Literature Presentation

Oxidation Catalysis of Nb(salan) Complexes: Asymmetric Epoxidation of Allylic Alcohols Using Aqueous Hydrogen Peroxide as an Oxidant

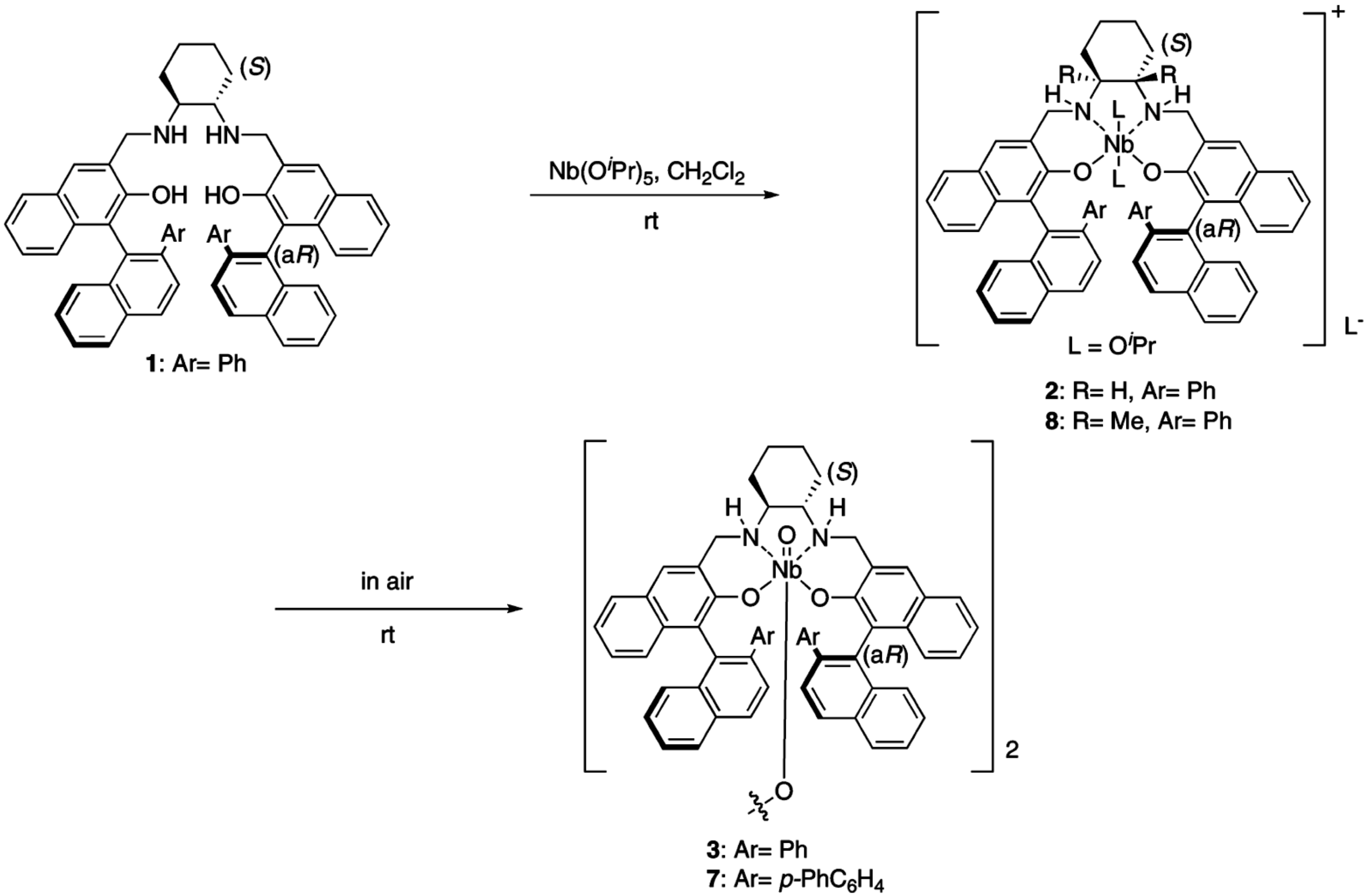
Egami, H.; Oguma, T.; Katsuki, T. *J. Am. Chem. Soc.* **2010**, ASAP.

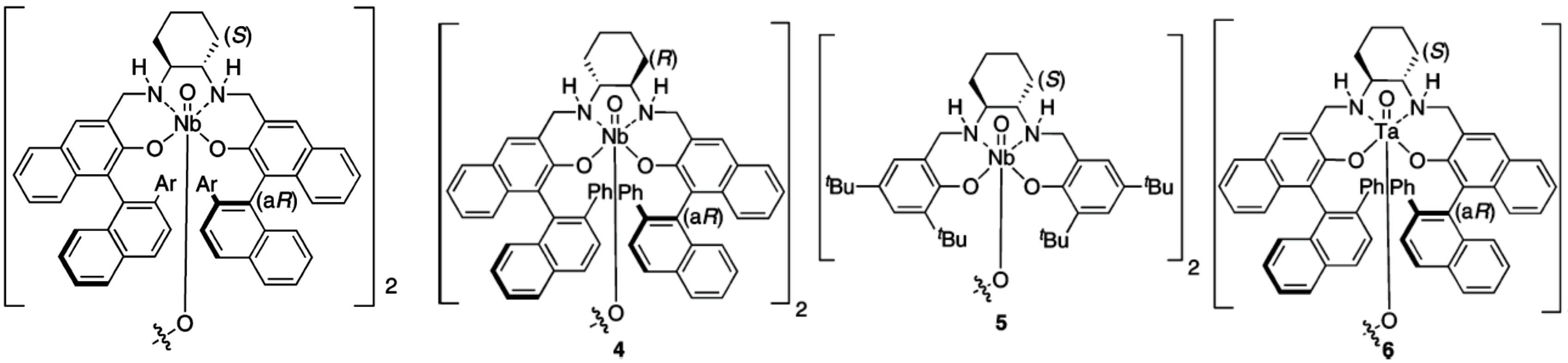
Wynter Gilson

April 16, 2010

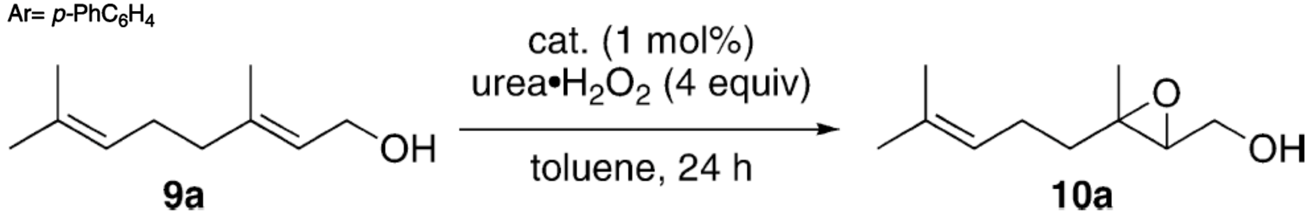
Wulff Group

Preparation of Catalyst



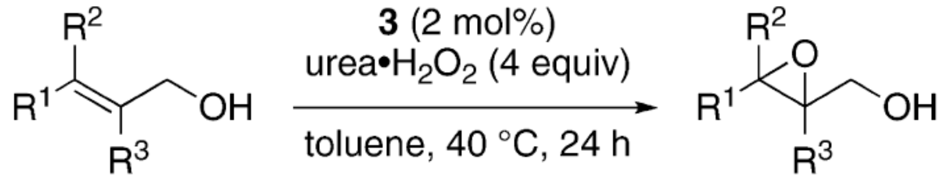


3: Ar= Ph
7: Ar= *p*-PhC$_6$H$_4$

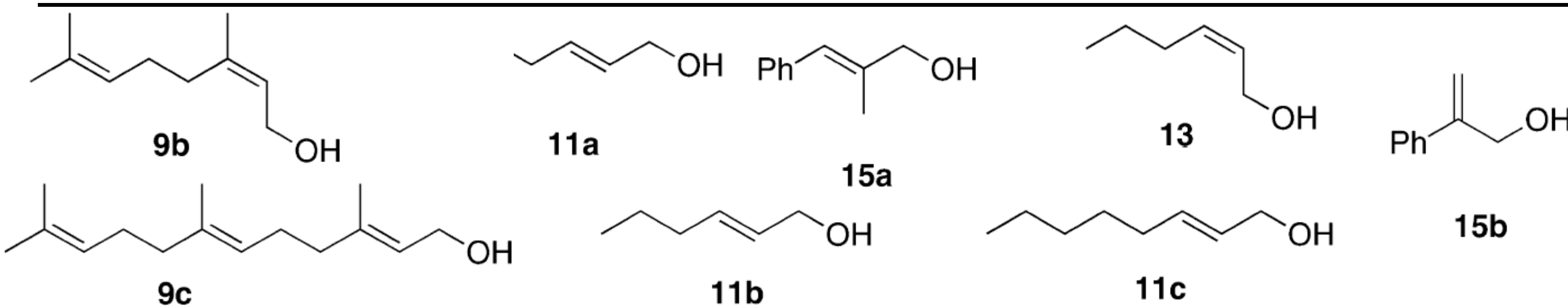


entry	cat.	solvent	T (°C)	yields (%)	ee (%)[b]
1	**3**	toluene	20	24	68
2	**4**	toluene	20	10	−42
3	**5**	toluene	20	N.R.[c]	
4	**6**	toluene	20	13	42
5	**3**	toluene	40	61	81
6	**3**	toluene	60	32	67
7	**3**	CH_2Cl_2	40	22	68
8	**3**	THF	40	<5	
9	**3**	AcOEt	40	10	56
10	**3**	MeOH	40	40	rac
11[d]	**3**	toluene	40	83	81 (2*S*, 3*S*)
12	**7**	toluene	40	58	79 (2*S*, 3*S*)

Epoxidation of Various Allylic Alcohols

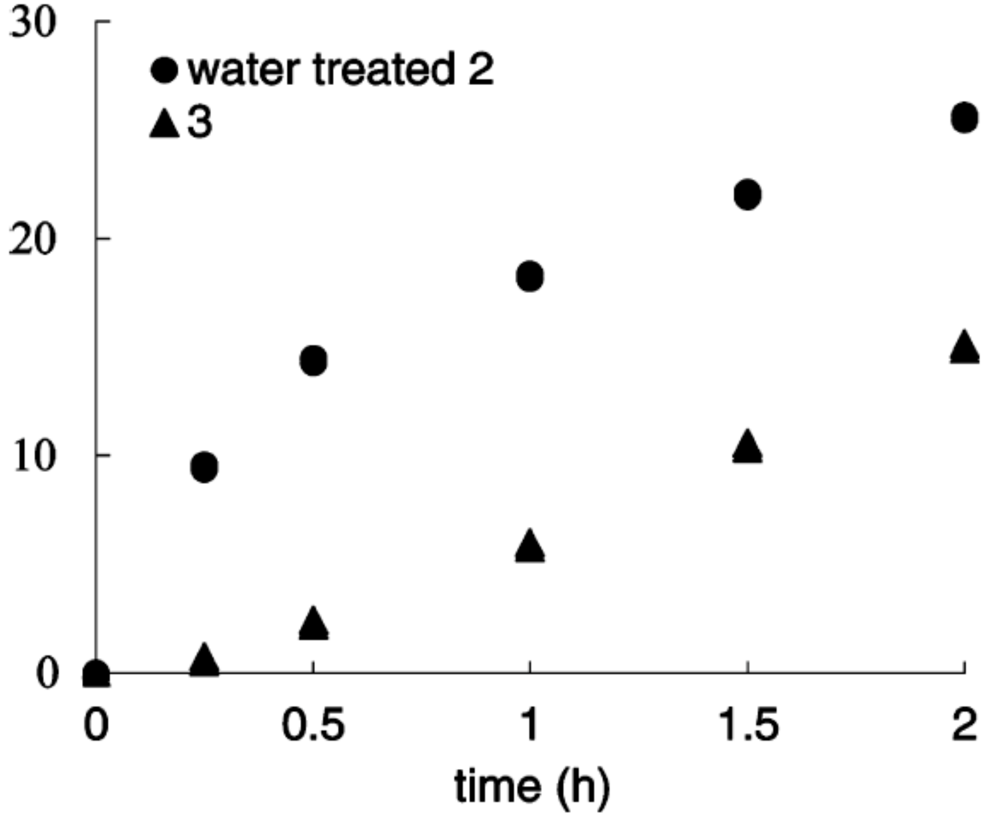


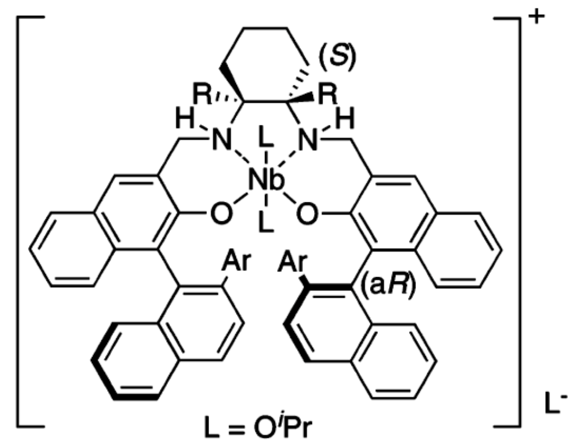
9, 11, 13, 15 → **10, 12, 14, 16**



entry	substrate	yield (%)	ee (%)[b]	config[c]
1	**9b**	66	80[d]	2*S*, 3*R*
2	**9c**	72	80[d]	2*S*, 3*S*
3	**11a**	83	79	2*S*, 3*S*
4	**11b**	78	80[d]	2*S*, 3*S*
5	**11c**	81	79[d]	2*S*, 3*S*
6	**13**	79	83[d]	2*S*, 3*R*
7	**15a**	86	72	2*S*, 3*S*
8	**15b**	83	68	2*S*

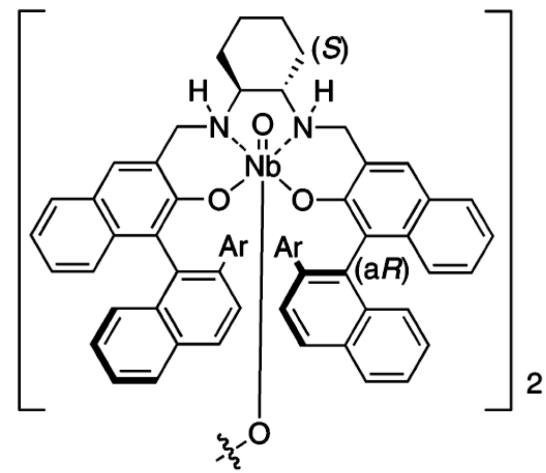
Induction period of Pretreated 2 vs 3





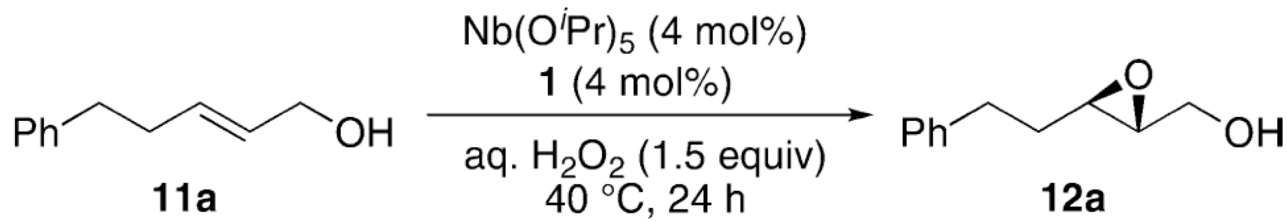
L = O^{i}Pr

2: R= H, Ar= Ph
8: R= Me, Ar= Ph



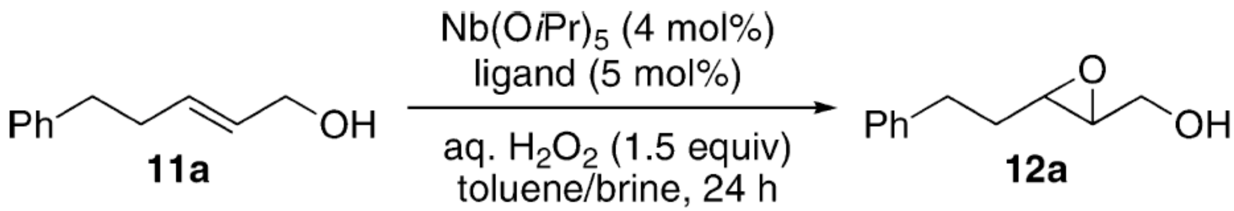
3: Ar= Ph
7: Ar= p-PhC_6H_4

Synthesis of Monomer Directly



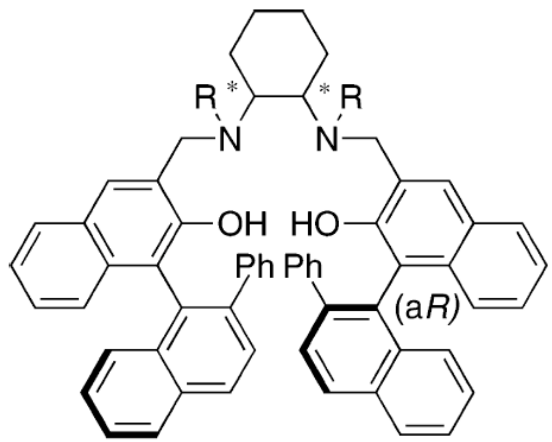
entry	solvent	yield (%)	ee (%)[b]
1[c]	toluene	53	58
2[c]	toluene/brine	74	80
3[d]	toluene	43	36
4[d]	toluene/H_2O	48	58
5[d]	toluene/brine	21	72

Optimization of the New Method

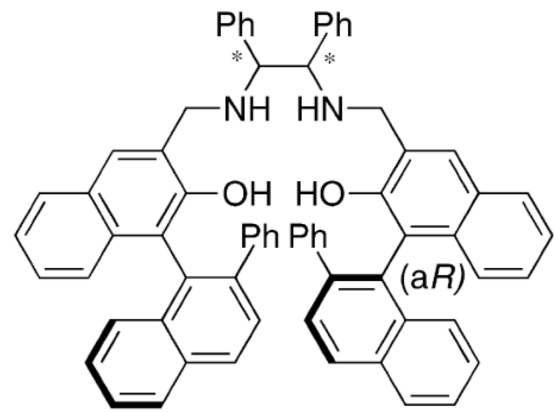


entry	temp (°C)	ligand	yield (%)	ee (%)[b]	config[c]
1[d]	40	**1**	74	80	2*S*, 3*S*
2	40	**1**	80	81	2*S*, 3*S*
3[e]	40	**1**	82	81	2*S*, 3*S*
4[f]	40	**1**	71	81	2*S*, 3*S*
5	20	**1**	28	75	2*S*, 3*S*
6	60	**1**	55	80	2*S*, 3*S*
7	40	**17**	31	48	2*R*, 3*R*
8	40	**18**	46	52	2*R*, 3*R*
9	40	**19**	72	87	2*S*, 3*S*
10[g]	40	**19**	76[h]	91	2*S*, 3*S*
11[g]	40	**20**	81[h]	92	2*S*, 3*S*
12	40	**21**	N.R.[i]		
13	40	**22**	N.R.[i]		

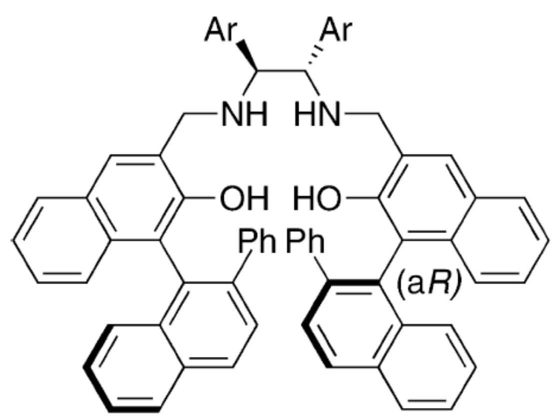
Various Ligands



1: (a*R*, *S*), N = H
17: (a*R*, *R*), N = H
22: (a*R*, *S*), N = Me



18: (a*R*, *R*)
19: (a*R*, *S*)



Ar = 1-naphthyl

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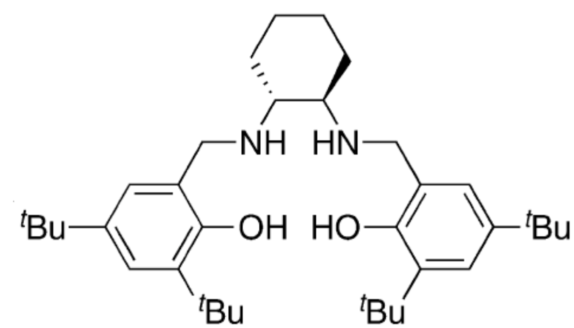

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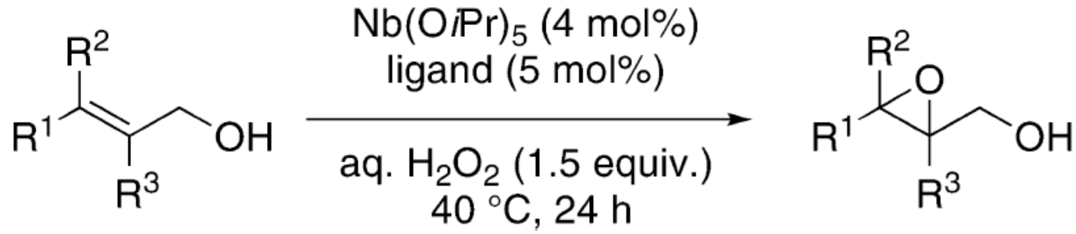
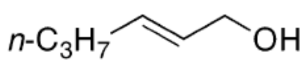
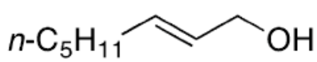
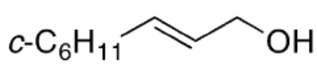
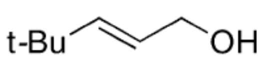
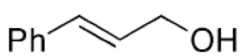
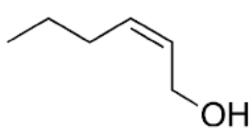
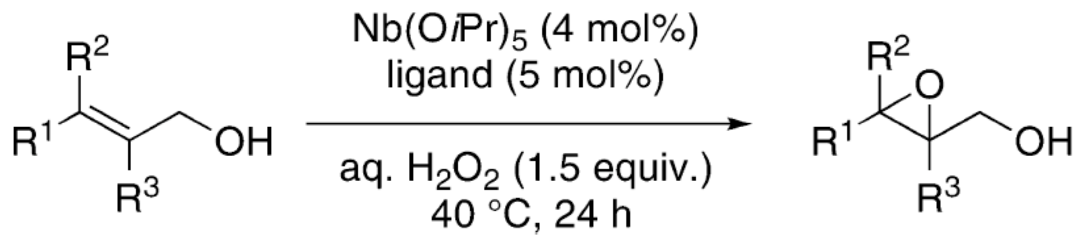
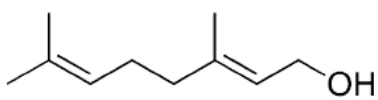
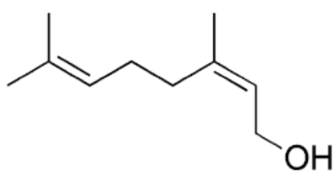
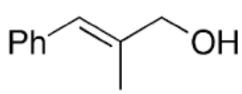
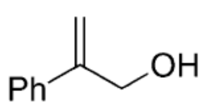
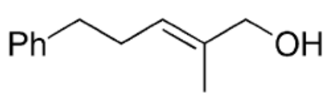
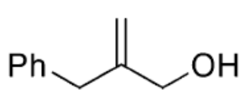
Epoxidation Using Ligands 20 and 1



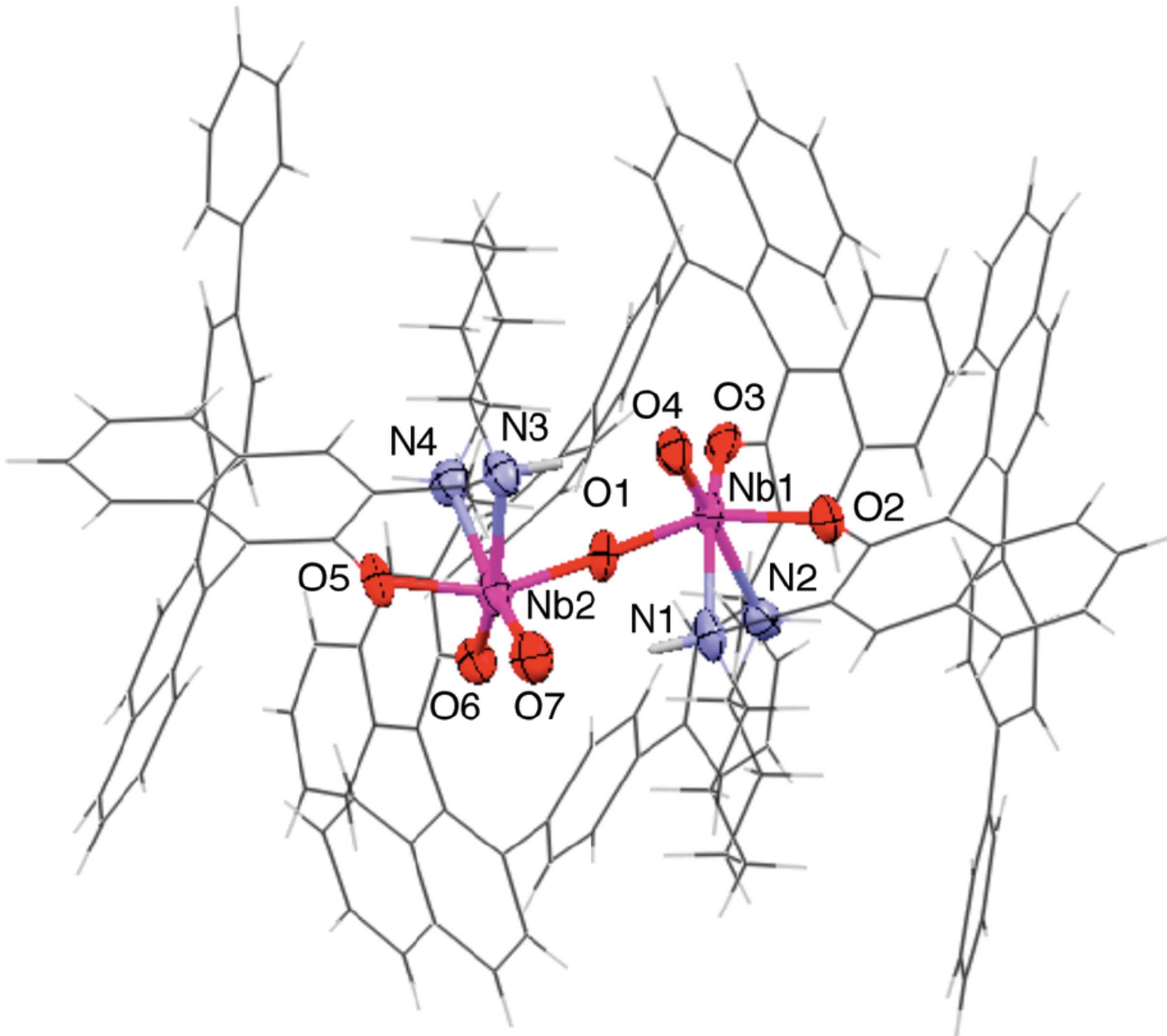
1		**11b**	**20**	$CHCl_3$/brine	57	91[e]	2*S*, 3*S*
2		**11c**	**20**	$CHCl_3$/brine	79	93[e]	2*S*, 3*S*
3		**11d**	**20**	$CHCl_3$/brine	82	93[e]	2*S*, 3*S*
4		**11e**	**20**	$CHCl_3$/brine	52	95[e]	2*S*, 3*S*
5		**11f**	**20**	$CHCl_3$/brine	61	74	2*S*, 3*S*
6		**13**	**1**	toluene/brine	52[f]	85[e]	2*S*, 3*R*

Epoxidation Using Ligands 1 and 18

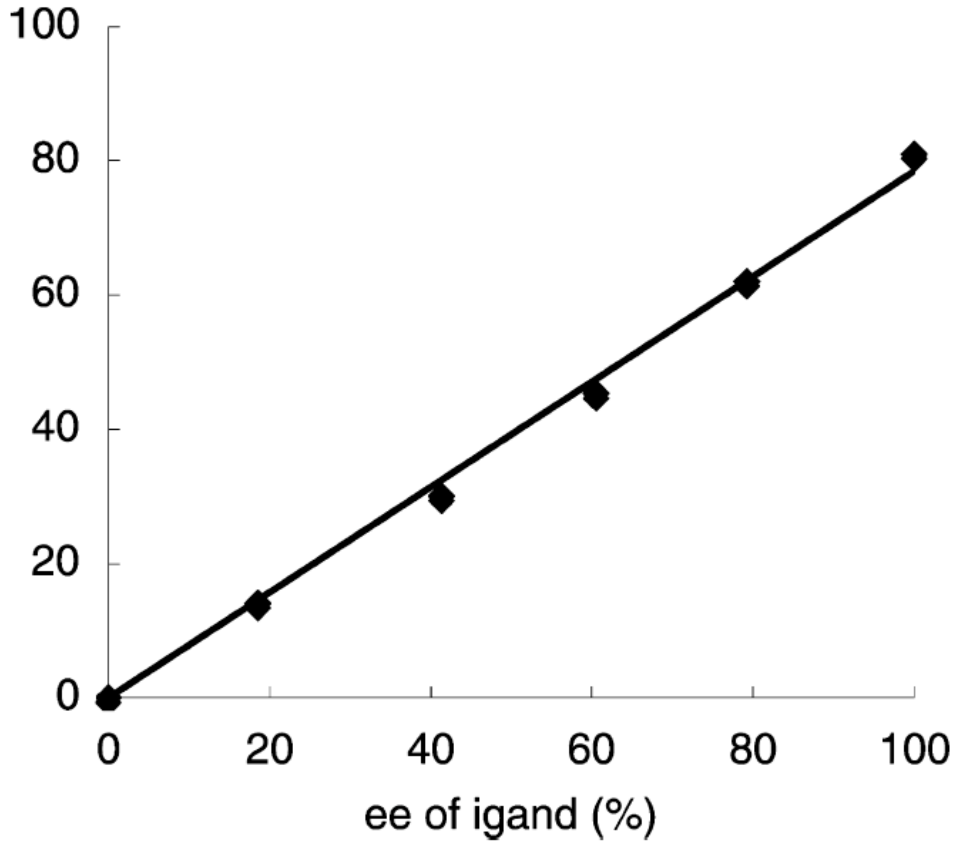


7		**9a**	**1**	$CHCl_3$/brine	82	84[e]	2*S*, 3*S*
8		**9b**	**1**	$CHCl_3$/brine	76	83[e]	2*S*, 3*R*
9		**15a**	**18**	C_6H_5F /brine	40	83	2*R*, 3*R*
10		**15b**	**18**	toluene/brine	43[f]	85	2*R*
11[g]		**15c**	**18**	C_6H_5F/brine	64	90	-
12		**15d**	**18**	toluene/brine	52[f]	90	2*R*

Crystal Structure of Dimer



Correlation Between ee's of Ligand 1 and *ee*'s of Product of 5-phenyl-2-pentenol



Proposed Mechanism