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Asymmetric Ring-Opening of Donor–Acceptor Cyclopropanes with Primary Arylamines Catalyzed by a Chiral Heterobimetallic Catalyst

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ABSTRACT An efficient catalytic asymmetric ring-opening reaction of donor-acceptor cyclopropanes with primary arylamines was developed. The reaction was achieved through the utilization of a chiral heterobimetallic catalyst, delivering a variety of chiral γ-amino acid derivatives in up to 93% yield and 99% *ee*. Stereochemical experiments suggest a dominant role for kinetic resolution in this asymmetric process, which is supported by a computational study of the reaction coordinate. A class of chiral bimetallic Lewis acid catalysts formed through a ligand exchange/transmetalation process was

introduced in this work. The symmetric structure of the bimetallic catalyst, i.e., $Yb(OTf)_3$-$Yb[\mathbf{P}]_3$, was confirmed with X-ray crystallography.

KEYWORDS asymmetric catalysis, donor–acceptor cyclopropanes, heterobimetallic, primary arylamines, ring-opening.

Chiral phosphoric acids (CPAs) play an important role in modern organocatalysis owing to their high modifiability, ease of handling as well as their environmentally friendly nature.[1-2] In the evolution of chiral Brønsted acid catalysis, the combination of chiral phosphoric acids with metal catalysts has emerged as a new and powerful strategy to achieve enhanced acidity and flexibility of the catalytic systems.[3] In general, combined metal–phosphoric acid catalysis can be classified into the following types: relay catalysis, binary acid catalysis, anion directed catalysis and phosphate metal catalysis (Type I - IV, Figure 1).[3e]

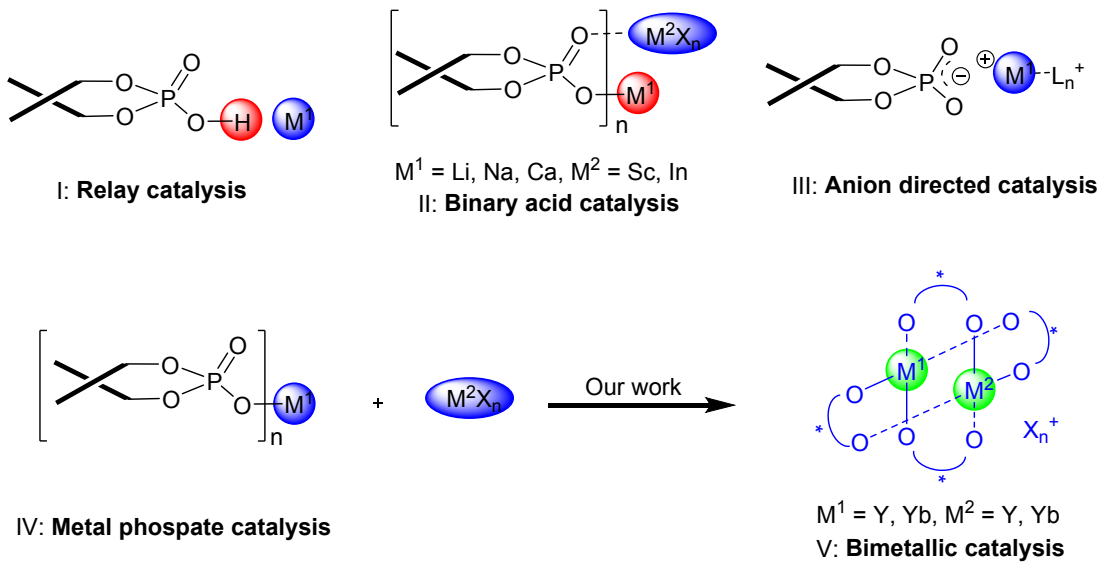
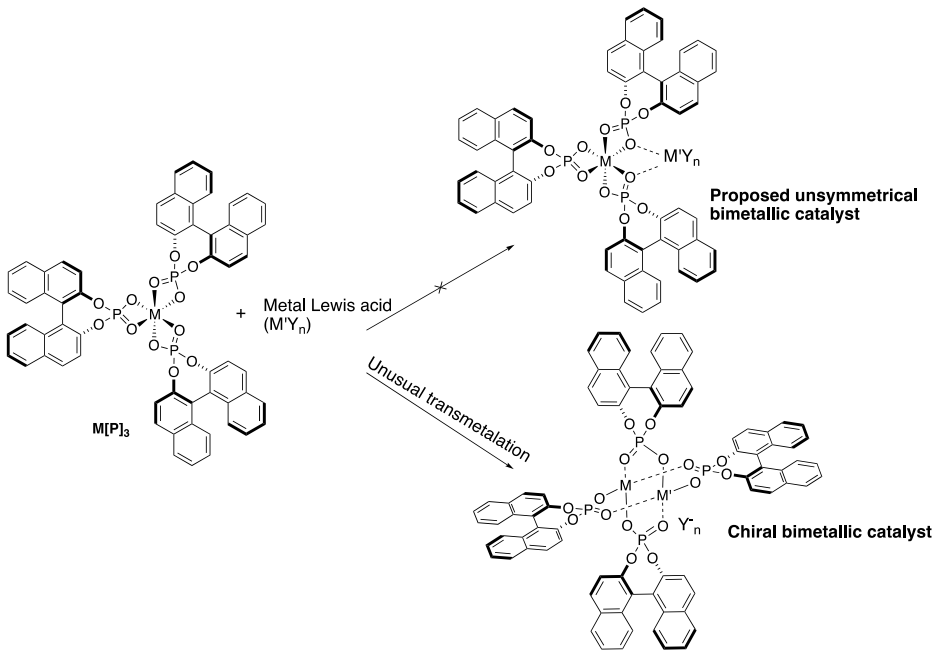


Figure 1. Catalyst types derived from combining phosphoric acids with metals.

To further expand the utility of combined metal–phosphoric acid catalysis, we have introduced a new class of chiral bimetallic Lewis acid catalyst (Type V, Figure 1).[4a] Current asymmetric metal Lewis acid catalysis mainly relies on metal/chiral ligand approach. However, when combined with a chiral ligand, the activity of the metal Lewis acid often decreases significantly. We considered developing a new type of chiral bimetallic Lewis acid. This new type of chiral bimetallic catalysts could serve a complementary strategy to the traditional metal/chiral ligand approach, opening up new opportunities in asymmetric catalysis. Chiral phosphoric acids, i.e. binaphthyl phosphoric acids, appeared to be an

ideal platform to serve the purpose. We speculated that a metal binaphthyl phosphate would be able to bind another metal in one structural entity to form an unsymmetrical bimetallic complex (Scheme 1). Interestingly, an unusual ligand exchange/transmetalation occurred, and a symmetrical bimetallic complex was formed (Scheme 1). The bimetallic phosphate complex is expected to provide multi-binding sites for the reacting substrates and required transition state, making it possible to better control the stereoselectivity. Very importantly, the bimetallic nature of the catalyst may possibly engender bifunctional activity of the catalyst, enabling reaction patterns and activation modes different from those of other existing catalytic systems.[4] This type of bimetallic catalysts have shown much enhanced activity and/or enantioselectivity than each individual metal salt.[4] The easy accessibility and manipulability of this new type of chiral bimetallic catalysts are expected to find broad applications in asymmetric catalysis.



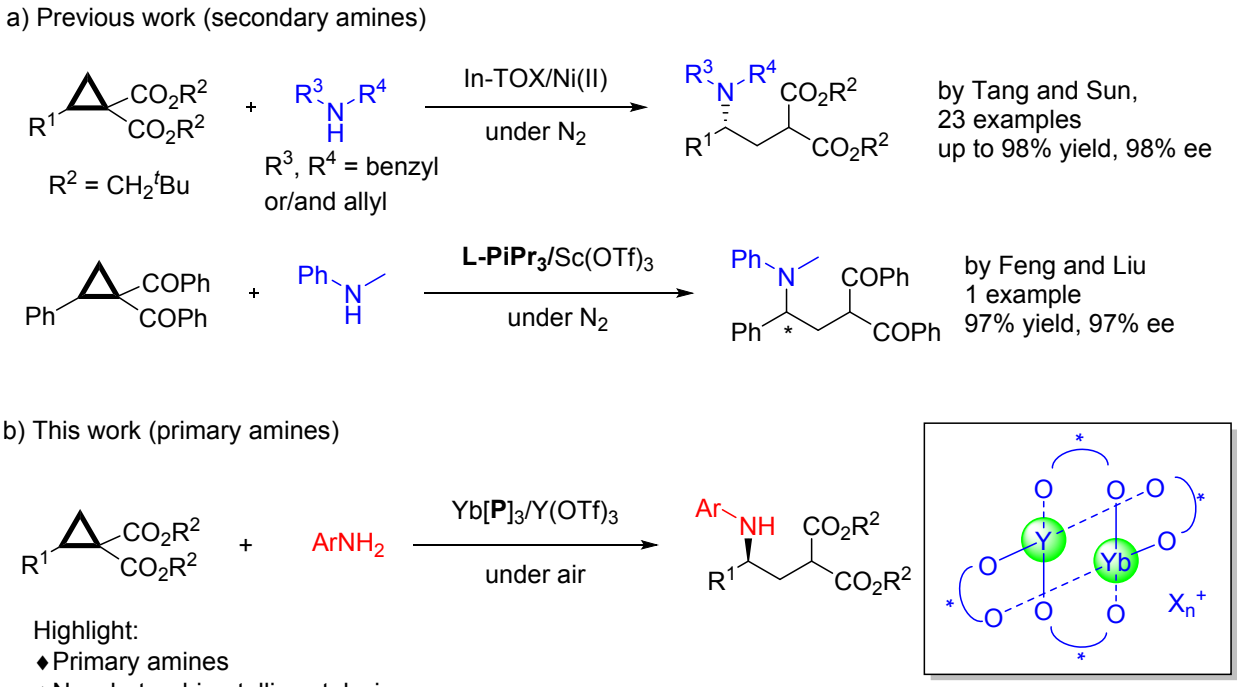
Scheme 1. Formation of chiral bimetallic catalysts.

Donor-acceptor (D-A) cyclopropanes serving as 1,3-dipolar synthons have received increased attention in recent years.[5-8] Ring-opening reaction of D-A cyclopropanes has evolved into an effective strategy to assemble functionalized carbon scaffolds. Asymmetric ring-opening reactions of D-A cyclopropanes with heteroatom nucleophiles such as thiols, alcohols, water, amines, as well as acids have been developed (Scheme 2a).[8d-h] Among the nitrogen nucleophiles, functionalized allylic amines (mainly 2^{o} amines) pioneered by Tang group are routinely used in asymmetric ring-opening reactions of D-A cyclopropanes.[8d,e] In contrast, there is only one single example of asymmetric ring-

opening of cyclopropyl ketones with a secondary arylamine (i.e., *N*-methylaniline) described by Feng and Liu (Scheme 2b).[8g] Asymmetric ring-opening reactions of D-A cyclopropanes with primary arylamines, however, remains an open challenge in the organic synthetic community. This is likely due to the following challenges: 1) As compared with secondary amines, primary amine possesses more degree of freedom, thus making it harder to control the stereoselectivity. 2) As compared with aliphatic amines, the nucleophilicity of anilines is much lower, requiring stronger acid catalyst and elevated temperatures to open the cyclopropane ring. It is more difficult to control the stereoselectivity at higher temperature. 3) It is hard to stop the reaction at the ring-opening stage as D-A cyclopropanes are 1,3-dipolar synthons. Further reaction of the resulting secondary amine with the diester groups or another cyclopropane could happen to give tertiary amine products.[8g]

All reported asymmetric ring-opening reactions of donor-acceptor cyclopropanes are based on chiral metal complexes of oxazolines or *N,N'*-dioxides.[6-8] Both classes possess limited binding sites for substrates. We decided to tackle this challenge reaction using the

chiral bimetallic Lewis acid developed in our laboratory. Herein, the development of an asymmetric ring-opening of D-A cyclopropanes with primary arylamines is reported. This research not only offers new reaction patterns to be exploited for asymmetric synthesis, but also provides insight into controlling factors in stereoselectivity, which are not well understood. The syntheses developed could be used for the construction of many chiral *γ*-amino acid derivatives and γ-lactams, which are important structural motifs for many biologically active compounds.[9]



Scheme 2. Ring-opening reactions of D-A cyclopropanes with amines.

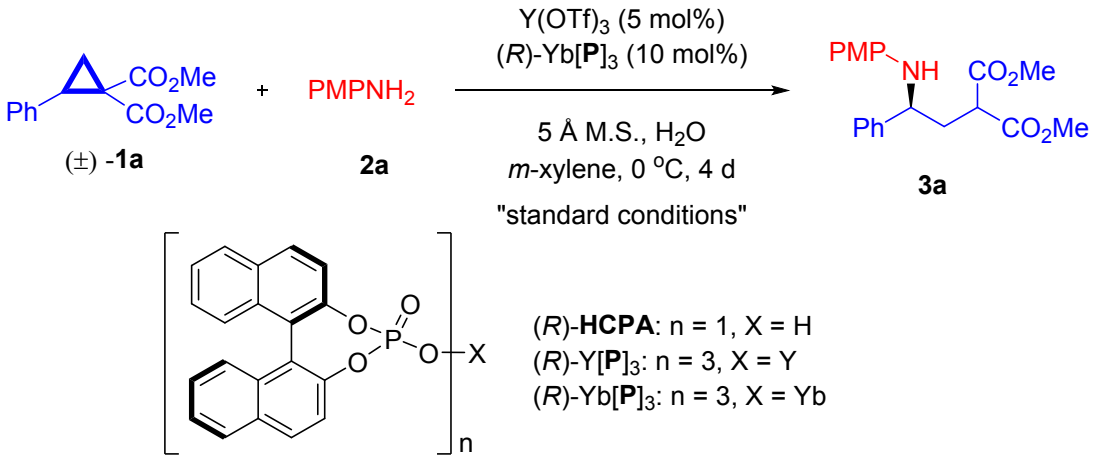
Racemic dimethyl 2-phenylcyclopropane-1,1-dicarboxylate (**1a**) and *p*-anisidine (**2a**) were initially chosen as model substrates (Table 1). When either $Y(OTf)_3$ or (*R*)-Yb[**P**]$_3$ was used solely as the Lewis acid catalyst, only trace amounts of product were observed (Table 1, entries 2 & 3). When $Y(OTf)_3$ and (*R*)-Yb[**P**]$_3$ were combined, a major product was obtained (Table1, entry 9). This product turned out to be the desired ring-opening product **3a** based on the analysis of its ^{1}H and ^{13}C NMR spectroscopic data and Mass Spectrometry data. It should be noted that the occurrence of this reaction requires the presence of both $Y(OTf)_3$ and (*R*)-Yb[**P**]$_3$. These data suggest a bifunctional nature of the $Y(OTf)_3$-Yb[**P**]$_3$ catalyst in this reaction, highlighting a unique set of activity expected for the bimetallic catalyst. Optimized reaction conditions were obtained after evaluating an array of reaction parameters including solvents, temperature, and additives (Table S1-5 in SI). The primary conditions for the reaction of **1a** (0.5 mmol) and **2a** (0.1 mmol) involve 5 mol% of $Y(OTf)_3$, 10 mol% of (*R*)-Yb[**P**]$_3$ in *m*-xylene at 0 °C with addition of 5 μL of H_2O and 10 mg of 5 Å molecular sieves as additives, producing **3a** in good yield and

enantioselectivity (entry 1). The data demonstrate that both the metal phosphate (*R*)-Yb[**P**]$_3$ and metal salt Y(OTf)$_3$ are crucial to this reaction. Replacement of (*R*)-Yb[**P**]$_3$ with (*R*)-Y[**P**]$_3$ enhanced the yield, however, resulting in lower *ee* value (entry 4).

The combination of Y(OTf)$_3$ with *(R*)-HCPA (HCPA = 1,1′-binaphthyl-2,2′-diyl hydrogenphosphate) resulted in higher *ee* values, however, the activity of the reaction was much lower (entry 5). If a chiral Brønsted acid, i.e. (*R*)-HCPA, was used, the reaction did not proceed (entry 6). When more Y(OTf)$_3$ was used, yield of the reaction remained similar, but enantioselectivity decreased moderately (entry 7). Replacing Y(OTf)$_3$ with YCl_3 led to substantially lower yield (entry 8). These data suggest that this ring-opening reaction cannot be easily catalysed by a simple Brønsted or Lewis acid. It is worthy of mention that co-addition of water and molecular sieves as additives was crucial to obtain higher enantioselectivity, albeit at the cost of activity.[10] If no additive was added, the reaction gave 93% yield with 86% *ee* (entry 9). The addition of water significantly enhanced the enantioselectivity, however, the activity also decreased significantly (entry 10, 57% yield, 92% *ee*). On the other hand, the addition of 5 Å molecular sieves without

added H_2O resulted in excellent conversion, but with much lower *ee* (entry 11). A comparable result was achieved when increasing the reaction concentration (entry 12, 86% yield, 90% *ee*). It is speculated that water can mediate the interaction between the substrate and the catalyst through hydrogen bonding and coordinating to the metal, and molecular sieves serve to control the minor amount of water presence in the reaction. We also screened other conditions such as other solvents and metals; the results are compiled in SI (Table S1-5). The absolute configuration of **3a** was established unambiguously to be *S* by X-ray crystallographic analysis (Table 2, CCDC 1864175).[11]

Table 1. Condition screening and optimization.[a]



Entry	variation from standard conditions	Yield (%)[b]	ee (%)[c]
1	none	70	93

2	without (*R*)-Yb[**P**]$_3$	trace	-
3	without Y(OTf)$_3$	trace	-
4	(*R*)-Y[**P**]$_3$ instead of (*R*)-Yb[**P**]$_3$	86	87
5	(*R*)-**HCPA** instead of (*R*)-Yb[**P**]$_3$	28	95
6	(*R*)-**HCPA** instead of (*R*)-Yb[**P**]$_3$/Y(OTf)$_3$	0	-
7	7.5 mol% of Y(OTf)$_3$	75	88
8	YCl_3 instead of Y(OTf)$_3$	8	95
9	without 5 Å M.S. and H_2O	93	86
10	without 5 Å M.S.	57	92
11	without H_2O	92	63
12[d]	**0.5 mL of *m*-xylene**	**86**	**90**

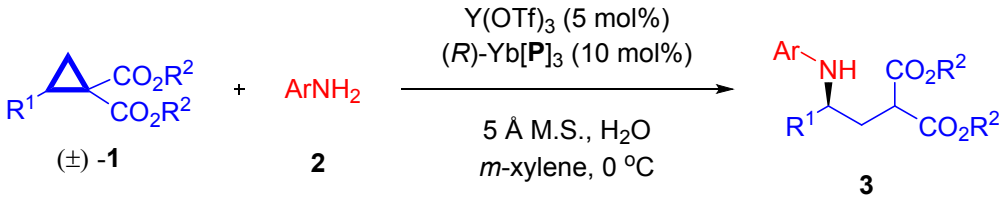
[a]Standard reaction conditions: **1a** (0.5 mmol), **2a** (0.1 mmol), Y(OTf)$_3$ (5 mol%), (*R*)-Yb[**P**]$_3$ (10 mol%), 5 Å M.S. (10 mg), and H_2O (5 μL) at 0 oC in *m*-xylene (1.0 mL) for 4 days. [b]Isolated yield. [c]Determined by chiral-phase HPLC. [d]Average of two runs.

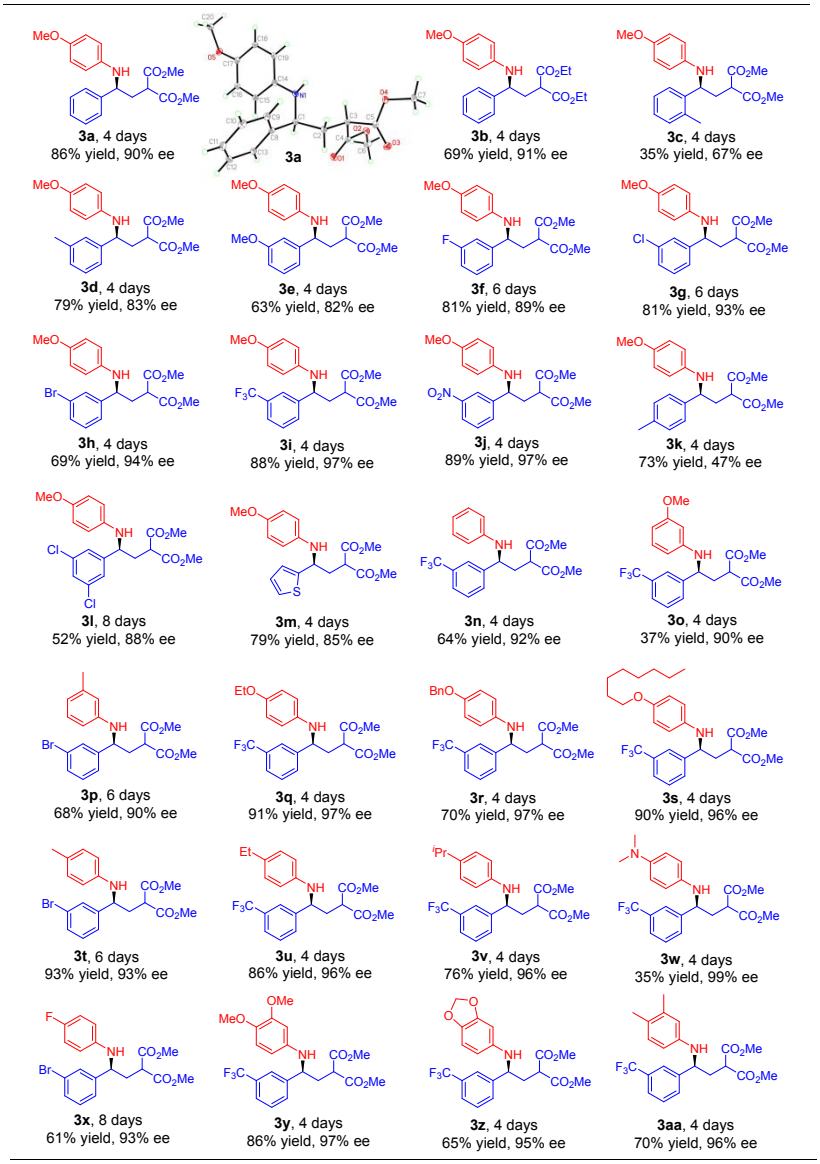
With optimized conditions in hand (Table 1, entry 12), the generality of this protocol for different substrates was investigated. To examine the scope of cyclopropanes, various substituents at the 1- and 2- positions of the cyclopropane were tested (Table 2). Changing the ester group from methyl to ethyl slightly increased the enantioselectivity, but the reactivity decreased moderately (**3a** & **3b**). The aryl substituent at the 2-position of cyclopropane was investigated next. In general, *meta*-substituted phenyl groups (**3d-j**)

displayed high reactivities and enantioselectivities (63-89% yields, and 82-97% *ees*). *Ortho*-substituted phenyl group (**3c**) showed much lower reactivity and enantioselectivity, likely due to both electronic and steric factors. For *para*-substituted phenyl group (**3k**), the reactivity remained similar to that of *meta*-substituted phenyl groups, however, the enantioselectivity decreased significantly (73% yield, 47% *ee*). For the *meta* substituents on the 2-phenyl ring, electron-withdrawing groups (**3f-j**) gave higher enantioselectivities and yields than electron-donating groups (**3d-e**). *Meta*-disubstituted phenyl groups (**3l)** displayed inferior results as compared with their mono-substituted analogues (**3g**). Thiophen-2-yl cyclopropane could also be employed as a substrate, leading to good yield and enantioselectivity (**3m**, 79% yield, 85% *ee*). The scope of primary amines was also explored. Importantly, substitution at different positions of the aniline nucleophile was well tolerated. Aniline gave the ring-opening product (**3n**) in 64% yield and 92% *ee.* An exception was dimethyl-4-phenylenediamine, which produced the ring-opening product **3w** in lower yield (35%), but with excellent *ee* (99%); all other *para*-substituted anilines with electron-rich substituents provided adducts with excellent yields and *ee* (**3q-v**). It is notable that strongly electron-deficient 4-fluoroaniline was effective in this reaction,

affording the ring-opening product in good yield and *ee* (**3x**, 61% yield, 93% *ee*). The reactivity of 3-methylaniline (**3p**, 68% yield, 90% *ee*) is superior to 3-methoxyaniline (**3o**, 37% yield, 90% *ee*). Disubstituted anilines reacted smoothly with cyclopropanes under the reaction conditions, forming

Table 2. Substrate scope of the reaction.[a-c]



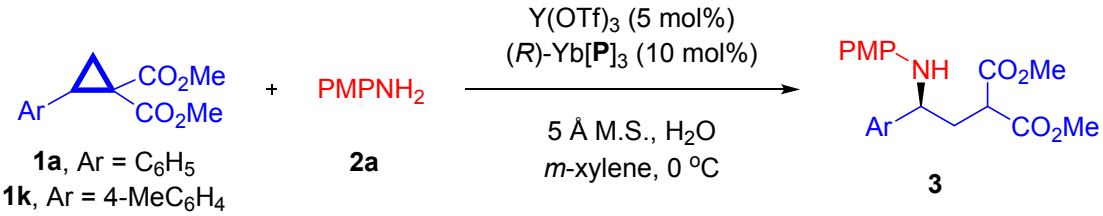


[a]Standard reaction conditions: **1** (0.5 mmol), **2** (0.1 mmol), (*R*)-Yb[**P**]$_3$ (10 mol%), Y(OTf)$_3$ (5 mol%), 5 Å M.S. (10 mg), and H_2O (5 μL) at 0 °C in *m*-xylene (0.5 mL). [b]Isolated yield. [c]Determined by chiral-phase HPLC.

the secondary amines in good yields with excellent enantioselectivities (**3y**-**3aa**, 65-86% yield, 95-97% *ee*).

To gain some mechanistic insight of this reaction, (*R*)- and (*S*)-isomers of **1a** and **1k** were used as mechanistic probes. As shown in Table 3, stereospecific ring-openings were observed for both the (*R*) and (*S*) enantiomers. It was found that an inconspicuous rate preference was conferred for (*R*)-**1a** and (*R*)-**1k**, with unchanged *ee* for the recovered cyclopropane. These data suggest a simple kinetic resolution rather than a dynamic kinetic resolution process for the ring-opening reaction. As such, it is likely that an S_N2-type ring-opening primarily dominates the reaction.

Table 3. Stereochemical Experiments.[a]



1a, Ar = C_6H_5
1k, Ar = 4-MeC_6H_4

2a

3

Substrate	*t* (d)	Yield of **3** (%)[b]	*ee* of recovered **1** (%)[c]	*ee* of **3** (%)[c]
(±)-**1a**	2	25	-30	91
(*R*)-**1a**	2	77	96	98
(*S*)-**1a**	2	38	-98	-92
(±)-**1k**	5	25	-15	58

(*R*)-**1k**	6	53	98	99
(*S*)-**1k**	6	19	-99	-99

[a]Reaction conditions: **1** (0.1 mmol), **2a** (0.1 mmol), $Y(OTf)_3$ (5 mol%), (*R*)-Yb[**P**]$_3$ (10 mol%), 5 Å M.S. (10 mg), and H_2O (5 μL) at 0 °C in *m*-xylene (0.5 mL). [b]Isolated yield. [c]Determined by chiral-phase HPLC.

In order to further understand the reaction profile, the relationship between the *ee* value of (*R*)-Yb[**P**]$_3$ and that of product (**3h**) was studied through mixing different ratios of (*R*)-Yb[**P**]$_3$ and

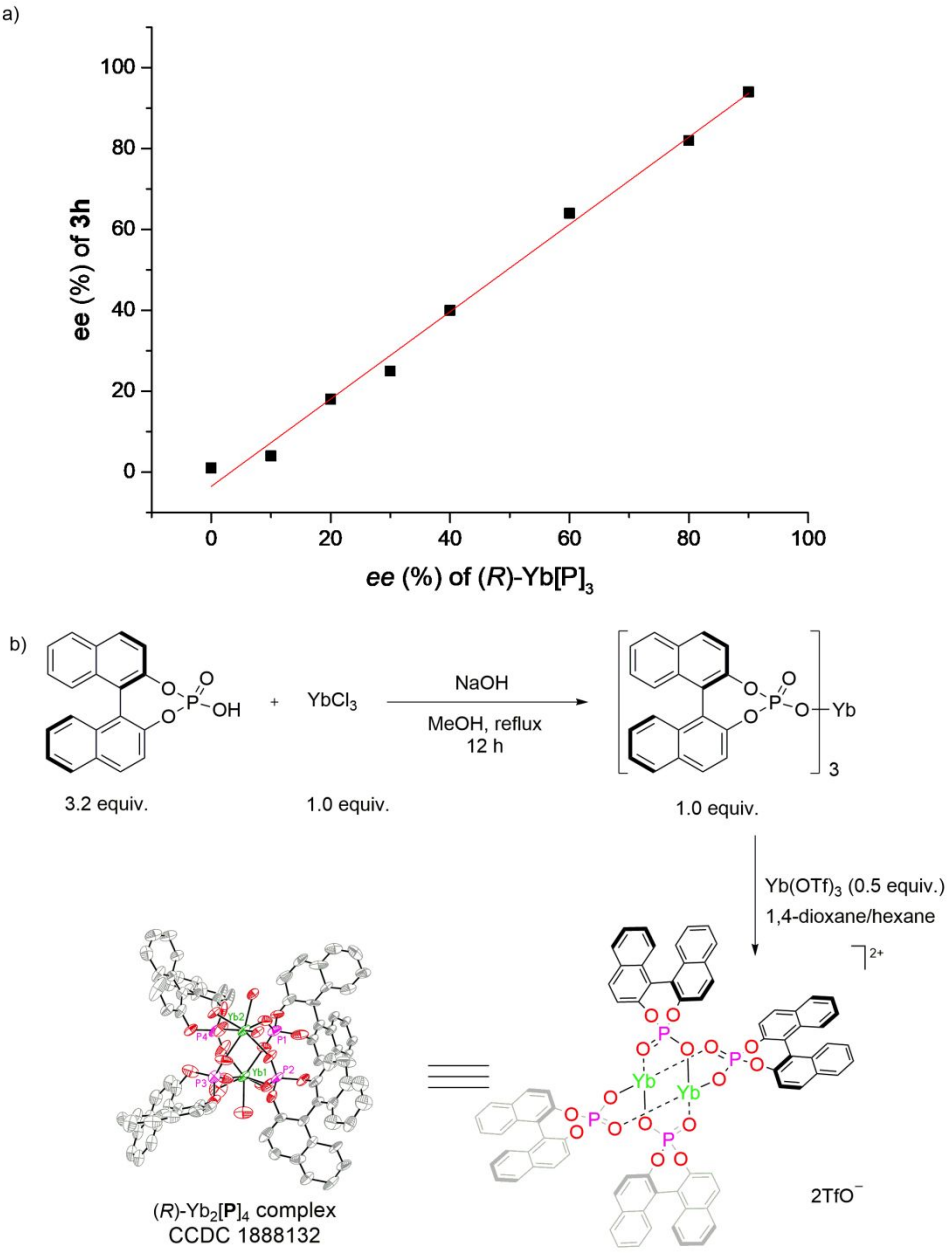


Figure 2. Identification of bimetallic catalyst.

(*S*)-Yb[**P**]$_3$ (Figure 2a). A linear effect was observed, suggesting that the main catalytic active species should be highly uniform. While attempts to grow single crystals for the

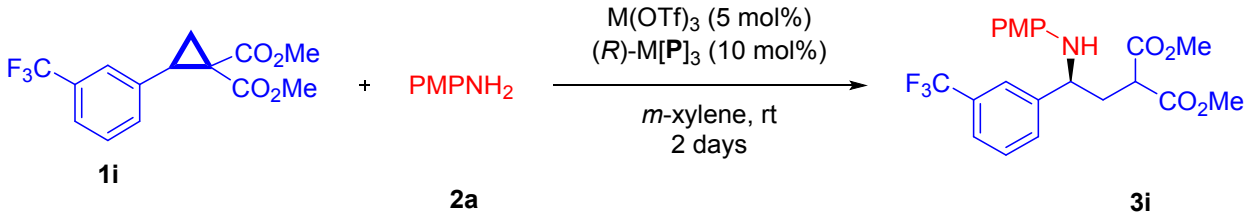
heterobimetallic catalyst $Y(OTf)_3$-Yb[**P**]$_3$ were not successful, single crystals suitable for X-ray diffraction studies were obtained for the homobimetallic catalyst $Yb(OTf)_3$-Yb[**P**]$_3$ from 1,4-dioxane/hexane (Figure 2b, CCDC 1888132).[11] X-ray crystallographic analysis revealed a symmetrical binuclear metal complex with the two metals sharing four bridged phosphate ligands. It appears that transmetalation between $Yb(OTf)_3$ and (*R*)-Yb[**P**]$_3$ occurred, resulting in the formation of the symmetrical binuclear metal complex. This structure is consistent with a $Y(OTf)_3$-Y[**P**]$_3$ (Y_2[**P**]$_4$) complex described previously by our group.[4a] It should be noted that the structures of these bimetallic complexes represent new coordination chemistry for rare earth metals.

Considering that rare earth metals have similar coordination chemistry and Lewis acidities, several chiral bimetallic complexes composed of different metal ions and chiral phosphates were prepared. The catalytic properties of these bimetallic complexes were investigated at room temperature using simple kinetic resolution between 2.0 equivalent of *rac*-**1i** and 1.0 equivalent of **2a** (Table 4). The Sc^{3+} ion is the smallest (and hence most Lewis acidic) rare earth metal cation (Z/r^3; Z = charge and *r* = ionic radius).[12a] The

corresponding $Sc(OTf)_3$-Sc[**P**]$_3$ showed moderate reactivity and no enantioselective induction (entry 1). These results indicate that bimetallic complex (*R*)-Sc_2[**P**]$_4$ did not form, and a background reaction dominated the process. La^{3+} ion is the largest lanthanide trication. Similar to $Sc(OTf)_3$-Sc[**P**]$_3$, $La(OTf)_3$-La[P]$_3$ produced a racemic product **3i** in very low yield (entry 2). Although the *ee* of product is low, (*R*)-Ce_2[**P**]$_4$ displayed increased enantioselectivity (entry 3). Sm^{3+} cation, whose ionic radius is about 0.958 Å, was also examined. The corresponding Sm_2[**P**]$_4$ complex afforded the product in 54% yield with 77% *ee* (entry 4). Yttrium and ytterbium phosphate complexes were compared (entries 5 & 6). (*R*)-Yb_2[**P**]$_4$ was superior to (*R*)-Y_2[**P**]$_4$, which is consistent with the results obtained earlier in this work. Although Lu^{3+} is smaller than Yb^{3+}, the Lewis acidity of the former is weaker due to its incomplete 4f orbital.[12a] As it turned out, (*R*)-Lu_2[**P**]$_4$ gave the product in moderate yield with high enantioselectivity (entry 7). The ee values of the recovered cyclopropane were measured for each experiment, and the selectivity factors were calculated based on these values (Table 4). (*R*)-Yb_2[**P**]$_4$ displayed highest selectivity factor followed by (*R*)-Y_2[**P**]$_4$. Based on these data, a trend was identified: bimetallic complexes with decreasing ionic radius within a certain range (1.032 Å to 0.868 Å) give

rise to increasing enantiomeric control (entries 2-7). We speculate that a rare-earth metal ion with too small radius, such as Sc^{3+}, will not go through ligand exchange with the corresponding metal phosphate to form the bimetallic complex due to the structural confinement of metal phosphate, for example (*R*)-Sc[**P**]$_3$. On the other hand, for metals that can form the bimetallic compounds, the enantioselectivity of the bimetallic catalyst increases with a decrease of the metal ionic radius due to the tighter coordination sphere of the bimetallic complexes.

Table 4. Test of bimetallic catalyst.[a]



1i **2a** **3i**

Entry	Cat.	r_{M}^{3+} (Å)	Yield (%)[b]	*ee* of recovered **1i** (%)[c]	*ee* of **3i** (%)[c]	*s*[d]
1	(*R*)-Sc$_2$[**P**]$_4$	0.754	36	n.d	1	-
2	(*R*)-La$_2$[**P**]$_4$	1.032	14	n.d	0	-
3	(*R*)-Ce$_2$[**P**]$_4$	1.01	4	n.d	10	-

4	(*R*)-Sm_2[**P**]$_4$	0.958	54	32	77	11
5	(*R*)-Y_2[**P**]$_4$	0.900	80	48	82	16
6	(*R*)-Yb_2[**P**]$_4$	0.868	70	56	92	39
7	(*R*)-Lu_2[**P**]$_4$	0.861	53	39	81	13

[a]Reaction conditions: **1i** (0.2 mmol), **2a** (0.1 mmol), M(OTf)$_3$ (5 mol%), (*R*)-M[**P**]$_3$ (10 mol%), at room temperature in *m*-xylene (1.0 mL). [b]Isolated yield. [c]Determined by chiral-phase HPLC. [d]Selectivity factors (*s*), calculated according to the following equation: $s = \ln[(1 - C)(1 - ee_1)]/\ln[(1 - C)(1 + ee_1)]$, $C = (ee_1)/(ee_1 + ee_3)$.

To further understand the selectivity and reactivity of the bimetallic catalyst, the electronic structure and selectivity of Yb(OTf)$_3$-Yb[**P**]$_3$ complex was studied computationally with two-layer ONIOM (B3LYP:UFF) for geometry optimization followed by single-point calculations with *m*-xylene solvation at 0 °C. Since Y(OTf)$_3$-Y[**P**]$_3$ and Yb(OTf)$_3$-Yb[**P**]$_3$ showed similar activity and enantioselectivity for this ring-opening reaction, the X-ray crystallographic data for Yb(OTf)$_3$-Yb[**P**]$_3$ were used in our initial guess for the geometry of Y(OTf)$_3$-Yb[**P**]$_3$ catalyst through substituting one Yb with Y in the crystal structure. Y(III) and Yb(III) are expected to have similar lability due to their similar charge-to-size ratios. The calculations were based on the reaction of substrates (±)-**1a** and *p*-anisidine. It is speculated that **1a** binds to one of the metals of the bimetallic

$Y(OTf)_3$-Yb[**P**]$_3$ catalyst and is thus activated. Calculations reveal that the binding of (*R*)-**1a** with Yb is about 3–6 kcal/mol lower than the other three possible bindings, i.e., (*S*)-**1a**-Yb, (*R*)-**1a**-Y and (*S*)-**1a**-Y. Ligand substitution for (*R*)-**1a**-Yb is favored energetically by -10.1 kcal/mol (see SI). Transition state calculations suggest that the anticlockwise conformations (**TSYbS**) is the most favored than the clockwise (**TSYR** and **TSYbR**) conformations (Figure 3). The free energy difference ($\Delta\Delta G^{\ddagger}$) between **TSYbR** and **TSYbS** is 2.0 kcal/mol. Boltzmann analysis of the calculated TSs (**TSYbR** and **TSYbS**) predicts enantiomeric excess of 95% at the experimental temperature of 0 °C, which is close to the experimental ee value of 90% (**3a**). When (±)-**1a** binds to the catalytic center, steric clashing between (*S*)-**1a** and BINOL phosphate blocks the anisidine C that is the site of attack on the cyclopropane ring, leading to a distortion of the catalyst in the transition state. Optimized geometries indicate that **TSYbR** is more distorted than **TSYbS**. The most favored transition state **TSYbS** leads (*R*)-reactant to (*S*)-intermediate with *S* configuration at the chiral carbon, which is consistent with the absolute configuration of product **3a** identified with X-ray crystallography. Hence, both experimental and computational data support that this ring-opening reaction of cyclopropane with arylamine is through a two-

step S_N2/proton transfer mechanism, and the S_N2 reaction is the rate- and enantio-determining step of the overall reaction.

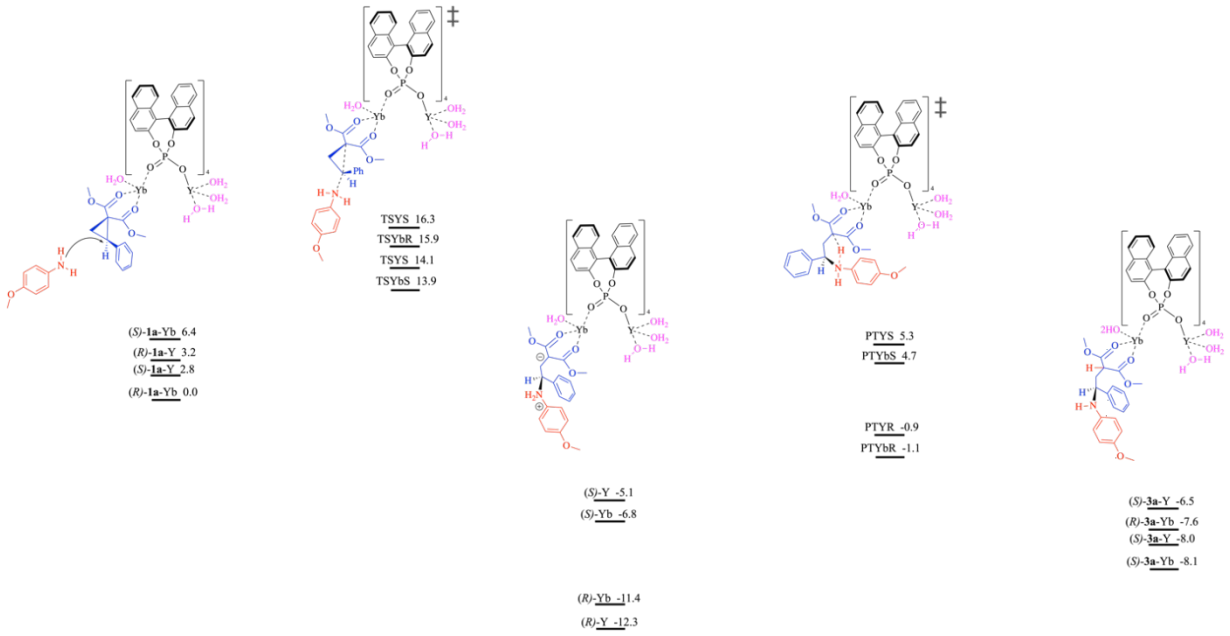
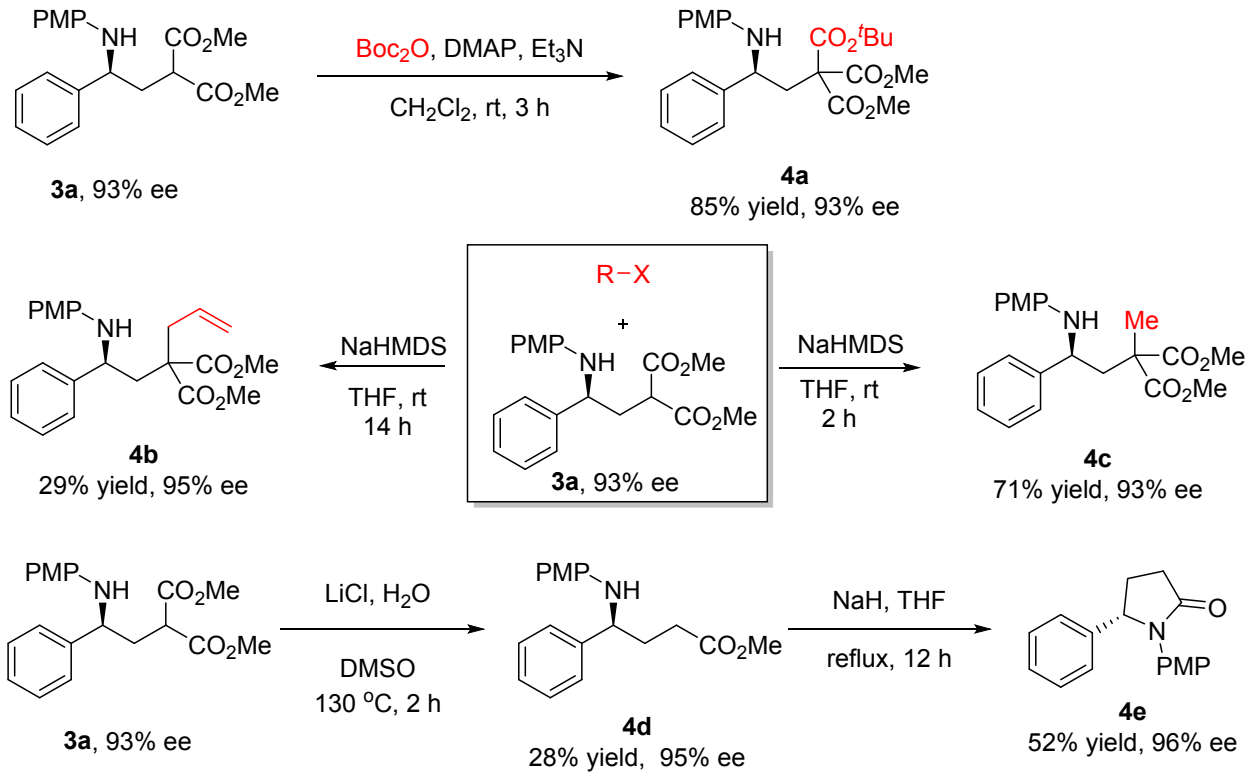


Figure 3. Free energy surface (in kcal/mol) modelled with S_N2 (**TSM±**) and proton transfer (**PTM±**) transition states, M=Y or Yb for *R*- and *S*-enantiomers.

To further highlight the prospect of this reaction, transformations of the ring-opening product **3a** (Scheme 3) were investigated. Triester **4a** was easily obtained from **3a** in 85% yield with 93% *ee*. Allylation product **4b** and methylation product **4c** were generated readily at the malonate moiety of **3a** without any loss of enantioselectivity. Decarboxylation of **3a** was difficult, requiring higher temperature and resulting in γ-amino

acid **4d** with low yield. This is likely due to the presence of the amino group in **3a**. Subsequent cyclization of **4d** with NaH gave optically active γ-lactam **4e** in moderate yield with 96% *ee*.



Scheme 3. Versatile synthetic transformations.

In summary, an efficient enantioselective ring-opening reaction of donor-acceptor cyclopropanes with primary arylamines has been successfully developed through a novel chiral heterobimetallic Lewis acid catalyst. These bimetallic catalysts displayed bifunctional catalytic properties, which enabled this difficult reaction to occur with ease.

Our study has shown that the enantioselectivity of these rare-earth bimetallic catalysts is closely related to the size of the metal ions. Stereochemical experiments suggest that this asymmetric ring-opening reaction can be ascribed to kinetic resolution and that a S_N2-type of ring-opening primarily dominates the process. Computational studies support the primary role of kinetic resolution in this asymmetric synthesis. An X-ray crystal structure was obtained for $Yb(OTf)_3$-Yb[**P**]$_3$, revealing a symmetrical Yb-Yb center bridged with four chiral phosphate ligands which represents new coordination chemistry for rare earth metals. These data further confirm the occurrence of a novel ligand exchange/transmetalation process in the formation of the bimetallic complex. The utility of the ring-opening products (chiral *γ*-amino acid derivatives) has also been demonstrated through useful organic transformations. The extension of these bimetallic complexes to other group of metals and the exploitation of these chiral bimetallic Lewis acid catalysts in other organic transformations are underway.

ASSOCIATED CONTENT

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Notes

The authors declare no competing financial interest.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures, ^{1}H and ^{13}C NMR and other characterization data, single crystal X-ray analysis, computational methods.

Crystallographic data for *(R)*-$Yb_2[\mathbf{P}]_4$ complex (CIF), Crystallographic data for **3a** (CIF).

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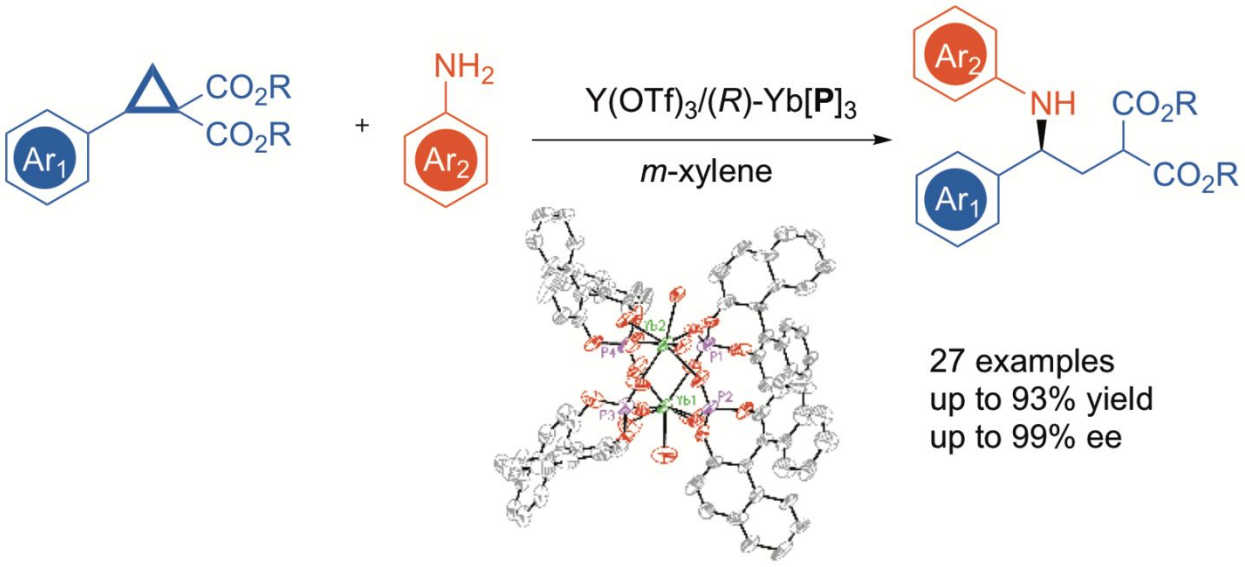

An efficient asymmetric ring-opening reaction of donor-acceptor cyclopropanes with primary arylamines was achieved through a chiral heterobimetallic catalyst.