Advanced Synthesis & Catalysis

Supporting Information

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Extensive Re-Investigations of Pressure Effects in Rh Catalyzed Asymmetric Hydrogenations.

Mohamad Alame, Nathalie Pestre and Claude de Bellefon*

Laboratoire de Génie des Procédés Catalytiques
UMR 2214, CNRS-CPE Lyon
69616 Villeurbanne, France.
Claude.debellefon@lgpc.cpe.fr

I-Criteria for assessment of pressure effect on ee: ee variation = Δee

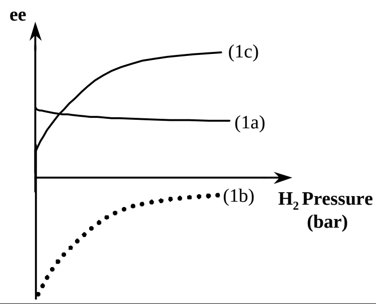
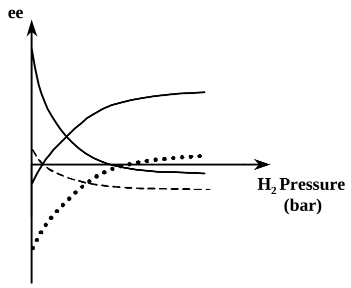
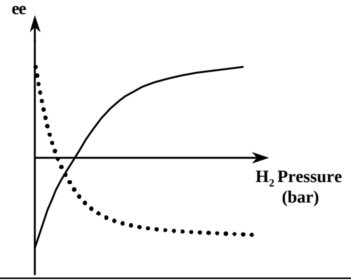
In order to quantify the observed influence of hydrogen pressure on enantiomeric excess, a variation factor (Δee) is proposed, taking into consideration the enantiomeric excess difference between maximal and minimal pressure used in the experiment :

$$\Delta ee = |ee_{max}| - |ee_{min}|$$

When the enantiomeric excess, whatever the pressure of hydrogen, is close to zero ($|ee|<+4$), this catalyst is not consider. When the enantiomeric excess is sufficiently important at least for one of two values ($|ee| \geq +4$), two cases are considered (Table 1a):

- Case 1: ee_{min} and ee_{max} have the same sign :
  The result verifies the condition $|ee| > +4$. One of the enantiomers is thus majority for all the pressure range of the study. The evolutions of enantiomeric excess are considered as (1a) Negligible if $-4 \leq \Delta ee \leq +4$, (1b) negative if $\Delta ee < -4$ and (1c) positive if $\Delta ee > +4$.
- Case 2: There is change of the majority enantiomer between the minimal and maximal pressure, i.e. enantiomeric excess sign changes. Two types of behavior are suggested:
  - o The results verify the condition $|ee_{max}|$ <u>or</u> $|ee_{min}| \geq +4$ (2a). The effect of the pressure is remarkable. For this situation, the tools proposed with case 1 are used.
  - o The results verify the condition $|ee_{max}|$ <u>and</u> $|ee_{min}| \geq +4$ (2b). Whatever the value of Δee, both beneficial and detrimental effects are taken into account.

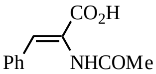
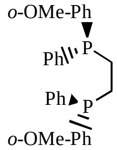
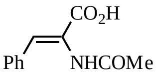
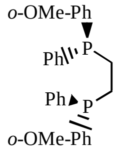
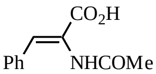
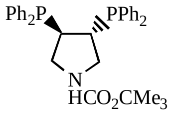
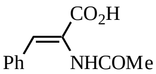
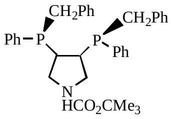
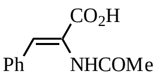
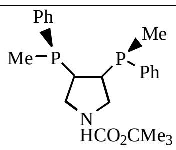
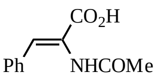
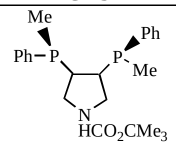
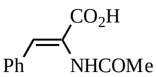
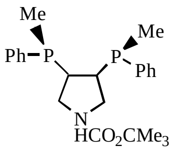
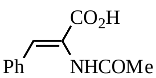
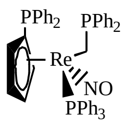
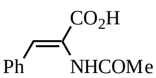
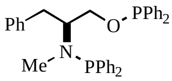
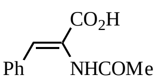
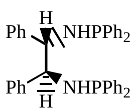
Table 2sup: Quantification of the hydrogen effect on the enantiomeric excess.

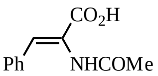
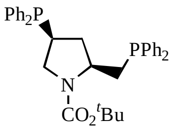
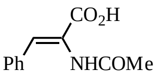
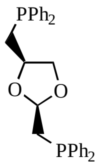
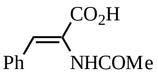
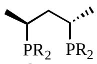
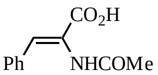
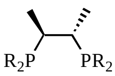
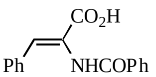
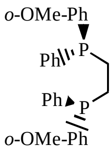
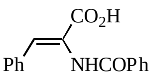
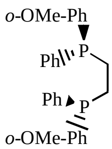
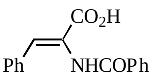
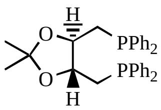
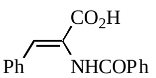
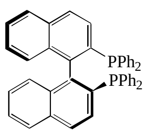
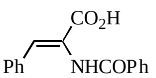
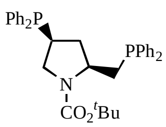
Situation		Condition	Δee	Effect on Δee	Examples
Case 1 ee_{max} and ee_{min} have the same sign $\|ee\| \geq +4$	1a		$-4 < \Delta ee < +4$	?	
	1b		$\Delta ee < -4$	?	
	1c		$\Delta ee > +4$	?	
Case 2 ee_{max} and ee_{min} have different signs	2a	$\|ee_{max}\|$ <u>or</u> $\|ee_{min}\|$ $\geq +4$	case 1a, 1b, 1c are used		
	2b	$\|ee_{max}\|$ <u>and</u> $\|ee_{min}\|$ $\geq +4$	For all the value of Δee	? and ?	

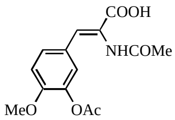
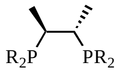
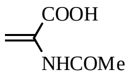
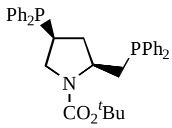
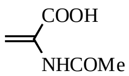
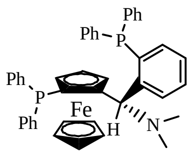
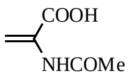
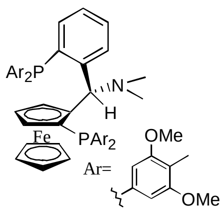
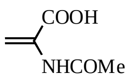
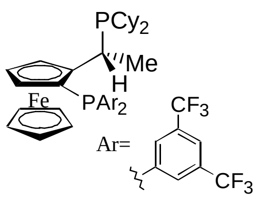
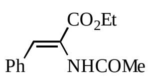
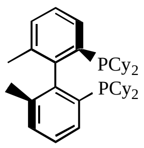
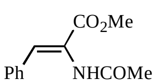
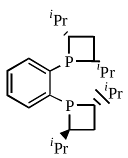
NB : Detrimental↓, Beneficial↑, Negligible↔.

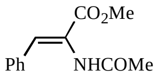
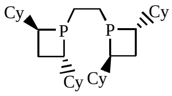
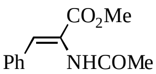
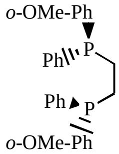
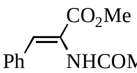
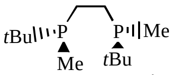
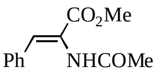
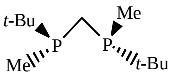
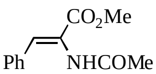
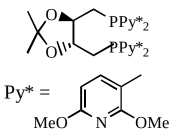
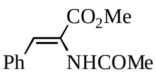
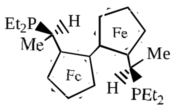
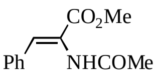
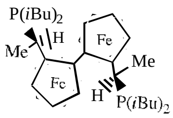
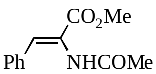
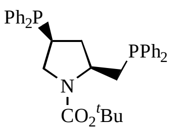
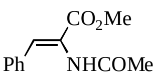
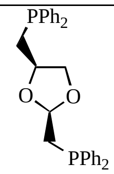
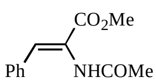
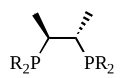
$ee_{max, min}$ = enantiomeric excess observed with maximal and minimal hydrogen pressures.

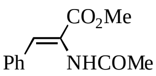
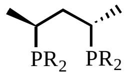
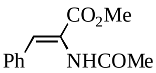
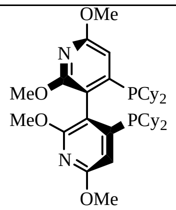
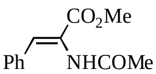
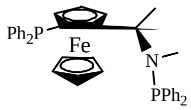
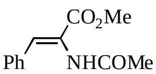
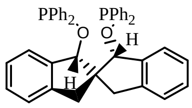
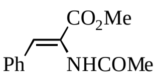
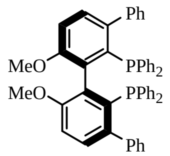
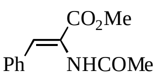
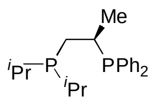
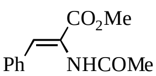
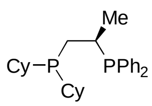
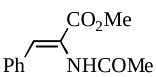
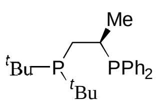
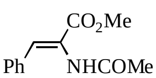
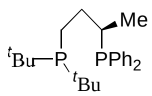
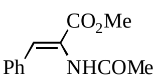
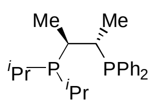
II-Literature survey on 110 Rh/chiral diphosphine/substrate reaction systems.

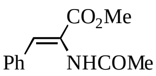
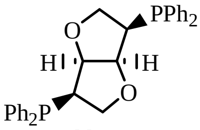
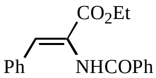
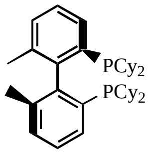
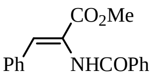
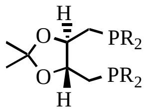
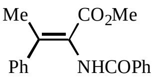
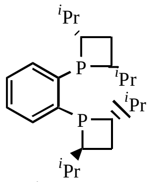
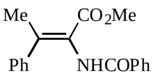
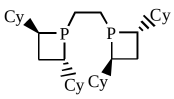
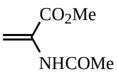
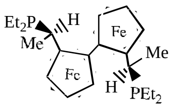
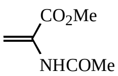
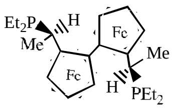
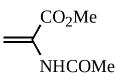
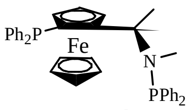
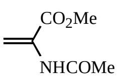
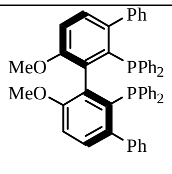
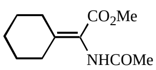
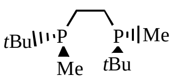
Entry	Substrate	Ligand	Conditions*	Δee **	Ref.
1	 **S1**	 **(*R*,*R*)-DiPAMP**	S/Rh = 2000 [Rh] = 2.10^{-4} *i*-PrOH à 88 % T = 25 **P_{H_2} : 3,5-27**	ee_{min} = +92,8 ee_{max} = +92,8 Δ**ee** = 0 **Negligible**	1
2	 **S1**	 (*R*,*R*)-DiPAMP	S/Cata [c] = 200 3 mL [bmim][BF_4] 9 mL *i*PrOH T = 55 t = 1 h **P_{H_2} : 2,5-7,5**	ee_{min} = +92 ee_{max} = +91 Δ**ee** = -1 **Negligible**	2
3	 **S1**	 **C2-4**	[S] = 0,1 S/Rh = 200-2000 T = 22 30-50 mL MeOH **P_{H_2} : 1-50**	ee_{min} = +98 ee_{max} = +98 Δ**ee** = 0 **Negligible**	3
4	 **S1**	 **C2-11**	[S] = 0,1 S/Rh = 200-2000 T = 22 30-50 mL MeOH **P_{H_2} : 1-75**	ee_{min} = +74,5 ee_{max} = +78 Δ**ee** = +4,5 **Beneficial**	3
5	 **S1**	 **C2-5**	[S] = 0,1 S/Rh = 200-2000 T = 22 30-50 mL MeOH **P_{H_2} : 1-75**	ee_{min} = +64 ee_{max} = +59,4 Δ**ee** = -4,6 **Detrimental**	3
6	 **S1**	 **C2-6**	[S] = 0,1 S/Rh = 200-2000 T = 22 30-50 mL MeOH **P_{H_2} : 1-75**	ee_{min} = +34,1 ee_{max} = +26,4 Δ**ee** = -7,7 **Detrimental**	3
7	 **S1**	 **C2-12**	[S] = 0,1 S/Rh = 200-2000 T = 22 30-50 mL MeOH **P_{H_2} : 1-75**	ee_{min} = +20,9 ee_{max} = +42,4 Δ**ee** = +21,5 **Beneficial**	3
8	 **S1**	 **X3-7**	n_S = 3 S/Rh = 200 [f] T = 20-23 **P_{H_2} : 0,3-90**	ee_{min} = +76 ee_{max} = +40 Δ**ee** = -36 **Detrimental**	4
9	 **S1**	 **PheNOP**	[S] = 0,002 S/Rh = 100 T = 20°C C_6H_6/MeOH = 1 : 1 **P_{H_2} : 1-40**	ee_{min} = -22 ee_{max} = -68 Δ**ee** = +46 **Beneficial**	5
10	 **S1**	 **X4-4**	[Rh] [c] = $2\text{-}2{,}5.10^{-3}$ S/Rh = 125 T = 25 t = 10-40 min χ = 90-100 EtOH **P_{H_2} : 1-5**	ee_{min} = -93,8 ee_{max} = -91 Δ**ee** = -2,8 **Negligible**	6

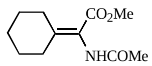
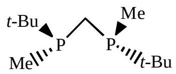
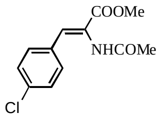
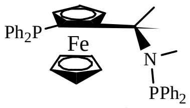
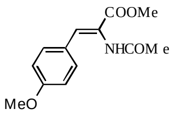
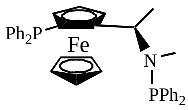
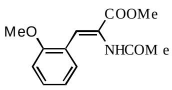
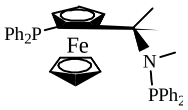
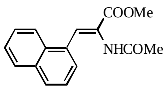
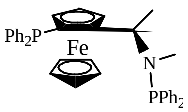
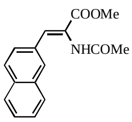
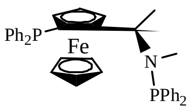
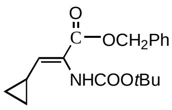
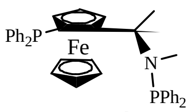
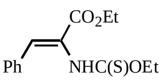
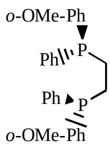
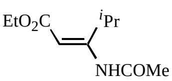
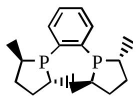
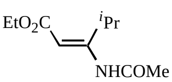
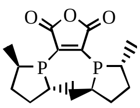
Entry	Substrate	Ligand	Conditions*	Dee **	Ref.
11	 **S1**	 **(*S*,*S*)-BPPM**	n_{Rh}[d] = 0,01 n_S = 1 12 mL EtOH T = 25 t = 3-15 h **P_{H_2} : 1-20**	ee_{min} = +87 ee_{max} = +82,3 Dee = -4,7[h] **Detrimental**	7
12	 **S1**	 **(*R*,*R*)-DIOXOP**	[S] = 0,1 [Rh][d] = 4.10^{-3} 10 mL EtOH χ = 100 **P_{H_2} : 1-50**	ee_{min} = -13 ee_{max} = +32 Dee = +32 **Beneficial** D**ee = -13** **Detrimental**	8
13	 **S1**	 R : p-$C_6H_4NHMe_2)BF_4$ **C3-1**	n_{Rh} = 0,025 S/Rh = 100 10 mL MeOH T°$_{amb}$ χ = 100 **P_{H_2} : 1-14**	ee_{min} = +91 ee_{max} = +58 Dee = -33[h] **Detrimental**	9
14	 **S1**	 R : p-$C_6H_4NMe_2$ **C2-2**	n_{Rh} = 0,025 S/Rh = 100 10 mL MeOH T°$_{amb}$ χ = 100 **P_{H_2} : 1-14**	ee_{min} = +87 ee_{max} = +82 Dee = -5[h] **Detrimental**	9
15	 **S2**	 **(*R*,*R*)-DiPAMP**	[S]=0,15 S/Rh[c]=800 MeOH ou EtOH T = 50 25 mL de liquide **P_{H_2} : 3-27**	ee_{min} = -93 ee_{max} = -78 Dee = -15[h] **Detrimental**	10
16	 **S2**	 **(*R*,*R*)-DiPAMP**	n_{Rh} = 0,01[d] n_S = 1 12 mL EtOH T = 25 t = 3-15h **P_{H_2} : 1-100**	ee_{min} = -64 ee_{max} = -31 Dee = -33 **Detrimental**	7
17	 **S2**	 **(*R*,*R*)-DIOP**	n_{Rh} = 0,01[d] n_S = 1l 12mL EtOH T = 25 t = 3-15h **P_{H_2} : 1-50**	ee_{min} = +55,2 ee = 0 Dee = -55,2[i] **Detrimental** ee = 0 ee_{max} = -5 Dee = +5[i] **Beneficial**	7
18	 **S2**	 **(S)-BINAP**	n_S = 0,5-1,0 1 % mol de Rh 20-30 mL EtOH T°$_{amb}$ **P_{H_2} : 4-50,7**	ee_{min} = +96 ee_{max} = +71 Dee = - 25[h] **Detrimental**	11
19	 **S2**	 **(*S*,*S*)-BPPM**	n_{Rh} = 0,01[d] n_S = 1 12 mL EtOH T = 25 t = 3-15h **P_{H_2} : 1-100**	ee_{min} = +84 ee_0 = 0 Dee = -84[i] **Detrimental** ee_0 = 0 ee_{max} = -8,4 Dee = +8,4[i] **Beneficial**	7

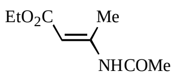
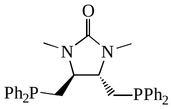
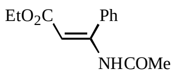
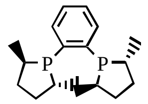
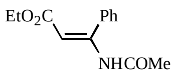
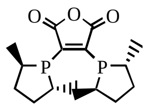
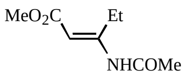
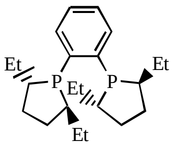
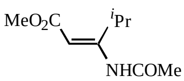
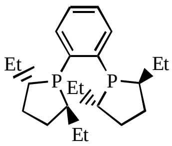
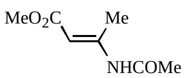
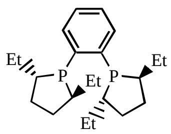
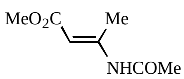
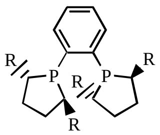
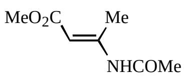
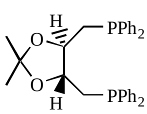
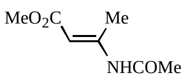
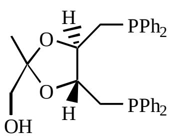
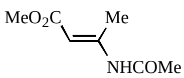
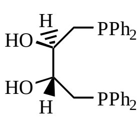
Entry	Substrate	Ligand	Conditions*	Dee **	Ref.
20	 **S3**	 R : p-$C_6H_4NMe_2$ **C2-2**	n_{Rh} = 0,025 S/Rh = 100 10 mL MeOH T°$_{amb}$ χ = 100 **P_{H_2} : 1-14**	ee_{min} = +93 ee_{max} = +88 Dee = - 5[h] **Detrimental**	9
21	 S4	 **(*S*,*S*)-BPPM**	n_{Rh} = 0,01[d] n_S = 1 12 mL MeOH T = 25 t = 3-15 h **P_{H_2} : 1-20**	ee_{min} = +95,2 ee = 0 Dee = -95,2[h, i] **Detrimental** ee = 0 ee_{max} = -22 Dee = +22[h, i] **Beneficial**	7
22	 S4	 (*S*,*S*)-TANIAPHOS	<u>3 mL MeOH:</u> <u>3mL (omim)BF$_4$/H$_2$0 (3/1):</u> S/Rh[c] = 200 T = 25 t = 3 h **P_{H_2} : 1-10**	ee_{min} = +98 ee_{max} = +99 Dee = +1[h] **Negligible** ee_{min} = +99 ee_{max} = +98 Dee =-1[h] **Negligible**	12
23	 S4	 (R,S) 3,5OMe Taniaphos	<u>3 mL MeOH:</u> <u>3mL (omim)BF$_4$/H$_2$0 (3/1):</u> S/Rh[c] = 200 T = 25 t = 3 h **P_{H_2} : 1-10**	ee_{min} = +97 ee_{max} = +96 Dee = + 1[h] **Negligible** ee_{min} = +99 ee_{max} = +99 Dee =0[h] **Negligible**	12
24	 **S4**	 **(R,S)Cy-3,5trifluoroMe Josiphos**	<u>3 mL MeOH:</u> <u>3mL (omim)BF$_4$/H$_2$0 (3/1):</u> S/Rh[c] = 200 T = 25 t = 3 h **P_{H_2} : 1-10**	ee_{min} = +97 ee_{max} = +84 Dee = -13[h] **Detrimental** ee_{min} = +99 ee_{max} = +92 Dee = -7[h] **Detrimental**	12
25	 **S5**	 **(*R*)-BICHEP**	[S] = (2-15).10^{-3} S/Rh = 100 T = 25 t = 10 min χ : 100 THF **P_{H_2} : 1-5**	ee_{min} = -97 ee_{max} = -95 Dee = -2[h] **Negligible**	13
26	 **S6**	 **(*S*,*S*)-^{i}Pr-CnrPHOS**	1 % mole Rh[e] T°$_{amb}$ t = 20 h CH_2Cl_2/benzène **P_{H_2} : 10-100**	ee_{min} = +82 ee_{max} = +90 Dee = +8 **Beneficial**	14

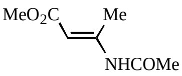
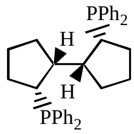
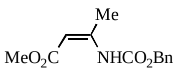
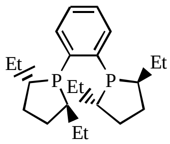
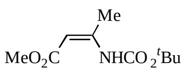
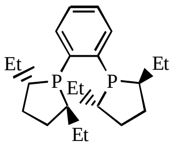
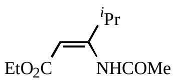
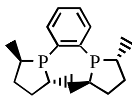
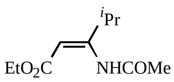
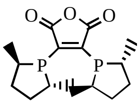
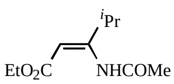
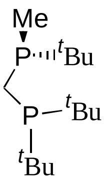
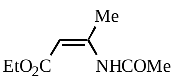
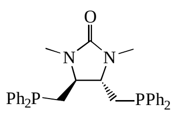
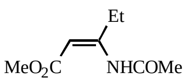
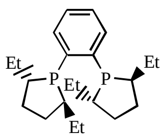
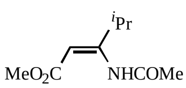
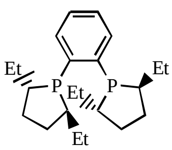
Entry	Substrate	Ligand	Conditions*	Dee**	Ref.
27	 **S6**	 **C2-1**	1 % mole Rh[e] T°$_{amb}$ t = 20 h CH_2Cl_2/benzène **P_{H_2} : 10-100**	ee$_{min}$ = +15 ee$_{max}$ = +70 **Dee** = +55[a] **Beneficial**	14
28	 **S6**	 **(*R*,*R*)-DiPAMP**	[S] = 0,4 [Rh][c] = $4{,}5.10^{-4}$ MeOH T = 25 **P_{H_2} : 1,6-9**	ee$_{min}$ = -92,1 ee$_{max}$ = -73,8 **Dee** = -18,3 **Detrimental**	15
29	 **S6**	 **(*R*,*R*)-^{t}Bu-BisP***	n_S = 1 n_{Rh} = 0,002 T°$_{amb}$ **P_{H_2} : 2-80**	ee$_{min}$ = +98 ee$_{max}$ = +98 **Dee** = 0[a] **Negligible**	16
30	 **S6**	 **(*R*,*R*)-^{t}Bu-MiniPHOS**	n_S = 1 n_{Rh} = 0,002 T°$_{amb}$ **P_{H_2} : 2-80**	ee$_{min}$ = +97 ee$_{max}$ = +95 **Dee**=-2[a] **Negligible**	16
31	 **S6**	 **C4-1**	n_S = 0,1 n_{Rh} = 0,001 2 mL de MeOH T = 25 t = 1 h **P_{H_2} : 3-100**	ee$_{min}$ = -61 ee$_{max}$ = -50 **Dee** = -11 **Detrimental**	17
32	 **S6**	 **(*R*,*R*)-(*S*,*S*)-EtTRAP**	S:Rh[c]:L=100:1:1,1 T = 30 MeOH t = 24 h χ : 100 % **P_{H_2} : 1-100**	ee$_{min}$ = +18 ee$_{max}$ = -79 **Dee** = -18[h, i] **Detrimental** **Dee** = +79[h, i] **Beneficial**	18
33	 **S6**	 **(*R*,*R*)-(*S*,*S*)-*i*BuTRAP**	S:Rh[c]:L=100:1:1,1 T = 30 MeOH t = 24 h χ : 100 % **P_{H_2} : 1-100**	ee$_{min}$ = -84 ee$_{max}$ = -83 **Dee** = -1[h] **Negligible**	18
34	 **S6**	 **(*S*,*S*)-BPPM**	n_{Rh} = 0,01[d] n_S = 1 12 mL EtOH T = 25 t = 3-15 h **P_{H_2} : 1-20**	ee$_{min}$ = +95 ee$_{max}$ = +89,7 **Dee** = -5,3[h] **Detrimental**	7
35	 **S6**	 **(*R*,*R*)-DIOXOP**	[S] = 0,1 [Rh][d] = 4.10^{-3} 10 mL EtOH χ : 100% **P_{H_2} : 1-50**	ee$_{min}$ = -1 ee$_{max}$ = +33 **Dee** = +34 **Beneficial**	8
36	 **S6**	 R : p-$C_6H_4NMe_3$,BF_4 **C2-3**	[Rh] = 0,025 S/Rh = 100 10 mL MeOH T°$_{amb}$ χ : 100 % **P_{H_2} : 1-14**	ee$_{min}$ = +75 ee$_{max}$ = +75 **Dee** = 0[h] **Negligible**	9

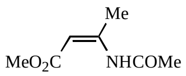
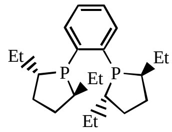
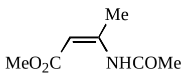
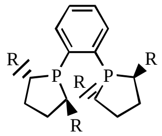
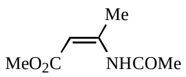
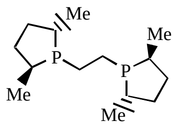
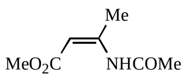
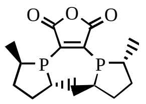
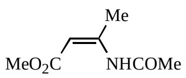
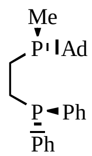
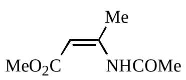
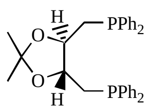
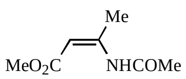
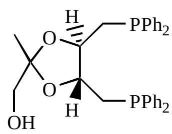
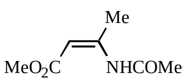
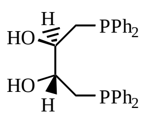
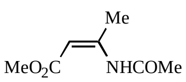
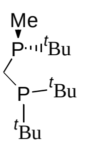
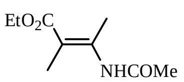
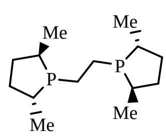
Entry	Substrate	Ligand	Conditions[*]	Dee[**]	Ref.
37	 **S6**	 R : p-$C_6H_4NMe_2$ **C3-2**	[Rh] = 0,025 S/Rh = 100 10 mL MeOH $T°_{amb}$ χ : 100 % **P_{H_2} : 1-14**	ee_{min} = +76 ee_{max} = +38 Dee = -38[h] **Detrimental**	9
38	 **S6**	 **(*S*)-Cy-P-Phos**	[Rh-L][c] = 10^{-5} S/Cata[c] = 100 0,2 mL Acetone T = 25 t = 2 h **P_{H_2} : 1-35**	ee_{min} = +95 ee_{max} = +86 Dee = -9 **Detrimental**	19
39	 **S6**	 (*R*,*S*)-BoPhos	n_{Rh} = 10[e] Ligand/ Rh = 1.2 6 mL THF T = 25 t = 6 h **P_{H_2} : 1-21**	ee_{min} = +99,1 ee_{max} = +96,8 Dee = -2,8[h] **Negligible**	19
40	 **S6**	 **(R)-SpiroBIP**	S/Cata = 100 Ligand/ Rh[c] = 1.2 4 mL MeOH T = 25 t = 24 h **P_{H_2} : 5-50**	ee_{min} = +94 ee_{max} = +80 Dee = -14 **Detrimental**	20
41	 **S6**	 **(S)-*o*-Ph-MeO-BIPHEP**	S/Cata = 100 $[Rh(NBD)_2]SbF_6$ CH_2Cl_2 T = 25 t = 24 h **P_{H_2} : 1,6-4**	ee_{min} = -98 ee_{max} = -97 Dee = -1[h] **Negligible**	21
42	 **S6**	 C2-7	S/Cata = 100 [Rh (L)*]PF_6 [Rh] = 2,5 10^{-6} 10 mL THF T = 25 t = (12-60 min) **P_{H_2} : 5-60**	ee_{min} = -56 ee_{max} = -57 Dee = +1 **Negligible**	22
43	 **S6**	 C2-9	S/Cata = 100 [Rh (L)*]PF_6 [Rh] = 2,5 10^{-6} 10 mL THF T = 25 t = 60 min **P_{H_2} : 5-10**	ee_{min} = -42 ee_{max} = -48 Dee = +6[h] **Beneficial**	23
44	 **S6**	 C2-8	S/Cata = 100 [Rh (L)*]PF_6 [Rh] = 2,5 10^{-6} 10 mL THF T = 25 t = (4-6 h) **P_{H_2} : 5-10**	ee_{min} = -29 ee_{max} = -30 Dee = +1[h] **Negligible**	23
45	 **S6**	 C3-6	S/Cata = 100 [Rh (L)*]PF_6 [Rh] = 2,5 10^{-6} 10 mL THF T = 25 t = (6-12 min) **P_{H_2} : 5-10**	ee_{min} = -20 ee_{max} = -20 Dee = 0[h] **Negligible**	23
46	 **S6**	 C2-10	S/Cata = 100 [Rh (L)*]PF_6 [Rh] = 2,5 10^{-6} 10 mL THF T = 25 t = (6-12 min) **P_{H_2} : 5-10**	ee_{min} = -58 ee_{max} = -52 Dee = -6[h] **Detrimental**	23

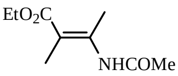
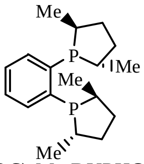
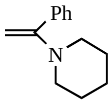
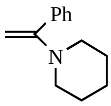
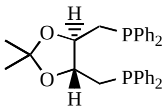
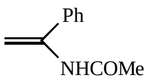
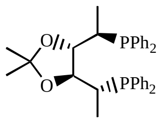
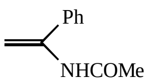
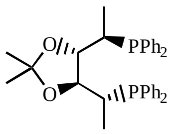
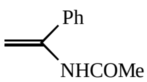
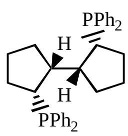
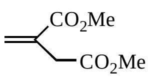
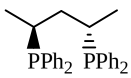
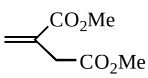
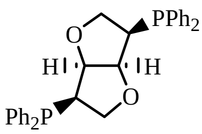
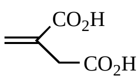
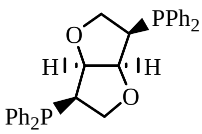
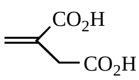
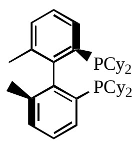
Entry	Substrate	Ligand	Conditions*	Dee **	Ref.
47	 **S6**	 **ddppm**	n_{Rh} = 1 [c] S/ Cata = 100 15 mL MeOH T = 25 **P_{H_2} : 1-3,5**	ee_{min} = +30 ee_{max} = +36 **D**ee = +6 [h] **Beneficial**	22
48	 **S7**	 **(*R*)-BICHEP**	[Rh][d] = 0,02-0,2.10^{-3} S/Rh = 100 T = 25 THF t = 10 min **P_{H_2} : 1-5**	ee_{min} = -96 ee_{max} = -92 **D**ee = -4[h] **Detrimental**	13
49	 **S8**	 R : p-$C_6H_4NMe_2$ **C4-2**	[Rh] = 0,025 S/Rh = 100 10 mL MeOH T°$_{amb}$ χ : 100 % **P_{H_2} : 1-91**	ee_{min}= -7 ee_{max} = +2,5 **D**ee = -9,5[h, i] **Detrimental**	9
50	 **S9**	 **(*S*,*S*)-^{i}Pr-CnrPHOS**	1 % mole Rh[e] T°$_{amb}$ t = 20 h CH_2Cl_2/benzène **P_{H_2} : 10-100**	ee_{min} = -38 ee_{max} = +80 **D**ee = - +38[*a*] **Detrimental** **D**ee = +80[*a*] **Beneficial**	14
51	 **S9**	 **C2-1**	1 % mole Rh[e] T°$_{amb}$ t = 20 h CH_2Cl_2/benzène **P_{H_2} : 10-100**	ee_{min} = +32 ee_{max} = +78 **D**ee = +46[*a*] **Beneficial**	14
52	 **S10**	 **(*R*,*R*)-(*S*,*S*)-EtTRAP**	S:Rh:L = 100:1:1,1[c] $C_2H_4Cl_2$ T = 60 t = 24 h χ? 100 % **P_{H_2} : 0,5-100**	ee_{min} = +96 ee_{max} = +2 **D**ee = -94 **Detrimental**	18
53	 **S10**	 **(*R*,*R*)-(*S*,*S*)-EtTRAP**	S:Rh:TRAP=1:0,01:0,011[c] n_S = 0,05 T = 60 1 mL $C_2H_4Cl_2$ **P_{H_2} : 0,5-1**	ee_{min} = +96 ee_{max} = +70 **D**ee = -26[a] **Detrimental**	24
54	 **S10**	 (*R*,*S*)-BoPhos	n_{Rh} = 10 [e] Ligand/ Rh = 1.2 6 mL THF T = 25 t = 6 h **P_{H_2} : 0.6-20.6**	ee_{min} = +98.5 ee_{max} = +95.2 **D**ee = -3,3[h] **Negligible**	25
55	 **S10**	 **(S)-*o*-Ph-MeO-BIPHEP**	S/Cata = 100 $[Rh(NBD)_2]SbF_6$ CH_2Cl_2 T = 25 t = 24 h **P_{H_2} : 1,6-4**	ee_{min} = >-99 ee_{max} = >-99 **D**ee = 0 [h] **Negligible**	26
56	 **S11**	 **(*R*,*R*)-^{t}Bu-BisP***	n_S = 1 n_{Rh} = 0,002 T°amb **P_{H_2} : 2-80**	ee_{min} = +85 ee_{max} = +64 **D**ee = -21[a] **Detrimental**	16

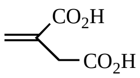
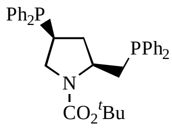
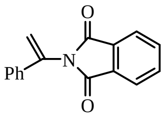
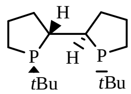
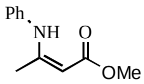
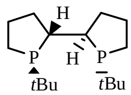
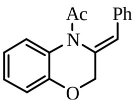
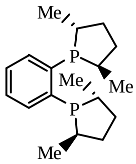
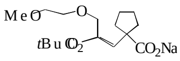
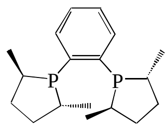
Entry	Substrate	Ligand	Conditions*	Dee**	Ref.
57	 **S11**	 **(*R*,*R*)-^{t}Bu-MiniPHOS**	$n_S = 1$ $n_{Rh} = 0{,}002$ T°amb **P_{H_2} : 2-80**	$ee_{min} = +85$ $ee_{max} = +64$ **Dee**=-21[a] **Detrimental**	16
58	 **S12**	 (*R*,*S*)-BoPhos	$n_{Rh} = 10$[e] Ligand/ Rh = 1,2 6 mL THF T = 25 t = 6 h **P_{H_2} : 0.6-20.6**	$ee_{min} = +98{,}8$ $ee_{max} = +97{,}2$ **Dee** = -1,6[h] **Negligible**	25
59	 **S13**	 (*R*,*S*)-BoPhos	$n_{Rh} = 10$[e] Ligand/ Rh = 1.2 6 mL THF T = 25 t = 6 h **P_{H_2} : 0.6-20.6**	$ee_{min} = +98{,}1$ $ee_{max} = +97{,}3$ **Dee**=-0,8[h] **Negligible**	25
60	 **S14**	 **(*R*,*S*)-BoPhos**	$n_{Rh} = 10$[e] Ligand/ Rh = 1,2 6 mL THF T = 25 t = 6 h **P_{H_2} : 1-21**	$ee_{min} = +97{,}7$ $ee_{max} = +96{,}7$ **Dee** = -1[h] **Negligible**	25
61	 **S15**	 **(*R*,*S*)-BoPhos**	$n_{Rh} = 10$[e] Ligand/ Rh = 1,2 6 mL THF T = 25 t = 6 h **P_{H_2} : 0.6-20.6**	$ee_{min} = +99{,}3$ $ee_{max} = +97{,}1$ **Dee** = -0,4[h] **Negligible**	25
62	 **S16**	 (*R*,*S*)-BoPhos	$n_{Rh} = 10$[e] Ligand/ Rh = 1,2 6 mL THF T = 25 t = 6 h **P_{H_2} : 1-21**	$ee_{min} = +98{,}1$ $ee_{max} = +97{,}6$ **Dee** = -0,5[h] **Negligible**	25
63	 **S17**	 (*R*,*S*)-BoPhos	$n_{Rh} = 10$[e] Ligand/ Rh = 1,2 6 mL THF T = 25 t = 6 h **P_{H_2} : 1-21**	$ee_{min} = +98{,}6$ $ee_{max} = +96{,}6$ **Dee** = -2[h] **Negligible**	25
64	 **S18**	 **(*R*,*R*)-DiPAMP**	[S] = 0,15 S/Rh = 100[c] MeOH ou EtOH T = 50 25 mL de liquide **P_{H_2} : 3-27**	$ee_{min} = -62$ $ee_{max} = -56$ **Dee** = -6[h] **Detrimental**	10
65	 **S19**	 **(*R*,*R*)-Me-DuPHOS**	n_{Rh}[c] = 0,005 $n_S = 0{,}5$ 7,5 mL MeOH T = 25 t = 1 h **P_{H_2} : 1-90**	$ee_{min} = -98{,}6$ $ee_{max} = -67{,}8$ **Dee** = -30,8 **Detrimental**	27
66	 **S19**	 **(*R*,*R*)-Me-MALPHOS**	n_{Rh}[c] = 0,005 $n_S = 0{,}5$ 7,5 mL MeOH T = 25 t = 1 h **P_{H_2} : 1-90**	$ee_{min} = -97{,}3$ $ee_{max} = -90{,}1$ **Dee** = -7,2 **Detrimental**	27

Entry	Substrate	Ligand	Conditions*	Dee**	Ref.
67	 **S20**	 **(*S*,*S*)-Me-BDPMI**	Rh:L:S=0,01:0,012:1[c] T°$_{amb}$ MeOH[b] **P_{H_2} : 1-7**	ee_{min} = +92,3 ee_{max} = +91,5 **Dee** = -0,8[h] **Negligible**	28
68	 **S21**	 **(*R*,*R*)-Me-DuPHOS**	n_{Rh}[c] = 0,005 n_S = 0,5 7,5 mL MeOH T = 25 t = 1 h **P_{H_2} : 1-90**	ee_{min} = -96,3 ee_{max} = -81,5 **Dee** = -14,8 **Detrimental**	27
69	 **S21**	 **(*R*,*R*)-Me-MALPHOS**	n_{Rh}[c] = 0,005 n_S = 0,5 7,5 mL MeOH T = 25 t = 1 h **P_{H_2} : 1-90**	ee_{min} = -88,3 ee_{max} = -88,9 **Dee** = +0,6 **Negligible**	27
70	 **S22**	 **(*S*,*S*)-Et-DuPHOS**	n_{Rh}[c] = 0,01 n_S = 1 15 mL MeOH T = 25 **P_{H_2} : 1-30**	ee_{min} = -98,5 ee_{max} = -98,7 **Dee** = 0,2[h] **Negligible**	29
71	 **S23**	 **(*S*,*S*)-Et-DuPHOS**	n_{Rh}[c] = 0,01 n_S = 1 15 mL MeOH T = 25 **P_{H_2} : 1-30**	ee_{min} = +99 ee_{max} = +99 **Dee** = 0[a, h] **Negligible**	29
72	 **S24**	 **(*S*,*S*)-Et-DuPHOS**	n_{Rh} = 0,01[c] n_S = 1 15 mL MeOH[b] T = 25 **P_{H_2} : 1-45**	ee_{min} = -97 ee_{max} = -96 **Dee** = -1 **Negligible**	30
73	 **S24**	 R : -CH_2OMe **(*S*,*S*)-Me-BasPHOS**	n_{Rh} = 0,01[c] n_S = 1 15 mL MeOH T = 25 **P_{H_2} : 1-45**	ee_{min} = +98 ee_{max} = +96 **Dee** = -2[a] **Negligible**	29
74	 **S24**	 **(*R*,*R*)-DIOP**	n_{Rh} = 0,01[c] n_S = 1 15 mL MeOH T = 25 **P_{H_2} : 1-30**	ee_{min} = +71 ee_{max} = +71 **Dee** = 0[a, h] **Negligible**	29
75	 **S24**	 **(*R*,*R*)-HO-DIOP**	n_{Rh} = 0,01[c] n_S = 1 15 mL MeOH T = 25 **P_{H_2} : 1-30**	ee_{min} = +71 ee_{max} = +70 **Dee** = -1[a, h] **Negligible**	29
76	 **S24**	 **C4-3**	n_{Rh} = 0,01[c] n_S = 1 15 mL MeOH T = 25 **P_{H_2} : 1-30**	ee_{min} = +57 ee_{max} = +38 **Dee** = -19[a, h] **Detrimental**	29

Entry	Substrate	Ligand	Conditions*	Dee**	Ref.
77	 **S24**	 **(R,R)-BICP**	Rh:L:S=0,01:0,012:1[e] T°$_{amb}$ toluène **P_{H_2} : 1-50**	ee_{min} = +94,9 ee_{max} = +96,1 Dee = +1,2 **Negligible**	31
78	 **S25**	 **(*R*,*R*)-Et-DuPHOS**	n_{Rh} = 0,01[c] n_S = 1 15 mL MeOH T = 25 **P_{H_2} : 1-30**	ee_{min} = -80 ee_{max} = -38 Dee = -38 [a, h] **Detrimental**	29
79	 **S26**	 **(*R*,*R*)-Et-DuPHOS**	n_{Rh} = 0,01[c] n_S = 1 15 mL MeOH T = 25 **P_{H_2} : 1-30**	ee_{min} = -79 ee_{max} = -66 Dee = -13 [a, h] **Detrimental**	29
80	 **S27**	 **(*R*,*R*)-Me-DuPHOS**	n_{Rh}[c] = 0,005 n_S = 0,5 7,5 mL MeOH T = 25 t = 1 h **P_{H_2} : 1-90**	ee_{min} = -3,6 ee_{max} = +75,1 Dee = +78,7 **Beneficial**	27
81	 **S27**	 **(*R*,*R*)-Me-MALPHOS**	n_{Rh}[c] = 0,005 n_S = 0,5 7,5 mL MeOH T = 25 t = 1 h **P_{H_2} : 1-90**	ee_{min} = -69,4 ee_{max} = -34 Dee = -35,4[i] **Detrimental**	27
82	 **S27**	 C1-1	S/Cata = 100 $[Rh(COD)_2]BF_4$ [S] = 0,2 10^{-3} 2,5 mL EtOAc T = 25 t = 15 min **P_{H_2} : 0.4-3.4**	ee_{min} = -92 ee_{max} = -66 Dee = -26 **Detrimental**	32
83	 **S28**	 **(*S*,*S*)-Me-BDPMI**	Rh:L:S=0,01:0,012:1[c] T°amb MeOH[b] **P_{H_2} : 1-7**	ee_{min} = +94,6 ee_{max} = +91,3 Dee = -3,3[h] **Negligible**	28
84	 **S29**	 **(*R*,*R*)-Et-DuPHOS**	n_{Rh} = 0,01[c] n_S = 1 15 mL MeOH T = 25 **P_{H_2} : 1-30**	ee_{min} = -68 ee_{max} = -28 Dee = -40[h] **Detrimental**	29
85	 **S30**	 **(*R*,*R*)-Et-DuPHOS**	n_{Rh} = 0,01[c] n_S = 1 15 mL MeOH T = 25 **P_{H_2} : 1-30**	ee_{min} = +31 ee_{max} = -72 Dee = -31 [a, i] **Detrimental** Dee = +72 [a, i] **Beneficial**	29

Entry	Substrate	Ligand	Conditions*	Dee**	Ref.
86	 **S31**	 **(*R*,*R*)-Et-DuPHOS**	n_{Rh} = 0,01[c] n_S = 1 15 mL MeOH T = 25 **P_{H_2} : 1-45**	ee_{min} = -86,7 ee_{max} = -35 D**ee** = -51,7 **Detrimental**	30
87	 **S31**	 R : $-CH_2OMe$ **(*S*,*S*)-Me-BASPHOS**	n_{Rh} = 0,01[c] n_S = 1 15 mL MeOH T = 25 **P_{H_2} : 1-45**	ee_{min} = +67 ee_{max} = +57 D**ee** = -10[a] **Detrimental**	29
88	 **S31**	 **(*S*,*S*)-Me-BPE**	T°$_{amb}$ MeOH **P_{H_2} : 1-30**	ee_{min} = +67 ee_{max} = +25 D**ee**=-42[a,h] **Detrimental**	33
89	 **S31**	 **(*R*,*R*)-Me-MALPHOS**	n_{Rh}[c] = 0,005 n_S = 0,5 7,5 mL MeOH T = 25 t = 1 h **P_{H_2} : 1-90**	ee_{min} = -83 ee_{max} = -61,3 D**ee** = -21,7 **Detrimental**	27
90	 **S31**	 **(*S*)-BisP***	n_S = 1 n_{Rh} = 2.10^{-3} 2 mL MeOH **P_{H_2} : 3-45**	ee_{min} = -57,4 ee_{max} = -70,5 D**ee** = +13,1 **Beneficial**	34
91	 **S31**	 **(*R*,*R*)-DIOP**	n_{Rh} = 0,01[c] n_S = 1 15 mL MeOH T = 25°C **P_{H_2} : 1-30**	ee_{min} = +17 ee_{max} = +26 D**ee** = +9 [a, h] **Beneficial**	29
92	 **S31**	 **(*R*,*R*)-HO-DIOP**	n_{Rh} = 0,01[c] n_S = 1 15 mL MeOH T = 25 **P_{H_2} : 1-30**	ee_{min} = +36 ee_{max} = +32 D**ee** = -4 [a, h] **Detrimental**	29
93	 **S31**	 **C4-3**	n_{Rh} = 0,01[c] n_S = 1 15 mL MeOH T = 25 **P_{H_2} : 1-30**	ee_{min} = +37 ee_{max} = +17 D**ee** = -20 [a, h] **Detrimental**	29
94	 **S31**	 **C1-1**	S/Cata = 100 $[Rh(COD)_2]BF_4$ [S] = 0,2 10^{-3} 2,5 mL THF T = 25 t = 15 min **P_{H_2} : 0.4-3.4**	ee_{min} = +99 ee_{max} = +94 D**ee** = -5 **Detrimental**	32
95	 **S39**	 (R,R)-Me-BPE	$[Rh(COD)_2]$OTF (4-10 mL) MeOH T = 25 t = (72-96 h) **P_{H_2} : 1-5**	ee_{min} = +35 ee_{max} = +49 D**ee**=+14[h] **Beneficial**	35

Entry	Substrate	Ligand	Conditions*	Dee**	Ref.
96	 **S39**	 (S,S)-Me-DUPHOS	$[Rh(COD)_2]OTF$ (4-10 mL) MeOH T = 25 t = 72 h **P_{H_2} : 1-5**	ee_{min} = +5 ee_{max} = +1 Dee=+9[h] **Beneficial**	35
97	 **S32**	 **(*R*,*R*)-bdpch**	n_S = 1 n_{Rh} = 0,01 15 mL MeOH **P_{H2} : 1-50**	ee_{min} = +32 ee_{max} = +30 Dee = -2[h] **Negligible**	36
98	 **S32**	 **(*R*,*R*)-DIOP**	n_S = 1 n_{Rh} = 0,01 15 mL MeOH **P_{H_2} : 1-50**	ee_{min} = +39 ee_{max} = +32 Dee = -7[h] **Detrimental**	36
99	 **S33**	 **(*R*,*S*,*S*,*R*)-DIOP***	S:Rh:L=1:0,02:0,02[g] n_S = 0,25 T°$_{amb}$ t = 60h 3 mL MeOH **P_{H_2} : 1-50**	ee_{min} = +98,8 ee_{max} = +97,2 Dee = -1,6 **Negligible**	37
100	 **S33**	 **(*R*,*S*,*S*,*R*)-DIOP***	S/Rh[c] = 10 T°$_{amb}$ t = 10 h χ : 100 % [c] CH_2Cl_2 (2mL) **P_{H2} : 1-5**	ee_{min} = +98 ee_{max} = +98 Dee = 0[h] **Negligible**	38
101	 **S33**	 **(*R*,*R*)-BICP**	S/Rh/L=1:0,01:0,011 [c] n_S = 0,5 T°$_{amb}$ t = 24 h χ : 100 % 4 mL toluène **P_{H_2} : 1-3**	ee_{min} = +80,2 ee_{max} = +86,3 Dee = +6,1[h] **Beneficial**	39
102	 **S34**	 (*SS*)-BDPP	S/Rh = 500 $[Rh(NBD)_2Cl_2]$ MeOH T = 25 t = 5-10 min **P_{H_2} : 1-20**	ee_{min} = +70,8 ee_{max} = +63,1 Dee = -10,7 [h] **Detrimental**	40
103	 **S34**	 **ddppm**	n_{Rh} = 1 [c] S/ Cata = 100 15 mL MeOH T = 25 **P_{H_2} : 1-20**	ee_{min} = -41 ee_{max} = -31 Dee = -10 [h] **Detrimental**	41
104	 **S35**	 **ddppm**	n_{Rh} = 1 [c] S/ Cata = 100 15 mL MeOH T = 25 **P_{H_2} : 1-3,5**	ee_{min} = -64 ee_{max} = -59 Dee = -5 [h] **Detrimental**	41
105	 **S35**	 **(*R*)-BICHEP**	[Rh][d] = (0,02-0,2).10^{-3} [S] = (2-20).10^{-3} EtOH t = 5 min **P_{H_2} : 1-5**	ee_{min} = +93 ee_{max} = +85 Dee = -8 **Detrimental**	13

Entry	Substrate	Ligand	Conditions*	Dee **	Ref.
106	 **S35**	 **(*S*,*S*)-BPPM**	n_{Rh} = 0,01[d] n_S = 1 12 mL MeOH T = 25 t = 3-15 h **P_{H_2} : 1-20**	ee_{min} = -91,3 ee_{max} = -85,3 D**ee** = -6[h] **Detrimental**	1
107	 **S36**	 **(R,S)-TangPhos**	S/Cata = 100 $[Rh(NBD)_2]SbF_6$ EtOAc T = 25 t = 18 h **P_{H_2} : 10-30**	e_{min} = +96 ee_{max} = +98 D**ee** = + 2 [h] **Negligible**	42
108	 **S37**	 **(R,S)-TangPhos**	S/Cata = 100 $[Rh(NBD)_2]SbF_6$ 1mL THF T = 25 t = 18-24 h **P_{H_2} : 6-95**	ee_{min} = -93 ee_{max} = -73 D**ee** = -20 **Detrimental**	43
109	 **S38**	 **(*R*,*R*)-Me-DuPHOS**	S/Cata = 100 Ligand/ Rh [c] = 1,1 4 mL MeOH T = 25 t = 16 h **P_{H_2} : 2-14**	ee_{min} = +97 ee_{max} = +94 D**ee** = + 3 **Negligible**	44
110	 **S40**	 **(*R*,*R*)-Me-DuPHOS**	[S] = 0,6 S/Rh = 2500[c] MeOH T = 20 **P_{H_2} : 5-40**	ee_{min} = +99 ee_{max} = +99 D**ee** = 0[a] **Negligible**	45

* : [concentration] ($kmol.m^{-3}$), T : temperature (°C), t : reaction time, P_{H2} : hydrogen pressure (Bar), n : quantity (mmol), ? : substrate conversion (%). S : substrate.

** : ee_i : initial enantiomeric excess (at low hydrogen pressure), ee_f : final enantiomeric excess (at high hydrogen pressure).

[a] : the configuration of the major enantiomer is not indicated. [b] : solvent effect. [c] : BF_4^-, [d] : ClO_4^-, [e] : OTf^- , [f] : PF_6^-, [g] : SbF_6^-, [h] : only two pressures were investigated. [i] : inversion of major enantiomer.

Other general operating conditions : solvents are generally alcohols, the Rh/L ratio is unity.

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III-Sign of derivative of ee with hydrogen concentration

Reaction scheme:

$$\text{Mac} + H_2 \rightarrow \text{R} \qquad (R)$$
$$\text{Mac} + H_2 \rightarrow \text{S} \qquad (S)$$

Mechanism:

$$\text{Mac} + \text{Rh*} \underset{k_{-1R}}{\overset{k_{1R}}{\rightleftharpoons}} I_R \qquad \text{(1R)}$$

$$\text{Mac} + \text{Rh*} \underset{k_{-1S}}{\overset{k_{1S}}{\rightleftharpoons}} I_S \qquad \text{(1S)}$$

$$I_R + H_2 \xrightarrow{k_{2R}} \text{Rh*} + \text{R} \qquad \text{(2R)}$$

$$I_S + H_2 \xrightarrow{k_{2S}} \text{Rh*} + \text{S} \qquad \text{(2S)}$$

Rate laws:

$$r_R = \frac{k_{1R}k_{2R}}{\left(k_{-1R} + k_{2R}[H_2]_L\right)} \frac{[Mac][Rh]_{tot}[H_2]_L}{\left(1 + \frac{k_{1R}[Mac]}{k_{-1R} + k_{2R}[H_2]_L} + \frac{k_{1S}[Mac]}{k_{-1S} + k_{2S}[H_2]_L}\right)}$$

$$r_S = \frac{k_{1S}k_{2S}}{\left(k_{-1S} + k_{2S}[H_2]_L\right)} \frac{[Mac][Rh]_{tot}[H_2]_L}{\left(1 + \frac{k_{1R}[Mac]}{k_{-1R} + k_{2R}[H_2]_L} + \frac{k_{1S}[Mac]}{k_{-1S} + k_{2S}[H_2]_L}\right)}$$

The instantaneous enantioselectivity ratio is given by: $\frac{r_R}{r_S} = \frac{k_{1R}k_{2R}}{k_{1S}k_{2S}}\left(\frac{k_{-1S} + k_{2S}[H_2]_L}{k_{-1R} + k_{2R}[H_2]_L}\right)$

Knowing that the mass balances for species R and S in a batch reactor with no limitations by mass transfer are:

$$\frac{d[R]}{dt} = \bar{r}_R \qquad \text{and} \qquad \frac{d[S]}{dt} = \bar{r}_S$$

It follows: $\frac{r_R}{r_S} = \frac{k_{1R}k_{2R}}{k_{1S}k_{2S}}\left(\frac{k_{-1S} + k_{2S}[H_2]_L}{k_{-1R} + k_{2R}[H_2]_L}\right) = \frac{d[R]}{d[S]}$

Under constant hydrogen concentration (or constant hydrogen pressure in a mass transfer free reactor), this ratio is constant and can be integrated to give the integral enantioselectivity ratio :

$$\frac{[R]}{[S]} = \frac{k_{1R}k_{2R}}{k_{1S}k_{2S}}\left(\frac{k_{-1S} + k_{2S}[H_2]_L}{k_{-1R} + k_{2R}[H_2]_L}\right)$$

The derivative of this ratio with hydrogen concentration writes :

$$\frac{d\frac{[R]}{[S]}}{d[H_2]_L} = \frac{k_{1R}k_{2R}k_{1S}k_{-1S}}{\left(k_{1S}k_{-1R} + k_{1S}k_{2R}[H_2]_L\right)^2}\left(\frac{k_{-1R}}{k_{-1S}} - \frac{k_{2R}}{k_{2S}}\right)$$

Because kinetic constants and concentrations are always positive, the sign of this derivative, which indicates the increase or decrease of enantioselectivity with hydrogen concentration is given by :

$$sign\left(\frac{d\frac{[R]}{[S]}}{d[H_2]_L}\right) = sign\left(\frac{k_{-1R}}{k_{-1S}} - \frac{k_{2R}}{k_{2S}}\right)$$

Similarly for the enantiomeric excess ee: By definition: $ee = \frac{\frac{R}{S}-1}{\frac{R}{S}+1}$

It follows: $$ee = \frac{k_{1R}k_{2R}k_{-1S} - k_{-1R}k_{1S}k_{2S} + (k_{1R}k_{2R}k_{2S} - k_{1S}k_{2S}k_{2R})[H_2]_L}{k_{1R}k_{2R}k_{-1S} + k_{-1R}k_{1S}k_{2S} + (k_{1R}k_{2R}k_{2S} + k_{1S}k_{2S}k_{2R})[H_2]_L}$$

The derivative of ee with hydrogen concentration writes :

$$\frac{dee}{d[H_2]_L} = \frac{2k_{1R}k_{2R}k_{2S}k_{1S}}{\left(k_{1R}k_{2R}k_{-1S} + k_{1S}k_{2S}k_{-1R} + (k_{1R}k_{2R}k_{2S} + k_{1S}k_{2S}k_{2R})[H_2]_L\right)^2}(k_{-1R}k_{2S} - k_{-1S}k_{2R})$$

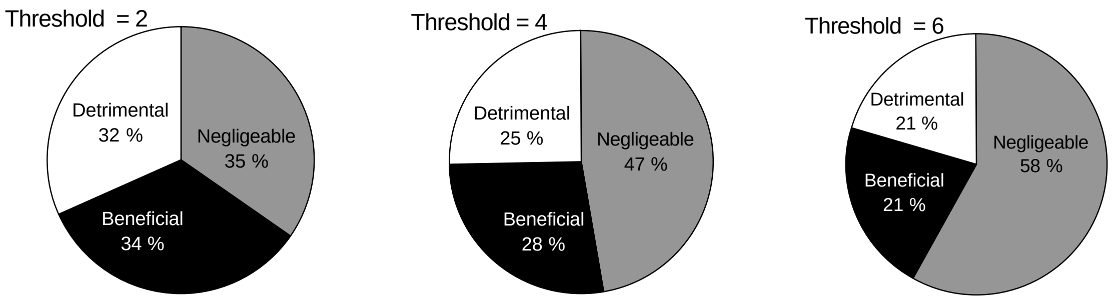
Because kinetic constants and concentrations are always positive, the sign of this derivative, which indicates the increase or decrease of enantioselectivity with hydrogen concentration is given by :

$$sign\left(\frac{dee}{d[H_2]_L}\right) = sign(k_{-1R}k_{2S} - k_{-1S}k_{2R}) = sign\left(\frac{k_{-1R}}{k_{-1S}} - \frac{k_{2R}}{k_{2S}}\right)$$

IV-Influence on the threshold on conclusions

The influence of the threshold of Δee fixed for the statistical analysis has been checked.

Thus, different threshold values, i.e. 2, 4 and 6, have been investigated. The results are reported in the figures and table below:



Threshold	Δee	%	Number
	Not taken (|ee| <5 %)		12
6	Negligeable (-6 < Δee|< 6)	58,1	90
	Beneficial (Δee > 6)	21,3	33
	Detrimental (Δee < -6)	20,6	32
4	Negligeable (-5 < Δee|< 5)	47,1	73
	Beneficial (Δee > 4	27,7	43
	Detrimental (Δee < -4	25,2	39
2	Negligeable (-2 < Δee|< 2)	34,8	54
	Beneficial (Δee > 2	33,5	52
	Detrimental (Δee < -2	31,6	49

It is clear that the level of the threshold does not have an influence on the conclusion about the equal repartition of detrimental and beneficial pressure effect on ee. In the main text, a threshold value of 4 has been used.

V-List of the chiral diphosphines used in this work.

Entry	Name	Full name	CAS N°	Ref
1	(*R*)-BINAP	(*R*)-(+)-2,2'-bis(diphénylphosphino)-1,1'-binaphthyl	76189-55-4	STREM
2	(*R*)-5,5'-Br_2-BINAP	(*R*)-(+)-2,2'-bis(diphénylphosphino)-5,5'-dibromo-1,1'-binaphthyl		1
3	(*R*)-5,5'-CN_2-BINAP	(*R*)-(+)-2,2'-bis(diphénylphosphino)-5,5'-dicyano-1,1'-binaphthyl		2
4	(*R*)-5,5'-$(CH_2NH_2)_2$-BINAP	(*R*)-(+)-2,2'-bis(diphénylphosphino)-5,5'-diaminométhyl-1,1'-binaphthyl		2
5	(*R*)-5,5'-$(C_8F_{17})_2$-BINAP	(*R*)-(+)-2,2'-bis(diphénylphosphino)-5,5'-diperfluorooctyl-1,1'-binaphthyl		3
6	(*R*)-5,5'-Me_2-BINAP	(*R*)-(+)-2,2'-bis(diphénylphosphino)-5,5'-dimétyl-1,1'-binaphthyl		1
7	(*R*)-5,5'-Ph_2-BINAP	(*R*)-(+)-2,2'-bis(diphénylphosphino)-5,5'-diphényl-1,1'-binaphthyl		1
8	(*R*)-5,5'-$(COOH)_2$-BINAP	(*R*)-(+)-2,2'-bis(diphénylphosphino)-5,5'-dicarbonyl-1,1'-binaphthyl		1
9	(*R*)-4,4'-Br_2-BINAP	(*R*)-(+)-2,2'-bis(diphénylphosphino)-4,4'-dibromo-1,1'-binaphthyl		4
10	(*R*)-4,4'-CN_2-BINAP	(*R*)-(+)-2,2'-bis(diphénylphosphino)-4,4'-dicyano-1,1'-binaphthyl		2
11	(*R*)-4,4'-$(CH_2NH_2)_2$-BINAP	(*R*)-(+)-2,2'-bis(diphénylphosphino)-4,4'-diaminométhyl-1,1'-binaphthyl		2
12	(*R*)-4,4'-$(C_{10}F_{21})_2$-BINAP	(*R*)-(+)-2,2'-bis(diphénylphosphino)-4,4'-diperfluorodécyl-1,1'-binaphthyl		3
13	(*R*)-4,4'-Me_2-BINAP	(*R*)-(+)-2,2'-bis(diphénylphosphino)-4,4'-dimétyl-1,1'-binaphthyl		4
14	(*R*)-4,4'-Ph_2-BINAP	(*R*)-(+)-2,2'-bis(diphénylphosphino)-4,4'-diphényl-1,1'-binaphthyl		4
15	(*R*)-Tol-BINAP	(*R*)-(+)-2,2'-bis(di-*p*-tolylphosphino)-1,1'-binaphthyl	99646-28-3	STREM
16	(*R*)-*p*-OMe-BINAP	(*R*)-(+)-2,2'-bis(di(*p*-méthoxyphényl)phosphino)-1,1'-binaphthyl		5
17	(*R*)-*p*-OH-BINAP	(*R*)-(+)-2,2'-bis(di(*p*-hydroxyphényl)phosphino)-1,1'-binaphthyl		6
18	(*R*)-*p*-NMe_2-BINAP	(*R*)-(+)-2,2'-bis(di(*p*-diméthylaniline)phosphino)-1,1'-binaphthyl		6
19	(*R*)-*p*-O^--BINAP	(*R*)-(+)-2,2'-bis(di(*p*-alcoolatephényl)phosphino)-1,1'-binaphthyl		6
20	(*R*)-*p*-$^+NMe_3$-BINAP	(*R*)-(+)-2,2'-bis(di(*p*-triméthylaniline)phosphino)-1,1'-binaphthyl		6
21	(*R*)-6,6'-$(C_{12}H_{25})_2$-*p*-OH-BINAP	(*R*)-(+)-2,2'-bis(di(*p*-hydroxyphényl)phosphino)-6,6'dodécyl-1,1'-binaphthyl		6
22	(*R*)-6,6'-$(C_{12}H_{25})_2$-*p*-O^--BINAP	(*R*)-(+)-2,2'-bis(di(*p*-alcoolatephényl)phosphino)-6,6'dodécyl-1,1'-binaphthyl		6
23	(*R*)-3,5-Xylyl-BINAP	(*R*)-(+)-2,2'-bis(di(3,5-Xylyl)phosphino)-1,1'-binaphthyl	137219-86-4	STREM
24	(*R*)-Cy-SONIPHOS	(*R*)-(+)-6,6'-Bis(diphénylphosphino)-1,1'-biphényl-2,2'-diylbis(cyclohexylcarboxylate)	398128-03-5	STREM
25	(*R*)-C_3-TUNEPHOS	(*R*)-(-)-1,13-Bis(diphénylphosphino)-7,8-dihydro-6H-dibenzo[f,h][1,5]dioxonin	301847-89-2	STREM
26	(*R*)-DifluoroPHOS	(*R*)-(-)-5,5'-Bis(diphénylphosphino)-2,2,2',2'-Tetrafluoro-4,4'-bi-1,3-benzodioxole	503538-69-0	STREM
27	(*R*)-SYNPHOS	(*R*)-(+)-6,6'-Bis(diphénylphosphino)-2,2',3,3'-tetrahydro-5,5'-bi-1,4-benzodioxin		STREM
28	(*R*)-Cl-OMe-BIPHEP	(*R*)-(+)-5,5'-Dichloro-6,6'-diméthoxy-2,2'-bis(diphénylphosphino)-1,1'-biphényl	185913-97-7	STREM
29	(*R*,*S*)-Xyl-Ph-JOSIPHOS	(*R*)-(-)-1-[(*S*)-2-(Dicyclohexylphosphino)-ferrocényl]éthyldi(3,5-diméthylphényl)phosphine	184095-69-0	STREM
30	(*R*)-(*S*)-^{t}Bu-Ph-JOSIPHOS	(*R*)-(-)-1-[(*S*)-2-(Dicyclohexylphosphino)-ferrocényl]éthyl-di-t-buthylphosphine	155830-69-6	STREM
31	(*R*)-(*S*)-JOSIPHOS	(*R*)-(-)-1-[(*S*)-2-(diphénylphosphino)-ferrocényl]éthyldi-cyclohexylphosphine	155806-35-2	STREM
32	(*R*)-(*S*)-Cy-*p*-OMe-Xyl-JOSIPHOS	(*R*)-(-)-1-[(*S*)-2Bis-(3,5-diméthyl-4-méthoxyphénylphosphino)-ferrocényl]éthyldicyclohexylphosphine	360048-63-1	STREM
33	(*R*)-(*S*)-Ph-Cy-JOSIPHOS	(*R*)-(-)-1-[(*S*)-2-(Dicyclohexylphosphino)-ferrocényl]éthyldiphénylphosphine	158923-09-2	STREM
34	(*R*)-(*S*)-Cy-Cy-JOSIPHOS	(*R*)-(-)-1-[(*S*)-2-(Dicyclohexylphosphino)-ferrocényl]éthyldicyclohexylphosphine	167416-28-6	STREM
35	(*R*)-(*S*)-^{t}Bu-Cy-JOSIPHOS	(*R*)-(-)-1-[(*S*)-2-(Diphénylphosphino)-ferrocényl]éthyldi-t-butylphosphine	158923-11-6	STREM
36	(*R*)-Ph-CTH-P-PHOS	(*R*)-(+)-2,2',6,6'-tetraméthoxy-4,4'-bis(diphénylphosphino)-3,3'-bipyridine	221012-82-4	STREM
37	(*R*)-Xylyl-CTH-P-PHOS	(*R*)-(+)-2,2',6,6'-tetraméthoxy-4,4'-bis(di(3,3'xylyl)phosphino)-3,3'-bipyridine	442905-33-1	STREM
38	(*R*)-PHANPHOS	(*R*)-(-)-4,12-Bis(diphénylphosphino)-[2,2]-paracyclophane	192463-40-4	STREM
39	CTH-(*S*)-3,5Xyl-PHANPHOS	(*S*)-(+)-4,12-Bis(di(3,5-Xylyl)phosphino)-[2,2]-*p*-cyclophane		STREM
40	(*R*,*R*)-Me-DUPHOS	(-)-1,2-bis((2*R*,5*R*)-2,5-diméthylphospholano)benzène	147253-67-6	STREM
41	(*R*,*R*)-Et-DUPHOS	(-)-1,2-bis((2*R*,5*R*)-2,5-diéthylphospholano)benzène	136705-64-1	STREM
42	(*S*,*S*)-^{i}Pr-DUPHOS	(-)-1,2-Bis((2*S*,5*S*)-2,5-di-*i*-propylphospholano)benzène	147253-69-8	STREM
43	(*R*,*R*)-Me-BPE	(+)-1,2-bis((2*R*,5*R*)-2,5-diméthylphospholano)éthane	129648-07-3	STREM
44	(*R*,*R*)-Et-BPE	(+)-1,2-bis((2*R*,5*R*)-2,5-diéthylphospholano)éthane	136705-62-9	STREM
45	(*S*,*S*)-BDPP	(2*S*,4*S*)-(-)-2,4-bis-(diphénylphosphino)pentane	77876-39-2	STREM
46	(*S*,*S*)-CHIRAPHOS	(2*S*,3*S*)-(-)-bis(diphénylphosphino)butane	64896-28-2	STREM
47	(*R*)-PROPHOS	*R*-(+)-1,2-bis(diphénylphosphino)propane	67884-32-6	STREM
48	(*R*,*R*)-DIOP	(4*R*,5*R*)-(-)-O-Isopropylidéne-2,3-dihydroxy-1,4-bis(diphénylphosphino)butane	32305-98-9	STREM
49	(*S*,*S*)-BPPM	(-)-(2*S*,4*S*)-2-diphénylphosphinométhyl-4-diphénylphosphino-1-t-butoxycarbonylpyrrolidine	61478-28-2	STREM
50	(*S*,*S*,*R*,*R*)-TANGPHOS	(1*S*,1'*S*,2*R*,2'*R*)-(+)-1,1'-Di-t-buthyl-[2,2']-diphospholane	470480-32-1	STREM
51	CARBOPHOS	Methyl a-D-glucopyranoside-2,6-dibenzoate-3,4-di(bis(3,5-diméthylphényl)phosphinite)	158214-06-3	STREM
52	(*R*,*R*)-NORPHOS	(2*R*,3*R*)-(-)-2,3-bis(diphénylphosphino)-bicyclo[2.2.1]hept-5-ene	71042-54-1	STREM
53	(*R*)-BINAPHANE	(*R*,*R*)-(-)-1,2-Bis{(*R*)-4,5-dihydro-3H-binaphto[1,2-c:2',1'-e]phosphepino}benzène	253311-88-5	STREM
54	(*S*)-BINAPINE	(3*S*,3'*S*,4*S*,4'*S*,11bs,11'bs)-(+)-4,4'Di-t-butyl-4,4',5,5'-tetrahydro-3,3'-bi-3H-dinaphtho [2,1-c:1',2'-e]phosphine	610304-81-9	STREM
55	(*S*,*S*)-Et-FERROTANE	(-)-1,1'-Bis((2*S*,4*S*)-2,4-diéthyl-phosphonato)ferrocéne, min95%	290347-66-9	STREM
56	(*R*,*S*)-3,5-trifluoro-*o*-PPh_2-Ph-L	(*R*)-(-)-1-[(*R*)-2-(2'Diphénylphosphinophényl)-ferrocényl]éthyldi(bis-3,5-trifluorométhylphényl)phosphine	387868-06-6	STREM

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