CHEMISTRY
A European Journal

A Journal of
ChemPubSoc Europe

Accepted Article

Title: Palladium-Catalyzed Enantioselective Alkoxycarbonylation of Propargylic Carbonates with (R)- or (S)-3,4,5-(MeO)3-MeOBIPHEP

Authors: Wanli Zhang and Shengming Ma

To be cited as: *Chem. Eur. J.* 10.1002/chem.201701194

Link to VoR: http://dx.doi.org/10.1002/chem.201701194

Supported by
ACES

WILEY-VCH

10.1002/chem.201701194

COMMUNICATION

WILEY-VCH

Palladium-Catalyzed Enantioselective Alkoxycarbonylation of Propargylic Carbonates with (*R*)- or (*S*)-3,4,5-(MeO)$_3$-MeOBIPHEP

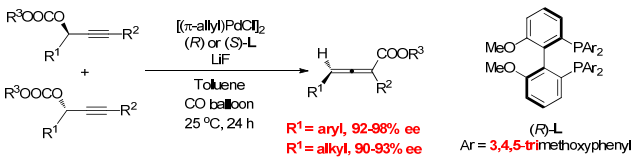
Wanli Zhang[b] and Shengming Ma*[a,c]

Abstract: (*R*)- and (*S*)-3,4,5-(MeO)$_3$-MeOBIPHEP have been identified as the efficient chiral ligands for the palladium-catalyzed highly enantioselective synthesis of 2,3-allenoates from easily available different types of racemic propargylic carbonates with 90-98% ee and decent yields. The potentials of the products have been demonstrated with high chirality transfer efficiency.

Allenes are a class of compounds characterized by two cumulated carbon-carbon double bonds exhibiting extraordinary activities as building blocks or even as chiral ligands in organic synthesis.[1-2] This unique structure has also been found in a great number of natural products and pharmaceutical molecules, which gave rise to ample interest in the synthesis of allenes.[1a,3] Recently, many methodologies for the synthesis of allenes have been developed,[4] however, controlling the axial chirality in trisubstitued allenes, especially the trisubstitued 2,3-allenoates, which are extremely useful precursors for the synthesis of other allenes due to the versatile reactivity of the ester functionality, remains a hard nut to crack.[5] A common method to generate optically active such compounds is through kinetic resolution of racemic compounds (Scheme 1a):[6] Chiral trisubstituted allenoates were recovered in the 1,3-dipolar cycloaddition of racemic 2,3-allenoates using bisphosphoric acid catalyst with 35-48% yield and 85-99% ee, together with the products, 3-methylenepyrrolidine derivatives, with 39-57% yield and 64-94% ee; another efficient access to enantiomerically enriched trisubstituted allenoates relies on the dynamic kinetic resolution-based isomerization of 1-substituted 3-alkynoates with the recovery of the starting 3-alkynoates even after 24 h, which is barely possible to separate from 2,3-allenoates (Scheme 1b);[7] another approach utilizes organozinc reagents as the nucleophile through the corresponding S_N2' substitution with optically active propargylic mesylates (Scheme 1c).[8] With the help of DMSO, 2,3-allenoates could be afforded with 87% yield and 98% ee, whereas only one example of trisubstituted allenoate was displayed; synthesis of optically active trisubstituted allenoates may also be realized through Pd-catalyzed alkoxycarbonylation of optically active propargylic mesylates in 69-90% yield and 80-99% ee (Scheme 1d);[9] asymmetric olefination of ketenes is another option albeit using at least a stoichiometric amount of chiral ylide (Scheme 1e).[10]

Catalytic enaotioselective synthesis is the most ideal strategy in consideration of costs and atom economy. In the presence of chiral phosphite ligand, chiral 2,3-allenoates can be synthesized enatioselectively through Pd-catalyzed asymmetric *β*-hydride elimination of the not-readily-available stereodefined enol triflates (Scheme 1f).[11] However, only 20% ee was detected in the synthesis of trisubstituted allenoates. Applying intermolecular addition of nitroalkanes to activated enynes to the synthesis of chiral trisubstituted allenoates is also feasible (Scheme 1g).[12] High yields and excellent enatioselectivities were observed in the tandem addition/isomerization process, albeit in some cases the alkynoate intermediates were detected, which can be further transferred into allenoates under the identical reaction conditions. Asymmetric C-H insertion of *α*-diazoesters into terminal alkynes is an alternative access to chiral trisubstituted allenoates (Scheme 1h).[13] Catalyzed by copper(I) complexes and chiral cationic guanidinium salts, enantiomerically enriched allenoates may be produced. Apart from these, chiral trisubstituted allenoates may be synthesized from the relatively complicated cyclopropenonylmethyl acetates catalyzed by Lewis base with good yields and enatioselectivities (Scheme 1i).[14]

In 2013, our laboratory disclosed a catalytic asymmetric synthesis of 2,3-allenoates with ECNU-Phos starting from propargylic carbonates.[15] However, the enantioselectivity is not satisfactory in many cases. Herein, we report our recent results in identifying (*R*)- or (*S*)-3,4,5-(MeO)$_3$-MeOBIPHEP as the ligand for a very general Pd-catalyzed highly enantioselective synthesis of chiral trisubstituted allenoates from cheap and readily available differently substituted 2-alkynylic carbonates generally with 90~98% ee (Scheme 2).



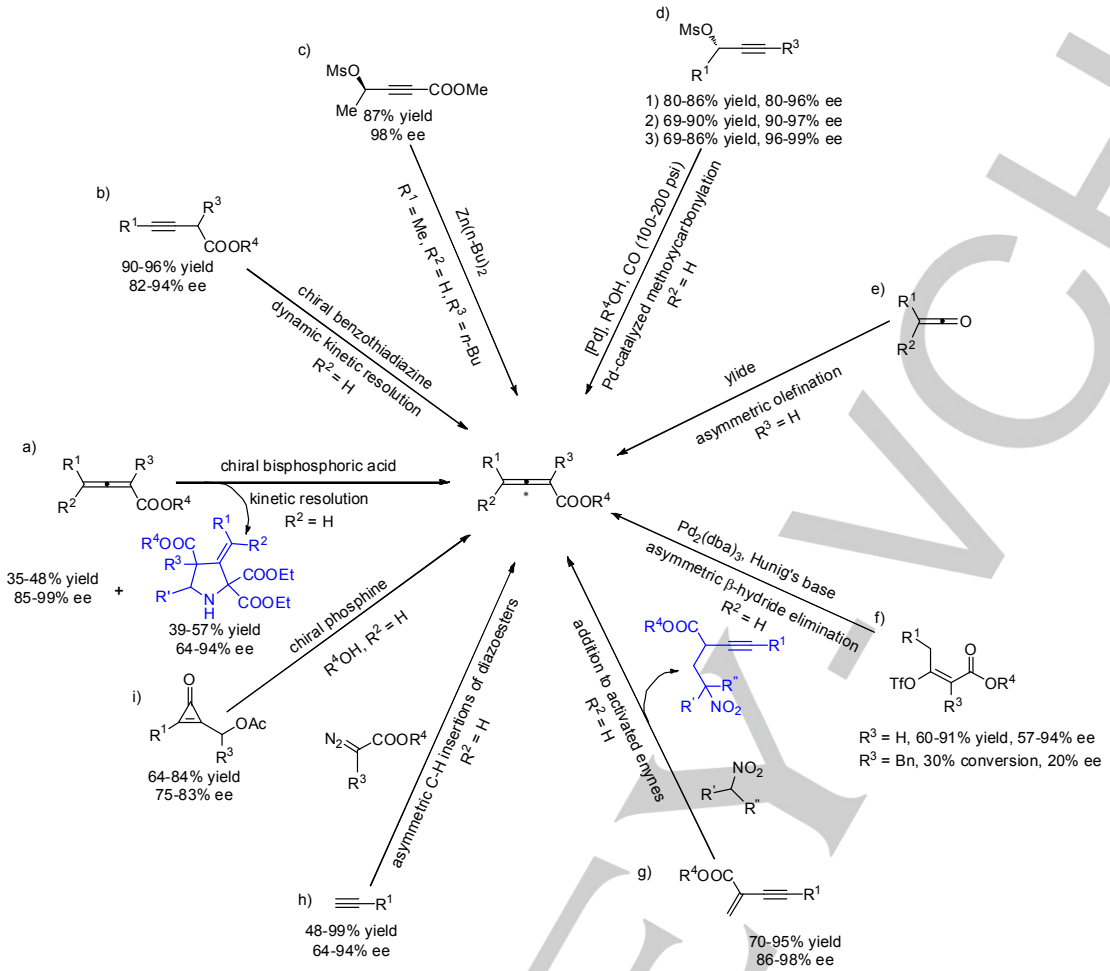
Scheme 2. Enantioselective synthesis of 2,3-allenoates from racemic propargylic carbonates

Racemic methyl 1-phenyl-2-heptyn-1-yl carbonate [(±)-**1a**] was used as the model compound with [(π-allyl)PdCl]$_2$ as the catalyst at room-temperature to investigate the ligand effect for this methoxycarbonylation reaction. Our attempt was to finely tune the electronic property of the phosphorus atoms in the BIPHEP skeleton: Firstly, changing the aryl substituents of the coordinating phosphorus atom from 3,5-dimethoxy to 3,5-dimethyl [(*R*)-**L1**] leads to 90% recovery of the starting material, (R_a)-**2a** was detected with only 4% yield (Table 1, entry 1). By replacing the aryl substituents with 4-methylphenyl in order to

[a] Prof. Dr. S. Ma
State Key Laboratory of Organometallic Chemistry,
Shanghai Institute of Organic Chemistry,
Chinese Academy of Sciences,
345 Lingling Lu, Shanghai 200032, P. R. China.
E-mail: masm@sioc.ac.cn
[b] W. Zhang
Shanghai Key Laboratory of Green Chemistry and Chemical Process,
College of Chemistry and Molecular Engineering,
East China Normal University,
3663 North Zhongshan Lu, Shanghai 200062, P. R. China
[c] Prof. Dr. S. Ma
Department of Chemistry, Fudan University,
220 Handan Lu, Shanghai 200433, P. R. China

Supporting information for this article is given via a link at the end of the document.

10.1002/chem.201701194



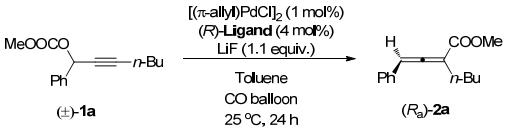
Scheme 1. Reported methods for the synthesis of chiral trisubstituted 2,3-allenoates

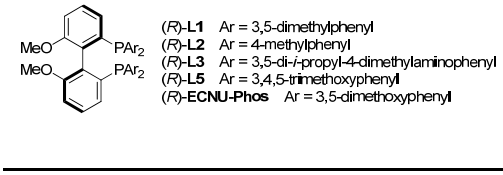
decrease the electron-density of the phosphorous atom, (*R*)-**L2** leads to inferior results (Table 1, entry 2). To our disappointment, when electron-richer ligands (*R*)-3,5-*i*-Pr_2-4-Me_2N-MeOBIPHEP [(*R*)-**L3**] and (*R*)-Ph-Garphos [(*R*)-**L4**] were surveyed, the carbonate (±)-**1a** remains mostly unreacted and only trace amount of the target product was detected (Table 1, entries 3 and 4). Interestingly, when 3,4,5-trimethoxy groups were introduced**, i.e.,** (*R*)-**L5**, after stirring at room temperature for 24 h, (R_a)-**2a** was obtained in 55% yield with 98% ee (Table 1, entry 6)! Inspired by this observation, the catalyst-loading was increased in an attempt to raise the conversion of this methoxycarbonylation progress. To our delight, when 3 mol% [(π-allyl)PdCl]$_2$ was used in combination with 9 mol% (*R*)-**L5**, the desired product (R_a)-**2a** was obtained in 85% yield and 97% ee with the starting material being completely converted (Table 1, entry 7). By comparison, when (*R*)-**ECNU-phos** was used, (R_a)-**2a** was produced in 78% yield with only 92% ee (Table 1, entry 5).[15]

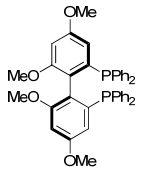
With this optimized chiral ligand in hand, other experimental parameters were inspected to further optimize the reaction conditions. Firstly, [(π-allyl)PdCl]$_2$ was replaced by [(π-cinnamyl)PdCl]$_2$, the product was obtained with 58% yield and 97% ee (Table 2, entry 2). In consideration of the cost, [(π-allyl)PdCl]$_2$ was used for further study.[16] Among the solvents surveyed, toluene was shown to be the best (Table 2, entries 3-8); 1,4-dioxane was also effective, albeit with a decreased yield and poorer enatioselectivity (Table 2, entry 3); the enatioselectivity and yield dropped further when THF was used (Table 2, entry 4); the methoxycarbonylation proceeded slowly in DCM to afford only 19% of (R_a)-**2a** after 24 h of stirring (Table 2, entry 5); when MTBE, DMF, or CH_3CN was applied, the catalyst system was ineffective with a trace amount of target products being detected (Table 2, entries 6-8).

10.1002/chem.201701194

Table 1. Pd-catalyzed enantioselective methoxycarbonylation of propargylic carbonates (±)-**1a**-ligand effect [a]





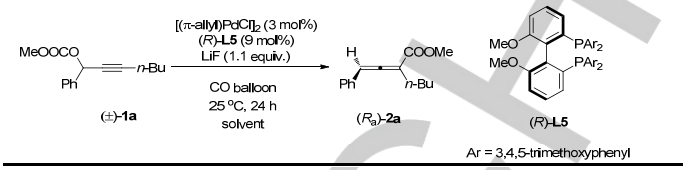


Entry	Ligand	(R_a)-**2a**		Recovery of (±)-**1a** (%) [b]
		Yield (%)	ee (%)	
1	(*R*)-**L1**	4 [b]	-	90
2	(*R*)-**L2**	6 [b]	-	87
3	(*R*)-**L3**	6 [b]	-	80
4	(*R*)-**L4**	4 [b]	-	92
5 [c]	(*R*)-**ECNU-Phos**	78 [d]	92 [e]	21
6 [f]	(*R*)-**L5**	55 [d]	98 [e]	28
7 [c]	(*R*)-**L5**	85 [d]	97 [e]	N.D.

[a] Reaction conditions: (±)-**1a** (0.2 mmol), [(π-allyl)PdCl]$_2$ (1 mol%), (*R*)-**Ligand** (4 mol%) and LiF (1.1 equiv.) at 25 °C in toluene (2.0 mL) under 1 atm of CO unless otherwise noted. [b] Determined by ^{1}H NMR analysis using 1,3,5-trimethylbenzene as the internal standard. [c] 0.1 mmol (±)-**1a** was used in combination with 3 mol% [(π-allyl)PdCl]$_2$ and 9 mol% (*R*)-**Ligand**. [d] Isolated yields. [e] ee values of 2,3-allenoates were determined by HPLC. [f] The reaction was carried out with 0.1 mmol (±)-**1a**.

After further optimization, it is apparent that when 3 mol% [(π-allyl)PdCl]$_2$ and 9 mol% (*R*)-**L5** were applied as the chiral catalyst in toluene under 1 atm of CO with 1.1 eqiuv LiF as additive, 2,3-allenoates (R_a)-**2** can be obtained in the highest yield and enantiopurity after 24 h of stirring at room temperature (25 °C). With this optimized condition in hand, the substrate scope has been investigated: When 1-aryl propargylic carbonates were used, (*R*)-**L5** exhibited excellent activity, producing (R_a)-**2** with very high enatioselectivities and recoveries of starting materials were not detected. When the simple phenyl-substitued substrate (±)-**1a** was applied, (*R*)-**L5** resulted in 86% yield and 97% ee on 1 mmol scale (Table 3, entry 1). Different substituents may be introduced into the Ar' group: both the electron-donating groups and electron-withdrawing groups are well tolerated, affording the corresponding allenonates in good yields with excellent enatioselectivities (Table 3, entries 2-5). Aryl groups with *m*-Cl and *p*-Cl make no difference, furnishing the target products (R_a)-**2f** and (R_a)-**2g** with 82~84% yields and 97-98% ee (Table 3, entries 6 and 7). The reactions of naphthyl-substituted substrates **1h** and **1i** were easily carried out to afford (R_a)-**2h** and (R_a)-**2i** with 80% yield and excellent

Table 2. Optimization of reaction conditions[a]

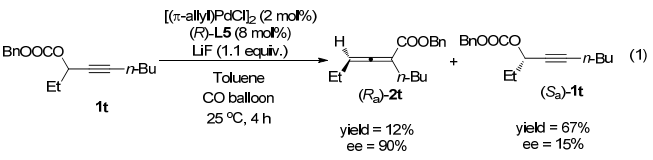


Entry	Solvent	(R_a)-**2a**		Recovery of (±)-**1a** (%) [d]
		Yield (%) [b]	ee (%) [c]	
1	Toluene	85	97	N.D.
2 [e]	Toluene	58	97	20
3	1,4-dioxane	70	95	N.D.
4	THF	50	92	N.D.
5	DCM	19 [d]	-	56
6	MTBE	N.D.	-	77
7	DMF	5 [d]	-	N.D.
8	CH_3CN	5 [d]	-	81

[a] Reaction conditions : (±)-**1a** (0.1 mmol), [(π-allyl)PdCl]$_2$ (3 mol%), (*R*)-**L5** mol%) and LiF (1.1 equiv.) at 25 °C in toluene (2.0 mL) under 1 atm of C unless otherwise noted, THF = tetrahydrofuran, MTBE = methyl tert-bu ether, DMF = N,N'-dimethylformamide, DCM = dichloromethane. [b] Isolat yield. [c] ee values of 2,3-allenoates were determined by HPLC. Determined by ^{1}H NMR analysis using 1,3,5-trimethylbezene as the inter standard. [e] 0.2 mmol (±)-**1a**, 1 mol% [(π- cinnamyl)PdCl]$_2$, and 4 mol% (*R* **L5** were used.

enatioselectivities (Table 3, entries 8 and 9). The R^2 group is also very flexible: methyl, isopropyl, long-chain *n*-hexadecyl, phenethyl, 4-chloroethyl, and cyclohexyl performed very well in this reaction, affording the products with good yields and no less than 92% ee (Table 3, entries 10-16). Compared to (*R*)-**ECNU-Phos**, an impressive enantioselectivity has been observed (Table 3, entries 1', 3', 7', and 13'). The reaction of the substrate with Ar' and R^2 both being phenyl is very slow.

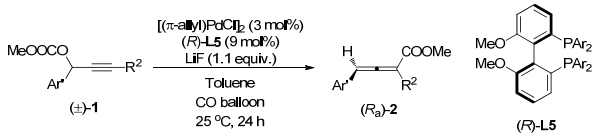
Furthermore when R^1 group is methyl, allenoates **2q**-**s** may be accessed with ees higher than 91% using (*R*)-**L5** (Table 4, entries 1-3). Changing R^1 group from methyl to ethyl, (R_a)-**2t** and (R_a)-**2u** were provided with 90% ee using (*R*)-**L5** (Table 4, entries 4, 5). Further lengthening R^1 group to *n*-butyl, *n*-hexyl, and *n*-undecyl didn't impact the enantioselectivity by (*R*)-**L5**, affording allenoates with 90-93% ee. By contrast, (*R*)-**ECNU-phos** resulted in these allenoates with only 83%-84% ee (Table 4, entries 5', 6', 7', 8', 9', and 10'). The lower yielding nature for substrates with R^1 being alkyl substituents may be caused by the difficulty in removing leaving groups as compared with the reaction of substrates with R^1 being an aryl group, in which the carbonate group is placed at benzylic position. In addition, it should be noted that the ee of the recovered starting material is 15%, indicating that the reaction is at least pattically a kinetic resolution process (eq. 1).



10.1002/chem.201701194

(*S*)-**L5** was also effective in this methoxycarbonylation process, affording the *S*-products (Scheme 3). When Ar' group is phenyl and phenyl substituted with electron-donating group, the enantiomers could be obtained with similar yields and ees. The chlorine-substituted substrate (±-**1n**) could be transformed into the desired enantiomer with 97% ee. It is worth mentioning that an allyl group can also be accommodated, affording (S_a)-**2o** with 84% yield and 95% ee.

Table 3. Substrate scope of enatioenriched allenoates synthesis from racemic 1-aryl propargylic carbonates (±)-1 [a]

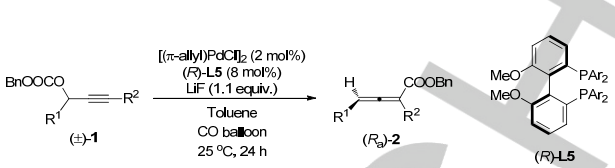


Ar = 3,4,5-trimethoxyphenyl

Entry	(±)-1		Yield of (R_a)-2 [b]	ee of (R_a)-2 [c]
	Ar'	R^2		
1	Ph	*n*-Bu (**1a**)	86 (**2a**)	97
1' [d]	Ph	*n*-Bu (**1a**)	77 (**2a**)	93
2	4-MeC_6H_4	*n*-Bu (**1b**)	80 (**2b**)	98
3	3-MeOC_6H_4	*n*-Pr (**1c**)	88 (**2c**)	97
3' [e]	3-MeOC_6H_4	*n*-Pr (**1c**)	85 (**2c**)	92
4 [f]	4-NCC_6H_4	*n*-Bu (**1d**)	72 (**2d**)	95
5 [f]	4-MeO_2CC_6H_4	*n*-Bu (**1e**)	79 (**2e**)	96
6	3-ClC_6H_4	*n*-Bu (**1f**)	84 (**2f**)	97
7	4-ClC_6H_4	*n*-Bu (**1g**)	82 (**2g**)	98
7' [g]	4-ClC_6H_4	*n*-Bu (**1g**)	87 (**2c**)	91
8 [h]	1-naphthyl	*n*-Bu (**1h**)	80 (**2h**)	95
9 [h]	2-naphthyl	*n*-C_8H_{17} (**1i**)	80 (**2i**)	93
10	Ph	Me (**1j**)	85 (**2j**)	92
11	Ph	*i*-Pr (**1k**)	84 (**2k**)	98
12	Ph	*n*-$C_{16}H_{33}$ (**1l**)	86 (**2l**)	97
13	Ph	$(CH_2)_2$Ph (**1m**)	81 (**2m**)	97
13' [i]	Ph	$(CH_2)_2$Ph (**1m**)	79 (**2m**)	93
14	Ph	$(CH_2)_4$Cl (**1n**)	83 (**2n**)	97
15	Ph	allyl (**1o**)	85 (**2o**)[g]	95
16	4-EtC_6H_4	Cy (**1p**)	83 (**2p**)	97

[a] Reaction conditions : (±)-**1** (1.0 mmol), [(π-allyl)PdCl]$_2$ (3 mol%), (*R*)-**L5** (9 mol%) and LiF (1.1 equiv.) at 25 °C in toluene (5.0 mL) under 1 atm of CO unless otherwise noted. [b] Isolated yield. [c] ee values of 2,3-allenoates were determined by HPLC. [d] with (*R*)-**ECNU-phos**; 17% of **1a** was recovered.[15] [e] with (*R*)-**ECNU-phos**; 6% of **1c** was recovered.[15] [f] The reaction was carried out in 35 °C. [g] with (*R*)-**ECNU-phos**.[15] [h] The reaction was carried out for 26 h. [i] with (*R*)-**ECNU-phos**; 10% of **1m** was recovered. [15]

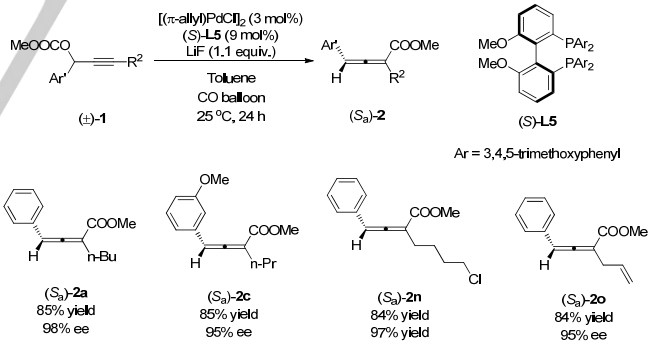
Table 4. Substrate scope of enatioenriched allenoates synthesis from racemic 1-alkyl-substuituted propargylic carbonates (±)-**1**[a]



Ar = 3,4,5-trimethoxyphenyl

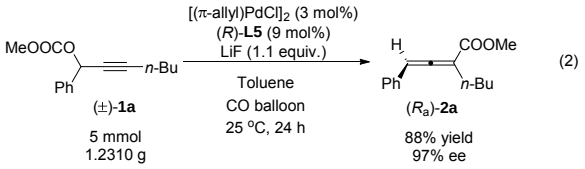
Entry	(±)-1		Yield of (R_a)-2 [b]	ee of (R_a)-2 [c]	Recovery of (±)-1 [d]
	R^1	R^2			
1	Me	*i*-Pr (**1q**)	23 (**2q**)	92	66
2	Me	*n*-Bu (**1r**)	31 (**2r**)	91	54
3	Me	*n*-C_6H_{13}(**1s**)	24 (**2s**)	92	61
4	Et	*n*-Bu (**1t**)	38 (**2t**)	90	49
5	Et	*n*-C_8H_{17} (**1u**)	38 (**2u**)	90	60
5' [e]	Et	*n*-C_8H_{17} (**1u**)	52 (**2u**)	85	26
6 [f]	*n*-Bu	*n*-Pr (**1v**)	25 (**2v**)	92	66
6' [e]	*n*-Bu	*n*-Pr (**1v**)	51 (**2v**)	84	21
7 [f]	*n*-Bu	*n*-C_7H_{15} (**1w**)	27 (**2w**)	90	67
7' [e]	*n*-Bu	*n*-C_7H_{15} (**1w**)	52 (**2w**)	84	18
8 [f]	*n*-C_6H_{13}	*n*-Bu (**1x**)	24 (**2x**)	91	65
8' [e]	*n*-C_6H_{13}	*n*-Bu (**1x**)	54 (**2x**)	83	15
9 [f]	*n*-C_6H_{13}	*n*-C_8H_{17} (**1y**)	27 (**2y**)	93	58
9' [e]	*n*-C_6H_{13}	*n*-C_8H_{17} (**1y**)	50 (**2y**)	84	22
10 [f]	*n*-$C_{11}H_{23}$	*n*-Pr (**1z**)	35 (**2z**)	90	56
10' [e]	*n*-$C_{11}H_{23}$	*n*-Pr (**1z**)	54 (**2z**)	84	15

[a] Reaction conditions : (±)-**1** (1.0 mmol), [(π-allyl)PdCl]$_2$ (2 mol%), (*R*)-**L5** (8 mol%) and LiF (1.1 equiv.) at 25 °C in toluene (5.0 mL) under 1 atm of CO unless otherwise noted. [b] Isolated yield. [c] ee values of 2,3-allenoates were determined by HPLC. [d] Determined by ^{1}H NMR analysis using 1,3,5-trimethylbenzene as the internal standard. [e] The reaction was carried out with (*R*)-**ECNU-phos**. [f] The reactions were carried out at 20 °C, data for reactions carried out at 25 °C are available in supporting information.

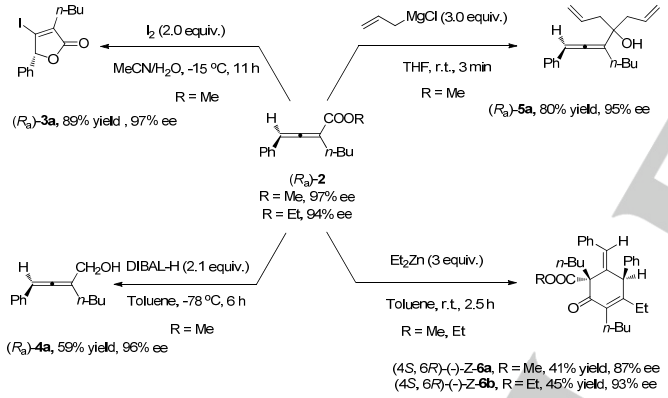


Scheme 3. (*S*)-3,4,5-(MeO)$_3$-MeOBIPHEP accelerated Pd-catalyzed methoxycarbonylation

The practicality was demonstrated by applying 5 mmol of (±)-**1a**, affording (R_a)-**2a** in 88% yield and 97% ee with the standard catalytic formula (eq. 2).



As a class of very useful compounds in organic synthesis, the 2,3-allenoates may be easily transformed into other versatile chemicals with high ee (Scheme 4): treated with I_2 at -15 °C, the lactone (R_a)-**3a** could be afforded in 89% yield with 97% ee; in the presence of DIBAL-H, (R_a)-**2a** may be transferred into trisubstituted 2,3-allenol (R_a)-**4a** with 96% ee, which is the versatile starting materials for halides, mesylates, tosylates, amines, thiols, etc.;[17] (R_a)-**2a** may also undergo 1,2-addition reaction with allyl magnesium chloride,[18] furnishing the chiral tertiary *α*-allenols (R_a)-**5a** in 80% yield and 95% ee; reactions of 2,3-allenoates with organozinc compounds is an efficient access to 5-benzylidenecyclohex-2-enones through double Michael addition/cyclization:[19] after stirring for 2.5 h at room temperature, (4*S*,6*R*)-(–)-*Z*-**6a** can be afforded with 87% ee, interestingly utilizing the ethyl ester led to a much higher chirality transfer efficiency, furnishing (4*S*, 6*R*)-(–)-*Z*-**6b** with 93% ee.



Scheme 4. Synthetic applications of 2,3-allenoate (R_a)-**2**

In summary, we have succeeded in establishing a chiral catalyst system consisting of [(π-allyl)PdCl]$_2$ and (*R*) or (*S*)-3,4,5-(MeO)$_3$-MeOBIPHEP that facilitates the Pd-catalyzed highly enantioselective alkoxycarbonylation of readily available racemic propargylic carbonates, affording the optically active 2,3-allenoates with 90–98% ee. Further studies in this area are being conducted in our laboratory.

Experimental Section

To a flame-dried Schlenk flask (100 mL) were added [(π-allyl)PdCl]$_2$ (56.1 mg, 0.15 mmol) and (*R*)-**L5** (438.2 mg, 0.45 mmol). After addition of each chemical, the flask was degassed and refilled with argon for three times to ensure the complete exclusion of air. Then freshly distilled toluene (15 mL) was added under argon. The resulting mixture was stirred for 1 hour at room temperature, which was followed by the addition of anhydrous LiF (143.3 mg, 5.5 mmol) (kept in a glove box) and (±)-**1a** (1.2310 g, 5.0 mmol)/toluene (10 mL) sequentially. The mixture was then frozen with a liquid nitrogen bath, degassed to remove the argon inside completely, and refilled with CO by a balloon of CO for three times. Then the solution was stirred at 25 °C for 24 h. After that, the mixture was diluted with Et_2O (25 mL), washed with brine (20 mL), and dried over anhydrous Na_2SO_4. The resulting mixture was filtered through a short column silica gel (5.0 cm) eluted with Et_2O (50 mL), and concentrated. The residue was purified by column chromatography on silica gel to afford (R_a)-**2a**[15] (1.0129 g, 88%) as an oil [eluent: petroleum ether (b.p. 60-90 °C)/ethyl ether = 250/1]: 97% ee (HPLC conditions: IC column, hexane/*i*-PrOH = 200/1, 0.5 mL/min, λ = 214 nm, t_R (minor) = 5.4 min, t_R (major) = 6.9 min); $[\alpha]^{23}_D$ = -47.4 (*c* = 1.04, $CHCl_3$) [93% ee, $[\alpha]^{21}_D$ = -47.3 (c = 1.15, $CHCl_3$)] [15]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38-7.22 (m, 5 H, Ar-H), 6.53 (t, *J* = 2.8 Hz, 1 H, =CH), 3.74 (s, 3 H, CH_3), 2.45-2.29 (m, 2 H, CH_2), 1.53-1.32 (m, 4 H, 2 x CH_2), 0.89 (t, *J* = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.1, 167.2, 132.5, 128.8, 127.7, 127.2, 104.3, 98.3, 52.2, 30.2, 28.6, 22.3, 13.8.

Acknowledgements

Financial support from National Natural Science Foundation of China (grant No.21690063) are greatly appreciated.

Keywords: alkoxycarbonylation • allenoates • enatioselective catalysis • palladium • propargylic carbonates

[1] For selected reviews, see: (a) N. Krause, A. S. K. Hashimi, *Modern Allene Chemistry*, *Vol. 1*, Wiley-VCH, Weinheim, 2004; (b) A. S. K. Hashmi, *Angew. Chem.* **2000**, *112*, 3737-3740; *Angew. Chem. Int. Ed.* **2000**, *39*, 3590-3593; (c) R. Zimmer, C. U. Dinesh, E. Nandanan, F. A. Khan, *Chem. Rev.* **2000**, *100*, 3067-3125; (d) J. A. Marshall, *Chem. Rev*. **2000**, *100*, 3163-3185; (e) R. W. Bates, V. Satcharoen, *Chem. Soc. Rev*. **2002**, *31*, 12-21; (f) L. K. Sydnes, *Chem. Rev*. **2003**, *103*, 1133-1150; (g) M. Tius, *Acc. Chem. Res*. **2003**, *36*, 284-290; (h) S. Ma, *Acc. Chem. Res.* **2003**, *36*, 701-712; (i) L.-L. Wei, H. Xiong, R. P. Hsung, *Acc. Chem. Res.* **2003**, *36*, 773-782. (j) S. Ma, *Chem. Rev.* **2005**, *105*, 2829-2871; (k) S. Ma, *Aldrichim. Acta* **2007**, *40*, 91-102; (l) S. Ma, *Acc. Chem. Res*. **2009,** *42*, 1679-1688; (m) C. Aubert, L. Fensterbank, P. Garcia, M. Malacria, A. Simonneau, *Chem. Rev.* **2011**, *111*, 1954-1993; (n) S. Yu, S. Ma, *Angew. Chem.* **2012**, *124*, 3128-3167; *Angew. Chem. Int. Ed.* **2012**, *51*, 3074-3112; (o) J. Ye, S. Ma, *Acc. Chem. Res.* **2014**, *47*, 989-1000.

[2] For selected examples of using allenes as ligands or catalysts, see: (a) I. Sato, Y. Matsueda, K. Kadowaki, S. Yonekubo, T. Shibata, K. Soai, *Helv. Chim. Acta.* **2002**, *85*, 3383-3387; (b) S. Löhr, J. Averbeck, M. Schurmann, N. Krause, *Eur. J. Inorg. Chem.* **2008**, 552-556; (c) X. Pu, X. Qi, J. M. Ready, *J. Am. Chem. Soc.* **2009**, *131*, 10364-10365; (d) F. Cai, X. Pu, X. Qi, V. Lynch, A. Radha, J. M. Ready, *J. Am. Chem. Soc.* **2011**, *133*, 18066-18069; (e) A. Vanitcha, C. Damelincourt, G. Gontard, N. Vanthuyne, V. M. Mansuy, L. Fensterbank, *Chem. Commun.* **2016**, *52*, 6785-6788.

[3] For reviews on allenes in natural products and molecular materials, see: (a) A. Hoffmann-Röder, N. Krause, *Angew. Chem.* **2004**, *116*, 1216–1236; *Angew. Chem. Int. Ed.* **2004**, *43*, 1196-1216; (b) P. Rivera-Fuentes, F. Diederich, *Angew. Chem.* **2012,** *124*, 2872-2882; *Angew. Chem. Int. Ed.* **2012**, *51*, 2818-2828.

[4] For reviews on the synthesis of allenes, see: (a) A. Hoffmann-Röder, N. Krause, *Angew. Chem.* **2002**, *114*, 3057–3059; *Angew. Chem. Int. Ed.* **2002**, *41,* 2933-2935; (b) N. Krause, A. Hoffmann-Röder, *Tetrahedron* **2004**, *60*, 11671-11697; (c) G. B. Hammond, *ACS Symp. Ser.* **2005**, *911*, 204-215; (d) K. M. Brummond, J. E. DeForrest, *Synthesis* **2007**,

795-818; (e) M. Ogasawara, *Tetrahedron: Asymmetry* **2009**, *20*, 259-271; (f) S. Yu, S. Ma, *Chem. Commun.* **2011**, 5384-5418; (g) R. K. Neff, D. E. Frantz, *ACS Catal.* **2014**, *4*, 519-528; (h) J. Ye, S. Ma, *Org. Chem. Front.* **2014**, *1*, 1210-1224; (i) R. K. Neff, D. E. Frantz, *Tetrahedron* **2015**, *71*, 7-18.

[5] For selected examples for the synthesis of trisubstitued allenes, see: (a) Y. Matsumoto, M. Naito, Y. Uozumi, T. Hayashi, *J. Chem. Soc., Chem. Commun.* **1993**, 1468-1469; (b) Z. Wan, S. Nelson, *J. Am. Chem. Soc.* **2000**, *122*, 10470-10471; (c) B. D. Sherry, F. D. Toste, *J. Am. Chem. Soc.* **2004**, *126*, 15978-15979; (d) M. Ogasawara, A. Okada, S. Watanabe, L. Fan, K. Uetake, K. Nakajima, T. Takahashi, *Organometallics* **2007**, *26*, 5025-5029; (e) R. V. Kolakowski, M. Manpadi, Y. Zhang, T. J. Emge, L. Williams, *J. Am. Chem. Soc.* **2009**, *131*, 12910-12911; (f) W. Zhang, S. Zheng, N. Liu, J. B. Werness, I. A. Guzei, W. Tang, *J. Am. Chem. Soc.* **2010**, *132*, 3664-3665; (g) C. M. Sapu, J. E. Bäckvall, J. Deska, *Angew. Chem.* **2011**, *123*, 9905-9908; *Angew. Chem. Int. Ed.* **2011**, *50*, 9731-9734; (h) M. Yang, N. Yokokawa, H. Ohmiya, M. Sawamura, *Org. Lett.* **2012**, *14*, 816-819; (i) H. Li, D. Müller, L. Guénée, A. Alexakis, *Org. Lett.* **2012**, *14*, 5880-5883; (j) J. Dabrowski, F. Haeffner, A. Hoveyda, *Angew. Chem.* **2013**, *125*, 7848-7853; *Angew. Chem. Int. Ed.* **2013**, *52*, 7694-7699; (k) M. Wang, Z. Liu, X. Zhang, P. Tian, Y. Xu, T.-P. Loh, *J. Am. Chem. Soc.* **2015**, *137*, 14830-14833; (l) Y. Liu, X. Liu, H. Hu, J. Guo, Y. Xia, L. Lin, X. Feng, *Angew. Chem.* **2016**, *128*, 4122-4126; *Angew. Chem. Int. Ed.* **2016**, *55*, 4054-4058; (m) Q. Yao, Y. Liao, Y. Lin, X. Lin, J. Ji, X. Liu, X. Feng, *Angew. Chem.* **2016**, *128*, 1891-1895; *Angew. Chem. Int. Ed.* **2016**, *55*, 1859-1863; (n) W.-D. Chu, L. Zhang, Z. Zhang, Q. Zhou, F. Mo, Y. Zhang, J. Wang, *J. Am. Chem. Soc.* **2016**, *138*, 14558-14561.

[6] J. Yu, W. Chen, L. Gong, *Org. Lett.* **2010**, *12*, 4050-4053.

[7] T. Inokuma, M. Furukawa, T. Suzuki, T. Kimachi, Y. Kobayashi, Y. Takemoto, *ChemCatChem.* **2012**, *4*, 983-985.

[8] K. Kobayashi, H. Naka, A. E. H. Wheatley, Y. Kondo, *Org. Lett.* **2008**, *10*, 3375-3377.

[9] (a) J. A. Marshall, M. A. Wolf, *J. Org. Chem.* **1996**, *61*, 3238-3239; (b) J. A. Marshall, G. S. Bartley, E. M. Wallace, *J. Org. Chem.* **1996**, *61*, 5729-5735; (c) J. A. Marshall, M. A. Wolf, E. M. Wallace, *J. Org. Chem.* **1997**, *62*, 367-371; (d) Y. Wang, S. Ma, *Adv. Synth. Catal.* **2013**, *355*, 741-750; (e) Y. Wang, W. Zhang, S. Ma, *Org. Chem. Front.* **2014**, *1*, 807-811.

[10] (a) J. Yamazaki, T. Watanabe, K. Tanaka, *Tetrahedron: Asymmetry* **2001**, *12*, 669-675; (b) C. Li, X. Sun, Q. Jing, Y. Tang, *Chem. Commun.* **2006**, 2980-2982; (c) C. Li, X. Wang, X. Sun, Y. Tang, J. Zheng, Z. Xu, Y. Zhou, L. Dai, *J. Am. Chem. Soc.* **2007**, *129*, 1494-1495.

[11] I. T. Crouch, R. K. Neff, D. E. Frantz, *J. Am. Chem. Soc.* **2013**, *135*, 4970-4973.

[12] H. Qian, X. Yu, J. Zhang, J. Sun, *J. Am. Chem. Soc.* **2013**, *135*, 18020-18023.

[13] Y. Tang, Q. Chen, X. Liu, G. Wang, L. Lin, X. Feng, *Angew. Chem.* **2015**, *127*, 9648 –9652; *Angew. Chem. Int. Ed.* **2015**, *54*, 9512-9516.

[14] Y. Wei, W. Zhao, Y. Yang, Z. Zhang, M. Shi, *ChemCatChem.* **2015**, *7*, 3340-3349.

[15] Y. Wang, W. Zhang, S. Ma, *J. Am. Chem. Soc.* **2013**, *135*, 11517-11520.

[16] Recent price per gram according to J&K Chemicals: $[(\pi\text{-allyl})PdCl]_2$ vs. $[(\pi\text{-cinnamyl})PdCl]_2$ = 784:1257 (in CNY).

[17] J. Ye, W. Fan, S. Ma, *Chem. Eur. J.* **2013**, *19*, 716-720.

[18] B. Chen, Z. Lu, G. Chai, C. Fu, S. Ma, *J. Org. Chem.* **2008**, *73*, 9486-9489.

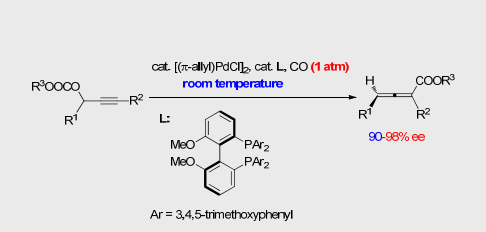
[19] Z. Lu, G. Chai, S. Ma, *Angew. Chem.* **2008**, *120*, 6134–6137; *Angew. Chem. Int. Ed.* **2008**, *47*, 6045-6048.

10.1002/chem.201701194

WILEY-VCH

COMMUNICATION

A catalytic highly enantioselective synthesis of 2,3-allenoates from easily available racemic propargylic carbonates utilizing (*R*)- or (*S*)-3,4,5-$(MeO)_3$-MeOBIPHEP and Pd has been developed, obtaining optically active allenoates with 90-98% ee and decent yields.



*Wanli Zhang and Shengming Ma**

Page No. – Page No.

Palladium-Catalyzed Enantioselective Alkoxycarbonylation of Propargylic Carbonates with (*R*)- or (*S*)-3,4,5-$(MeO)_3$-MeOBIPHEP