Multiselective Diels−Alder Reaction

CHM 612

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Presented By
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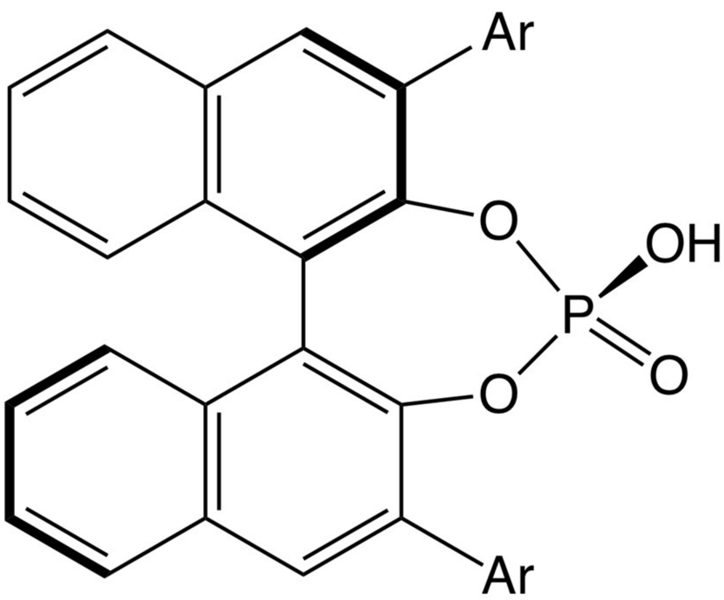
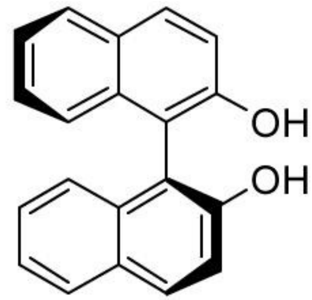
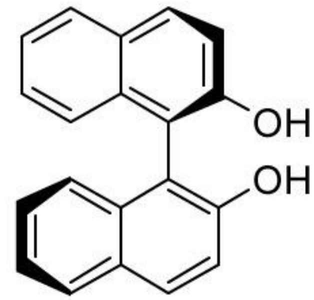
- **Nitu Kumari**

BINOL-derived phosphoric acid catalysts





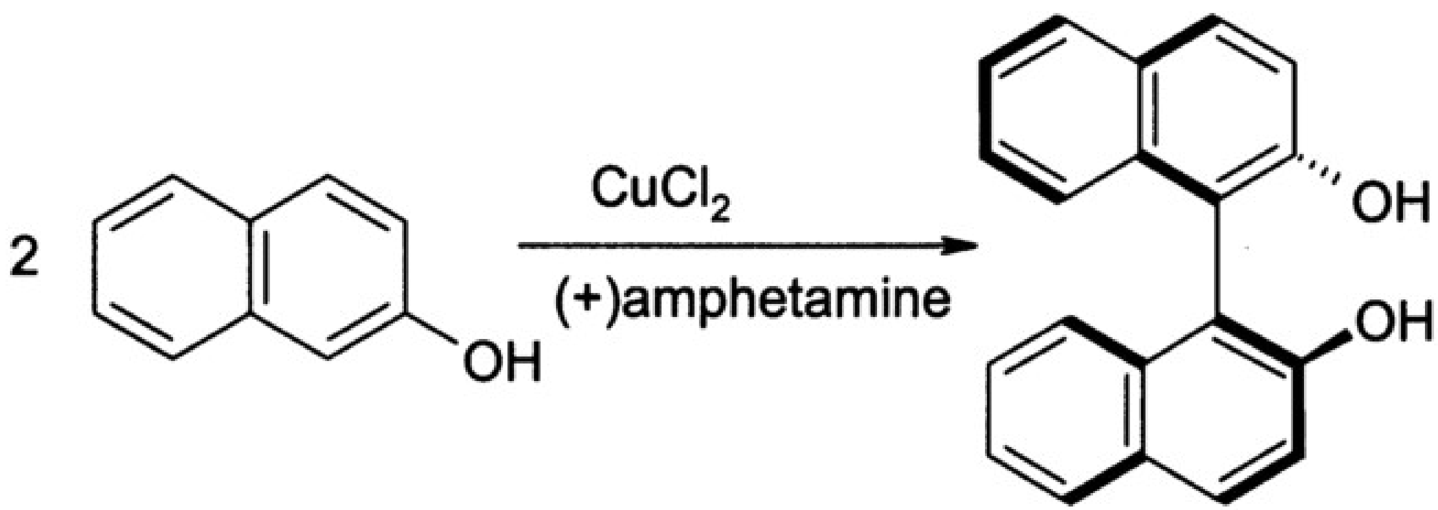
(*S*)-BINOL ((*S*)-1)



(*R*)-BINOL ((*R*)-1)

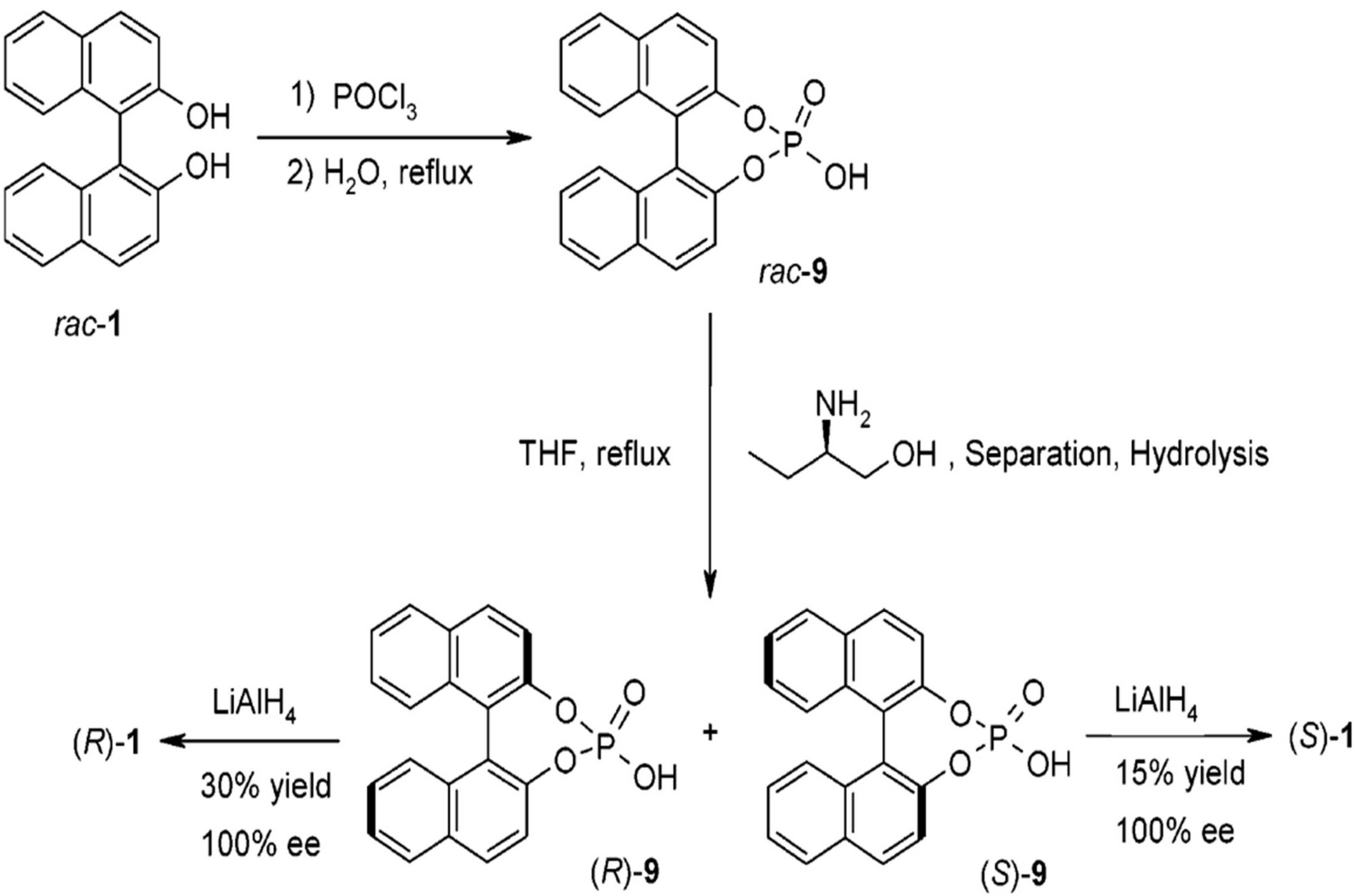
Axial chirality

Prepration

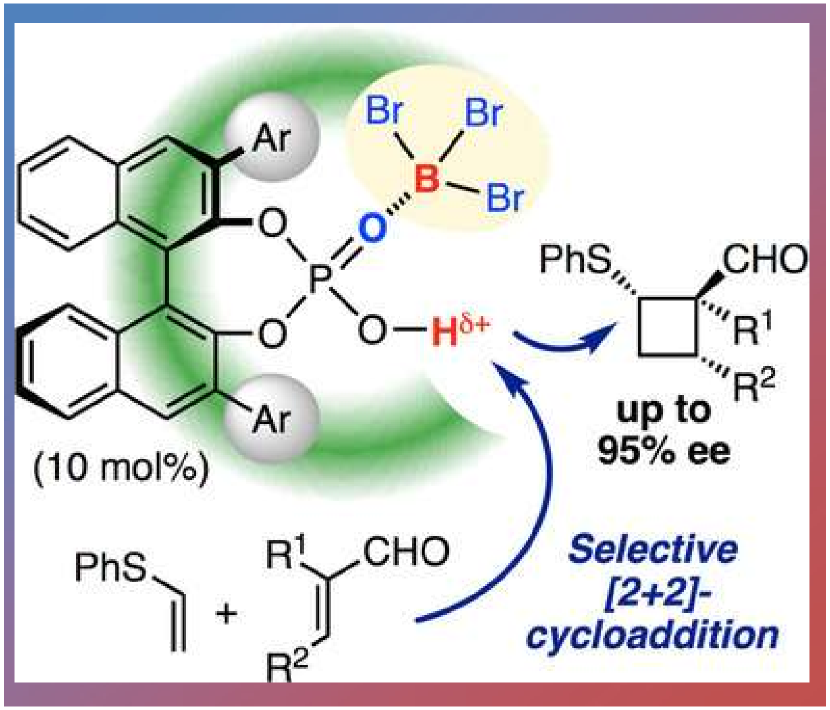


S-BINOL

1-1' Bi -2- Naphthol

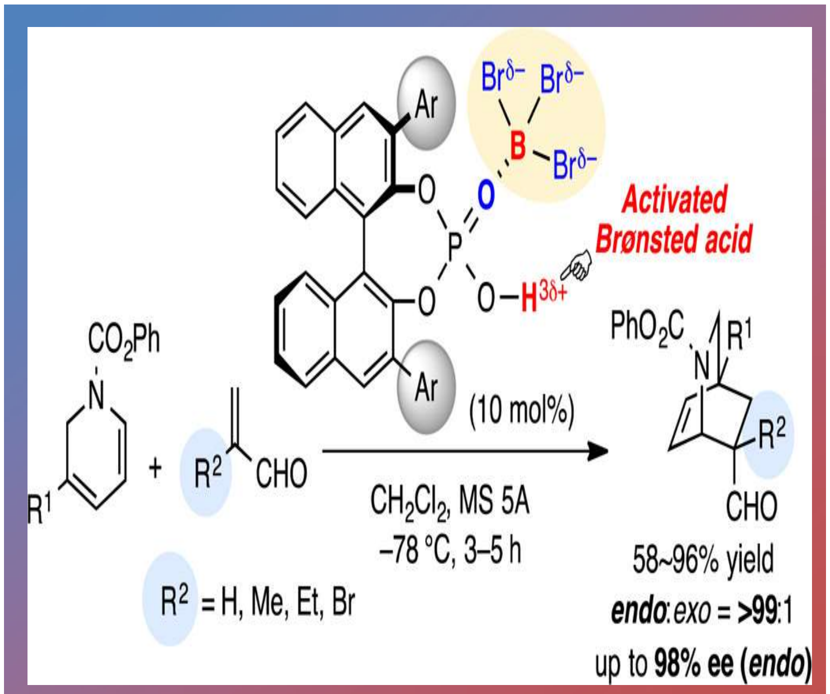


OH
OH
1) POCl3
2) H2O, reflux
O
O
P
O
OH
rac-1
rac-9
THF, reflux
NH2
OH , Separation, Hydrolysis
LiAlH4
(R)-1
30% yield
100% ee
(R)-9
+
(S)-9
LiAlH4
(S)-1
15% yield
100% ee



Diels−Alder

- **Boron Tribromide-Assisted Chiral Phosphoric Acid Catalysts for Enantioselective [2+2] Cycloaddition**



- **Boron Tribromide-Assisted Chiral Phosphoric Acid Catalyst for a Highly Enantioselective Diels–Alder Reaction of 1,2-Dihydropyridines**

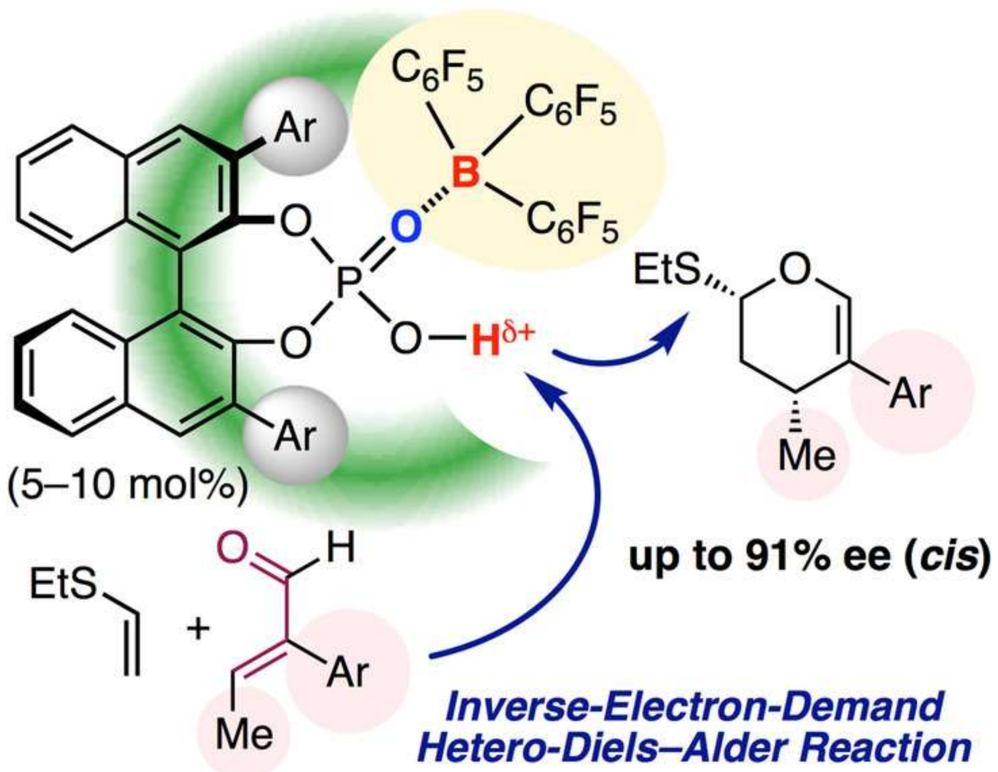
J. Am. Chem. Soc. 2015, 137, 42, 13472−13475

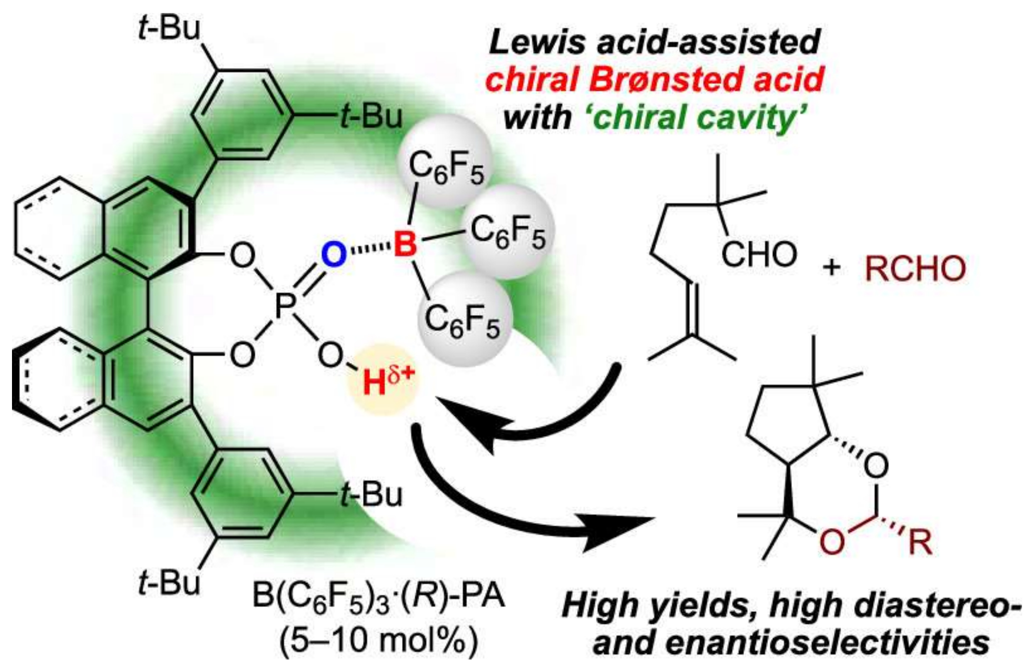
•Manabu Hatano† Yuta Goto† Atsuto Izumiseki† Matsujiro Akakura‡ Kazuaki Ishihara*†

Hetero Diels−Alder

Tris(pentafluorophenyl)borane-Assisted Chiral Phosphoric Acid Catalysts for Enantioselective Inverse-Electron-Demand Hetero-Diels-Alder Reaction of α,β-Substituted Acroleins

Enantio- and Diastereoselective Carbonyl-Ene Cyclization−Acetalization Tandem Reaction Catalyzed by Tris(pentafluorophenyl)borane-Assisted Chiral Phosphoric Acids

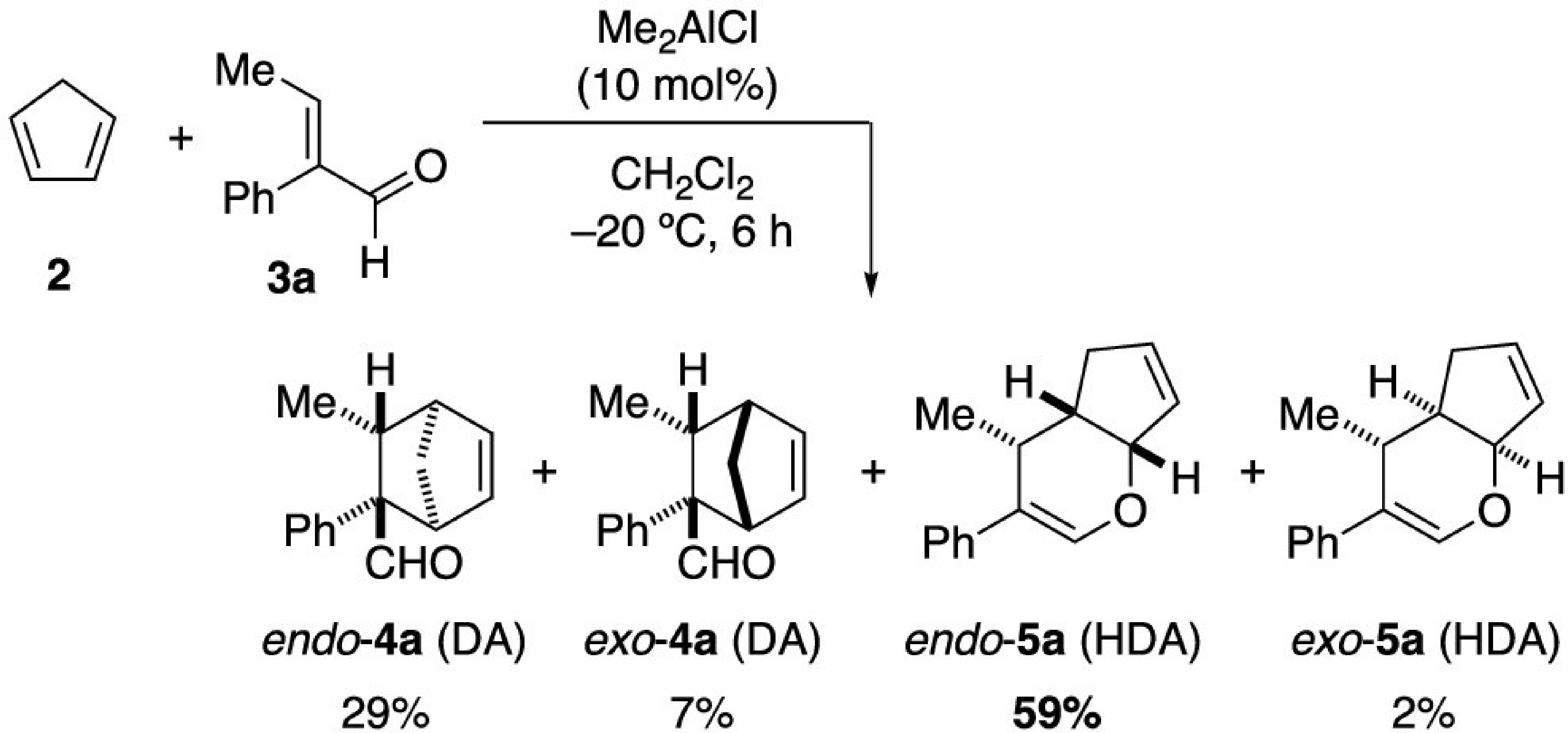




06 March 2019

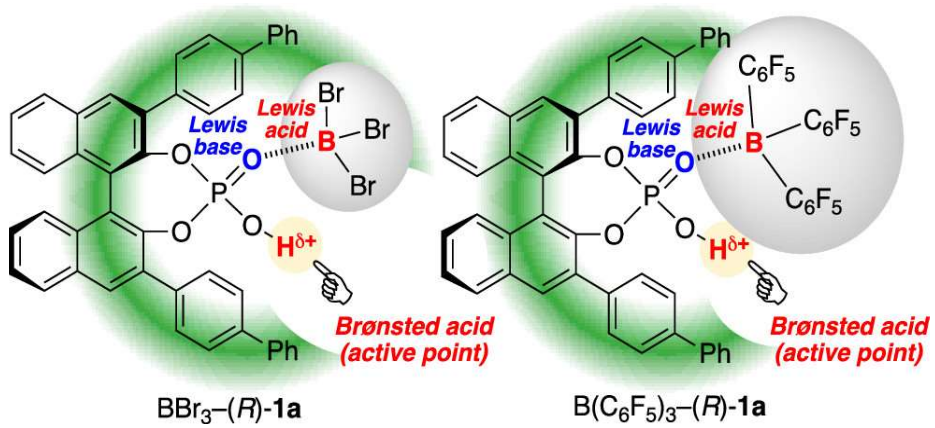
ACS Catal. 2021, 11, 10, 6121−6127

Diels−Alder (DA) reactions, in which the enantio-, endo/exo-, π-facial, regio-, site-, and substrateselectivity are possible.



During the present study, we found that Davies had reported the Me2AlCl-catalyzed HDA reaction of α-arylacroleins (3) and cyclopentadiene (2), in which the undesired competitive DA reaction also occurred

Selectivity can be controlled

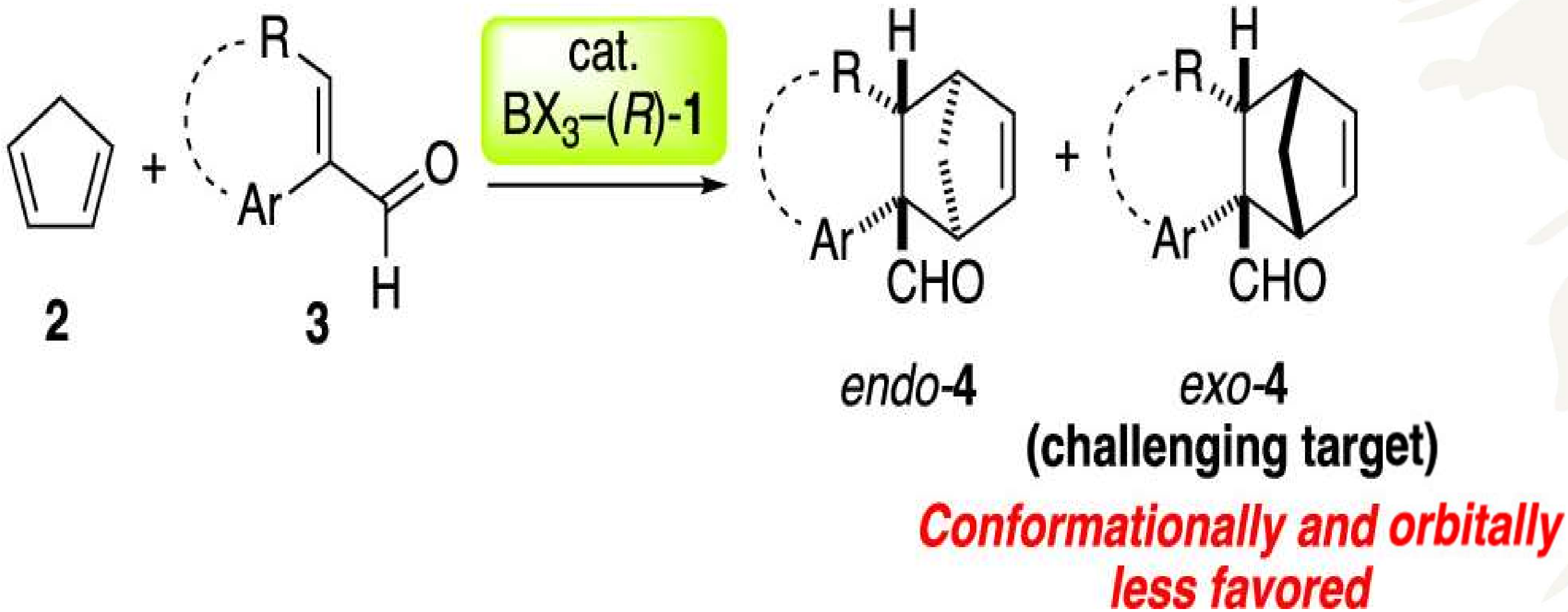


- Catalysts for multiselective carbon−carbon-bond-forming reactions

- The rational design of achiral acid-assisted chiral Lewis- or Brønsted-acid catalysts

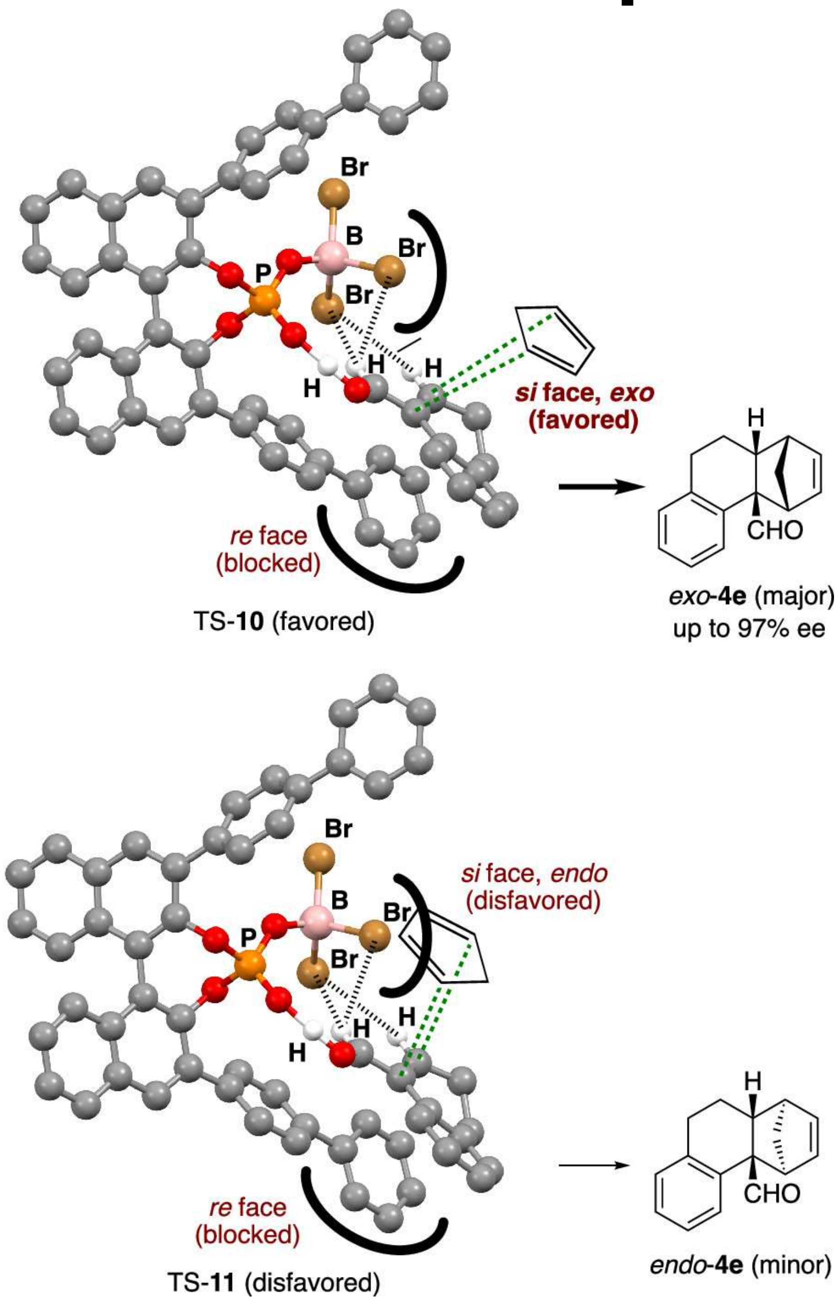
- In particular, by taking advantage of the chiral-cavity control exerted by BX3-(R)-1, unusual exo-DA productsmight be obtained by overcoming the orbital preference

(b) **This work** (Multiselective DA reaction supressing HDA reaction)

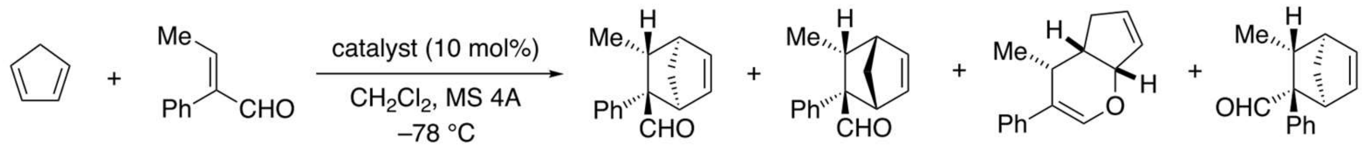


•Manabu Hatano†, Yuta Goto†, Atsuto Izumiseki†, Matsujiro Akakura‡, and Kazuaki Ishihara*†

Mechanistic Aspects



Optimization of the Catalysts in the Reaction of α-Phenylcrotonaldehyde (3a) with Cyclopentadiene (2)a



entry	catalyst	reaction time (h)	yield (%)[b]	ratio (%) *endo*-4a	ratio (%) *exo*-4a	ratio (%) *endo*-5a	ratio (%) 6a	ee (%) of *exo*-4a
1	(*R*)-**1a**	24	0					
2	BBr_3-(*R*)-**1a**	2.5	83	1	66	17	16	94
3	BBr_3-(*R*)-**1a**	48	79	2	67	16	15	95
4	BCl_3-(*R*)-**1a**	2.5	87	5	63	29	3	78
5	$B(C_6F_5)_3$-(*R*)-**1a**	24	53	26	15	57	2	−3[c]
6	BBr_3	7	15	13	13	53	21	
7[d]	$B(C_6F_5)_3$	4	84	27	27	46	0	
8	$C_6F_5SO_3H$	24	36	17	36	39	8	


Thank You