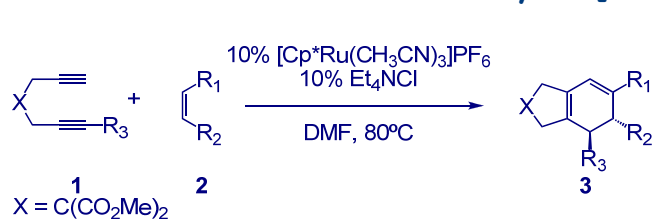


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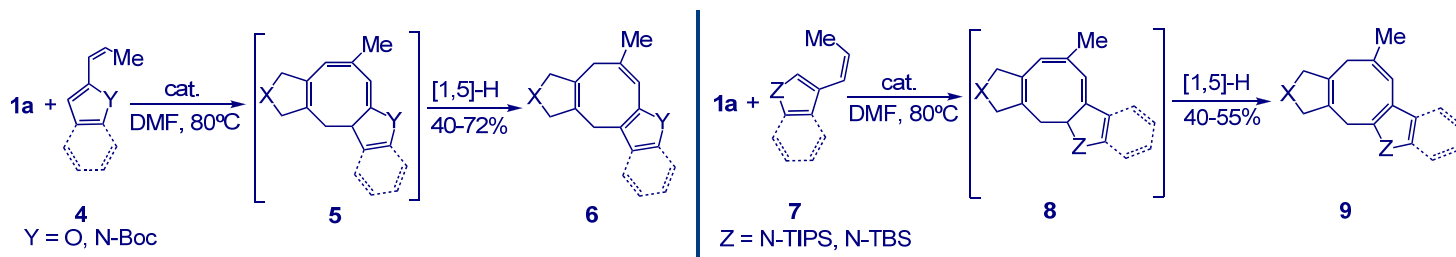
## "Formal" Ru-Catalyzed [2+2+2] Cycloadditions of 1,6-Diynes to Alkenes



R <sub>3</sub>	Diyne	R <sub>1</sub>	R <sub>2</sub>	Alkene	Cyclohexadiene	Yield
H	1a	CO <sub>2</sub> Me	H	2a	3aa	62
H	1a	CH <sub>2</sub> OE <sup>+</sup>	H	2b	3ab	90
H	1a	C <sub>5</sub> H <sub>11</sub>	H	2c	3ac	67
H	1a	CO <sub>2</sub> Me	CO <sub>2</sub> Me	2d	3ad	61
Me	1b	CO <sub>2</sub> Me	H	2a	3ba	90
Me	1b	CH <sub>2</sub> OE <sup>+</sup>	H	2b	3bb	70
Me	1b	C <sub>5</sub> H <sub>11</sub>	H	2c	3bc	69
Me	1b	CO <sub>2</sub> Me	CO <sub>2</sub> Me	2d	3bd	70
CO <sub>2</sub> Me	1c	CO <sub>2</sub> Me	H	2a	3ca	68
CO <sub>2</sub> Me	1c	CH <sub>2</sub> OE <sup>+</sup>	H	2b	3cb	70
CO <sub>2</sub> Me	1c	C <sub>5</sub> H <sub>11</sub>	H	2c	3cc	63
CO <sub>2</sub> Me	1c	CO <sub>2</sub> Me	CO <sub>2</sub> Me	2d	-	-
Ph	1d	CO <sub>2</sub> Me	H	2a	3da	40
Ph	1d	CH <sub>2</sub> OE <sup>+</sup>	H	2b	3db	78
Ph	1d	C <sub>5</sub> H <sub>11</sub>	H	2c	3dc	47
Ph	1d	CO <sub>2</sub> Me	CO <sub>2</sub> Me	2d	-	-

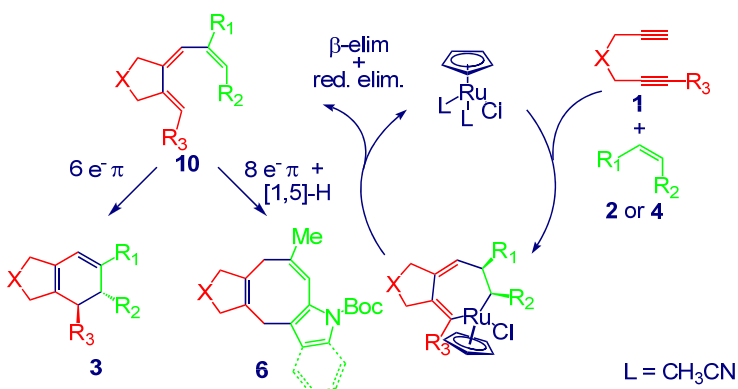
Recently, in our research group, we have developed the "formal" Ru-catalyzed [2+2+2] cycloaddition between unsubstituted 1,6-diynes **1a** to alkenes to afford 1,3-cyclohexadienes.<sup>1</sup> Regioselective polysubstituted 1,6-cyclohexadienes can be prepared using unsymmetrical 1,6-diynes **1b-d**.<sup>2</sup>

## "Formal" Ru-Catalyzed [4+2+2] Cycloadditions of 1,6-Diynes to Vinylheteroarenes



When the reaction was performed using heteroarenes such as 2-(*cis*-1-propenyl)heteroarenes **4** and 3-(*cis*-1-propenyl)heteroarenes **7** cyclooctatrienes **6** and **9** were obtained in quite good yields. The reaction takes place through the initial formation of cyclooctatrienes **5** and **8** by a "formal" Ru-catalyzed [4+2+2] cycloaddition reaction<sup>3</sup> followed by a [1,5]-hydrogen shift.

## Mechanism of the "Formal" Ru-Catalyzed Cycloaddition Reactions



The proposed mechanism involves the initial Ru-catalyzed linear coupling between diynes **1** and the double bond of alkenes **2** or vinylheteroarenes **4** to give polyenes **10**. These polyenes evolve through a disrotatory 6e<sup>-</sup>π electrocyclization to afford cyclohexadienes **3** (in the case of alkenes **2**), or through a conrotatory 8e<sup>-</sup>π electrocyclization followed by a [1,5]-hydrogen shift to afford cyclooctatrienes **6** (in the case of vinylheteroarenes **4**).

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**References:** <sup>1</sup> J.A. Varela, S. G. Rubín, C. González-Rodríguez, L. Castedo, C. Saá, *J. Am. Chem. Soc.* **2006**, *128*, 9262.  
<sup>2</sup> S. García-Rubín, J. A. Varela, L. Castedo, C. Saá, *Chem. Eur. J.* **2008**, in press.  
<sup>3</sup> J.A. Varela, L. Castedo, C. Saá, *Org. Lett.* **2003**, *5*, 2841.