

## Silver(I)-catalyzed $\beta$ -hydride migration from $\alpha$ -diazo esters: mild and stereoselective synthesis of (1*E*,3*E*)-dienes and mechanistic insights

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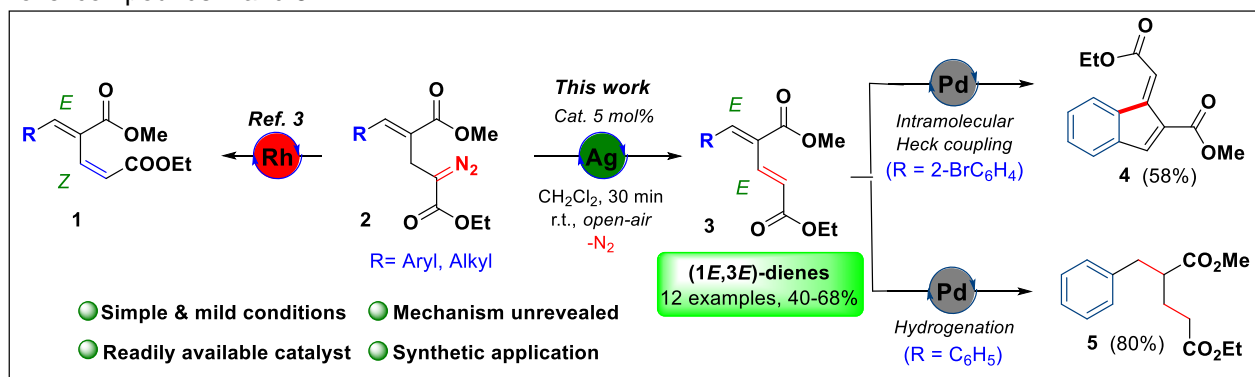
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### ABSTRACT

The structural motif of 1,3-dienes is of considerable significance, as they are frequently encountered in a plethora of natural products and biologically active compounds.<sup>[1]</sup> Consequently, the control of diastereoselectivity in 1,3-dienes reactions has emerged as a crucial objective in the advancement of efficient synthetic methodologies, given the pivotal role of stereochemistry in the domains of drug discovery and total synthesis.<sup>[2]</sup> In a previous work from our group, conjugated 1,3-dienes of *E,Z* configuration (**1**) were diastereoselectively synthesized through the  $\beta$ -hydride migration of donor-acceptor diazo compounds **2** with rhodium(II) catalysts.<sup>[3]</sup> In the current investigation, the introduction of silver(I) triflate as the catalyst also induces the decomposition of the aforementioned diazo compounds **2**, although the resulting 1,3-dienes **3** possess *E,E* configuration (Scheme). The computational results indicated that the formation of dienes **3** is dependent on the formation of a C=C double bond with *E* geometry. A simplified model combined with microkinetic simulations<sup>[4]</sup> was employed to identify the key factors influencing this stereoselectivity, where the extrusion of molecular N<sub>2</sub> was found to be the rate determining step.<sup>[5]</sup> The synthetic versatility of (1*E*,3*E*)-diene **3** was evaluated with selected palladium-catalyzed post-functionalizations, resulting in the formation of novel compounds **4** and **5**.



**Scheme.** Silver-catalyzed diastereoselective synthesis of (1*E*,3*E*)-dienes **3** from donor-acceptor diazo compounds **2**.

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