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Hydroalkynylative cyclization of 1,6-enynes with terminal alkynes†

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A rhodium-catalyzed highly regio- and enantioselective hydroalkynylation, generating *cis*-hydrobenzofuranone-tethered enynes has been developed. The reaction proceeds with a selective head-to-head insertion and symmetry breaking Michael addition cascade. One product was produced from tens of possible isomers through precise control of chemo-, regio-, and stereoselectivities using a single rhodium catalyst. Notable features of this method include 100% atom-economy, mild reaction conditions and a very broad substrate scope.

Introduction

Conjugated enynes are a type of privileged structure distributed in a number of natural products[1] and luminescent materials.[2] They are also very important building blocks widely used in organic synthesis.[3] The most attractive and atom-economic pathway to conjugated enynes is the transition-metal catalyzed direct addition of a terminal alkyne C–H bond to a second alkyne moiety.[4,5] Generally the acceptor alkynes are electron-deficient internal alkynes.[4] Hydroalkynylation[6] of a second terminal alkyne, also termed cross-dimerization of two different terminal alkynes is more challenging. This reaction could in principal produce six possible cross-dimerization products and six homodimerization side products (Scheme 1a). Ideally, the metal catalyst should selectively produce one isomer from 12 similar isomers, and consequently very few examples have been reported.[5] Taking advantage of the steric and electronic differences of two alkynes, so controlling chemo- and regioselectivity is a possible solution. For instance, silyl alkynes were usually chosen to couple with aryl or aliphatic alkynes to give different products depending on the choice of catalyst.[5d,e] However, in all these reactions, undesired isomers were always produced together with the major product.[5] Consequently, the development of a new synthetically useful strategy to realize selective cross-hydroalkynylation reactions to access conjugated enynes[7] is important.

Generally, a metal acetylide complex was selectively formed, and subsequent *syn* insertion into the other triple bond usually

led to two different alkenyl metal intermediates because both head-to-head and head-to-tail insertion are possible.

Completely selective formation of one intermediate over another similar intermediate is generally unlikely and most reactions reported always led to one major product together with other isomers as minor products.[5] When aryl alkynes were reacted with propargyl alcohol, head-to-head dimers were obtained as a major product in the presence of a palladium
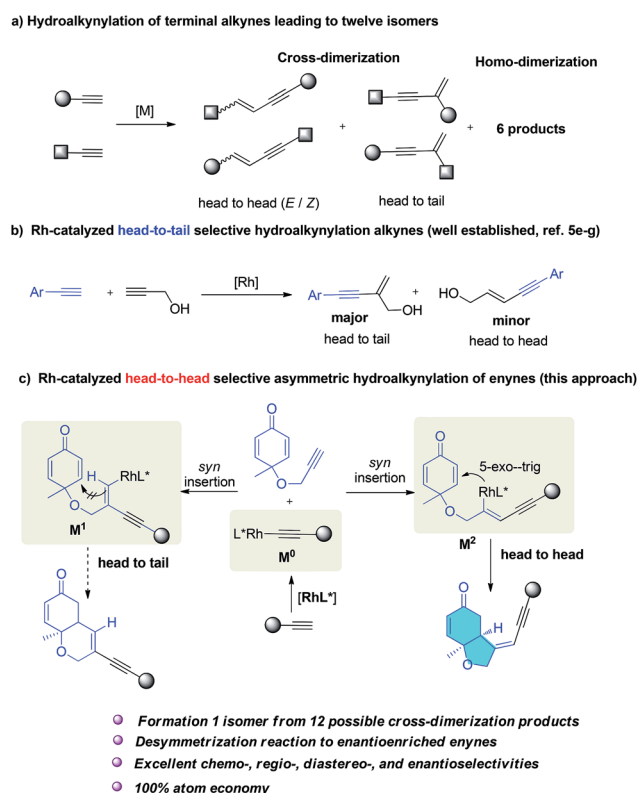
Scheme 1 Rh-catalyzed cross-hydroalkynylation of terminal alkynes.

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catalyst,[5c,j] but when rhodium catalyst was employed, head-to-tail dimers were obtained as a major product, together with some head-to-head isomers as byproducts (Scheme 1b).[5e–g] Herein, we report the first Rh-catalyzed asymmetric cross-hydroalkynylation of 1,6-enynes *via* a selective head-to-head insertion and symmetry breaking Michael addition cascade. As illustrated in Scheme 1c, rhodium acetylide (M^0) was selectively formed from a terminal alkyne and its subsequent *syn* addition to the alkyne moiety of enynes could generate two vinyl rhodium intermediates (M^1, M^2). M^2 can undergo a fast 5-*exo*-trig cyclization to form the final bicyclic products. However, M^1 bearing a *trans* C–Rh bond cannot undergo the Michael addition to form stabilized ring products. A possible E/Z isomerization[8] of M^1 might generate a *cis* C–Rh bond which could undergo Michael addition, but this will involve a much higher activation energy. Consequently, the formation of M^2 would be preferred, delivering the head-to-head products selectively. More importantly, when a chiral phosphine ligand was applied, enantioenriched enynes bearing an important chiral *cis*-hydrobenzofuran moiety were obtained. This is a unique scaffold present in many bioactive natural products including incarviditone,[9a] iso-ambrox[9b] haterumaimide I,[9c] and milling-tonine A.[9d] To date, no examples of synthesis of chiral enynes by asymmetric cross-hydroalkynylation process have been reported.

Results and discussion

A cyclohexadienone tethered terminal alkyne (**1a**) was selected as one partner in this reaction, because this prochiral electron-deficient diene is an excellent Michael acceptor with which to build chiral *cis*-hydrobenzofuranones by organo- or transition-metal-catalyzed desymmetrization reactions.[10,11] The aromatic alkyne (**2a**), bearing an alkyne proton which is more acidic than that in aliphatic alkynes,[12] was chosen as the second partner to react with the enyne (**1a**) in the presence of a rhodium catalyst. The rhodium catalyst might react with **2a** to form phenyl-ethynyl rhodium, and upon subsequent hydroalkynylation of **1a**, deliver the cyclization products. To test this hypothesis, the reaction was performed in dichloroethane (DCE) at rt overnight in the presence of 5 mol% of [Rh(COD)Cl]₂ and 10 mol% of *S*-BINAP. The desired head-to-head bicyclo[4.3.0] product (**3a**) was obtained in 72% isolated yield as a single diastereomer, and no head-to-tail bicyclo[4.4.0] product was observed in the reaction (Table 1, entry 1). These results are contrary to previous rhodium-catalyzed reactions which give head-to-tail structures as major products[5e–g] (Scheme 1b) and indicate the viability of the proposed reaction shown in Scheme 1c. In addition, HPLC analysis shows that the enantioselectivity of this reaction is as high as 94% ee.

Next, we sought to optimize the reaction conditions, obtaining the results shown in Table 1. We first examined various diphosphine ligands (entries 1–6). Increasing the steric hindrance of the phosphine substituents led to lower enantio-selectivities (entries 2 and 3). Biphenyl ligands such as SEGPHOS (**L4**) and MeO-BIPHEP (**L5**) gave almost quantitative yields but lower enantioselectivity (entries 4 and 5). When DIOP (**L6**) was employed, the highest 98% ee was obtained but with much lower

Table 1 Optimization of reaction conditions[a]

Entry	Catalyst	Ligand	Solvent	Yield[b]/%	ee[c]/%
1	[Rh(cod)Cl]₂	**L1**	DCE	72	94
2	[Rh(cod)Cl]₂	**L2**	DCE	94	79
3	[Rh(cod)Cl]₂	**L3**	DCE	50	83
4	[Rh(cod)Cl]₂	**L4**	DCE	98	77
5	[Rh(cod)Cl]₂	**L5**	DCE	99	88
6	[Rh(cod)Cl]₂	**L6**	DCE	48	98
7	[Rh(cod)Cl]₂	**L1**	MeOH	62	99
8	[Rh(cod)Cl]₂	**L1**	THF	0	—
9	[Rh(cod)Cl]₂	**L1**	DMF	Trace	—
10	[Rh(cod)Cl]₂	**L1**	Toluene	59	92
11	[Rh(cod)Cl]₂	**L1**	DCE : MeOH = 3 : 1	81	98
12	[Rh(cod)Cl]₂	**L1**	DCE : MeOH = 1 : 1	66	97
13[d]	**[Rh(cod)Cl]₂**	**L1**	**DCE : MeOH = 3 : 1**	**92**	**99**
14	[Rh(cp*)Cl₂]₂	**L1**	DCE	0	—
15	NiCl₂·6H₂O	**L1**	DCE	0	—
16	Ni(acac)₂	**L1**	DCE	0	—

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), catalyst (5 mol%), and ligand (10 mol%), solvent (2 mL), rt. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase. [d] **1a** (0.2 mmol), **2a** (0.4 mmol), [Rh(cod)Cl]₂ (2.5 mol%), and **L1** (5 mol%).

yield (entry 6). The solvent effect was then investigated (entries 7–12). The reaction in MeOH was much more rapid, leading to 99% ee but lower isolated yield (62%, entry 7). We observed that when DCE was added to the MeOH solvent, a higher reaction yield was obtained without any obvious decrease in enantiose-lectivity (entries 11 and 12). Increasing the concentration of substrates and lowering the catalyst loading to 5 mol% in the mixed solvent (DCE : MeOH = 3 : 1) led to 92% isolated yield and 99% ee, and represents the optimal conditions (entry 13). When the Rh(I) catalyst was replaced by a Rh(III) catalyst (entry 14) or nickel catalysts (entries 15 and 16), no product was formed. Under the optimized conditions, this atom-economic reaction produces chiral hydrobenzofuranone-tethered enynes in high yield with extremely high enantioselectivity. Notably, the rhodium catalyst produced a single product from tens of possible products counting two new chiral centers by precise control of the chemo-, regio-, diastereo-, and enantioselectivities. Such reactions are very rare in organic synthesis.
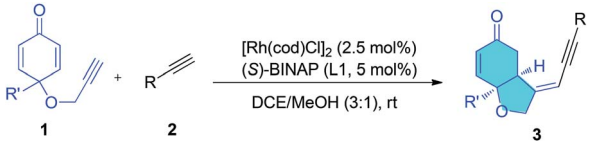
Having established the optimal conditions for this asymmetric enyne hydroalkynylation reaction, the scope of terminal alkynes was investigated. As shown in Table 2, various aromatic terminal alkynes reacted with enyne **1a** under the optimized conditions, and the corresponding head-to-head hydroalkynylation products (**3a–3q**) were produced in good yields (50–97%) and excellent enantioselectivity (92% to >99% ee). Various electron-withdrawing or electron-donating functional groups at the *para*, *ortho*, or *meta*- positions do not affect this reaction (entries 1–11). Electron-donating groups generally favor the reaction and electron-withdrawing groups lead to slightly lower yields. Functional groups such as alkoxyl (**3c**), halogens (**3d–3f**), CF₃ (**3c**), and even an unprotected hydroxyl group (**3i, 3j**) are all tolerated. In the case of **2j**, the 2-hydroxymethyl group led to decreased enantioselectivity (92% ee), but when the hydroxyl group was protected, 99% ee was obtained (entries 10 and 11). Terminal alkynes containing heterocycles, including indole and thiophene also reacted smoothly under the standard

conditions, delivering corresponding enantioenriched enynes in good yields and with 96–99% ee (entries 14–16). Remarkably, the ferrocene-derived alkyne (**2q**) was also suitable for this reaction and gave the cyclization product (**3q**) in 80% yield and with over 99% ee (entry 17). Two single crystals of products **3m** and **3p** were grown to confirm their structures and stereochemistry. The absolute configuration of these two products were established as *S* and *S* by X-ray crystallography (Scheme 2).

Selective cross-dimerization of two aliphatic alkynes is more challenging and is unprecedented. The cyclopropyl alkyne (**2r**) and cyclohexenyl alkyne (**2u**) react equally well under these conditions and give the corresponding bicyclic products (**3r, 3u**) in excellent yields (89% and 96%) and enantioselectivity (>99% ee), (entries 18 and 21). Simple linear aliphatic alkynes (**2s, 2t**) were converted to the corresponding bicyclic enynes in acceptable yields with excellent enantioselectivities (99% and 98% ee), (entries 19 and 20). The scope of the enynes was also studied. Enynes containing aliphatic groups such as ethyl or the bulkier isopropyl, and a phenyl group at the prochiral quaternary carbon center all reacted smoothly to give the corresponding desymmetrization products in excellent yields and enantioselectivities (entries 22–25). The nitrogen bridged enyne (**1e**) was also amenable to this transformation, giving the nitrogen heterocycle (**4**) in 94% yield and 98% ee (eqn (1)).

In a large scale reaction, 1.14 g of **3a** was isolated in 86% yield and 99% ee with low catalyst loading, demonstrating the remarkable practicality of this method (eqn (2)). Further synthetic transformations of the bicyclic enynes were explored (Scheme 3). Selective reduction of the ketone group by NaBH₄ afforded an allyl alcohol (**5**) in 93% yield with 98% ee. Pd/C-catalyzed hydrogenation of **3a** with a balloon of H₂ led to complete hydrogenation of the enyne moiety in the side chain and enone affording ketone (**6**) in 95% yield. Conjugated borylation of **3a** with B₂Pin₂ in the presence of CuI gave the borate (**7**) in 72% yield and 99% ee. The silyl enol ether (**8**) was prepared to undergo a gold-catalyzed intramolecular Conia-ene reaction, the addition of enol ether to alkyne moiety to yield cyclized products, but the desired tricyclic product was not formed, and instead, a phenol tethered enyne (**9**) was produced in 85% yield through an aromatized C–O bond cleavage. It should be noted that formally, this is a *meta*-functionalization reaction of phenol, which is very difficult to achieve by known methods.

**Table 2** Substrate scope of alkene trifluoromethylthiosulfonylation reactions[a]

Entry	1 (R')	2 (R)	3	Yield[b]/%	ee[c]/%
1	**1a** (Me)	**2a** (C₆H₅)	**3a**	92	99
2	**1a**	**2b** (4-MeC₆H₄)	**3b**	83	98
3	**1a**	**2c** (4-MeOC₆H₄)	**3c**	90	98
4	**1a**	**2d** (4-FC₆H₄)	**3d**	92	>99
5	**1a**	**2e** (4-ClC₆H₄)	**3e**	67	>99
6	**1a**	**2f** (4-BrC₆H₄)	**3f**	66	>99
7	**1a**	**2g** (4-CF₃C₆H₄)	**3g**	73	99
8	**1a**	**2h** (3-MeC₆H₄)	**3h**	80	99
9	**1a**	**2i** (3-OHC₆H₄)	**3i**	64	99
10	**1a**	**2j** (2-CH₂OHC₆H₄)	**3j**	50	92
11	**1a**	**2k** (2-CH₂OTBSC₆H₄)	**3k**	58	99
12	**1a**	**2l** (1-naphthyl)	**3l**	81	99
13	**1a**	**2m** (2-naphthyl)	**3m**	78	98
14	**1a**	**2n** (3-indolyl)	**3n**	68	96
15	**1a**	**2o** (3-thienyl)	**3o**	96	>99
16	**1a**	**2p** (2-thienyl)	**3p**	97	99
17	**1a**	**2q** (ferrocenyl)	**3q**	80	>99
18	**1a**	**2r** (cyclopropyl)	**3r**	89	>99
19	**1a**	**2s** (C₆H₅CH₂CH₂CH₂⁻)	**3s**	55	>99
20	**1a**	**2t** (C₆H₅OCH₂⁻)	**3t**	46	98
21	**1a**	**2u**	**3u**	96	>99
22	**1b** (Et-)	**2a** (C₆H₅)	**3v**	93	>99
23	**1b** (Et-)	**2d** (4-FC₆H₄)	**3w**	81	>99
24	**1c** (i-propyl)	**2a**	**3x**	86	97
25	**1d** (C₆H₅)	**2a**	**3y**	89	99

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.4 mmol), [Rh(cod)Cl]₂ (2.5 mol%), and **L1** (5 mol%), rt. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase.


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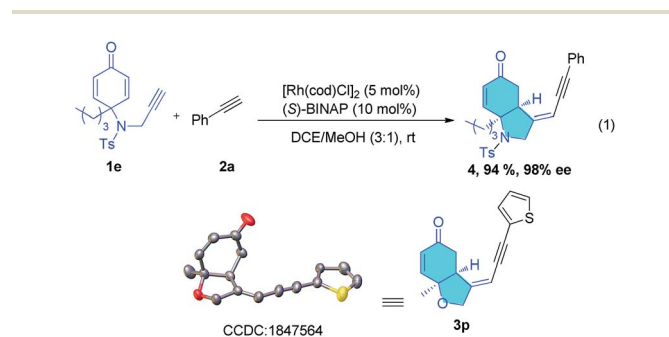
Scheme 2 X-ray crystallographic structure of **3p**.
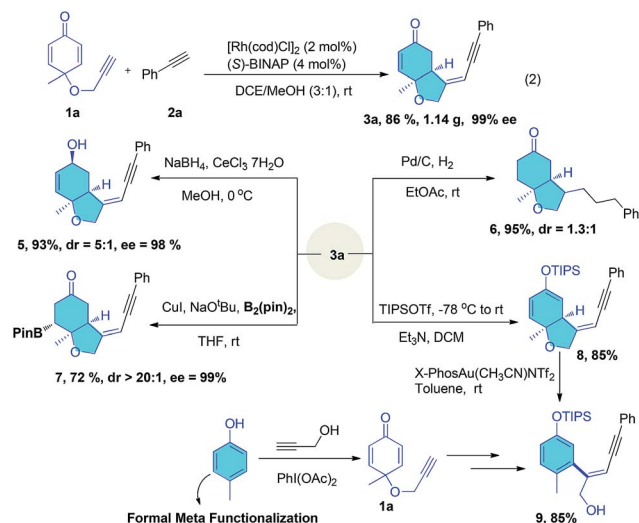
Scheme 3 Scale-up experiment and further synthetic applications of bicyclic enynes.

To gain insight into the hydroalkynylation process, we conducted deuterium labelling experiments (Scheme 4). The standard reaction in MeOD led to **3a-D** with 50% deuterium content at the methylene position adjacent to the ketone (eqn (3)).
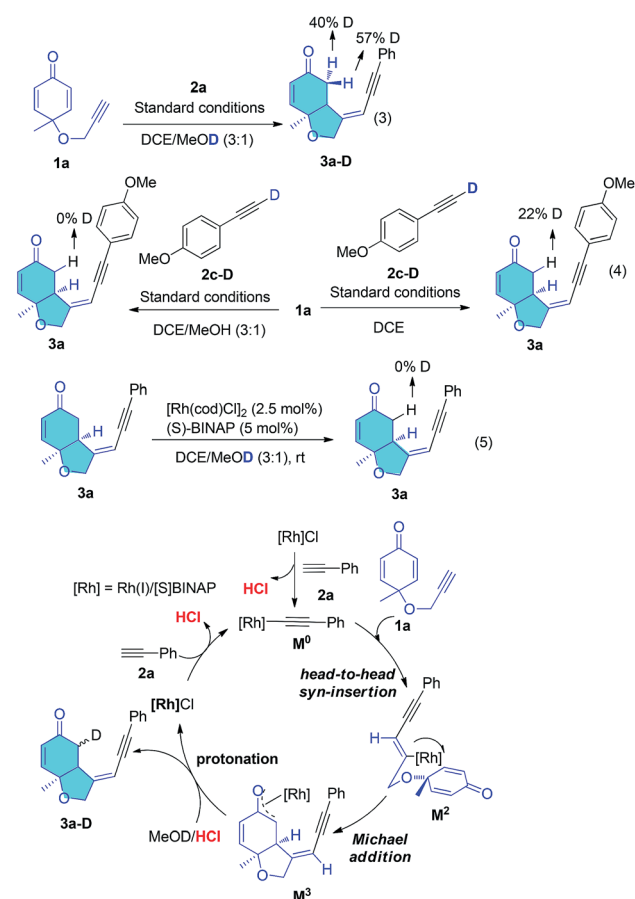
Scheme 4 Control experiments and proposed mechanism.

When the deuterated alkyne **2c-D** was subjected to the reaction in MeOH, the CH$_2$ was not deuterated at all, but when the reaction was performed in DCE solution, the proton was 22% deuterated (eqn (4)). Product **3a** was not deuterated under standard conditions in MeOD (eqn (5)). These results indicate that the origin of this hydrogen could be the alkyne proton and solvent. Based on these results and previous reports, a plausible mechanism is proposed and shown in Scheme 4. Rh(I) catalyst reacted with **2a** forming Rh(I) acetylide **M⁰** and released catalytic amount of HCl, which might exchange with solvent methanol and played a very important role in the final protonation step. Rh(I) acetylide **M⁰** went through head-to-head insertion afforded the vinyl rhodium intermediate (**M²**). Asymmetric Michael addition to this prochiral diene gave an Rh(I) enolate (**M³**), which was protonated by HCl/MeOH to form the product (**3a**) and Rh(I)Cl. This final unselective protonation of Rh(I) enolate (**M³**) with HCl/MeOD could result in both protons of the methylene group being deuterated, which would be consistent with eqn (3). If the first formation of Rh(I) acetylide **M⁰** was oxidative addition, then the final step should be reductive elimination and the proton of the methylene group should come from the terminal alkyne, which fails to agree with eqn (3). If [Rh(COD)OMe]₂ catalyst was used instead of chloride catalyst, much slower reaction and lower yield was observed, because this catalyst reacted with terminal alkyne only produce neutral methanol, but not acid.

Conclusions

In summary, we have developed a highly enantioselective Rh-catalyzed hydroalkynylation reaction that can be used for the synthesis of enantioenriched *cis*-hydrobenzofuranone-tethered enynes. Although many isomers are possible, a single head-to-head regioisomer was obtained in this reaction. Notable features of this approach include 100% atom-economy, mild reaction conditions, a very broad substrate scope, and precise control of chemo-, regio-, diastereo- and enantioselectivity by a single catalyst. Further application of this strategy is in progress in our laboratory.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Notes and references

1 (*a*) P. Lan, L. E. White, E. S. Taher, P. E. Guest, M. G. Banwell and A. C. Willis, *J. Nat. Prod.*, 2015, **78**, 1963; (*b*)

P. Nussbaumer, I. Leitner, K. Mraz and A. Stütz, *J. Med. Chem.*, 1995, **38**, 1831.

2 Y. Liu, M. Nishiura, Y. Wang and Z. Hou, *J. Am. Chem. Soc.*, 2006, **128**, 5592.

3 (*a*) P. McGee, G. Bétournay, F. Barabé and L. Barriault, *Angew. Chem., Int. Ed.*, 2017, **56**, 6280; (*b*) J. Cheng and T.-P. Loh, *J. Am. Chem. Soc.*, 2015, **137**, 42; (*c*) Y. Wang, P. Zhang, D. Qian and J. Zhang, *Angew. Chem., Int. Ed.*, 2015, **54**, 14849; (*d*) W. Zhang, S. Zheng, N. Liu, J. B. Werness, I. A. Guzei and W. Tang, *J. Am. Chem. Soc.*, 2010, **132**, 3664.

4 (*a*) B. M. Trost, M. T. Sorum, C. Chan, A. E. Harms and G. Rühter, *J. Am. Chem. Soc.*, 1997, **119**, 698; (*b*) B. M. Trost, B. R. Taft, J. T. Masters and J.-P. Lumb, *J. Am. Chem. Soc.*, 2011, **133**, 8502.

5 For a review, see: (*a*) B. M. Trost and J. T. maters, *Chem. Soc. Rev.*, 2016, **45**, 2212; For recent examples, see:(*b*) Q. Liang, K. M. Osten and D. Song, *Angew. Chem., Int. Ed.*, 2017, **56**, 6317; (*c*) M. G. Lauer, B. R. Headford, O. M. Gobble, M. B. Weyhaupt, D. L. Gerlach, M. Zeller and K. H. Shaughnessy, *ACS Catal.*, 2016, **6**, 5834; (*d*) O. Rivada-Wheelaghan, S. Chakraborty, L. J. W. Shimon, Y. Ben-David and D. Milstein, *Angew. Chem., Int. Ed.*, 2016, **55**, 6942; (*e*) R. Azpíroz, L. Rubio-Pérez, R. Castarlenas, J. J. Pérez-Torrente and L. A. Oro, *ChemCatChem*, 2014, **6**, 2587; (*f*) H.-D. Xu, R. Zhang, X. Li, S. Huang, W. Tang and W.-H. Hu, *Org. Lett.*, 2013, **15**, 840; (*g*) H. M. Peng, J. Zhao and X. Li, *Adv. Synth. Catal.*, 2009, **351**, 1371; (*h*) R. H. Platel and L. L. Schafer, *Chem. Commun.*, 2012, **48**, 10609; (*i*) C.-C. Lee, Y.-C. Lin, Y.-H. Liu and Y. Wang, *Organometallics*, 2005, **24**, 136; (*j*) C. Jahier, O. V. Zatolochnaya, N. V. Zvyagintsev, V. P. Ananikov and V. Gevorgyan, *Org. Lett.*, 2012, **14**, 2846; (*k*) C.-H. Jun, Z. Lu and R. H. Crabtree, *Tetrahedron Lett.*, 1992, **33**, 7119.

6 Rh-catalyzed asymmetric hydroalkynylation of alkene moiety has been well developed, see: (*a*) X.-Y. Bai, W.-W. Zhang, Q. Li and B.-J. Li, *J. Am. Chem. Soc.*, 2018, **140**, 506; (*b*) K.-L. Choo and M. Lautens, *Org. Lett.*, 2018, **20**, 1380; (*c*) Y. Zhi, J. Huang, N. Liu, T. Lu and X. Dou, *Org. Lett.*, 2017, **19**, 2378; (*d*) X.-Y. Bai, Z.-X. Wang and B.-J. Li, *Angew. Chem., Int. Ed.*, 2016, **55**, 9007; (*e*) X. Dou, Y. Huang and T. Hayashi, *Angew. Chem., Int. Ed.*, 2016, **55**, 1133; (*f*) Q. Yang, P. Y. Choy, B. Fan and F. Y. Kwong, *Adv. Synth. Catal.*, 2015, **357**, 2345; (*g*) B.-M. Fan, Q.-J. Yang, J. Hu, C.-L. Fan, S.-F. Li, L. Yu, C. Huang, W. W. Tsang and F. Y. Kwong, *Angew. Chem., Int. Ed.*, 2012, **51**, 7821; (*h*) T. Nishimura, T. Sawano and T. Hayashi, *Angew. Chem., Int. Ed.*, 2009, **48**, 8057; (*i*) T. Nishimura, X.-X. Guo, N. Uchiyama, T. Katoh and T. Hayashi, *J. Am. Chem. Soc.*,

2008, **130**, 1576; (*j*) D. F. Cauble, J. D. Gipson and M. J. Krische, *J. Am. Chem. Soc.*, 2003, **125**, 1110.

7 Z. Yan, X.-A. Yuan, Y. Zhao, C. Zhu and J. Xie, *Angew. Chem., Int. Ed.*, 2018, **57**, 12906.

8 C. Clarke, C. A. Incerti-Pradillos and H. W. Lam, *J. Am. Chem. Soc.*, 2016, **138**, 8068.

9 (*a*) Y.-Q. Chen, Y.-H. Shen, Y.-Q. Su, L.-Y. Kong and W.-D. Zhang, *Chem. Biodiversity*, 2009, **6**, 779; (*b*) K. Zhao, G.-J. Cheng, H. Yang, H. Shang, X. Zhang, Y.-D. Wu and Y. Tang, *Org. Lett.*, 2012, **14**, 4878; (*c*) J. M. Castro, S. Salido, J. Altarejos, M. Nogueras and A. Sánchez, *Tetrahedron*, 2002, **58**, 5941; (*d*) M. J. Uddin, S. Kokubo, K. Ueda, K. Suenaga and D. Uemura, *J. Nat. Prod.*, 2001, **64**, 1169; (*e*) T. Hase, K. Ohtani, R. Kasai, K. Yamasaki and C. Picheansoonthon, *Phytochemistry*, 1996, **41**, 317.

10 For a review on desymmetrization reactions: (*a*) X.-P. Zeng, Z.-Y. Cao, Y.-H. Wang, F. Zhou and J. Zhou, *Chem. Rev.*, 2016, **116**, 7330; For organo-catalyzed desymmetrization of cyclohexadienone, see:(*b*) X. Su, W. Zhu, Y. Li and J. Zhang, *Angew. Chem., Int. Ed.*, 2015, **54**, 6874; (*c*) S. Takizawa, T. M.-N. Nguyen, A. Grossmann, D. Enders and H. Sasai, *Angew. Chem., Int. Ed.*, 2012, **51**, 5423; (*d*) Q. Gu and S.-L. You, *Chem. Sci.*, 2011, **2**, 1519; (*e*) Q. Gu, Z.-Q. Rong, C. Zheng and S.-L. You, *J. Am. Chem. Soc.*, 2010, **132**, 4056; (*f*) N. T. Vo, R. D. M. Pace, F. O'Hara and M. J. Gaunt, *J. Am. Chem. Soc.*, 2008, **130**, 404; (*g*) Q. Liu and T. Rovis, *J. Am. Chem. Soc.*, 2006, **128**, 2552; (*h*) W. Yao, X. Dou, S. Wen, J. Wu, J. J. Vittal and Y. Lu, *Nat. Commun.*, 2016, **7**, 13024.

11 For metal-catalyzed desymmetrization of cyclohexadienone, see: (*a*) T. Shu, L. Zhao, S. Li, X.-Y. Chen, C. von Essen, K. Rissanen and D. Enders, *Angew. Chem., Int. Ed.*, 2018, **57**, 10985; (*b*) X. Zhou, Y. Pan and X. Li, *Angew. Chem., Int. Ed.*, 2017, **56**, 8163; (*c*) J. Chen, X. Han and X. Lu, *Angew. Chem., Int. Ed.*, 2017, **56**, 14698; (*d*) R. Kumar, Y. Hoshimoto, E. Tamai, M. Ohashi and S. Ogoshi, *Nat. Commun.*, 2017, **8**, 32; (*e*) Z.-T. He, X.-Q. Tang, L.-B. Xie, M. Cheng, P. Tian and G.-Q. Lin, *Angew. Chem., Int. Ed.*, 2015, **54**, 14815; (*f*) P. Liu, Y. Fukui, P. Tian, Z.-T. He, C.-Y. Sun, N.-Y. Wu and G.-Q. Lin, *J. Am. Chem. Soc.*, 2013, **135**, 11700; (*g*) Z.-T. He, B. Tian, Y. Fukui, X. Tong, P. Tian and G.-Q. Lin, *Angew. Chem., Int. Ed.*, 2013, **52**, 5314; (*h*) J. Keilitz, S. G. Newman and M. Lautens, *Org. Lett.*, 2013, **15**, 1148; (*i*) T. L. N. Nguyen, C. A. Incerti-Pradillos, W. Lewis and H. W. Lam, *Chem. Commun.*, 2018, **54**, 5622; (*j*) K. K. Gollapelli, S. Donikela, N. Manjula and R. Chegondi, *ACS Catal.*, 2018, **8**, 1440.

12 A. J. Kresge and P. Pruszynski, *J. Org. Chem.*, 1991, **56**, 4808.