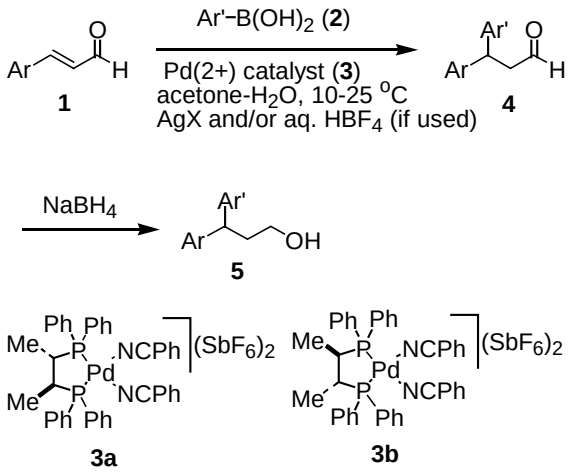
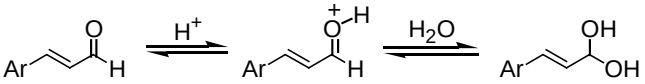
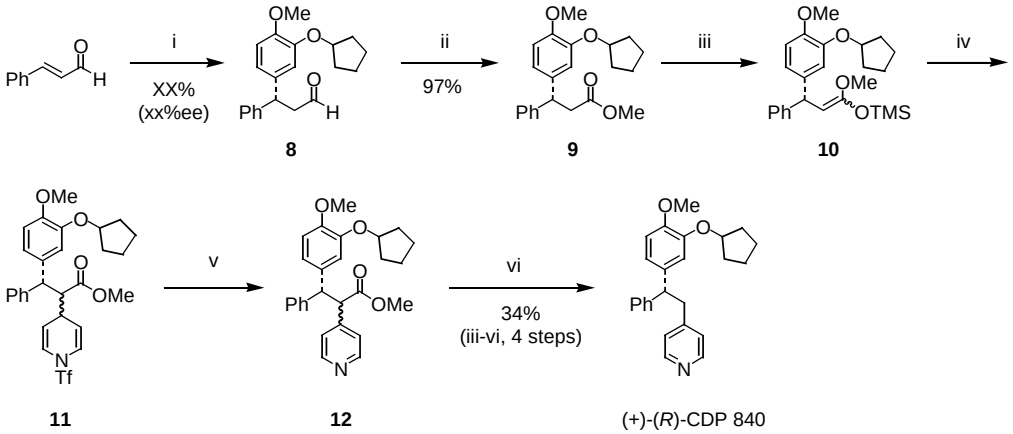

Ar'−B(OH)2 (2)
Pd(2+) catalyst (3)
acetone-H2O, 10-25 °C
AgX and/or aq. HBF4 (if used)
Ar
O
H
1
Ar'
4
NaBH4
OH
5
Ph
Me
P
Pd
NCPh
(SbF6)2
3a
3b

Scheme 1.



1 **6** **7**

Scheme 2.



(i) 3-(*c*-C_5H_9O)-4-MeOPhB$(OH)_2$ (2 eq), [Pd(*R*,*R*-chiraphos) $(PhCN)_2$]$(SbF_6)_2$ (**3b**, 0.5 mol%), acetone, aq HBF_4, 10 ^oC, 20 h.
(ii) I_2 (2.5 eq), KOH (2.5 eq), MeOH, 0 to 20 °C, 20 h.
(iii) LDA (1.5 eq), TMSCl (2 eq), THF, -78°C to rt, 3 h.
(iv) $PyTf_2O$ (3 eq), CH_2Cl_2, 0 °C, 1 h.
(v) *t*BuONa (3 eq), DMSO, 20 °C, 20 min.
(vi) (a) EtOH- water, NaOH, reflux, 0.5 h. (b) dioxane-water, conc. HCl, reflux, 5 h.

Scheme 3. Synthesis of CDP 840

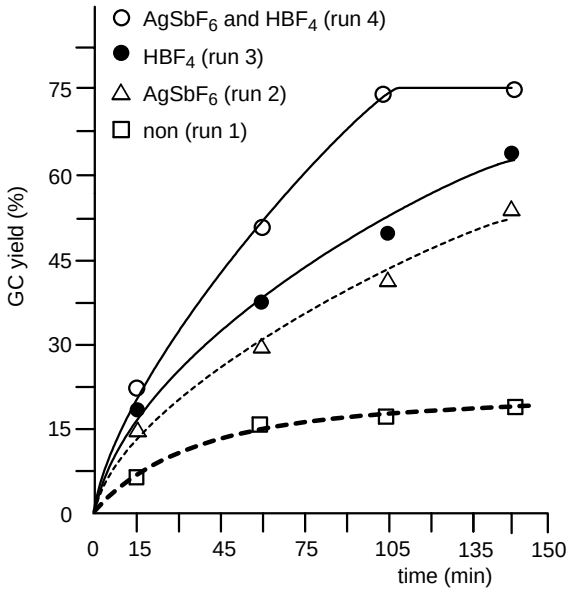
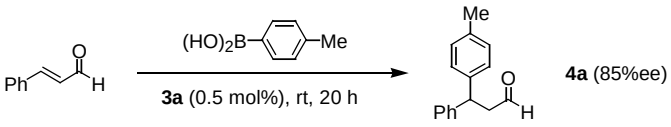


Figure 1. Effects of $AgSbF_6$ and HBF_4 on Reaction Rates (see, Table 1)

Table 1: Reaction conditions[a]



4a (85%ee)

run	AgX (mol%)	solvent and acid	yield/%	method
1	none	acetone/H_2O (10/1)	54	
2	$AgSbF_6$ (10)	acetone/H_2O (10/1)	75	
3	none	acetone/H_2O/HBF_4 (20/2/1)	81	A
4	$AgSbF_6$ (10)	acetone/H_2O/HBF_4 (20/2/1)	70	B
5	$AgBF_4$ (10)	acetone/H_2O/HBF_4 (20/10/1)	64	C

a) A mixture of PhCH=CHCHO (0.5 mmol), 4-MePhB$(OH)_2$ (1 mmol), Pd(*S*,*S*-chiraphos)$(PhCN)_2$] $(SbF_6)_2$ (**3a**, 0.5 mol%), AgX (10 mol%, if used) and 42wt% HBF_4 (0.1 ml, if used) in acetone (2 ml) and water (0.2 or 1 ml) was stirred for 20 h at room temperature.

Table 2. Asymmetric 1,4-Addition of Arylboronic Acids to β-Arylenals

run	**1** (Ar=)	**2** (Ar'=)	method[a]	temp/°C	yield/%[b]	product No	%ee[c]
1	Ph	3-MeOPh	A	10	29	**4b**	92
2	Ph	3-MeOPh	C	10	78	**4b**	92
3	Ph	2-MeOPh	B	rt	trace	**4c**	-
4	Ph	4-MeOPh	B	rt	59	**4d**	86
5	Ph	3-(*n*-C_4H_9O)Ph	C	rt	76	**4e**	91
6	Ph	3-($PhCH_2O$)Ph	C	10	76	**4f**	90
7	Ph	3,4-$(MeO)_2$Ph	A	10	66	**4g**	92
8	Ph	3-Me-4-MeOPh	A	10	61	**4h**	90
9	Ph	3-(*c*-C_5H_9O)-4-MeOPh[d]	A	10	72 (70)	**4i**	94 (*S*)
10	Ph	3,5-Me_2-4-MeOPh	A	10	80	**4j**	88
11	Ph	4-PhPh	A	10	79	**4k**	97
12	4-MeOPh	3-MeOPh	B[e]	10	78	**4l**	91
13	2-MeOPh	3-MeOPh	B	rt	72	**4m**	91
14	2-naphthyl	3-MeOPh	B	rt	86 (89)	**4n**	90
15	2-naphthyl	3-(*c*-C_5H_9O)-4-MeOPh[d]	C	rt	80 (80)	**4o**	94
16	4-MePh	3-MeOPh	C	10	78	**4p**	91
17	4-PhPh	3-MeOPh	B	rt	76 (70)	**4q**	90
18	4-PhPh	3-(*c*-C_5H_9O)-4-MeOPh[d]	C	rt	80(75)	**4r**	93

a) see, Table 1. Method A: acetone/H_2O/aq 42wt% HBF_4(20/2/1); method B: acetone/H_2O/aq 42wt% HBF_4 (20/2/1) and $AgSbF_6$ (10 mol%); method C: acetone/H_2O/aq 42wt% HBF_4(20/10/1) and $AgBF_4$ (10 mol%).
b) NMR yields and isolated yields are in parentheses.
c) Enantiomeric excess of the corresponding alcohol derivatives (**5**) obatined by reduction **4** with $NaBH_4$.
d) 3-cyclopentyloxy-4-methoxyphenyl group. e) in acetone/aq 42wt% HBF_4(20/1) and $AgSbF_6$ (10 mol%).