New approach for the synthesis of pinane-derived bis-phosphines

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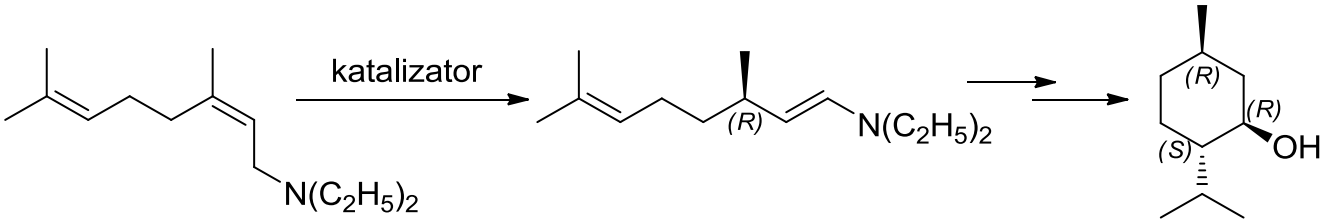
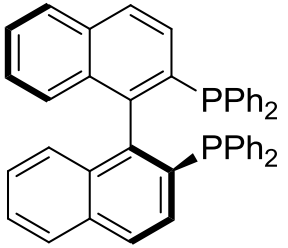
Application of bisphosphine ligands

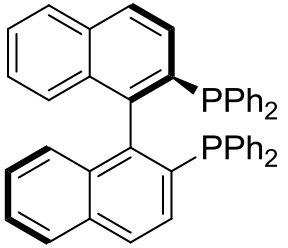
Asymmetric isomerization



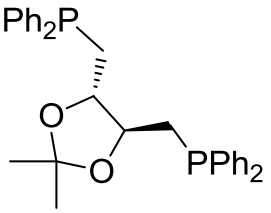
catalyst	Yield [%]	ee [%]
$Co(acac)_2$/(+)-DIOP/$^{i}Bu_2AlH$	87	35 (R)
$Co(acac)_2$/(R)-BINAP/$^{i}Bu_2AlH$	97	20 (R)
[Rh{(+)-DIOP}(COD)]$^{+}$	100	22 (R)
[Rh(R,S-BPPFA)]$^{+}$	-	-
[Rh{(R)-BINAP}(COD)]$^{+}$	100	97 (S)
[Rh{(S)-BINAP}(COD)]$^{+}$	100	97 (R)



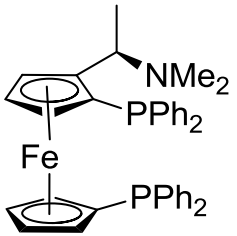
(S)-BINAP



(R)-BINAP



(+)-DIOP

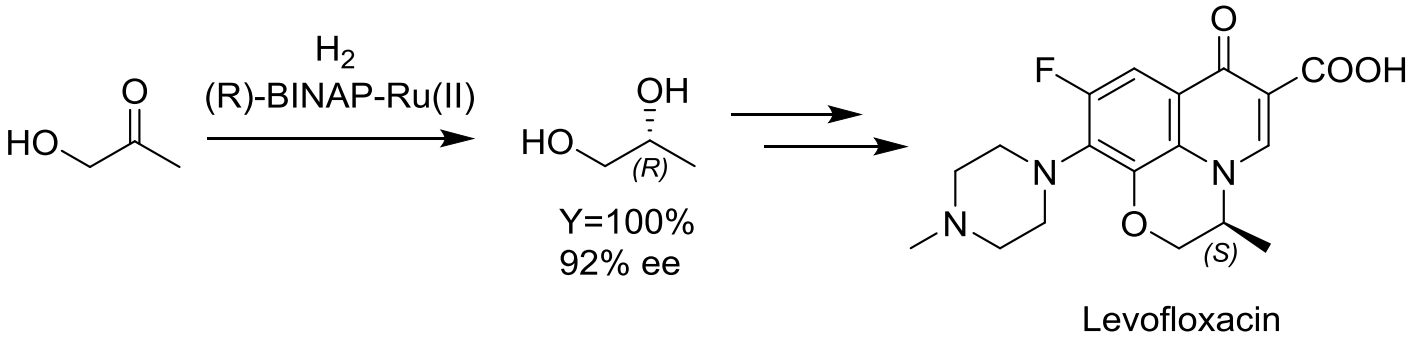


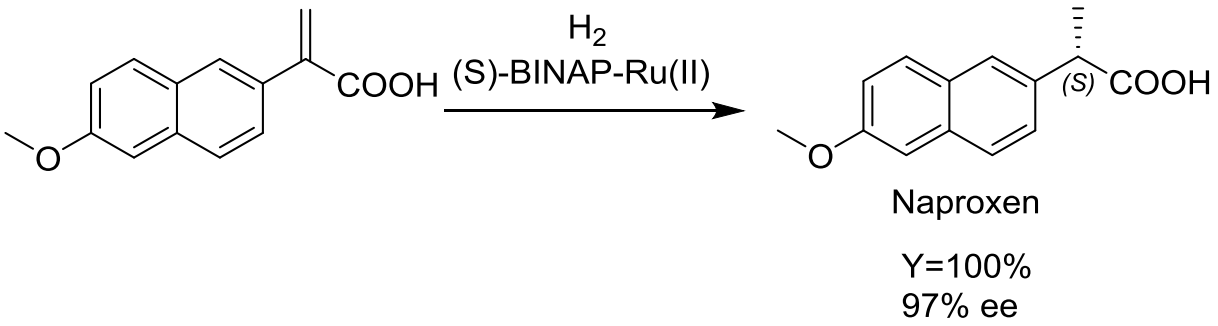
(R,S)-BPPFA

Akutagawa S.; *Topics in Catalysis*; **1997**; *4*; 271-274

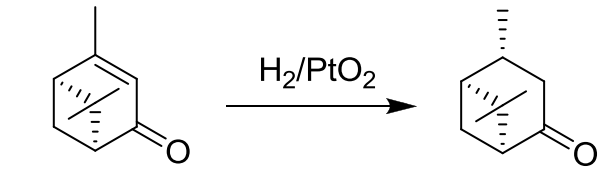
Application of bisphosphine ligands

Asymmetric hydrogenation

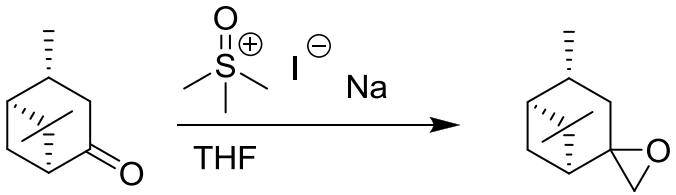




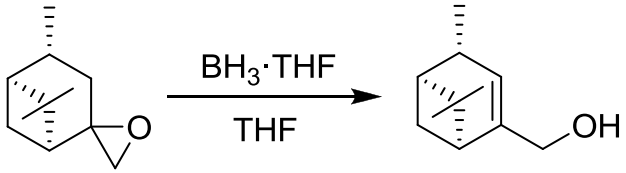
Allylic alcohol synthesis – from verbenone



(–)-Verbenone 93%

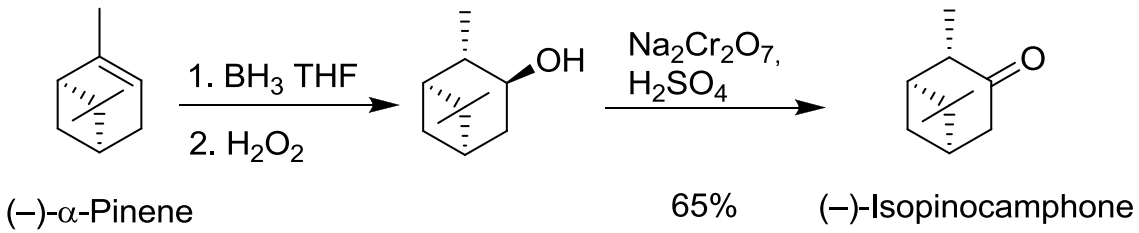


73%



70%

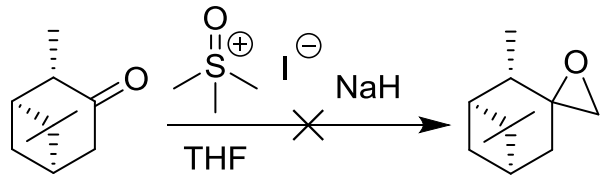
Allylic alcohol synthesis – from isopinocamphone

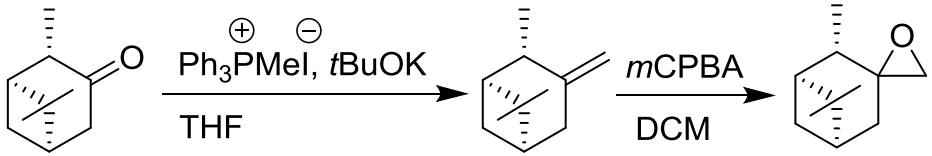


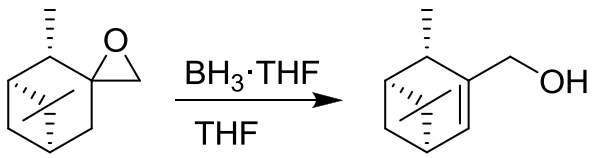
(–)-α-Pinene

65%

(–)-Isopinocamphone

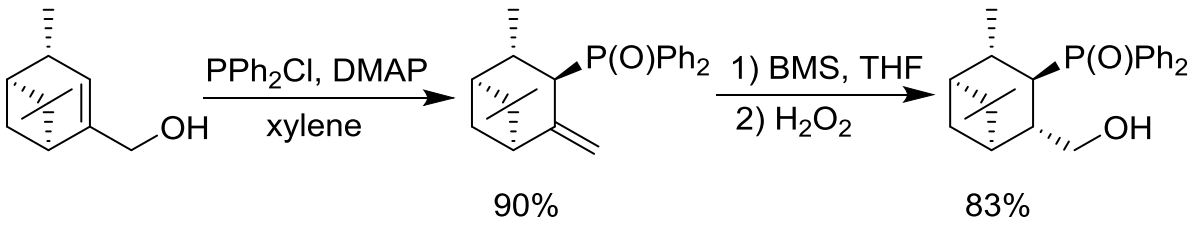


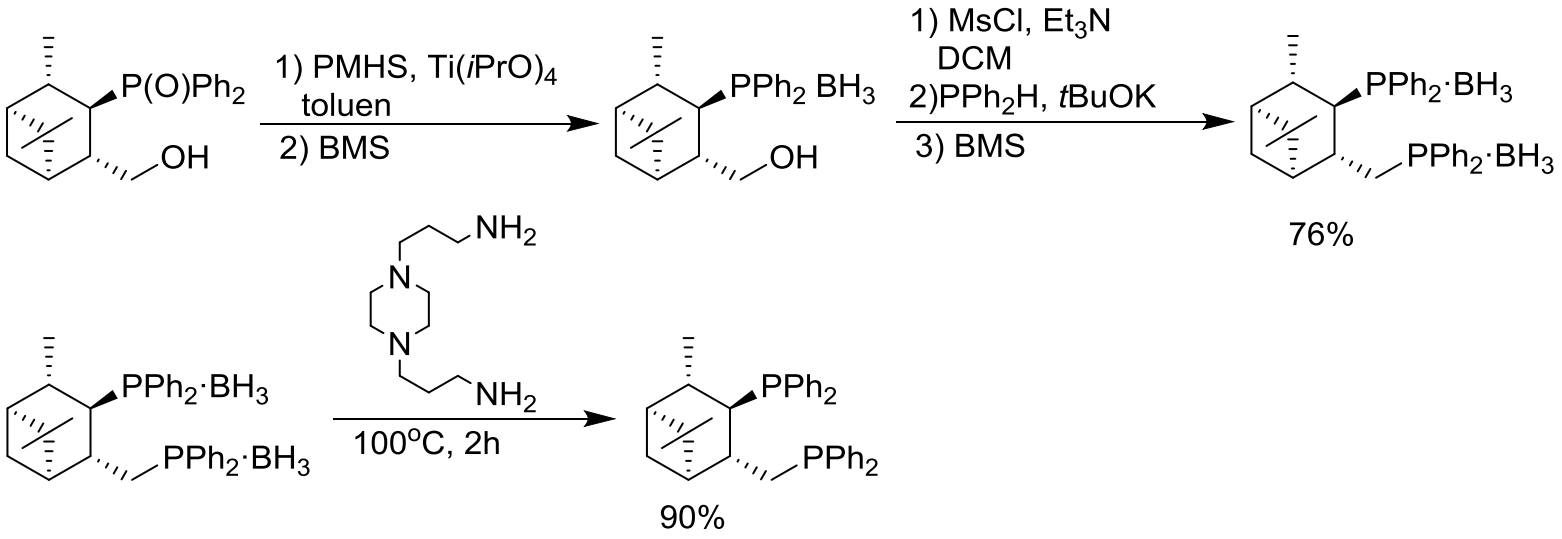


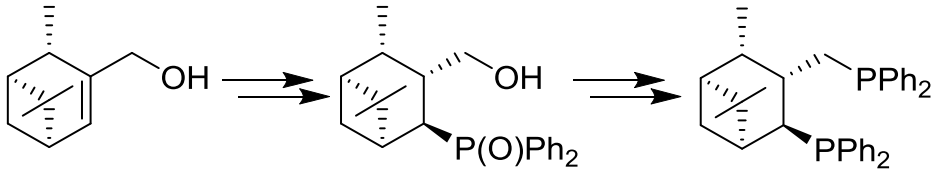


45%

Bis-phosphine synthesis







Summary

We have shown the synthesis of regio-isomeric bis-phosphines starting from (–)-α-pinene, through regio-isomeric ketones – verbenone and isopinocamphone.