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Recent Progress of Symmetrically Substituted 1,1-Binaphthyls for Asymmetric Catalytic Hydrogenation

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In the present work, a review on recent progress of symmetrically substituted 1,1-binaphthyls for asymmetric catalytic hydrogenation is presented.

Key Words: Substituted 1,1-binaphthyls, Asymmetric catalytic hydrogenation, Review.

INTRODUCTION

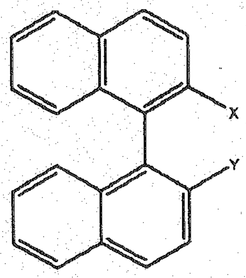
Chiral symmetrically substituted 1,1′-binaphthyl (BINAP) catalysts is an interesting topic in asymmetric catalytic fields. Chiral binaphthyl was first prepared in 1873; the absolute configuration was determined in 1971[1-3]. The development of molecular biology and modern instrumentation techniques have led to the remarkable achievements in asymmetric synthesis. Numerous BINAP analogous and other binaphthyl derivatives have been synthesized and applied in asymmetric catalysis[4].

Hydrogention of ketones, olefins, acrylic esters, enamides and α-dehydroamino acid derivatives and β-keto esters are the fundamental tools for synthesis of chiral amino acids, optically active secondary alcohols and for the synthesis of β-peptides, β-lactam antibiotics and many important drugs.

Brusse *et al.*[5] described the non-symmetric substituted 1,1′-binaphthyls for enantioselective catalysis. This review deals with the typical examples of symmetrically substituted 1,1′-binaphthyls and the application to the typical hydrogenation reactions.

Application of symmetrically substituted 1,1′-binaphthyls for asymmetric catalytic hydrogenation

There are many methods to prepare the racemization of binaphthyls[6-11]. The best method available for 1,1′-binaphthyl is reported by Ullmann and Bicleckin[12], who treat 1-iodonaphthylalene with copper power at 285°C, obtaining a 74% yield. Chiral symmetrically substituted 1,1′-binaphthyl with a great deal of structure diversity has been introduced since 1979. Representative structural features of these novel ligands are shown in Fig. 1. In general, they are all derivatives of H_8-bi-1,1′-2-binaphthol and H_8-bi-1,1′-2-binaphthylamine, etc.[13] (Fig. 1).

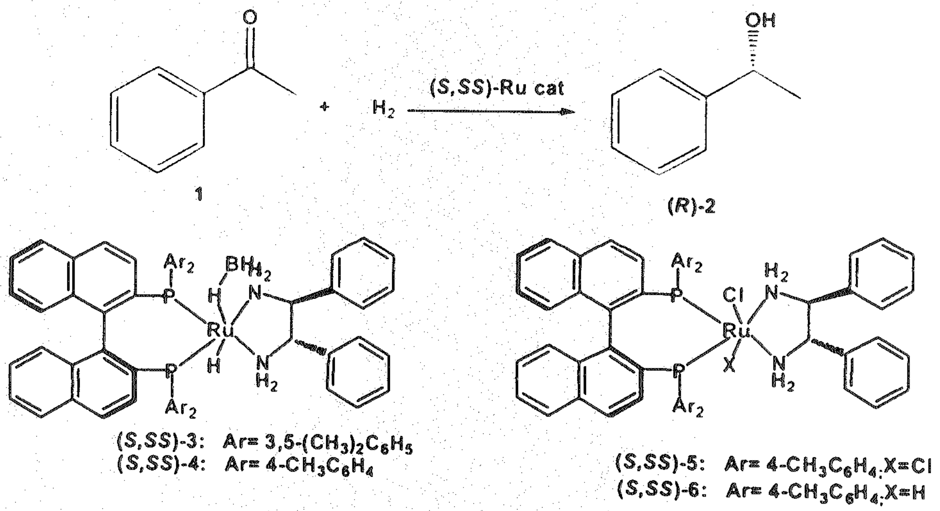


X, Y = PAr_2, OH, OR, NR_2, SR

Fig. 1.

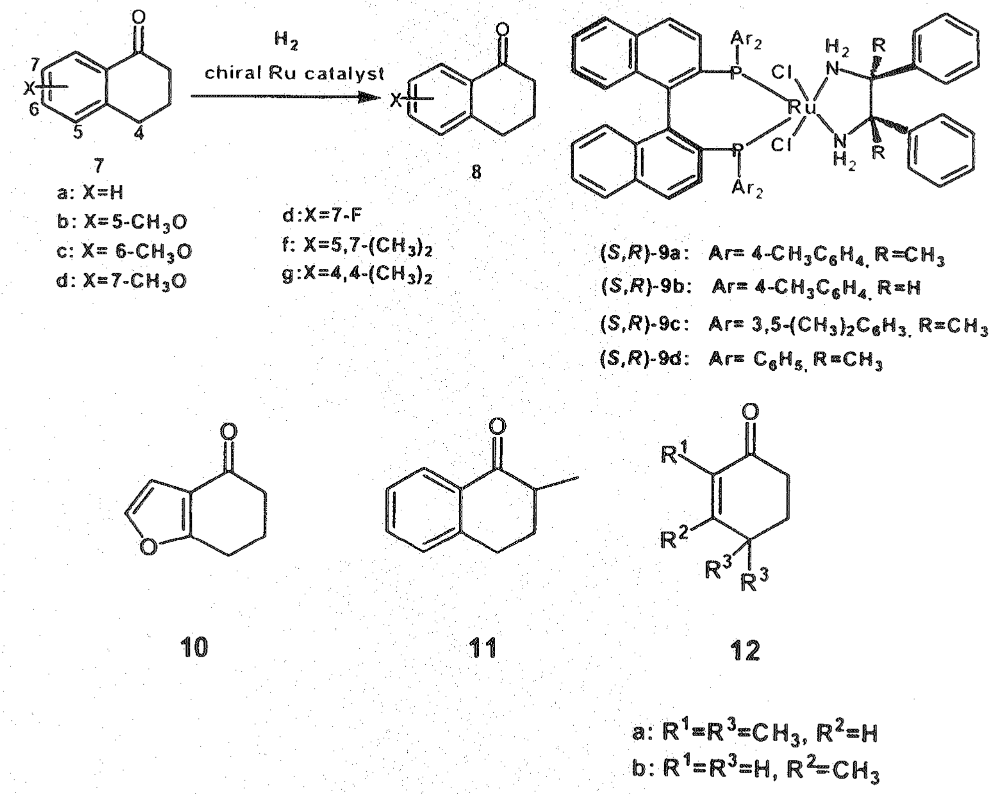
(1) BINAP/diamine ruthenium(II) complexes for hydrogenation of ketones

Noyori and co-workers[14, 15] have achieved enantioselective ketonic hydrogenation and developed many reactive catalyst systems for hydrogenation of ketone esters, of alky-aryl ketones and even of alkyl ketones. For example, Sandoval *et al.*[16] recently reported a series of BINAP/diamine ruthenium(II) complexes for hydrogenation of ketones. Noyoji *et al.*[14–16] used the catalysts **4–6** to the simple acetophenone (**Scheme-1**).



Scheme-1. Asymmetric hydrogenation of acetophenone (**1**) to (R)-1-phenylethanol [(R)-2] with (S)-BINAP/(S,S)-BINAP Ru(II) catalyst

But for 1-tetralone derivatives and some methylated 2-cyclohexenones, the catalysts **4–6** seems not suitable, because the ketone enantiofaces are differentiated on the chiral molecular surface of the saturated RuH_2, in order to get high efficiency. Ohkuma *et al.*[17] revised the structure of the catalysts, using the chiral BINAP/1,4-diamine ruthenium(II) complexes to replace the BINAP/1,2-diamine ruthenium(II) complexes and the results are found satisfactory (**Scheme-2**, Table-1).



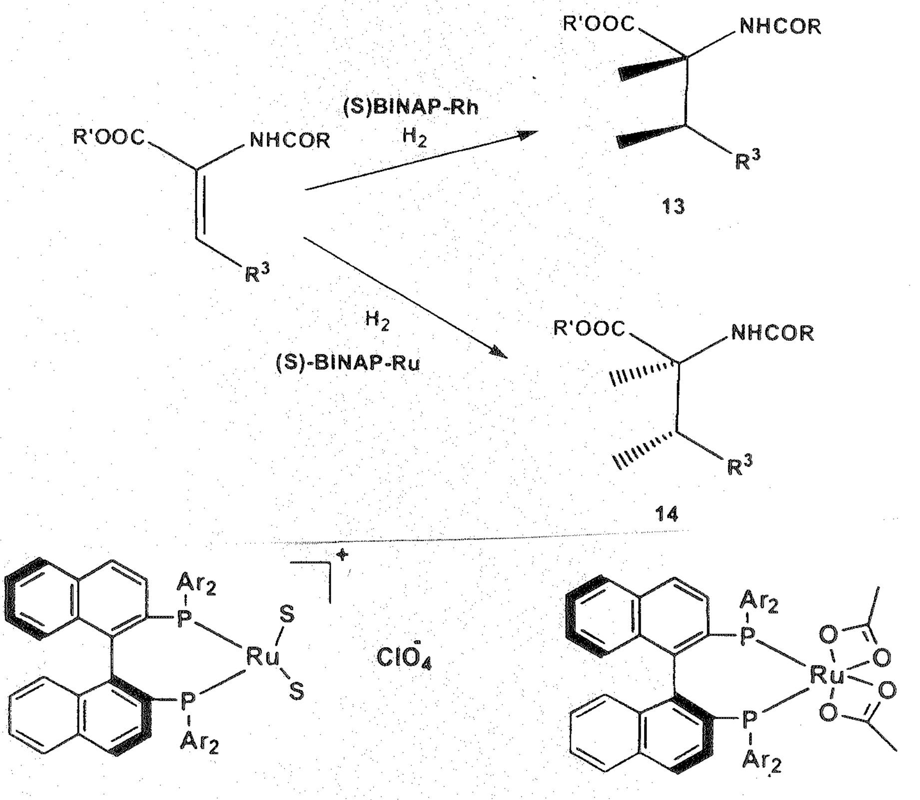
Scheme-2

TABLE-1
ASYMMETRIC HYDROGENATION OF CYCLIC KETONES

Ketone	Ru catalyst	S/C	Base [mM]	Time (h)	Yield (%)	ee (%)
7a	(S,R)-9c	3000	10	8	99.6	99
7b	(S,R)-9a	10000	20	2	100.0	98
7c	(S,R)-9a	55000	20	14	100.0	98
7d	(S,R)-9a	1000	50	13	98.0	92
7e	(S,R)-9c	3300	20	8	100.0	99
7f	(S,R)-9c	3000	20	8	100.0	98
7g	(S,R)-9d	3300	30	2	99.9	95
10	(S,R)-9a	12000	20	14	98.0	96
11	(S,R)-9d	10000	16	16	97.0	87
12a	(S,R)-9a	10000	20	7	99.5	96
12b	(S,R)-9b	1000	20	8	100.0	30

(2) BINAP/ruthenium(II) complexes as catalyst for hydrogenation of ketones, olefins and β-keto esters

Noyori and co-workers[18] had also studied the asymmetric hydrogenation of α-(acylamino)acrylic esters catalyzed by BINAP/ruthenium(II) diacetate complexes. They got the saturated products in > 90% ee (**Scheme-3**).



(*S*)-BINAP-Rh(I)[(*S*)-15]

(*S*)-BINAP-Rh(II)[(*S*)-16

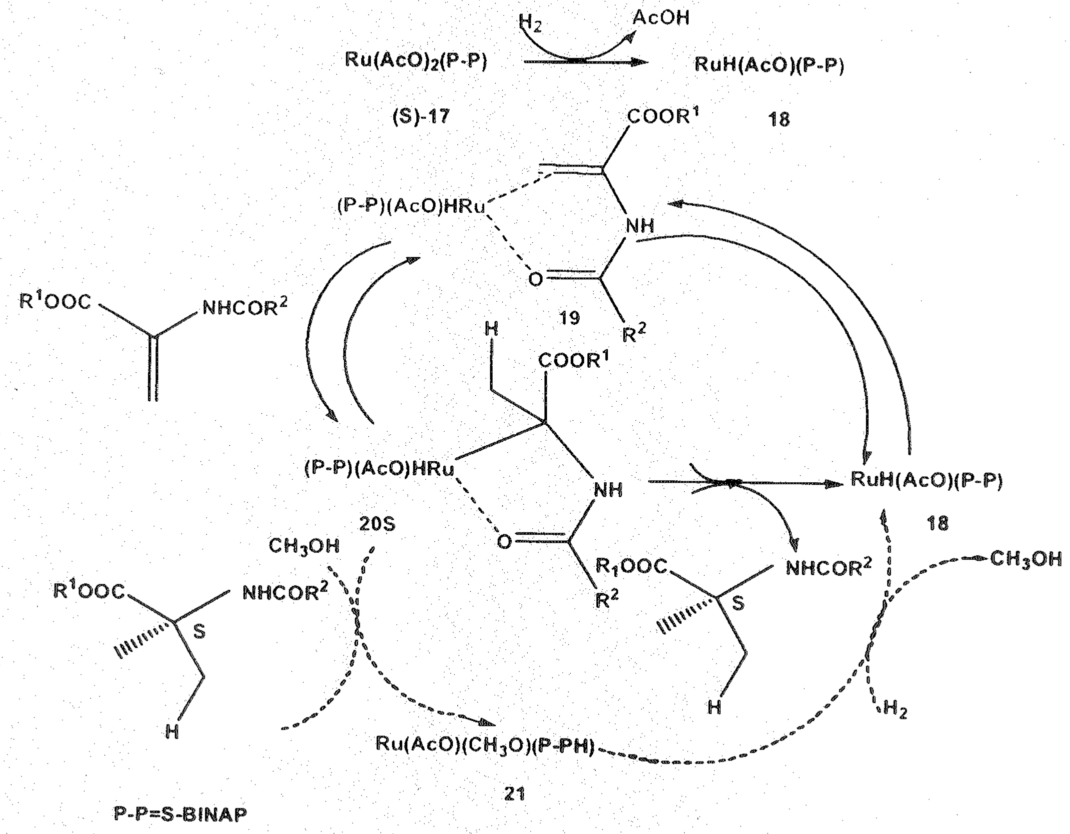
Scheme-3. Asymmetric hydrogenation of α-(acylamino)acrylic esters by (s)-BINAP Rh(I) or Rh(II) complexes

In this study, at first, they put forward the proposed mechanism (catalytic major cycle, **Scheme-4**), then made the compution on kinetics and detailed analysis isotope labelling patterns through the NMR spectra. But in conclusion the detection of true catalytic Ru complexes is diffcult and most spectroscopically observable complexes are not directly involved in the catalytic cycle (**Scheme-4**).

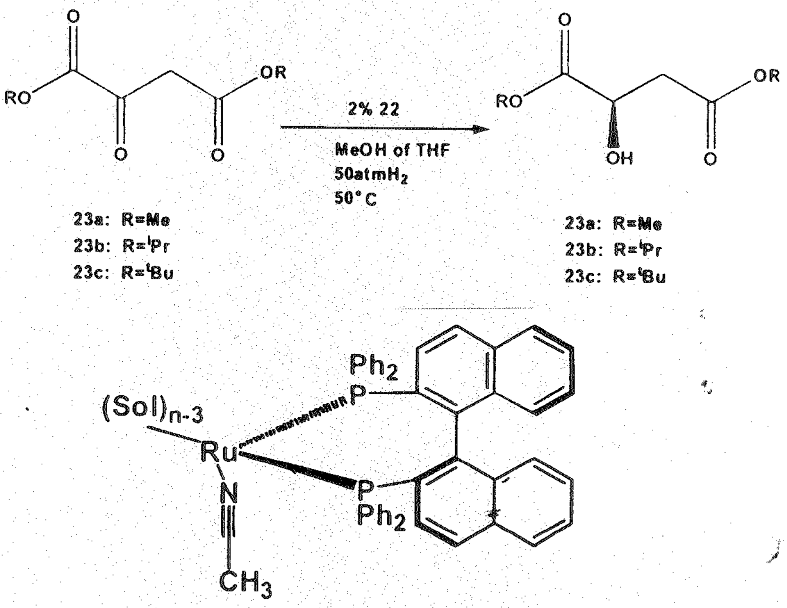
Bergens and co-workers[19] made up this in an enantioselective ketone hydrogenation. They reported the mechanistic investigation on the ketone hydrogenation catalyzed by BINAP/ruthenium(II) complexes. They first completely tested the putative catalytic intermediate structural characterization of a diasteromeric ketone-catalyst compound (**Scheme-5**).

Bergens *et al.*[19] described the NMR experiment to characterize the catalyst-substrate species according to their broad structural features, fine structural features, substrate signals and absolute configurations, BINAP signals and correlations and low-temperature studies (**Scheme-6**).

The use of racemic catalysts in catalytic asymmetric synthesis has been reported in different manners[20a]. "Chiral activator" and "chiral poisoning" are often used for asymmetric reaction, for example. Mikami *et al.*[20a, b] developed a system of theory, "the chiral activator" and "chiral poisoning' (**Scheme-7**).



Scheme-4. Mechanism of (s)-BINAP-Ru-catalyzed hydrogenation of α-(acylamino)acrylic esters in methanol



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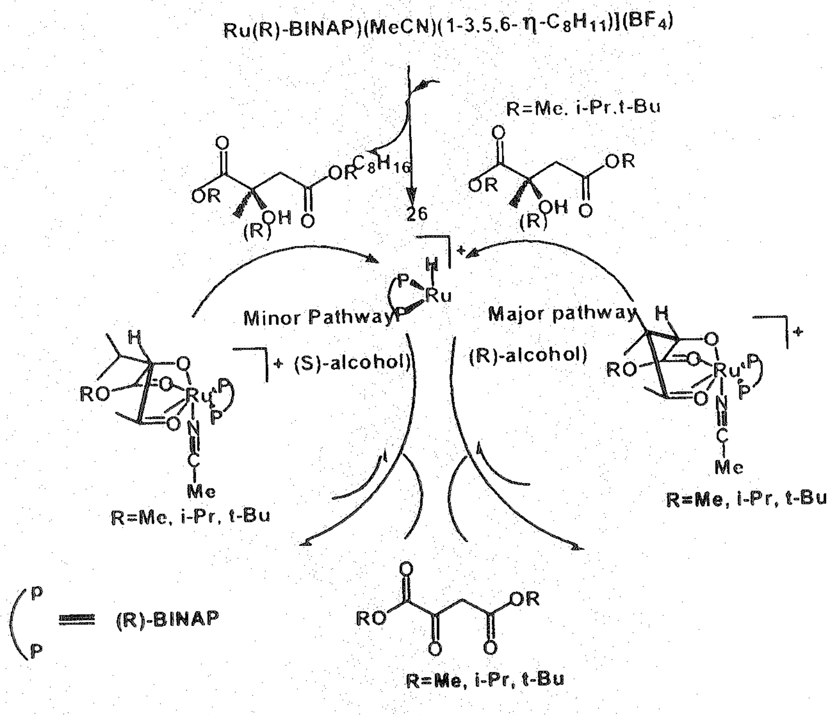
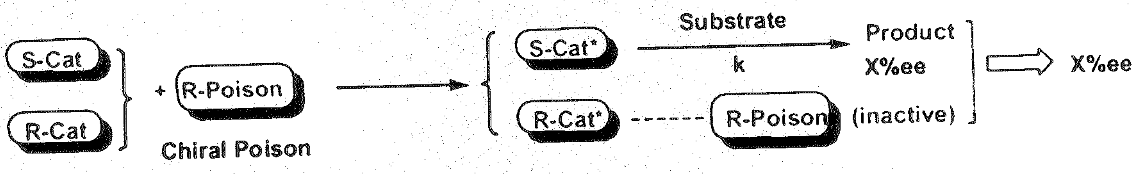
Substrate	ee(R)(MeOH)	ee(R)(THF)
23a	59	59
23b	68	66
23c	82	80

Scheme-5

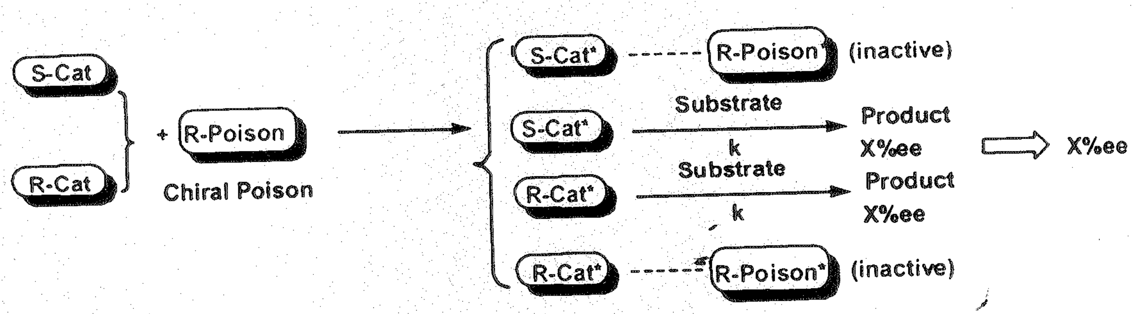


Scheme-6

a) Selective Complexation

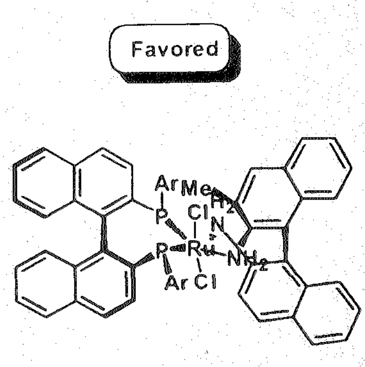


b)Nonselective Complexation



Scheme-7. Chiral poisoning of racemic catalyst

Bergens *et al.*[19] also reported asymmetric activation/deactivation of racemic Ru catalysts for highly enantioselective hydrogenation irrespective of ketonic substrates; they designed a molecular 3,3′-dimethyl-2,2′-diamino-1,1′-BINAP as a chiral poison for complete complexation of $RuCl_2$ (binaps)(dmf)n with chiral diamines to give *trans*-Ru(binaps)(diamine)complexes. Complete enantiomer recognition of the racemic BINAP-RuCl$_2$ was found to be effective for enantioselective hydrogenation of β-keto esters using enantipure DM-DABN as chiral poison (Table-2). Hydrogenation of methyl-3-oxobutanoate gave (R)-methyl-3-hydroxybutanoate with 92.4% ee in quantitative yield.



(S)-BINAP-Ru(II)Cl$_2$/(S)-DM-DABN

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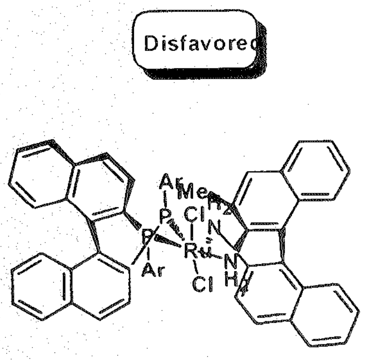

(R)-BINAP-Ru(II)Cl$_2$/(S)-DM-DABN

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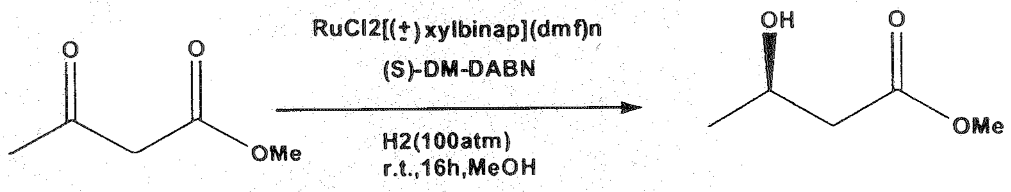


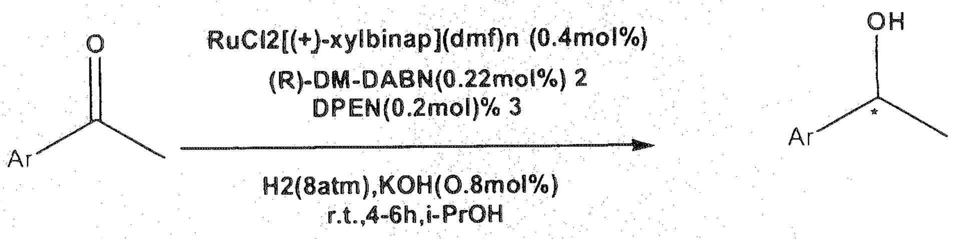
30 R-31

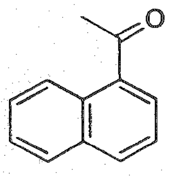
TABLE-2

HYDROGENATION OF METHYL 3-OXOBUTANOATE 30 BY RACEMIC BINAP-Ru(II) CATALYST THROUGH CHIRAL POISONING

Entry	Cat.	Deact	Yield (%)	ee (%)
30	28(±)	0.5eq	100	99.3
30	(R)-28	None	100	99.9

The efficiency of this asymmetric activation/deactivation protocol was reflected, regardless of the ketonic substrates, in the high enantioselective in the asymmetric hydrogenation (Table-3). All ketones employed can be hydrogenated at room temperature with enantiomeric excesses higher than 90% e.e. in the same quantitive yield. A superiority of the asymmetric activation/deactivation protocol significantly shown in the case of (2-naphthyl)-ethanol using complex 28 is increased up to 91% ee in contrast to only 45% ee without 2,2,4,4-trimethyl-2-cyclohexenone was also hydrogened in high enantioselectivity (92%) by changing the chirality of DPEN from S to R.

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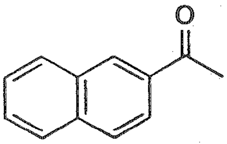
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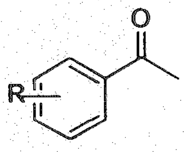

a: R=H
b: R=o=Me
c: R=m-Me
d: R=p-Me

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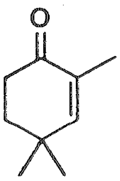
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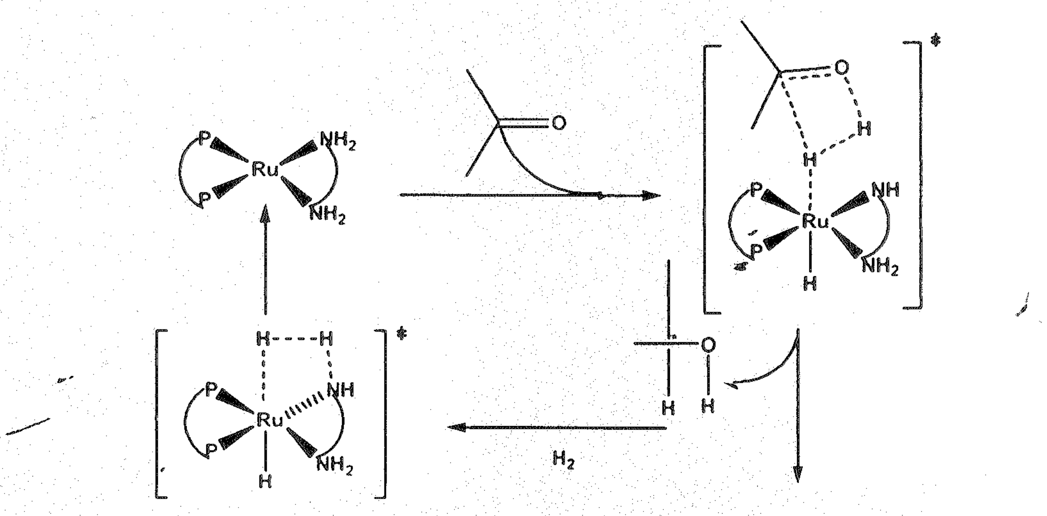
TABLE-3
HYDROGENATION OF KETONES BY THE RACEMIC [$RuCl_2$(xylbinap)] COMPLEX THROUGH ASYMMETRIC ACTIVATION/DEACTIVATION

Ketones	2	3	yield [%]	ee [%]
32	+	(S, S)	> 99	96 (R)
33	+	(S, S)	> 99	91 (R)
34a	+	(S, S)	> 99	95 (R)
34b	+	(S, S)	> 99	95 (R)
34c	+	(S, S)	> 99	95 (R)
34d	+	(S, S)	> 99	93 (R)
35	+	(R, R)	> 99	92 (R)

They also proposed the mechanism of hydrogenation and focussed on the hydro- genation-splitting step of amide complex **(Scheme-8)**.



Scheme-8

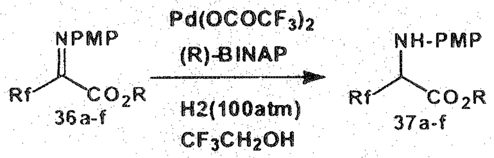
(3) BINAP/Pd complexes for hydrogenation of α-fluorinated iminoesters

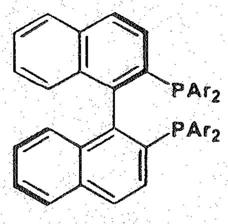
Chiral fluorinated amino acids are an important class of nonnatural molecules. Recently several excellent examples of catalytic enantioselective reaction of non-fluorinated imines such as reduction, alkylation, cyanoation, Mannich-type reactions and aza Diels-Alder reactions have been reported, especially catalytic hydrogenation of ketimines[21–24].

Several authors[25, 26] reported palladium(II) trifluoroacetate and 2,2-bis-(diphenylphosphino-1,1′-binaphthyl promoted asymmetric hydrogenation of α-fluorinated iminoesters and got the ee up to 91%.

Under the optimum condition, they compared palladium compounds, and other chiral ligands DIOP (8% ee), CHIRAPHOS (5% ee) and BPPFA (1% ee); the combination of palladium trifluoroacetate and BINAP gave the best results to afford highly enantioenriched β-fluorinated α-amino esters.

The key for getting the good results (Table-4) is that they used the solvent fluorinate alcohol; it is rationalized as a stabilizer of active catalyst or hydrogen bond donor. But the role of TFE and mechanistic studies in this hydrogenation has not been clarified yet.





38 (R)-BINAP

TABLE-5
ASYMMETRIC HYDROGENATION OF α-FLUORINATED IMINOESTERS

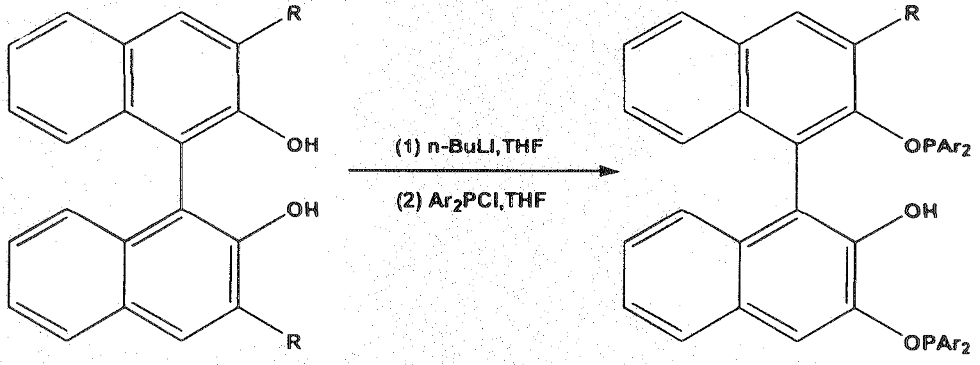
Entry	R_f	R	Yield (%)	ee (%)
36a	CF_3	Et	> 99	98(R)
36b	CF_3	*t*-Bu	92	85(R)
36c	CF_3	Bu	95	84(R)
36d	$CClF_2$	*t*-Bu	69	81(R)
36e	C_7F_{15}	Bu	98	61(R)
36f	CHF_2	Bu	75	30(R)

(4) Chiral *ortho*-substituted BINAPO for hydrogenation of acrylates and β-keto esters

Although many effective chiral BINAP/metal complexes have been reported in past. Novel family of chiral ligands have to be developed in asymmetric catalytic reaction.

Zhou *et al.*[27] have reported a novel family of BINOL-derived phosphinite ligands for the first highly enantioselective hydrogenation of β-aryl-substituted (β-acylamino)acylates and β-keto esters.

They first explored the ligand-Ru complexes to the asymmetric catalytic hydrogenation of aryl-substituted (β-acylamino)acylates (Table-5), substrates are employed, surprisingly, ee values increased dramatically when an aryl was introduced in the *o*-BINAP ligand, up to 99% ee has been achieved (entry 4). When using **43** as the ligands, the effects of the substituted groups on Ar of **45** are not too rigid, the same is R group, Me changed to Et, the ee% are all in range 95–99%.



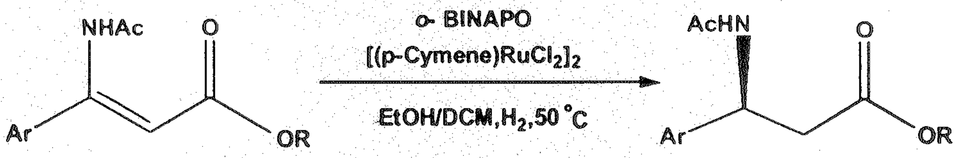
39

40:BINAPO

39: R=H, Ar=Ph
39: R=Me, Ar=Ph
39: R=Ph, Ar=Ph
39: R=3,5-$Me_2C_6H_3$, Ar=Ph
39: R=Ph,Ar=3,5-$Me_2C_6H_3$

41:Me-O-BINAP
42:Ph-o-BINAP
43:Xylyl-o-BINAP
44:Ph-o-Xylyl-BINAP

TABLE-5
ASYMMETRIC HYDROGENATION OF β-ARYL-SUBSTITUTED β-(ACYLAMINO)ACRYLATES

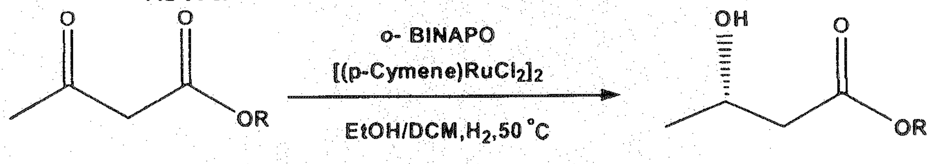


45 **46**

Entry	Ligands	Ar of 45	R of 45	ee (%)	Config.
1	BINAPO	Ph	Me	2	S
2	41	Ph	Me	22	S
3	42	Ph	Me	98	S
4	43	Ph	Me	99	S
5	44	Ph	Me	97	S
6	44	Ph	Et	98	S
7	44	*p*-F-C_6H_4	Me	99	S
8	44	*p*-MeO-C_6H_4	Me	99	S

They further expanded the utility of the *o*-BINAP ligand system (Table-6); high enantioselectivite hydrogenation of β-aryl-substituted-β-keto esters was achieved with most substrates (93%–99% ee) except for entry 6.

TABLE-6
ASYMMETRIC HYDROGENATION OF β-KETO ESTERS

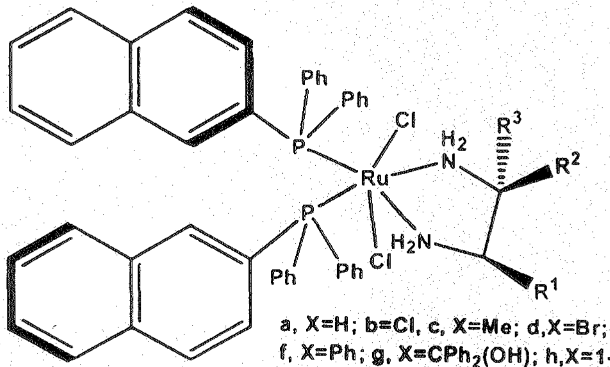


47 48

Entry	Ligand	Ar of 47	R of 47	ee (%)	Config.
1	43	Ph	Et	99	R
2	43	*p*-F-C_6H_4	Et	93	R
3	43	*p*-Cl-C_6H_4	Et	98	R
4	43	*p*-Br-C_6H_4	Et	96	R
5	43	*p*-Me-C_6H_4	Et	95	R
6	43	*p*-MeO-C_6H_4	Et	87	R
7	43	*o*-Me-C_6H_4	Et	90	R
8	43	*o*-MeO-C_6H_4	Et	98	R
9	43	Me	Me	96	S
10	44	Me	Et	96	S
11	44	ClMe	Et	98	R

(5) 4,4′-Substituted BINAP/ruthenium(II) complexes for hydrogenation of ketones

Lin *et al.*[28, 29] were encouraged to prepare a family of tunable precatalysts Ru(4,4′-BINAP)(chiral diamine)Cl_2 (complex **49**), and used for highly enantioselective hydrogenation of aromatic ketones. Asymmetric hydrogenation reactions of aromatic ketones were carried out with 0.1% of precatalysts 49a–k in the presence of KO^{t}Bu, when he used **49a–k** as the ligands for the acetophenone; the good results can reach up to 97.1%, but with the research on the substitutes of phenyl, in general, the ee % become lower slightly.



49 a-k; R1=R2=Ph, R3=H
50 l-k; R1=iPr,R2=R3=4-MeOPh

a, X=H; b=Cl, c, X=Me; d,X=Br; e,X=I
f, X=Ph; g, X=CPh$_2$(OH); h,X=1-*cyclo*-Pentanol;
i,X=P(O)(OEt)$_2$;j=X=TMS; k, X=P(O)(OH)$_2$

TABLE-7
ENANTIOMERIC EXCESSES (%) FOR ASYMMETRIC HYDROGENATION OF KETONES WITH Ru[(R)-4,4′-BINAP][(R)-DPEN]Cl_2

Entry	Ar, R	50i	50j	50k
34a	Ph, Me	97.3	98.5	98.5
51	Ph, Et	98.3	99.4	98.5
32	1-Naphthyl, Me	99.5	99.8	99.5
52	4-*t*-Bu-Ph, Me	99.3	99.6	99.2
33	2-Naphthyl, Me	98.7	98.8	99.2
34d	4-Me-Ph, Me	98.3	98.4	98.6
54	4-MeO-Ph	99.0	98.3	98.6
55	4-Cl-Ph	97.1	96.1	98.2

Asymmetric hydrogenation reactions of aromatic ketones were carried out with 0.1% of precatalysts **49a–k** in the presence of KO^{t}Bu, the ee values vary significantly among, for the hydrogenation of acetophenone to generate 1-phenylethanol, a moderate ee of 83.0%, the small substituted in the 4,4-position of BINAP in **49b–e** only slightly affect the ee, while the bulky 4,4′-position substituents in **49i–k** drastically enhance the ee for the hydrogenation aromatic ketones.

At the same time, they[28, 29] examined the performance of precatalysts **50i–k** with a more sterically demanding chiral diamine, DAIPEN, shown in Table-7, a range of aromatic ketones can be readily hydrogenated with complete conversions and ee's in the range of 98.2–99.8%. These catalysts indicate that they need a tunable catalyst platform for a practical asymmetric hydrogenation of different substrates.

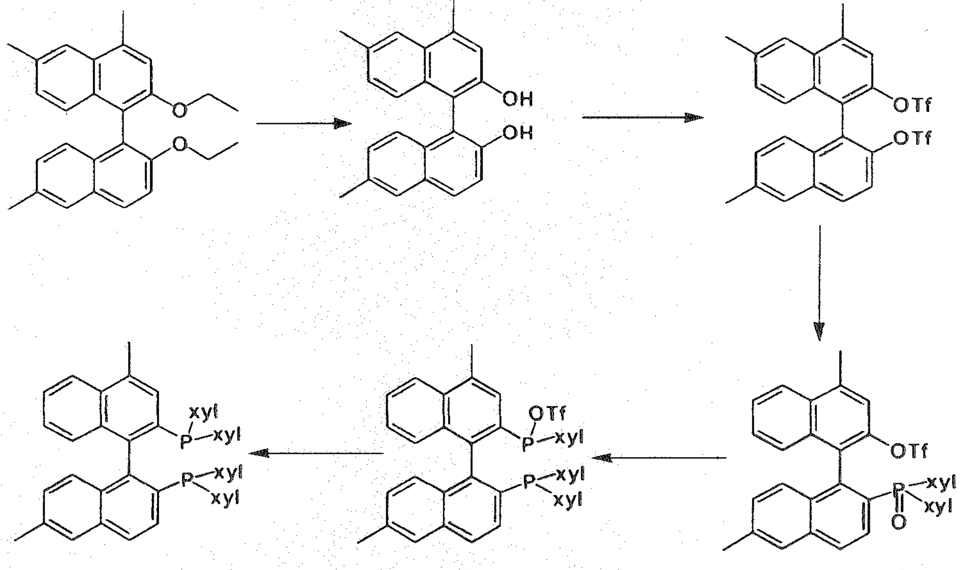
After that they[28, 29] developed a family of 4,4′-substituted XylBINAP ligands for heterogeneous asymmetric of hydrogenation of aromatic ketones. They adopted several steps to synthesize a family of complexes **(Scheme-9).**

These Ru complexes were used for asymmetric hydrogenation of aromatic ketones in a highly enantioselective manner with complete conversion. Only with 0.1% catalyst, nearly 100% conversion and 100 ee% for the most of the aromatic ketones examined, and these results are the best of the literature reported.

(6) Ruthenium(II)/phosphineamidiate catalyst for hydrogenation of enamides and α-dehydroamino acid derivatives

With the development of the asymmetric catalysis, more and more chiral binaphthyl derivative catalysts are studied. Recently, ruthenium(II)/phosphoramidites catalyst and ruthenium(II)/phosphine-phosphite catalyst showed highly efficiency for hydrogenation.

Bidentate ligands tend to be more effective in chiral induction than monodentate ligands. Feringa and co-workers[30] reported the new monodentate phos-



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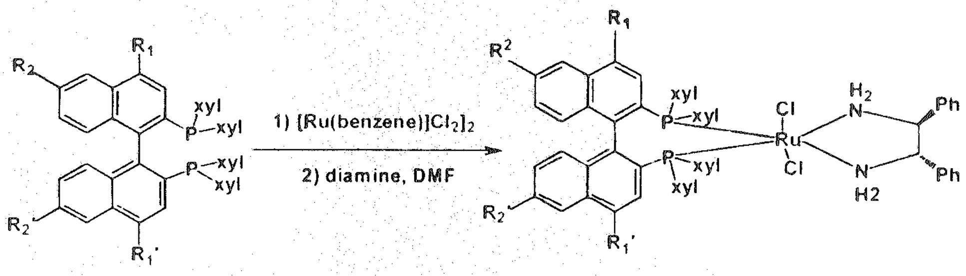
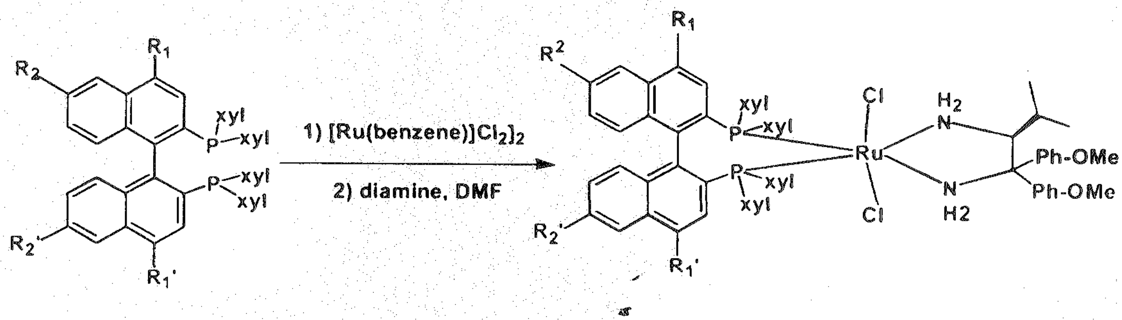


57(R)-L_1: R_1=R'=TMS, R_2=R_2'=H
58(R)-L_2: R_1=R'=Ph, R_2=R_2'=Cl
59(R)-L_3: R_1=R'=R_2=R_2'=CH_3

(R,RR)-60 [(R)-L_1)Ru (R,R)-DPEN)Cl_2
(R,RR)-60 [(R)-L_3)Ru (R,R)-DPEN)Cl_2
(R,RR)-60 [(R)-L_4)Ru (R,R)-DPEN)Cl_2

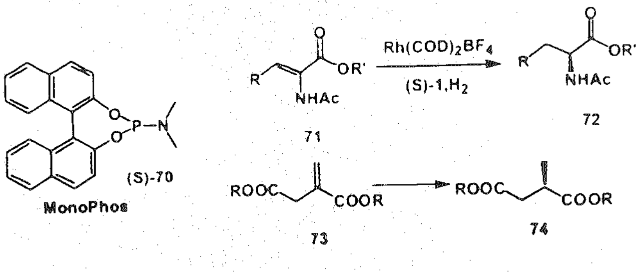


63(R)-L_1: R_1=R'=TMS, R_2=R_2'=H
64(R)-L_2: R_1=TMS, R_1'=H, R_2=R_2'=H
65(R)-L_3: R_1=R'=Ph,R_2=R_2'=Cl
65(R)-L_4: R_1=R'=R_2=R_2'=CH_3

(R,RR)-66 [(R)-L_1)Ru (R,R)-DAIPEN)Cl_2
(R,RR)-67 [(R)-L_1)Ru (R,R)-DAIPEN)Cl_2
(R,RR)-68 [(R)-L_4)Ru (R,R)-DAIPEN)Cl_2
(R,RR)-69 [(R)-L_4)Ru (R,R)-DAIPEN)Cl_2

Scheme-9

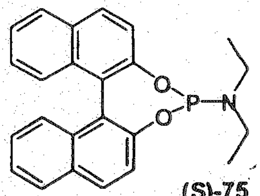
phoramidites ligands for the highly enantioselective rhodium-catalyzed hydrogenation of olefins with ee up to 99.8%. They considered the solvents, catalyst loading, H_2 pressure effect, after screening and got the excellent ee % of different substrates **(Scheme-10).**



Scheme-10

Substrate	Solvent	0°C (ee%)	25°C (ee%)	Config.
71 R = H, R' = Me	CH_2Cl_2		99.0	R
71 R = H, R' = Me	EtOAc	99.8	99.6	R
71 R = Ph, R' = Me	CH_2Cl_2	97.6	95.0	R
71 R = Ph, R' = Me	EtOAc	98.4	93.2	R
71 R = *p*-OAc-*m*-OMePh, R' = Me	CH_2Cl_2	96.3	95.1	R
71 R = *p*-OAc-*m*-OMePh, R' = Me	EtOAc	98.7		R
71 R = H, R' = H	EtOAc		98.7	R
71 R = Ph, R' = Me	CH_2Cl_2		80.5	R
71 R = Ph, R' = Me	EtOAc		97.1	R
73 R = Me	CH_2Cl_2	94.4	87.0	S
73 R = H	CH_2Cl_2		96.6	S
73 R = H	EtOAc		96.0	S

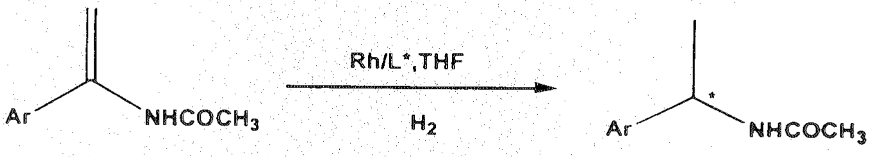
Albert[31] reported the monodentate phosphoramidite ligand, which is the S-monophos (ligand **S-70**), the others which are derived from BINOL, (S)-2,2'-O,O-(1,1'-binaphthyl)-dioxo-N,N-diethylphospholidine (ligand **75**) for the hydrogenation of enamides again in order.



(S)-75
MonoPhos

They used the [Rh(S-monophos)(COD)]BF_4 (ligand **S-70**)[3], for the hydrogenation of enamides, he changed many reaction conditions, such as the solvents, temperature, hydrogenation pressure and get the satisfactory results of different substrates (ee 50–96%)[31].

They also used the complexes [Rh(S)-2,2'-O,O-(1,1'-binaphthyl)-dioxo-N,N-diethylphospholidine](COD)]BF_4 for the hydrogenation of enamides[32] after screening the conditions highly ee% (up to 99.6%) was resulted (Table separately).



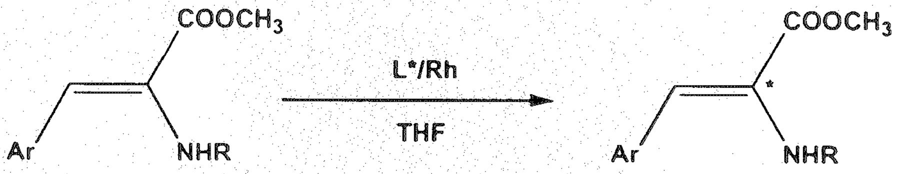
76a-i

77

Scheme-11

Entry	Substrate	Ar	S/C (mol/mol)	Temp. (°C)	Time (h)	Yield (%)	ee (%)
1	76a	C_6H_5	100	room temp.	4	> 99	95 (87)
2	76a	C_6H_5	100	5	4	> 99	99 (90)
3	76a	C_6H_5	200	5	8	> 99	97
4	76a	C_6H_5	400	5	12	> 99	96
5	76b	*p*-F_3C-C_6H_5	100	room temp.	4	> 99	97 (89)
6	76b	*p*-F_3C-C_6H_5	100	5	4	> 99	99.6 (92)
7	76c	*p*-Br-C_6H_5	100	5	4	> 99	99 (91)
8	76d	*p*-MeO-C_6H_5	100	room temp.	6	> 99	93
9	76e	*p*-MeO-C_6H_5	100	5	6	> 99	98
10	76f	*p*-Me-C_6H_5	100	5	6	> 99	98
11	76g	*m*-MeO-C_6H_5	100	5	6	> 99	98
12	76h	*m*-Me-C_6H_5	100	5	6	> 99	98
13	76i	1-naphthyl	100	5	18	85	59

In the same way, they also used these catalysts for the hydrogenation of α-dehydroamino acid derivatives (**Scheme-12**). The results are better than for the enamides, no matter the different groups on the substrates of Ar and R, the ee% is found to be very good, nearly 100% (**Scheme-12**).



78

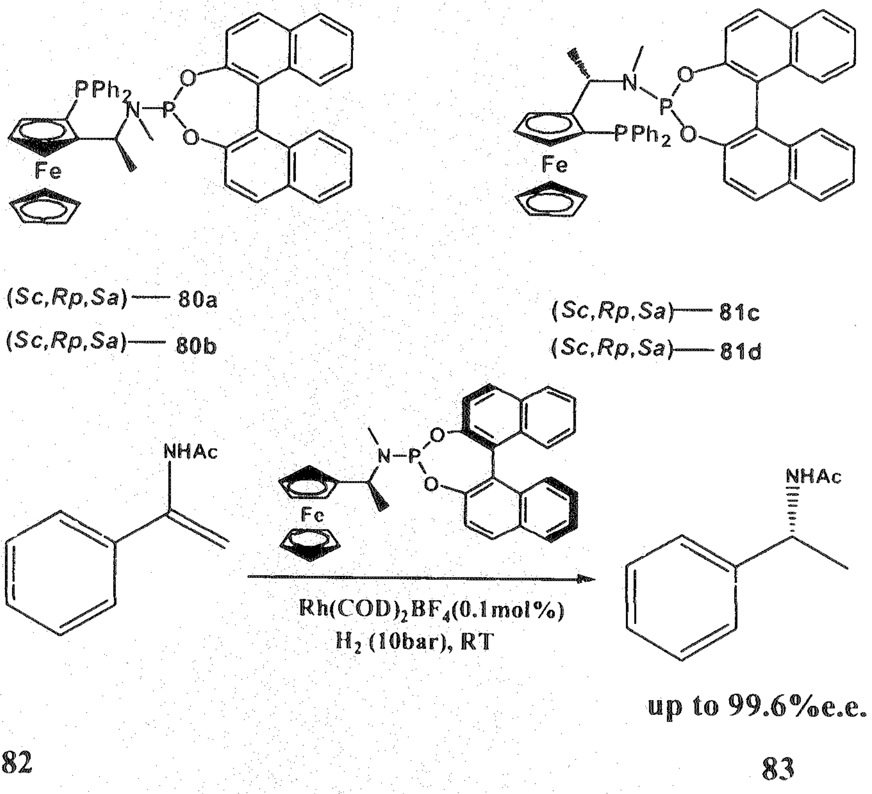
79

Scheme-12

Zheng and Hu[33] have also developed a new family of air-stable, highly unsymmetrical ferrocene-based phosphine-phosphoramidites bidentate ligands (**Scheme-13**), and applied to the hydrogenation of enamides (up to 99.6% ee), itaconate (up to 99.9% ee), and methyl(Z)-acetamidocinnamate (up to 99.9% ee).

(7) Ruthenium(II)/phosphite catalyst for hydrogenation of α, β-unsaturated carboxylic acid derivatives

Chiral ligands from the chiral pool have recently attracted a great deal of interest, because they are easily available from nature, for example, phosphine-phosphite ligand for the hydrogenation, Brunner *et al.*[34] reported moderate enantioselectivities (up to 35%). Until recently, Ruiz *et al.*[35] developed a new class of efficient catalysts, which was for the asymmetric hydrogenation of α,β-unsaturated carboxylic acid derivatives; they got satisfactory results, the enantioselectivities (up to 99%).



(Sc,Rp,Sa)— 80a
(Sc,Rp,Sa)— 80b

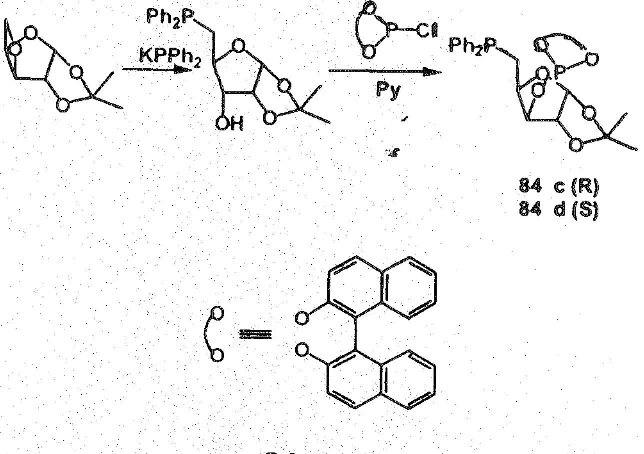
(Sc,Rp,Sa)— 81c
(Sc,Rp,Sa)— 81d

82

83

Scheme-13

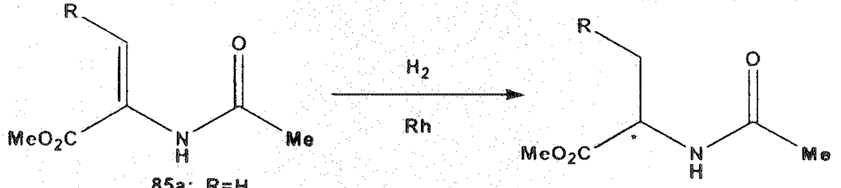
The ligands which are a series of novel phosphine-phosphites, derived from D-(+)-xylose; they studied the varied biphenyl substituents in the phosphate moiety greatly affected the enantioselectivity and has also made the mechanism study, but only one point, their catalysts are limited to two kinds of substrates (**Scheme-14**).



84 c (R)
84 d (S)

Scheme-14

ASYMMETRIC HYDROGENATION OF METHYL (N)-ACETAMIDOACRYLATE 85a AND METHYL (Z)-(N)-ACETAMIDOCINNAMATE (85b) WITH [(Rh(COD)$_2$BF$_2$ (84)



85a: R=H
85b: R=Ph

86

Entry	Substrate	Solvent	Ligand	TOF	Yield (%), time (min)	ee (%)
1	86a	CH_2Cl_2	**84c**	318	100 (20)	97.6 (R)
2	86a	CH_2Cl_2	**84d**	330	100 (20)	98.3 (S)
3	86b	CH_2Cl_2	**84c**	212	100 (30)	94.3 (R)
4	86b	CH_2Cl_2	**84c**	212	100 (30)	91.0 (S)

Conclusion

This review reports some examples of symmetric substituted 1,1′-binaphthyls, and their application to the typical asymmetric catalytic hydrogenation reactions. In the past, many researchers have made great contribution to hydrogenation for industrial application. But some new high efficient catalysts are requires to be devised and developed further, such as to increase the diversity of the ligands, employed the more broader metal ions as the Lewis acids. The mechanisms are still waiting to be cleared and determined.

REFERENCES

1. (a) V. von Richter, *Chem. Ber.*, **6**, 1252 (1873); (b) R. Pummerer, E. Prell and A. Rieche, *Chem. Ber.*, **59**, 2159 (1926).
2. (a) J. Jacques and C. Fouquey, *Tetrahedron Lett.*, 4617 (1971); (b) E.P. Kyba, G.H. Gokel and F. De Jong, *J. Org. Chem.*, **42**, 4173 (1977).
3. P. Kocovsky, S. Vyskocil and M. Smrcina, *Chem. Rev.*, **103**, 3213 (2003).
4. (a) R.Nojori, Asymmetric Catalysis in Organic Synthesis, Wiley, New York (1994); Ojima, Catalytic Asymmetric Synthesis, 2nd Edn., Wiley, New York (2000); (b) M. McCarty and P.J. Guiry, *Tetrahedron*, **57**, 3809 (2001).
5. (a) J. Brusse and A.C.A. Jansen, *Tetrahedron Lett.*, **24**, 3261 (1983); (b) J. Brusse, L.G. Groenedijk, J.M. TeKoppele and A.C.A. Jansen, *Tetrahedron*, **41**, 3313 (1985).
6. J. Brusse and A.C.A. Jansen, *Tetrahedron Lett.*, **24**, 3261 (1983).
7. M. Smrcina, V.J.S. Polakova and P. Kocovsky, *J. Org. Chem.*, **59**, 2156 (1994).
8. F.K. Toda, K. Tanaka and S. Iwata, *J.O. Chem.*, **54**, 3007 (1989).
9. (a) H. Yamamoto, H. Fukushima, Y. Okamoto, K. Hatada and M. Nakazaki, *J. Chem. Soc., Chem. Commun.*, 1111 (1984); (b) F. Diederich, M.R. Hester and M.A. Uyeki, *Angew. Chem., Int. Ed. Engl.*, **27**, 1705 (1988).
10. M. Smrcina, M. Lorenc, V. Hanus and P. Kocovsky, *Synlett.*, 231 (1991).
11. M. Smrcina, M. Lorenc, V. Hanus, P. Sedmera and P. Kocovsky, *J. Org. Chem.*, **57**, 1917 (1992).
12. Ullmann and Bielecki, *Ber.*, **34**, 2184.
13. A. Korostylev, V.I. Tararov, C. Fischer, A. Monsees and A. Borner, *J. Org. Chem.*, **69**, 3220 (2004).
14. R. Noyoji and T. Ohkuma, *Angew. Chem., Int. Ed. Engl.*, **40**, 40 (2001).
15. R. Noyoji, *Angew. Chem., Int. Ed. Engl.*, **41**, 2008 (2002).

16. C.A. Sandoval, T. Ohkuma, K. Muniz, R. Noyoji, *J. Am. Chem. Soc.*, **125,** 13490 (2003).
17. T. Ohkuma, T. Hattori, H. Ooka, T. Inoue and R. Noyori, *Org. Lett.*, **6,** 2681 (2004).
18. M. Kitamura, M. Tsukamoto, Y. Bessho, M. Yoshimura, U. Kobs, M. Widhalm and. R. Noyori, *J. Am. Chem. Soc.*, **124,** 6649 (2002).
19. C.J.A. Daley and S.H. Bergens, *J. Am. Chem. Soc.*, **124,** 3680 (2002).
20. (a) K. Mikami, Y. Yusa and T. Korenaga, *Org. Lett.*, **4,** 1643 (2002); (b) K. Mikami, T. Korenaga, Y. Yusa and M. Yamanaka, *Adv. Synth. Catal.*, **345,** 246 (2003).
21. For reviews, see: (a) H.-U. Blaser and F. Spindler, in: E.N. Jacobsen, A. Pfaltz and H. Yamamoto (Eds.), Comprehensive Asymmetric Catalysis, Springer, Berlin, Vol. 1, pp. 247–265 (1999). (b) C. Bolm, *Angew. Chem., Int. Ed. Engl.*, **32,** 232 (1993).
22. Ti-catalyzed asymmetric hydrogenation of imines: (a) C.A. Willoughby and S.L. Buchwald, *J. Am. Chem. Soc.*, **114,** 7562 (1992). (b) ———, *J. Am. Chem. Soc.*, **116,** 8952 (1994). (c) ———, *J. Am. Chem. Soc.*, **116,** 11703 (1994). Hydrosilylation of imines: (d) ———, ,*J. Org. Chem.*, **58,** 7627 (1993). (e) X. Verdaguer, U.E.W. Lange, M.T. Reding and S.L. Buchwald, *J. Am. Chem. Soc.*, **118,** 6784 (1996). (f) X. Verdaguer, U.E.W. Lange and S.L. Buchwald, *Angew. Chem., Int. Ed. Engl.*, **37,** 1103 (1998).
23. Ru-catalyzed asymmetric hydrogenation of imines: (a) W. Oppolzer, M. Wills, C. Starkemann and G. Bernardinelli, *Tetrahedron Lett.*, **31,** 4117 (1990). Hydrogen transfer to imines: (b) N. Uematsu, A. Fujii, S. Hashiguchi, T. Ikariya and R. Noyori, *J. Am. Chem. Soc.*, **118,** 4916 (1996). (c) R. Noyori and S. Hashiguchi, *Acc. Chem. Res.*, **30,** 97 (1997). (d) K.H. Ahn, C. Ham, S.K. Kim and C.W. Cho, *J. Org. Chem.*, **62,** 7047 (1997). (e) E. Vedejs, P. Trapencieris and E. Suna, *J. Org. Chem.*, **64,** 6724 (1999).
24. Rh-catalyzed asymmetric hydrogenation of imines: (a) A.G. Becalski, W.R. Cullen, M.D. Fryzuk, B.R. James, G.-J. Kang and S. Rettig, *J. Inorg. Chem.*, **30,** 5002 (1991). (b) J. Bakos, A.Ä. Orosz, B. Heil, M. Laghmari, P. Lhoste and D. Sinou, *J. Chem. Soc. Chem. Commun.*, 1684 (1991). C. Lensink and J.G. de Vries, *Tetrahedron: Asymmetry,* **3,** 235 (1992). Hydrogen transfer to imines: (c) J. Mao and D.C. Baker, *Org. Lett.*, **1,** 841 (1999). Hydrogenation of acylhydrazones: (d) M.J. Burk and J.E. Feaster, *J. Am. Chem. Soc.*, **114,** 6266 (1992). (e) M.J. Burk, J.P. Martinez, J.E. Feaster and N. Cosford, *Tetrahedron*, **50,** 4399 (1994).
25. Ir-catalyzed asymmetric hydrogenation of imines: (a) F. Spindler, B. Pugin and H.-U. Blaser, *Angew. Chem., Int. Ed. Engl.*, **29,** 558 (1990). (b) A. Togni, *Angew. Chem., Int. Ed. Engl.*, **35,** 1475 (1996). (c) T. Morimoto and K. Achiwa, *Tetrahedron: Asymmetry.*, **6,** 2661 (1995). (d) R. Sablong and J.A. Osborn, *Tetrahedron Lett.*, **37,** 4937 (1996). (e) P. Schnider, G. Koch, R. Prétôt, G. Wang, F.M. Bohnen, C. Krüger and A. Pfaltz, *Chem. Eur. J.*, **3,** 887 (1997). (f) S. Kainz, A. Brinkmann, W. Leitner and A. Pfaltz, *J. Am. Chem. Soc.*, **121,** 6421 (1999).
26. H. Abe, H. Amii and K. Uneyama, *Org. Lett.* **3,** 313 (2001).
27. Y.G. Zhou, W.J. Tang, W.B. Wang, W.G. Li and X.M. Zhang, *J. Am. Chem. Soc.*, **124,** 4952 (2002).
28. A. Hu, H.L. Ngo and W.B. Lin, *Org. Lett.*, **6,** 2937 (2004).
29. H.L. Ngo and W.B. Lin, *J. Org. Chem.*, **70,** 1177 (2005).
30. M.V.D. Berg, A.J. Minnaard, E.P. Schudde, J.D. Vries and B.L. Feringa, *J. Am. Chem. Soc.*, **122,** 11539 (2000).
31. X. Jia, R.W. Guo, X.S. Li, X.S. Yao and S.C.C. Albert, *Tetrahedron Lett.*, **43,** 5541 (2002).
32. X. Jia, X.S. Li, L.J. Xu, Q. Shi, X.S. Yao and S.C.C. Albert, *J. Org. Chem.*, **68,** 4539 (2003).
33. X.P. Hu and Z. Zheng, *Org. Lett.*, **6,** 3585 (2004).
34. H. Brunner and W. Pieronczyk, *Chem. Res. Synop.*, **3,** 76 (1980).
35. O. Pamies, M. Dieguez, G. Net, A. Ruiz, C. Claver, *J. Org. Chem.*, **66,** 8364 (2001).

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