Ru-Catalyzed [2+2+2] Cycloaddition of *o*-Alkenylarylacetylenes with Alkynes: a New Entry to Dihydrobiphenylenes

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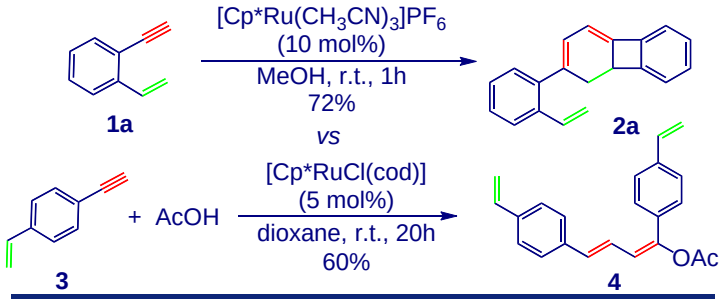
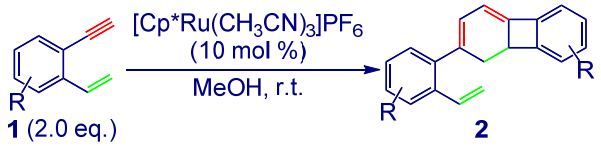
Cycloaddition *vs* Linear Coupling Reactions

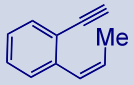
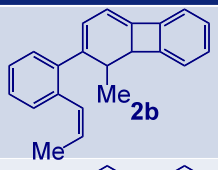
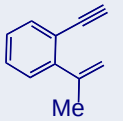
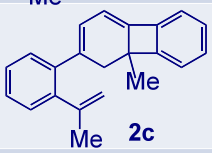
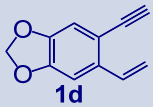
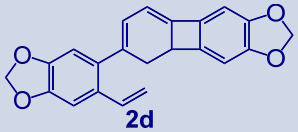
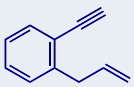
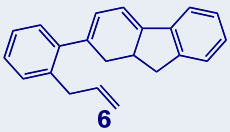
New Ru-catalyzed dimerization of *o*-vinylphenylacetylene **1a** to dihydrobiphenylene **2a** has been recently described in our group.[1]

Surprisingly, this result contrasts with the linear coupling observed for *p*-vinylphenylacetylene **3** to give 1,3-dienylacetate **4**.[2]

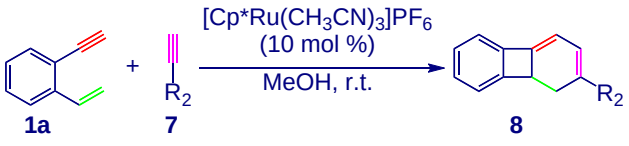


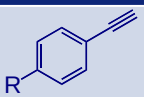
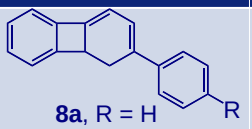
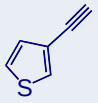
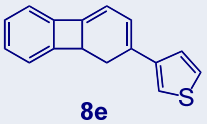
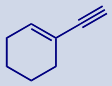
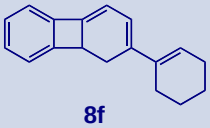
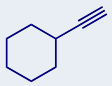
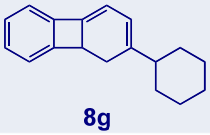
Ru(II)-Catalyzed Dimerization of *o*-Alkenylarylacetylenes to Dihydrobiphenylenes



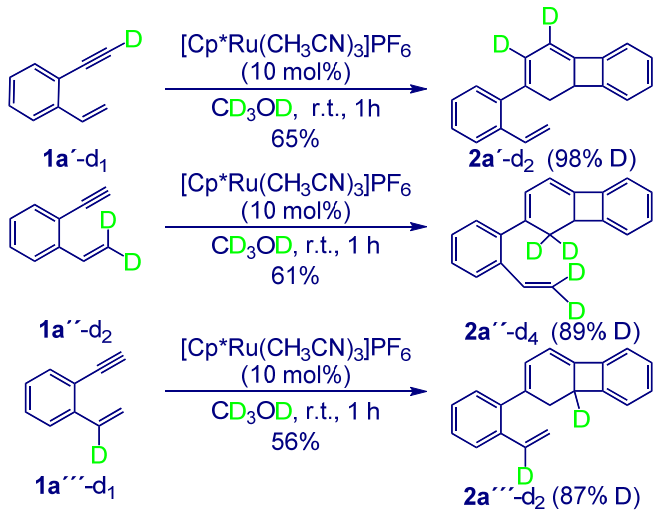
Entry	Substrate	Product	Yield (%)
1	 **1b**	 **2b**	55
2	 **1c**	 **2c**	63
3	 **1d**	 **2d**	70
4	 **5**	 **6**	33

Ru(II)-Catalyzed [2+2+2] Cycloaddition of *o*-Vinylphenylacetylene 1a with Alkynes

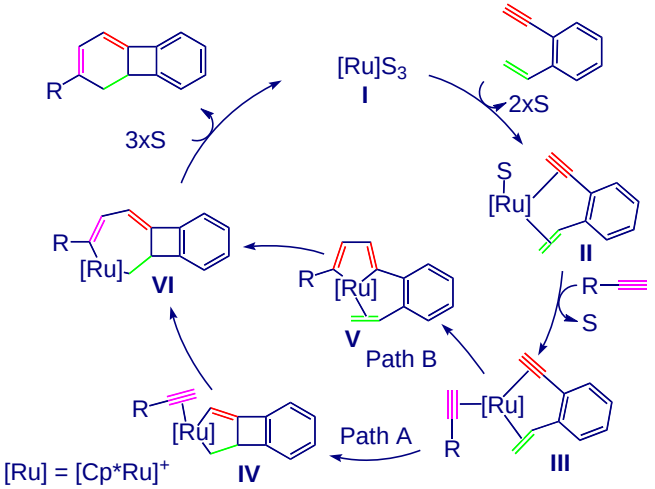


Entry	Substrate	Product	Yield (%)
1	 **7a**, R = H **7b**, R = Me **7c**, R = OMe **7d**, R = CF_3	 **8a**, R = H **8b**, R = Me **8c**, R = OMe **8d**, R = CF_3	65 (**6a**) 70 (**6b**) 88 (**6c**) 26 (**6d**)
2	 **7e**	 **8e**	55
3	 **7f**	 **8f**	85
4	 **7g**	 **8g**	35

Deuterium Labeling Experiments



Mechanistic Proposal



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References: [1] García-Rubín, S.; González-Rodríguez, C.; García-Yebra, C.; Varela, J. A.; Esteruelas, M. A.; Saá, C. *Angew. Chem., Int. Ed.* **2014**, *53*, 1841.
[2] Le Paith, J.; Monnier, F.; Dérien, S.; Dixneuf, P. H.; Clot, E.; Eisenstein, O. *J. Am. Chem. Soc.* **2003**, *125*, 11964