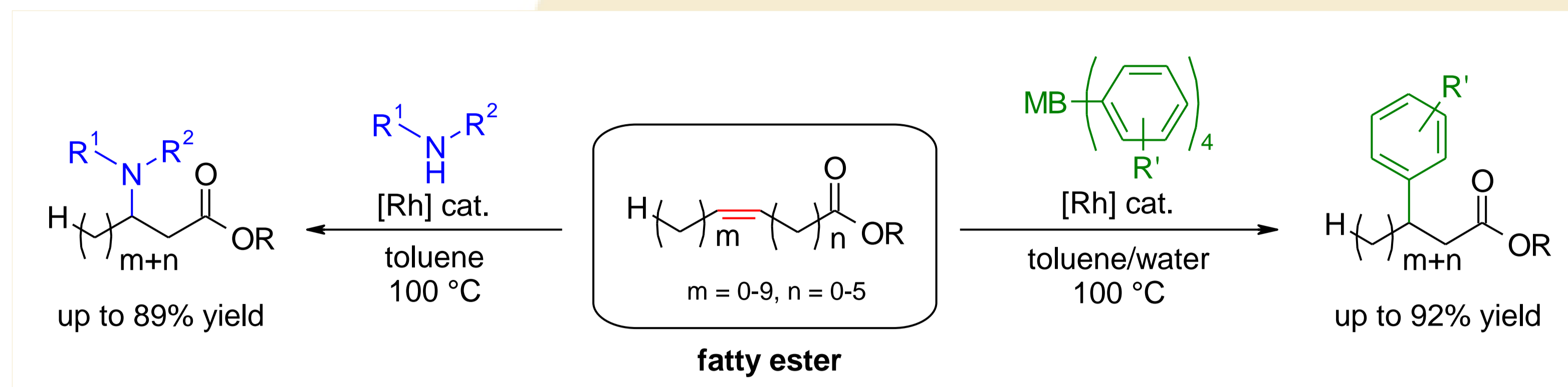


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Rhodium-phosphite catalysts^[1] effectively mediate the double-bond migration within unsaturated esters and transform them into a constantly renewing equilibrium mixture of double-bond isomers. Selectively, the conjugated species are continuously removed via 1,4-addition under formation of β -aryl or β -amino esters. The new method can be applied to a range of substrates, such as fatty esters of different chain lengths and double-bond positions, and several C- and N-nucleophiles.^[2]

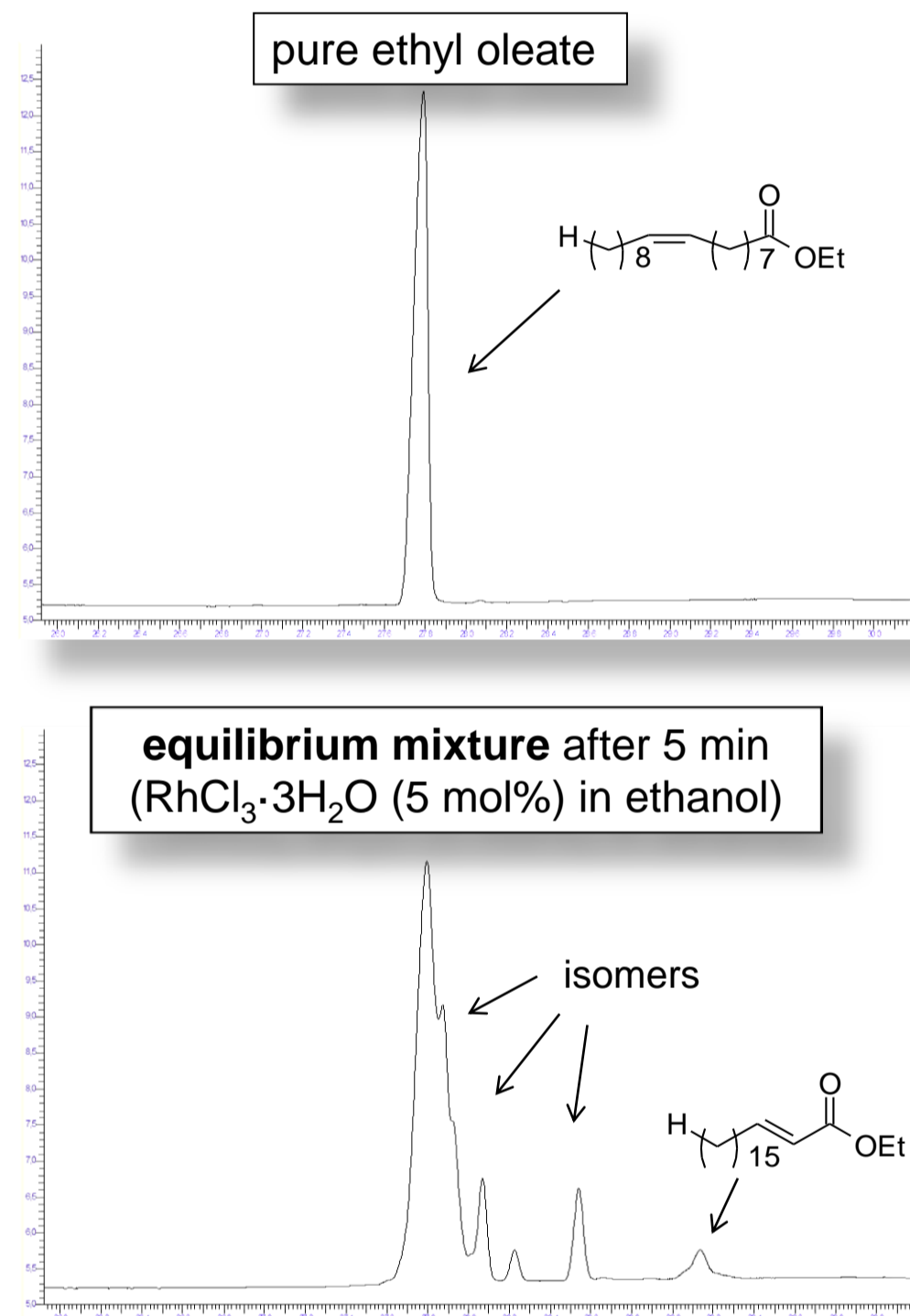
Development of a bifunctional catalyst

First, we identified catalysts that are capable of both migrating double-bonds in the presence of ester groups and establishing a dynamic equilibrium of double-bond isomers.^[3]

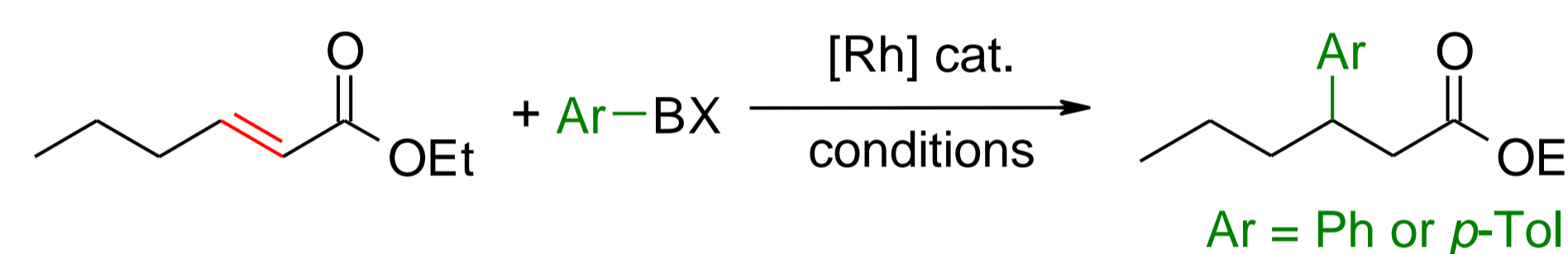
Screening of isomerization catalysts

#	Catalyst (mol%)	Solvent	Temp. (°C)	Isomerization of ethyl oleate
1	H ₂ PtCl ₆ (1)/HSiMe ₂ Cl (4)	none	70	–
2	Ru(CO)(PPh ₃) ₃ HCl (5)	CHCl ₃	70	+
3	PdCl ₂ (5)	EtOH	80	+
4	Fe(CO) ₅ (20)	<i>n</i> -octane	125	++
5	RhCl ₃ ·3H ₂ O (2)	EtOH	80	++
6	Rh(COD)(acac) (1.5)/biphephos (1.5)	toluene	90	++
7	Rh(acac)(CO) ₂ (1.5)/biphephos (1.5)	toluene	90	++
8	[Rh(Cl)(COD)] ₂ (0.75)/biphephos (1.5)	toluene	90	+

GC analysis of the equilibrium



Second, we evaluated active isomerization catalysts for the conjugate addition of aryl nucleophiles to our model substrate ethyl 2-hexenoate. We screened several arylboron compounds under especially adapted conditions:

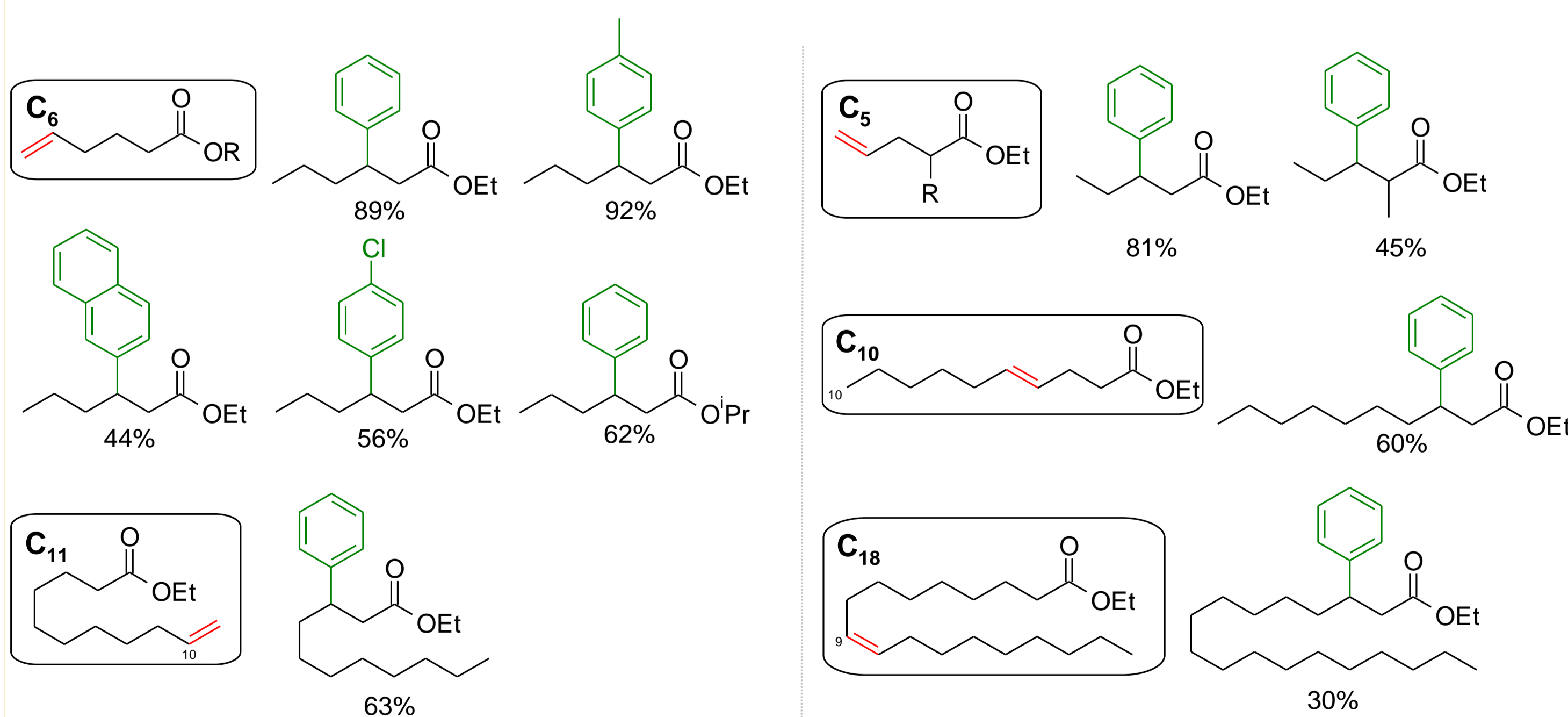
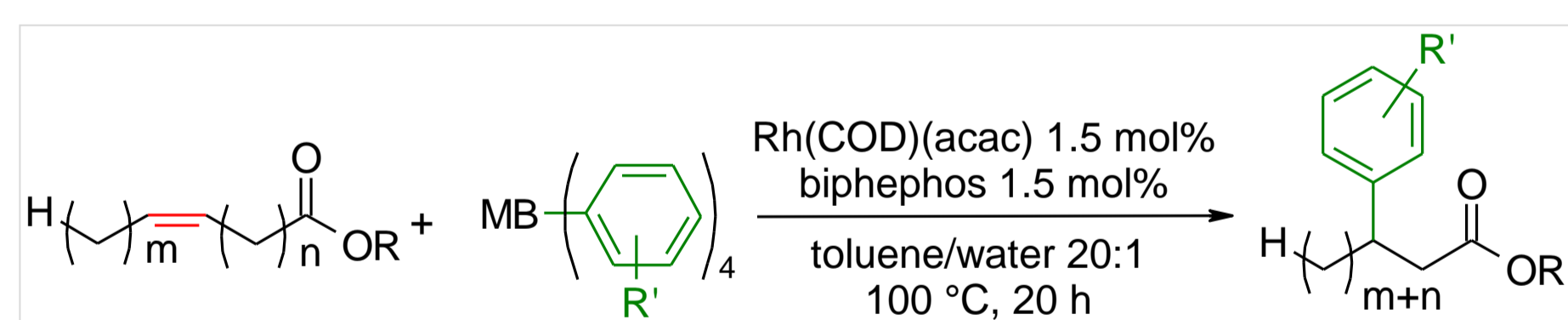


#	Ar-BX	Equiv.	Catalyst	Cond.	Yield (%) ^[a]
1	phenylboronic acid	1.2	RhCl ₃ ·3H ₂ O	A	1
2	potassium phenyltrifluoroborate	2.4	Rh(COD)(acac)	B	8
3	"	1.2	[Rh(Cl)(COD)] ₂	B	53
4	phenylboronic acid MIDA ester	1.2	Rh(acac)(CO) ₂	C	1
5	"	1.2	[Rh(Cl)(COD)] ₂	C	79
6	<i>p</i> -tolylboroxine	0.7	[Rh(Cl)(COD)] ₂	D	76
7	sodium tetraphenylborate	1.5	Rh(COD)(acac)	E	95

Reaction conditions: Enolate (0.5 mmol), rhodium catalyst (3 mol% Rh), biphephos ligand (3 mol%), argon atmosphere, conditions A: toluene/water 1.5/0.5 mL, 80 °C, 16 h; B: toluene/water 1.9/0.1 mL, 110 °C, 16 h; C: 5 equiv. K₃PO₄, dioxane/water 1.7/0.3 mL, 60 °C, 16 h; D: 3 equiv. KF, toluene/water 1.5/0.5 mL, 60 °C, 16 h; E: toluene/water 3.0/0.15 mL, 100 °C, 16 h. [a] GC yields were determined using *n*-dodecane as the internal standard.

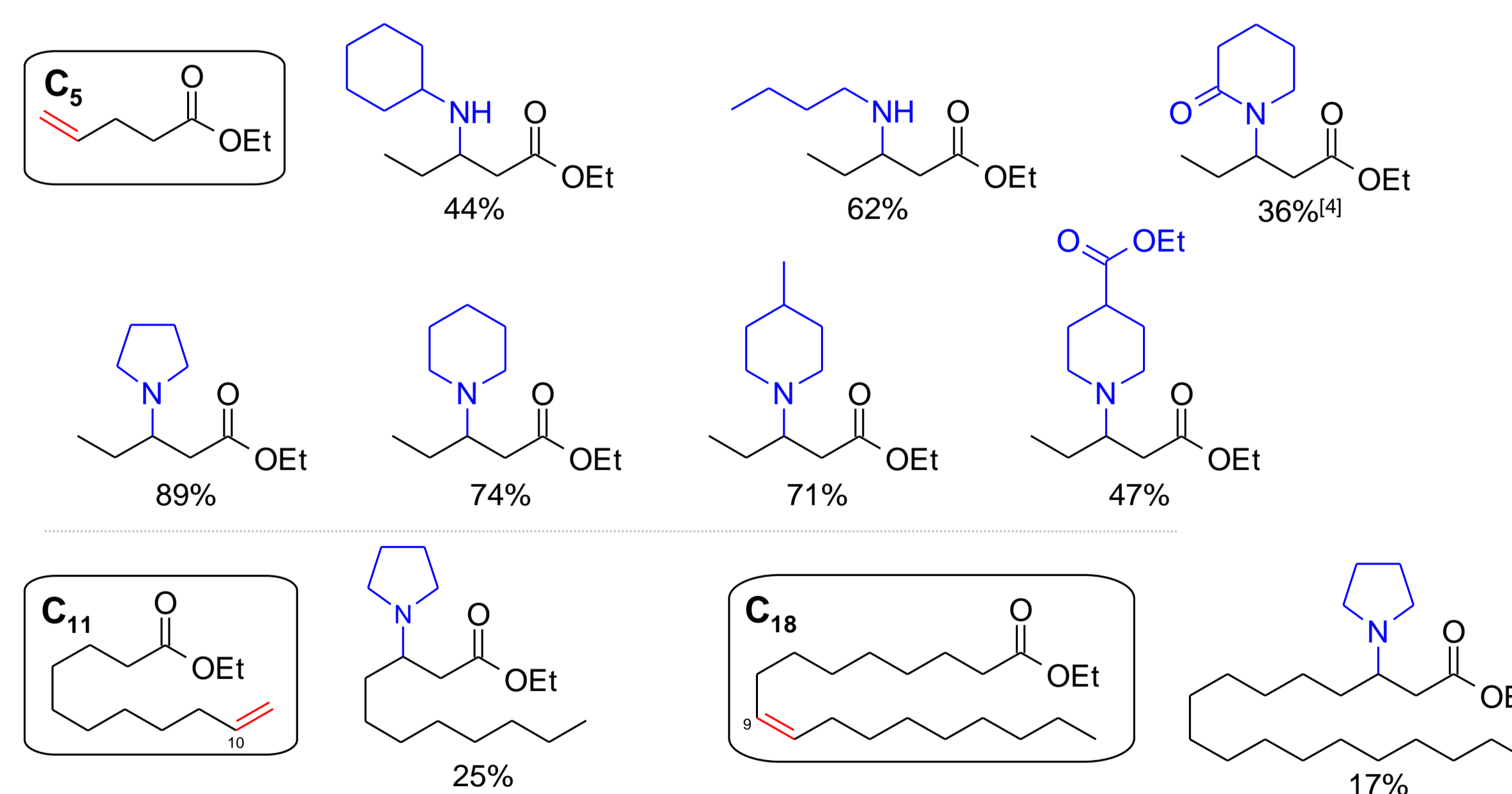
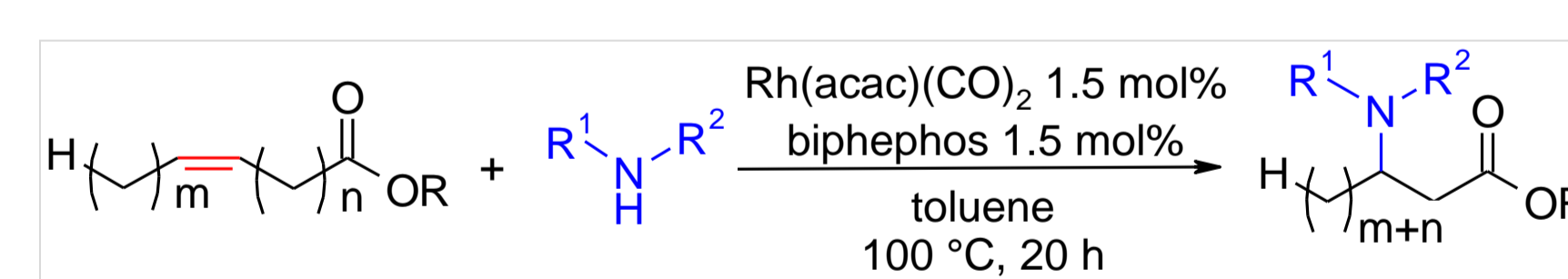
Isomerizing Michael-addition of C-nucleophiles

Under optimized conditions, unsaturated substrates with different chain lengths and double-bond positions were converted into the corresponding β -arylated esters.



Isomerizing Michael-addition of N-nucleophiles

We extended the protocol to amine nucleophiles: Under slightly different conditions, several β -amino esters are accessible via isomerizing Aza-Michael addition.



On the basis of this concept, we are currently developing new isomerizing transformations, particularly for the conversion of renewable feedstocks into valuables.

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

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