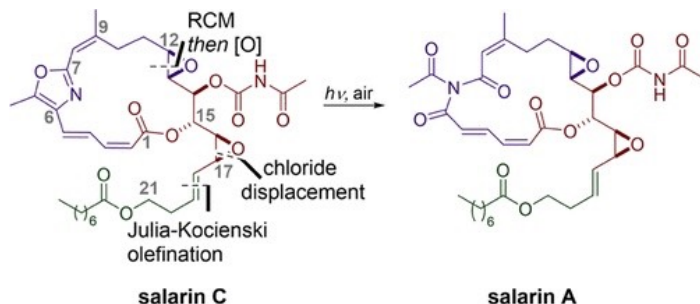
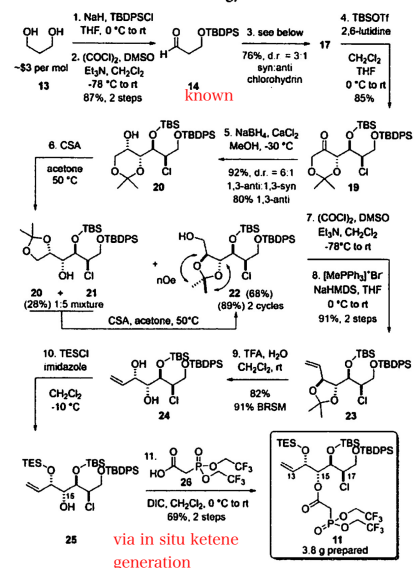


1.4% yield over 24 steps from methyl acetoacetate or 1.0% yield in 23 steps from 1,3-propanediol.

all macrocyclic intermediates were stable provided they were kept away from sunlight



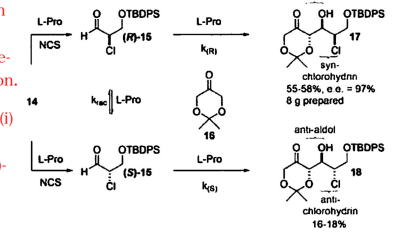
Scheme 1. Preparation of Phosphone 11 via  $\alpha$ -Chlorination DKR Aldol Strategy



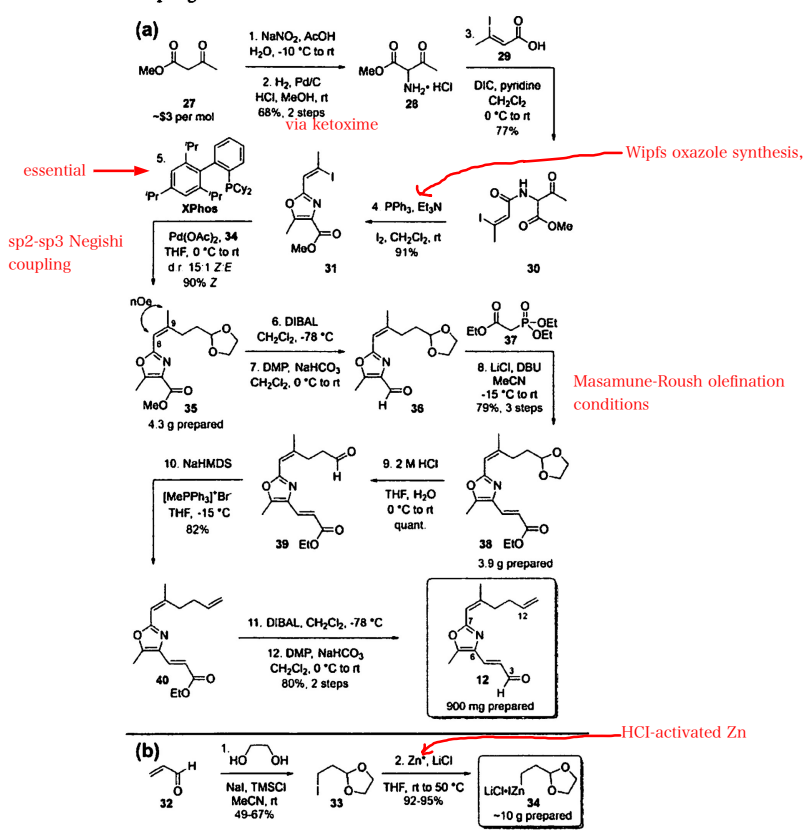
one-pot & chlorination dynamic kinetic resolution (DR) proline-catalyzed aldol reaction.

proline catalyzes the (i) chlorination, (ii) interconversion of (R)- and (S)-15, and (iii) subsequent aldol reaction with ketone 16,

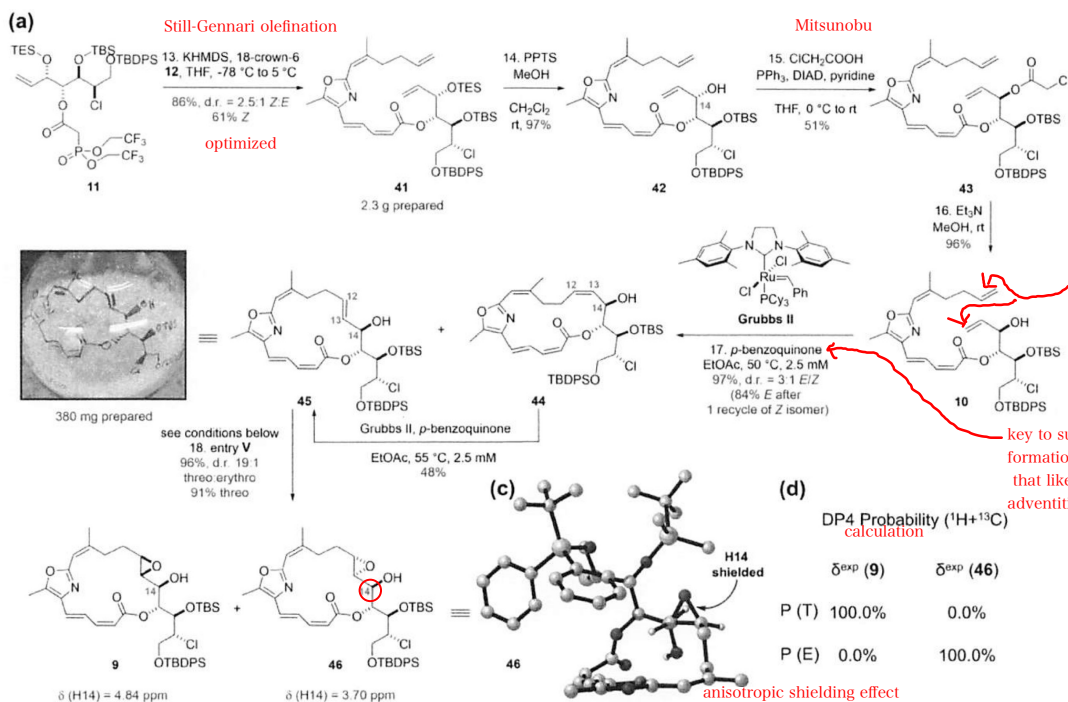
$\alpha$ -chlorination DKR aldol reaction



Scheme 2. Preparation of Key Oxazole 12 and Organozinc Coupling Partner 34



stable during purification



the enhanced reactivity relative to internal olefins

key to suppressing the formation of minor side products that likely result from adventitious ruthenium hydrides

Sharpless: kinetically mismatched

following Teranishi's pioneering work

Entry	Reagent	Solvent	T (°C)	t (h)	d.r. (T:E)	Yield
I	VO(acac) <sub>2</sub> , (10 mol%), <sup>t</sup> BuOOH	C <sub>6</sub> H <sub>6</sub>	rt	3 h	1:1	65%
II	VO(acac) <sub>2</sub> , (10 mol%), <sup>t</sup> BuOOH	CH <sub>2</sub> Cl <sub>2</sub>	-20	24 h	3:1	42%
III	VO(acac) <sub>2</sub> (10 mol%), <sup>t</sup> BuOOH, 3 Å MS	CH <sub>2</sub> Cl <sub>2</sub>	rt	1 h	2.5:1	74%
IV	Ti(OPr) <sub>4</sub> , (1.2 eq), <sup>t</sup> BuOOH, 3 Å MS	CH <sub>2</sub> Cl <sub>2</sub>	rt	1 h	11:1	89%
V	Ti(OPr) <sub>4</sub> , (1.2 eq), <sup>t</sup> BuOOH, 3 Å MS	CH <sub>2</sub> Cl <sub>2</sub>	-20 to -5	1 h	19:1	96%

reproducibility problems attributed to water

