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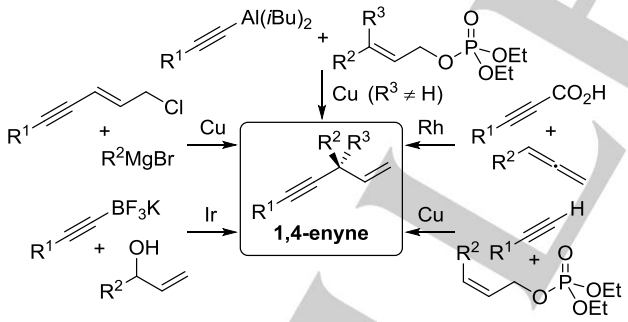
Asymmetric Synthesis of Chiral 1,4-Enynes via Organocatalytic Alkenylation of Propargyl Alcohols with Trialkenylboroxines

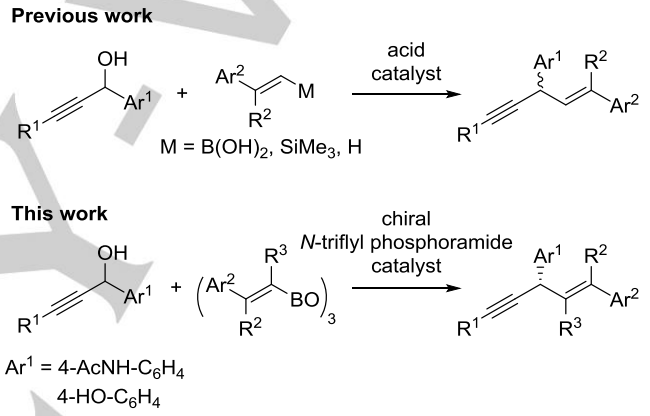
Jian-Fei Bai,[a] Kento Yasumoto,[a] Taichi Kano* [a] and Keiji Maruoka*[a,b]

Abstract: A highly enantioselective synthesis of 1,4-enynes is described via an organocatalytic reaction between propargyl alcohols and trialkenylboroxines. Our strategy relies on the acid-mediated generation of the carbocationic intermediate from propargyl alcohols followed by enantioselective alkenylation with trialkenylboroxines. A range of chiral 1,4-enynes were obtained in moderate to good yields with high levels of enantioselectivity. Use of a highly acidic chiral *N*-triflyl phosphoramide catalyst, which has two distant Lewis basic oxygen atoms, was found to be crucial for both high reactivity and selectivity in the present reaction.

Chiral 1,4-enynes are important and versatile synthetic intermediates.[1] Both alkenyl and alkynyl groups on the chiral center at the 3-position can serve as handles for further elaboration, respectively.[2] Various synthetic approaches to 1,4-enynes have been developed thus far.[3] Asymmetric synthesis of chiral 1,4-enynes has also been achieved by transition metal-catalyzed enantioselective allylic substitution (Scheme 1).[4] In recent years, the development of effective and environmentally benign methods using non-metal catalysts has attracted much attention. In this context, alkenylation of propargyl alcohols is an alternative promising approach to 1,4-enynes, in which the carbocation intermediate is generated by the acid-mediated elimination of the hydroxy group (Scheme 2).[5-7] To the best of our knowledge, however, the catalytic asymmetric variant has not been developed, probably due to the difficulty on enantioface selection of the carbocation intermediate by the chiral acid catalyst. Thus, we became interested in a chiral Brønsted acid-catalyzed synthesis of chiral 1,4-enynes. Herein we report an organocatalytic enantioselective alkenylation of propargyl alcohols with trialkenylboroxines.



Scheme 1. Transition metal-catalyzed asymmetric synthesis of 1,4-enynes.



Scheme 2. Synthesis of 1,4-enynes by alkenylation of propargyl alcohols.

We first examined the reaction of propargyl alcohol **1a** with boroxine **2a** in dichloromethane at room temperature. In this reaction, boroxine **2a** was employed as a nucleophile instead of (*E*)-stylylboronic acid which readily forms **2a** by dehydration.[8] A highly acidic chiral *N*-triflyl phosphoramide (*S*)-**4a**[9] was selected as catalyst with the expectation that the carbocation intermediate would be generated from propargyl alcohol **1a** by elimination of the hydroxy group, along with the generation of water. When the reaction was performed in the presence of 5 mol% of (*S*)-**4a**, the desired 1,4-enyne **3a** was obtained in good yield but with low enantioselectivity (Table 1, entry 1). To improve the stereoselectivity, propargyl alcohol **1b** having an acetamido group at the *para*-position, which can be the handle for further functionalization, was then used. To our delight, the enantioselectivity was drastically increased without loss of reactivity (entry 2). The fine-tuning of the catalyst structure led to a slight increase in enantioselectivity, and (*S*)-**4b** was found to be the optimal catalyst (entry 3). On the other hand, the yield and enantioselectivity were significantly decreased with a phosphoric acid catalyst (*S*)-**5** (entry 7). Among the solvents tested, chloroform proved to be most effective in terms of both yield and enantioselectivity (entry 9). The concentration of the solution was found to affect the stereoselectivity, and the reaction at a lower

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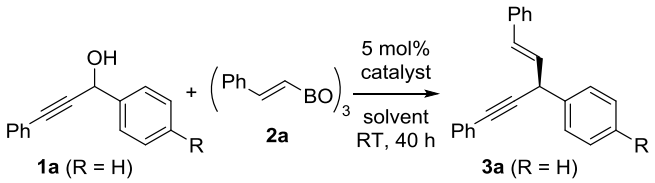
concentration resulted in higher enantioselectivity (entry 14). Addition of molecular sieve 5A caused a substantial decrease in yield (entry 15). When diisopropyl (*E*)-styrylboronate was used as a nucleophile instead of **2a**, decreased yield and enantioselectivity were observed (entry 16). Use of (*E*)-styrylboronic acid pinacol ester led to complete suppression of the desired alkenylation (entry 17).

Table 1. Catalyst and solvent screening for the alkenylation of propargyl alcohol **1** with boroxine **2a**.[a]

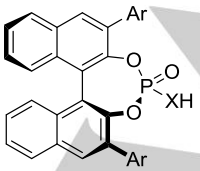


1a (R = H)
1b (R = AcNH)

3a (R = H)
3b (R = AcNH)

Entry	1	Catalyst	Solvent	Yield [%][b]	Ee [%][c]
1[d]	**1a**	(*S*)-**4a**	CH_2Cl_2	76	28
2	**1b**	(*S*)-**4a**	CH_2Cl_2	76	85
3	**1b**	(*S*)-**4b**	CH_2Cl_2	80	88
4	**1b**	(*S*)-**4c**	CH_2Cl_2	64	85
5	**1b**	(*S*)-**4d**	CH_2Cl_2	70	87
6	**1b**	(*S*)-**4e**	CH_2Cl_2	77	81
7	**1b**	(*S*)-**5**	CH_2Cl_2	8	–24
8[e]	**1b**	(*S*)-**4b**	CH_2Cl_2	92	87
9[e]	**1b**	(*S*)-**4b**	$CHCl_3$	88	89
10[e]	**1b**	(*S*)-**4b**	$ClCH_2CH_2Cl$	85	82
11[e]	**1b**	(*S*)-**4b**	THF	53	4
12[e]	**1b**	(*S*)-**4b**	1,4-dioxane	49	5
13[e,f]	**1b**	(*S*)-**4b**	$CHCl_3$	84	64
14[g,h]	**1b**	(*S*)-**4b**	$CHCl_3$	72	91
15[g,h,i]	**1b**	(*S*)-**4b**	$CHCl_3$	57	87
16[g,h,j]	**1b**	(*S*)-**4b**	$CHCl_3$	61	73
17[g,h,k]	**1b**	(*S*)-**4b**	$CHCl_3$	n.d.	-

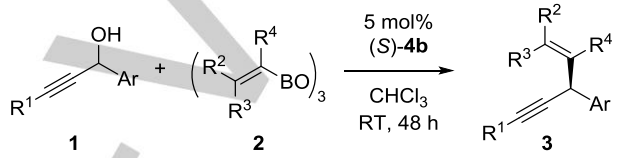
[a] Use of **1** (0.06 mmol), **2a** (0.02 mmol), a catalyst (0.003 mmol) and a solvent (2 mL). [b] Determined by ^{1}H-NMR with 1,2-dichloroethane as internal standard. [c] Determined by chiral HPLC methods. [d] Performed for 24 h. [e] Use of **1b** (0.072 mmol). The yield is based on **2a**. [f] Use of $CHCl_3$ (0.6 mL). [g] Performed for 48 h. [h] Use of $CHCl_3$ (3 mL). [i] Use of molecular sieve 5A (50 mg). [j] Use of (*E*)-styryl-B(O*i*Pr)$_2$ instead of **2a**. [k] Use of (*E*)-styryl-B(pin) instead of **2a**. pin = pinacolato. n.d. = not detected. Ad = adamantyl.



(*S*)-**4a** (Ar = 4-*t*Bu-2,6-(*i*Pr)$_2$-C_6H_2, X = NTf)
(*S*)-**4b** (Ar = 4-(1-Ad)-2,6-(*i*Pr)$_2$-C_6H_2, X = NTf)
(*S*)-**4c** (Ar = 2,4,6-(*c*Pent)$_3$-C_6H_2, X = NTf)
(*S*)-**4d** (Ar = 2,4,6-(*c*Hex)$_3$-C_6H_2, X = NTf)
(*S*)-**4e** (Ar = 2,4,6-(*i*Pr)$_3$-C_6H_2, X = NTf)
(*S*)-**5** (Ar = 2,4,6-(*i*Pr)$_3$-C_6H_2, X = O)

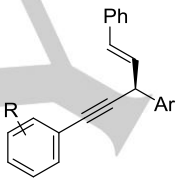
With the optimized conditions in hand, a variety of propargyl alcohols **1** and boroxines **2** were tested to study the scope of the developed methodology (Table 2). The reaction proved tolerant to electron-donating and electron-withdrawing groups on the aromatic ring on the alkynyl terminus, giving moderate to good yields and high enantioselectivities (**3c**-**3i**). A number of other propargyl alcohols **1** having heteroaryl, alkenyl, alkyl and silyl groups performed equally well, and comparable yields and selectivities were observed (**3j**-**3p**). Several boroxines **2** also served as effective coupling partners, providing the corresponding products with good yields and enantioselectivities (**3q**-**3v**). While introduction of an α-substituent on the styryl group slightly reduced the enantioselectivity (**3t**), the reaction of a boroxine bearing 2-indenyl group showed excellent enantioselectivities (**3u** and **3v**).[10]

Table 2. Alkenylation of propargyl alcohols **1** with boroxines **2**.[a]

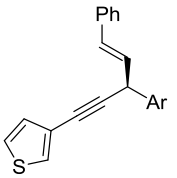


1 **2** **3**

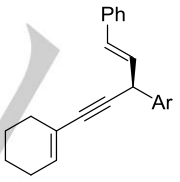
Ar = 4-AcNH-C_6H_4



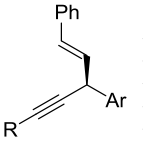
3b R = H 70%, 91% ee
3c R = 4-MeO 67%, 93% ee
3d R = 4-Me 77%, 90% ee
3e R = 4-Br 83%, 90% ee
3f R = 3-MeO 77%, 91% ee
3g R = 3-Cl 70%, 90% ee
3h R = 2-MeO 60%, 92% ee
3i R = 2-Cl 79%, 90% ee



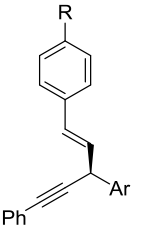
3j 65%, 91% ee



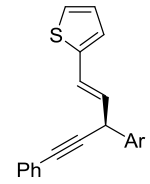
3k 67%, 90% ee



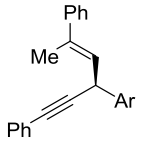
3l R = Bn 68%, 90% ee
3m R = Pr 74%, 92% ee
3n R = *c*Pr 77%, 90% ee
3o R = *t*Bu 66%, 92% ee
3p R = Me_3Si 78%, 92% ee



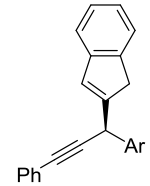
3q R = Me 83%, 91% ee
3r R = Br 63%, 90% ee



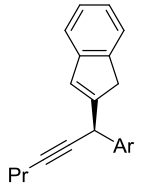
3s 85%, 89% ee



3t 86%, 84% ee



3u 86%, 96% ee[b]



3v 89%, 98% ee[b]

[a] Use of **1** (0.09 mmol), **2** (0.03 mmol), (*S*)-**4b** (0.0045 mmol) and $CHCl_3$ (4.5 mL). Yield of isolated product given. The enantiomeric excess was determined by chiral HPLC methods. [b] Performed for 24 h.

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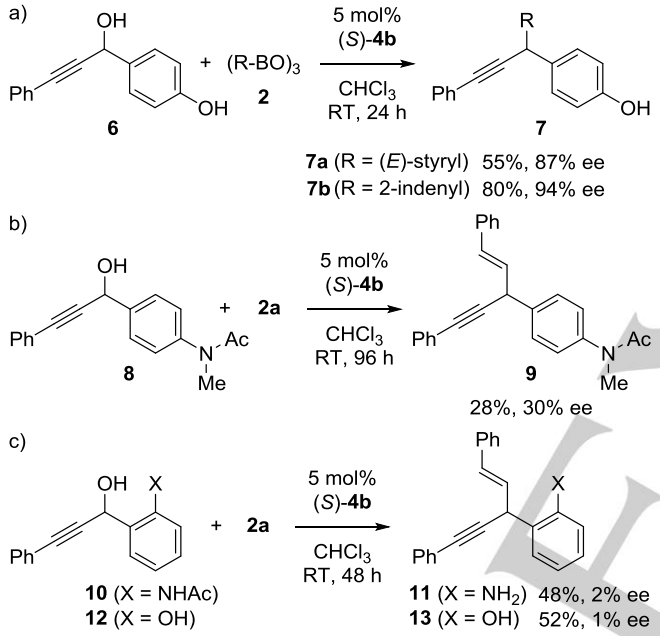
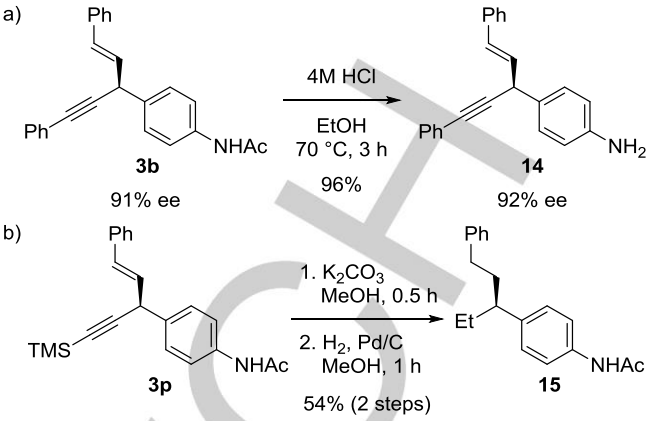
While propargyl alcohols **1** having a *p*-acetamidophenyl group proved to be an excellent substrate for the reaction, the application of the present method to a propargyl alcohol **6** with a *p*-hydroxyphenyl substituent also provided satisfactory results (Scheme 3a). On the other hand, introduction of a methyl group to *p*-acetamido group significantly decreased the reaction rate and stereoselectivity (Scheme 3b) The reactions of propargyl alcohols **10** and **12** having an *ortho*-substituted phenyl group gave almost racemic products, respectively (Scheme 3c). Interestingly, the acetamido group at the *ortho*-position was hydrolyzed during the reaction. These results suggested that a hydrogen bond donor, which can be engaged in a hydrogen bonding with the oxygen atom of the catalyst, might be required as a substituent at the *para* position for high yield and stereoselectivity.



Scheme 3. Alkenylation of propargyl alcohols having a *para*- or *ortho*-substituted phenyl group.

When the product **3b** was treated with 4N HCl, the acetamido group was hydrolyzed to amino group, which can be used as a synthetic handle for further functionalization, without loss of optical purity (Scheme 4a). Hydrogenation of the alkenyl and alkynyl groups of **3p** afforded the product **15** bearing two different alkyl groups (Scheme 4b). The absolute stereochemistry at the benzylic carbon of **15** was determined to be *S* by comparison with **15** which was synthesized from the known compound.



Scheme 4. Transformation and absolute configuration determination of alkenylation products.

Based on the above preliminary results, plausible catalytic cycle and transition states **TS1** and **TS2** were proposed (Figure 1). First, the acid catalyst **4** promotes the elimination of hydroxy group of propargyl alcohol **1** (X = AcNH) or **6** (X = OH), and the generated cationic intermediate interacts with the catalyst through the hydrogen bonding as shown in either **TS1** or **TS2**.[11,12] The Lewis basic oxygen atom on the phosphorus atom is close to the sterically hindered aryl substituent of the catalyst, and might preferably interact with the sterically less hindered acetamido or hydroxy group as shown in **TS1**. Interconvertible *cis* and *trans* isomers of the cationic intermediate are generated during this process, and one geometric isomer might preferentially participate in the reaction. The boroxine or the corresponding boronic acid,[13] which is generated in-situ by hydrolysis of the boroxine, can be activated as a nucleophile by formation of the ate complex with the deprotonated catalyst, and the carbon-carbon bond formation with the neighboring cationic intermediate might then occur to afford the product **3** or **7** stereoselectively. The borane salt of the catalyst is readily hydrolyzed as the catalyst is regenerated. In this reaction, interaction of two distant oxygen atoms of the catalyst with both nucleophile and electrophile may be crucial for obtaining high yields and selectivities.[11] In this scenario, the two oxygen atoms of the phosphoric acid catalyst as Lewis bases might be too close to each other (Table 1, entry 3 vs. 7).

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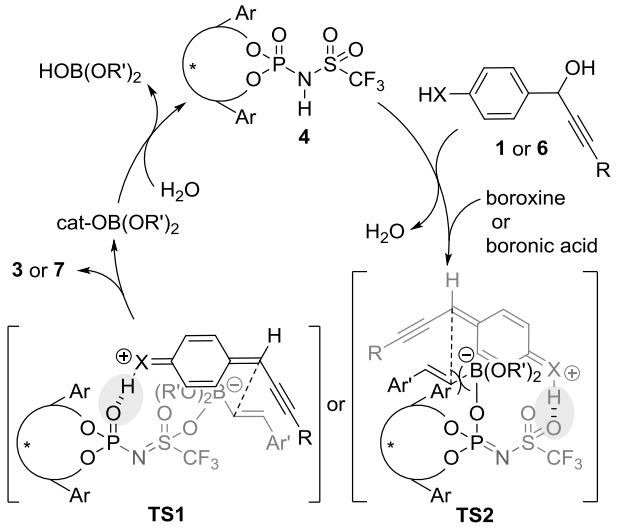

Figure 1. Proposed catalytic cycle and transition state models.

An organocatalytic asymmetric synthesis of 1,4-enynes has been realized. In this process, readily available propargyl alcohols bearing a hydrogen bond donor and trialkenylboroxines can be employed and a highly acidic chiral *N*-triflyl phosphoramide was found to be the optimal Brønsted acid catalyst. This asymmetric alkenylation of propargyl alcohols with trialkenylboroxines offers an alternative approach to the asymmetric synthesis of 1,4-enynes, and will probably find application in the synthesis of a range of chiral compounds having alkynyl, alkenyl or alkyl carbon chains.

Acknowledgements

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Keywords: organocatalysis • asymmetric catalysis • Brønsted acids • alkenes • alkynes

[1] For selected examples as synthetic intermediates in total synthesis, see: a) M. Jacobson, R. E. Redfern, W. A. Jones, M. H. Aldridge, *Science* **1970**, *170*, 542; b) G. Stork, M. Isobe, *J. Am. Chem. Soc.* **1975**, *97*, 4745; c) K. Iida, M. Hirama, *J. Am. Chem. Soc.* **1994**, *116*, 10310; d) V. Hickmann, M. Alcarazo, A. Fürstner, *J. Am. Chem. Soc.* **2010**, *132*, 11042; e) R. Bajpai, D. P. Curran, *J. Am. Chem. Soc.* **2011**, *133*, 20435.

[2] For selected examples on transformations of 1,4-enynes, see: a) T. P. Heffron, T. F. Jamison, *Org. Lett.* **2003**, *5*, 2339; b) T. P. Heffron, J. D. Trenkle, T. F. Jamison, *Tetrahedron* **2003**, 59, 8913; c) X. Shi, D. J. Gorin, F. D. Toste, *J. Am. Chem. Soc.* **2005**, *127*, 5802; d) B. A. Bhanu Prasad, F. K. Yoshimoto, R. Sarpong, *J. Am. Chem. Soc.* **2005**, *127*, 12468; e) A. Buzas, F. Gagosz, *J. Am. Chem. Soc.* **2006**, *128*, 12614; f) D. Vasu, A. Das, R.-S. Liu, *Chem. Commun.* **2010**, *46*, 4115; g) T. Sato, T. Onuma, I. Nakamura, M. Terada, *Org. Lett.* **2011**, *13*, 4992.

[3] For selected examples on synthesis of 1,4-enynes, see; a) C. A. Correia, C.-J. Li, *Adv. Synth. Catal.* **2010**, *352*, 1446; b) Q. Wang, Y. Kobayashi, *Tetrahedron Lett.* **2010**, *51*, 5592; c) K. Ren, P. Li, L. Wang, X. Zhang, *Tetrahedron* **2011**, *67*, 2753; d) P. Trillo, A. Baeza, C. Nájera, *J. Org. Chem.* **2012**, *77*, 7344; e) C. Liu, F. Yang, T. Wang, *Chin. J. Chem.* **2014**, *32*, 387; f) Q. Yang, Y. Zhou, J. Chen, X. He, J. Xu, F. Y. Kwong, B. Fan, *Eur. J. Org. Chem.* **2015**, 5330; g) Z. Yang, R. K. Kumar, P. Liao, Z. Liu, X. Li, X. Bi, *Chem. Commun.* **2016**, *52*, 5936.

[4] a) J. A. Dabrowski, F. Gao, A. H. Hoveyda, *J. Am. Chem. Soc.* **2011**, *133*, 4778; b) H. Li, A. Alexakis, *Angew. Chem.* **2012**, *124*, 1079; *Angew. Chem. Int. Ed.* **2012**, *51*, 1055; c) J. Y. Hamilton, D. Sarlah, E. M. Carreira, *Angew. Chem.* **2013**, *125*, 7680; *Angew. Chem. Int. Ed.* **2013**, *52*, 7532; d) Y. Makida, Y. Takayama, H. Ohmiya, M. Sawamura, *Angew. Chem.* **2013**, *125*, 5458; *Angew. Chem. Int. Ed.* **2013**, *52*, 5350; e) A. Harada, Y. Makida, T. Sato, H. Ohmiya, M. Sawamura, *J. Am. Chem. Soc.* **2014**, *136*, 13932; f) C. P. Grugel, B. Breit, *Org. Lett.* **2018**, *20*, 1066.

[5] a) G. W. Kabalka, Z. Wu, Y. Ju, *Org. Lett.* **2004**, *6*, 3929; b) Y. Nishimoto, M. Kajioka, T. Saito, M. Yasuda, A. Baba, *Chem. Commun.* **2008**, 6396; c) M.-L. Yao, T. R. Quick, Z. Wu, M. P. Quinn, G. W. Kabalka, *Org. Lett.* **2009**, *11*, 2647; d) S. Biswas, S. Maiti, U. Jana, *Eur. J. Org. Chem.* **2009**, 2354; e) V. J. Meyer, M. Niggemann, *Eur. J. Org. Chem.* **2011**, 3671; f) H.-L. Yue, W. Wei, M.-M. Li, Y.-R. Yang, J.-X. Ji, *Adv. Synth. Catal.* **2011**, *353*, 3139; g) S. Peng, L. Wang, J. Wang, *Org. Biomol. Chem.* **2012**, *10*, 225; h) G.-B. Huang, X. Wang, Y.-M. Pan, H.-S. Wang, G.-Y. Yao, Y. Zhang, *J. Org. Chem.* **2013**, *78*, 2742; i) F. Han, L. Yang, Z. Li, Y. Zhao, C. Xia, *Adv. Synth. Catal.* **2014**, *356*, 2506; j) D. Leboeuf, M. Presset, B. Michelet, C. Bour, S. Bezzenine-Lafoll|e, V. Gandon, *Chem. Eur. J.* **2015**, *21*, 11001; k) J. R. Cabrero-Antonino, M. Tejeda-Serrano, M. Quesada, J. A. Vidal-Moya, A. Leyva-Pérez, A. Corma, *Chem. Sci.* **2017**, *8*, 689; l) S. Yaragorla, R. Dada, A. Pareek, *Chemistry Select* **2018**, *3*, 495; m) K. Čebular, S. Stavber, *Pure Appl. Chem.* **2018**; *90*, 377.

[6] a) B. St. Onge, J. R. Green, *Synlett* **2017**, *28*, 2923; b) M. Ueda, D. Nakakoji, T. Morisaki, I. Ryu, *Eur. J. Org. Chem.* **2017**, 7040.

[7] For related alkenylation and alkylation of alcohols or their derivatives with boron compounds, see; a) Y. Kobayashi, Y. Tokoro, K. Watatani, *Eur. J. Org. Chem.* **2000**, 3825; b) G. W. Kabalka, M.-L. Yao, S. Borella, *Org. Lett.* **2006**, *8*, 879; c) Y. M. A. Yamada, S. M. Sarkar, Y. Uozumi, *J. Am. Chem. Soc.* **2012**, *134*, 3190; d) Y. Luan, S. E. Schaus, *J. Am. Chem. Soc.* **2012**, *134*, 19965; e) J. Y. Hamilton, D. Sarlah, E. M. Carreira, *J. Am. Chem. Soc.* **2013**, *135*, 994; f) H.-B. Wu, X.-T. Ma, S.-K. Tian, *Chem. Commun.* **2014**, *50*, 219; g) K. M. Fisher, Y. Bolshan, *J. Org. Chem.* **2015**, *80*, 12676; h) C. Li, Y. Zhang, Q. Sun, T. Gu, H. Peng, W. Tang, *J. Am. Chem. Soc.* **2016**, *138*, 10774; i) S. Liu, X. Zeng, G. B. Hammond, B. Xu, *Adv. Synth. Catal.* **2018**, *360*, 3667; j) D. Tian, C. Li, G. Gu, H. Peng, X. Zhang, W. Tang, *Angew. Chem.* **2018**, *130*, 7294; *Angew. Chem. Int. Ed.* **2018**, *57*, 7176.

[8] a) C. L. Cioffi, W. T. Spencer, J. J. Richards, R. J. Herr, *J. Org Chem.* **2004**, *69*, 2210; b) A. L. Korich; P. M. Iovine, *Dalton Trans.* **2010**, *39*, 1423.

[9] a) D. Nakashima, H. Yamamoto, *J. Am. Chem. Soc.* **2006**, *128*, 9626; b) P. Jiao, D. Nakashima, H. Yamamoto, *Angew. Chem.* **2008**, *1200*, 2445; *Angew. Chem. Int. Ed.* **2008**, *47*, 2411; c) A. Jolit, C. F. Dickinson, K. Kitamura, P. M. Walleser, G. P. A. Yap, M. A. Tius, *Eur. J. Org. Chem.* **2017**, 6067; d) N. Li, D.-F. Chen, P.-S. Wang, Z.-Y. Han, L.-Z. Gong, *Synthesis* **2014**, *46*, 1355.

[10] The reaction of boroxines having an alkyl group at the alkenyl terminus and triphenylboroxine resulted in no reaction.

[11] Two oxygen atoms of chiral phosphoramide catalysts are engaged in the intramolecular S_N2' cyclization, see: M. Shimizu, J. Kikuchi, A. Kondoh, M. Terada, *Chem. Sci.* **2018**, *9*, 5747.

[12] For recent examples of chiral Brønsted acid-catalyzed reactions via *para*-quinone methide-type intermediates, see: a) C. Yue, F. Na, X. Fang, Y. Cao, J. C. Antilla, *Angew. Chem.* **2018**, *130*, 11170; *Angew. Chem. Int. Ed.* **2018**, *57*, 11004; b) X.-L. Jiang, S.-F. Wu, J.-R. Wang, G.-J. Mei, F. Shi, *Adv. Synth. Catal.* **2018**, *360*, 4225; c) Z.-P. Zhang, K.-X. Xie, C. Yang, M. Li, X. Li, *J. Org. Chem.* **2018**, *83*, 364 and references cited therein

[13] The in-situ generated boronic acid might be the actual nucleophile, since the product yield decreased without loss of enantioselectivity in the

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presence of dehydrating agents such as $MgSO_4$ and MS5A (Table 1, entry 14 vs. 15).

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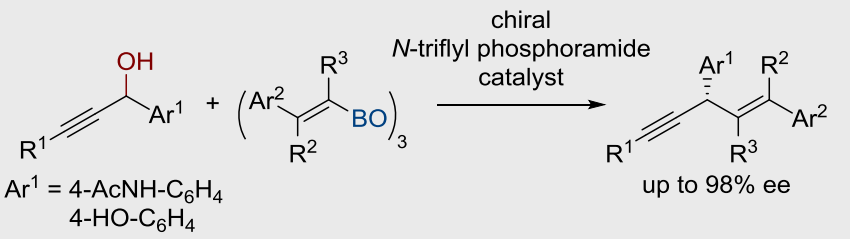

Chiral 1,4-enynes were synthesized by an organocatalytic alkenylation of propargyl alcohols with trialkenylboroxines with high enantioselectivity. A highly acidic chiral *N*-triflyl phosphoramide, which has two distant Lewis basic oxygen atoms, was identified as an effective catalyst in terms of both reactivity and selectivity.

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