

Systemes fluorés

- Immiscible with common organic solvents at RT: the “third liquid phase” allows recovery of catalyst
- Miscible at elevated temperature
- Monophasic catalysis et elevated temperature with biphasic product-catalysis separation at lower temperatures
- High solubility of oxygen in fluorocarbons: aerobic oxidation
- Rather expensive compared to regular organic solvents
- Catalyst needs to be solubilized in fluoruous phase
 - “fluorophilic” ligands
 - Incorporate “fluorous ponytail”
- Extremely long lifetime in the environment
- Fluorous catalysis without fluoruous solvents

Systemes fluorés

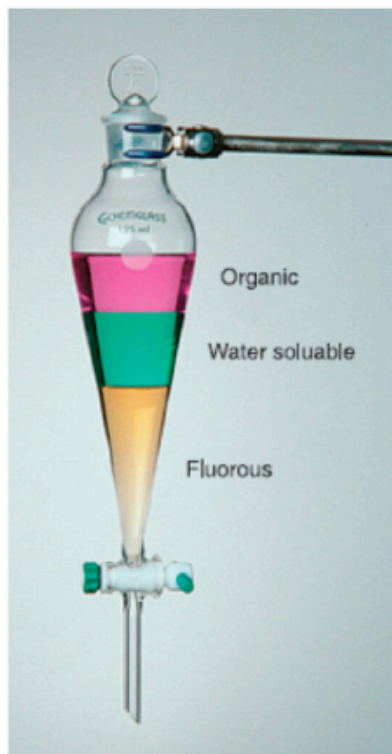
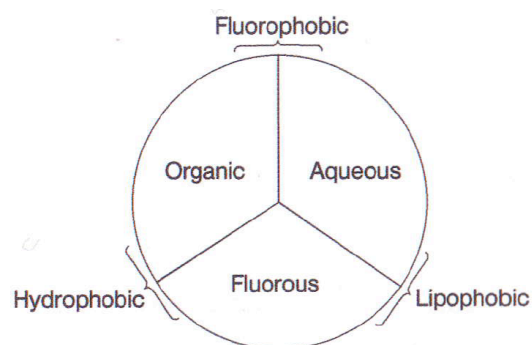
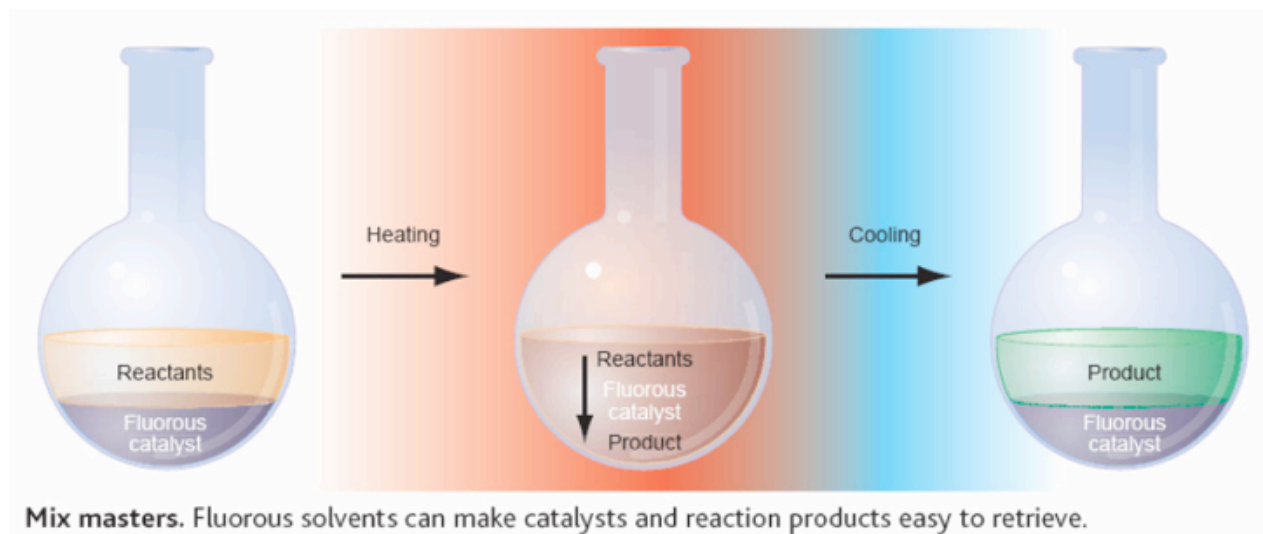
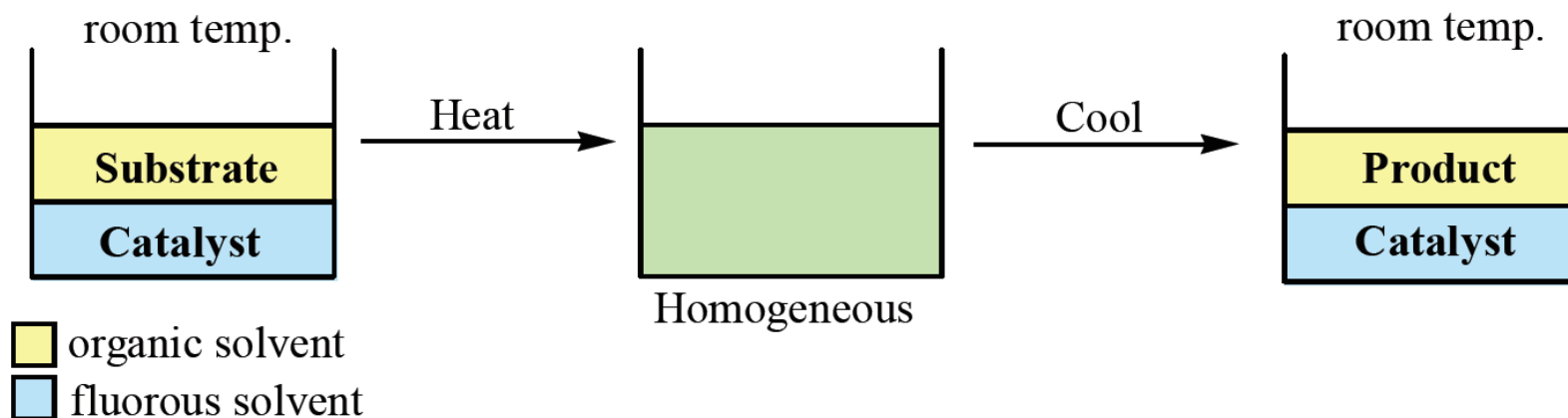


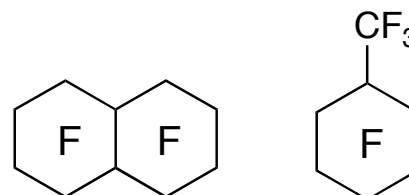
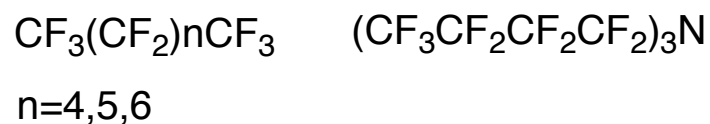
Fig. 1. A photograph of a typical three-phase liquid-liquid extraction is shown with an organic (yellow), inorganic (blue), and fluorous (clear) phases. [Illustration from (65)]



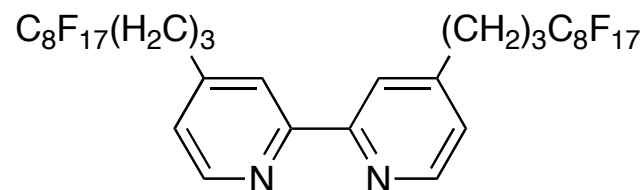
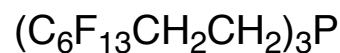
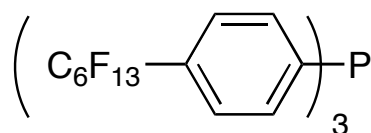
Systemes fluorés



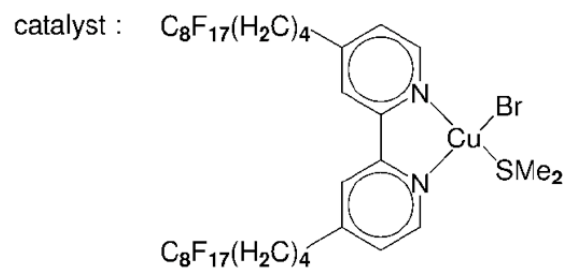
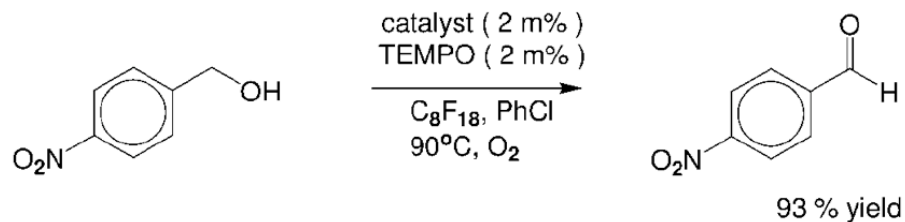
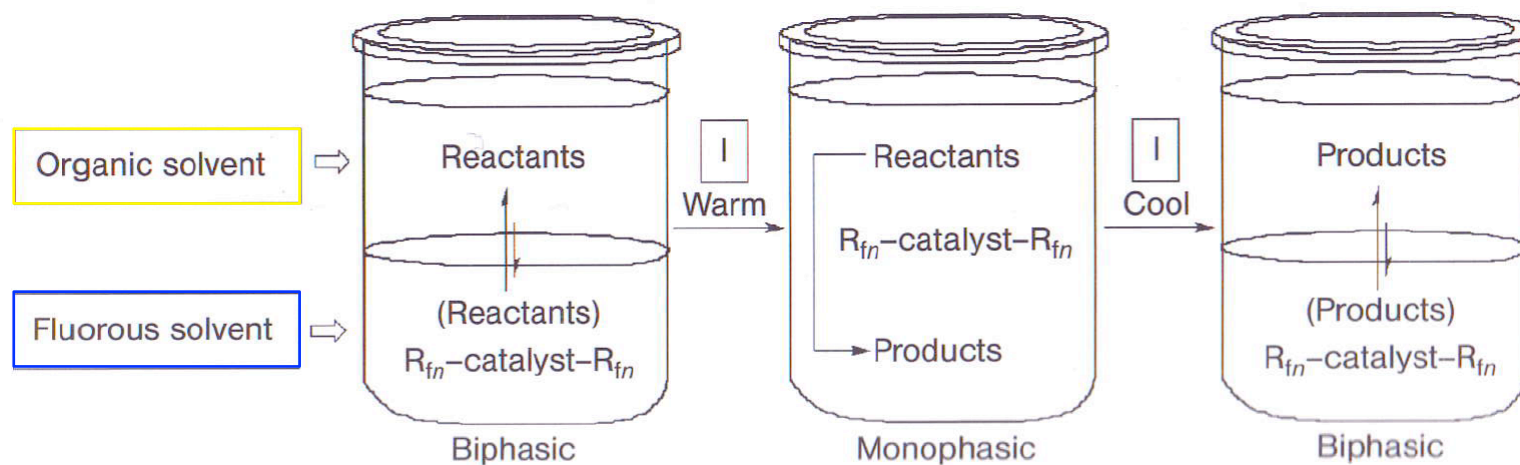
Fluorous solvents:



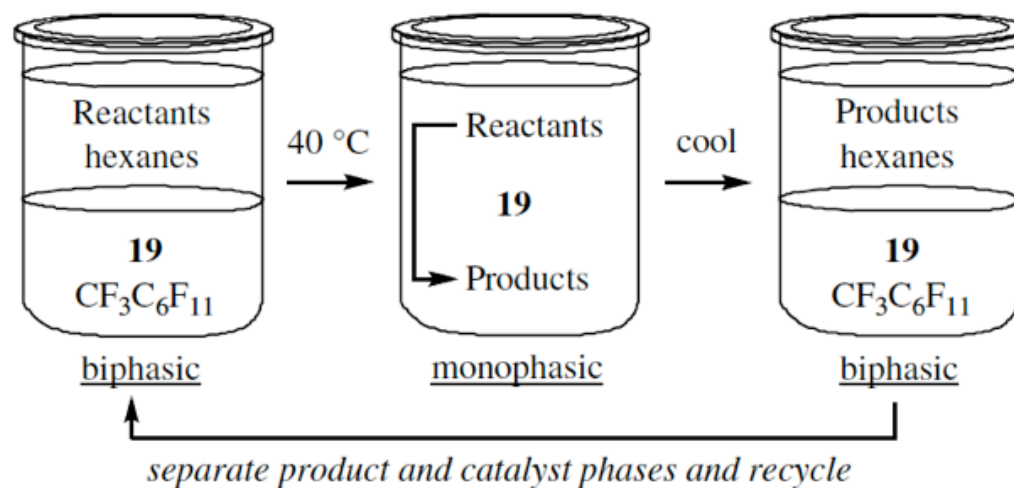
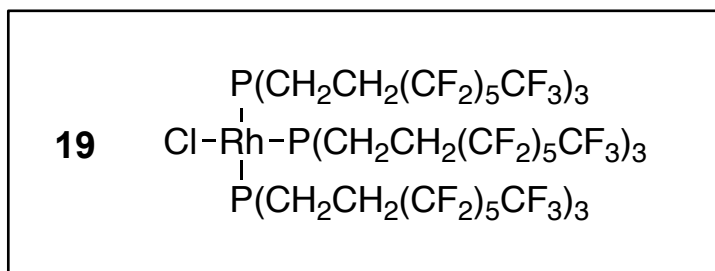
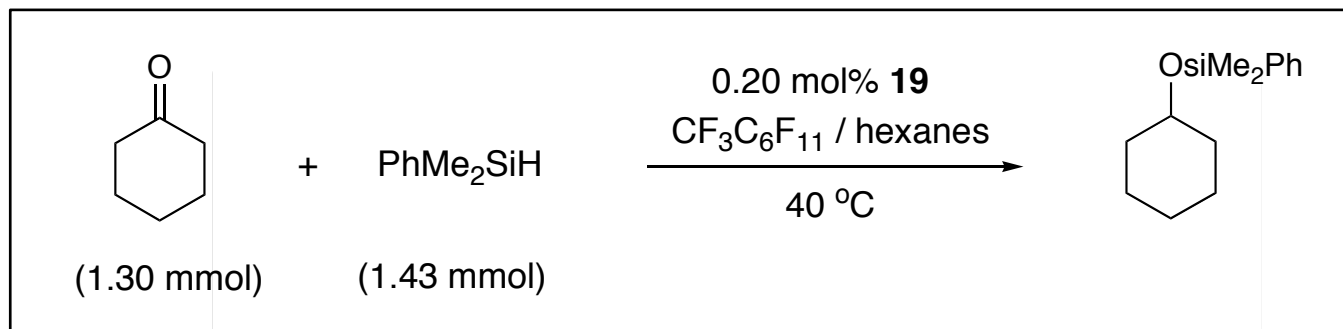
Fluorous ligands:



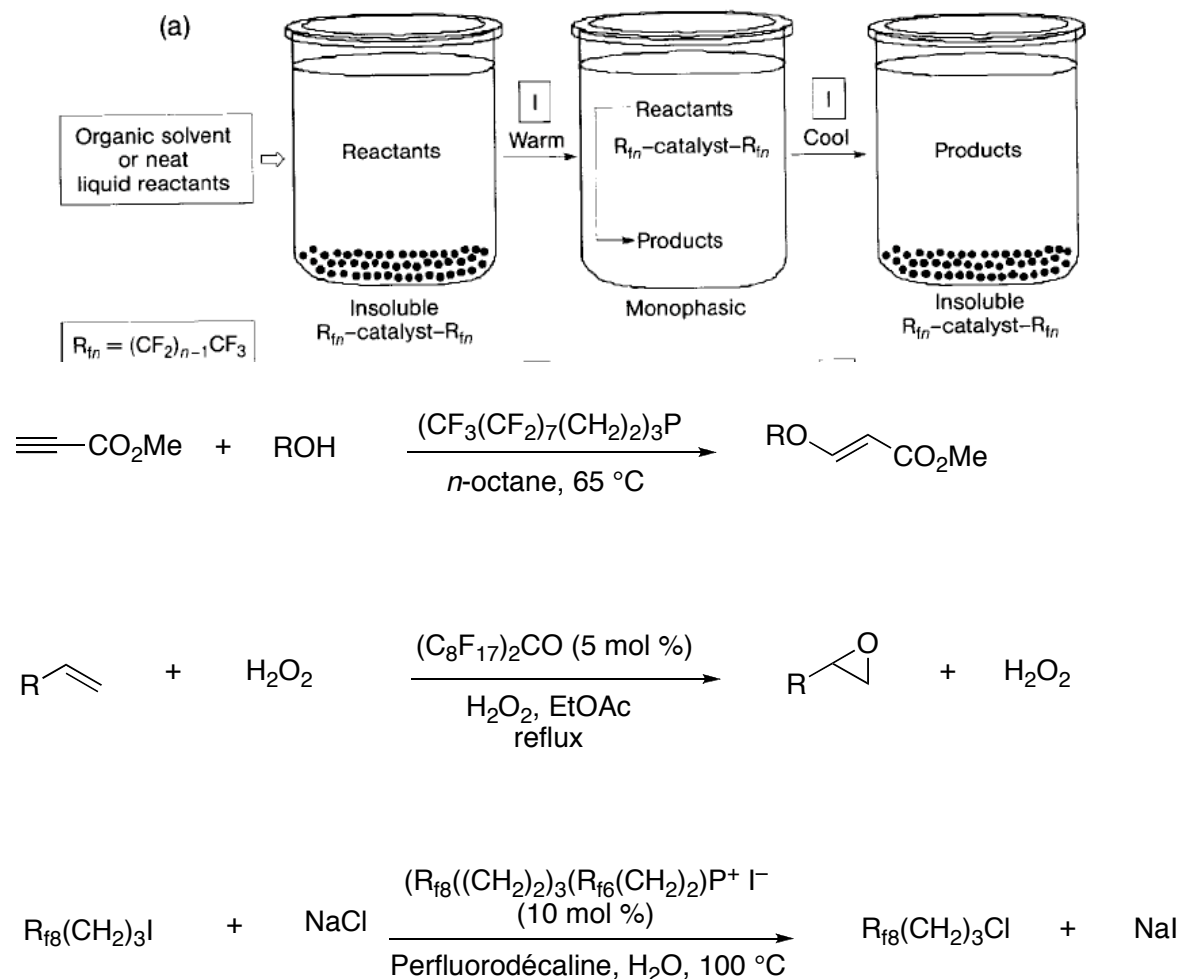
Systemes fluorés



Systemes fluorés



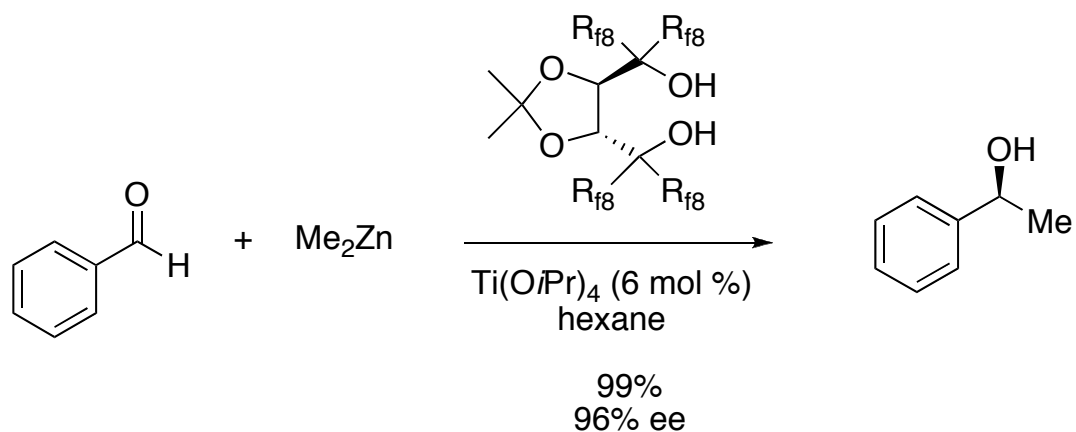
Systemes fluorés



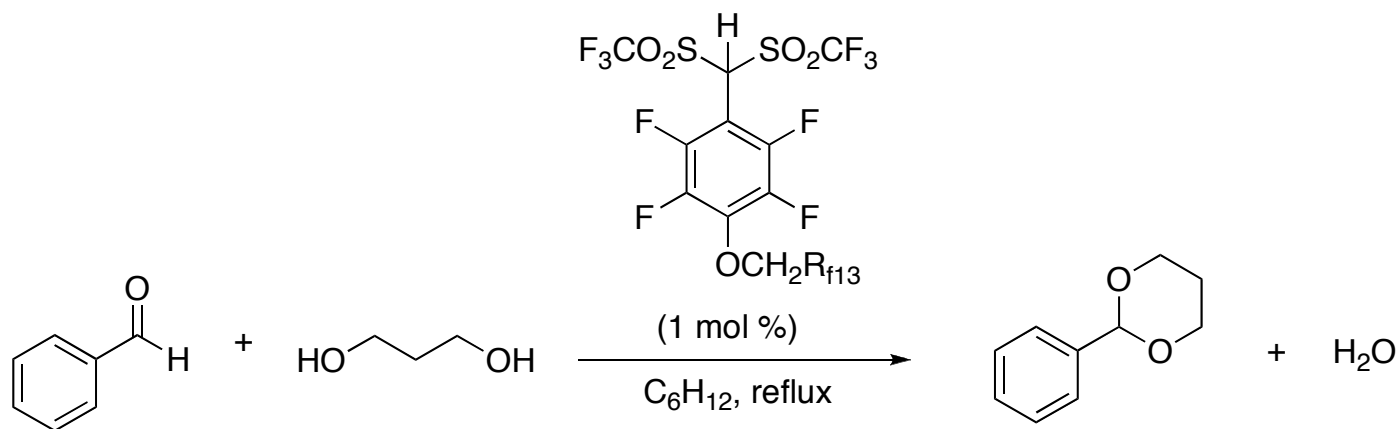
Catalyseur précipité en refroidissant

Wende, M.; Gladysz, J. A., *J. Am. Chem. Soc.* **2003**, *125*, 5861
 van Vliet, M. C. A.; Arends, I. W. C. E.; Sheldon, R. A., *Chem. Commun.* **1999**, 263
 Emnet, C.; Weber, K. M.; Vidal, J. A.; Consorti, C. S.; Stuart, A. M.; Gladysz, J. A.,
Adv. Synth. Catal. **2006**, *348*, 1625

Systemes fluorés



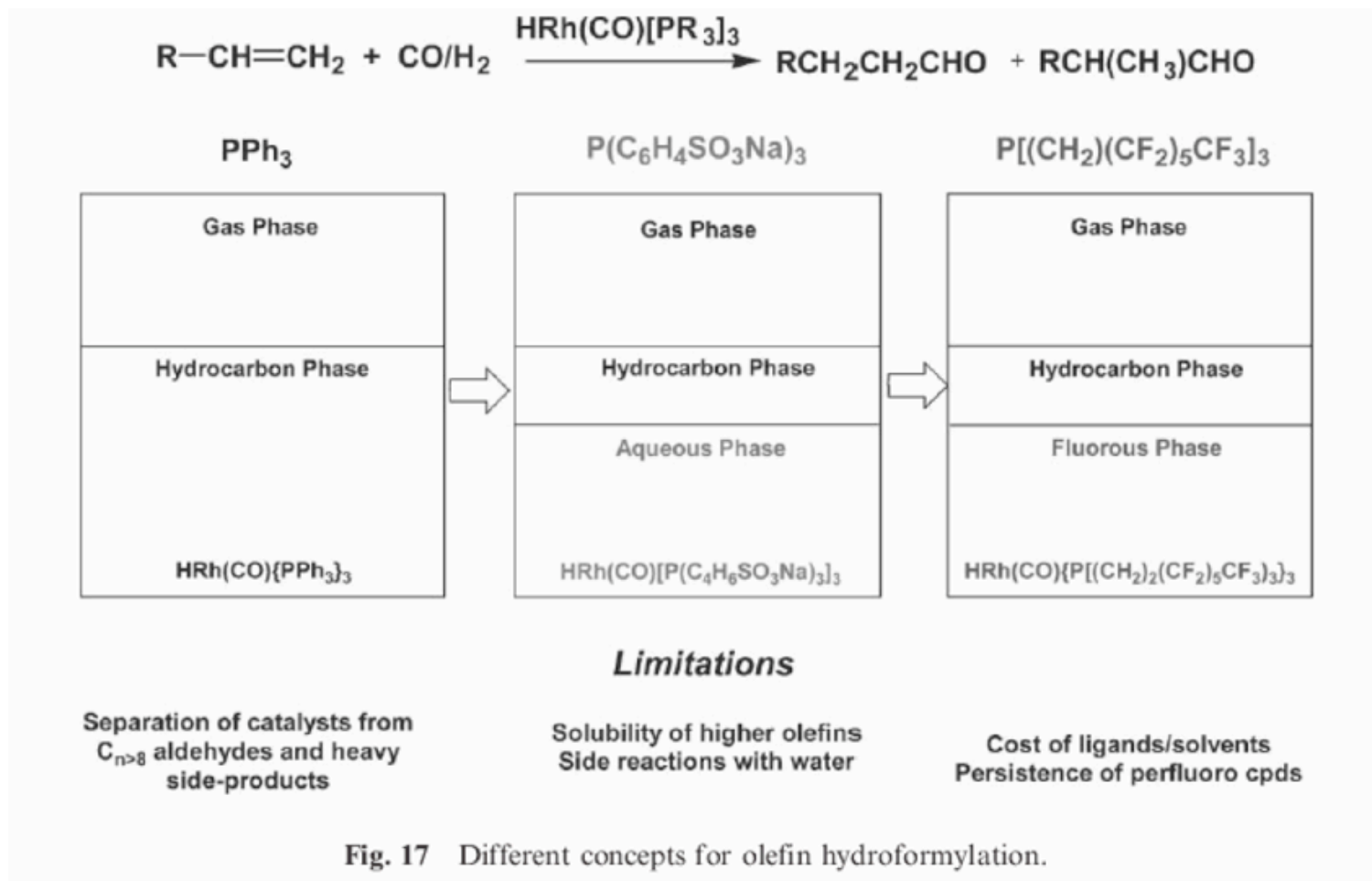
Catalyseur précipité par ajout de PhMe froid



Catalyseur précipité en refroidissant à 0 °C

Sokeirik, Y. S.; Mori, H.; Omote, M.; Sato, K.; Tarui, A.; Kumadaki, I.; Ando, A.,
Org. Lett. **2007**, *9*, 1927
 Ishihara, K.; Hasegawa, A.; Yamamoto, H., *Synlett* **2002**, 1299

Systemes fluorés



“Green Chemistry and Catalysis”

Sheldon, R. A.; Arends, I.; Hanefeld, U. Eds, Wiley-VCH 2007

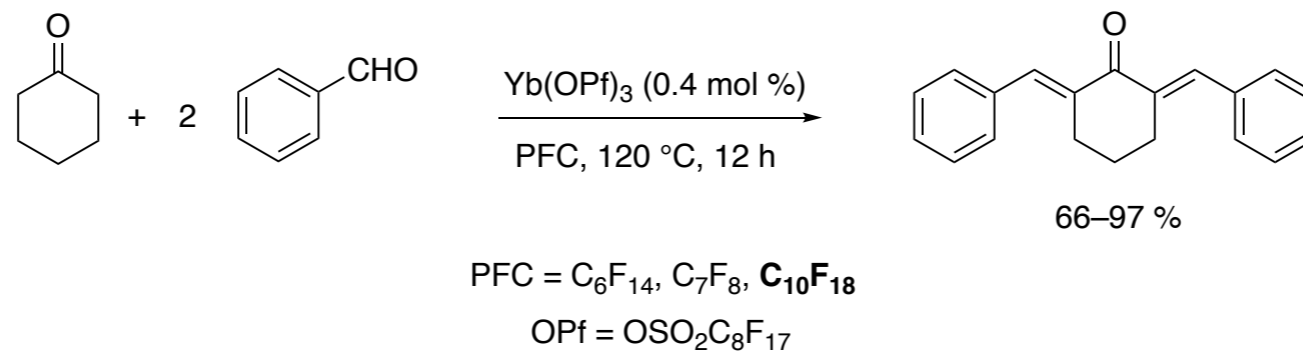
“Green Solvents for Sustainable Organic Synthesis: State of the Art”

Sheldon, R. A., *Green Chem.* **2004**, *7*, 267–278

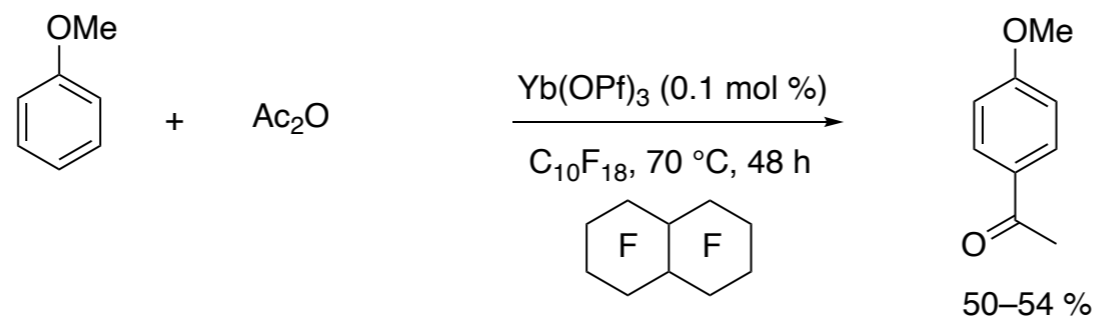
Solvants fluorés

Exemples

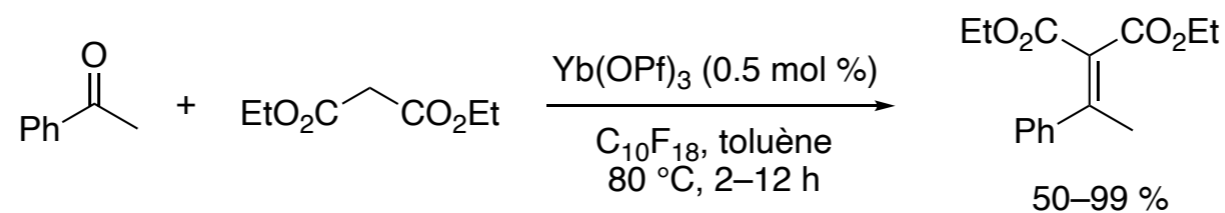
● Condensation aldolique



● Acylation de Friedel-Crafts



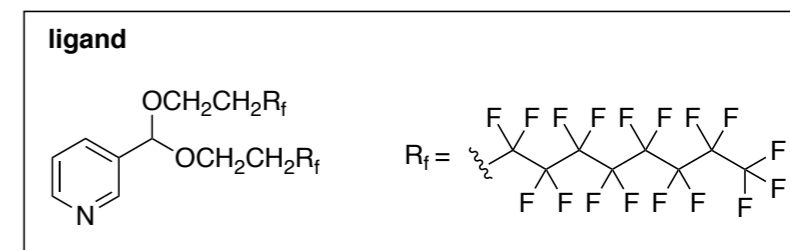
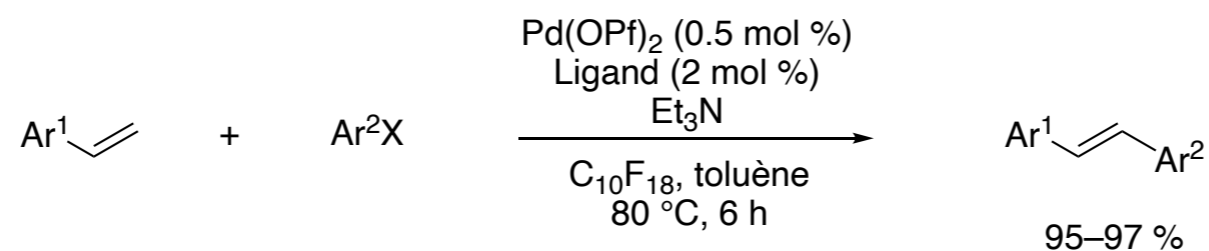
● Condensation de Knoevenagel



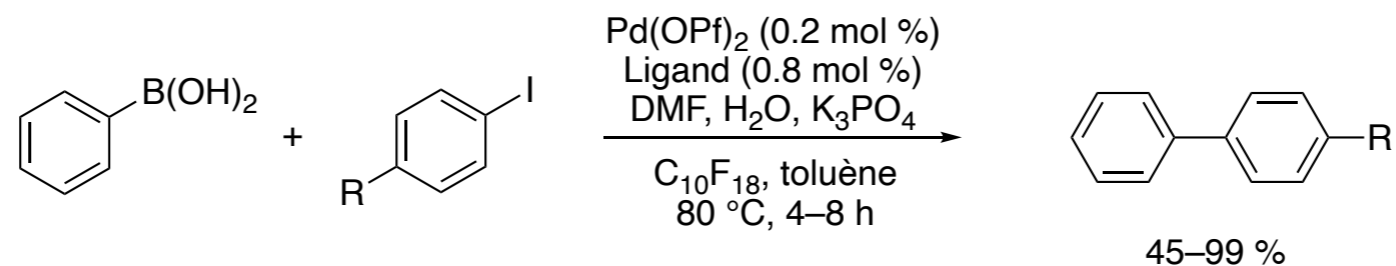
Solvants fluorés

Exemples

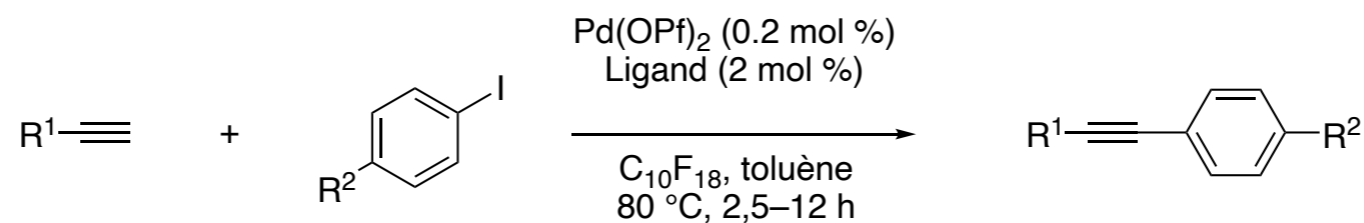
● Réaction de couplage de Heck



● Réaction de couplage de Suzuki-Miyaura



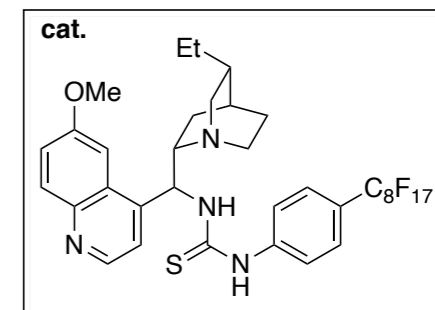
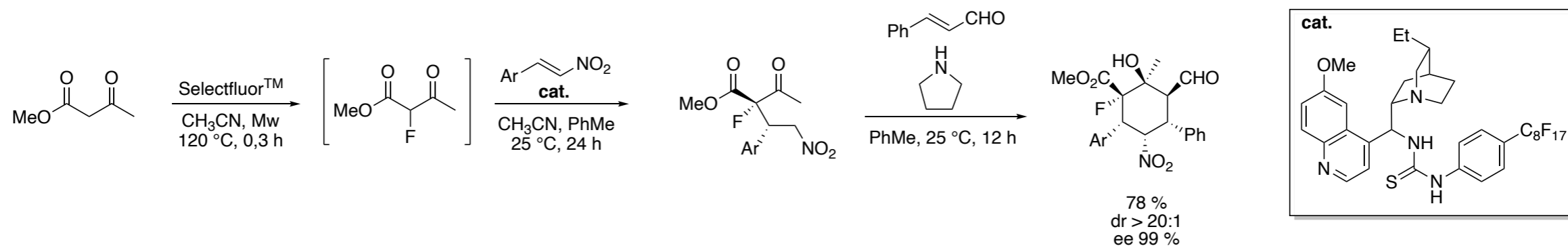
● Réaction de couplage de Sonogashira



Solvants fluorés

Exemple en synthèse stéréosélective

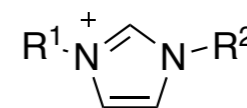
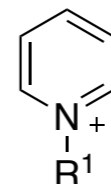
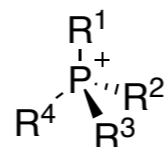
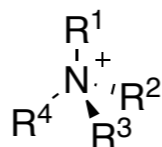
- Fluorous catalyst easily recovered by fluorous solid-phase extraction in 94–97% yield and >98% purity



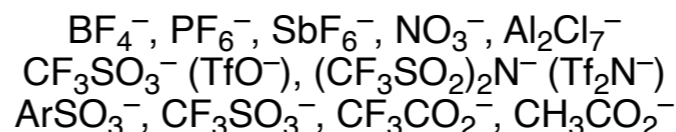
Liquides ioniques

Généralités

- Sels de cations organiques



- Anions divers :



- Utilisés comme solvants organiques
- Polarité et hydrophobie peuvent être réglées
 - Possibilité d'optimisation : rendement, sélectivité, solubilité des substrats, séparation du produit
 - Solvants de conception : > 1 million liquides ioniques vs. 600 solvants organiques « classiques »
- Applicables pour des systèmes biphasiques et recyclage de catalyseurs
- Très conducteurs
- Sels ioniques qui doivent être liquides à la température d'utilisation (température ambiante, « RTIL »)
- Souvent coûteux
- Questions importantes au sujet de leur toxicité, biodégradabilité
- Récupération du produit et recyclage du catalyseur
 - Extraction possible du produit avec un solvant organique, mais apparence de contradiction avec le fait d'utiliser un liquide ionique pour remplacer un solvant organique
- Solvants appropriés pour faire de la biocatalyse

Liquides ioniques

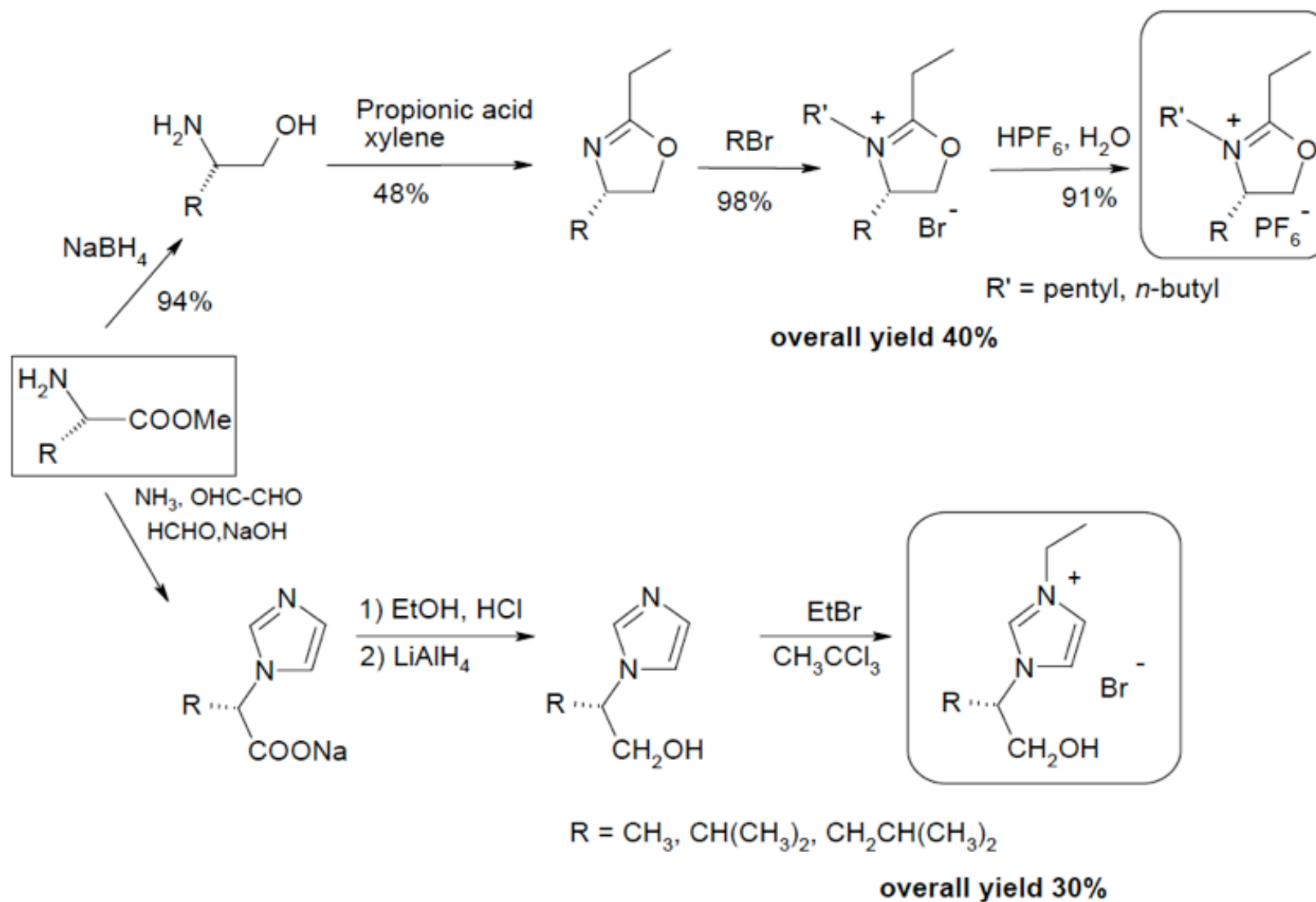
- Premier procédé industriel : mars **2003**



The BASIL reactor. Upper phase, the solvent-free pure product, lower phase, ionic liquid.

The **BASIL** process was developed and is operated by the **BASF**. Et the meeting, Matthias Masse (BASF) revealed that the use of the **BASIL** process increases the productivity of their alkoxyphenylphosphine formation process by a factor of 80 000 compared with the conventional process.

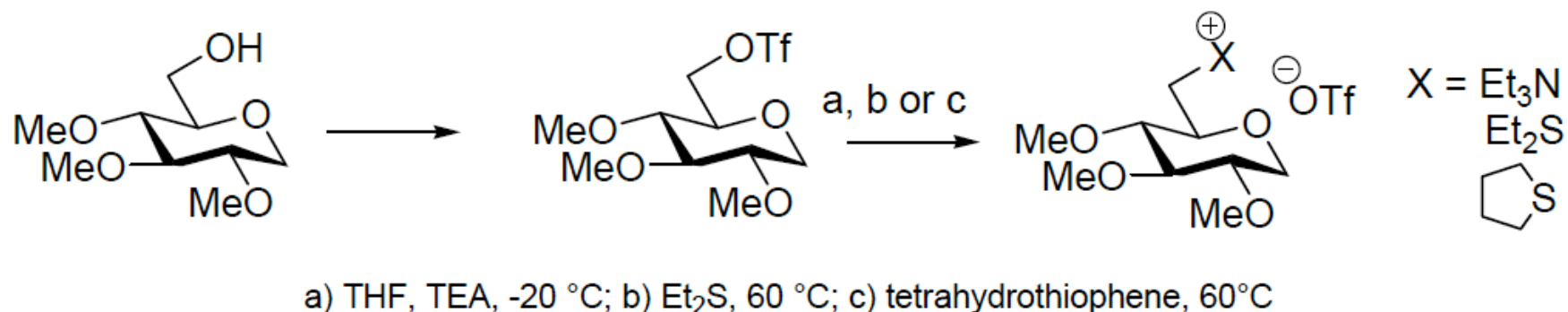
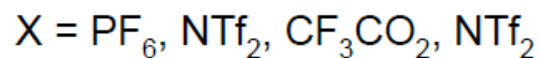
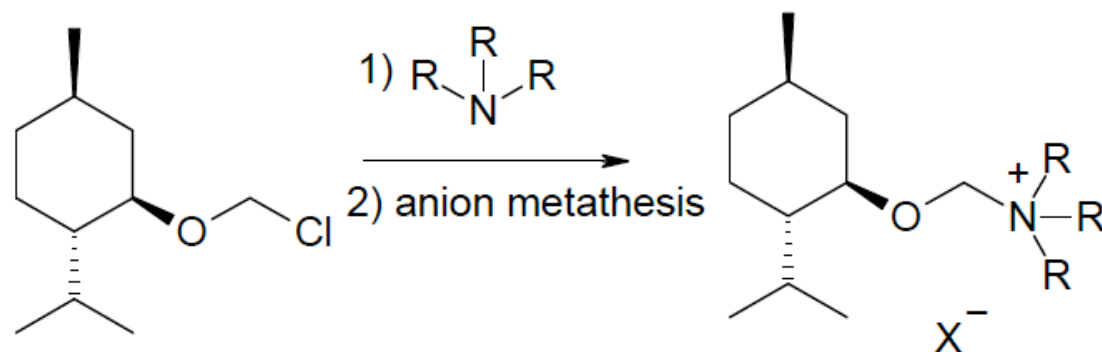
Liquides ioniques



Bao, W.; Wang, Z.; Li, Y., *J. Org. Chem.* **2003**, *68*, 591–593

Guilen, F.; Brégeon, D.; Plaquevent, J. C., *Tetrahedron Lett.* **2006**, *47*, 1245–1248

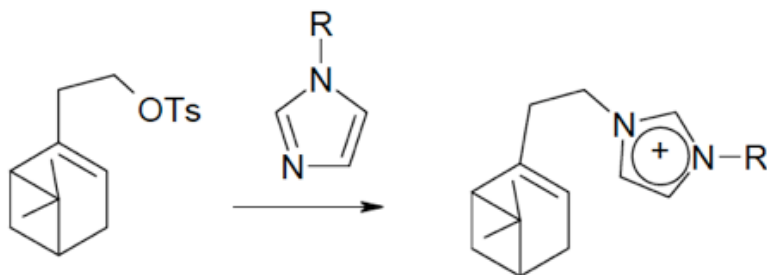
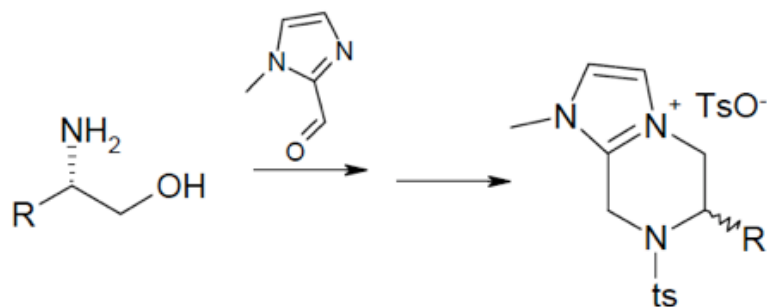
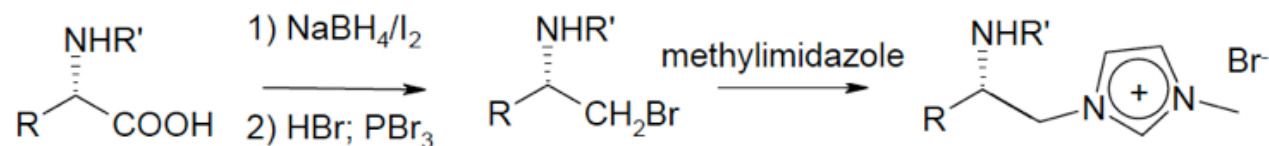
Liquides ioniques



Pernak, J.; Feder-Kubis, J., *Chem. Eur. J.* **2005**, *11*, 4441

Poletti, L.; Chiappe, C.; Lay, L.; Pieraccini, D.; Politi, L.; Russo, G.,
Green Chem. **2007**, *9*, 337–341

Liquides ioniques

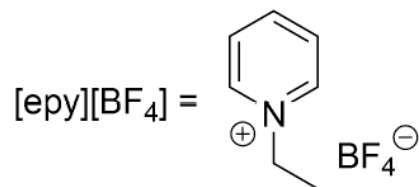
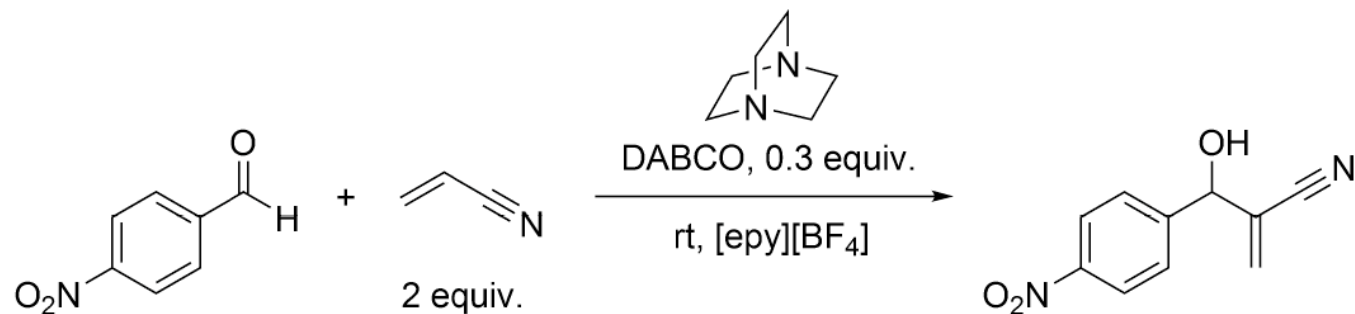


Luo, S.-P.; Xu, D.-Q.; Yue, H.-D.; Wang, L.-P.; Yang, W. L.; Xu, Z.-Y., *Tetrahedron: Asymmetry* **2006**, *17*, 2028

Ni, B.; Garre, S.; Headly, A. D., *Tetrahedron Lett.* **2007**, *48*, 1999

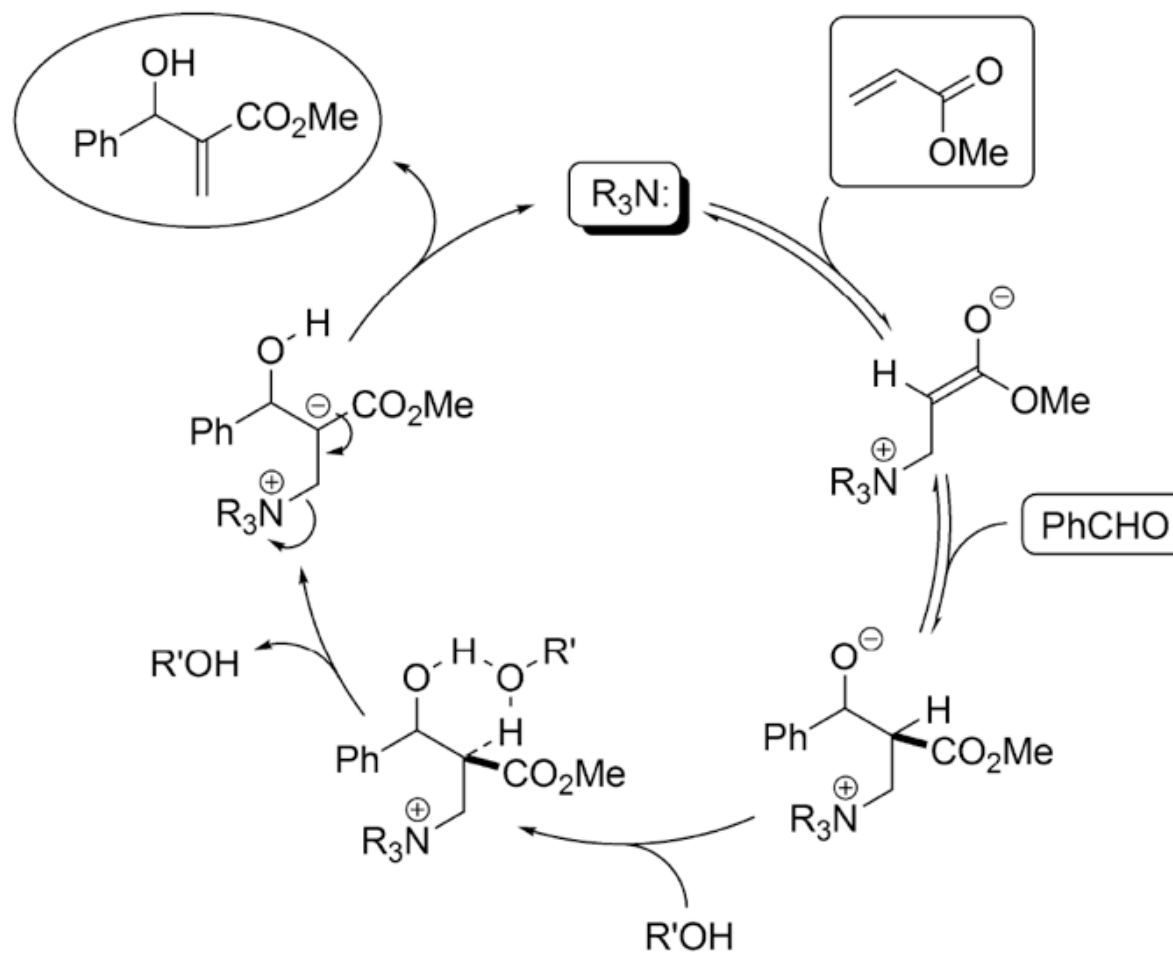
Balczewski, P.; Bachowska, B.; Bialas, T.; Biczak, R.; Wieczorek, W. M.; Balinska, A., *J. Agr. Food Chem.* **2007**, *55*, 1881

Liquides ioniques

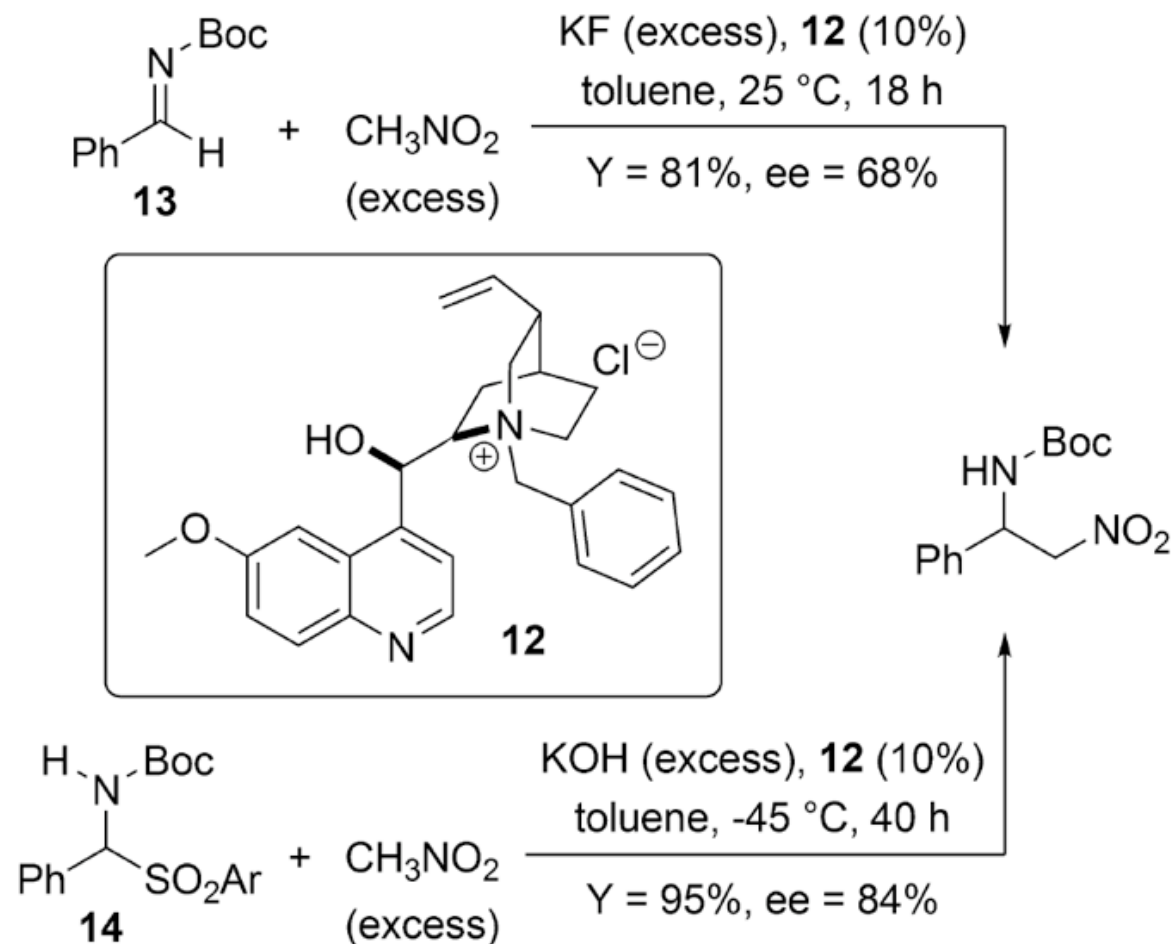


Entry	Solvent	Time (h)	Yield (%)
1	CH ₃ CN	48	32
2	THF	48	40
3	[bmim] [BF ₄]	12	48
4	[bupy] [NO ₄]	5	72
5	[epy] [BF ₄]	2	92

Liquides ioniques



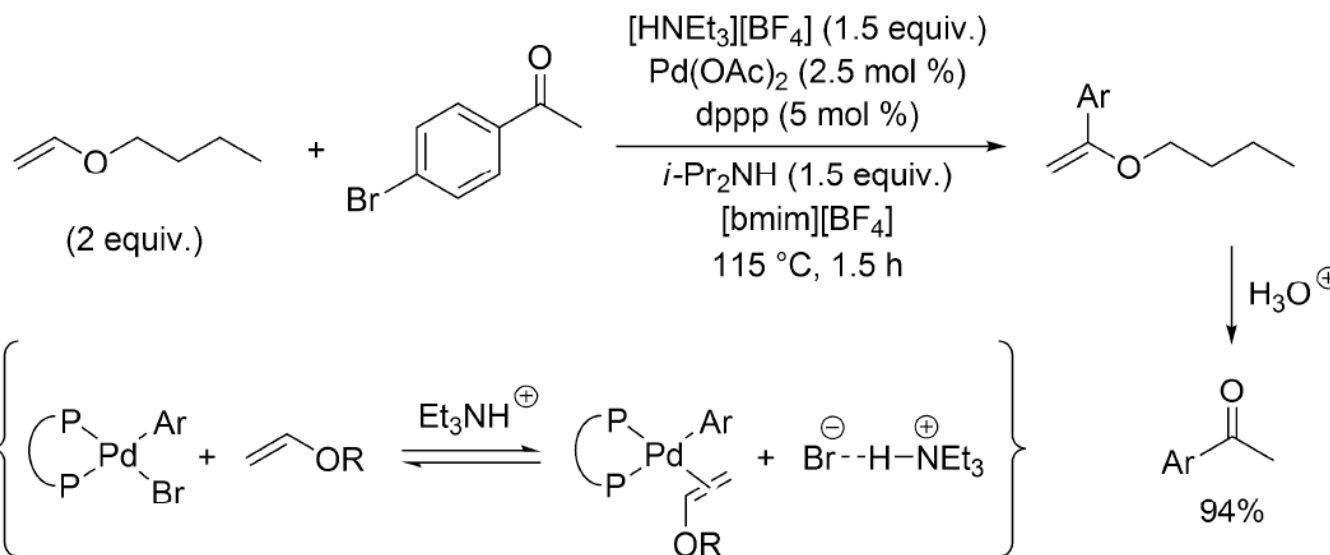
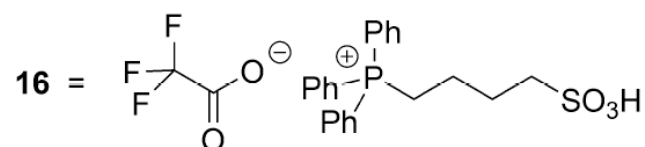
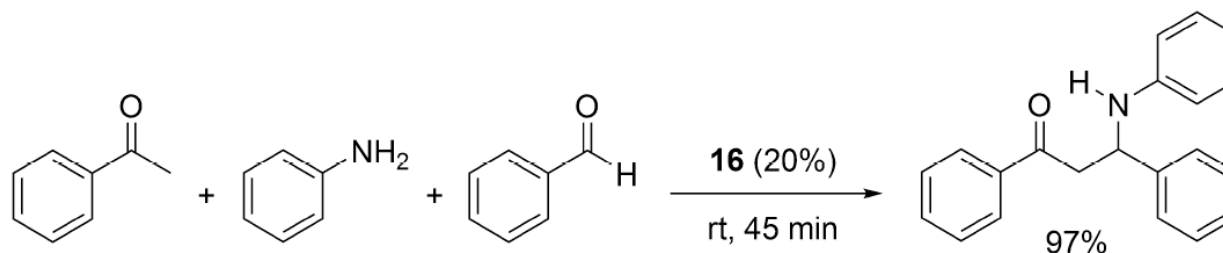
Liquides ioniques



Fini, F.; Sgarzani, V.; Pettersen, D.; Herrera, R. P.; Bernardi, L.; Ricci, A., *Angew. Chem. Int. Ed. Eng.* **2005**, *44*, 7975–7978

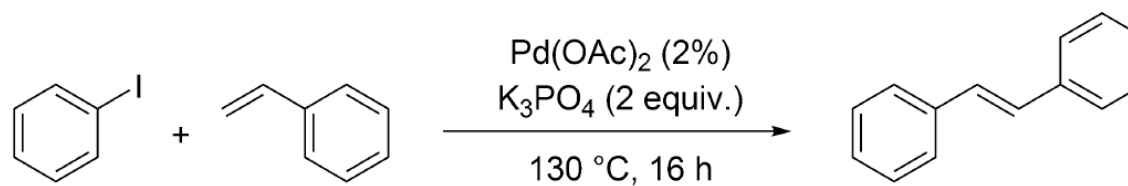
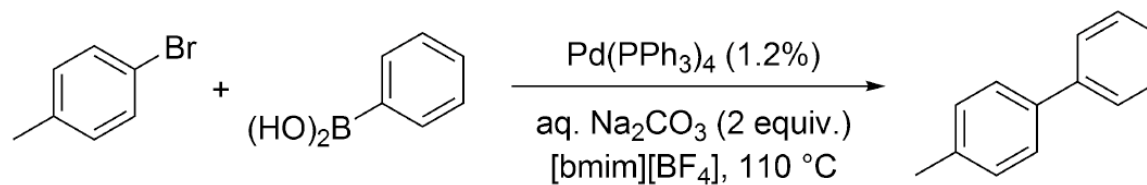
Palomo, C.; Oiarbide, M.; Laso, A.; Lopez, R., *J. Am. Chem. Soc.* **2005**, *127*, 17622–17623

Liquides ioniques



Sahoo, S.; Joseph, T.; Halligudi, S. B., *J. Mol. Catal. A: Chem.* **2006**, *244*, 179–182
 Mo, J.; Xiao, J., *Angew. Chem. Int. Ed. Eng.* **2006**, *45*, 4152–4157

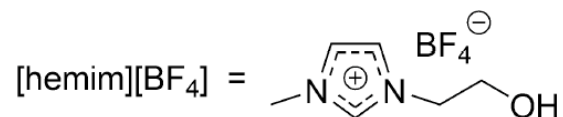
Liquides ioniques



[bmim][BF₄] Y = 18%

[hemim][Cl] Y = 42%

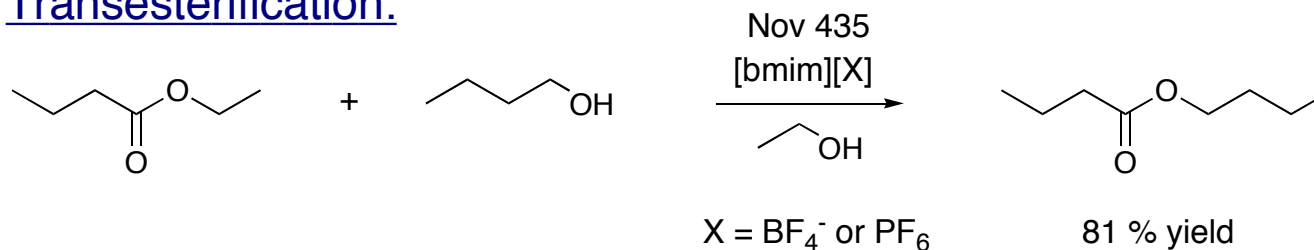
[hemim][BF₄] Y = 97%



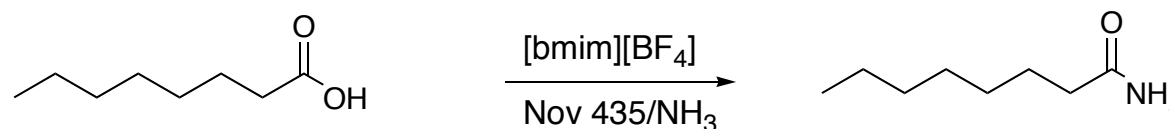
McLachlan, F.; Mathews, C. J.; Smith, P. J.; Welton, T., *Organometallics* **2003**, 22, 5350–5357
 Zhou, L.; Wang, L., *Synthesis* **2006**, 2653–2658

Liquides ioniques

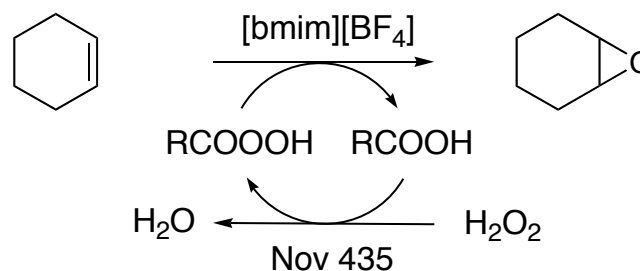
Transesterification:



Ammoniolysis:



Perhydrolysis:



“Lipase-catalyzed reactions in ionic liquids”

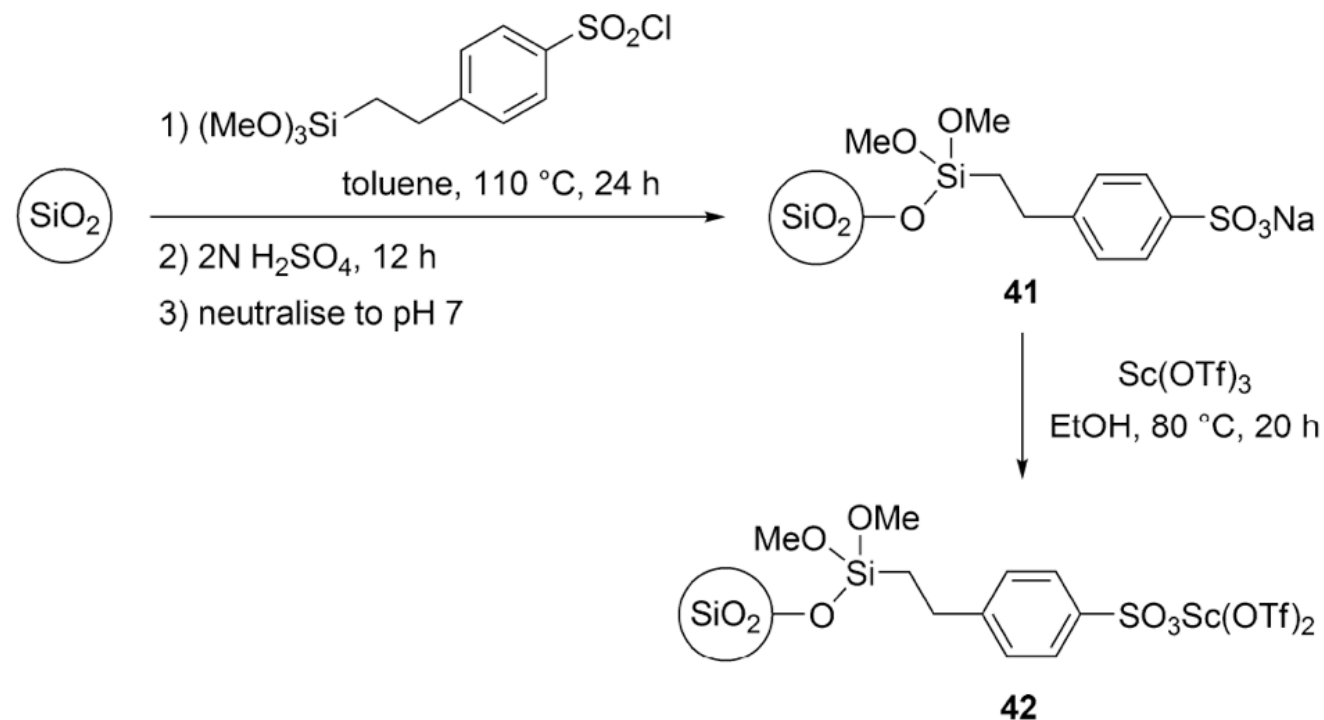
Madeira Lau, R.; van Rantwijk, F.; Seddon, K. R.; Sheldon, R. A., *Org. Lett.* **2000**, 2, 4189–4191

“Biocatalysis in Ionic Liquids”

van Rantwijk, F.; Sheldon, R. A., *Chem. Rev.* **2007**, 107, 2757–2785

Acides de Lewis

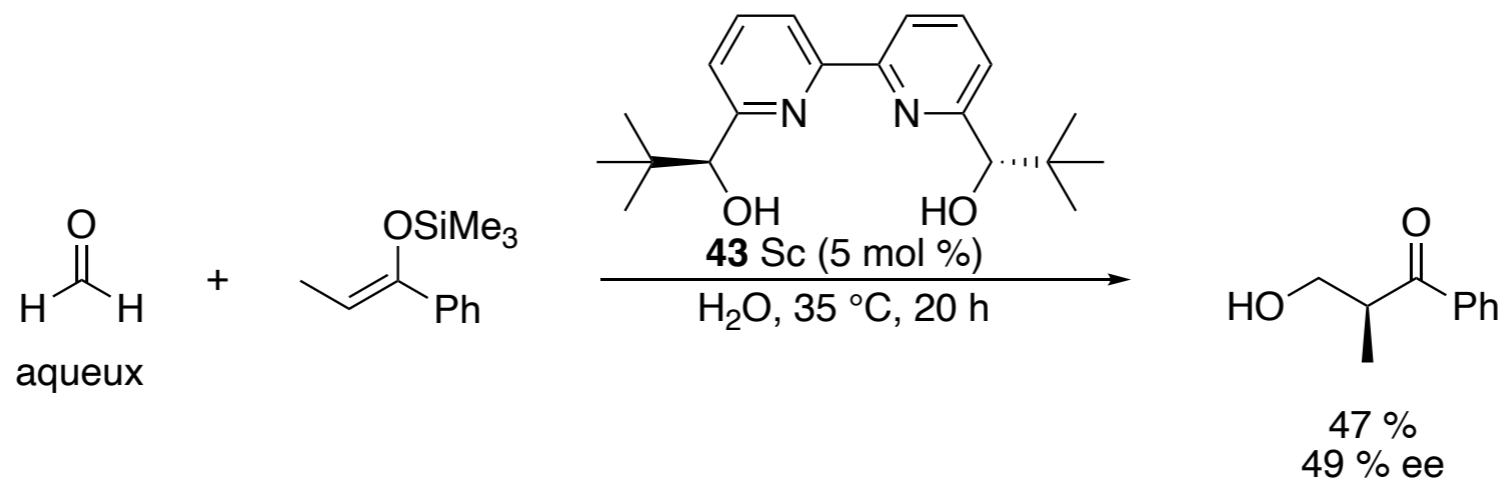
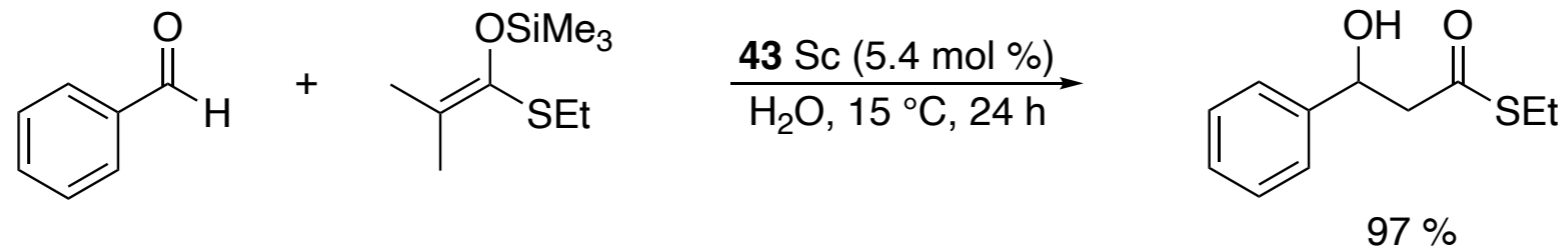
–Liquides ioniques combinés



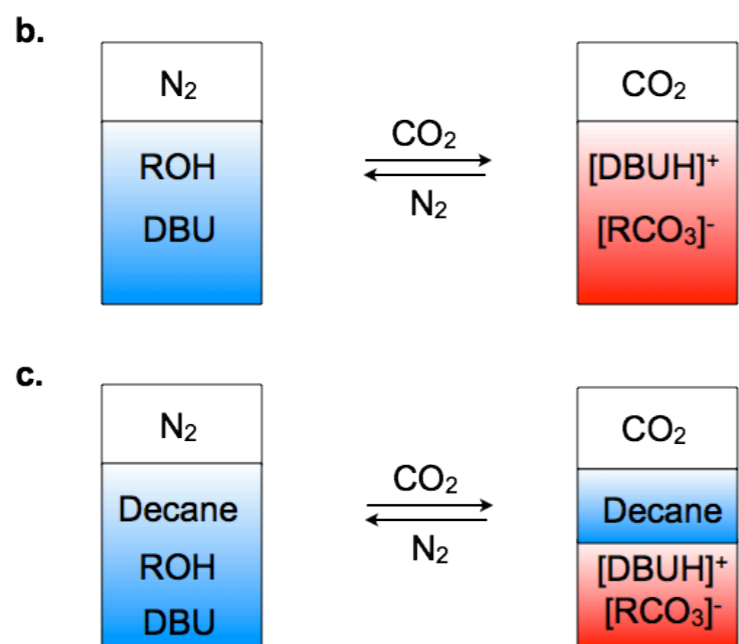
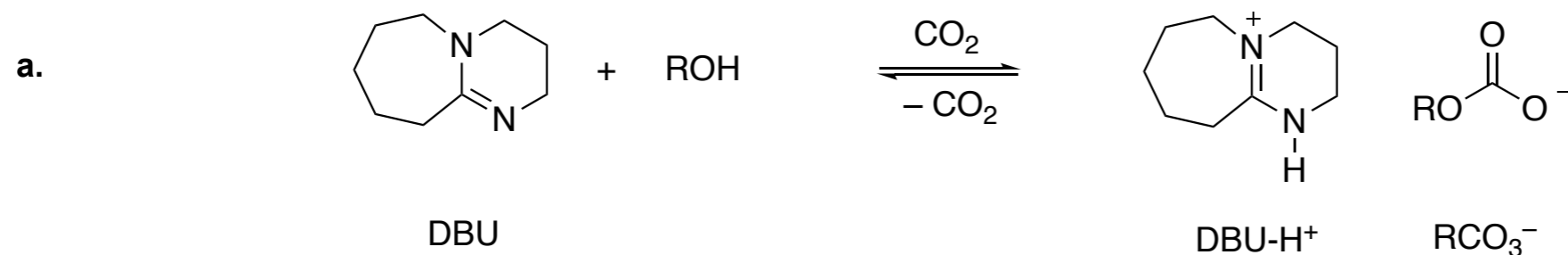
A hydrophobic IL, 1-butyl-3-decylimidazolium hexafluoroantimonate [dbim][SbF₆], was then chosen for particle impregnation, thus creating a lipophilic environment around the particle where reactions can take place. Thus, **42** is added to a solution of [dbim][SbF₆] in ethyl acetate to give, after solvent removal under reduced pressure, a fine powder of SiO₂-Sc-IL (**43**).

Acides de Lewis – Liquides ioniques combinés

- Le rôle du liquide ionique imprégné sur le support solide est de créer un environnement hydrophobe sur la surface du matériau silice, où le catalyseur, lié de manière ionique à l'espaceur, exerce son rôle pour promouvoir la réaction souhaitée.



Solvents intelligents



The “switching” of a switchable solvent.

a. Protonation of DBU (1,8-diazobicyclo-[5, 4, 0]-undec-7-ene) in the presence of an alcohol and carbon dioxide is reversed when CO₂ is removed.

b. Polarity switching in the reaction shown in a, in which CO₂ causes a nonpolar liquid (shown in blue) mixture of hexanol and DBU to change over one hour into a polar, ionic liquid (shown in red); nitrogen gas reverses the process by stripping out CO₂ from the reaction.

c. The different polarity of each liquid under the two conditions is illustrated by the miscibility of decane with the hexanol/DBU mixture under nitrogen, before exposure to CO₂: however, decane separates out once the mixture becomes polar in the presence of CO₂. Again, N₂ reverses the process.