Rhodium-Catalyzed C–H Functionalization and Seven-membered Ring Formation

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Dr. Hong Mei

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Communication

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Straightforward Assembly of Benzoxepines by Means of a Rhodium(III)-Catalyzed C–H Functionalization of *o*-Vinylphenols

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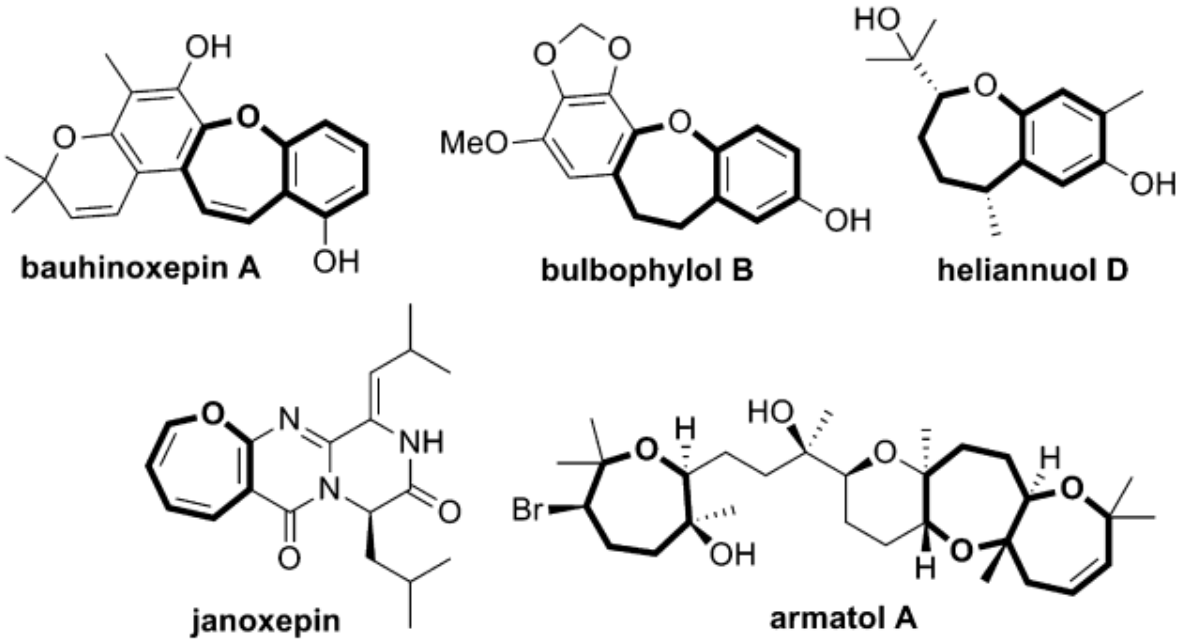
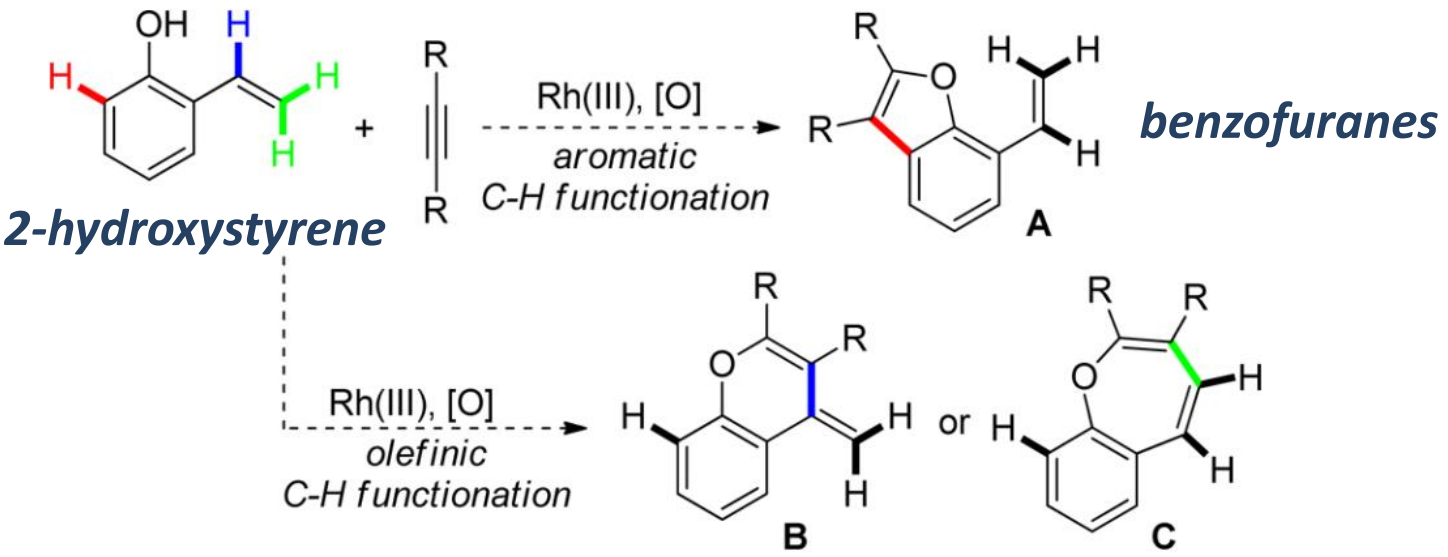
Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CIQUS) and Departamento de Química Orgánica, Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain



Different Annulation Options for o-Vinylphenols

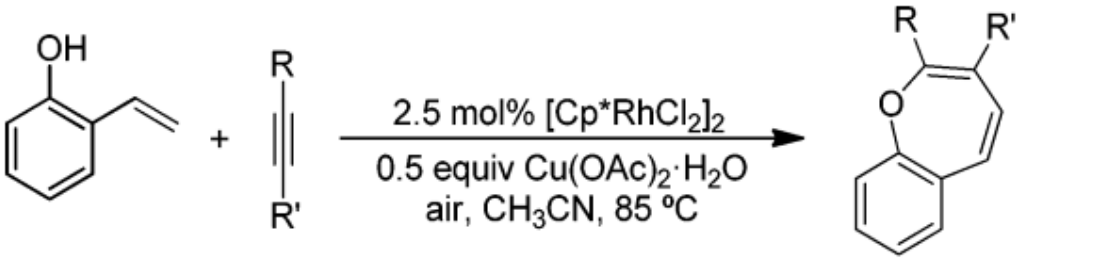
three different C–H positions



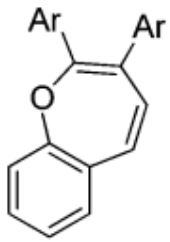
A Formal (5 + 2) Cycloaddition Reaction

Morimoto, K.; Hirano, K.; Satoh, T.; Miura, M. *J. Org. Chem*. **2011**, *76*, 9548−9551.

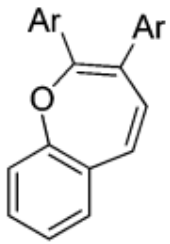
Scope with Respect to the Alkyne Component



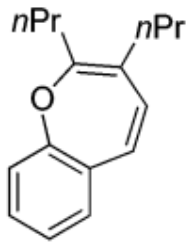
1a **2b-i** **3**



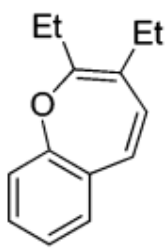
3ab, 85%
Ar = *p*OMePh



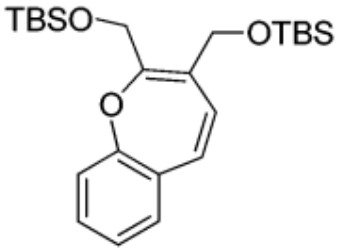
3ac, 71%
Ar = *p*CF_3Ph



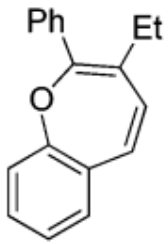
3ad, 56%



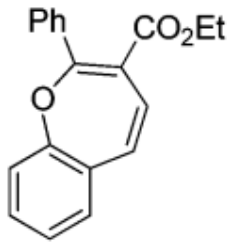
3ae, 52%



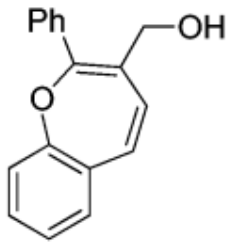
3af, 65%



3ag, 85% (14:1)

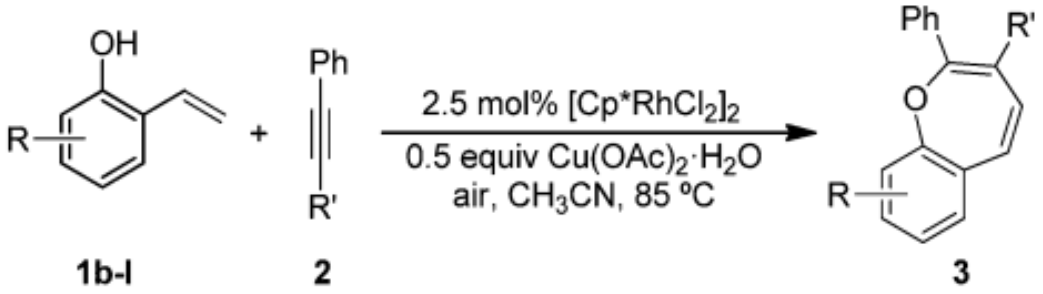


3ah, 99% (8:1)

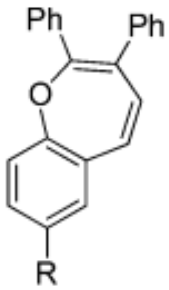


3ai, 65% (11:1)

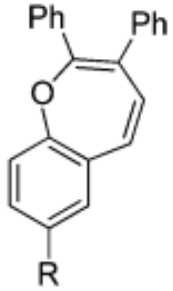
Phenols Equipped with Different Substituents



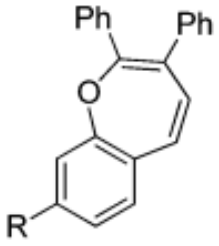
1b-l **2** **3**



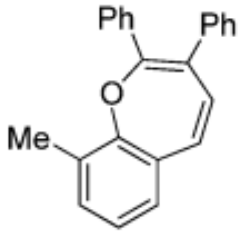
3ba, R = OMe, 84%
3ca, R = Me, 60%
3da, R = Ph, 89%



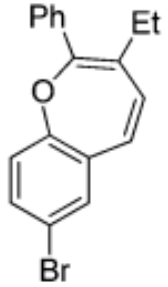
3ea, R = Cl, 78%
3fa, R = Br, 80%
3ga, R = CO_2Me, 69%



3ha, R = OMe, 88%
3ia, R = Me, 90%
3ja, R = Br, 78%
3ka, R = CF_3, 86%

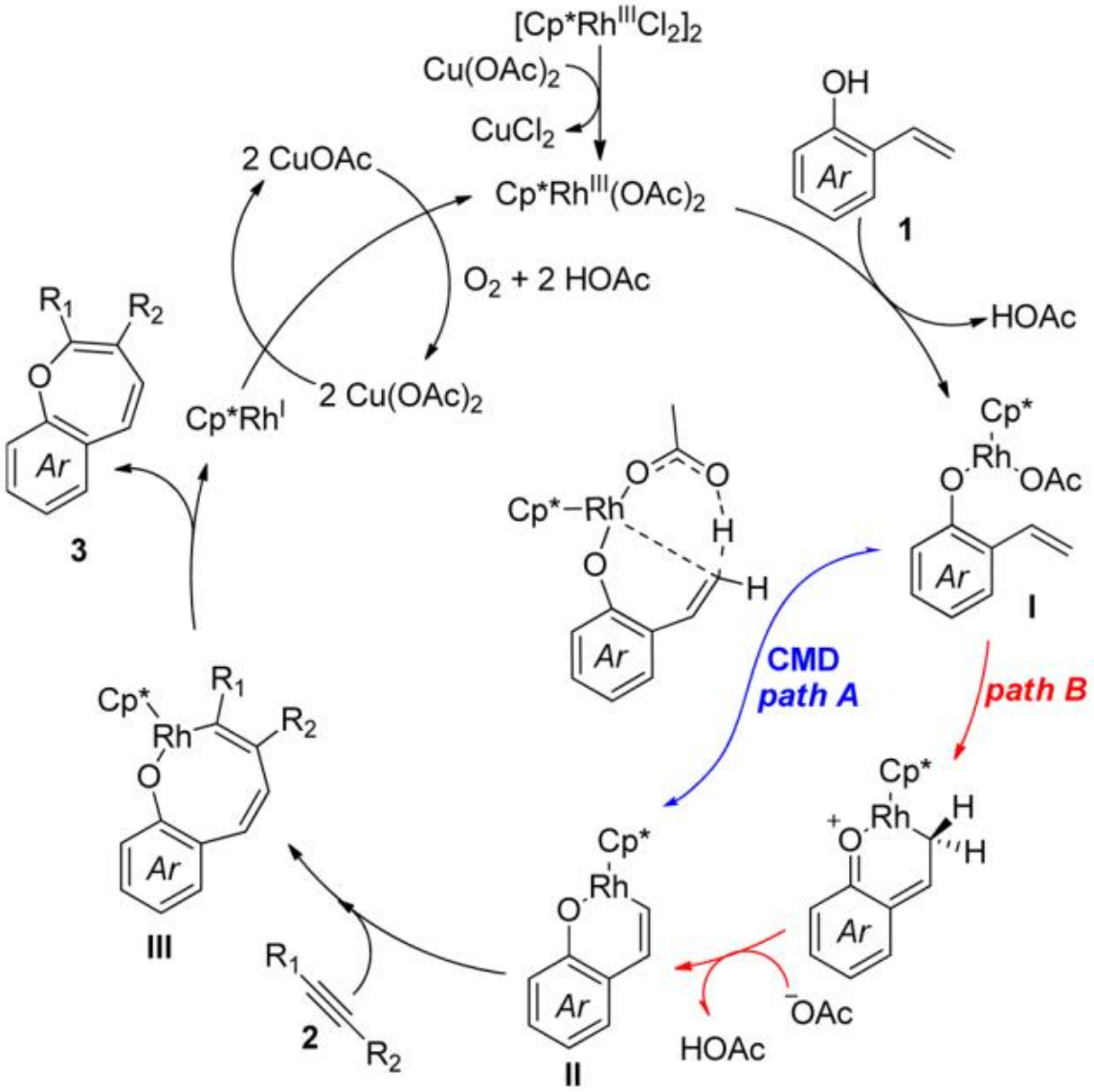


3la, 71%



3fg, 68% (≥20:1)

Proposed Mechanistic Cycle



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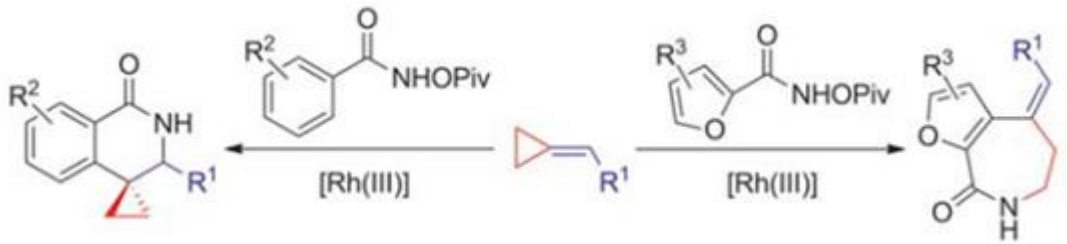
Rh(III)-catalyzed C–H activation/cycloaddition of benzamides and methylenecyclopropanes: divergence in ring formation†

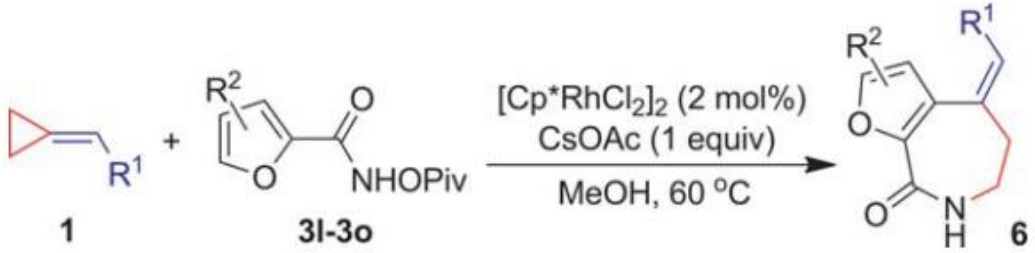
Cite this: *Chem. Sci.*, 2013, **4**, 3421

Sunliang Cui,* Yan Zhang and Qifan Wu

benzamide ***furan-2-carboxamide***

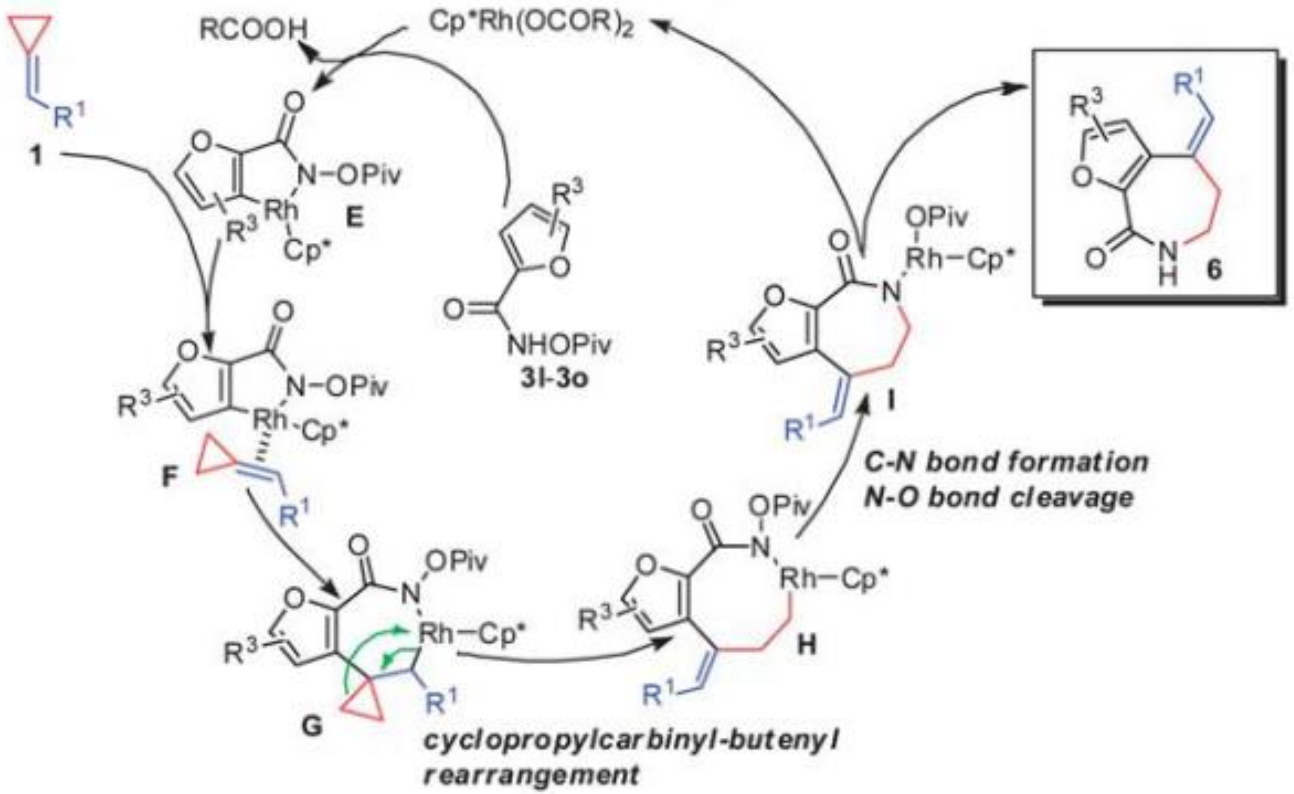


spiro dihydroisoquinolinone ***furan-fused azepinone***



1 3l-3o 6

Proposed mechanism



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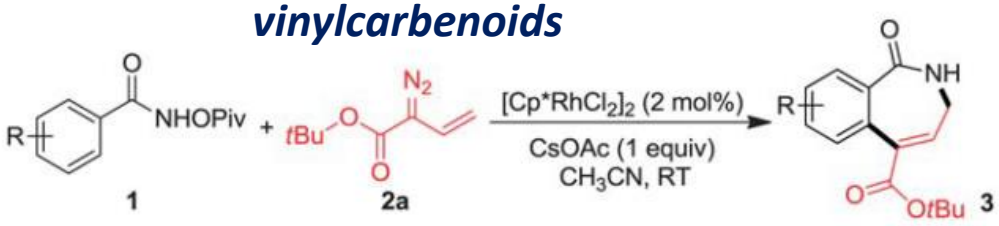
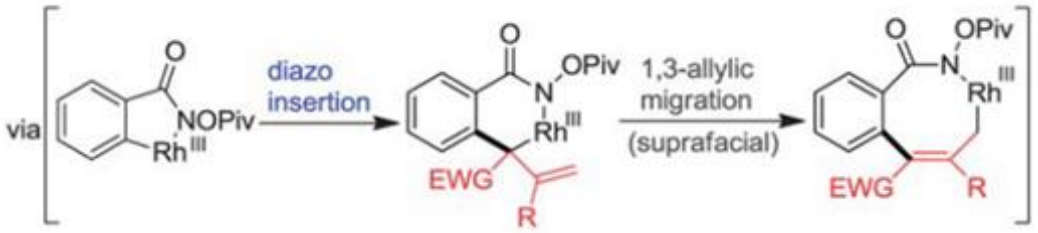
Cite this: *Chem. Sci.*, 2013, **4**, 3912

Rh(III)-catalyzed C–H activation/[4 + 3] cycloaddition of benzamides and vinylcarbenoids: facile synthesis of azepinones†

Sunliang Cui,* Yan Zhang, Dahai Wang and Qifan Wu

vinylcarbenoids





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C–H Activation

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Mild Rhodium(III)-Catalyzed Cyclization of Amides with α,β-Unsaturated Aldehydes and Ketones to Azepinones: Application to the Synthesis of the Homoprotoberberine Framework**

*Zhuangzhi Shi, Christoph Grohmann, and Frank Glorius**