Literature-1

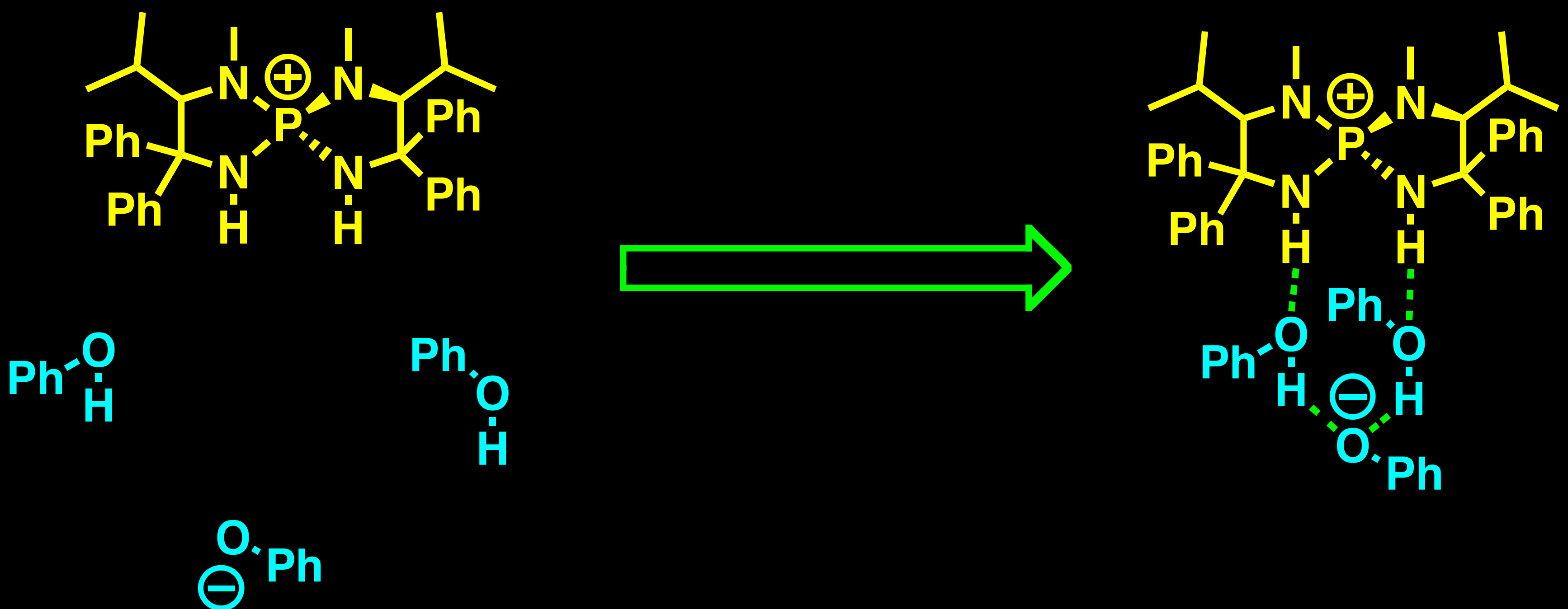
Kishor Mohanan

Chiral Supramolecular Catalysis

Chiral Organic Ion Pair Catalysts Assembled Through a Hydrogen-Bonding Network

Takashi Ooi and co-workers, SCIENCE, 2009, 326, 120

Nagoya University



Ph
Ph
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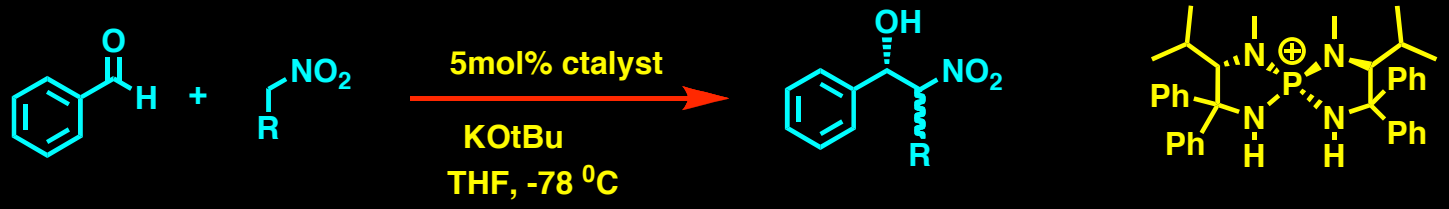
Ph

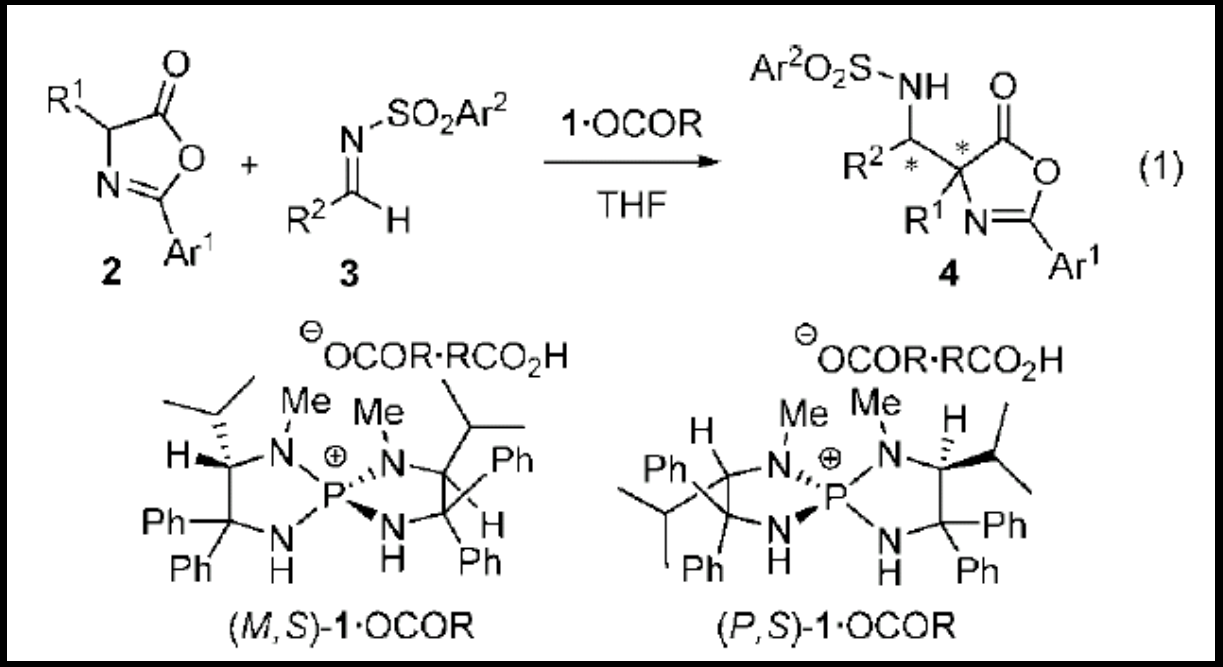
Background….



19:1 dr (anti:syn)

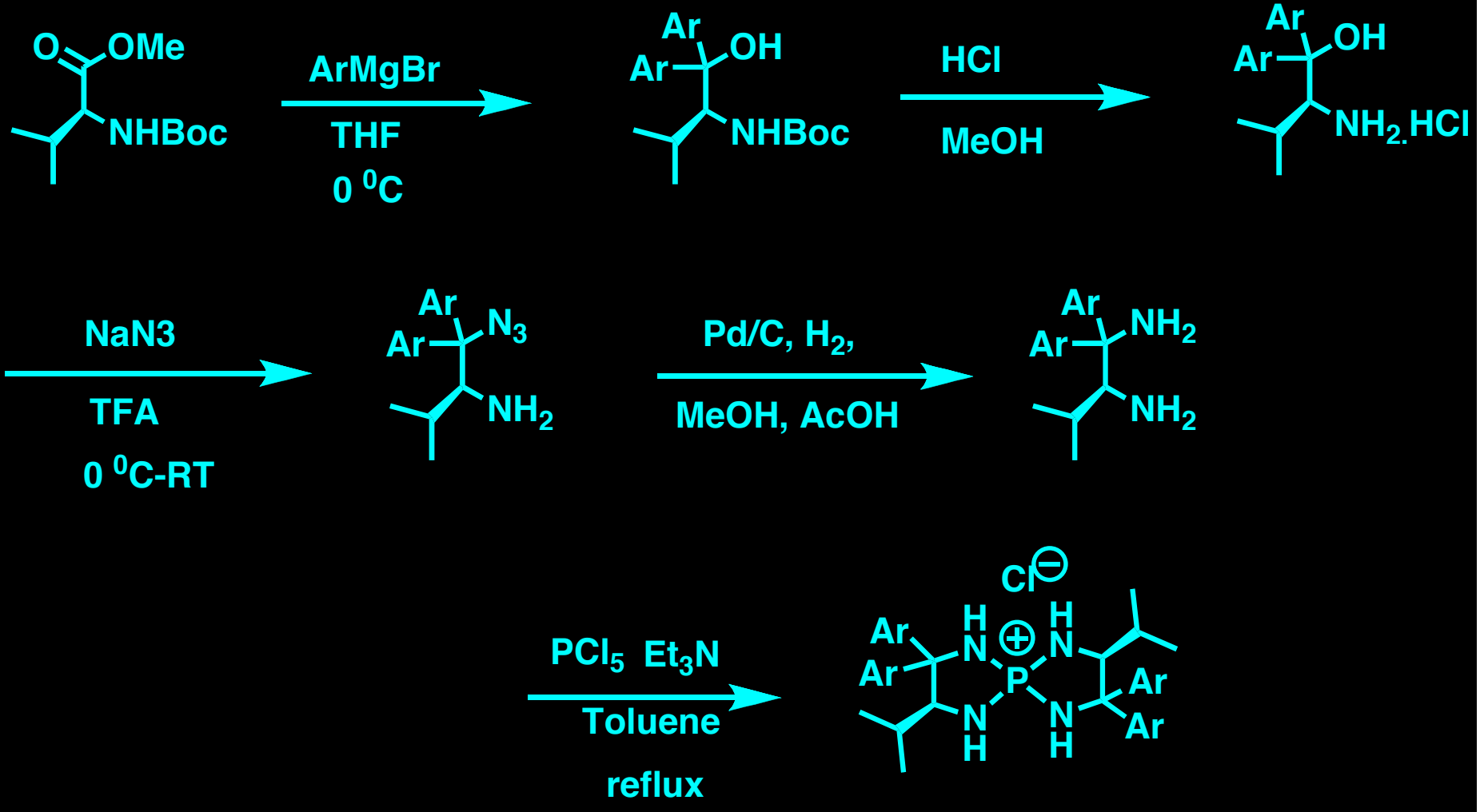
Up to 97% ee

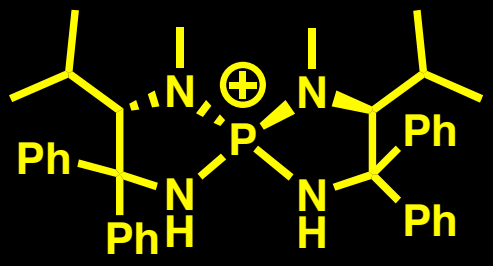
Takashi Ooi and co-workers, J. Am. Chem. Soc. 2007, 129, 12392

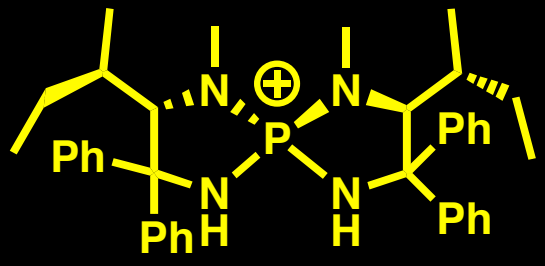


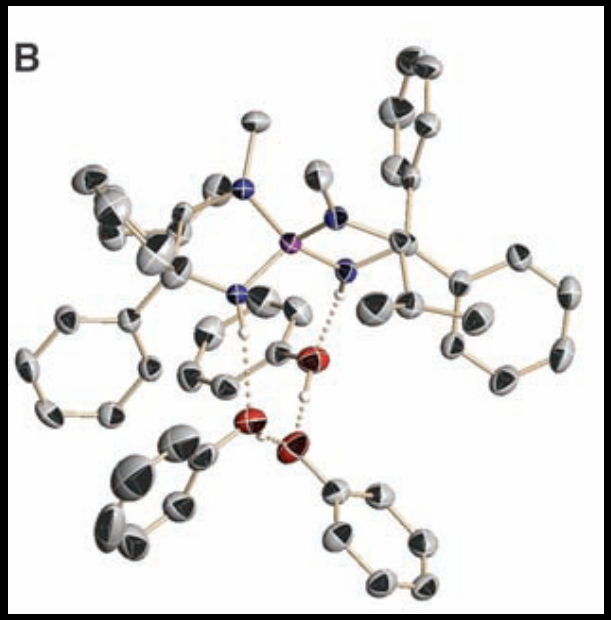
Takashi Ooi and co-workers, J. Am. Chem. Soc. 2008, 130, 14088

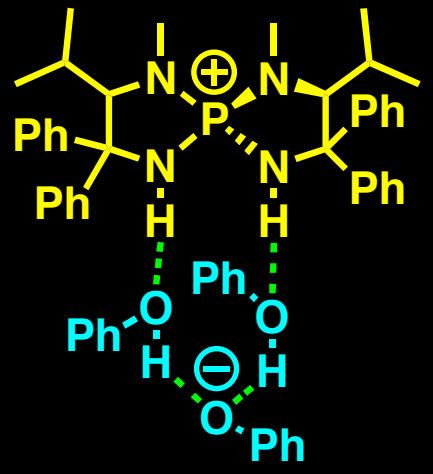
Synthesis of the catalyst….



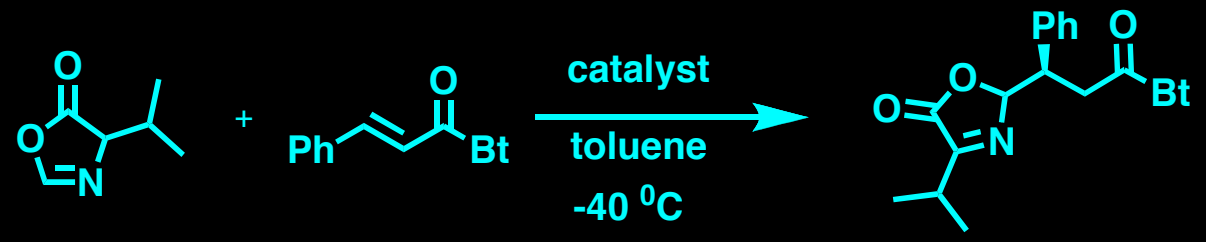


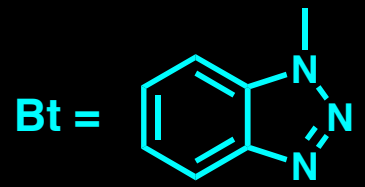


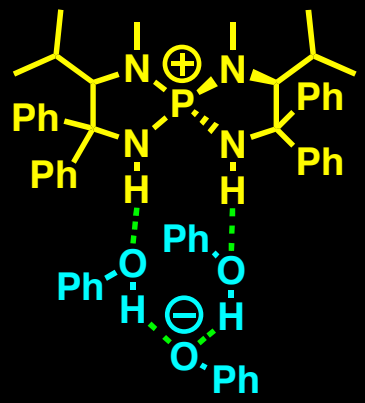


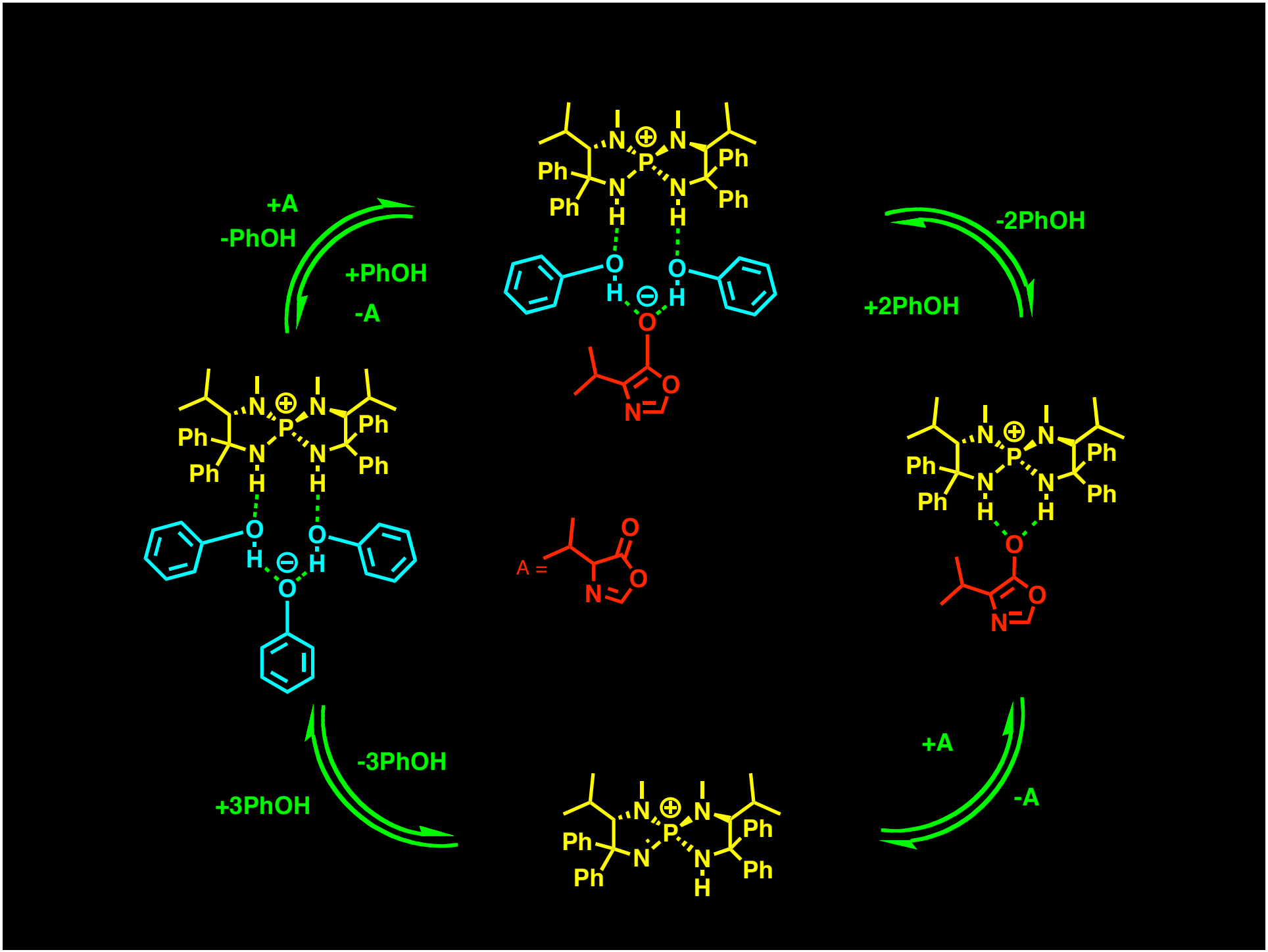


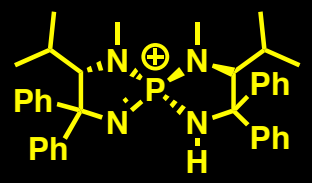
X-ray analysis of the supramolecular assembly


catalyst
toluene
-40 0C
Ph
O
Bt
N
dr = 20:1
ee up to 98%

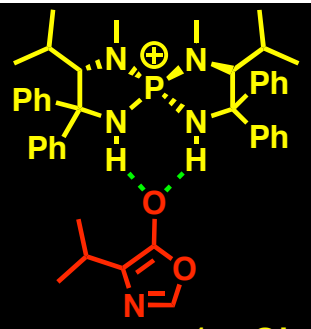

Bt =
N
N
N


N
P
N
Ph
Ph
Ph
Ph
H
H
Ph
O
Ph
H
O
H
O
Ph

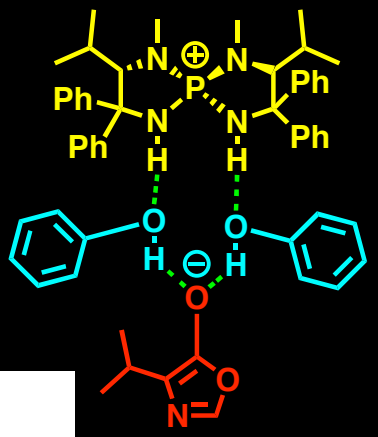

+A
-PhOH
+PhOH
-A
-2PhOH
+2PhOH
-3PhOH
+3PhOH
+A
-A
A =

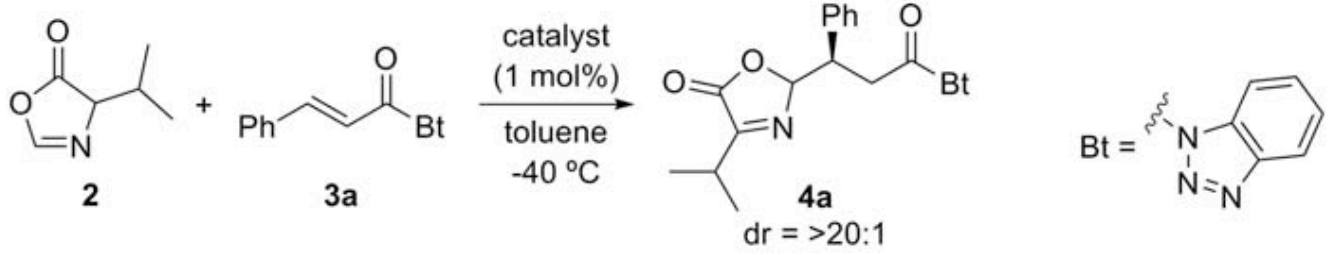


1a’

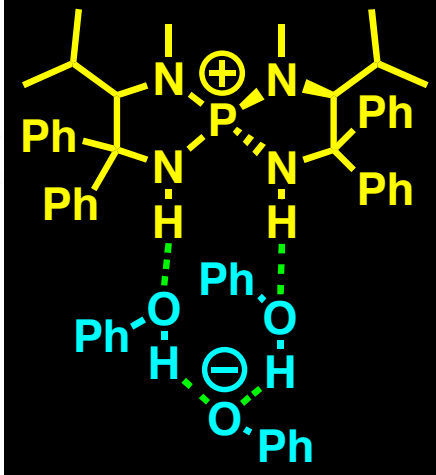


1a.2’

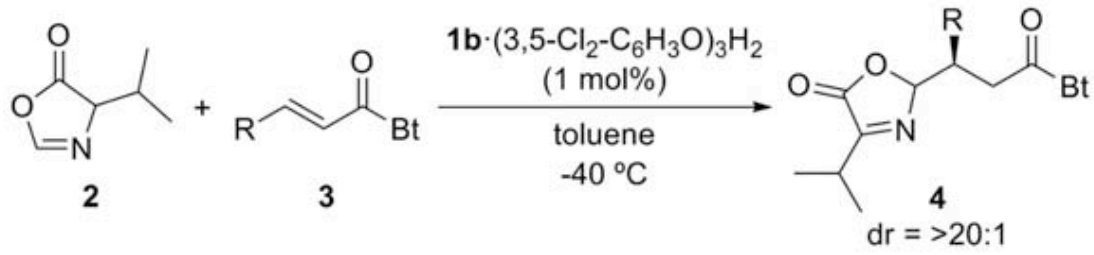




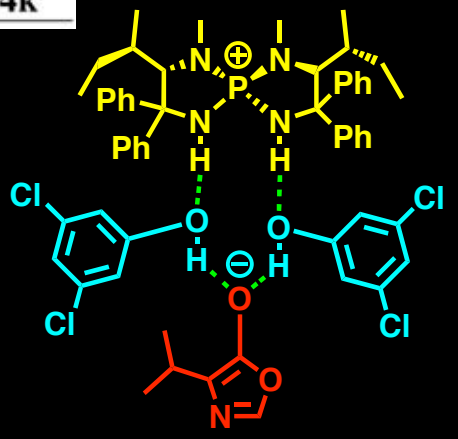
Entry	Catalyst	Conc (mM)	Time (h)	Yield (%)	ee (%)
1	**1a**·$(PhO)_3H_2$	1	6	99	60
2	**1a’**	1	2	99	34
3	**1a’** + 3PhOH	1	10	98	62
4	**1a·2’** + 3PhOH	1	16	87	61
5	**1a**·(4-Me–$C_6H_4O)_3H_2$	1	4	96	58
6	**1a**·(4-Cl–$C_6H_4O)_3H_2$	1	10	97	75
7	**1a**·(2-Cl–$C_6H_4O)_3H_2$	1	12	94	63
8	**1a**·(3-Cl–$C_6H_4O)_3H_2$	1	6	93	70
9	**1a**·(3,5-Cl_2–$C_6H_3O)_3H_2$	1	16	92	80
10*	**1a**·(3,5-Cl_2–$C_6H_3O)_3H_2$	2	24	99	85
11†	**1a**·(3,5-Cl_2–$C_6H_3O)_3H_2$	5	18	98	89
12‡	**1a**·(3,5-Cl_2–$C_6H_3O)_3H_2$	10	20	94	89
13§	**1a**·(3,5-Cl_2–$C_6H_3O)_3H_2$	10	4	99	87
14§	**1b**·(3,5-Cl_2–$C_6H_3O)_3H_2$	10	4	95	95



1a.$(PhO)_3H_2$

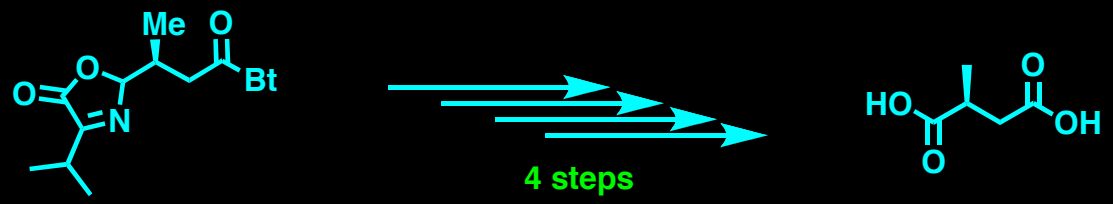


Entry	R (3)	Time (h)	Yield (%)	ee (%)	Prod
1	4-MeO–C_6H_4 (**3b**)	24	98	97	**4b**
2	4-Br–C_6H_4 (**3c**)	21	98	98	**4c**
3	2-Me–C_6H_4 (**3d**)	8	90	93	**4d**
4	3-Br–C_6H_4 (**3e**)	4	96	95	**4e**
5	1-Naph (**3f**)	12	91	95	**4f**
6	2-Furyl (**3g**)	22	91	96	**4g**
7	Me (**3h**)	2	97	96	**4h***
8	$Me(CH_2)_4$ (**3i**)	1	96	95	**4i**
9	$Ph(CH_2)_2$ (**3j**)	2	92	96	**4j**
10	Cyclohexyl (**3k**)	4	93	98	**4k**



To summarize….

- Design of functional supramolecular catalysis
- The stereocontrolling ability can be fine tuned by modifying both chiral and achiral components
- Functionalization without loss of optical purity



1) DBU, CH_3OH, CH_2Cl_2 2) DBU, CH_3OH 3) $NaNO_2$, AcOH, Ac_2O 4) LiOH, H_2O_2, H_2O, THF

Thank YOU