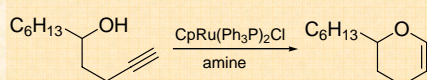


A major research area in organic chemistry is the development of new metal-catalyzed cyclizations. The facility of generation of Ru-vinylidene complexes by direct reaction with terminal alkynes makes these species an economical intermediates for evaluating their catalytic transformations into cyclic compounds.¹ Here we report an easy and efficient cycloisomerization of α, ω -alkynols into cyclic vinyl ethers under basic conditions.

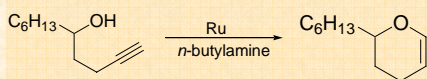
OPTIMIZATION

Solvent Optimization



Solvent	Time (h)	T (°C)	Yield (%)
<i>n</i> -butylamine	12	90	35
<i>n</i> -butylamine	6	130	60
isopropylamine	24	90	25
di-isopropylamine	24	90	S.M.
tri-ethylamine	24	90	S.M.
pyrrolidine	72	90	S.M.
pyridine	24	130	32
bi-pyridine	24	90	S.M.

For solvent optimization, *n*-butylamine and pyridine gave the best results.

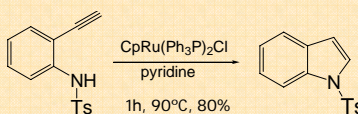
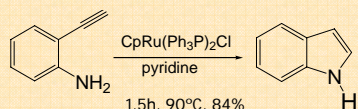


10% Catalyst	Time (h)	T (°C)	Yield (%)
CpRu(Ph ₃ P) ₂ Cl	6	130	60
Cp [*] Ru(CH ₃ CN) ₃ PF ₆	24	130	S.M.
CpRu(dppm)Cl	72	130	S.M.

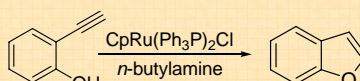
Of the three catalysts, CpRu(Ph₃P)₂Cl is the only one that worked.

So the best conditions to this kind of reactions are those with *n*-butylamine and pyridine as solvents and CpRu(Ph₃P)₂Cl as catalyst!

Indole series

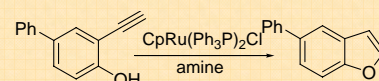


CYCLOISOMERIZATIONS



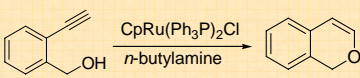
Time (h)	T (°C)	Yield (%)
72	60	20
72	90	35
72	130	45

Here it is shown that temperature plays an important role.

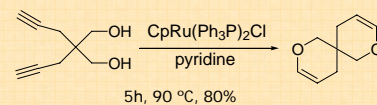


Solvent	Time (h)	T (°C)	Yield (%)
<i>n</i> -butylamine	4	130	50
	48	130	50
pyridine	2	90	84
	1,5	130	84

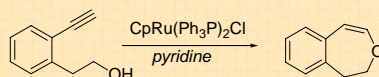
With pyridine as a solvent, the yield is higher and shorter times are needed!



Time (h)	T (°C)	Yield (%)
62	60	75
6	90	90
3	130	90



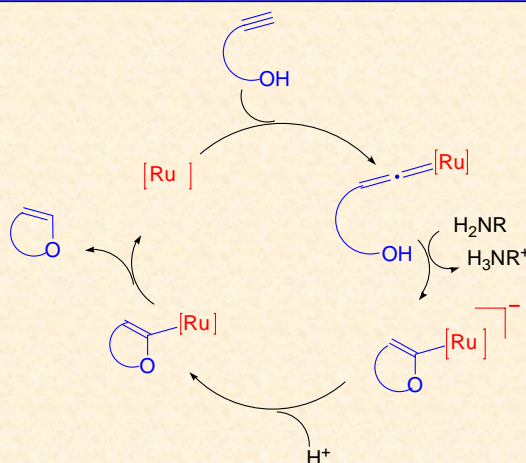
Double cycloisomerization to spiroheterocycles worked!



6 h, 130 °C, 60%

First time 7-membered ring synthesized!

POSSIBLE CATALYTIC CYCLE



Acknowledgements. This work was supported by the Ministerio de Educación y Ciencia (Spain) and the European Regional Development Found (CTQ2005-08613) and by the Xunta de Galicia (PGIDT00PXI20908). A.V.-F. Thanks the Xunta de Galicia for a grant and C.G.-R. And J.A.V. thank the M.E.C. for a predoctoral grant (BES-2003-0939) and a Ramón y Cajal research contract, respectively