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Hydrazines and Azides via the Metal-Catalyzed Hydrohydrazination and Hydroazidation of Olefins
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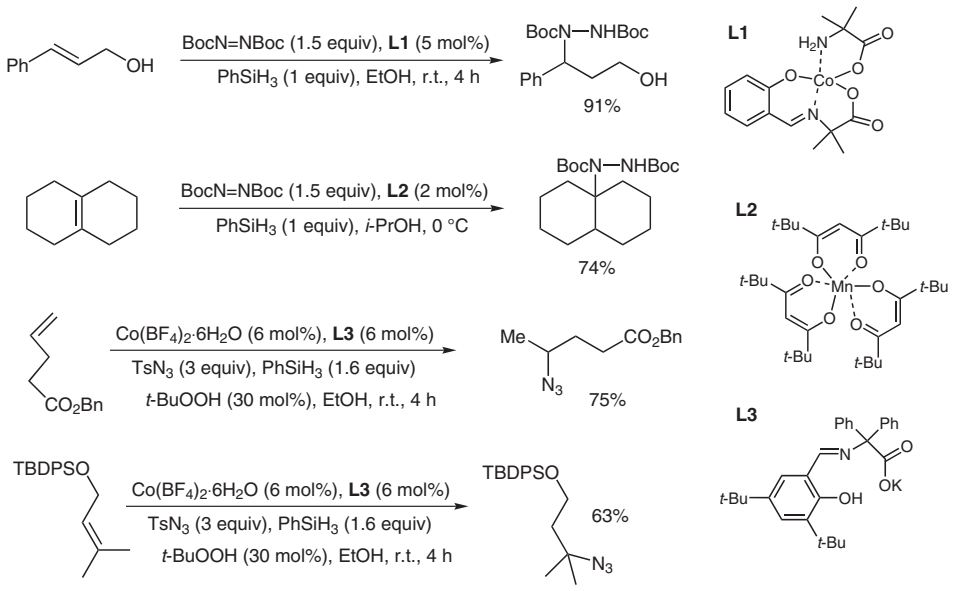
Co-Catalyzed Hydrohydrazination and Hydroazidation of Olefins



Significance: The authors reported a new, extremely broad and versatile method for the introduction of a nitrogen substituent into alkenes. The catalysts and reaction conditions are optimized for the preparation of alkyl azides and alkyl Boc-hydrazines, based on a novel catalytic procedure. Easily available starting materials and catalysts are used in this method. Due to the high selectivity of the method, it offers an excellent functional-group compatibility. The versatility of this approach is demonstrated by the preparation of a variety of functionalized organic azides and hydrazides.

Comment: This reaction can also be considered an elegant and versatile method of Markovnikov amination, since the products, which are formed very regioselectively, are easily reduced to the corresponding amines. Mechanistically, the process is believed to include the addition of Co(III)-H to the C=C bond, followed by the either radical or Co-bound intermediate addition to azo- or azido-species. The use of a 'radical clock' (cyclization with a suitably placed double bond) demonstrated the formation of free radical species, although they may not be involved in the main reaction pathway.

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