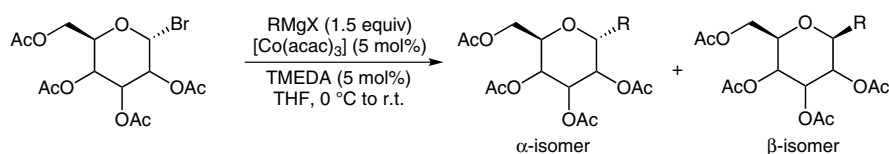
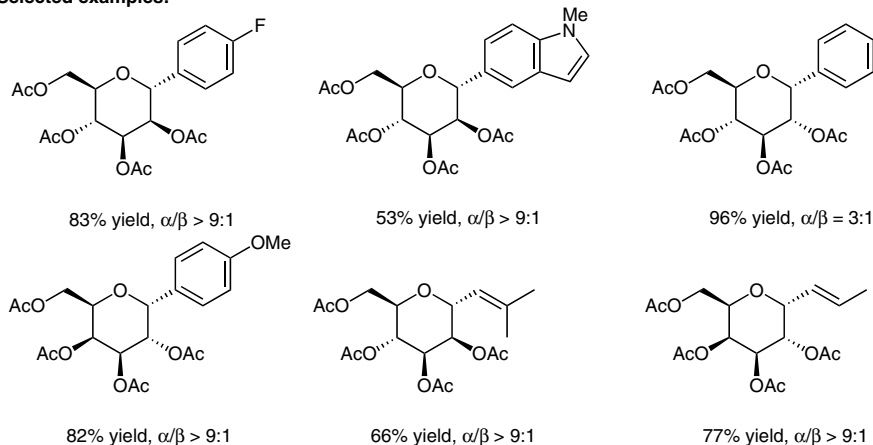


L. NICOLAS, P. ANGIBAUD, I. STANSFIELD, P. BONNET, L. MEERPOEL, S. REYMOND,*
J. COSSY* (ESCPi PARISTECH, JANSSEN RESEARCH & DEVELOPMENT, VAL DE REUIL,
FRANCE AND BEERSE, BELGIUM)
Diastereoselective Metal-Catalyzed Synthesis of C-Aryl and C-Vinyl Glycosides
Angew. Chem. Int. Ed. **2012**, *51*, 11101–11104.

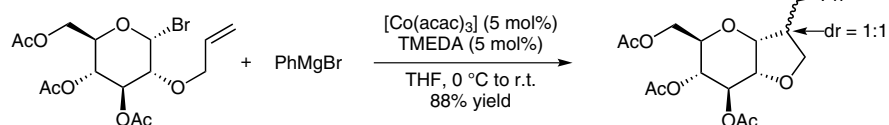
Cobalt-Catalyzed Cross-Coupling of 1-Bromo Glycosides and Grignard Reagents



Selected examples:



Mechanistic study:



Significance: Numerous metal-catalyzed cross-coupling methods to form anomeric C–C bonds exist, which are important for the synthesis of carbohydrate analogues such as C-glycosides (see Review below). However, β -elimination is a major drawback of these reactions. The authors report a new diastereoselective cobalt-catalyzed cross-coupling between 1-bromo glycosides and aryl and alkenyl Grignard reagents with moderate to good α -selectivity.

Review: L. Somsák *Chem. Rev.* **2001**, *101*, 81–136.

SYNFACTS Contributors: Mark Lautens, Jennifer Tsoung
Synfacts 2013, 9(1), 0078 Published online: 17.12.2012
DOI: 10.1055/s-0032-1317754; **Reg-No.:** L15612SF

Comment: The authors report that there was good α -selectivity for the cross-coupling reaction with mannose and galactose derivatives, but lower α/β ratios for glucose derivatives. Like most cobalt-catalyzed cross-coupling reactions, the stereoselectivity of this reaction supports a radical pathway. Treatment of a δ -olefinic 1-bromoglycoside produced an epimeric mixture of the bicyclic product, which would result from the formation of an anomeric radical that leads to a 5-*exo*-trig cyclization followed by cross-coupling with PhMgBr.