Os Better than Ru Catalysts in Synthesis of Benzoxepines via 7-*endo* Heterocyclization

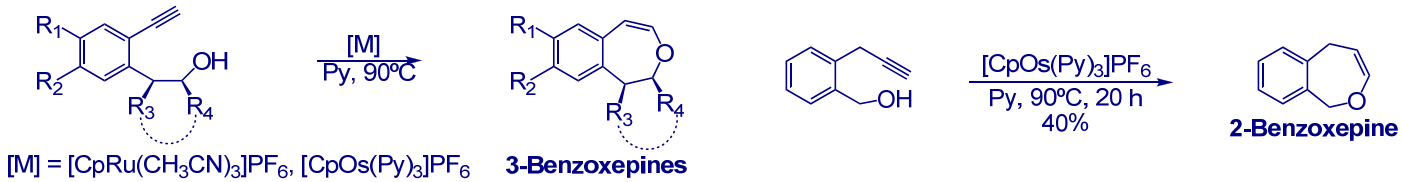
Carlos Saá,[a]*Alejandro Varela-Fernández,[a] C. García-Yebra,[b] Jesús A. Varela,[a] Miguel A. Esteruelas[b]

[a] *Dpt. Química Orgánica, Facultad de Química, Universidad de Santiago de Compostela, 15782 Santiago de Compostela, Spain.*

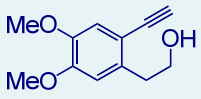
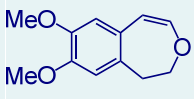
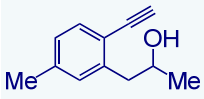
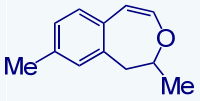
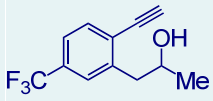
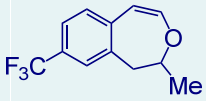
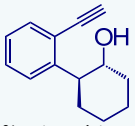
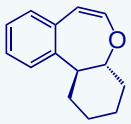
[b] *Dpt. Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain*

e-mail : carlos.saa@usc.es

Regioselective 7-*endo* Heterocyclization of Aromatic Alkynols to Benzoxepines via Catalytic Ru- and Os-Vinylidenes



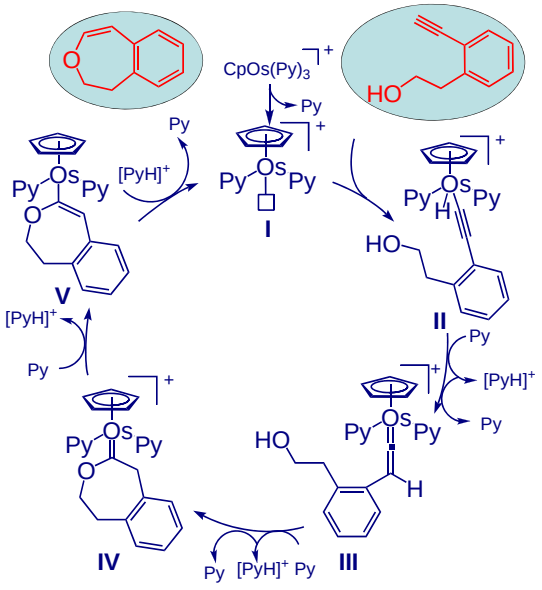
[M] = $[CpRu(CH_3CN)_3]PF_6$, $[CpOs(Py)_3]PF_6$ **3-Benzoxepines**

Entry	Aromatic Alkynols	3-Benzoxepines	[Ru][a] %	[Ru][a] h	[Os][b] %	[Os][b] h
1			28	5	60	0.5
2			31	1	68	1
3			29	1	63	0.5
4			32	4	56	1.5

[a] *Typical conditions*: 1 0% $[CpRu(CH_3CN)_3]PF_6$, 0.15M, Py, 90°C. [b]10% $[CpOs(py)_3]PF_6$, 0.15M, Py, 90°C.

Proposed Catalytic Cycle

After dissociation of py from the cationic Os(II) precatalysts, cationic unsaturated 16 e⁻ Os(II) could be formed acting as the catalytic species **I**. Formation of Os vinylidenes could be the key process of the catalytic cycle, which starts with the easy oxidative addition of the terminal alkyne to **I** to give the cationic hydride-alkynyl-Os(IV) species **II** followed by removal of the hydride as a proton by the pyridine and reprotonation at the C_β would afford the Os vinylidene **III**.[1] Then, the α electrophilic center of the vinylidene undergoes an intramolecular attack by the alcohol (7-*endo* heterocyclization)[2] to give the 2-oxocycloalkylidene Os intermediate **IV**, which in the presence of pyridine would evolve to the vinylic Os species **V**. Finally, protonation of the heterocyclic ligand would liberate the 3-benzoxepine.



Acknowledgements. We thank the MICINN (Spain) (CTQ2008-06557), Consolider Ingenio 2010 (CSD2007-00006) and the Xunta de Galicia (2007/XA084 and INCITE08PXIB209024PR). A. V.-F. thanks the USC for a predoctoral contract; C. G.-Y. thanks the Spanish MICINN and the University of Zaragoza for funding through the "Ramón y Cajal" program.

References: [1] Esteruelas, M. A., López, A. M., Oliván, M. *Coord. Chem. Rev.* **2007**, *22*, 2472.

[2] Alcazar, E., Pletcher, J. M., McDonald, F. E. *Org. Lett.* **2004**, *6*, 3877.