv	53%	45%
1 mol%	2 equiv	100%	98%

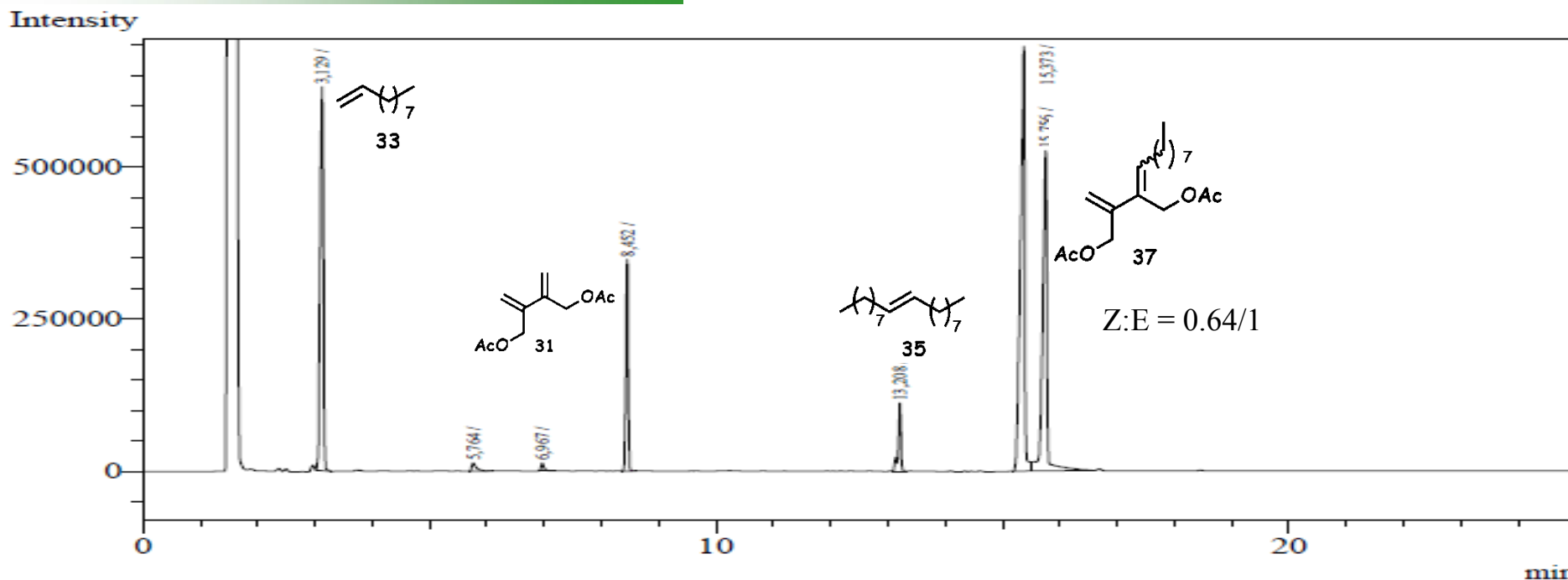
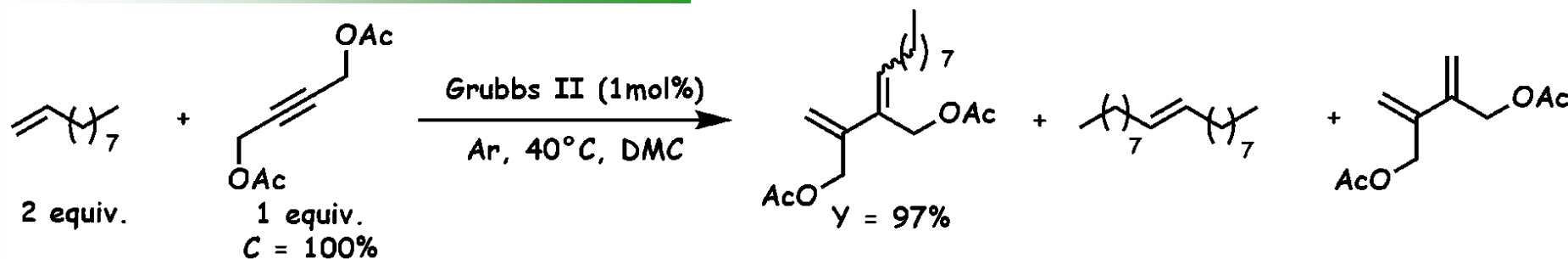
First generation catalysts are not efficient

2nd generation catalysts with a NHC ligand are efficient

Ene-yne cross metathesis : Kinetic study

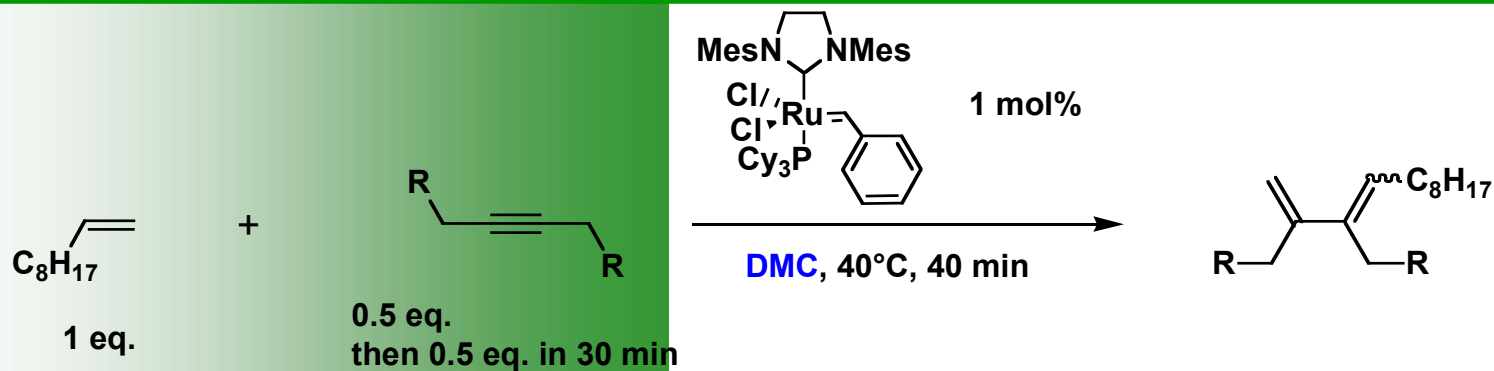


GC trace of the reaction mixture



Decene-alkyne cross metathesis

Continuous flow addition of the alkyne



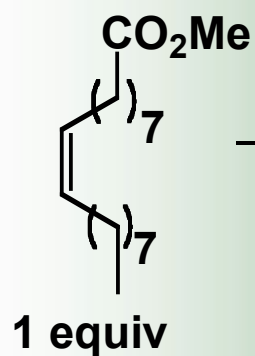
Alkyne	Product	stereoselectivity (Z:E)	Conversion, GC yield, isolated yield
		(0.64:1.0)	100%, 97%, 94%
		(0.88: 1.0)	100%, 87%, 71%
		(0.50:1.0)	100%, 90%, 76%
		(0.40: 1.0)	100%, 88%, 67%

Olefin cross-metathesis and sustainable development

Renewable olefins as substrates



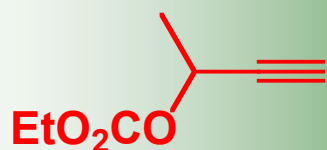
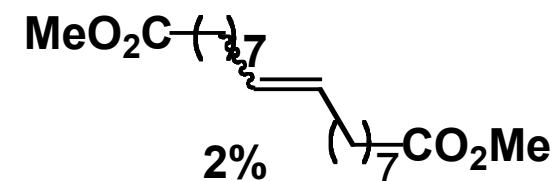
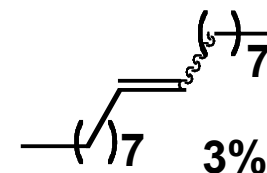
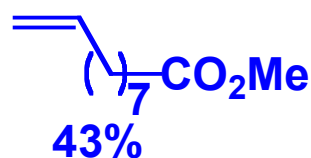
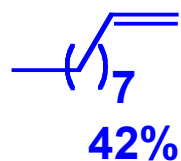
Other strategy : Ethenolysis + Ene-yne cross metathesis



cat.1 (2.5 mol%)

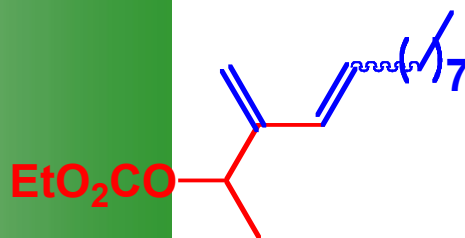
C_2H_4 , 1 bar
DMC, R.T.
Conv = 90%

cat.1: Hoveyda I
cat.2: Grubbs II

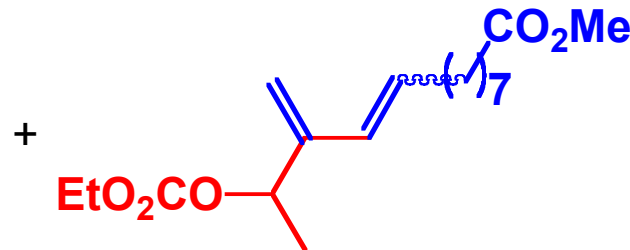


1 equiv.

cat.2 (1 mol%)
DMC, 40°C
2 h



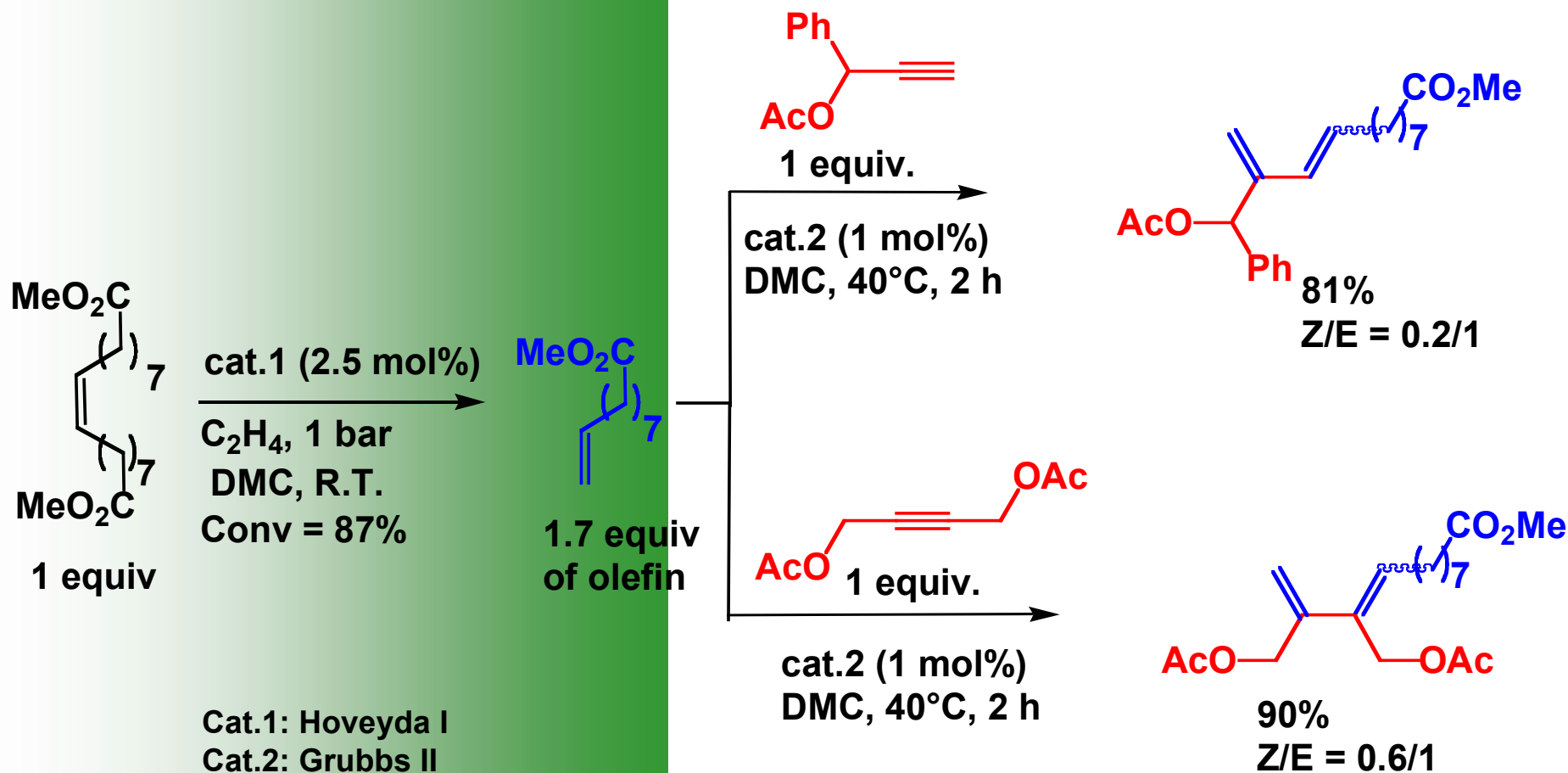
GC yield = 48%
Z/E = 0.45/1



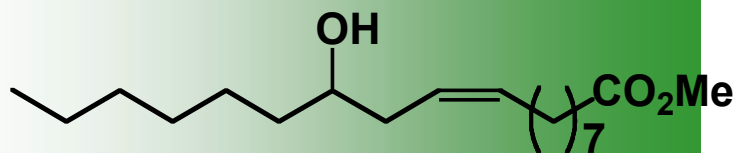
GC yield = 48%
Z/E = 0.1/1



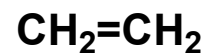
Ethenolysis + Cross-ene-yne metathesis from symmetrical substrate



Ethenolysis + Cross-ene-yne metathesis from ricinoleate

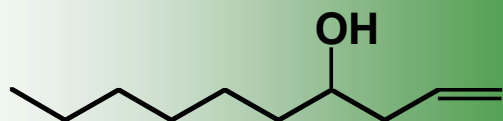


1 eq.

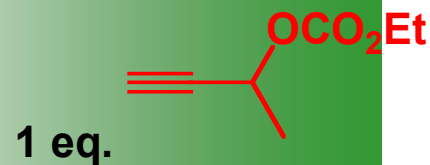


Hoveyda 2 (1 mol%)

C2H4, 1 bar
 DMC, R.T.
 Conv > 90%

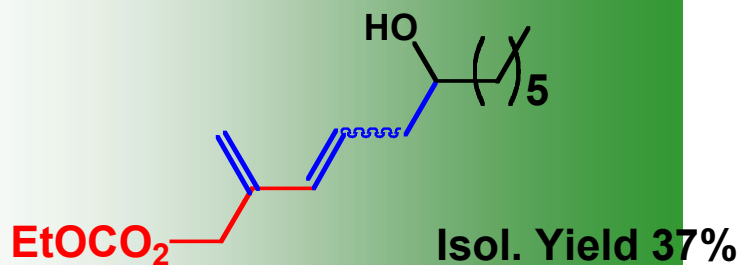


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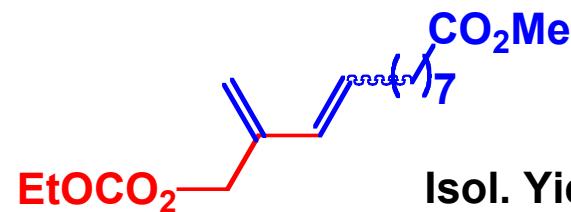


1 eq.

Hoveyda 2 (4 mol%)
 DEC, 100°C, 2 h
 conv. 95%



Isol. Yield 37%
 Z/E : 0.4:1

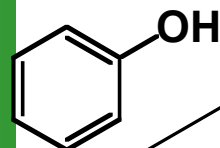
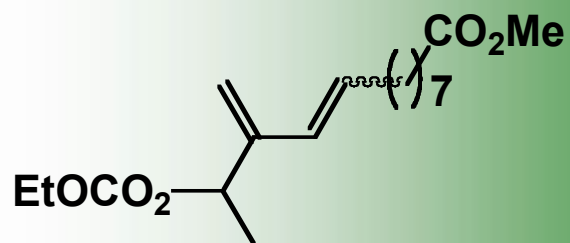


Isol. Yield 40%
 Z/E = 0.2:1

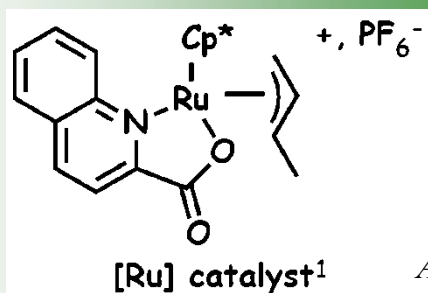
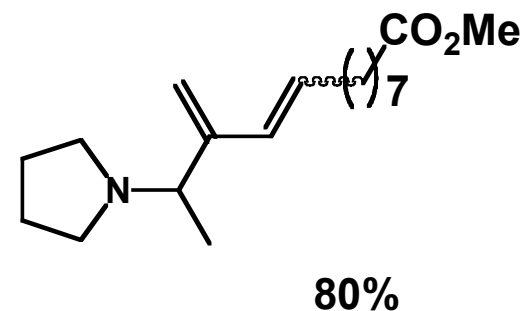
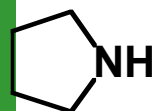
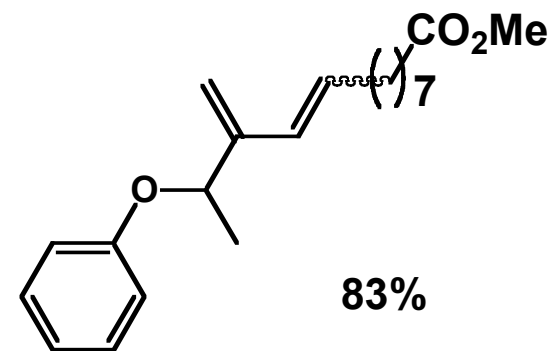
Nucleophilic substitution of the resulting allylic carbonates

Regioselective nucleophilic substitution

with the ester fragment

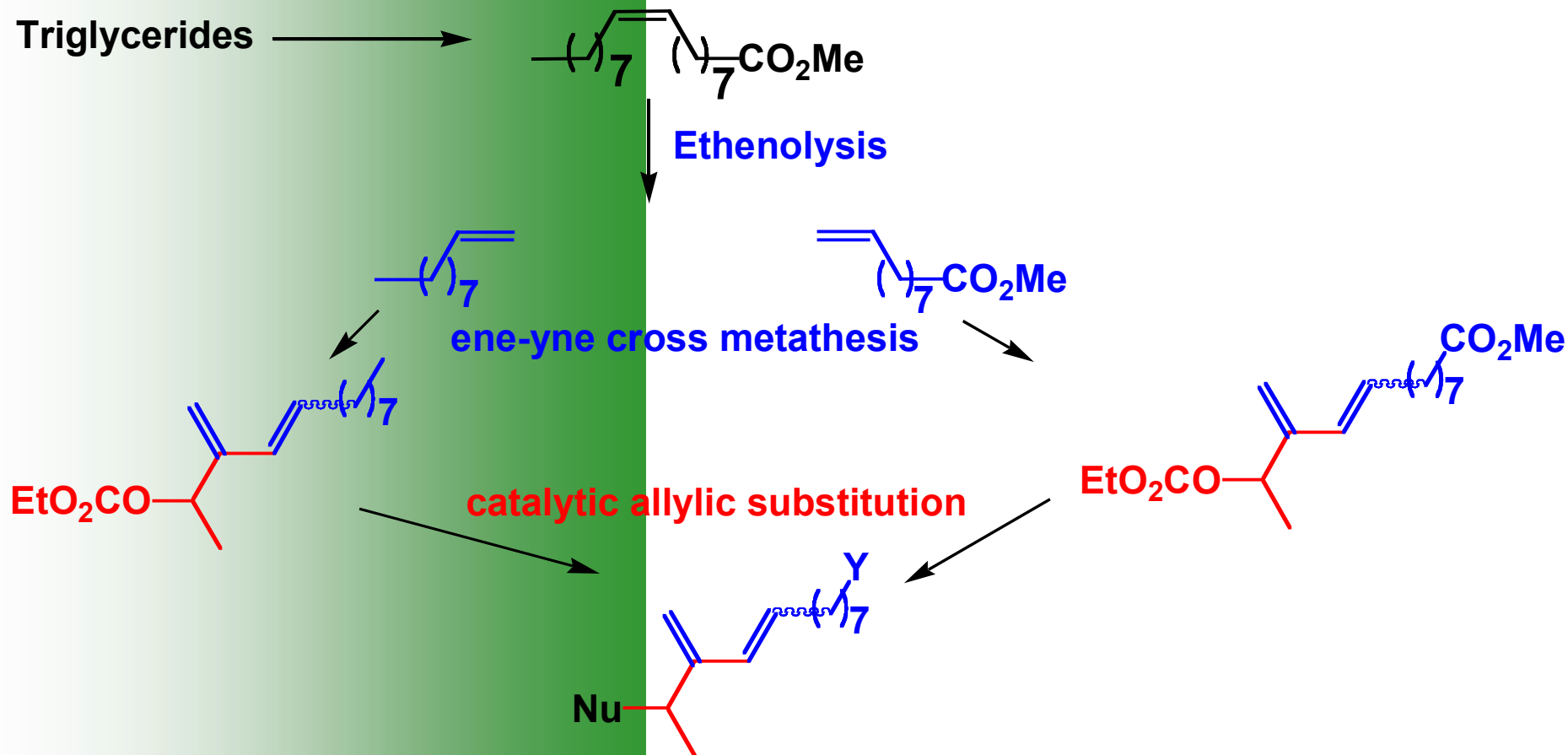


catalyst : 5 mol%
K₂CO₃, MeCN, r. t., 15 h



Adv. Synth. Catal. **2008**, 350, 1601

Olefin cross-metathesis and sustainable development



From mono-unsaturated substrates to polyfunctional fatty derivatives
Using 3 catalytic reactions in a green solvent (DMC)
And including 2 regioselective transformations

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CNRS, MENR, Université de Rennes1

