

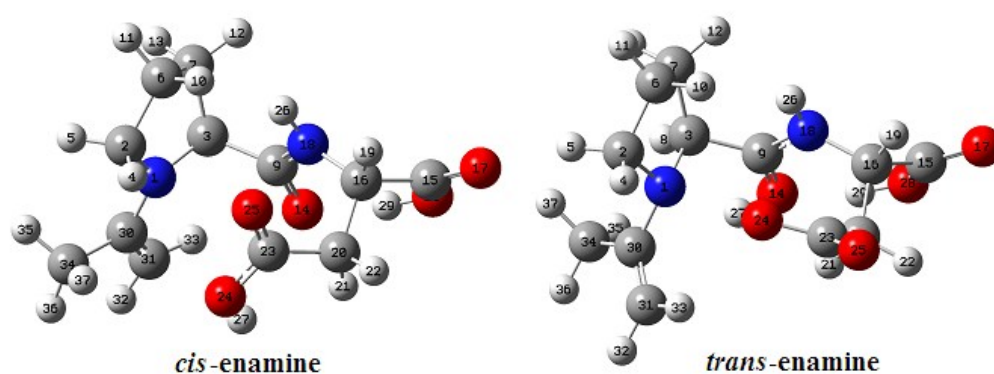
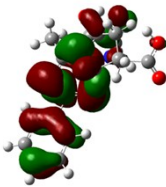
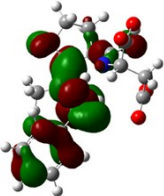
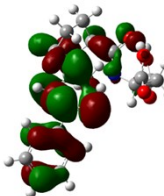
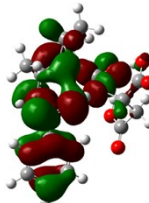
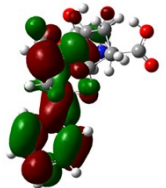
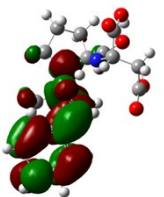
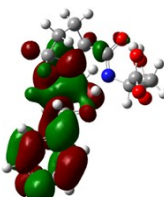
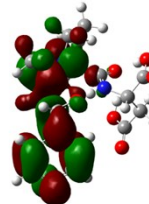
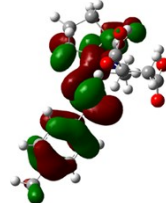
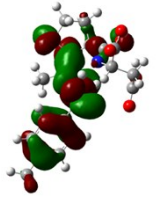
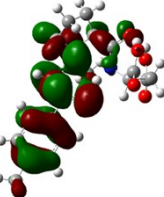
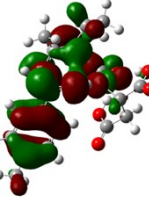
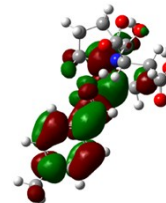
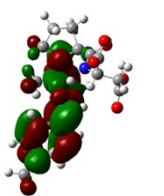
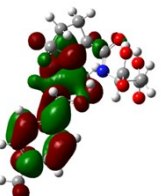
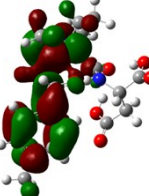
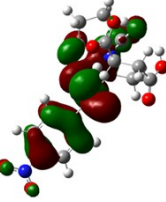
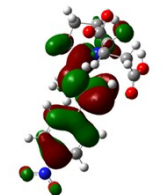
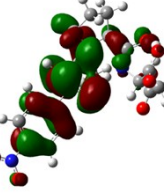
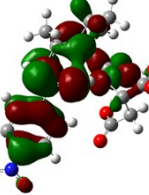


Fig.1 Structural models of two enamines

Table.1 Main geometric parameters of *cis*- and *trans*-enamines

	<i>cis</i> -enamine	<i>trans</i> -enamine
Bond distance/Å		
N ¹ -C ³⁰	1.39	1.45
C ³⁰ =C ³¹	1.36	1.34
C ³⁰ -C ³⁴	1.51	1.51
N ¹ -C ³	1.47	1.50
C ⁹ =O ¹⁴	1.25	1.25
C ⁹ -N ¹⁸	1.35	1.35
N ¹⁸ -H ²⁶	1.01	1.01
Bond angle/°		
N ¹ -C ³⁰ =C ³¹	124	118
N ¹ -C ³⁰ -C ³⁴	115	118
C ³⁰ -N ¹ -C ³	123	118
Dihedral angle/°		
C ³¹ =C ³⁰ -N ¹ -C ³	8	143
N ¹ -C ³⁰ -C ³⁴ -C ³¹	-179	176
C ² -N ¹ -C ³⁰ -C ³	165	128
C ⁹ -N ¹⁸ -H ²⁶ -O ¹⁴	2	1
C ¹⁵ -O ²⁸ -O ¹⁷ -H ²⁹	2	-2
C ²³ -O ²⁴ -O ²⁵ -H ²⁷	21	-5

Table.2 HOMO and LUMO orbitals of transition states in stereoselectivity determining step of three aromatic aldehydes in intermolecular aldol reaction

benzaldehyde	TS3-tR	TS3-cR	TS3-tS	TS3-cS
HOMO				
LUMO				
p-methyl benzaldehyde	TS3-tR	TS3-cR	TS3-tS	TS3-cS
HOMO				
LUMO				
p-nitro benzaldehyde	TS3-tR	TS3-cR	TS3-tS	TS3-cS
HOMO				

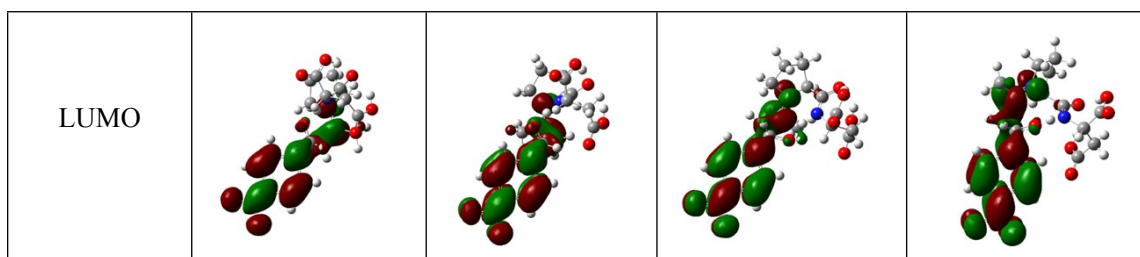


Table.3 The energy barrier in O-path calculated by using B3LYP method in different basis sets in gas phase

	$\Delta E(6-31G(d,p)/$ (kcal/mol)	$\Delta E(6-311++G(d,p)/$ (kcal/mol)
TS1	44.33	44.63
TS2-1	13.36	11.60
TS2-2 (<i>cis</i> -)	1.86	1.94
TS2-2 (<i>trans</i> -)	1.69	2.30
TS3- <i>tR</i>	14.94	16.31
TS3- <i>cR</i>	18.96	20.51
TS3- <i>tS</i>	21.59	22.67
TS3- <i>cS</i>	22.52	22.87
TS4- <i>tR</i>	42.74	48.93
TS4- <i>cR</i>	42.07	47.76
TS4- <i>tS</i>	42.58	48.63
TS4- <i>cS</i>	41.74	47.09

Cartesian coordinates of four transition states in third step in gas

calculated at the level of B3LYP/6-31G(d,p)

TS3-cR:

N	0.16441200	2.23481600	-0.39257700
C	0.42621300	3.32027500	0.58706300
C	1.42809900	1.76960700	-1.01664100
H	-0.02702300	3.06858600	1.54873600
H	-0.01930000	4.25481100	0.22705800
C	1.95500300	3.42460700	0.63697900
C	2.37760600	2.95657300	-0.76150800
H	1.25554500	1.60884100	-2.08457300
C	2.06286600	0.46681400	-0.49230500
H	2.35745000	2.75073100	1.39939400
H	2.28480600	4.43861700	0.87362900
H	3.41871300	2.64331500	-0.83458900
H	2.19603600	3.74256700	-1.50272500
O	3.16712600	0.17350200	-1.05792800
C	3.28685700	-1.36562800	1.74913400
C	2.02775900	-1.53257500	0.86622100
O	3.35086100	-1.82317100	2.86572800
N	1.46067200	-0.24315600	0.43357700
H	1.27351500	-1.97599700	1.51735500
C	2.33628900	-2.55288900	-0.27825300
H	3.34020100	-2.39036000	-0.67442900
H	2.29319100	-3.55578700	0.15155500
C	1.31022400	-2.48521100	-1.40265700
O	1.61692500	-1.66063700	-2.42984400
O	0.26319500	-3.09427600	-1.39393300
H	0.22807400	-0.08559900	0.83694500
H	2.40984900	-1.12947800	-2.19672200
O	4.31259200	-0.70720200	1.18668200
H	4.06188500	-0.39642200	0.27818000
C	-1.05884000	1.89238700	-0.79999300
C	-1.30877000	0.68815300	-1.49172000
H	-2.24560800	0.63523200	-2.03413300
H	-0.48147800	0.18314500	-1.98099900
C	-2.22158000	2.67468700	-0.26503600
H	-2.06827600	3.75401100	-0.34795500
H	-3.13731600	2.40316000	-0.78816000
H	-2.35757200	2.43016100	0.79623700
C	-3.87030500	-1.23460500	-0.71489000
C	-3.07823900	-0.59996700	0.25422500

C	-3.68548100	-0.10707900	1.41703100
C	-5.06422900	-0.22381200	1.59461700
C	-5.84800200	-0.83978100	0.61771800
C	-5.24621300	-1.35081800	-0.53626500
H	-3.40091300	-1.64720700	-1.60468100
H	-3.05779000	0.33503200	2.18310200
H	-5.52556600	0.15558800	2.50186900
H	-6.92070900	-0.93410700	0.75873600
H	-5.84931500	-1.84731600	-1.29063500
C	-1.59801100	-0.50913700	0.07825800
O	-0.91316800	-0.06076300	1.10494100
H	-1.17170500	-1.35236500	-0.47724300

TS3-cS:

N	1.12783200	2.31307000	-0.33514200
C	2.38404600	2.85711400	0.25424000
C	1.46086400	1.26744600	-1.33626500
H	2.41294700	2.62583500	1.32238400
H	2.39325200	3.94364500	0.13537900
C	3.51506600	2.19575300	-0.55151200
C	2.82143000	1.76375300	-1.85201300
H	0.69507500	1.24941200	-2.11482300
C	1.62355400	-0.16856400	-0.77093000
H	3.90174400	1.31902200	-0.02331800
H	4.34804000	2.88303900	-0.71366200
H	3.34633600	0.97320200	-2.38511600
H	2.67099600	2.61736500	-2.52135200
O	2.41340100	-0.92771600	-1.40897100
C	2.52435200	-1.85914400	1.69855600
C	1.16304200	-1.82409400	0.96332100
O	2.62054500	-2.07893600	2.87997500
N	0.96182600	-0.51917800	0.31037400
H	0.40145100	-1.86912800	1.74211900
C	1.04183200	-3.09940700	0.07411000
H	1.98713800	-3.29706600	-0.43555600
H	0.83301200	-3.93682000	0.74288000
C	-0.08695100	-3.04521300	-0.95172700
O	0.22999400	-2.48301600	-2.13548200
O	-1.19809100	-3.47400400	-0.73902300
H	0.14882100	0.13054700	0.82750900
H	1.13861100	-2.11570000	-2.09323100
O	3.61059800	-1.64420000	0.92579300
H	3.34490800	-1.50902200	-0.01413300
C	-0.06478600	2.85273100	-0.13502500

C	-1.28177100	2.20171000	-0.51868600
H	-2.09135100	2.88786700	-0.75675100
H	-1.19970200	1.40075300	-1.24890300
C	-0.16045100	4.06303300	0.74925300
H	0.52416000	4.85880700	0.44272700
H	-1.17693100	4.45515100	0.74395700
H	0.09012200	3.77792900	1.77836700
C	-4.24319300	1.19360100	0.37917400
C	-2.99498600	0.57548100	0.53196800
C	-2.87312500	-0.78654600	0.24558400
C	-3.97142200	-1.51860700	-0.20404300
C	-5.21086500	-0.89467900	-0.35877400
C	-5.34678100	0.46393300	-0.06011400
H	-4.35340100	2.25054100	0.61666700
H	-1.92091500	-1.28043300	0.38702300
H	-3.84345700	-2.57128700	-0.43481900
H	-6.06893100	-1.46338200	-0.70561900
H	-6.31178800	0.95181100	-0.16634100
C	-1.79298000	1.37936800	0.99591600
O	-0.77552300	0.75749000	1.54759800
H	-2.14638300	2.25772500	1.57068600

TS3-tR:

N	-0.23890700	2.15788400	0.43692700
C	0.18720700	2.84310800	-0.82350300
C	-1.70866500	2.04508100	0.50766000
H	0.89274500	2.21518900	-1.36075100
H	0.66083200	3.79189600	-0.54396500
C	-1.12231400	3.05999300	-1.59279500
C	-2.19790700	3.10372700	-0.49702900
H	-2.06833600	2.24538100	1.51880500
C	-2.23187700	0.64158700	0.13532600
H	-1.30192200	2.21679100	-2.26596600
H	-1.09064100	3.97001300	-2.19589400
H	-3.20403800	2.87550400	-0.85159800
H	-2.22010800	4.08464000	-0.01035300
O	-3.46401700	0.44771300	0.34725100
C	-2.71873500	-1.67389000	-1.97126900
C	-1.81793600	-1.61435100	-0.71438600
O	-2.44444500	-2.37008800	-2.91857000
N	-1.39385900	-0.24665900	-0.36988700
H	-0.89728200	-2.13123500	-0.98481200
C	-2.50606600	-2.40449000	0.44176600
H	-3.57900000	-2.20320900	0.45683800

H	-2.35941900	-3.46891800	0.24785200
C	-1.88709100	-2.08289300	1.79528400
O	-2.50642600	-1.09819000	2.49823600
O	-0.89671800	-2.61687400	2.23340200
H	-0.24973400	-0.07950300	-0.55338200
H	-3.18016900	-0.66380500	1.93616500
O	-3.84059900	-0.93650800	-1.92701700
H	-3.89329600	-0.43531700	-1.07538300
C	0.59048400	1.70815600	1.36642700
C	0.04011400	1.23292600	2.68187600
H	-0.66341300	0.40107300	2.57341100
H	0.85247800	0.90497800	3.32997000
H	-0.49303300	2.04681300	3.18690700
C	1.96654300	1.46754700	1.04791000
H	2.61147100	1.35025000	1.91498500
H	2.41607100	2.10080100	0.28859000
C	3.79643100	-0.22383300	-1.41617900
C	3.32330100	-0.40937100	-0.11316000
C	4.20177000	-0.86971800	0.87509800
C	5.53712600	-1.13019600	0.56928200
C	6.00669100	-0.93342300	-0.73132500
C	5.13194500	-0.48401200	-1.72285300
H	3.09545100	0.09871100	-2.17846800
H	3.83558800	-1.03739800	1.88594900
H	6.20841900	-1.49368600	1.34208100
H	7.04567000	-1.13914400	-0.97200500
H	5.48926100	-0.34497500	-2.73940700
C	1.86875400	-0.12548400	0.20971900
O	1.05673700	-0.02698800	-0.82576200
H	1.52686200	-0.77874200	1.03373700

TS3-ts:

N	0.28299900	2.20186300	-0.55098900
C	-0.03531100	3.15288200	0.55412200
C	1.74124000	1.97625800	-0.64116000
H	-0.77288800	2.72341100	1.23072100
H	-0.45687700	4.06147400	0.10937500
C	1.31395300	3.41791000	1.23283600
C	2.33452500	3.17637100	0.11255300
H	2.06189600	1.96281600	-1.68533500
C	2.21542700	0.63512200	-0.03568000
H	1.47142900	2.70592700	2.04903500
H	1.36408100	4.42479700	1.65269000
H	3.33986800	2.94953300	0.46670800

H	2.38677000	4.04099400	-0.55733300
O	3.47236100	0.50337700	0.02123500
C	2.41489400	-1.64995300	2.16129800
C	1.78026900	-1.63316800	0.75112700
O	1.99521900	-2.36288200	3.04068900
N	1.34187100	-0.28718900	0.32976800
H	0.85696100	-2.20569300	0.83435800
C	2.72592900	-2.36347700	-0.25202100
H	3.76715100	-2.09496800	-0.06264200
H	2.61392500	-3.43644400	-0.08345600
C	2.36262700	-2.08331300	-1.70752400
O	3.02717100	-1.04869800	-2.28622300
O	1.53408100	-2.70349300	-2.32775900
H	0.18405000	-0.30141600	0.20906500
H	3.56735900	-0.58903300	-1.61356900
O	3.48118600	-0.85171600	2.33801700
H	3.67264500	-0.34738100	1.50900100
C	-0.63117900	1.61554700	-1.30461000
C	-0.25232000	0.68786800	-2.40588000
H	-0.48203700	-0.31742300	-2.01045300
H	-0.90110100	0.85693500	-3.26882200
H	0.79108000	0.71310800	-2.71356300
C	-2.01914900	1.58489200	-0.90167500
H	-2.67943700	1.29058200	-1.71373800
H	-2.40005900	2.46246900	-0.38397700
C	-4.47562000	0.54585700	0.88779300
C	-3.46161000	-0.22291400	0.30345700
C	-3.78394300	-1.45669200	-0.27147700
C	-5.10303800	-1.90979200	-0.26732100
C	-6.11169900	-1.13601700	0.31086200
C	-5.79461600	0.09354500	0.89293900
H	-4.23065300	1.49902300	1.35314300
H	-2.98194500	-2.05177200	-0.69460700
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H	-6.57235800	0.69448300	1.35569600
C	-2.02451800	0.25737600	0.29027800
O	-1.11537300	-0.66939900	0.02621800
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