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Supporting Information

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SUPPORTING INFORMATION
of
Heterogeneous Enantioselective Hydrogenation of Aromatic Ketones Catalyzed by Cinchona- and Phosphine-Modified Ir Catalysts

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CONTENTS:

(A) Hydrogenation experiment

The hydrogenation was performed in a 20 ml stainless autoclave with a magnetic stirrer bar. The desired amounts of catalyst (20mg), diamine, LiOH, solvent and substrate were added into the autoclave and then the autoclave was sealed and purged with pure hydrogen several times. After the reactants were heated to the desired temperature, the reaction timing began.

(B) Details of the homogeneous hydrogenation catalyzed by Ir/phosphine/diamine

The hydrogenation was performed in a 20 ml stainless autoclave with magnetic stirrer bar. The desired amount of $[Ir(cod)Cl]_2$ (the molar of Ir is equal to the supported metal Ir used in heterogeneous hydrogenation), two equivalent of tpp (tppts, one equivalent of bisbi) compared to Ir, the same amount of diamine, LiOH, solvent compared to heterogeneous hydrogenation were added to the autoclave and them the autoclave was sealed and purged with pure hydrogen several times, the mixture was stirred under 50 °C and the hydrogen pressure of 6.0 MPa for one hour. Then the substrate was introduced, the reactants was heated to 30 °C and reacted under 6.0 MPa for three hour.

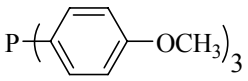
(C) ***Table 1:*** Effect of different solvents on asymmetric hydrogenation of acetophenone employing chiral diamine **2** as a modifier.[a]

Solvent	Yield [%]	*ee* [%]	Config[b]
MeOH	100	74	*R*
EtOH	10	34	*R*
*i*PrOH	6	37	*R*

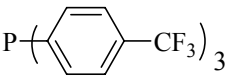
H_2O	5	20	*R*
THF	1	9	*R*
$CH_3CH_2CH_2OH$	6	42	*R*
$CH_3CH_2CH_2CH_2OH$	4	33	*R*
Toluene	2	22	*R*

[a] Reaction was carried out at 30 °C for modifier **2**. Substrate : in a 2 ml solution at [0.313 M], P_{H2} : 6.0 MPa. Substrate/Ir/diamine = 200:1:2, [LiOH] = 0.125mol L^{-1}. Reaction time : 3 hour. Products were analyzed by a GC instrument with an FID detector and β-DEX^{TM}120 capillary column. [b] Determined by sign of rotation.

(D) ***Table 2:*** Effect of different stabilizers on asymmetric hydrogenation of acetophenone employing chiral diamine **2** as a modifier.



motpp



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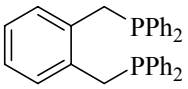
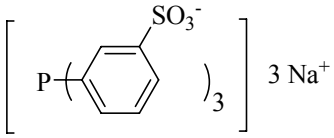
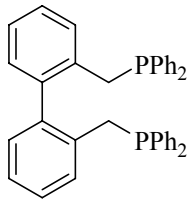


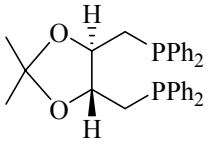
bdpx



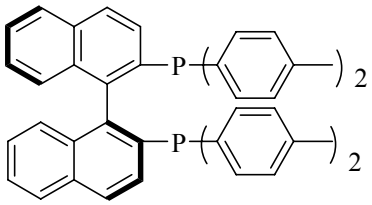
tppts



bisbi



(*S*,*S*)-diop



(*S*)-Tolbinap

Catalyst	Yield [%]	*ee* [%]	Config
3%Ir/SiO_2/2tpp	100	74	*R*
3%Ir/SiO_2/(*S*,*S*)-diop	3	50	*R*
3%Ir/SiO_2/(*S*,*S*)-diop[a]	2	4	*S*
3%Ir/SiO_2/bisbi	2	12	*R*
3%Ir/SiO_2/bdpx	4	34	*R*
3%Ir/SiO_2/(*S*)-Tolbinap	2	27	*R*
3%Ir/SiO_2/(*S*)-Tolbinap[a]	2	23	*S*
3%Ir/SiO_2/2motpp	80	63	*R*
3%Ir/SiO_2/2tftpp	81	54	*R*
3%Ir/SiO_2/2tppts	10	67	*R*

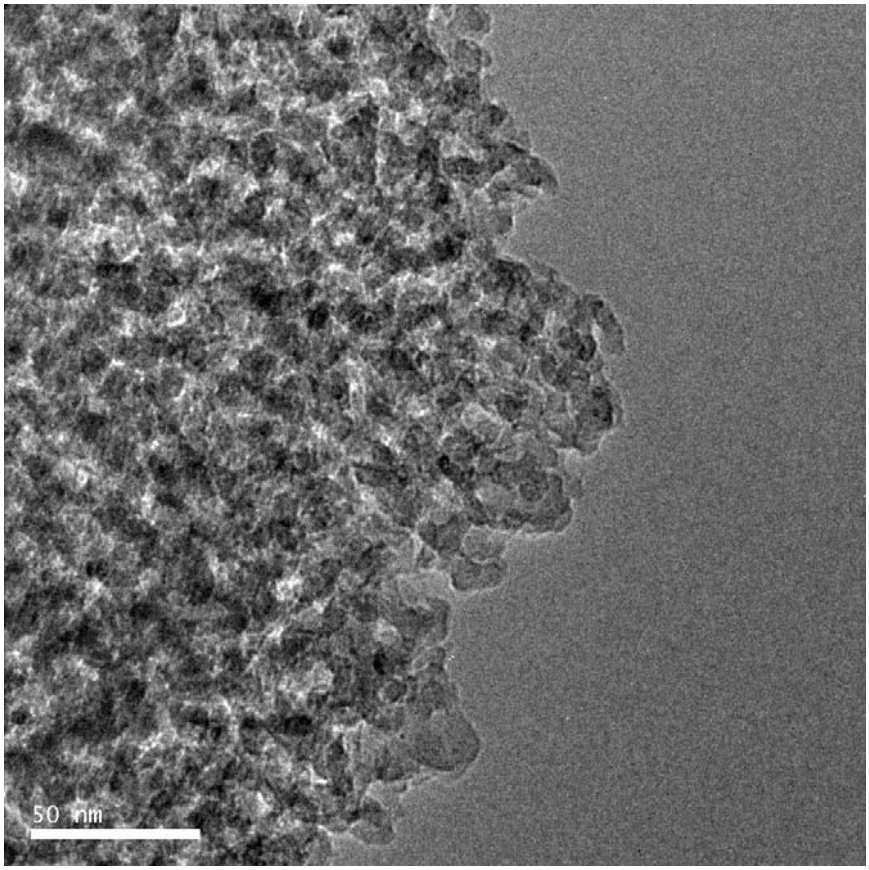
The reaction conditions are the same as in Table 1 except the stabilizer. Reaction time : 3 hour. [a] Diamine **1** was employed as a modifier. Reaction was carried out at 40°C for 10 hour.

(E) ***Table 3:*** Effect of different modifiers on asymmetric hydrogenation of acetophenone.

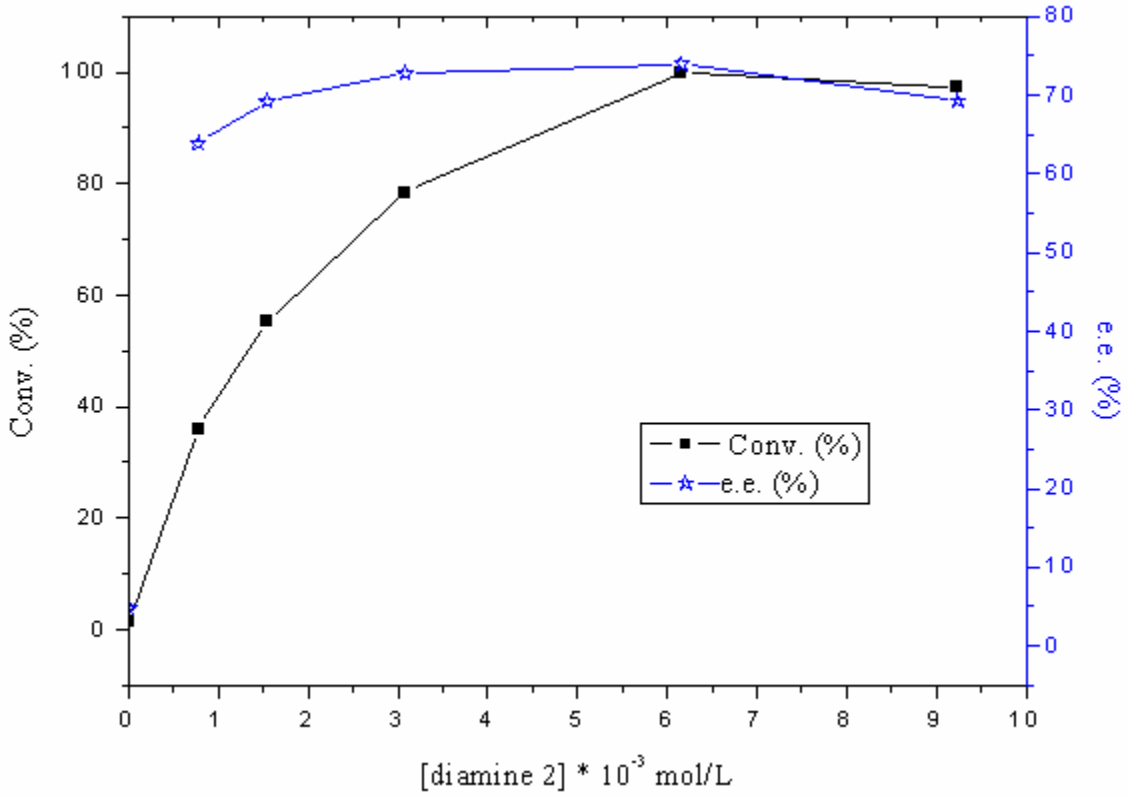
Modifiers	Yield [%]	*ee* [%]	Config
cinchonine[a]	2	34	*R*
cinchonidine[a]	3	34	*R*
quinine[b]	2	5	*R*

The reaction conditions are the same as in Table 1. [a] Reaction was carried out at 40°C for 3 hour. [b] Reaction was carried out at 40°C for 20 hour.

(F) ***Figure 1.*** HRTEM micrograph of 3%Ir/SiO_2/2tpp.

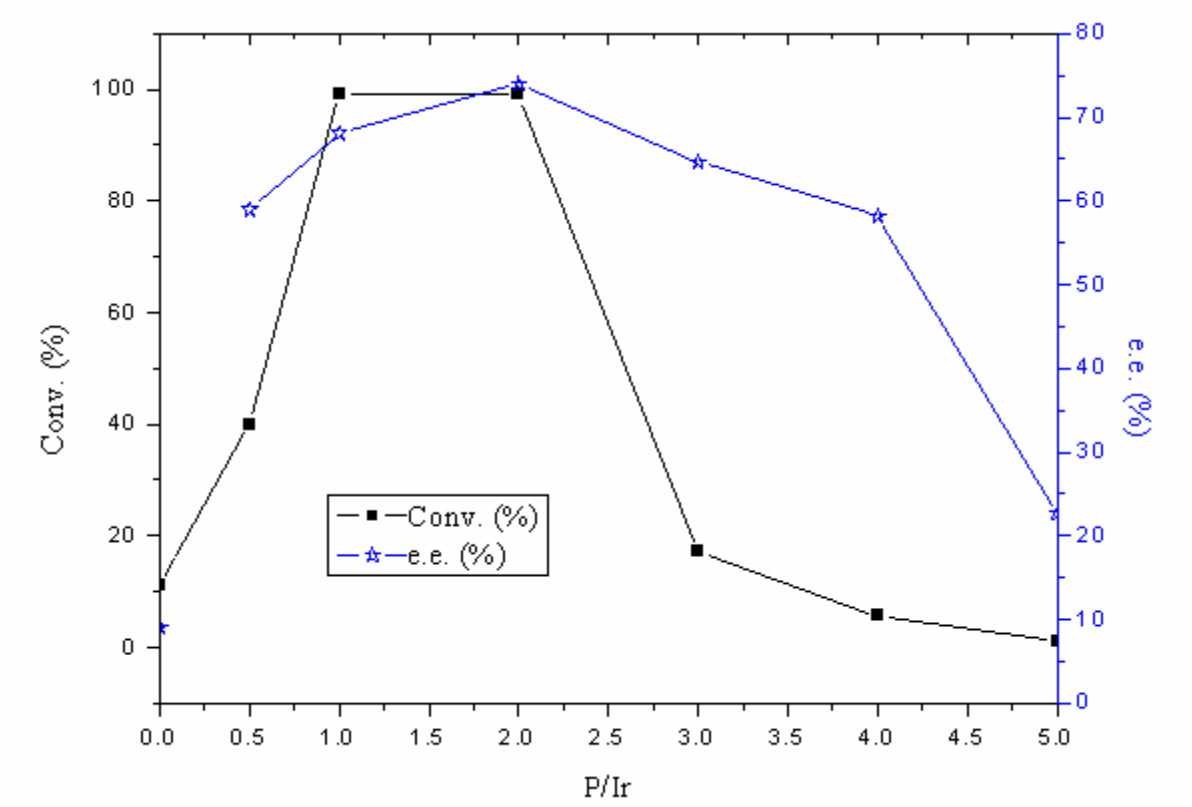


(G) ***Figure 2.*** Effect of modifier **2** concentration on asymmetric hydrogenation of acetophenone.



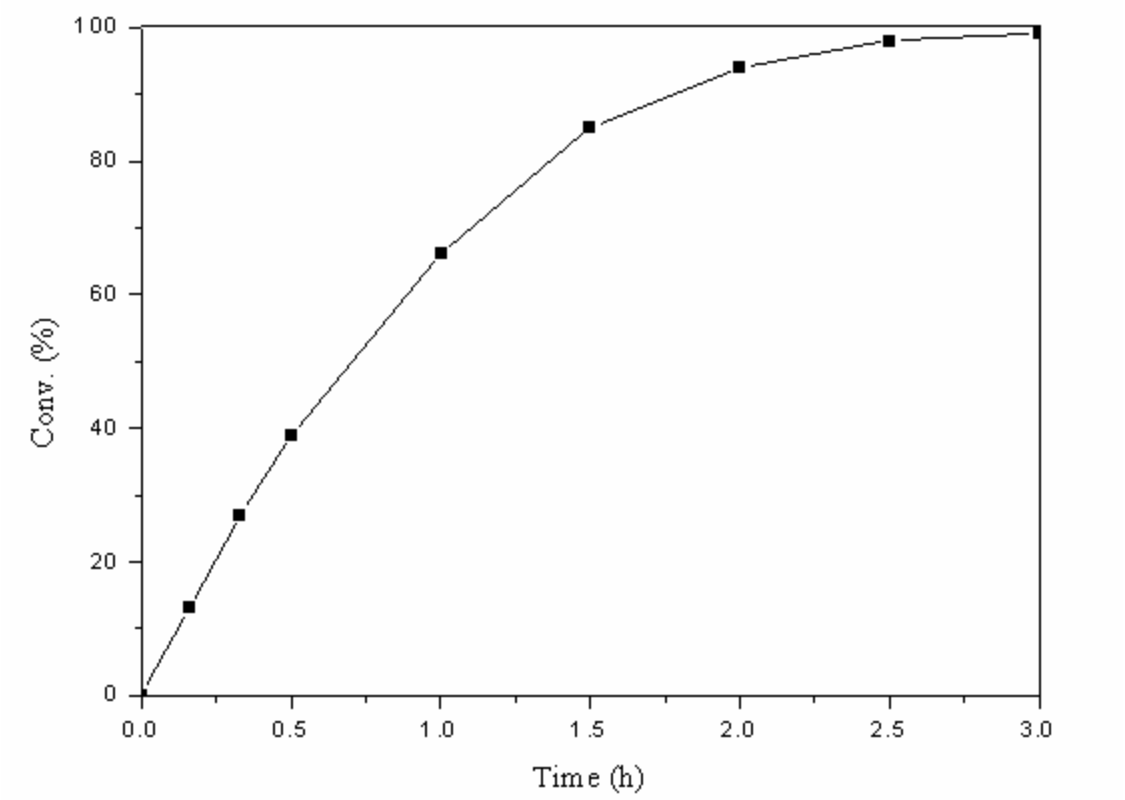
The reaction conditions are the same as in Table 1 except the concentration of diamine **2**. Reaction time : 3 hour.

(H) ***Figure 3.*** Effect of different P/Ir ratio on asymmetric hydrogenation of acetophenone employing chiral diamine **2** as a modifier.



The reaction conditions are the same as in Table 1 except the P/Ir ratio. Reaction time : 3 hour.

(I) ***Figure 4.*** Hydrogenation curve employing chiral diamine **2** on asymmetric hydrogenation of acetophenone.



The reaction conditions are the same as in Table 1.