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Chiral Ferrocenyl P,N-Ligands for Palladium-Catalyzed Asymmetric Formal [3 + 2] Cycloaddition of Propargylic Esters with β-Ketoesters: Access to Functionalized Chiral 2,3-Dihydrofurans

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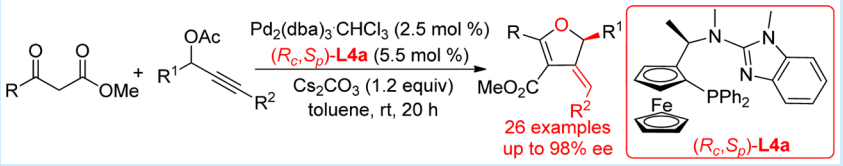
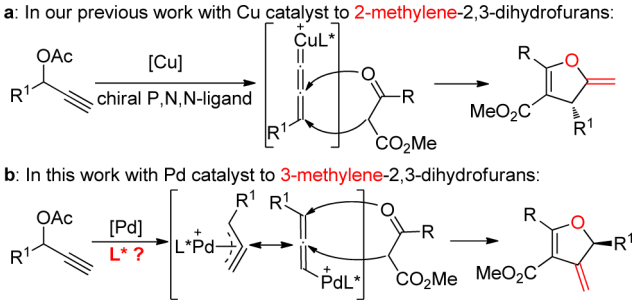
Supporting Information



ABSTRACT: A highly enantioselective palladium-catalyzed [3 + 2] cycloaddition of propargylic esters with β-ketoesters has been realized by employing a newly developed chiral ferrocene/benzimidazole-based P,N-ligand. This protocol features a good tolerance of functional groups in both propargylic esters and β-ketoesters, thereby delivering a variety of highly functionalized chiral 2,3-dihydrofurans bearing an exocyclic double bond at the 3-position in good yields and with high enantioselectivities (up to 98% ee).

2,3-Dihydrofurans are ubiquitous structural motifs in natural and synthetic products with wide-reaching biological activities, as well as useful synthetic intermediates for organic synthesis.[1] Among many approaches toward their synthesis,[2] the cycloaddition represents an attractive and powerful strategy, but catalytic asymmetric variants remain rare.[3] Recently, we discovered a Cu-catalyzed asymmetric [3 + 2] cycloaddition of propargylic esters with β-ketoesters via Cu-allenylidene intermediates, leading to highly functionalized chiral 2-methylene-2,3-dihydrofurans (Scheme 1a).[4] The success of this protocol, combined with the distinctive reaction pathway of propargylic esters with β-ketoesters observed under the catalysis of different transition metals,[5,6] encouraged us to explore a new asymmetric process to access to a complementary set of enantioenriched 2,3-dihydrofurans, in particular those with an exocyclic double bond at the 3-position that remain unavailable with the known synthetic methods.[3]

Scheme 1. Catalytic Asymmetric [3 + 2] Cycloaddition of Propargylic Esters with β-Ketoesters



In 1985, Tsuji and co-workers reported a palladium-catalyzed [3 + 2] cycloaddition of propargylic carbonates with β-ketoesters, leading to 3-alkylidene-2,3-dihydrofurans.[7] The reaction proceeds via the π-propargylpalladium or allenylpalladium intermediates, which are attacked consecutively by C- and O-nucleophilic atoms of β-ketoesters to give the cyclization product bearing an exocyclic double bond at the 3-position (Scheme 1b). Since this pioneering work, there have been several other studies of palladium-catalyzed cyclization of propargylic esters with bis-nucleophiles for the construction of structurally diverse carbo- and heterocyclic frameworks.[8] However, the stereochemistry of this methodology is rarely investigated,[9] and none has explored the possibility of accessing 3-alkylidene-2,3-dihydrofurans with control of the absolute stereochemistry. Given that the desired reactivity had been demonstrated, we believe that an appropriate chiral ligand would render this palladium-catalyzed asymmetric [3 + 2] cyclization enantioselective. However, the initial screening of the reaction with BINAP (**L1**), Trost's ligand (**L2**), and PHOX (**L3**), the privileged ligands for palladium-catalyzed asymmetric allylic transformation,[10] led to really disappointing performance (Table 1, entries 1−3), which clearly expresses the methodological difficulties. By the discovery of a novel chiral ferrocene/benzimidazole-based P,N-ligand, herein we described the first highly enantioselective palladium-catalyzed [3 + 2] cyclo-

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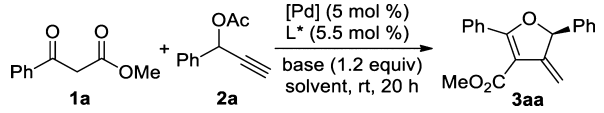
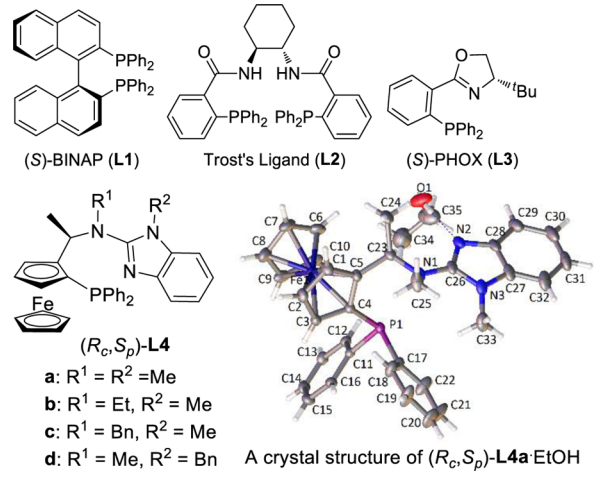
Table 1. Optimization of the Reaction Conditions[a]



entry	[Pd]	L*	base	yield (%)[b]	ee (%)[c]
1	$Pd_2(dba)_3{\cdot}CHCl_3$	**L1**	K_3PO_4	92	<10
2	$Pd_2(dba)_3{\cdot}CHCl_3$	**L2**	K_3PO_4	–	–
3	$Pd_2(dba)_3{\cdot}CHCl_3$	**L3**	K_3PO_4	–	–
4	$Pd_2(dba)_3{\cdot}CHCl_3$	**L4a**	K_3PO_4	78	97
5	$Pd_2(dba)_3{\cdot}CHCl_3$	**L4b**	K_3PO_4	75	96
6	$Pd_2(dba)_3{\cdot}CHCl_3$	**L4c**	K_3PO_4	75	92
7	$Pd_2(dba)_3{\cdot}CHCl_3$	**L4d**	K_3PO_4	73	89
8	$Pd(PPh_3)_4$	**L4a**	K_3PO_4	75	69
9	$Pd(OAc)_2$	**L4a**	K_3PO_4	54	93
10	$Pd_2(dba)_3{\cdot}CHCl_3$	**L4a**	none	–	–
11	$Pd_2(dba)_3{\cdot}CHCl_3$	**L4a**	Et_3N	–	–
12	$Pd_2(dba)_3{\cdot}CHCl_3$	**L4a**	^tBuOK	85	95
13	$Pd_2(dba)_3{\cdot}CHCl_3$	**L4a**	Cs_2CO_3	91	95
14[d]	$Pd_2(dba)_3{\cdot}CHCl_3$	**L4a**	Cs_2CO_3	86	95
15[e]	$Pd_2(dba)_3{\cdot}CHCl_3$	**L4a**	Cs_2CO_3	92	97

[a]The reaction was carried out using **1a** (0.3 mmol), **2a** (0.33 mmol), [Pd] (0.015 mmol, 5 mol %), **L*** (0.0165 mmol, 5.5 mol %), base (0.36 mmol, 1.2 equiv) in 3 mL of CH_2Cl_2 at room temperature for 20 h unless otherwise noted. [b]Yield of isolated product. [c]Determined by chiral HPLC. [d]The reaction solvent: DMSO. [e]The reaction solvent: toluene.

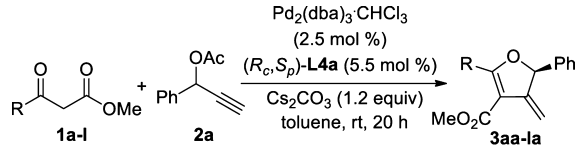


addition of propargylic esters with β-ketoesters, which generated highly functionalized chiral 3-alkylidene-2,3-dihydrofurans in good chemical yields and with high enantioselectivities (up to 98% ee).

Our recent study disclosed that the presence of the additional N-atoms in chiral P,N-ligands could significantly promote the reaction performance in the Pd-catalyzed asymmetric transformations,[11] which stimulated us to develop a series of novel and readily available chiral ferrocene/benzimidazole-based P,N-ligands for this cycloaddition.[12] The results in Table 1 disclosed that this newly developed P,N-ligand class was indeed efficient to this palladium-catalyzed cycloaddition, with ligand **L4a** giving the desired cycloadduct **3aa** in 78% yield and with up to 97% ee (entry 4), significantly superior to those previously studied ligands **L1**–**L3** (entries 1–3). Further modification of the ligand structure did not lead to improvements in the reaction performance (entries 5–7). We then focused our efforts on the optimization of the reaction conditions in order to further improve the reaction performance. The catalyst precursor exerted a large influence on the reaction performance. Thus, the use of $Pd(PPh_3)_4$ and $Pd(OAc)_2$ led to the decrease in both the yield and enantioselectivity (entries 8 and 9). The base additive proved to be crucial to the reaction since no reaction was observed in its absence (entry 10). The variation of base showed an obvious effect on the reaction rate and stereoselectivity. Thus, no cycloadduct **3aa** was detected by the use of Et_3N (entry 11), whereas the use of ^tBuOK or Cs_2CO_3 significantly improved the yields of the reaction (entries 12 and 13). The nature of the solvent showed little influence on both the yield and enantioselectivity, and all of the solvents tested showed excellent performance (entries 13–15), with toluene to be the optimal in terms of yield and enantioselectivity (entry 15).

With the optimal reaction conditions in hand, we then carried out the investigation on the substrate scope of β-ketoesters **1** by cycloaddition with **2a**, and the results are summarized in Table 2. The reaction well tolerated both

Table 2. Substrate Scope of β-Ketoesters[a]



entry	**1** (R)	**3**	yield (%)[b]	ee (%)[c]
1	**1b** (4-MeC_6H_4)	**3ba**	88	98
2	**1c** (4-$MeOC_6H_4$)	**3ca**	80	98
3	**1d** (4-FC_6H_4)	**3da**	91	97
4	**1e** (4-BrC_6H_4)	**3ea**	85	97
5	**1f** (4-ClC_6H_4)	**3fa**	87	97
6	**1g** (3-ClC_6H_4)	**3ga**	93	96
7[d]	**1h** (2-ClC_6H_4)	**3ha**	72	95
8	**1i** (2-naphthyl)	**3ia**	91	96
9	**1j** (2-thienyl)	**3ja**	88	97
10	**1k** (Me)	**3ka**	76	91
11	**1l** (Bn)	**3la**	70	96

[a]The reaction was carried out using **1** (0.3 mmol), **2a** (0.33 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (0.0075 mmol, 2.5 mol %), (R_c,S_p)-**L4a** (0.0165 mmol, 5.5 mol %), Cs_2CO_3 (0.36 mmol, 1.2 equiv) in 3 mL of toluene in a Schlenk tube at room temperature for 20 h. [b]Yield of isolated product. [c]Determined by chiral HPLC. [d]The reaction was performed at 50 °C.

electron-donating and -withdrawing groups at the *para*-position of the phenyl ring of β-ketoesters and gave the corresponding 2,3-dihydrofurans in high yields and with excellent enantioselectivities (entries 1–5). However, the substitution pattern of functionality on the phenyl ring showed a significant influence on the reactivity. Thus, both 4- and 3-Cl substituted β-ketoesters **1f** and **1g** gave the desired cycloadducts **3fa** and **3ga** in good yields and with high enantioselectivities (Table 2, entries 5 and 6), while no reaction was detected with the substrate **1h** bearing a 2-Cl substituent under the same reaction conditions presumably due to the steric hindrance. Fortunately, the substrate **1h** could be smoothly converted into the corresponding cycloadduct **3ha** in 72% yield and with an ee-value of 95% when the reaction was performed at 50 °C (entry 7). 2-Naphthyl-substituted substrate **1i** turned out to be a suitable reaction partner, giving the cycloadduct **3ia** in 91% yield and with 96% ee (entry 8). Heteroaromatic substrate **1j**

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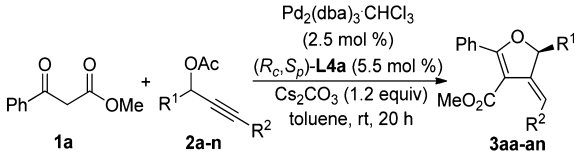
also worked well, providing the cycloadduct **3ja** in 88% yield and with 97% ee (entry 9). Remarkably, aliphatic β-ketoesters were well tolerated in this process, providing the corresponding cycloadducts **3ka** and **3la** in slightly decreased yields and with high enantioselectivities (entries 10 and 11).

Having investigated the scope of β-ketoesters, we next examined the scope of this catalytic asymmetric [3 + 2] cycloaddition with regard to propargylic esters. The results in Table 3 indicated that a series of aromatic propargylic esters

Table 3. Substrate Scope of Propargylic Esters[a]



entry	2 (R^1, R^2)	3	yield (%)[b]	ee (%)[c]
1	**2b** (4-MeC_6H_4, H)	**3ab**	94	97
2	**2c** (4-$MeOC_6H_4$, H)	**3ac**	93	96
3	**2d** (4-$CF_3C_6H_4$, H)	**3ad**	82	96
4	**2e** (4-FC_6H_4, H)	**3ae**	93	97
5	**2f** (4-BrC_6H_4, H)	**3af**	91	95
6	**2g** (4-ClC_6H_4, H)	**3ag**	88	96
7	**2h** (3-ClC_6H_4, H)	**3ah**	88	97
8	**2i** (2-ClC_6H_4, H)	**3ai**	70	98
9	**2j** (2-naphthyl, H)	**3aj**	86	95
10	**2k** (2-thienyl, H)	**3ak**	87	83
11[d]	**2l** (Me, H)	**3al**	85	56
12[d]	**2m** (Ph, Ph)	**3am**	88	89[e]
13[d]	**2n** (Ph, ^{n}Bu)	**3an**	82	95[f]
14[d]	**2o** (Bn, ^{n}Bu)	**3ao**	–	–

[a]The reaction was carried out using **1a** (0.3 mmol), **2** (0.33 mmol), $Pd_2(dba)_3$·$CHCl_3$ (0.0075 mmol, 2.5 mol %), (R_c,S_p)-**L4a** (0.0165 mmol, 5.5 mol %), Cs_2CO_3 (0.36 mmol, 1.2 equiv) in 3 mL of toluene in a Schlenk tube at room temperature for 20 h. [b]Yield of isolated product. [c]Determined by chiral HPLC. [d]The reaction was performed at 50 °C for 20 h by use of carbonates instead of acetates. [e]>95/5 E/Z ratio was determined by ^{1}H NMR. [f]92/8 E/Z ratio was determined by ^{1}H NMR.

could be utilized to give 2,3-dihydrofurans in high yields and excellent enantioselectivities, irrespective of the electronic property and position of the functionality (entries 1−9). The use of a heteroaromatic substrate (**2k**) led to a decrease in the enantioselectivity to 83% ee (entry 10). However, the reaction did not well tolerate aliphatic and internal propargylic acetates, giving very low conversion. In these cases, the use of carbonates instead of the corresponding acetates at an elevated reaction temperature (50 °C) was required (entries 11−13). For aromatic internal propargylic ester **2m**, the reaction exclusively gave rise to the cycloadduct **3am** bearing an E-exocyclic double bond in 88% yield and with 89% ee (entry 12). As for aliphatic internal propargylic ester **2n**, minimal erosion of the product ratio (E/Z = 92/8) but an improved enantioselectivity (95% ee) for E-isomer was observed (entry 13). However, the aliphatic internal propargylic ester **2o** (R^1 = Bn, R^2 = ^{n}Bu) gave only very low conversion (entry 14). For the reaction between two aliphatic substrates **1k** and **2l**, a mixture of 2,3-dihydrofuran and its furan isomer was obtained. The absolute configuration of the cycloadduct was unambiguously determined by X-ray structure analysis of **3ej**, to which an S-configuration was assigned.[13]

Based on the results, a plausible mechanism is proposed to explain the observed stereochemistry (Figure 1). The square-

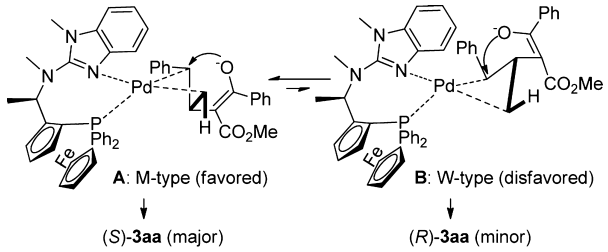
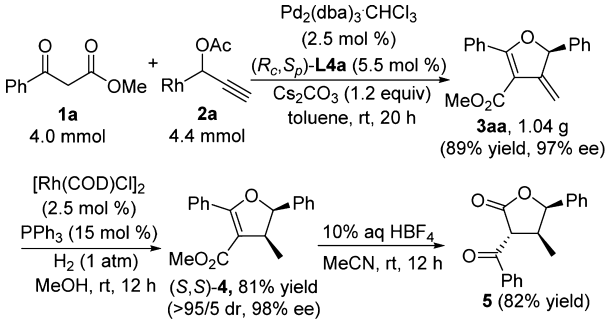


Figure 1. Proposed transition state for stereochemistry.

planar Pd-allyl intermediates give two possible orientations: M-type and W-type, in which the M-type (**A**) is favored due to the steric hindrance. The regioselective attack at the more congested π-allyl terminus according to the report by Larock[14] and the *trans*-effect[15] gives (*S*)-**3aa** as the major cycloadduct.

The practicality of the current methodology was demonstrated by a gram-scale synthesis, followed by the transformation of the cycloadduct **3aa** into the lactone **5**[16] (Scheme 2). The initial hydrogenation of **3aa** predominantly generated

Scheme 2. Synthetic Application



the *cis*-diastereoisomer (*S*,*S*)-**4** on the basis of the NOE experiment[13] without any loss in enantioselectivity. (*S*,*S*)-**4** was then converted into the corresponding lactone **5** by the formation of a new *S*-stereogeneric center based on the NOE experiment.[13]

In conclusion, we have developed a highly enantioselective palladium-catalyzed [3 + 2] cycloaddition of propargylic esters with β-ketoesters, a process for the generation of highly functionalized chiral 2,3-dihydrofurans bearing an exocyclic double bond at the 3-position that remain unavailable with the known synthetic methods. The key to achieving high enantioselectivity of the reaction is the use of a new and readily available chiral ferrocene/benzimidazole-based P,N-ligand. The reaction tolerates a variety of substitution patterns in both reaction partners. In particular, internal propargylic esters also were found to be suitable substrates for this cycloaddition. Due to the generality of the method and mild conditions employed, we believe this method will see considerable use in both academic and industrial settings.

■ ASSOCIATED CONTENT

Supporting Information

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Experimental procedures and characterization data for all new compounds (PDF)
X-ray crystallographic data for **L4a** (CIF)
X-ray crystallographic data for (*S*)-**3ej** (CIF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) (a) Lipshutz, B. H. *Chem. Rev.* **1986**, *86*, 795. (b) Merritt, A. T.; Ley, S. B. *Nat. Prod. Rep.* **1992**, *9*, 243. (c) Fraga, B. M. *Nat. Prod. Rep.* **1992**, *9*, 217. (d) Faul, M. M.; Huff, B. E. *Chem. Rev.* **2000**, *100*, 2407. (e) Elliott, M. C. *J. Chem. Soc., Perkin Trans. I* **2002**, 2301. (f) Hou, X.-L.; Yang, Z.; Yeung, K.-S.; Wong, H. N. C. *Prog. Heterocycl. Chem.* **2005**, *17*, 142. (g) Pettigrew, J. D.; Wilson, P. D. *Org. Lett.* **2006**, *8*, 1427.

(2) For selected recent examples, see: (a) Gais, H. J.; Reddy, L. R.; Babu, G. S.; Raabe, G. *J. Am. Chem. Soc.* **2004**, *126*, 4859. (b) Caliskan, R.; Pekel, T.; Watson, W. H.; Balci, M. *Tetrahedron Lett.* **2005**, *46*, 6227. (c) Bernard, A. M.; Frongia, A.; Piras, P. P.; Secci, F.; Spiga, M. *Org. Lett.* **2005**, *7*, 4565. (d) Xia, W.; Yang, C.; Patrick, B. O.; Scheffer, J. R.; Scott, C. *J. Am. Chem. Soc.* **2005**, *127*, 2725. (e) Bowman, R. K.; Johnson, J. S. *Org. Lett.* **2006**, *8*, 573. (f) Zhang, R.; Liang, Y.; Zhou, G.; Wang, K.; Dong, D. *J. Org. Chem.* **2008**, *73*, 8089. (g) Zheng, J.-C.; Zhu, C.-Y.; Sun, X.-L.; Tang, Y.; Dai, L.-X. *J. Org. Chem.* **2008**, *73*, 6909. (h) Chen, Z.; Zhang, J. *Chem. - Asian J.* **2010**, *5*, 1542. (i) Li, M.; Lin, S.; Dong, Z.; Zhang, X.; Liang, F.; Zhang, J. *Org. Lett.* **2013**, *15*, 3978. (j) Xia, L.; Lee, Y. R. *Adv. Synth. Catal.* **2013**, *355*, 2361.

(3) For organocatalytic Feist−Bènary reactions to form chiral 2,3-dihydrofurans, see: (a) Calter, M. A.; Phillips, R. M.; Flaschenriem, C. *J. Am. Chem. Soc.* **2005**, *127*, 14566. (b) Fan, L.-P.; Li, P.; Li, X.-S.; Xu, D.-C.; Ge, M.-M.; Zhu, W.-D.; Xie, J.-W. *J. Org. Chem.* **2010**, *75*, 8716. (c) Rueping, M.; Parra, A.; Uria, U.; Besselièvre, F.; Merino, E. *Org. Lett.* **2010**, *12*, 5680. (d) Dou, X.; Zhong, F.; Lu, Y. *Chem. - Eur. J.* **2012**, *18*, 13945. For catalytic asymmetric cycloaddition of diazo compounds, see: (e) Davies, H. M. L.; Ahmed, G.; Calvo, R. L.; Churchill, M. R. *J. Org. Chem.* **1998**, *63*, 2641. (f) Son, S.; Fu, G. C. *J. Am. Chem. Soc.* **2007**, *129*, 1046. (g) Zhou, J.-L.; Wang, L.-J.; Xu, H.; Sun, X.-L.; Tang, Y. *ACS Catal.* **2013**, *3*, 685. For Cu-catalyzed asymmetric [3 + 2] cycloaddition of propargylic esters with *β*-naphthol, see: (h) Shao, L.; Wang, Y.-H.; Zhang, D.-Y.; Xu, J.; Hu, X.-P. *Angew. Chem., Int. Ed.* **2016**, *55*, 5014. For other methods, see: (i) Ozawa, F.; Kubo, A.; Matsumoto, Y.; Hayashi, T. *Organometallics* **1993**, *12*, 4188. (j) Evans, D. A.; Sweeney, Z. K.; Rovis, T.; Tedrow, J. S. *J. Am. Chem. Soc.* **2001**, *123*, 12095. (k) Sinha, D.; Biswas, A.; Singh, V. K. *Org. Lett.* **2015**, *17*, 3302.

(4) Zhu, F.-L.; Wang, Y.-H.; Zhang, D.-Y.; Xu, J.; Hu, X.-P. *Angew. Chem., Int. Ed.* **2014**, *53*, 10223.

(5) For reviews on the catalytic transformation of propargylic derivatives, see: (a) Marion, N.; Nolan, S. P. *Angew. Chem., Int. Ed.* **2007**, *46*, 2750. (b) Marco-Contelles, J.; Soriano, E. *Chem. - Eur. J.* **2007**, *13*, 1350. (c) Ljungdahl, N.; Kann, N. *Angew. Chem., Int. Ed.* **2009**, *48*, 642. (d) Miyake, Y.; Uemura, S.; Nishibayashi, Y. *ChemCatChem* **2009**, *1*, 342. (e) Detz, R. J.; Hiemstra, H.; van Maarseveen, J. H. *Eur. J. Org. Chem.* **2009**, *2009*, 6263. (f) Ding, C.-H.; Hou, X.-L. *Chem. Rev.* **2011**, *111*, 1914. (g) Debleds, O.; Gayon, E.; Vrancken, E.; Campagne, J.-M. *Beilstein J. Org. Chem.* **2011**, *7*, 866. (h) Nishibayashi, Y. *Synthesis* **2012**, *2012*, 489. (i) Bauer, E. B. *Synthesis* **2012**, *44*, 1131. (j) Wen, J.-J.; Zhu, Y.; Zhan, Z.-P. *Asian J. Org. Chem.* **2012**, *1*, 108. (k) Reddy, C. R.; Ranjan, R.; Kumaraswamy, P.; Reddy, M. D.; Grée, R. *Curr. Org. Chem.* **2014**, *18*, 2603. (l) Zhang, D.-Y.; Hu, X.-P. *Tetrahedron Lett.* **2015**, *56*, 283.

(6) For examples on the catalytic asymmetric propargylic substitution with *β*-ketoesters, see: (a) Ikeda, M.; Miyake, Y.; Nishibayashi, Y. *Chem. - Eur. J.* **2012**, *18*, 3321. (b) Han, H.-Z.; Zhu, F.-L.; Wang, Y.-H.; Zou, Y.; Hu, X.-H.; Chen, S.; Hu, X.-P. *Org. Lett.* **2014**, *16*, 588. (c) Zhao, L.; Huang, G.; Guo, B.; Xu, L.; Chen, J.; Cao, W.; Zhao, G.; Wu, X. *Org. Lett.* **2014**, *16*, 5584. (d) Zhu, F.-L.; Zou, Y.; Zhang, D.-Y.; Wang, Y.-H.; Hu, X.-H.; Chen, S.; Xu, J.; Hu, X.-P. *Angew. Chem., Int. Ed.* **2014**, *53*, 1410. (e) Zhu, F.-L.; Wang, Y.-H.; Zhang, D.-Y.; Hu, X.-H.; Chen, S.; Hou, C.-J.; Xu, J.; Hu, X.-P. *Adv. Synth. Catal.* **2014**, *356*, 3231. (f) Huang, G.; Cheng, C.; Ge, L.; Guo, B.; Zhao, L.; Wu, X. *Org. Lett.* **2015**, *17*, 4894. For selected examples on the catalytic propargylic cycloaddition with *β*-ketoesters towards furan and pyrrole derivatives, see: (g) Cadierno, V.; Gimeno, J.; Nebra, N. *Chem. - Eur. J.* **2007**, *13*, 9973. (h) Cadierno, V.; Gimeno, J.; Nebra, N. *Adv. Synth. Catal.* **2007**, *349*, 382. (i) Liu, X.-T.; Huang, L.; Zheng, F.-J.; Zhan, Z.-P. *Adv. Synth. Catal.* **2008**, *350*, 2778. (j) Pan, Y.-M.; Zhao, S.-Y.; Ji, W.-H.; Zhan, Z.-P. *J. Comb. Chem.* **2009**, *11*, 103. (k) Yoshida, M.; Higuchi, M.; Shishido, K. *Tetrahedron* **2010**, *66*, 2675. (l) Yoshida, M.; Ohno, S.; Shishido, K. *Chem. - Eur. J.* **2012**, *18*, 1604. (m) Gujarathi, S.; Liu, X.; Song, L.; Hendrickson, H.; Zheng, G. *Tetrahedron* **2014**, *70*, 5267.

(7) (a) Tsuji, J.; Watanabe, I.; Minami, I.; Shimizu, I. *J. Am. Chem. Soc.* **1985**, *107*, 2196. (b) Minami, I.; Yuhara, M.; Watanabe, I.; Tsuji, J. *J. Organomet. Chem.* **1987**, *334*, 225.

(8) For reviews, see: (a) Tsuji, J.; Mandai, T. *Angew. Chem., Int. Ed. Engl.* **1996**, *34*, 2589. (b) Guo, L.-N.; Duan, X.-H.; Liang, Y.-M. *Acc. Chem. Res.* **2011**, *44*, 111. (c) Yoshida, M. *Chem. Pharm. Bull.* **2012**, *60*, 285. (d) Yoshida, M. *Heterocycles* **2013**, *87*, 1835. (e) Ye, J.; Ma, S. *Acc. Chem. Res.* **2014**, *47*, 989.

(9) For a review, see: (a) Hu, X.-H.; Liu, Z.-T.; Shao, L.; Hu, X.-P. *Synthesis* **2015**, *47*, 913. For examples, see: (b) Labrosse, J.-R.; Lhoste, P.; Sinou, D. *Org. Lett.* **2000**, *2*, 527. (c) Damez, C.; Labrosse, J.-R.; Lhoste, P.; Sinou, D. *Tetrahedron Lett.* **2003**, *44*, 557. (d) Yoshida, M.; Higuchi, M.; Shishido, K. *Org. Lett.* **2009**, *11*, 4752.

(10) (a) *Priviledged Chiral Ligands and Catalysts*; Zhou, Q.-L., Ed.; Wiley-VCH: Weinheim, Germany, 2011. (b) Helmchen, G.; Pfaltz, A. *Acc. Chem. Res.* **2000**, *33*, 336. (c) Trost, B. M.; Machacek, M. R.; Aponick, A. *Acc. Chem. Res.* **2006**, *39*, 747.

(11) Hu, X.-P.; Chen, H.-L.; Zheng, Z. *Adv. Synth. Catal.* **2005**, *347*, 541.

(12) For synthetic procedure for **L4**, see the Supporting Information.

(13) For details, see the Supporting Information.

(14) Larock, R. C.; Berrios-Peña, N. G.; Fried, C. A. *J. Org. Chem.* **1991**, *56*, 2615.

(15) Murray, S.; Hartley, F. *Chem. Rev.* **1981**, *81*, 365.

(16) Punirun, T.; Soorukram, D.; Kuhakarn, C.; Reutrakul, V.; Pohmakotr, M. *J. Org. Chem.* **2015**, *80*, 7946.

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