

# COPPER CATALYZED RING OPENING REACTIONS OF [1.1.1]PROPELLANE

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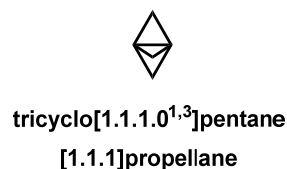
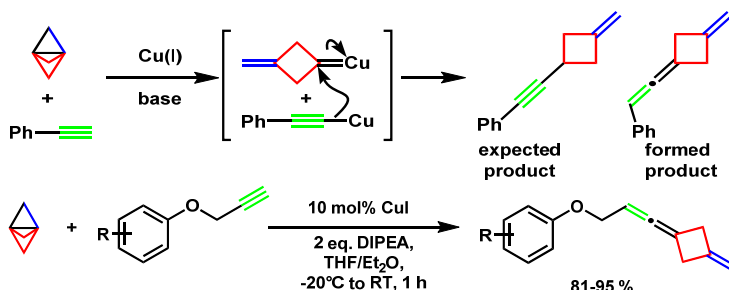
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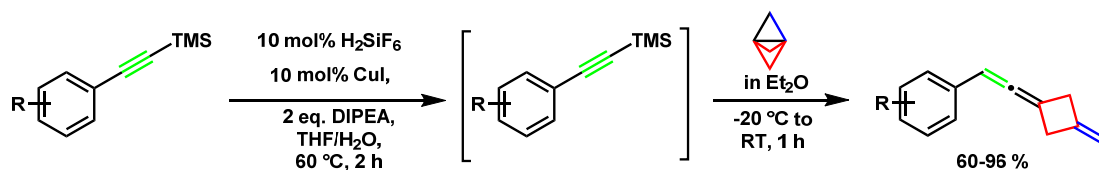
Bridged cyclic compounds, that has a direct bridgehead-bridgehead bond can be called propellanes.<sup>[1]</sup>

According to the literature, [1.1.1]propellane, in the presence of transition metals (Pd(II), Pt(I), Rh(II), Ir(I)), provide di- or trimerized products.<sup>[2]</sup> It was our interest to explore this chemistry further, to obtain practical synthetic procedures. In our hand, dimerization occurred in the presence of Fe(II) and Cu(I) as well. In the latter case, copper acetylides were an obvious choice of nucleophile to react with the suspected carbene intermediate. The only product of this reaction turned out to be an allene instead of the expected alynylcyclobutane.

The optimized parameters were expanded to produce allene derivatives in 81-95 % yield from propargyl ethers.



In contrast to terminal aryl acetylenes, the TMS derivatives are easy to synthesize. Our desilylation method,<sup>[3]</sup> that utilizes non-toxic H<sub>2</sub>SiF<sub>6</sub> solution could be implemented in the procedure, to form the terminal acetylene in situ. This step was also optimized to get the highest conversion values. After the desilylation, the same reaction conditions were used to form cyclobutanes, with very good yields.



[1] K. R. Mondanaro; W. P. Dailey, *Org. Synth.*, **1998**, 75, 98.

[2] Wiberg, K. B.; Waddell, S. T., *J. Am. Chem. Soc.*, **1990**, 112, 2194.

[3] Lasányi, D.; Mészáros, Á.; Novák, Z.; Tolnai, G. L., *J. Org. Chem.*, **2018**, 83, 8281.