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Pd-Catalyzed Enantioselective Hydroalkynylation of Cyclopropenes

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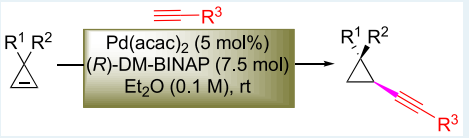
Supporting Information

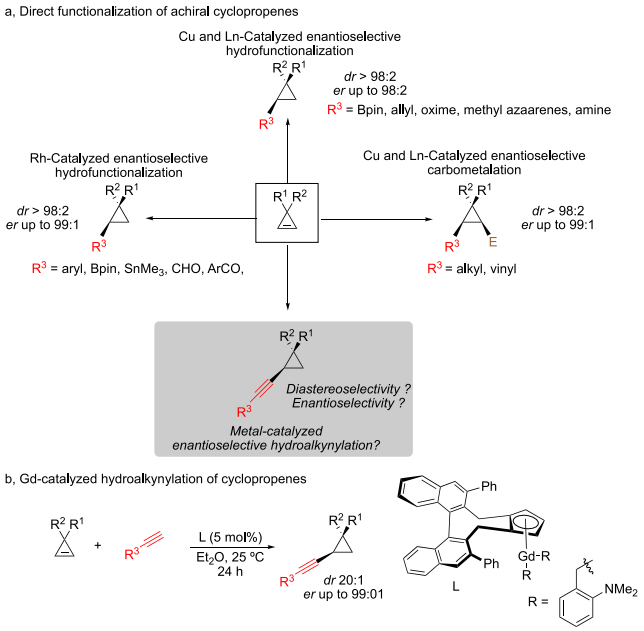
ABSTRACT: We report herein an easy, mild, and robust Pd-catalyzed enantioselective hydroalkynylation reaction of achiral cyclopropenes. Commercially available $Pd(acac)_2$ and (*R*)-DM-BINAP proved to be the best combination to reach high diastereo- and enantioselectivities.



KEYWORDS: *enantioselective, hydroalkynylation, cyclopropenes, cyclopropanes, palladium*

The diastereo- and enantioselective addition of organometallic species across unactivated 1,2-disubstituted double bonds (carbometalation) still stands nowadays as one of the most challenging transformations in organic synthesis.[1] Because of the release of ring strain, the addition on cyclopropenes represents a particular but successful case providing a new entry to a large variety of polysubstituted enantioenriched cyclopropanes.[2] In this context, and since the pioneering work of Lautens,[3] Fox,[4] and Nakamura,[5] the direct functionalization of achiral, unsaturated,[6] three-membered carbocycles have attracted much attention.[7] We and others have reported the catalytic enantioselective copper-, rhodium-, and lanthanide-catalyzed addition of sp^3- and sp^2-hydridized alkyl groups[8−10] as well as the addition of heteroelements[10a,11] with excellent diastereo- and enantioselectivities (Scheme 1a).

Scheme 1. Direct Functionalization of Achiral Unsaturated Cyclopropenes



However, an important but still missing transformation in this arsenal of direct functionalization of achiral unsaturated three-membered carbocycles was the introduction of alkynyl groups,[12] until the very recent report of Hou describing the highly diastereo- and enantioselective half-sandwich gadolinium-catalyzed enantioselective hydroalkynylation of cyclopropenes (Scheme 1b).[13] Because diastereo- and enantiomerically pure alkynyl cyclopropanes are motifs present in several natural products[14] and are considered as important building blocks in the construction of more complex skeletons,[15] we wanted to develop an alternative more efficient and easier approach to reach these scaffolds with high selectivities. The availability of palladium complexes combined with their robustness, ease of preparation and manipulation, and high functional group tolerance were key factors to investigate the Pd-catalyzed alkynylation reaction of cyclopropenes.[16] Additionally, and opposite to gadolinium complexes, most palladium (pre)catalysts can easily be handled outside a glovebox, advocating for their user-friendliness.

Cyclopropene **1a** and commercially available phenylacetylene were used as model substrates to explore the diastereo- and enantioselective Pd-catalyzed hydroalkynylation reaction. Various parameters such as the nature of the (i) catalyst, (ii) chiral ligand, and (iii) solvent were screened, as shown in Table 1. (See the Supporting Information for full details.) Our preliminary experiment was performed with $Pd(OAc)_2$ as the catalyst and (*S*)-DTBM-SEGPHOS as the ligand in $(CH_2Cl)_2$ for 16 h. Under this experimental condition, we were pleased to observe that alkynylated cyclopropane **2a** was formed with a moderate enantiomeric ratio (Table 1, entry 1, *er* 64:36).

On the basis of this initial finding, different chiral ligands were evaluated (Table 1, entries 2−6), and the commercially available (*R*)-DM-BINAP was found to be the best ligand (Table 1, entry 6, *er* 86:14). Using (*R*)-DM-BINAP as the most effective ligand, different solvents were tested (Table 1, entries 7−11), and DCM, THF, and Et_2O provided similar selectivities. Further additional screening of palladium salts and

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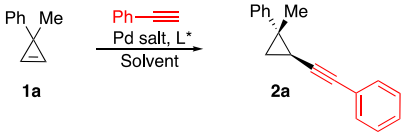
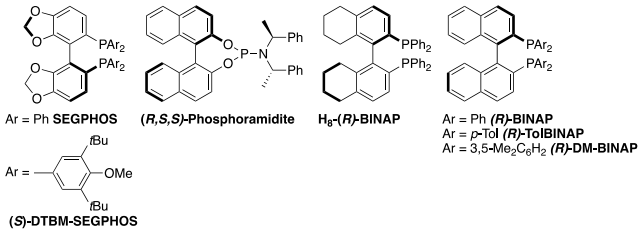
Table 1. Optimization of the Pd-Catalyzed Asymmetric Hydroalkynylation of Cyclopropene 1a

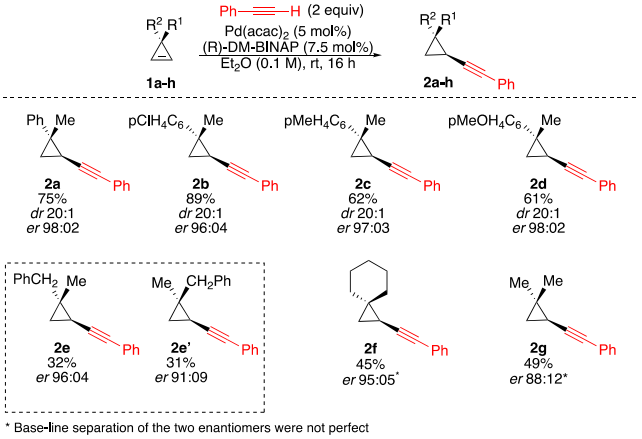


entry	Pd salt	L*	solvent	*er*[a]
1	$Pd(OAc)_2$	(*S*)-DTBM-SEGPHOS	DCE	36:64
2	$Pd(OAc)_2$	(*R,S,S*)-phosphoramidite	DCE	57:43
3	$Pd(OAc)_2$	H_8-(*R*)-BINAP	DCE	85:15
4	$Pd(OAc)_2$	(*R*)-BINAP	DCE	70:30
5	$Pd(OAc)_2$	(*R*)-Tol-BINAP	DCE	71:29
6	$Pd(OAc)_2$	(*R*)-DM-BINAP	DCE	86:14
7	$Pd(OAc)_2$	(*R*)-DM-BINAP	DCM	94:06
8[b]	$Pd(OAc)_2$	(*R*)-DM-BINAP	MeCN	ND
9[b]	$Pd(OAc)_2$	(*R*)-DM-BINAP	toluene	ND
10	$Pd(OAc)_2$	(*R*)-DM-BINAP	Et_2O	93:07
11	$Pd(OAc)_2$	(*R*)-DM-BINAP	THF	94:06
12	$Pd(OAc)_2$	(*R*)-DM-BINAP	DCM	90:10
13	$Pd(acac)_2$	(*R*)-DM-BINAP	DCM	95:05
14	$Pd(dpa)_2$	(*R*)-DM-BINAP	DCM	93:07
15	$(PdAllylCl)_2$	(*R*)-DM-BINAP	DCM	60:40
16	**$Pd(acac)_2$**	**(*R*)-DM-BINAP**	**Et_2O**	**98:02**[c]
17	$Pd(acac)_2$	(*R*)-DM-BINAP	THF	96:04
18[b]	$Pd(acac)_2$	(*R*)-DM-BINAP	DMF	ND
19[b]	$Pd(acac)_2$	(*R*)-DM-BINAP	DMSO	ND
20	$Pd(acac)_2$	(*R*)-DM-BINAP	acetone	93:07

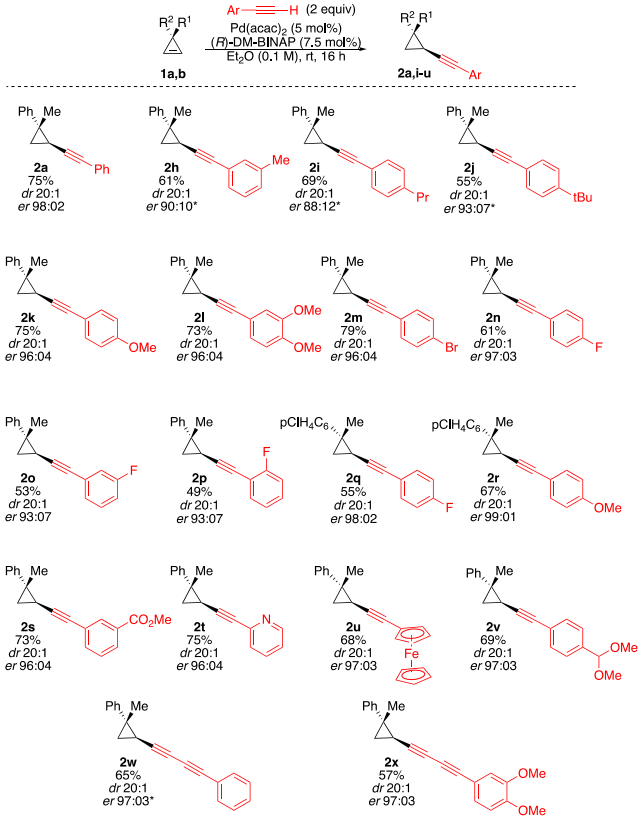
[a]Determined by chiral HPLC. [b]No detection of the desired product **2a**; cyclopropene **1a** was recovered. [c]Reactions were run on a 0.05 mmol scale using 2 equiv of the alkyne, Pd salt (5 mol %), and L* (7.5 mol %) in the corresponding solvent (0.1 M), and the reaction mixture was stirred at room temperature for 16 h. In all cases, conversion was >70%.



Scheme 2. Pd-Catalyzed Enantioselective Hydroalkynylation of Cyclopropenes



Scheme 3. Pd-Catalyzed Enantioselective Hydroalkynylation Reaction of Cyclopropenes with Different Terminal Alkynes



solvents (Table 1, entries 12–20) revealed that the ideal combination was $Pd(acac)_2$ with (*R*)-DM-BINAP in Et_2O (Table 1, entry 16). The desired alkynylcyclopropane **2a** was obtained with excellent enantio- and diastereoselectivity (*er* 98:02, *dr* 20:1). Having established the best experimental conditions for a mild Pd-catalyzed diastereo- and enantioselective hydroalkynylation reaction of achiral cyclopropenes **1a**, we then explored the nature of the substituents of the three-membered rings on the selectivity of the reaction.

As shown in Scheme 2, cyclopropenes bearing electron-withdrawing or -donating groups gave the corresponding hydroalkynylated cyclopropanes **2b–d** in good yield with constantly excellent diastereo- and enantioselectivity. When the cyclopropene possessing a benzyl group was treated under our experimental condition (**1e**, R^1 = Me, R^2 = CH_2Ph), the desired alkynyl cyclopropanes **2e** and **2e′** were isolated with good to excellent enantiomeric ratios but as an equimolar diastereoisomeric mixture of products, easily independently obtained by purification by column chromatography. Furthermore, cyclopropenes possessing identical groups on C_3 could easily be transformed into the expected products with high enantioselectivity (**2f**, Scheme 2), underlining that the aromatic ring present on the cyclopropenyl ring is not mandatory to reach good enantioselectivity.

Encouraged by this result, the simplest dimethyl cyclopropene was prepared and submitted to our catalytic Pd-catalyzed enantioselective alkynylation reaction. We were pleased to find that the desired alkynylated cyclopropane **2g** could be isolated in moderate yield with a promising

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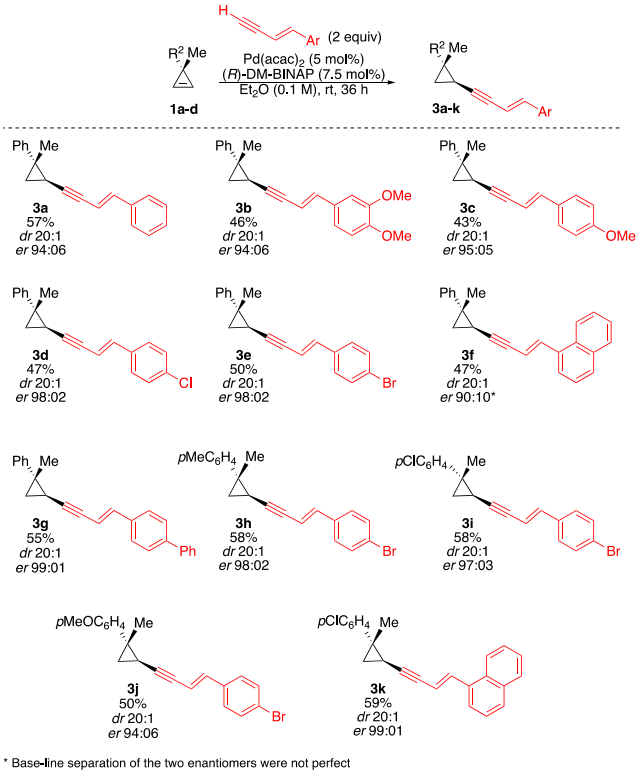
Scheme 4. Pd-Catalyzed Enantioselective Hydroalkynylation Reaction of Cyclopropenes with Terminal Enynes



* Base-line separation of the two enantiomers were not perfect

enantiomeric ratio of 88:12. In the last two cases, a substitution on C1 of the cyclopropenyl ring would lead to the creation of two quaternary stereocenters. Unfortunately, in this case, our catalytic procedure does not work anymore. Stimulated by these positive results, we then turned our attention to the nature of the nucleophilic alkynyl groups that could be introduced. A series of different substituted aromatic acetylenes were added to cyclopropane **1a**, and in all cases, excellent selectivities were observed. Alkyl substituents could be in either a meta or para position of the aromatic ring without drastically altering the diastereo- and enantioselectivity (Scheme 3, compare **2h** with **2i** and **2j**). Electron-donating groups provided the expected alkynylated cyclopropanes (**2k** and **2l**) with identical enantiomeric ratios. It is worth mentioning that electron-deficient *para*-bromo-phenyl acetylene could also be tolerated in this transformation and afford the desired cyclopropane **2m** in 79% yield with excellent diastereo- and enantioselective control (*dr* 20:1, *er* 96:04). Interestingly, *ortho*-, *meta*-, and *para*-fluoro-phenyl acetylene gave the desired fluoro-containing enantiomerically enriched alkynyl cyclopropanes (Scheme 3, **2n**–**p**) also with excellent stereocontrol. To establish the absolute configuration of the alkynyl cyclopropanes, product **2r** has been prepared, and the configuration was determined by X-ray diffraction analysis.[17] All other absolute configurations of products have been assigned by analogy.[18]

Various functional groups present on the alkynyl part can also be tolerated, such as ester, ferrocene, pyridine, and acetal (Scheme 3, **2s**–**v**). An important extension of this approach is the catalytic enantioselective addition of 1,3-butadiyn-1-ylbenzene. In the two examined cases (Scheme 3, **2w** and **2x**), the diynyl cyclopropanes were obtained with excellent diastereo- and enantioselectivities. It should be noted that TMS-substituted alkynes led to nearly racemic products with (*R*)-DM-BINAP, whereas alkyl-substituted alkynes did not lead to the expected products.

Encouraged by the excellent selectivity of the last two examples in Scheme 3, we were then wondering if this approach could be extended to more challenging systems, and we were particularly interested in the catalytic enantioselective addition of conjugated enynes. Thus a series of enynes were synthesized and tested under our standard conditions (Scheme 4). To our delight, cyclopropanes **3a**–**k** were isolated in moderate yield but with excellent diastereo- and enantioselectivity (*dr* 20:1, *er* up to 99:01). For instance, the Pd-catalyzed enantioselective addition of (*E*)-4-phenyl-3-buten-1-yne to **1a** provided the product **3a** in 57% yield with a 94:06 enantiomeric ratio. A variously substituted aromatic ring can be used without altering the diastereo- and enantioselectivities.

In conclusion, we have developed a friendly and easy to use Pd-catalyzed enantioselective hydroalkynylation reaction of achiral cyclopropenes by the addition of different terminal alkynes, diynes, and enynes with $Pd(acac)_2$ and commercially available (*R*)-DM-BINAP as a chiral ligand with excellent diastereo- and enantioselectivity. This hydroalkynylation reaction provides a simple, mild, and atom-economical approach toward a large variety of enantiomerically enriched alkynylated cyclopropanes.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.9b04960.

Experimental procedures, instrumentation used, conditional screening, ligands used, ^1H and ^{13}C NMR spectra of all new compounds, and HPLC traces of racemic and enantiomerically pure compounds (PDF)

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Notes

The authors declare no competing financial interest.

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(17) Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, accession number **2r**: 1897640.

(18) All compounds have very high positive values of optical rotation.

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