

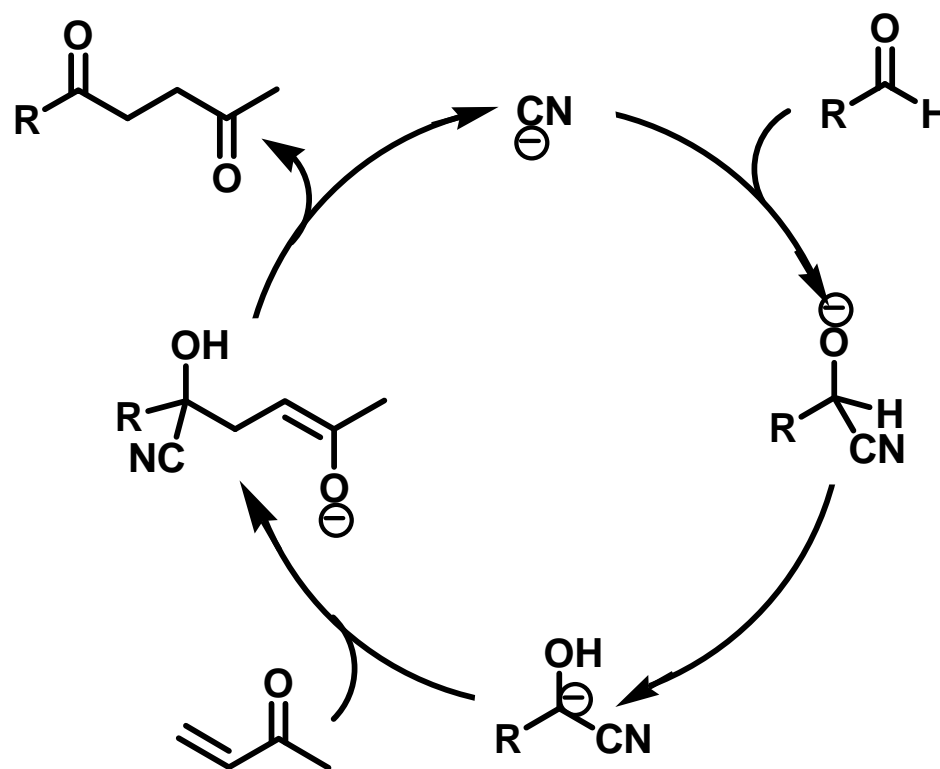
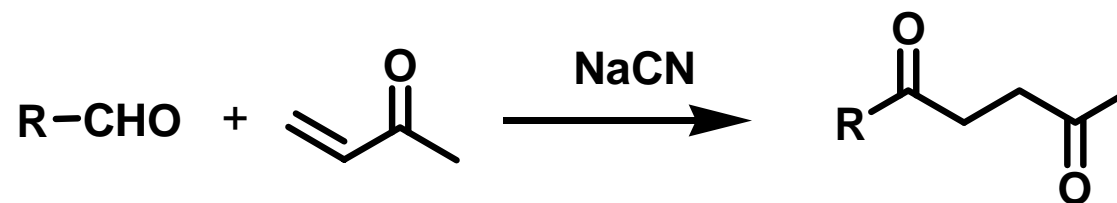
Séminaire bibliographique

22 mars 2007

Réaction de Stetter

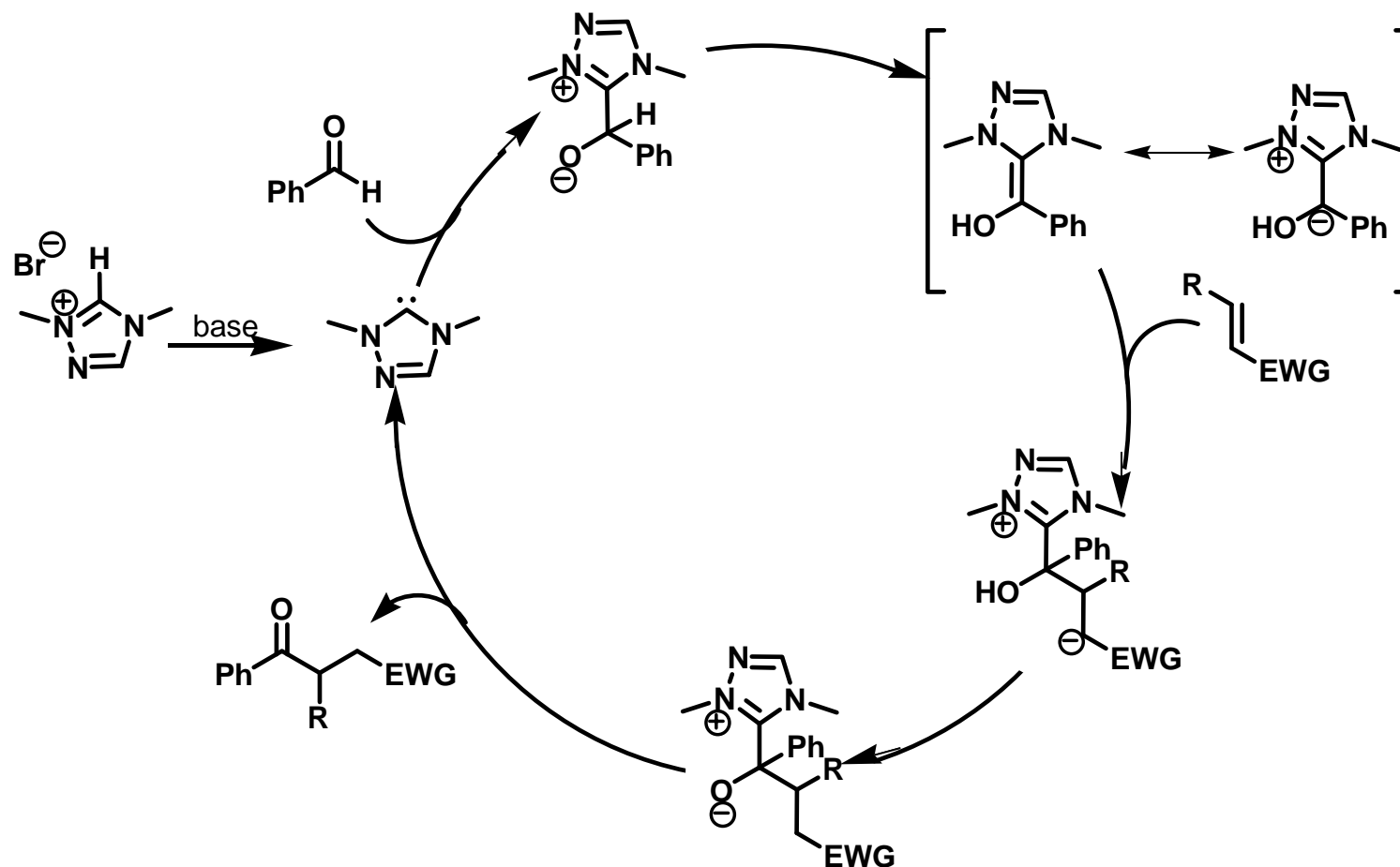
Corinne LAMIT

Synthèse catalytique de composés 1,4-dicarbonylés



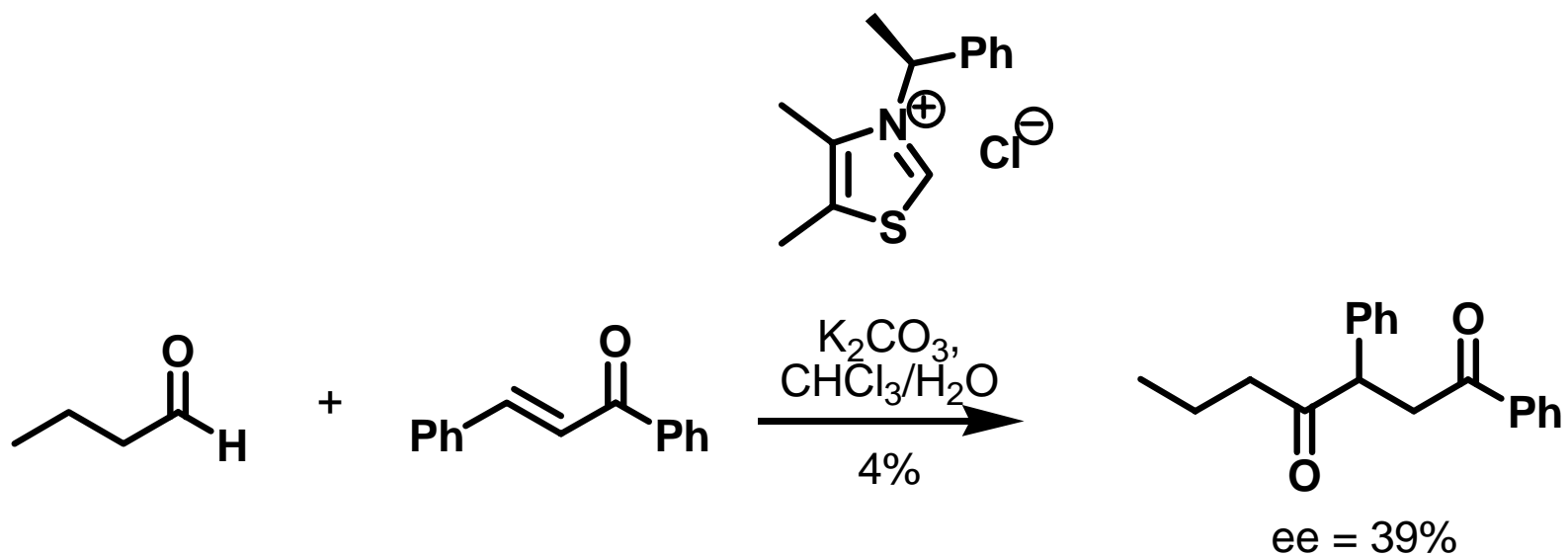
Hermann Stetter *Angew. Chem. Int. Ed.* **1976**, 15(11), 639-647

Synthèse catalytique de composés 1,4-dicarbonylés



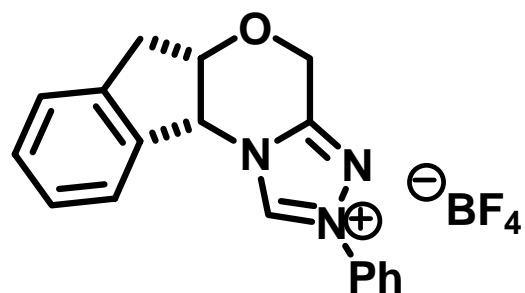
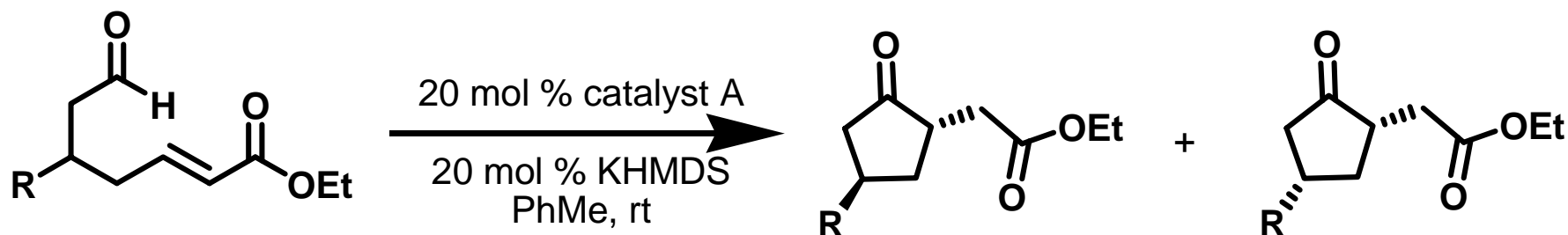
Enders D., Balensiefer T. *Acc. Chem. Res.* **2004**, 37(8), 534-541

Réaction de Stetter intermoléculaire



Enders D., Balensiefer T. *Acc. Chem. Res.* **2004**, 37(8), 534-541

Réaction de Stetter intramoléculaire : Synthèse de cyclopentanones 2,4 disubstituées



Catalyst A

R = Me

98% ee

97% yield

94% ee

Ph

98% ee

96% yield

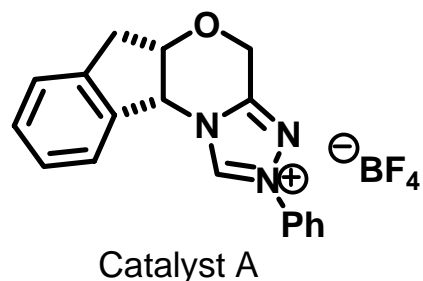
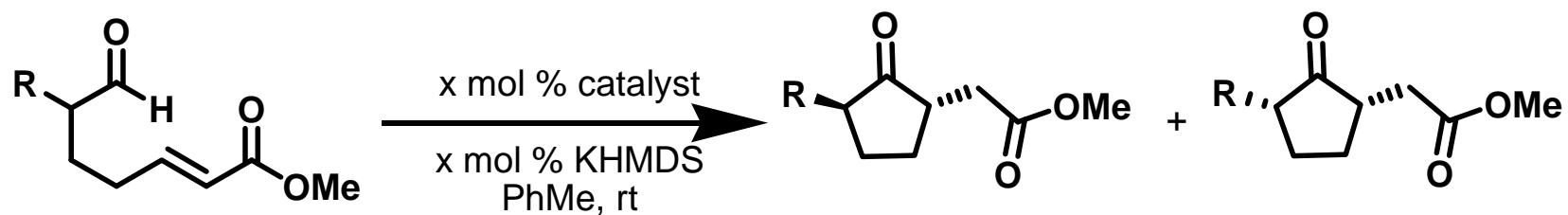
96% ee

trans

50:50

cis

Réaction de Stetter intramoléculaire : Synthèse de cyclopentanones 2,5 disubstituées

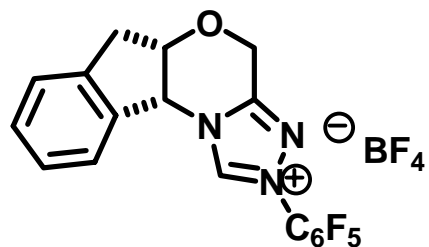
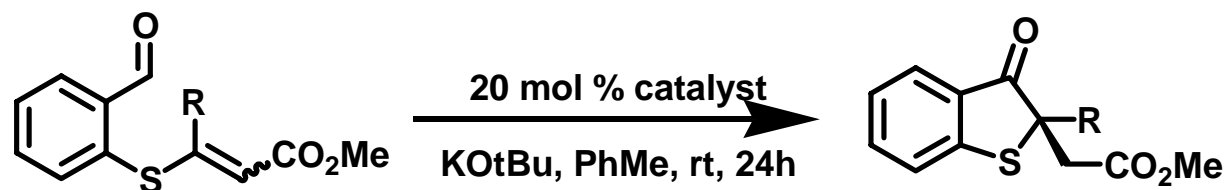


	trans	cis	
R = Me 50 mol % catalyst A	<5% ee	15:85 95% yield	<5% ee



iPr 20 mol % catalyst B	20% ee	3.5:96.5 74% conversion	6% ee
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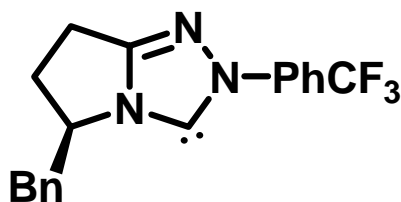
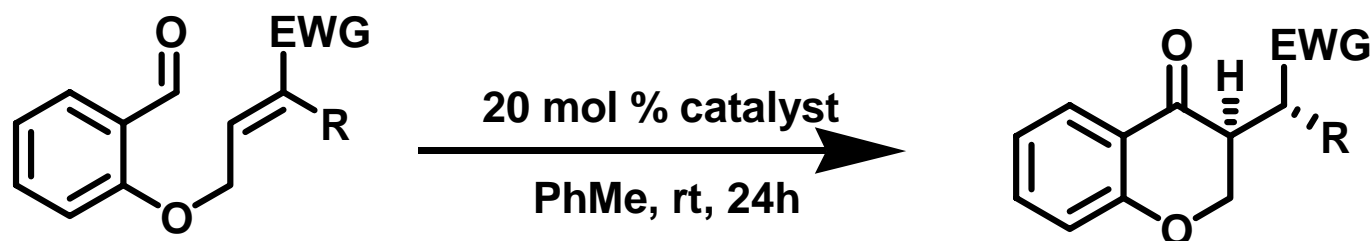
Réaction de Stetter intramoléculaire : Formation de centres quaternaires

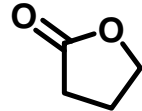
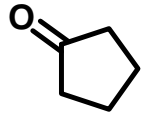


R		yield (%)	ee (%)
Et	E	90%	97%
	Z	89%	86%
Pr	E	83%	98%
	Z	85%	89%
CH ₂ CH ₂ Ph	E	91%	99%
	Z	92%	84%
CO ₂ Me	Z	85%	90%

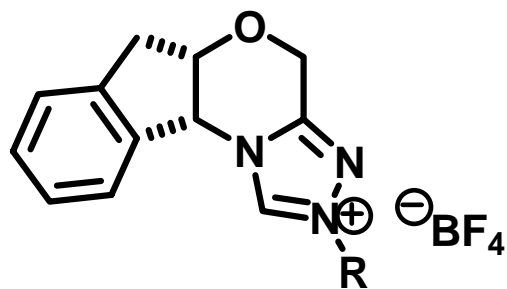
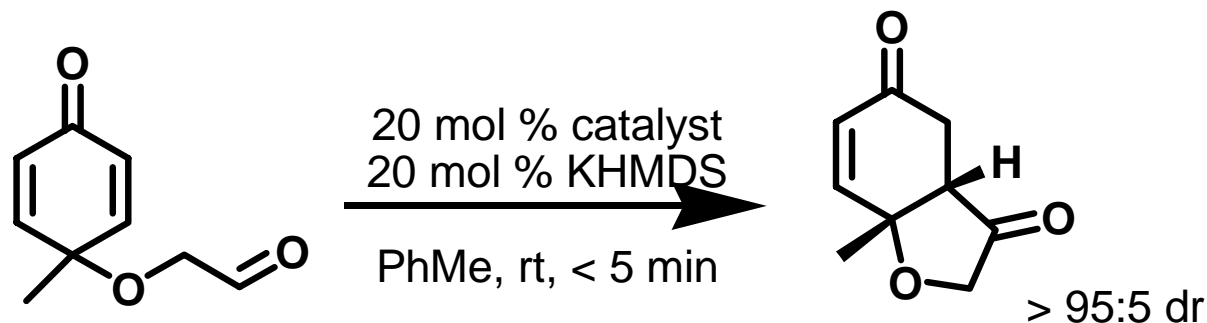
Moore J.L., Kerr M.S., Rovis T. *Tetrahedron* **2006**, 62, 11477-11482

Réaction de Stetter intramoléculaire :



R	EWG	yield (%)	ee (%)	dr (%)
Me	CO ₂ Et	94	95	30:1
Et	CO ₂ Et	95	92	35:1
n-Bu	CO ₂ Et	53	94	12:1
Bn	CO ₂ Et	80	84	20:1
CH ₂ CHCH ₂	CO ₂ Me	95	83	13:1
		95	94	10:1
		80	95	18:1
Me	COMe	85	55	10:1

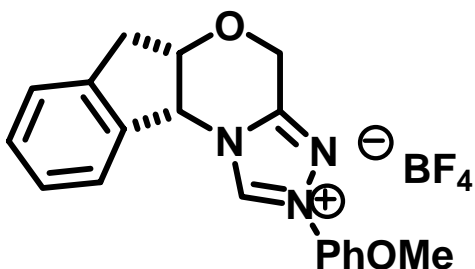
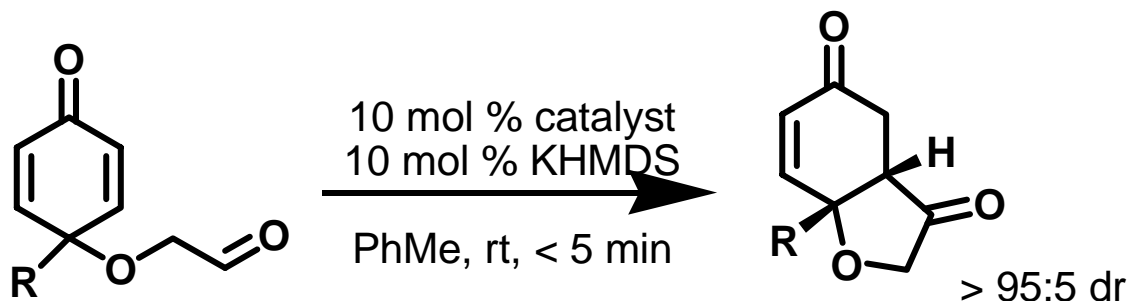
Réaction de Stetter intramoléculaire : Synthèse d'hydrobenzofuranones



R	yield (%)	ee (%)
4-OMePh	90	88
Ph	75	80
C ₆ F ₅	92	31

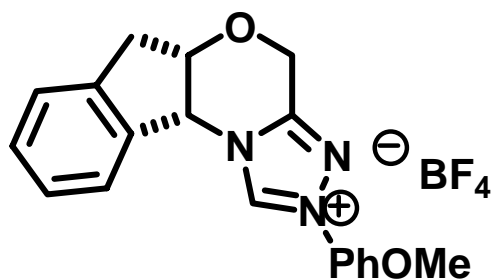
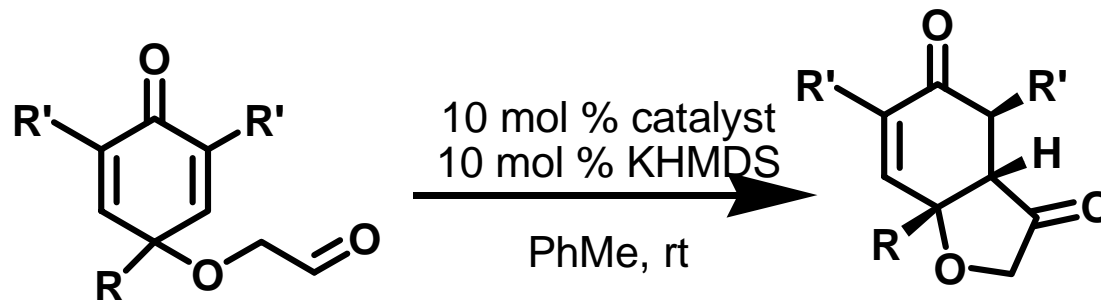
Liu Q., Rovis T. *J. Am. Chem. Soc.* **2006**, 128(8), 2552-2553

Réaction de Stetter intramoléculaire : Synthèse d'hydrobenzofuranones



R	yield (%)	ee (%)
Me	90	92
Et	86	94
iPr	87	94
iBu	86	94
Ph	87	88
4-BrPh	78	85
CH ₂ OAc	86	83
CH ₂ CH ₂ OMe	86	82
CH ₂ CH ₂ CO ₂ Me	94	87

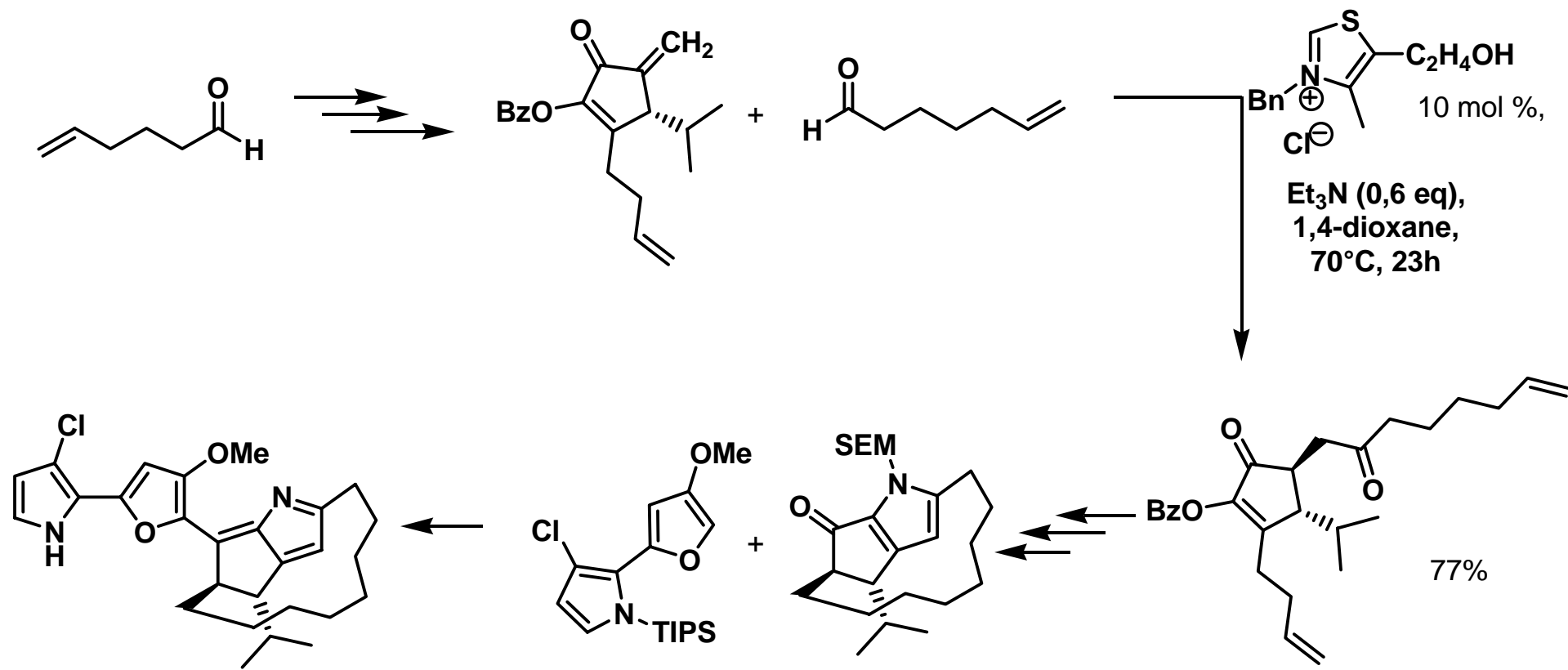
Réaction de Stetter intramoléculaire : Synthèse d'hydrobenzofuranones



R	R'	yield (%)	ee (%)
Me	Me	86	>99
Me	MeO	71	99
Me	^t Bu	80	>99
^t Bu	^t Bu	62	>99

Liu Q., Rovis T. *J. Am. Chem. Soc.* **2006**, 128(8), 2552-2553

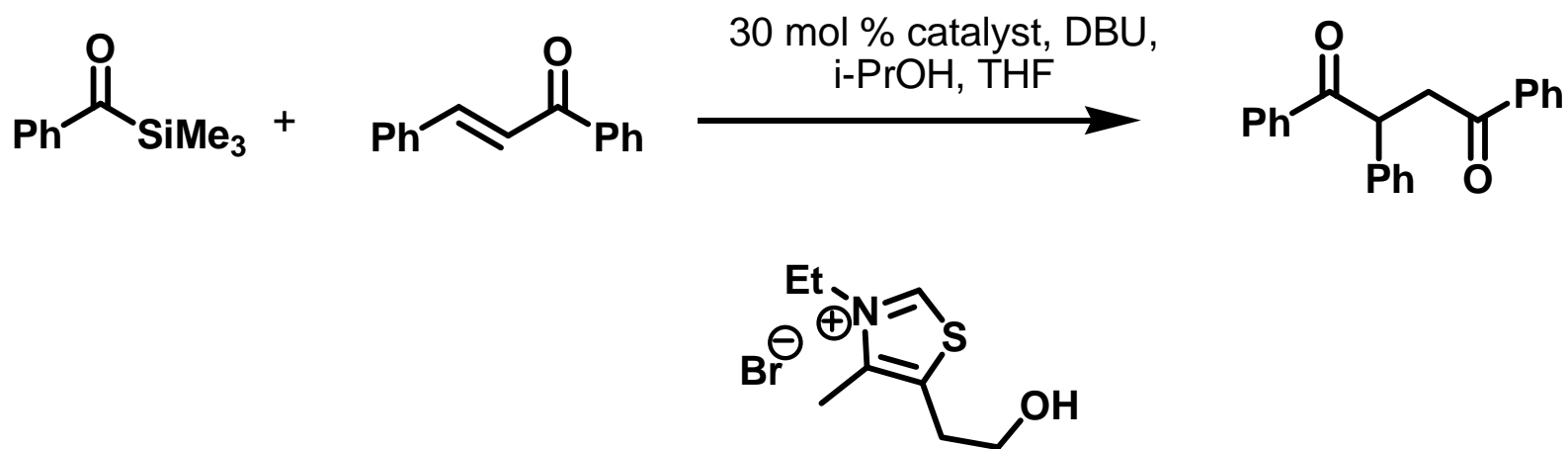
Synthèse de la Roséophilin



(22R,23R)-roseophilin,

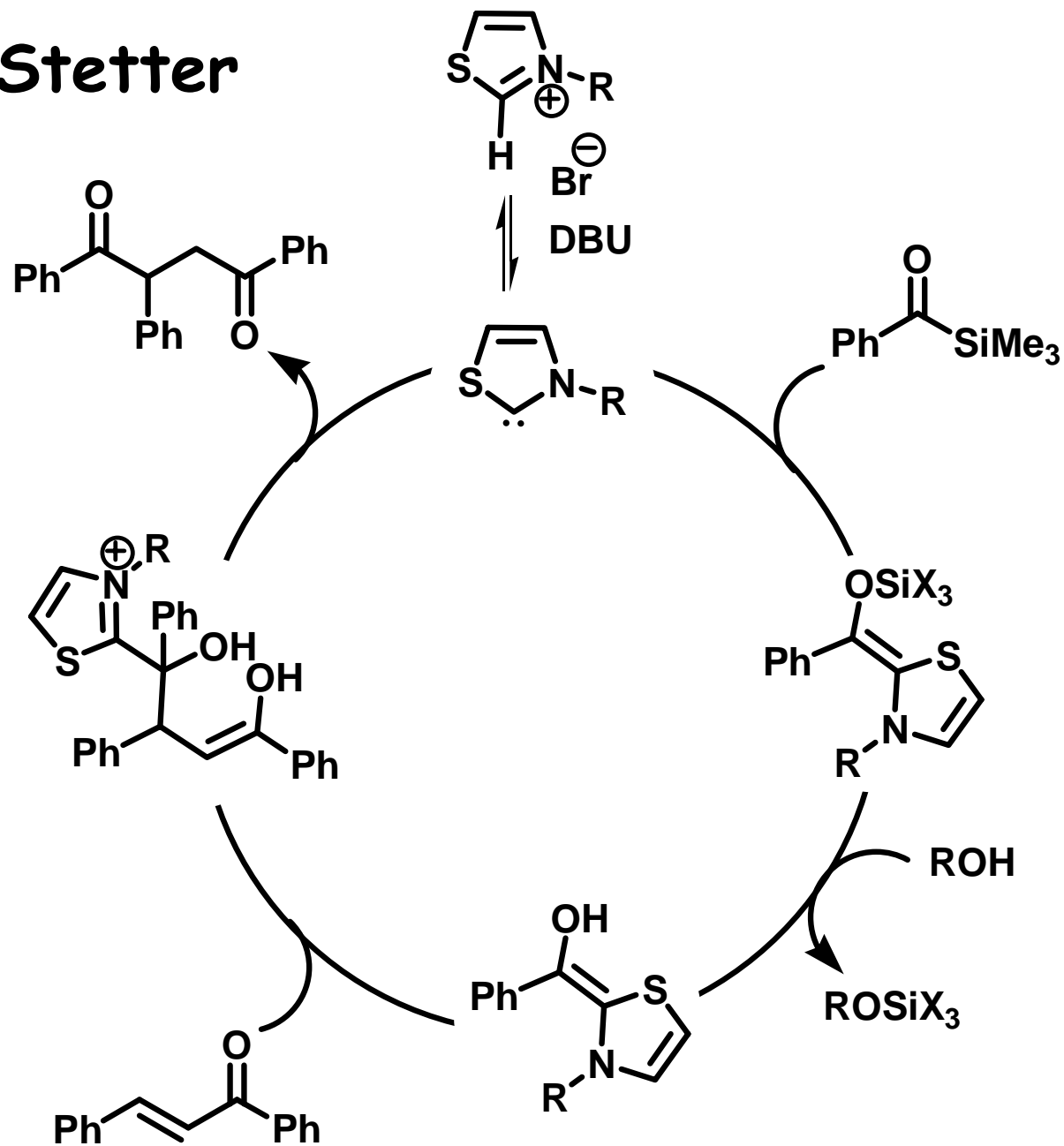
15 étapes, 7%

Réaction de sila-Stetter



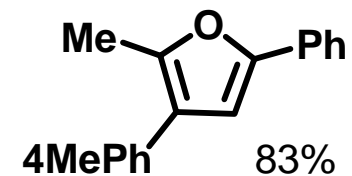
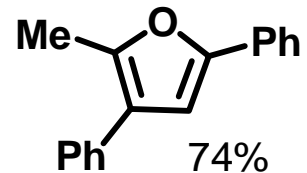
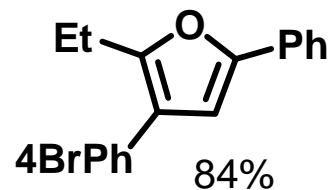
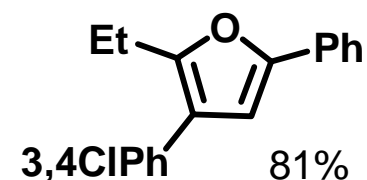
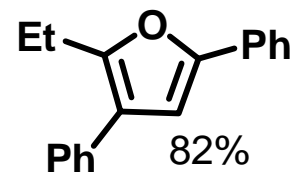
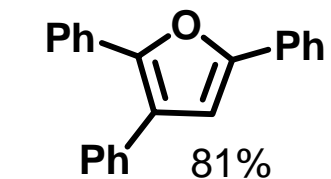
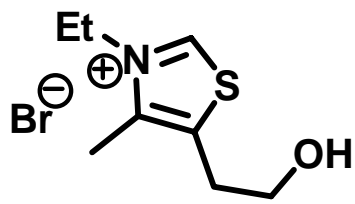
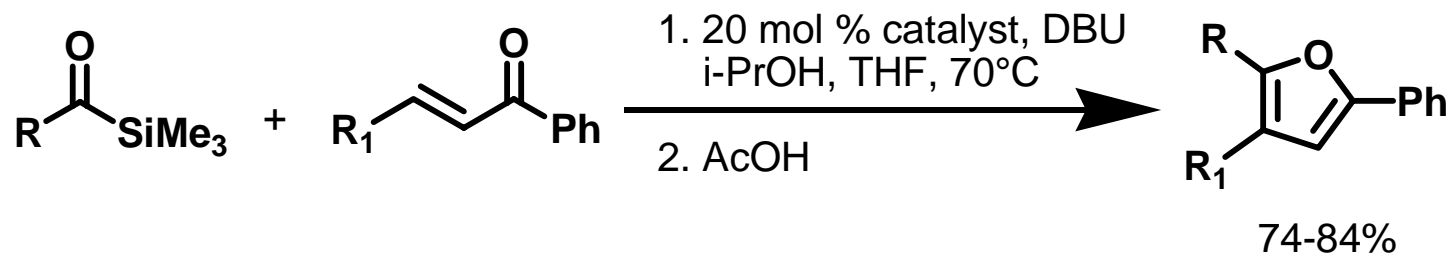
Mattson A.E., Bharadwaj A.R., Scheidt K.A. *J. Am. Chem. Soc.* **2004**, 126(8), 2314-2315

Réaction de sila-Stetter

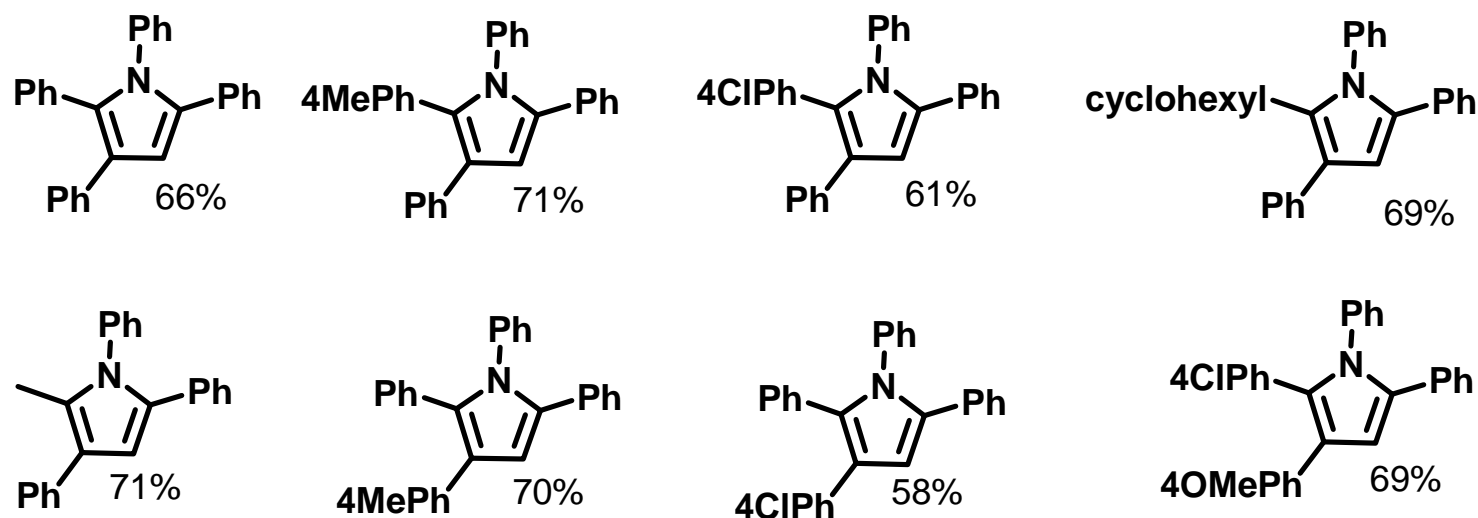
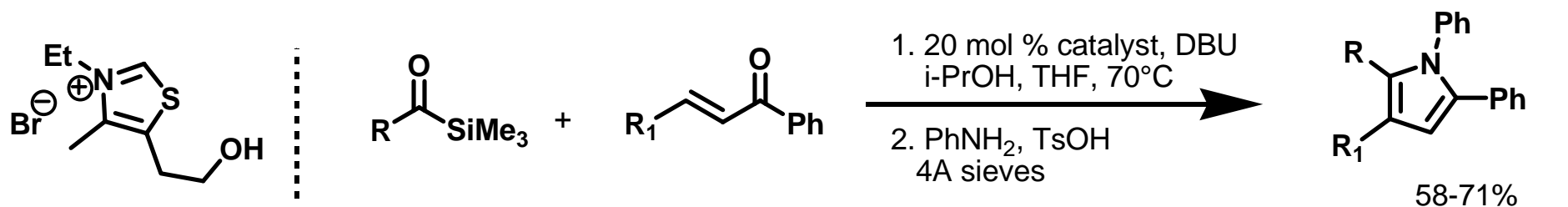


Réaction de sila-Stetter :

Synthèse de furanes



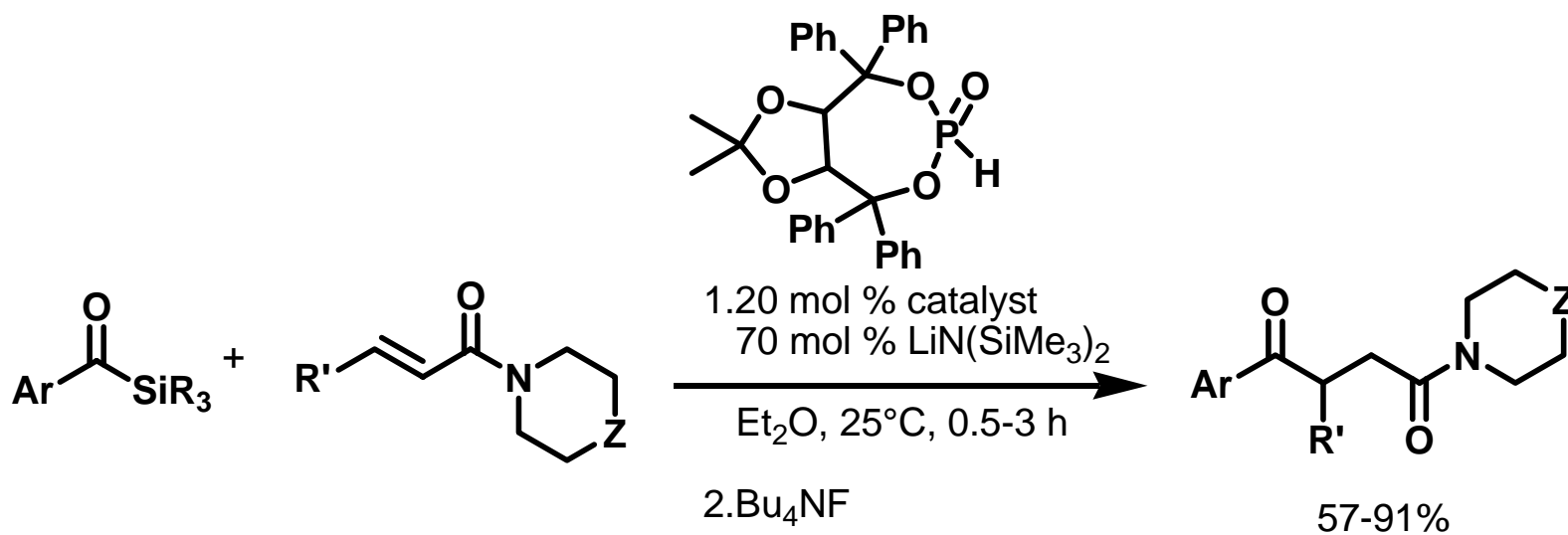
Réaction de sila-Stetter : Synthèse de pyrroles



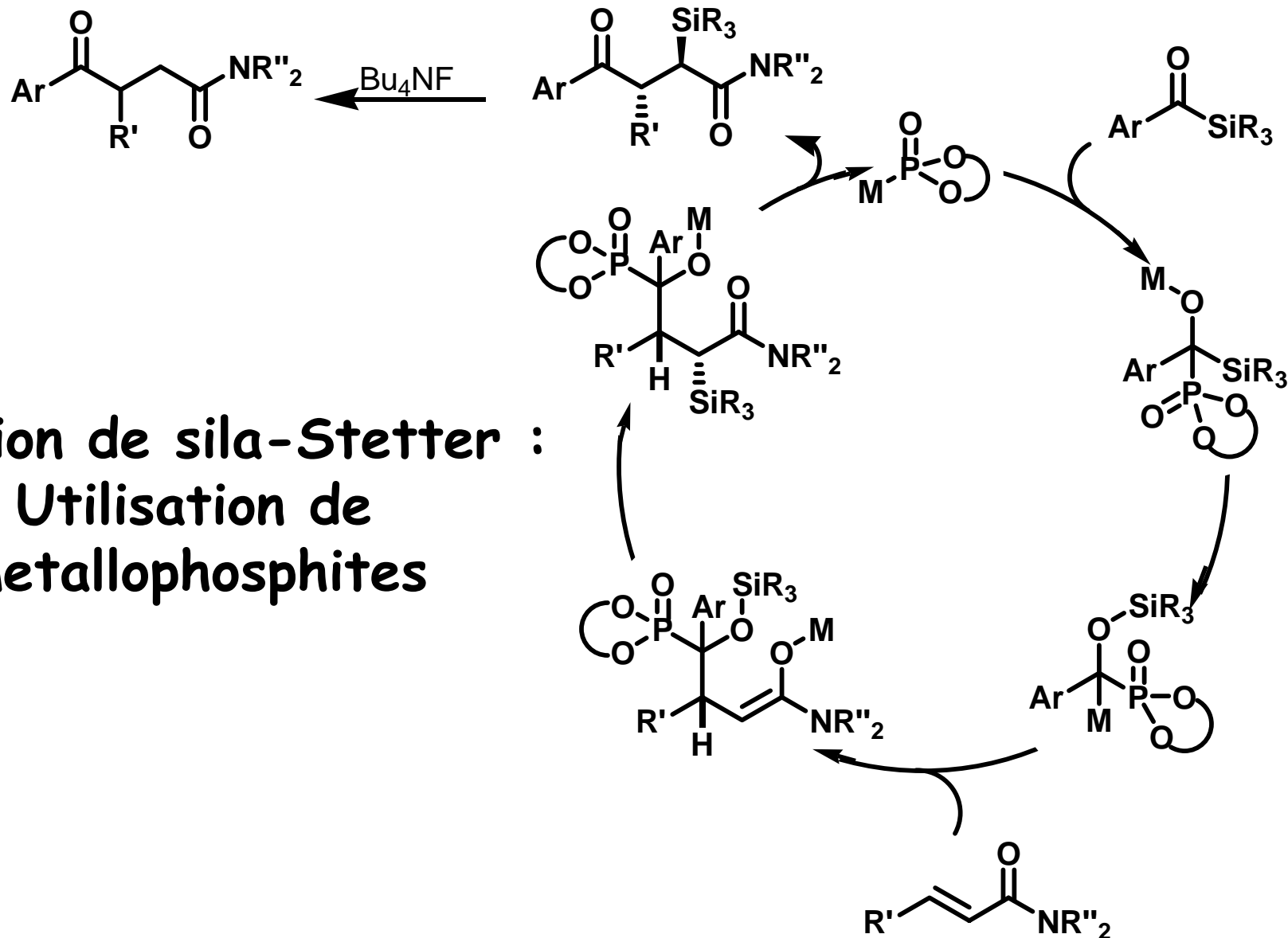
Mattson A.E., Bharadwaj A.R., Scheidt K.A. *J. Org. Chem.* **2006**, 71(15), 5715-5724

Bharadwaj A.R., Scheidt K.A. *Org. Lett.* 2004, 6(14), 2465-2468

Réaction de sila-Stetter : Utilisation de metallophosphites



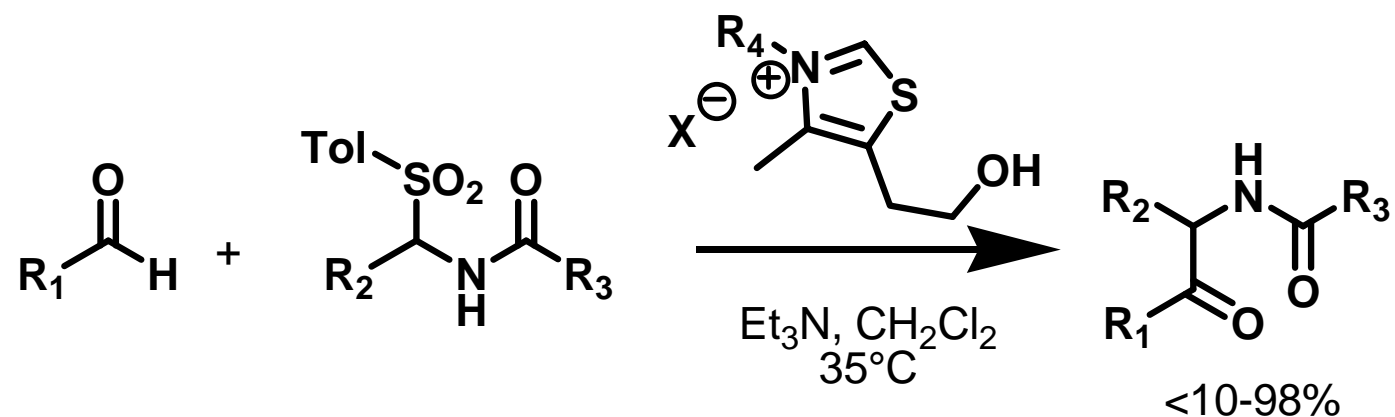
Nahm M.R., Linghu X., Potnick J.R., Yates C.M., White P.S., Johnson J. S.
Angew. Chem. Int. Ed. **2005**, 44, 2377-2379



Réaction de sila-Stetter :
Utilisation de
metallophosphites

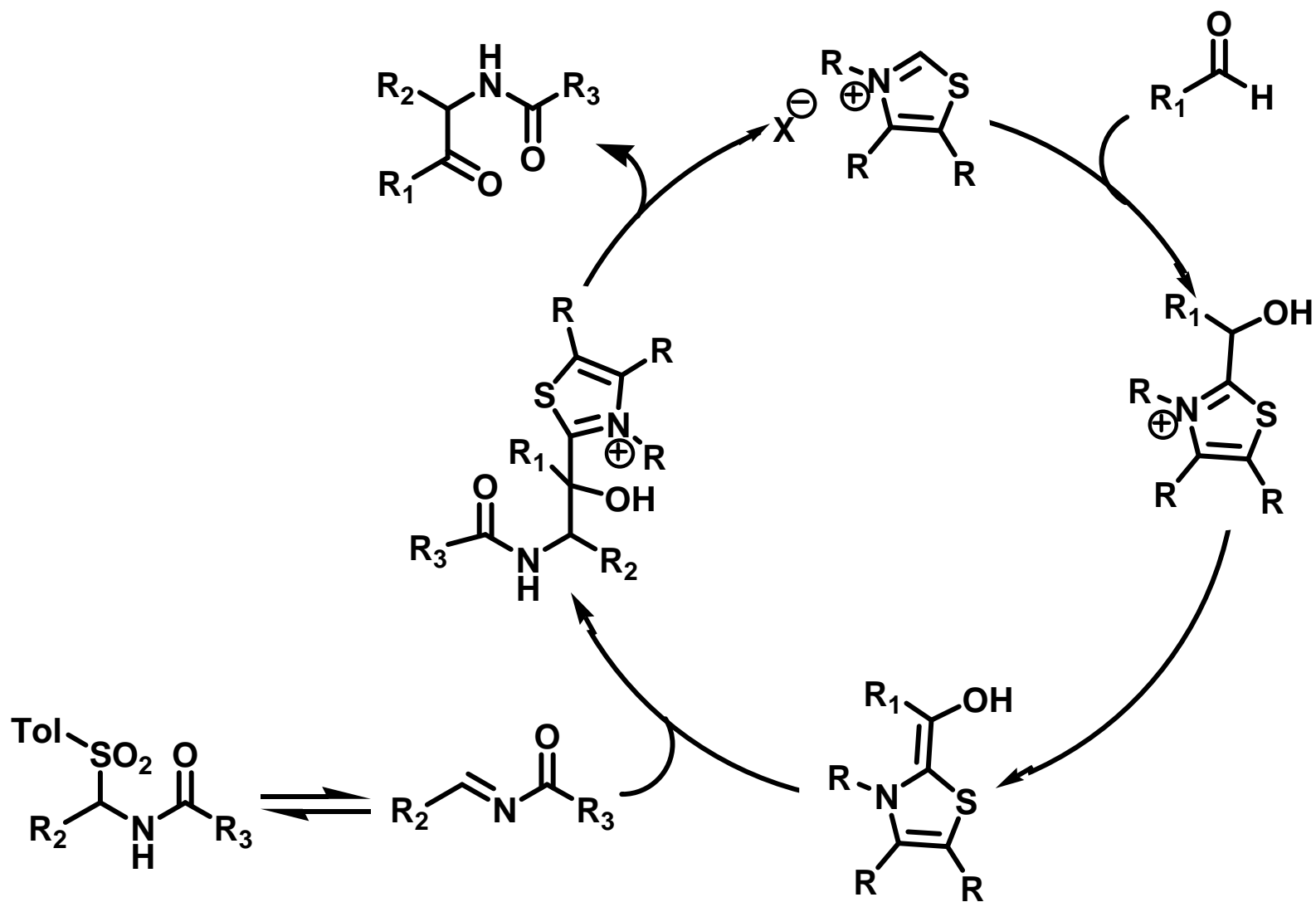
Nahm M.R., Linghu X., Potnick J.R., Yates C.M., White P.S., Johnson J. S. *Angew. Chem. Int. Ed.* **2005**, 44, 2377-2379

Synthèse d' α -amidocétones



Murry J.A., Frantz D.E., Soheili A., Tillyer R., Grabowski E.J.J., Reider P.J.
J. Am. Chem. Soc. **2001**, 123(39), 9696-9697

Synthèse d' α -amidocétones



Murry J.A., Frantz D.E., Soheili A., Tillyer R., Grabowski E.J.J., Reider P.J.
J. Am. Chem. Soc. **2001**, 123(39), 9696-9697