L. WU, F. WANG, P. CHEN, G. LIU* (SHANGHAI INSTITUTE OF ORGANIC CHEMISTRY, P. R. OF CHINA)
Enantioselective Construction of Quaternary All-Carbon Centers via Copper-Catalyzed Arylation of Tertiary Carbon-Centered Radicals
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Category
Metals in Synthesis

Key words
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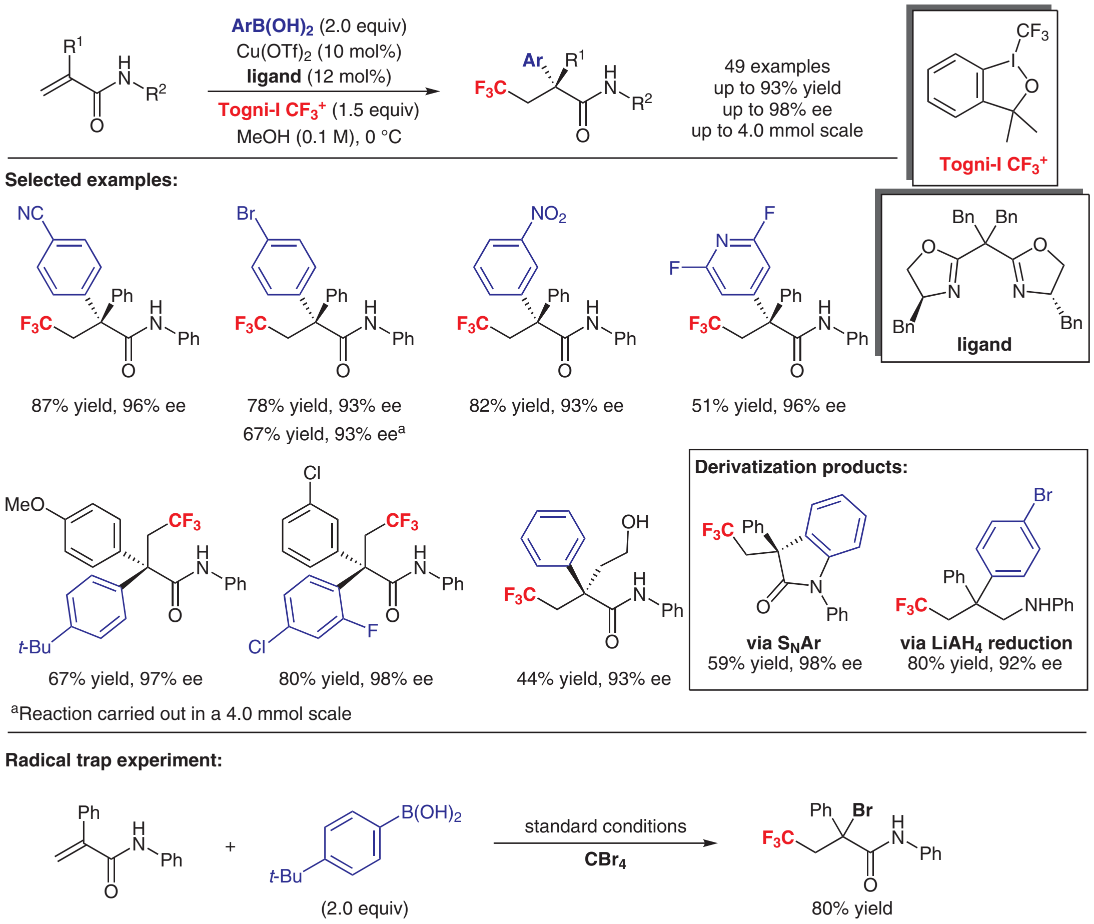
Enantioselective Arylative Trifluoromethylation of Alkenes



Significance: The asymmetric trapping of tertiary carbon-centered radicals represents a challenge in organic synthesis. The authors report an asymmetric coupling of tertiary radicals with L*Cu(II)–aryl species for the synthesis of enantiomerically enriched quaternary carbons. The tertiary carbon-centered radicals were generated via CF_3 radical addition. The trifluoromethylated products were obtained in moderate to high yields, and good to high enantioselectivities.

Comment: The scalability of this process was determined on a 4.0 mmol reaction, which provided the desired product with no erosion of enantioselectivity. Various derivatizations were performed on the trifluoromethylated products, such as cyclization (via nucleophilic aromatic substitution) and reduction of the carbonyl group. A radical trap experiment using CBr_4 generates an α-bromo amide in high yields, supporting the presence of benzylic radicals.

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