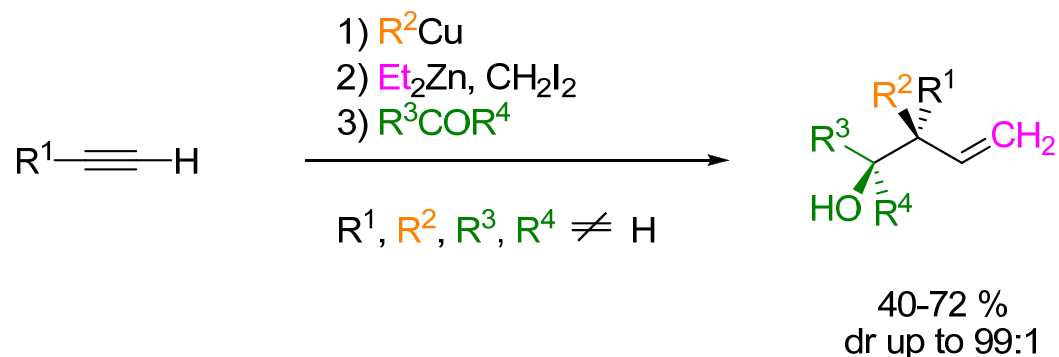


Highly Diastereoselective Preparation of Homoallylic Alcohols Containing Two Contiguous Quaternary Stereocenters in Acyclic Systems from Simple Terminal Alkynes



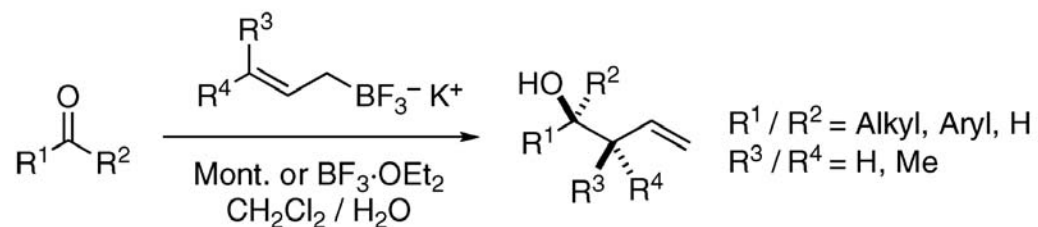
Bishnu Dutta, Noga Gilboa, and Ilan Marek
 JACS, ASAP

Bibliography

Preparation of homoallylic alcohols from different organometallic species :

. Bore

Batey et al., *Org. Lett.*, **2009**, *11*, 2631

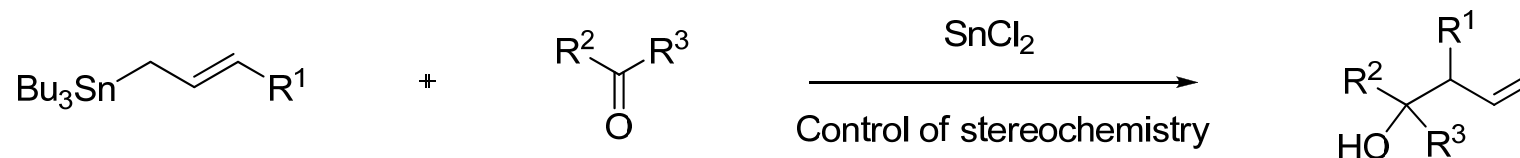


. Titanium

Takeda et al. *Chem.-Eur. J.*, **2009**, *15*, 2680

. Tin

Baba. et al., *J. Am. Chem. Soc.*, **2002**, *124*, 13442



. Silicium

Tietze et al., *J. Am. Chem. Soc.*, **2006**, *128*, 11483

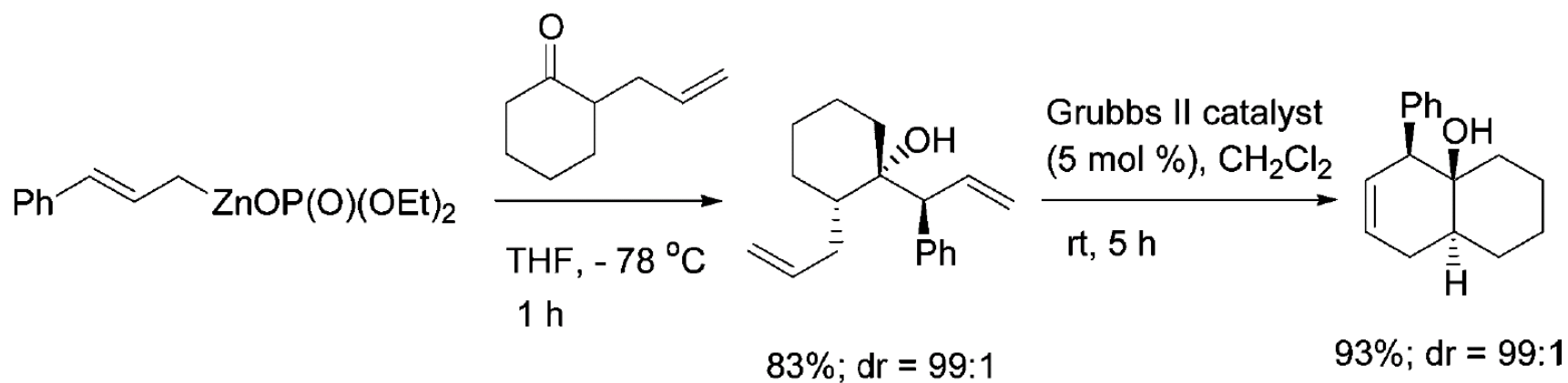
Bibliography

Preparation of homoallylic alcohols from different organometallic species :

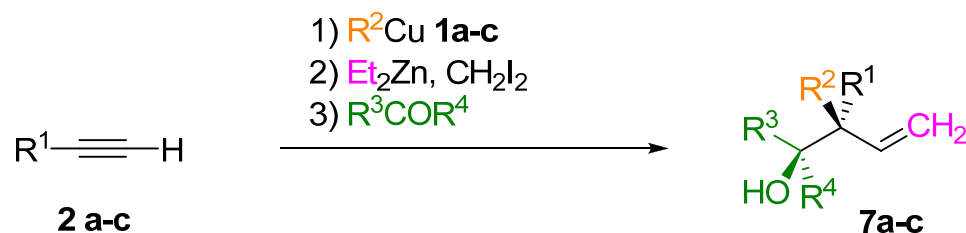
. Zinc

Knochel. et al., *Org. Lett.*, **2008**, *10*, 117

Knochel et al., *J. Am. Chem. Soc.*, **2007**, *129*, 5376



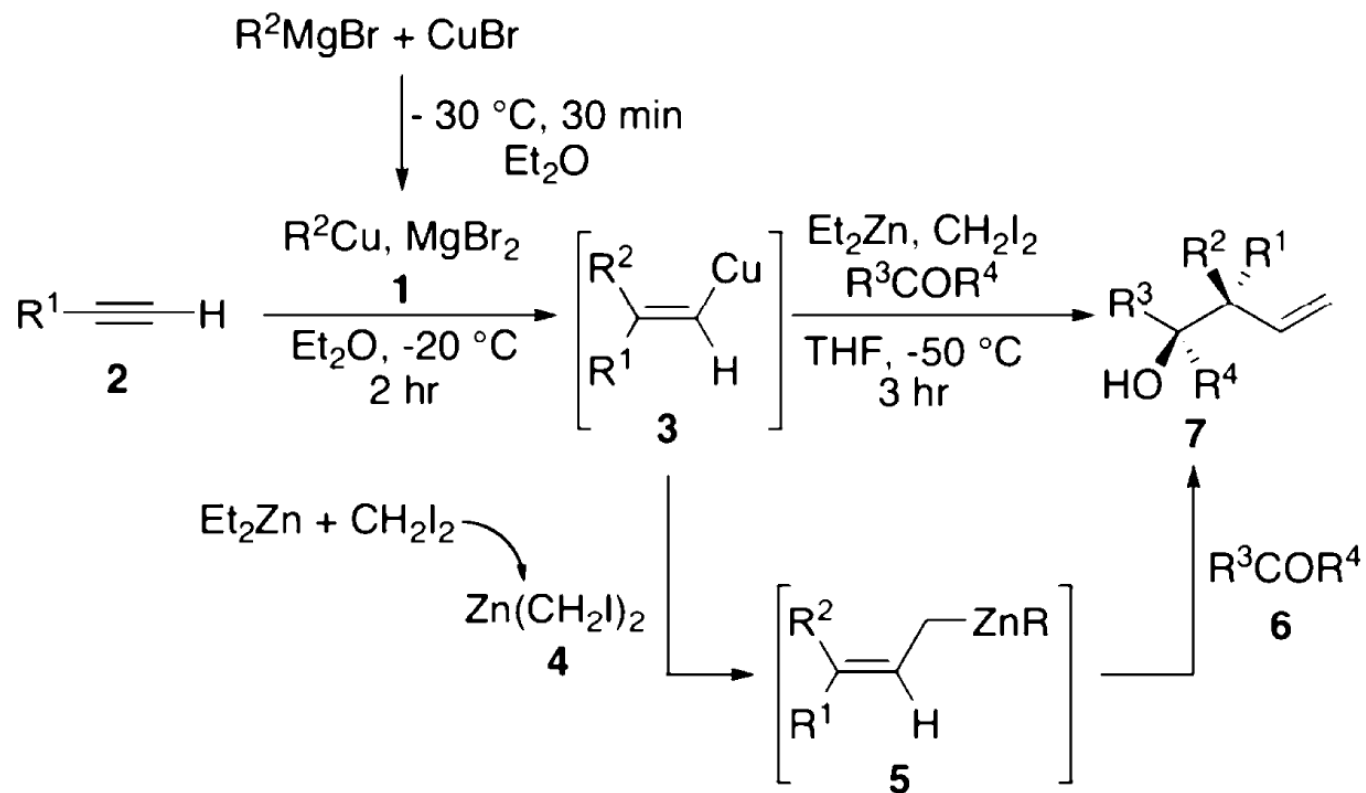
Scope of the reaction



entry	R ¹	R ²	R ³	R ⁴	pdts	Yield ^a %	dr ^b
1	C ₄ H ₉ (2a)	C ₂ H ₅ (1a)	C ₆ H ₅	CH ₃	7a	70	98/2
2	C ₂ H ₅ (2b)	C ₄ H ₉ (1b)	C ₆ H ₅	CH ₃	7b	72	97/3
3	C ₂ H ₅ (2b)	C ₄ H ₉ (1b)	C ₆ H ₅	C ₂ H ₅	7c	60	91/9
4	CH ₃ (2c)	C ₂ H ₅ (1a)	C ₆ H ₅	CH ₃	7d	60	99/1
5	CH ₃ (2c)	C ₂ H ₅ (1a)	C ₆ H ₅	C ₂ H ₅	7e	50	91/9
6	C ₄ H ₉ (2a)	C ₂ H ₅ (1a)	<i>p</i> CH ₃ O ₂ CC ₆ H ₄	CH ₃	7f	72	99/1
7	C ₂ H ₅ (2b)	C ₄ H ₉ (1a)	<i>p</i> CH ₃ O ₂ CC ₆ H ₄	CH ₃	7g	70	99/1
8	C ₄ H ₉ (2a)	C ₂ H ₅ (1a)	<i>p</i> -CH ₃ C ₆ H ₄	CH ₃	7h	60	98/2
9	CH ₃ (2c)	C ₂ H ₅ (1a)	<i>p</i> -BrC ₆ H ₄	CH ₃	7i	62	98/2
10	C ₄ H ₉ (2a)	C ₂ H ₅ (1a)	<i>p</i> -BrC ₆ H ₄	CH ₃	7j	60	97/3
11	CH ₃ (2c)	C ₂ H ₅ (1a)	<i>p</i> -MeOC ₆ H ₄	CH ₃	7k	55	97/3
12	CH ₃ (2c)	C ₂ H ₅ (1a)	2-naphthyl	CH ₃	7l	65	98/2
13	C ₄ H ₉ (2a)	C ₂ H ₅ (1a)	PhCH=CH	CH ₃	7m	40	98/2
14	C ₄ H ₉ (2a)	C ₂ H ₅ (1a)	2-thiophenyl	CH ₃	7n	55	90/10
15	C ₂ H ₅ (2b)	C ₄ H ₉ (1b)	2-thiophenyl	CH ₃	7o	57	90/10

^a Isolated yields. ^b Diastereoisomeric ratios determined by ¹H, ¹³C NMR and gas chromatography analysis of the crude reaction mixture.

How does it work ?



Conclusion

Preparation of homoallylic alcohols containing two contiguous stereocenters

From commercially available terminal alkynes

Construction of three carbon-carbon bonds in a single pot operation

15 examples , 40-72 %

Excellent control of the diastereoselectivity