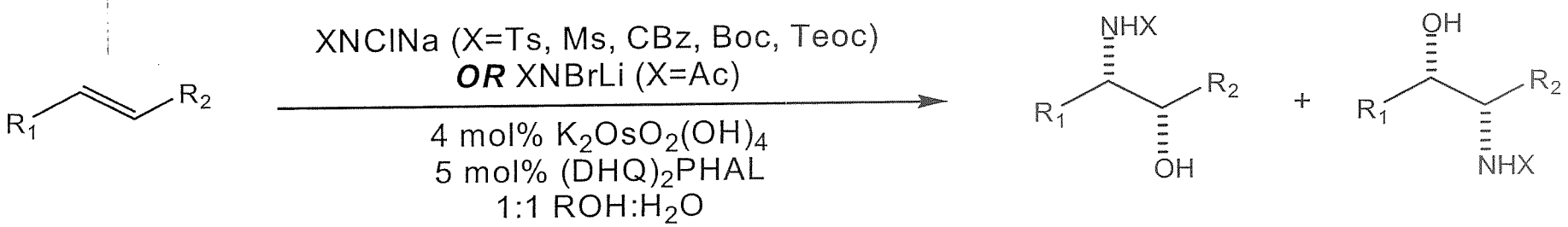
Asymmetric Aminohydroxylation of Alkenes

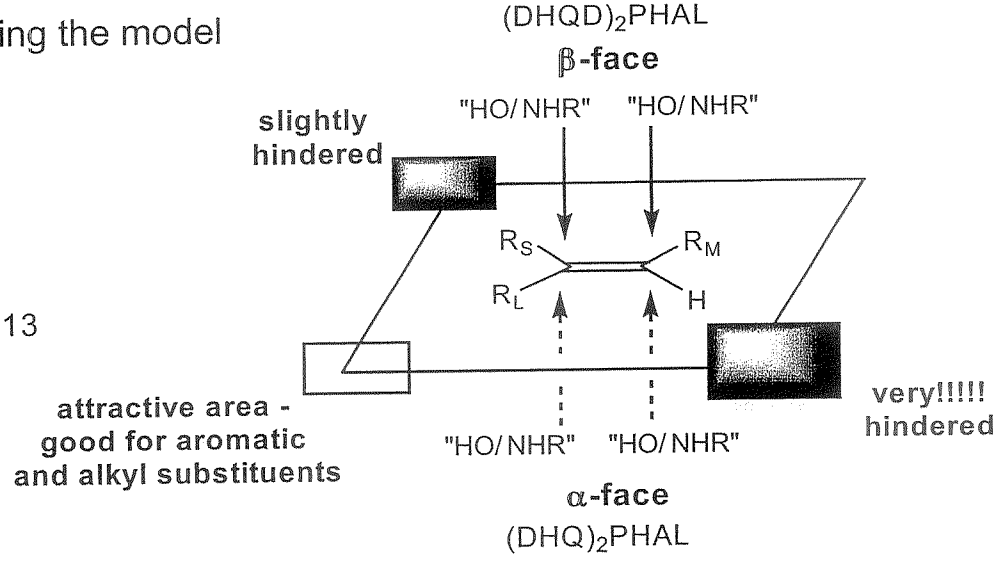


- originally developed with chloramine T (Na^+ClNTs^-), as for a racemic protocol developed by Sharpless in the 1980s 1980s

- found that the reaction works better with smaller N-substituents, (eg $MeSO_2$-), and even better still with salts of N-halocarbamates (NC(O)OR; ease of deprotection!) or N-haloamides

- regiocontrol is a problem, particularly with electronically unbiased alkene substituents

- in most respects the reaction is similar to the AD, including the model for asymmetric induction
  (note that, for a given olefin, the HO/NHR are delivered to the same face in both regioisomeric products)



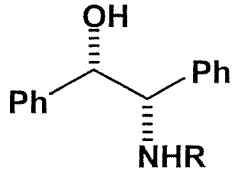
chloramine-T: *Angew.* ., **1996**, *35*, 451
chloramine-M: *Angew. Chem., Int. Ed. Engl.*, **1996**, *35*, 2810
halocarbamates: *Angew. Chem., Int. Ed. Engl.*, **1996**, *35*, 2813
haloamides: *Org. Lett.*, **2000**, *2*, 2221

REVIEW:
J. Chem. Soc. Perkin Trans. 1
2002, 2733.

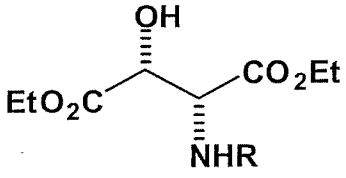
Scope of the asymmetric aminohydroxylation

(all reactions shown carried out with $(DHQ)_2$-PHAL; figure shown is *ee*)

Symmetrical trans-alkenes:

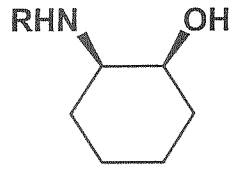


R = Ts	62
R = Ms	75
R = Cbz	91
R = Ac	94



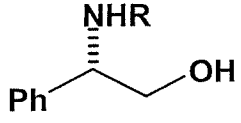
R = Ts	77
R = Ms	95
R = Cbz	84
R = Ac	- -

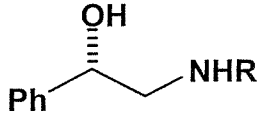
Symmetrical cis-alkenes:



R = Ts	45
R = Ms	66
R = Cbz	63
R = Ac	- -

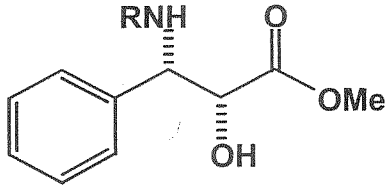
Styrenes:

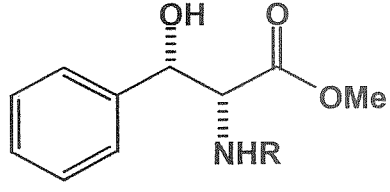




R = Ts	50	2 : 1
R = Ms	- -	- -
R = Cbz	93	1 : 1
R = Ac	88	1 : 6

Cinnamates (electronically distinguished):



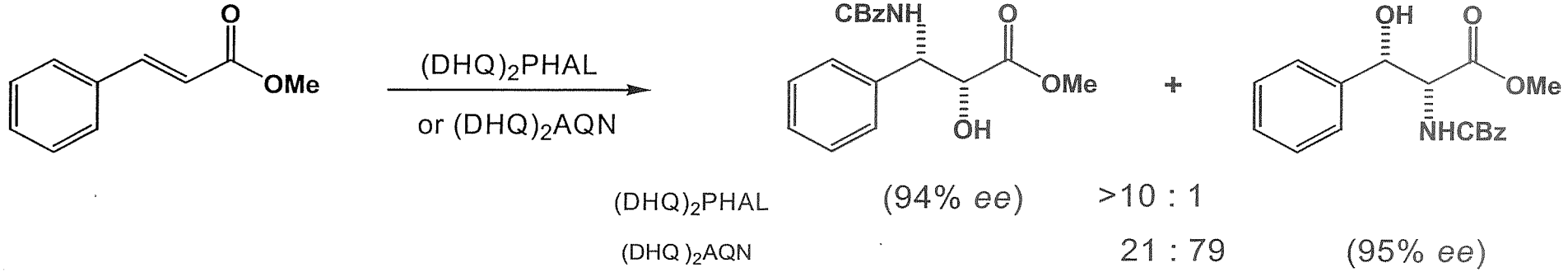


regiochemistry

R = Ts	81	5 : 1
R = Ms	95	9 : 1
R = Cbz	94	10 : 1
R = Ac*	99	20 : 1

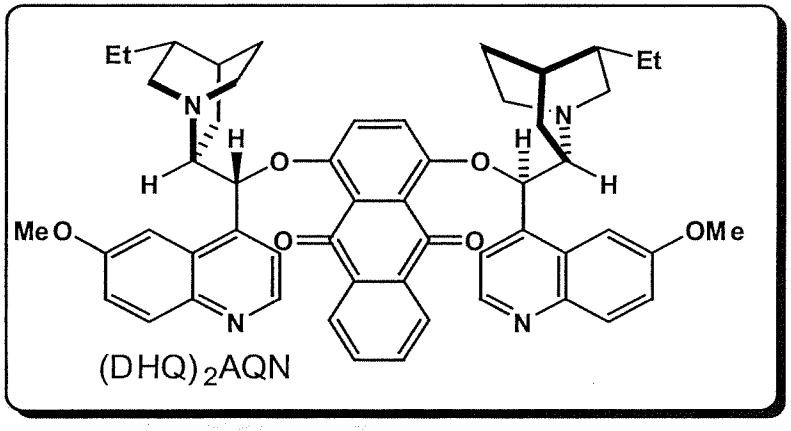
* - ^{i}Pr ester

Regiochemical control by adjustment of aromatic linking group



$(DHQ)_2PHAL$	(94% *ee*)	>10 : 1
$(DHQ)_2AQN$		21 : 79 (95% *ee*)

$(DHQ)_2PHAL$	(93% *ee*)	ca. 1 : 1
$(DHQ)_2AQN$		1 : 13 (88% *ee*)



Tetrahedron Lett., **1998**, *39*, 2507;
Angew. Chem., Int. Ed. Engl., **1997**, *36*, 1483