JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
pubs.acs.org/JACS

Rhodium-Catalyzed Asymmetric 1,4-Addition of α,β-Unsaturated Imino Esters Using Chiral Bicyclic Bridgehead Phosphoramidite Ligands

Ansoo Lee[†] and Hyunwoo Kim*[,†,‡]

[†]Department of Chemistry, KAIST, Daejeon 34141, Korea
[‡]Center for Nanomaterials and Chemical Reactions, Institute for Basic Science, Daejeon 34141, Korea

Supporting Information

ABSTRACT: A chiral bicyclic bridgehead phosphoramidite (briphos) prepared from 1-aminoindane is a highly efficient and selective ligand for rhodium(I)-catalyzed asymmetric 1,4-addition of arylboronic acids to α,β-unsaturated *N*,*N*-dimethyl-sulfamoyl imino esters at ambient temperature. This transformation provides a new class of chiral (*Z*)-γ,γ-diaryl-α,β-dehydroamino esters with excellent yield and enantioselectivity.

Rhodium-catalyzed asymmetric arylation[1] of aryl boronic acid derivatives to carbonyl,[2] imine,[3] and olefin[4] compounds is one of the most reliable and efficient C−Ar bond-forming reactions to construct tri- or tetra-substituted carbon centers in an enantioselective manner. Although arylation procedures have been widely explored for carbonyl compounds, the arylation of imines is still limited to 1,2-addition,[1] particularly the asymmetric 1,2-addition of imino esters provides phenyl glycine derivatives.[5] To the best of our knowledge, stereoselective 1,4-addition of aryl groups to α,β-unsaturated imino esters, providing γ,γ-diaryl-α,β-dehydroamino esters, has not been reported.[6−8] Because the α,β-dehydroamino ester derivatives are valuable structures found in many natural products and biologically active compounds[9] as well as ones used for stereoselective hydrogenation to provide unnatural amino esters,[10] the development of stereoselective 1,4-addition reaction of α,β-unsaturated imino esters is highly desired to obtain a new class of chiral unnatural dehydroamino or amino esters.

We recently reported bicyclic bridgehead phosphoramidites (briphos) as a new type of π-acceptor ligand where the geometrical constraints can reduce the σ-donor ability and enhance the π-acceptor ability (Figure 1a).[11] Briphos ligands have been shown to promote Rh(I)-catalyzed 1,4-addition of boronic acids to α,β-unsaturated *N*-tosyl ketimines under neutral conditions.[11] Given the beneficial properties of briphos in Rh(I)-catalyzed arylation, here we report asymmetric 1,4-addition of α,β-unsaturated imino esters using our newly designed chiral briphos ligands (Figure 1b). A series of chiral briphos ligands (**1a**−**h**) were prepared (Scheme 1). 2,2′-Dihydroxybenzophenone (**2**) was reacted with chiral primary amines to produce the corresponding imines, which were reduced by $NaBH_4$. The resulting secondary amines (**3**) were converted to briphos ligands (**1**) by the reaction with

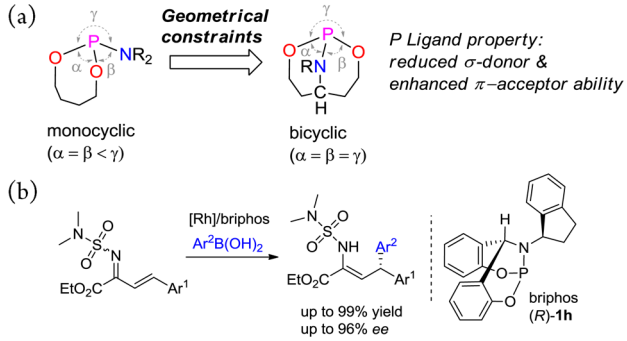
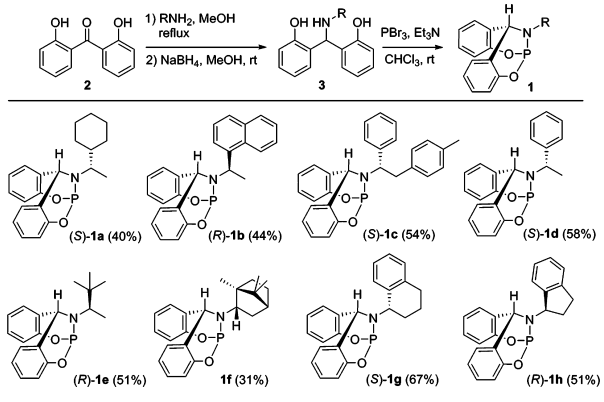


Figure 1. (a) Concept of controlling P ligand properties by geometrical constraints. (b) Scheme for Rh-catalyzed asymmetric 1,4-addition of arylboronic acids to α,β-unsaturated *N*,*N*-dimethyl-sulfamoyl imino esters.

Scheme 1. Synthesis of Chiral Briphos 1



phosphorus tribromide (PBr_3) in 31−67% overall yields (Scheme 1). Figure 2 shows the crystal structures of (*S*)-**1g** and (*R*)-**1h**. (See also the Supporting Information.) In both cases, the proton at the chiral carbon center is pointing toward the phosphorus atom, indicating that a rigid chiral environment is required for stereoselective reactions.

With chiral briphos ligands **1a**−**h** (Scheme 1), we explored the ligand effect on the Rh-catalyzed reaction between aryl boronic acid **6a** and α,β-unsaturated *N*,*N*-dimethyl-sulfamoyl

Received: July 12, 2015
Published: August 24, 2015

DOI: 10.1021/jacs.5b07034
J. Am. Chem. Soc. 2015, 137, 11250−11253

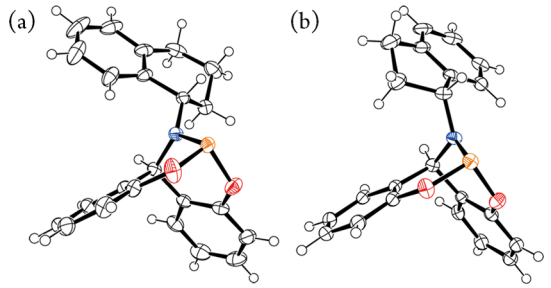
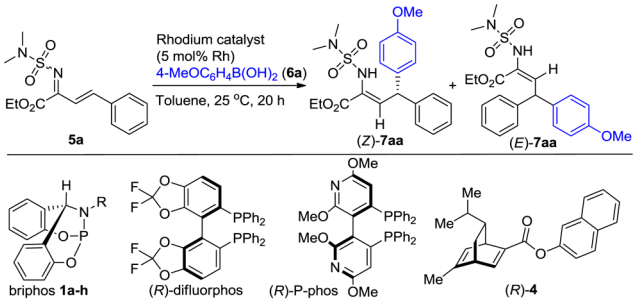


Figure 2. Crystal structures of (a) (*S*)-**1g** and (b) (*R*)-**1h**.

imino ester **5a** at ambient temperature. As shown in Table 1, briphos **1a**–**e** prepared from chiral amines with the acyclic

Table 1. Ligand Screening for Rh-Catalyzed 1,4-Addition of *α,β*-Unsaturated *N,N*-Dimethyl Sulfamoyl Iminoester 5a[a]



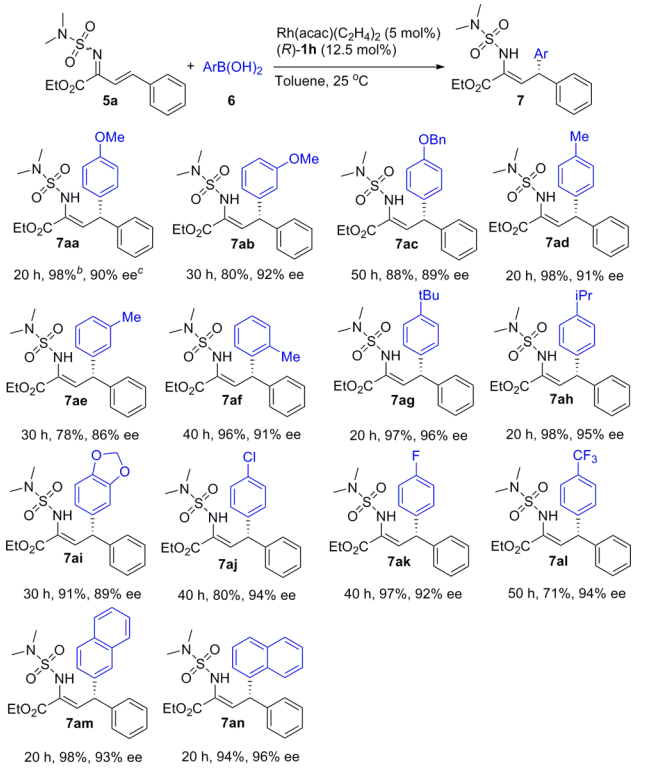
entry	L	ratio of (*Z*)/(*E*)-**7aa**[b]	yield of **7aa** (%)[c]	ee of **7aa** (%)[d]
1	(*S*)-**1a**	98/2	26	52(*S*)
2	(*R*)-**1b**	n.d.	trace	n.d.
3	(*S*)-**1c**	88/12	<10	n.d.
4	(*S*)-**1d**	>99/1	23	66(*R*)
5	(*R*)-**1e**	95/5	<5	n.d.
6	**1f**	n.d.	trace	n.d.
7	(*S*)-**1g**	97/3	27	96(*R*)
8	(*R*)-**1h**	>99/1	98	90(*S*)[e]
9[f,g]	(*R*)-**1h**	92/8	62	90(*S*)
10	(*R*)-difluorphos	n.d.	trace	n.d.
11	(*R*)-P-phos	n.d.	trace	n.d.
12	(*R*)-binap[h]	n.d.	trace	n.d.
13	(*S*)-monophos[i]	84/16	<5	n.d.
14	(*R*)-**4**	83/17	19	41(*R*)
15[f,g]	(*R*)-**4**	n.d.	8	51(*R*)
16[j]		71/29	65	

[a]Conditions: **5a** (0.2 mmol), **6a** (0.6 mmol), and $[Rh(acac)(C_2H_4)_2]$ (5 mol % Rh) were stirred in toluene (2.0 mL) at 25 °C for 20 h. [b]Determined by crude ^1H NMR spectra. 1,2-Arylation product was not detected. [c]Yield of isolated product. [d]Determined by chiral-phase HPLC analysis. [e]The absolute configuration of (*Z*)-**7aa** was determined by single-crystal X-ray crystallography (Supporting Information). [f]Reactions were carried out with KOH (100 mol %; 1.0 M in H_2O). [g]$[Rh(C_2H_4)_2Cl]_2$ (5 mol % Rh). [h]binap =2,2′-bis(diphenylphosphino)-1,1′-binaphthyl. [i]monophos = (3,5-dioxa-4-phosphacyclohepta[2,1-a:3,4-a′]dinaphthalen-4-yl)dimethylamine. [j]$[Rh(cod)OH]_2$ (5 mol % Rh).

secondary alkyl groups provided product **7aa** with lower than 26% yield with moderate enantioselectivity (entries 1–5). Briphos **1f** prepared from (+)-bornylamine was also inefficient (entry 6). Notably, briphos **1g** prepared from 1,2,3,4-tetrahydro-1-naphthylamine showed excellent stereoselectivity of 94% de and 96% ee, albeit with a poor isolated yield of 27% (entry 7). The reactivity problem of briphos **1g** was then addressed by the use of briphos **1h** prepared from 1-aminoindane. It appears that the bicyclic secondary alkyl group in the chiral briphos structure is essential to achieve high-level stereoselectivity. Briphos **1h** provided product (*Z*)-**7aa** with excellent yield (98%) and stereoselectivity (>98% de and 90% ee; entry 8). The addition of KOH resulted in decreased yield and diastereoselectivity without affecting the enantioselectivity (entry 9).[12] We also compared the ligand effect with ligands known to be efficient in the Rh-catalyzed arylation reactions. The difluorphos,[13] P-phos,[14] binap, and monophos were inactive for the reaction of *α,β*-unsaturated imino ester **5a** (entries 10–13). Chiral diene ligand **4** was also inefficient with or without KOH additives (entries 14 and 15). Because the use of $[Rh(cod)OH]_2$ resulted in a product with moderate yield and poor diastereoselectivity, other chiral diene ligands would not be very efficient for this type of reaction. Thus, our experiment shows that briphos **1h** is the most efficient ligand structure among the chiral ligands tested.

We then explored the reaction scope of Rh/**1h**-catalyzed 1,4-addition of *α,β*-unsaturated *N,N*-dimethyl-sulfamoyl imino esters. The survey of aryl boronic acids is summarized in Table 2. When aryl boronic acids **6** with electronic and steric functional groups were reacted with *α,β*-unsaturated imino ester **5a** in the presence of $[Rh(acac)(C_2H_4)_2]$ (5 mol % Rh) and (*R*)-**1h** (12.5 mol %), desirable (*Z*)-*γ,γ*-diaryl-*α,β*-

Table 2. Substrate Scope for Rh-Catalyzed 1,4-Addition of Various Arylboronic Acids 6 to *α,β*-Unsaturated Iminoester 5a[a]



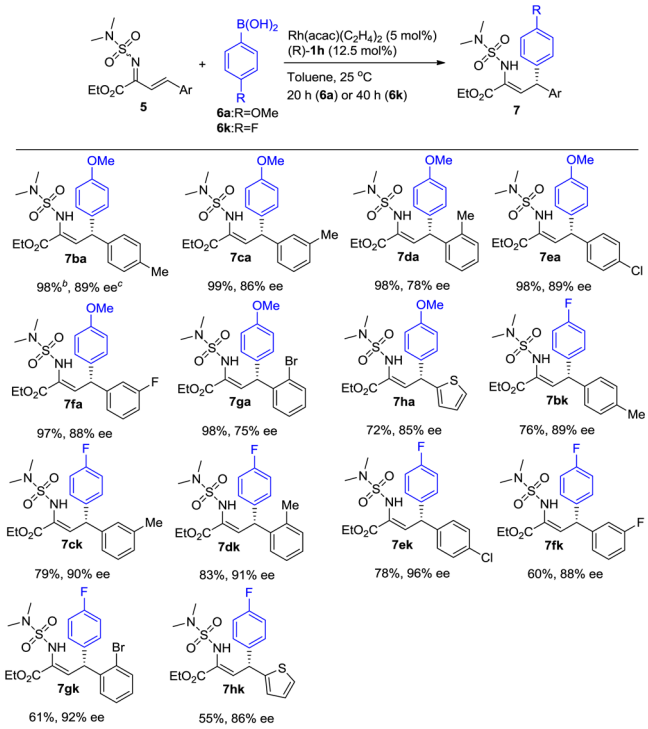
[a]Conditions: **5a** (0.2 mmol), **6** (0.6 mmol), $[Rh(acac)(C_2H_4)_2]$ (5 mol % Rh), and (*R*)-**1h** (12.5 mol %) were stirred in toluene (2.0 mL) at 25 °C. [b]Yield of isolated product. [c]Determined by chiral-phase HPLC analysis.

DOI: 10.1021/jacs.5b07034
J. Am. Chem. Soc. 2015, 137, 11250–11253

dehydroamino ester products **7aa**–**an** were produced with good yield (71–98%) and excellent stereoselectivity (86–96% ee). Our experiments showed that a highly stereoselective 1,4-addition of imino esters can be achieved with various aryl boronic acids at ambient temperature within 20–50 h.

The scope of α,β-unsaturated *N*,*N*-dimethyl-sulfamoyl imino esters was then studied. As shown in Table 3, two aryl boronic

Table 3. Substrate Scope for Rh-Catalyzed 1,4-Addition of Various Arylboronic Acids 6a,k to α,β-Unsaturated Iminoesters 5[a]



[a]Conditions: **5** (0.2 mmol), **6** (0.6 mmol), [Rh(acac)$(C_2H_4)_2$] (5 mol % Rh), and (*R*)-**1h** (12.5 mol %) were stirred in toluene (2.0 mL) at 25 °C. [b]Yield of isolated product. [c]Determined by chiral-phase HPLC analysis.

acids **6a** and **6k** were used to compare the reactivity and selectivity for the reaction with α,β-unsaturated imino esters **5b**–**h**. Although the more electron-rich 4-methoxyphenyl boronic acid, **6a**, showed better reactivity to complete the reaction within 20 h, the enantioselectivity of the products was somewhat reduced, particularly among imino esters with ortho-substituted phenyl groups (78% ee for **7da** and 75% ee for **7ga**). However, when the more electron-deficient 4-fluorophenylboronic acid, **6k**, was used, stereoselectivity greater than 86% ee was observed in all cases. Thus, chiral briphos **1h** can be an efficient ligand for Rh-catalyzed 1,4-addition of boronic acids to α,β-unsaturated *N*,*N*-dimethyl-sulfamoyl imino esters, providing a new class of (*Z*)-γ,γ-diaryl-α,β-dehydroamino esters.

For the asymmetric Rh(I)-catalyzed arylation reaction, various chiral ligands based on phosphorus,[15] diene,[16] sulfoxide,[17] NHC,[18] and its hybrid structures[19] with olefin, hetero atomic group (P, N, O, or S), and oxazoline have been creatively developed.[1] To achieve high-level stereoselectivity, ligand design largely relied on several privileged chiral ligand platforms such as 1,1′-binaphthyls or 1,1′-biphenyls as well as chelating effects to establish a rigid chiral environment. Thus, it is unusual to achieve high stereoselectivity from monodentate chiral ligands with only one carbon chiral center as found in chiral briphos **1h**. To gain insights into the origin of stereoselectivity, we performed DFT computation to find equilibrium geometries of the two possible conformer structures of [Rh{(*R*)-**1h**}$_2(C_2H_4)$Ph] prepared on the basis of the crystal structure of [Rh**1i**$_2$Cl]$_2$ (R = Ph in **1i**)[11] (Supporting Information). Among all possible local minima, the computation shows that [**Rh**]-**1** is the most stable conformer at least by about 1.61 kcal/mol relative to the other conformer [**Rh**]-**2** (Figure 3a). Thus, [Rh{(*R*)-

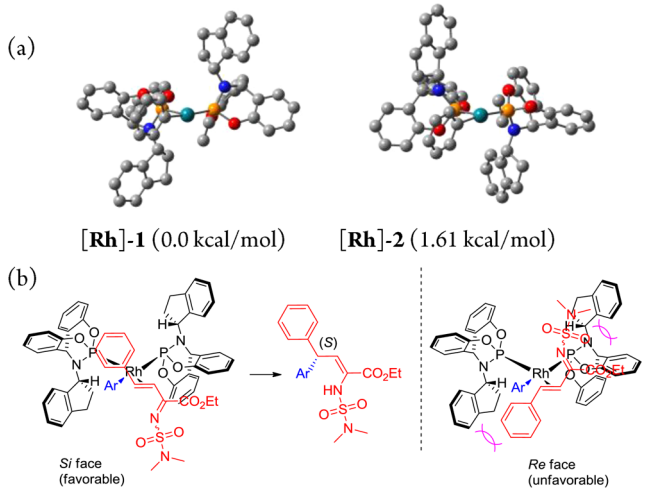
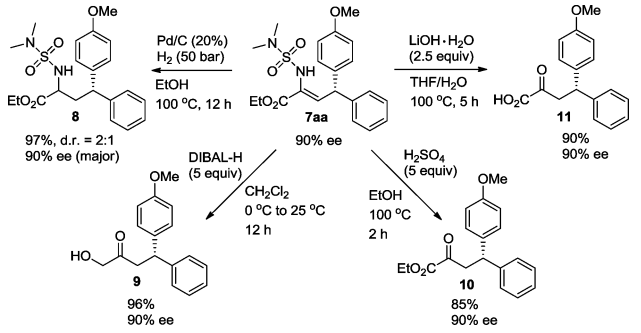


Figure 3. (a) Two calculated minimum structures of [Rh{(*R*)-**1h**}$_2(C_2H_4)$Ph]. (b) Proposed stereochemical pathway by [**Rh**]-**1**.

1h}$_2(C_2H_4)$Ph] is expected to form major conformer [**Rh**]-**1** analogous to the reported enantioselective model of Rh/(*S*)-BINAP proposed by Hayashi,[15d] thus allowing selective synthesis of the product with (*S*)-configuration (Figure 3b).

Finally, the utility of the dehydroamino ester products was demonstrated in Scheme 2. We could prepare **7aa** in gram scale

Scheme 2. Transformation of Dehydroamino Ester 7aa



(1.5 g) with 90% yield and 90% ee (Supporting Information). The hydrogenation of **7aa** by Pd/C gave γ,γ-diaryl amino ester **8** in a 2:1 diastereomeric ratio with complete retention of enantiopurity. The reduction of **7aa** by DIBAL-H provided hydroxy ketone **9**. Moreover, acidic or basic hydrolysis produced keto ester **10** or keto acid **11** in high yields, respectively.

We have developed a Rh(I)-catalyzed asymmetric 1,4-addition of arylboronic acids to α,β-unsaturated *N*,*N*-dimethyl-sulfamoyl imino esters using a newly designed chiral bicyclic bridgehead phosphoramidite (briphos) ligand (**1h**)

DOI: 10.1021/jacs.5b07034
J. Am. Chem. Soc. 2015, 137, 11250–11253

prepared from 1-aminoindane. This method represents a highly versatile and selective transformation to provide a new class of chiral (*Z*)-*γ*,*γ*-diaryl-*α*,*β*-dehydroamino esters that can be further modified to unnatural amino acids, hydroxy ketones, and keto acids, among others.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b07034.

Experimental procedures, spectroscopic and calculation data, and crystallographic details. (PDF)
Crystallographic details for (*R*)-**1h**. (CIF)
Crystallographic details for (*S*)-**1g**. (CIF)
Crystallographic details for (Z)-**7aa**. (CIF)

■ AUTHOR INFORMATION

Corresponding Author

*hwkim@kaist.edu

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful for the financial support provided by the Institute for Basic Science (IBS-R004-D1). This work was also supported by the National Institute of Supercomputing and Network/Korea Institute of Science and Technology Information (KCS-2014-C1-033). We also thank J. Kim and Prof. Y. Lee (KAIST) as well as Dr. A. J. Lough (University of Toronto) for X-ray analysis.

■ REFERENCES

(1) For reviews, see (a) Tian, P.; Dong, H.-Q.; Lin, G.-Q. *ACS Catal.* **2012**, *2*, 95. (b) Marques, C. S.; Burke, A. J. *ChemCatChem* **2011**, *3*, 635. (c) Edwards, H. J.; Hargrave, J. D.; Penrose, S. D.; Frost, C. G. *Chem. Soc. Rev.* **2010**, *39*, 2093. (d) Hayashi, T.; Yamasaki, K. *Chem. Rev.* **2003**, *103*, 2829. (e) Fagnou, K.; Lautens, M. *Chem. Rev.* **2003**, *103*, 169.

(2) (a) Zhu, T.-S.; Jin, S.-S.; Xu, M.-H. *Angew. Chem., Int. Ed.* **2012**, *51*, 780. (b) Cai, F.; Pu, X.; Qi, X.; Lynch, V.; Radha, A.; Ready, J. M. *J. Am. Chem. Soc.* **2011**, *133*, 18066. (c) Duan, H.-F.; Xie, J.-H.; Qiao, X.-C.; Wang, L.-X.; Zhou, Q.-L. *Angew. Chem., Int. Ed.* **2008**, *47*, 4351. (d) Shintani, R.; Inoue, M.; Hayashi, T. *Angew. Chem., Int. Ed.* **2006**, *45*, 3353.

(3) (a) Nishimura, T.; Noishiki, A.; Chit Tsui, G.; Hayashi, T. *J. Am. Chem. Soc.* **2012**, *134*, 5056. (b) Cui, Z.; Yu, H.-J.; Yang, R.-F.; Gao, W.-Y.; Feng, C.-G.; Lin, G.-Q. *J. Am. Chem. Soc.* **2011**, *133*, 12394. (c) Shintani, T.; Takeda, M.; Tsuji, T.; Hayashi, T. *J. Am. Chem. Soc.* **2010**, *132*, 13168. (d) Trincado, M.; Ellman, J. A. *Angew. Chem., Int. Ed.* **2008**, *47*, 5623. (e) Jagt, R. B. C.; Toullec, P. Y.; Geerdink, D.; de Vries, J. G.; Feringa, B. L.; Minnaard, A. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 2789.

(4) (a) So, C. M.; Kume, S.; Hayashi, T. *J. Am. Chem. Soc.* **2013**, *135*, 10990. (b) Pattison, G.; Piraux, G.; Lam, H. W. *J. Am. Chem. Soc.* **2010**, *132*, 14373. (c) Nishimura, T.; Wang, J.; Nagaosa, M.; Okamoto, K.; Shintani, R.; Kwong, F.-y.; Yu, W.-y.; Chan, A. S. C.; Hayashi, T. *J. Am. Chem. Soc.* **2010**, *132*, 464. (d) Sasaki, K.; Hayashi, T. *Angew. Chem., Int. Ed.* **2010**, *49*, 8145. (e) Wang, Z.-Q.; Feng, C.-G.; Zhang, S.-S.; Xu, M.-H.; Lin, G.-Q. *Angew. Chem., Int. Ed.* **2010**, *49*, 5780.

(5) For Rh-catalyzed asymmetric 1,2-addition to imino esters, see (a) Wang, H.; Jiang, T.; Xu, M.-H. *J. Am. Chem. Soc.* **2013**, *135*, 971. (b) Yamamoto, Y.; Takahashi, Y.; Kurihara, K.; Miyaura, N. *Aust. J. Chem.* **2011**, *64*, 1447. (c) Beenen, M. A.; Weix, D. J.; Ellman, J. A. *J. Am. Chem. Soc.* **2006**, *128*, 6304.

(6) For Cu-catalyzed 1,4-addition of diethyl zinc to imino esters, see Palacios, F.; Vicario, J. *Org. Lett.* **2006**, *8*, 5405.

(7) For an example of organocatalytic Friedel−Craft alkylation of indoles, see Bi, B.; Lou, Q.-X.; Ding, Y.-Y.; Chen, S.-W.; Zhang, S.-S.; Hu, W.-H.; Zhao, J.-L. *Org. Lett.* **2015**, *17*, 540.

(8) For selected examples of cycloadditions, see (a) He, L.; Laurent, G.; Retailleau, P.; Folléas, B.; Brayer, J.-L.; Masson, G. *Angew. Chem., Int. Ed.* **2013**, *52*, 11088. (b) Shi, Z.; Yu, P.; Loh, T.-P.; Zhong, G. *Angew. Chem., Int. Ed.* **2012**, *51*, 7825. (c) Zhou, S.-L.; Li, J.-L.; Dong, L.; Chen, Y.-C. *Org. Lett.* **2011**, *13*, 5874.

(9) (a) Oelke, A. J.; France, D. J.; Hofmann, T.; Wuitschik, G.; Ley, S. V. *Nat. Prod. Rep.* **2011**, *28*, 1445. (b) Valentekovich, R. J.; Schreiber, S. L. *J. Am. Chem. Soc.* **1995**, *117*, 9069. (c) Botes, D. P.; Tuinman, A. A.; Wessels, P. L.; Viljoen, C. C.; Kruger, H.; Williams, D. H.; Santikarn, S.; Smith, R. J.; Hammond, S. J. *J. Chem. Soc., Perkin Trans. 1* **1984**, 2311.

(10) For reviews, see (a) Etayo, P.; Vidal-Ferran, A. *Chem. Soc. Rev.* **2013**, *42*, 728. (b) Xie, J.-H.; Zhu, S.-F.; Zhou, Q.-L. *Chem. Soc. Rev.* **2012**, *41*, 4126. (c) Xie, J.-H.; Zhu, S.-F.; Zhou, Q.-L. *Chem. Rev.* **2011**, *111*, 1713.

(11) Lee, A.; Ahn, S.; Kang, K.; Seo, M.-S.; Kim, Y.; Kim, W. Y.; Kim, H. *Org. Lett.* **2014**, *16*, 5490.

(12) Addition of KOH resulted in partial decomposition of substrates and products: Wang, J.; Wang, M.; Cao, P.; Jiang, L.; Chen, G.; Liao, J. *Angew. Chem., Int. Ed.* **2014**, *53*, 6673.

(13) Genet, J.-P.; Ayad, T.; Ratovelomanana-Vidal, V. *Chem. Rev.* **2014**, *114*, 2824.

(14) Wu, J.; Chan, A. S. C. *Acc. Chem. Res.* **2006**, *39*, 711.

(15) (a) Korenaga, T.; Ko, A.; Uotani, K.; Tanaka, Y.; Sakai, T. *Angew. Chem., Int. Ed.* **2011**, *50*, 10703. (b) Boiteau, J.-G.; Imbos, R.; Minnaard, A. J.; Feringa, B. L. *Org. Lett.* **2003**, *5*, 681. (c) Reetz, M. T.; Moulin, D.; Gosberg, A. *Org. Lett.* **2001**, *3*, 4083. (d) Takaya, Y.; Ogasawara, M.; Hayashi, T.; et al. *J. Am. Chem. Soc.* **1998**, *120*, 5579.

(16) (a) Pattison, G.; Piraux, G.; Lam, H. W. *J. Am. Chem. Soc.* **2010**, *132*, 14373. (b) Cao, Z.; Du, H. *Org. Lett.* **2010**, *12*, 2602. (c) Gendrineau, T.; Chuzel, O.; Eijsberg, H.; Genet, J.-P.; Darses, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 7669. (d) Wang, Z.-Q.; Feng, C.-G.; Xu, M.-H.; Lin, G.-Q. *J. Am. Chem. Soc.* **2007**, *129*, 5336. (e) Paquin, J.-F.; Defieber, C.; Stephenson, C. R. J.; Carreira, E. M. *J. Am. Chem. Soc.* **2005**, *127*, 10850. (f) Tokunaga, N.; Otomaru, Y.; Okamoto, K.; Ueyama, K.; Shintani, R.; Hayashi, T. *J. Am. Chem. Soc.* **2004**, *126*, 13584.

(17) (a) Khiar, N.; Salvador, Á.; Valdivia, V.; Chelouan, A.; Alcudia, A.; Álvarez, E.; Fernández, I. *J. Org. Chem.* **2013**, *78*, 6510. (b) Chen, J.; Chen, J.; Lang, F.; Zhang, X.; Cun, L.; Zhu, J.; Deng, J.; Liao, J. *J. Am. Chem. Soc.* **2010**, *132*, 4552. (c) Chen, Q.-A.; Dong, X.; Chen, M.-W.; Wang, D.-S.; Zhou, Y.-G.; Li, Y.-X. *Org. Lett.* **2010**, *12*, 1928. (d) Bürgi, J. J.; Mariz, R.; Gatti, M.; Drinkel, E.; Luan, X.; Blumentritt, S.; Linden, A.; Dorta, R. *Angew. Chem., Int. Ed.* **2009**, *48*, 2768. (e) Mariz, R.; Luan, X.; Gatti, M.; Linden, A.; Dorta, R. *J. Am. Chem. Soc.* **2008**, *130*, 2172.

(18) Ma, Y.; Song, C.; Ma, C.; Sun, Z.; Chai, Q.; Andrus, M. B. *Angew. Chem., Int. Ed.* **2003**, *42*, 5871.

(19) (a) Ogasawara, M.; Tseng, Y.-Y.; Arae, S.; Morita, T.; Nakaya, T.; Wu, W.-Y.; Takahashi, T.; Kamikawa, K. *J. Am. Chem. Soc.* **2014**, *136*, 9377. (b) Chen, G.; Gui, J.; Li, L.; Liao, J. *Angew. Chem., Int. Ed.* **2011**, *50*, 7681. (c) Hahn, B. T.; Tewes, F.; Fröhlich, R.; Glorius, F. *Angew. Chem., Int. Ed.* **2010**, *49*, 1143. (d) Duan, W.-L.; Iwamura, H.; Shintani, R.; Hayashi, T. *J. Am. Chem. Soc.* **2007**, *129*, 2130. (e) Kuriyama, M.; Nagai, K.; Yamada, K.-i.; Miwa, Y.; Taga, T.; Tomioka, K. *J. Am. Chem. Soc.* **2002**, *124*, 8932.

DOI: 10.1021/jacs.5b07034
J. Am. Chem. Soc. 2015, 137, 11250−11253