

Fatty acids as feedstocks for new catalytic transformations



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The Raw Materials

Plant oils and their major components, **fatty acids**,

- are the most important renewable feedstocks for the chemical industry
- can be grown in most climate zones for low cost
- are pre-functionalized by nature with functional groups, such as COOR, OH, epoxides, double-bonds, triple-bonds,...
- should be considered as a **complementary resource** to crude oil.

The intensified industrial utilization of oleochemicals perfectly matches the principles of Green Chemistry and sustainability in general [1].

Project Aims

We explore new ways for value creation from fatty acids

- with innovative reaction concepts
 - using **transition-metal catalysis** as key technology.
- Our research focuses on the development of efficient ways to bio-based intermediates and fine chemicals. Starting from **unsaturated fatty acids**, we want to develop isomerizing transformations by
- making use of controlled catalytic double-bond migration
 - establishing a dynamic isomerization equilibrium
 - combining isomerization with **selective functionalization** of the fatty acid chain.

Method Development

We develop new methods for the valorization of fatty acids using **high-throughput experimentation**:

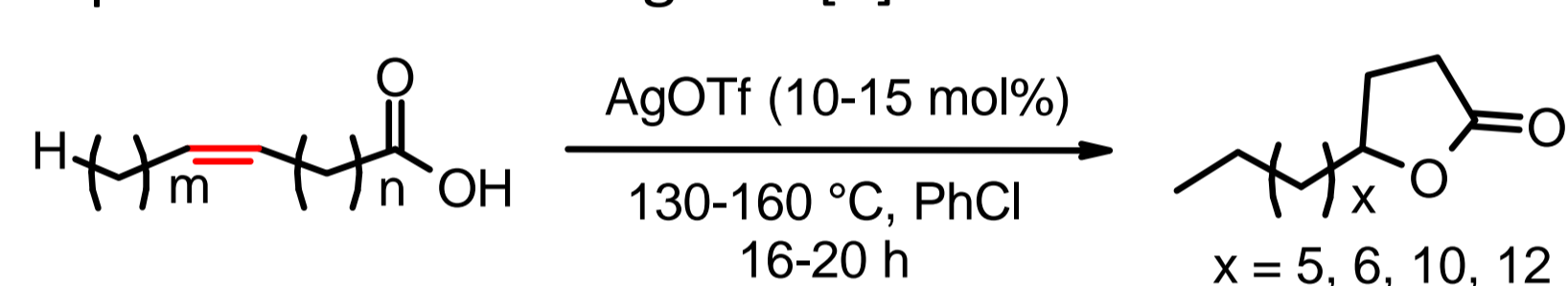
- parallel reaction setup for fast and efficient screening of catalysts and conditions
 - integrated electronic lab journal for rapid reaction design and **computer-aided data analysis** [2].
- After reaction optimization, we develop preparative-scale protocols for scale-up, considering industrial requirements:
- reliable, waste-minimized reactions
 - efficient and highly atom-economic processes
 - mild conditions, fast conversion and high selectivity

New catalytic transformations with fatty acid derivatives

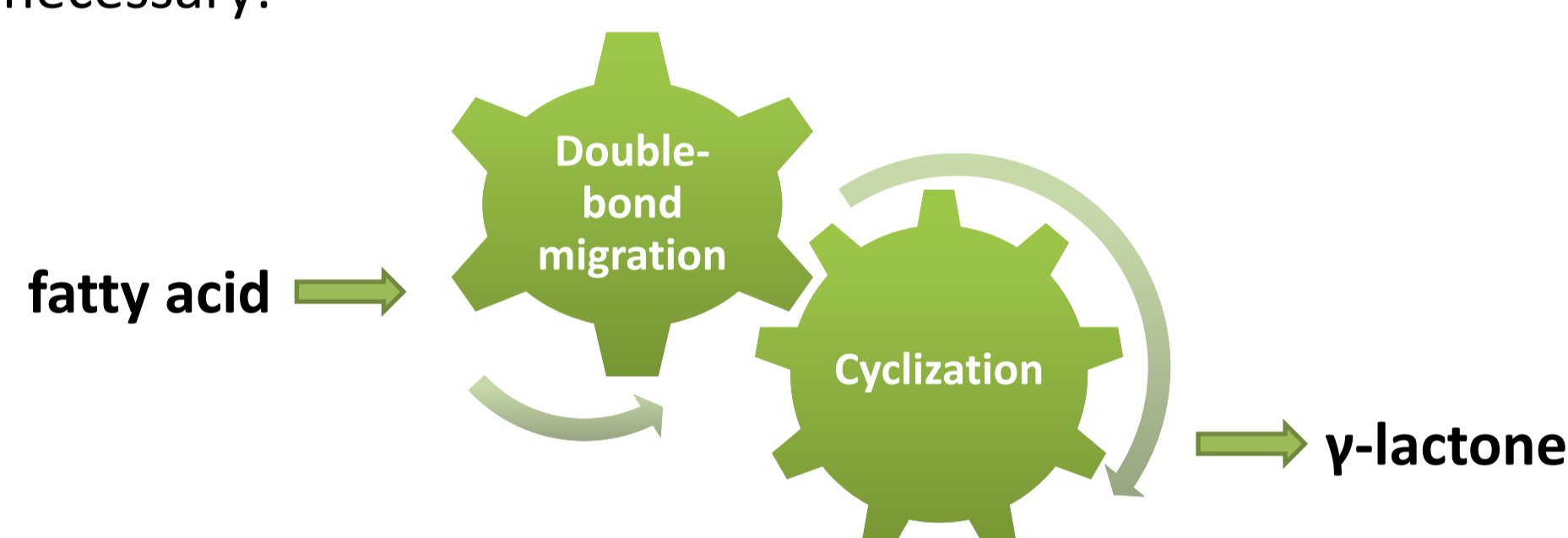
Isomerizing Lactone Synthesis

Long-chain γ -lactones are important for cosmetics, but they were hitherto synthesized from **unsaturated fatty acids** using stoichiometric amounts of corrosive acids [3].

We developed a silver-catalyzed **one-step method** that does not require hazardous reagents [4].



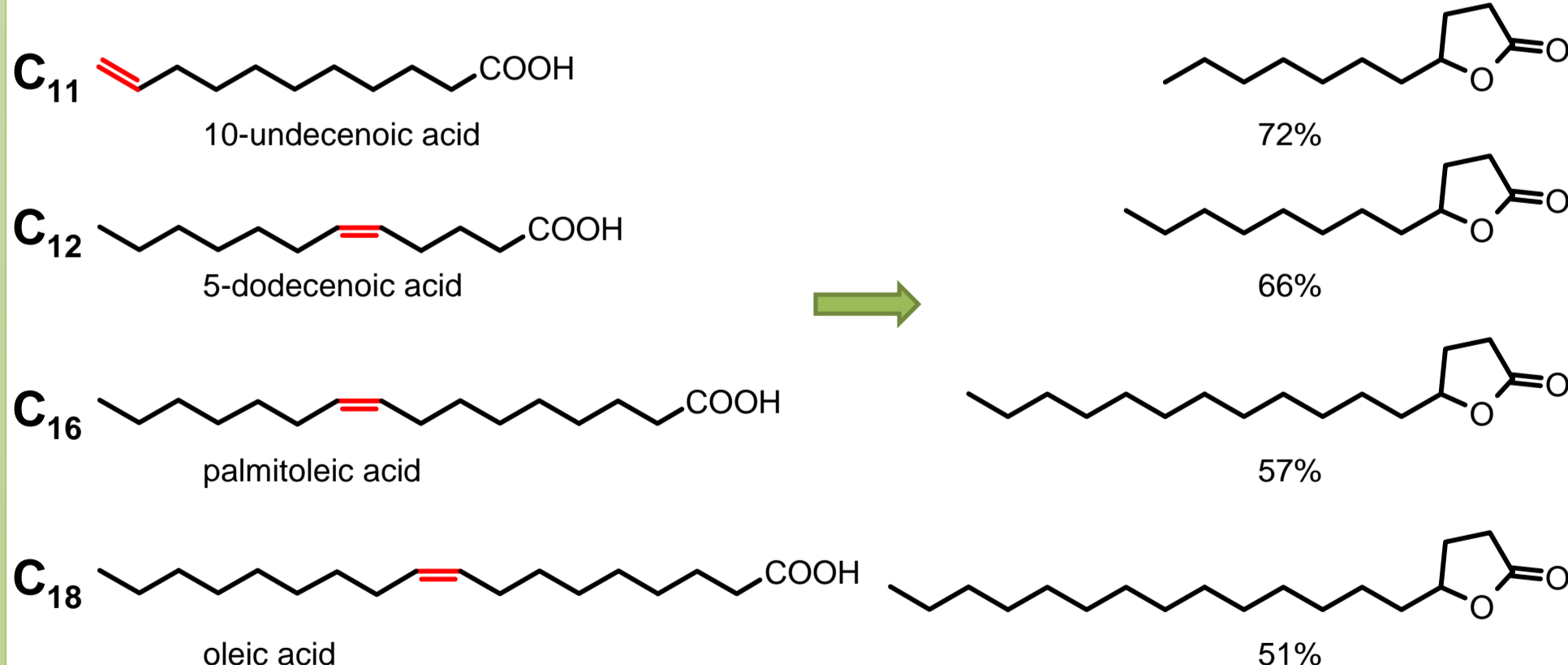
This reaction is based on a dynamic equilibrium of double-bond isomers, out of which only a single species reacts to the desired product. Two **intertwined catalytic cycles** are necessary:



An extensive screening led us to a **bifunctional silver catalyst** that mediates the double-bond migration and the cyclization:

Transition metal hydrides	No Activity
Mild Brønsted acids	No Activity
Lewis acids	Moderate Isomerization
Acidic Ionic Liquids	Isomerization +
Triflates, e.g. AgOTf	Formation of γ -lactones

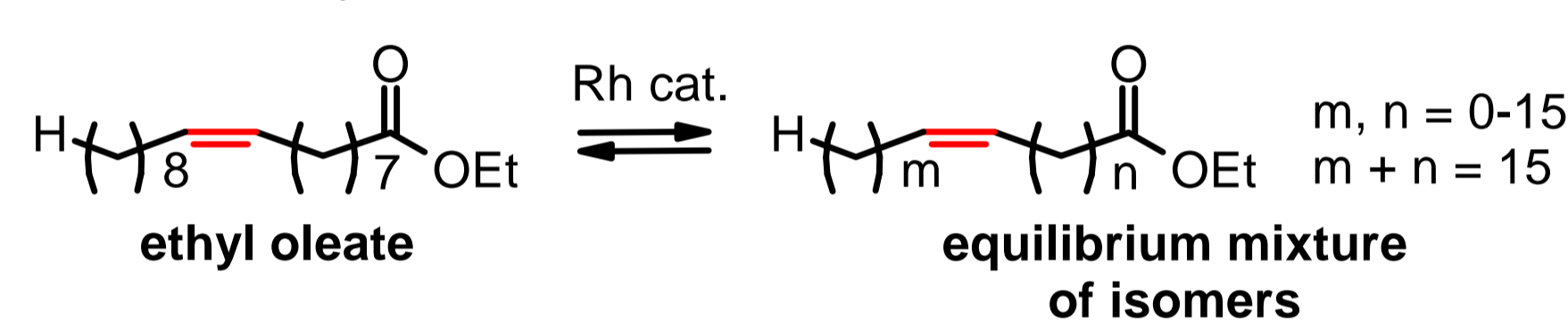
We obtained several **long-chain γ -lactones** from unsaturated fatty acids with various chain lengths and double-bond positions in high selectivities and good yields:



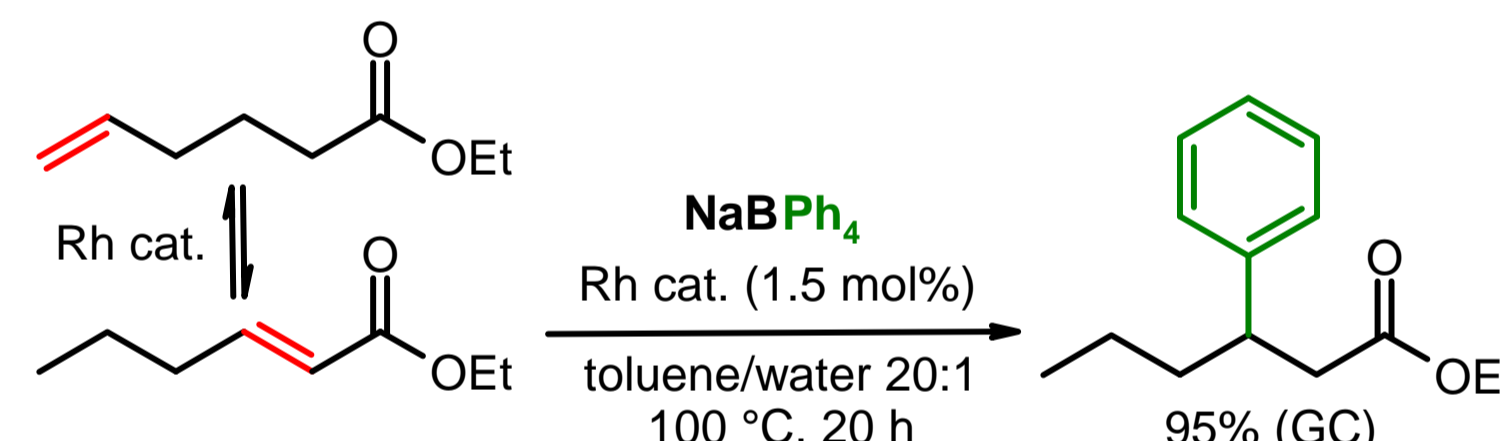
The results are encouraging for the development of further isomerizing cyclizations, such as the reaction of unsaturated amides to δ - or ϵ -lactams.

Isomerizing Michael Addition

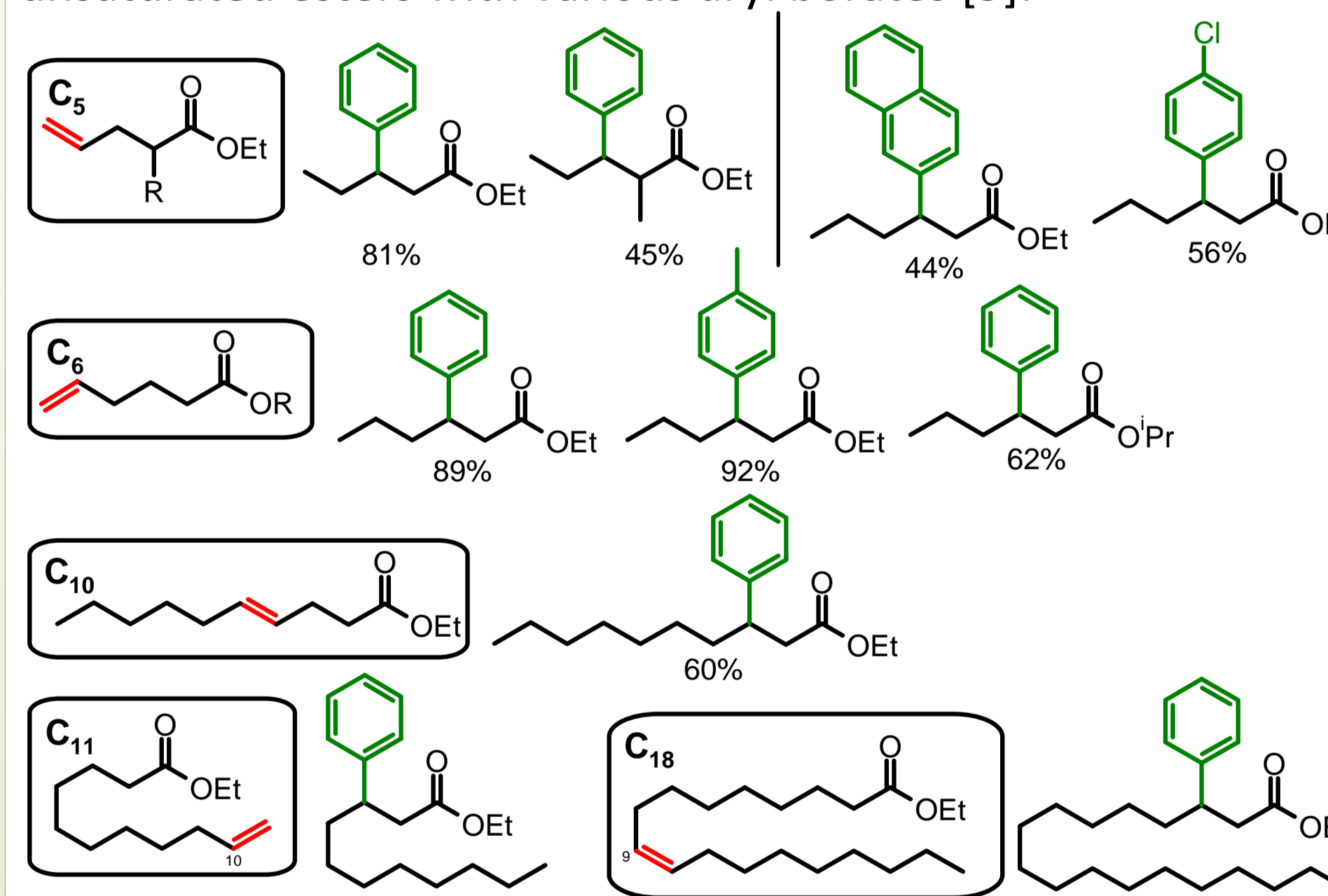
We also applied the concept of catalytic isomerizing transformations to **unsaturated fatty esters**. A rhodium catalyst rapidly converts the starting material into an equilibrium mixture of all possible double-bond isomers:



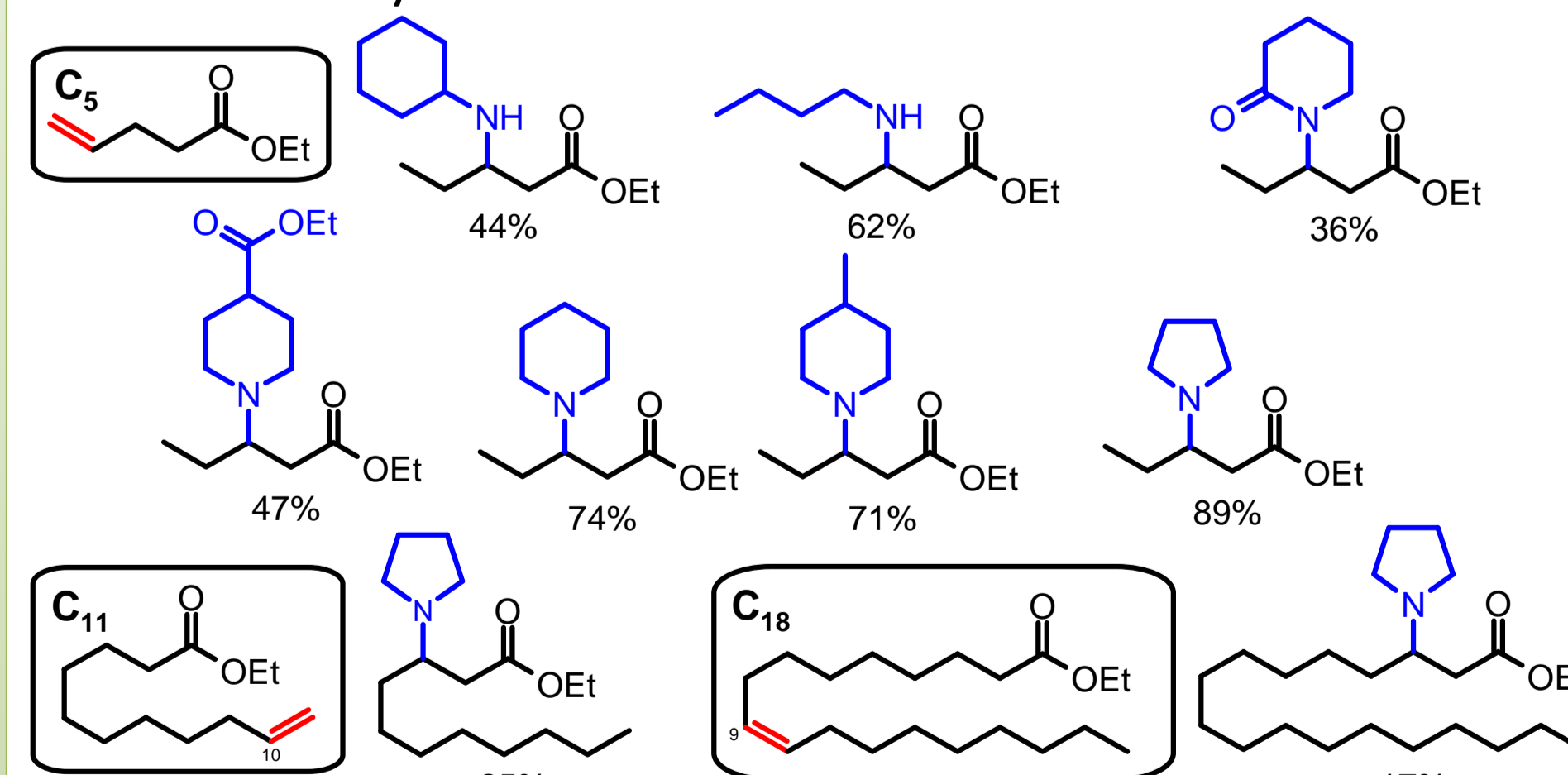
The *in situ* formed α,β -unsaturated isomer reacts irreversibly with an aryl nucleophile to yield a β -substituted ester via conjugate (Michael) addition:



With this **broadly applicable** protocol, we coupled several unsaturated esters with various aryl borates [5]:



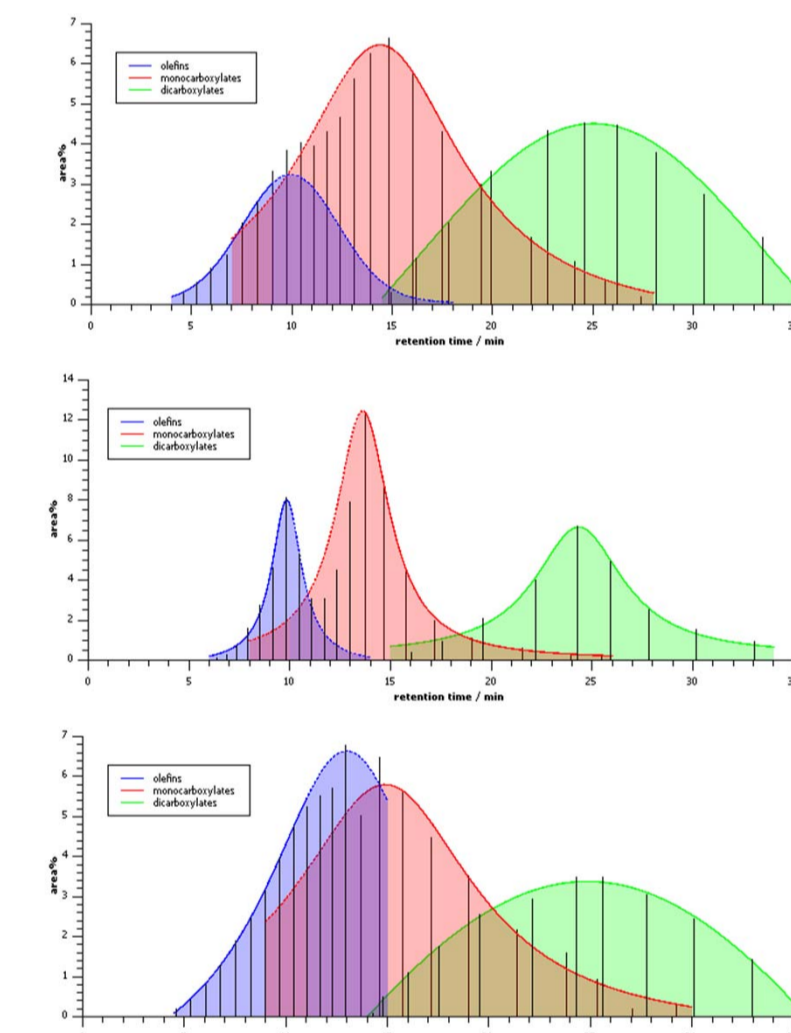
We successfully extended the method to **amines and lactams**:



Isomerizing Olefin Metathesis

The combination of controlled double-bond migration and olefin metathesis opens up new pathways to **useful product mixtures**. Polymer applications require defined compound mixtures as reaction feed, such as olefin cuts from crude oil. To produce these building blocks from renewable feedstocks, we developed a powerful bimetallic catalyst for the efficient isomerizing olefin metathesis of fatty acids and esters [6].

The **chain length distributions** can be tuned by the choice of catalyst and reaction conditions:

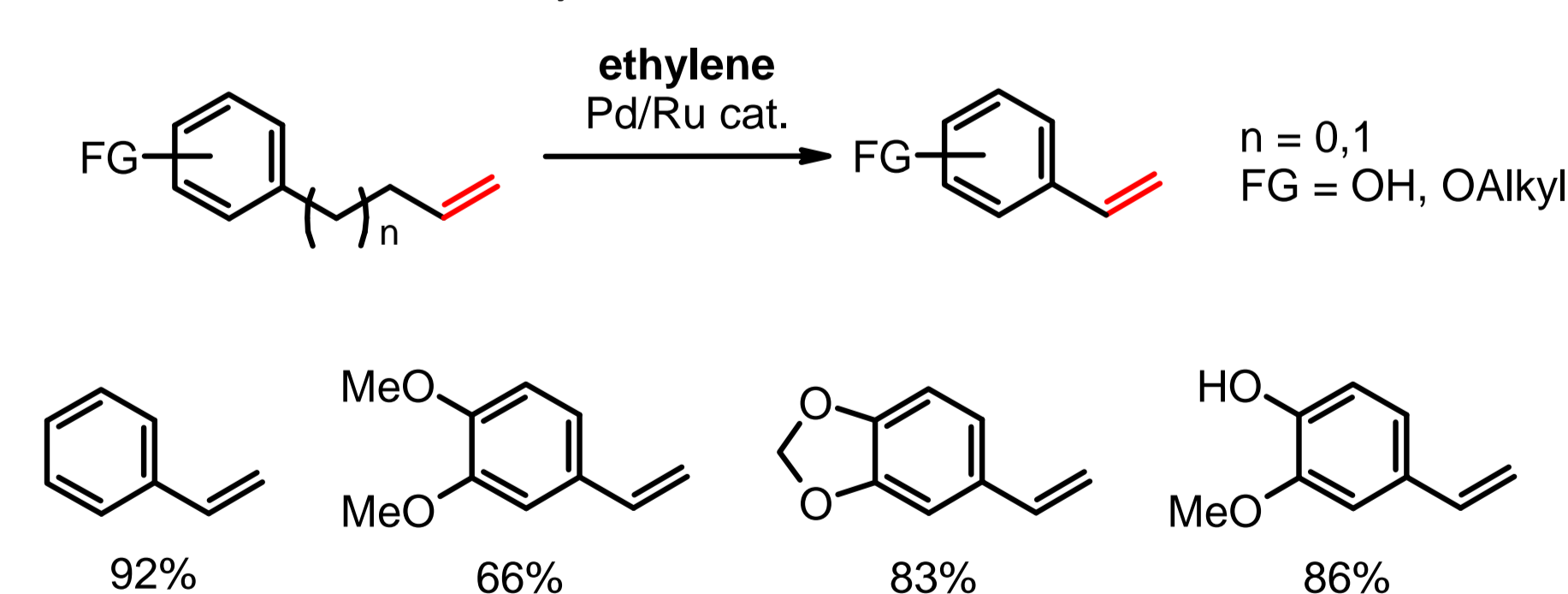


Most of the resulting olefins and dicarboxylates are not available from petrochemicals.

The new **Pd/Ru-based catalyst system**

- gives fast and high conversions at mild temperatures and with low catalyst loadings
- exhibits a broad substrate scope towards functional groups and natural products of technical quality
- does not require pre-activation of the isomerization catalyst, e.g. through hydride formation by additional base
- is broadly applicable to different variations of metathesis, such as self-metathesis, cross-metathesis and ethenolysis
- works solvent-independently and even solvent-free.

A **synthetic application** of this catalytic tool is the isomerizing ethenolysis of olefinic side-chains: Low-price phenylpropanoids, such as eugenol, are converted into yielding high-value functionalized styrenes:



Investigations are under way to elucidate mechanistic details and further applications of this cooperative catalysis.

Literature and further reading: (see also www.chemie.uni-kl.de/goossen)

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