Regio- and Stereoselective Synthesis of Cyclopentenones: Intermolecular Pseudo-Pauson–Khand Cyclization

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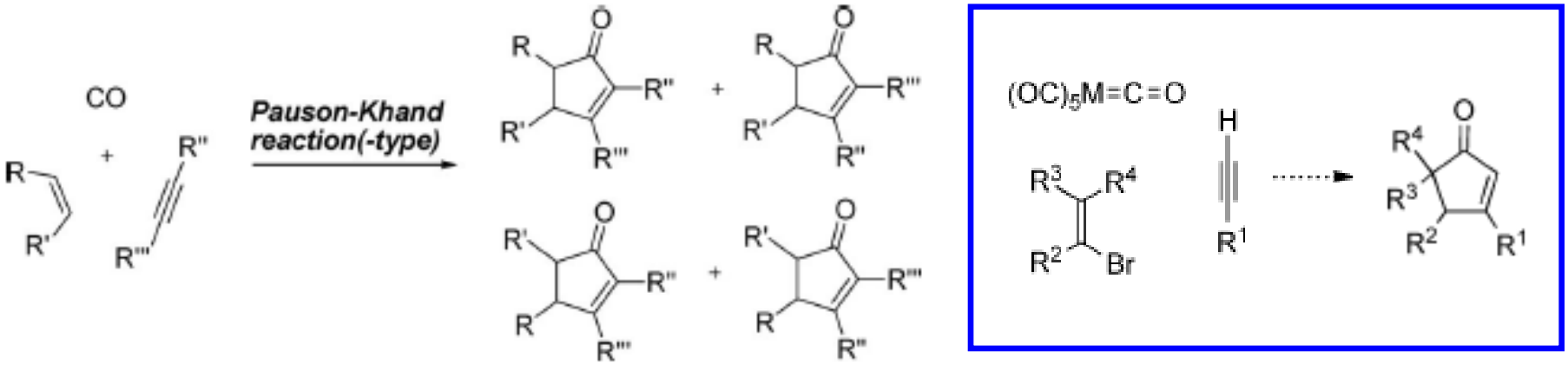
Dmitry VALYAEV RCC 24/01/2012

Réactions du type Pauson–Khand



Synthèse de cyclopentanones avec haute économie d'atomes

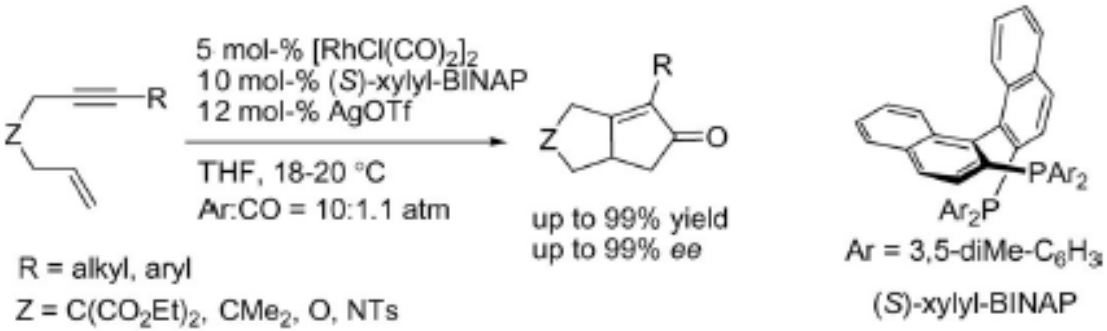
Bon rendement et contrôle de regiosélectivité de partie alcyne

Tolérance au présence de nombreux groups fonctionnelles (OH, OR, SR, CN, NR_2, amide, ester *etc.*)

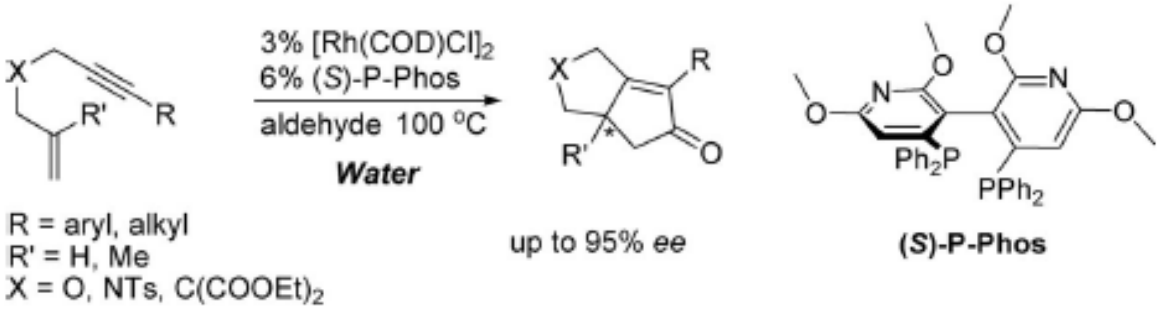
Grande variété de catalyseurs (complexes de Co, Rh, Ir, Ru, Ti, Ni, Pd) et mécanismes réactionnelles

Plusieurs sources de CO possible (CO gas, aldéhydes, esters)

Réaction de Pauson–Khand en version asymétrique



J. Org. Chem. **2008**, *73*, 7985

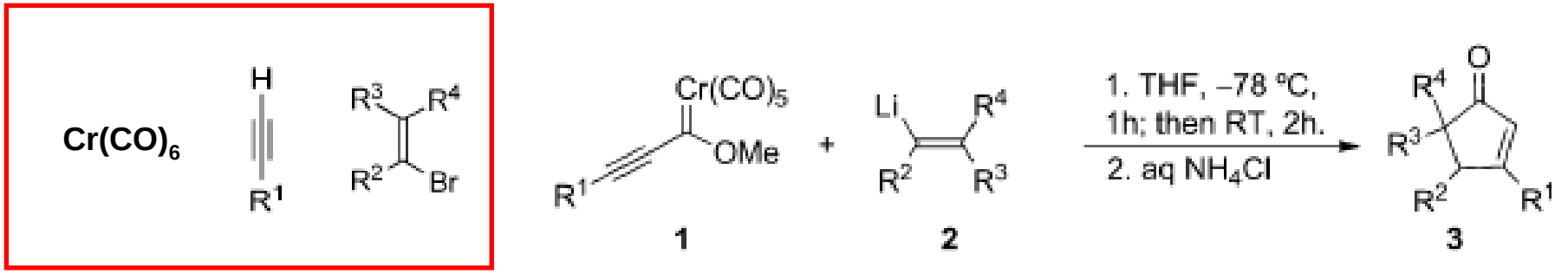


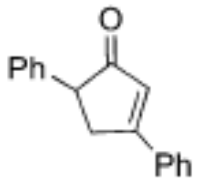
Chem. Eur. J. **2005**, *11*, 3872

X	R	% Yield	% *ee*
H	TMS	99	97
OMe	TMS	99	>99
F	TMS	99	78

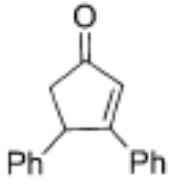
Angew. Chem. Int. Ed. **2007**, *46*, 5020

Formation de cyclopentanones à partir de complexes carbène de chrome

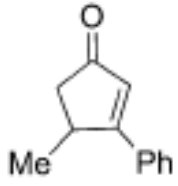




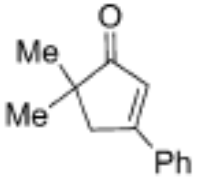
3a: 54%



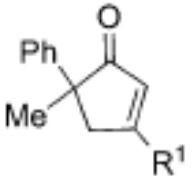
3b: 70% (X-ray)



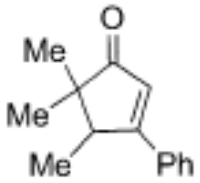
3c: 73%



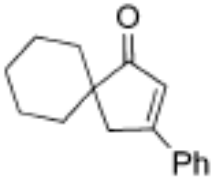
3d: 78%



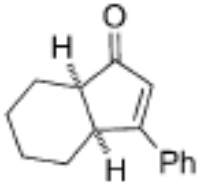
3e: R^1 = Ph, 72%
3f: R^1 = PCP, 62%



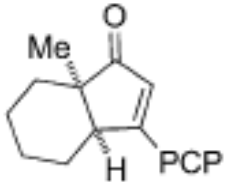
3g: 85%



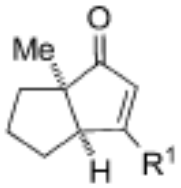
3h: 61%



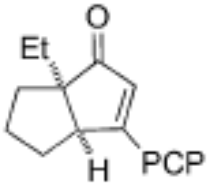
3i: 72%



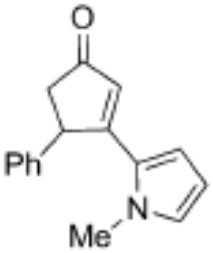
3j: 58%



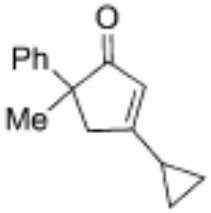
3k: R^1 = Ph, 65%
3l: R^1 = PCP, 68%
3m: R^1 = PTFP, 71%
3n: R^1 = PMP, 58%



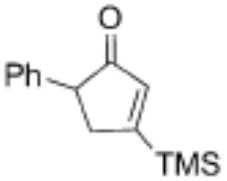
3o: 52%



3p: 75%

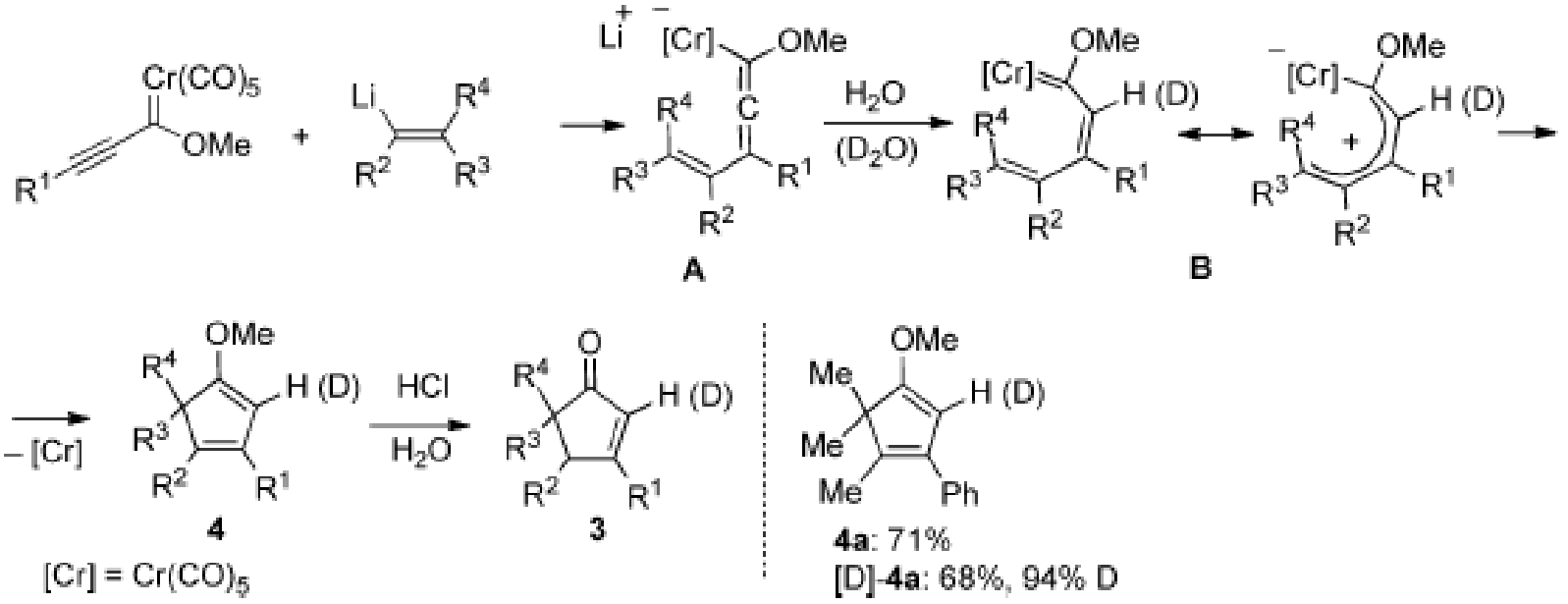


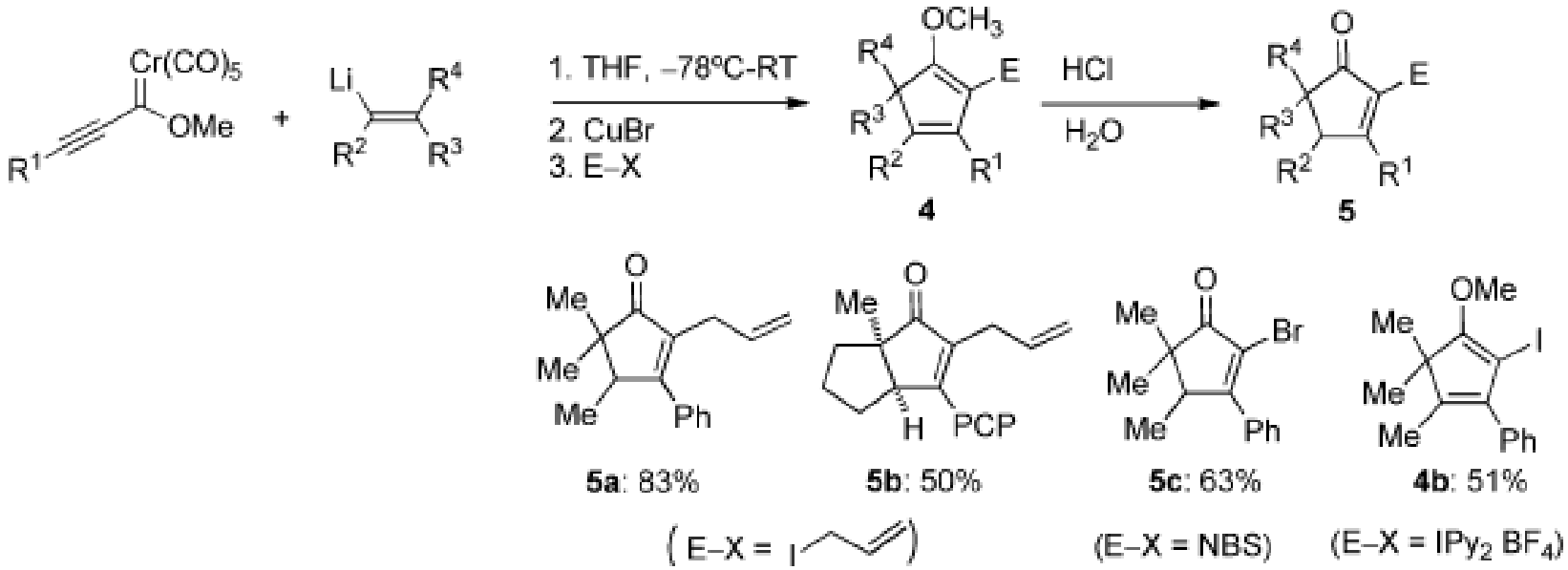
3q: 68%



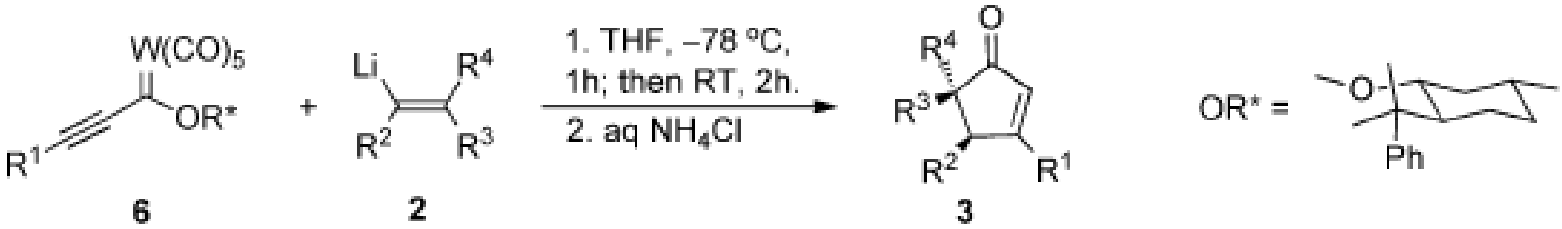
3r: 50%

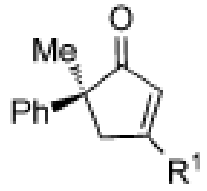
Mécanisme proposée de réaction *pseudo*-Pauson-Khand



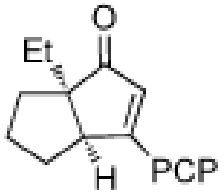


Réaction de *pseudo*-Pauson-Khand en version asymétrique

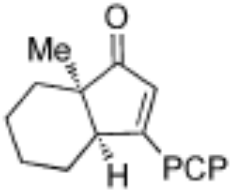




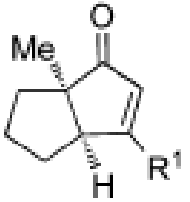
(+)-**3e**: R^1 = Ph, 48%, 92% *ee*
(+)-**3f**: R^1 = PCP, 55%, 87% *ee*



(–)-**3o**: 70%, 96% *ee*

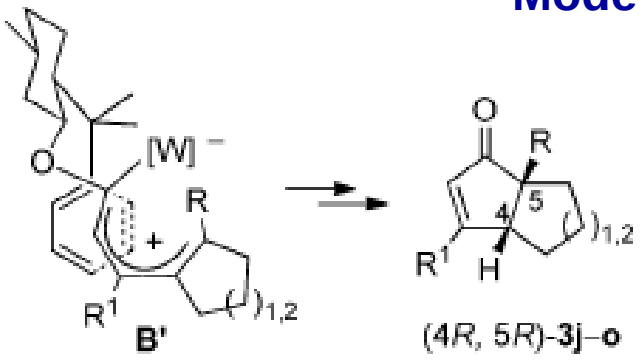


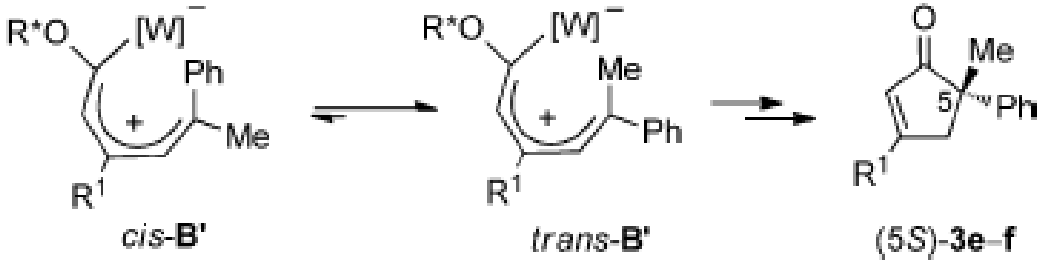
(+)-**3j**: 45%, 94% *ee*



(–)-**3k**: R^1 = Ph, 61%, 95% *ee*
(–)-**3l**: R^1 = PCP, 62%, > 99% *ee*
(+)-**3m**: R^1 = PTFP, 52%, 96% *ee*
(–)-**3n**: R^1 = PMP, 45%, 80% *ee*

Model d'induction proposée

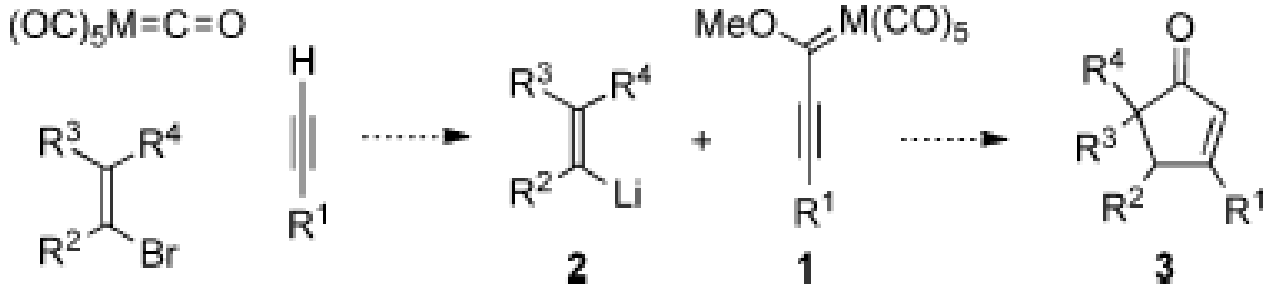




Effet de π-stacking

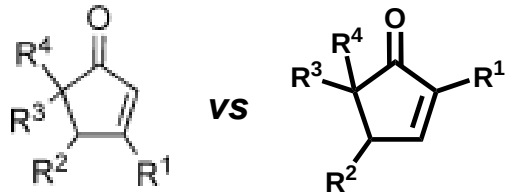
***E*- ou *Z*-vinyllithuim donnent la même résultat**

Conclusion

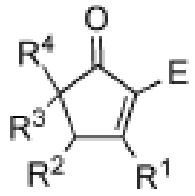


Vinyllithiums de type différents peuvent être appliquées (*Z*-, *E*- ou mélange) avec la contrôle complète de regiosélectivité de fragment alcène

Regiosélectivité de partie alcyne opposite au produits de réaction de Pauson-Khand classique pour les alcynes terminaux (substitution en position 3 *vs* position 2)



Installation facile des électrophiles dont les halogens en position stratégique 2 pour post-functionalisation



Synthèse énantiosélective de cyclopentanones possédants un centre quaternaire avec toute les substutuents carbonées