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Highly Regio- and Enantioselective Alkoxycarbonylative Amination of Terminal Allenes Catalyzed by a Spiroketal-Based Diphosphine/Pd(II) Complex

Jiawang Liu,[†] Zhaobin Han,[†] Xiaoming Wang,[†] Zheng Wang,*[,†] and Kuiling Ding*[,†,‡]

[†]State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China

[‡]Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300071, China

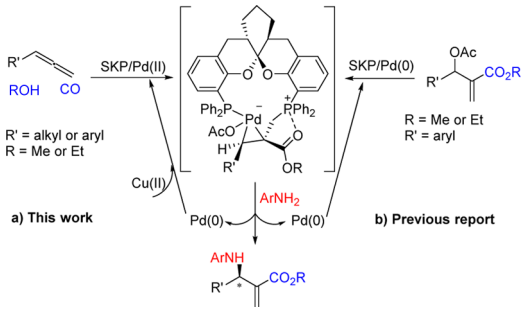
Supporting Information

ABSTRACT: An enantioselective alkoxycarbonylation−amination cascade process of terminal allenes with CO, methanol, and arylamines has been developed. It proceeds under mild conditions (room temperature, ambient pressure CO) via oxidative Pd(II) catalysis using an aromatic spiroketal-based diphosphine (SKP) as a chiral ligand and a Cu(II) salt as an oxidant and affords a wide range of α-methylene-β-arylamino acid esters (36 examples) in good yields with excellent enantioselectivity (up to 96% ee) and high regioselectivity (branched/linear > 92:8). Preliminary mechanistic studies suggested that the reaction is likely to proceed through alkoxycarbonylpalladation of the allene followed by an amination process. The synthetic utility of the protocol is showcased in the asymmetric construction of a cycloheptene-fused chiral β-lactam.

Allenes have been recognized as versatile building blocks in organic synthesis,[1] enabling numerous efficient transformations for rapid generation of molecular complexity.[2] The unique reactivity of the 1,2-diene structure renders allenes excellent flexibility to perform multicomponent or tandem reactions, providing elegant access to multifunctional molecules from readily available chemicals.[3] In this context, a typical mode for transition-metal-catalyzed allene transformation involves insertion into an R−M bond (hydrido−, carbo−, acyl−, or elemento−M in nature) to generate a transient π-allyl−M species that is trapped by an external or internal nucleophile, furnishing various functionalized olefins or cyclic compounds.[2,3] In the past two decades, this powerful strategy has been successfully extended to enantioselective functionalization of allenes[4] via asymmetric Pd,[5] Rh,[6] or Ni[7] catalysis. Despite the remarkable progress, however, significant challenges still remain in controlling the chemo-, regio-, and enantioselectivity, as multiple reactivities can be invoked on the two orthogonal cumulated C=C bonds in the catalysis.[2,3a,4,8] From a synthetic perspective, the development of new enantioselective tandem processes for allene functionalization that can selectively combine several compounds in one pot is highly desired[9] and holds promise for the rapid construction of chiral complex molecules without arduous and wasteful intermediate isolation in multistep syntheses. Herein we report the first regio- and enantioselective difunctionalization of simple terminal allenes with CO, methanol, and arylamines via a spiroketal-based diphosphine (SKP)/Pd(II)-catalyzed tandem alkoxycarbonylative amination process.

We recently reported a Pd(0)-catalyzed asymmetric allylic amination of racemic Morita−Baylis−Hillman (MBH) adducts wherein an aromatic SKP ligand[10] demonstrated excellent control of the regio- and enantioselectivity.[11] Mechanistic studies revealed that the SKP ligand plays a bifunctional role in the catalysis, forming a C−P σ bond with the terminal carbon of the allyl moiety and concomitantly coordinating with Pd in the key catalytic species (Scheme 1b).[12] We envisaged that such a phosphonium−Pd(II) species might be generated via an alternative route, i.e., by alkoxycarbonylpalladation of allenes with CO and alcohol as an acylating agent via oxidative Pd(II) catalysis (Scheme 1a).[13] This would effectively steer the course of the catalysis through the same key Pd species, allowing for more straightforward access to chiral α-methylene-β-arylamino acid esters[14] by obviating the tedious synthesis of MBH adducts. Although some studies have exploited Pd(II)-catalyzed oxidative carbonylation[15] of allenes to generate 2-alkoxycarbonyl π-allylpalladium species in harness with attack by a nucleophile,[16] to our knowledge no asymmetric variant has been reported to date.

Scheme 1. Reaction Design



Initial studies were focused on examining the feasibility of the strategy and optimizing the reaction conditions using 1-phenylallene (**1a**) and aniline (**2a**) as model substrates. The

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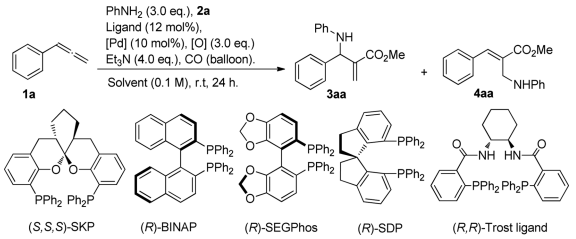
reactions were generally run at room temperature for 24 h under balloon pressure of CO in MeOH or MeOH-containing solvent with a Pd(II) salt (10 mol %) and a chiral diphosphine (12 mol %) as the catalyst and Et_3N (4.0 equiv) as the base. As shown in Table 1, the reaction catalyzed by $PdCl_2$/(*S*,*S*,*S*)-SKP in methanol gave the branched regioisomer **3aa** in only 7% yield in 24 h (entry 1), probably because of the absence of a stoichiometric oxidant necessary for regeneration of Pd(II) from the Pd(0) species formed in the amination step. Introduction of 3.0 equiv of $CuCl_2$ as an oxidant led to an increased yield of **3aa** (19%), albeit with a poor branched/linear (B/L) (**3aa**/**4aa**) ratio and ee (entry 2). $Cu(OAc)_2$ proved to be superior to $CuCl_2$ in this reaction, preferentially affording the branched product **3aa** in 52% yield with 74% ee (entry 3). Presumably, partial exchange of the acetate with the chloride in $PdCl_2$ gave coordinated acetate anions, which can serve as an internal base to facilitate the formation of a palladium alkoxide intermediate.[13a] Indeed, the beneficial effect of acetate was further corroborated with the use of $Pd(OAc)_2$ as the Pd(II) source, whereby **3aa** was obtained in significantly enhanced yield (73%) with 89% ee and 95:5 B/L selectivity (entry 4). After an extensive screening of reaction parameters (solvent, CO pressure, base, terminal oxidant, temperature, Pd precursor, etc.; for details, see Tables S1–S9), a 9:1 (v/v) MeOH/PhF solvent mixture was identified to be optimal, giving **3aa** in 89% yield with 92% ee and 96:4 B/L ratio (entry 5). This is in sharp contrast to the Pd(0)/SKP-catalyzed asymmetric allylic amination of MBH acetates,[11] wherein CH_2Cl_2 was optimal but MeOH was poor for catalysis. This distinction clearly indicated that different mechanistic details are present in the Pd(0)/SKP and Pd(II)/SKP routes to **3aa**/**4aa**, as also reflected by the need for a high MeOH concentration in the present catalysis (for catalyst activation). Further prolonging the reaction time from 24 to 40 h resulted in a slight improvement in the yield of **3aa** (entry 6), and this set of conditions was identified as conditions A in subsequent studies. Several other privileged chiral diphosphine ligands[17] were also evaluated in the catalysis, but unfortunately, all of them afforded less satisfactory results (entries 7–10). Some SKP ligands with different PAr_2 moieties were also found to be workable in the catalysis, but none showed significant improvement in activity or selectivities (Table S8). The use of 3.0 equiv of copper propionate [$Cu(OCOEt)_2$] as the oxidant at a reduced loading of SKP/$Pd(OAc)_2$ (5 mol %) afforded **3aa** in moderate yield (71%; entry 11), and extending the reaction time to 96 h afforded **3aa** in 87% yield with a 96:4 B/L ratio and 94% ee (entry 12, defined as conditions B).

The substrate scope of allenes for the SKP/$Pd(OAc)_2$-catalyzed reaction was first examined using **2a** as the nucleophile. In most cases, the reactions were conducted under conditions B, and the results are summarized in Table 2. The reaction appears to be quite compatible with various types of terminal allenes (**1a**–**p**), consistently affording the corresponding allylic amine products **3aa**–**pa** in good to excellent yields (up to 93%) with high B/L regioselectivities (>93:7) and excellent enantioselec-

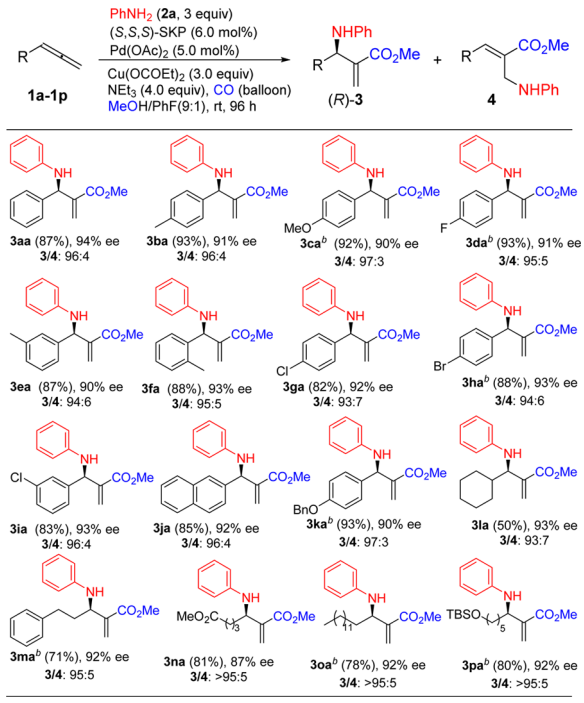
Table 1. Methoxycarbonylative Amination of 1-Phenylallene (1a) with Aniline (2a), CO, and MeOH[a]



entry	[Pd]/ligand	[O]	3aa/4aa[b]	yield (%)[c]	ee (%)[d]
1[e]	$PdCl_2$/(*S*,*S*,*S*)-SKP	none	36:64	7	N.D.
2[e]	$PdCl_2$/(*S*,*S*,*S*)-SKP	$CuCl_2$	50:50	19	40
3[e]	$PdCl_2$/(*S*,*S*,*S*)-SKP	$Cu(OAc)_2$	81:19	52	74
4[e]	$Pd(OAc)_2$/(*S*,*S*,*S*)-SKP	$Cu(OAc)_2$	95:5	73	89
5	$Pd(OAc)_2$/(*S*,*S*,*S*)-SKP	$Cu(OAc)_2$	96:4	89	92
6[f]	$Pd(OAc)_2$/(*S*,*S*,*S*)-SKP	$Cu(OAc)_2$	96:4	93	93
7	$Pd(OAc)_2$/(*R*)-BINAP	$Cu(OAc)_2$	64:36	54	3
8	$Pd(OAc)_2$/(*R*)-SEGPhos	$Cu(OAc)_2$	79:21	68	49
9	$Pd(OAc)_2$/(*R*)-SDP	$Cu(OAc)_2$	24:76	5	5
10	$Pd(OAc)_2$/Trost ligand	$Cu(OAc)_2$	72:28	<5	37
11[g]	$Pd(OAc)_2$/(*S*,*S*,*S*)-SKP	$Cu(OCOEt)_2$	95:5	71	92
12[g,h]	$Pd(OAc)_2$/(*S*,*S*,*S*)-SKP	$Cu(OCOEt)_2$	96:4	87	94

[a]Unless otherwise noted, all reactions were performed under 1 atm CO at rt for 24 h in the presence of **1a** (0.25 mmol), **2a** (0.75 mmol), [Pd] (10 mol %), ligand (12 mol %), Cu(II) salt (0.75 mmol), and Et_3N (1.0 mmol) in 9:1 (v/v) MeOH/PhF (2.5 mL). [b]Determined by ^1H NMR analysis. [c]Yields of isolated **3aa**. [d]Determined by chiral HPLC. [e]Methanol (2.5 mL) was used as the solvent. [f]40 h. [g][Pd] (5 mol %), SKP (6 mol %). [h]96 h.

Table 2. Substrate Scope of Allenes[a]



[a]Unless otherwise noted, the reactions were performed under conditions B. Data in parentheses are the yields of isolated **3**. In each case, the branched/linear (**3**/**4**) ratio was determined by ^1H NMR analysis of the crude product, while the ee value for **3** was determined by chiral HPLC. [b]Reactions were conducted under conditions A.

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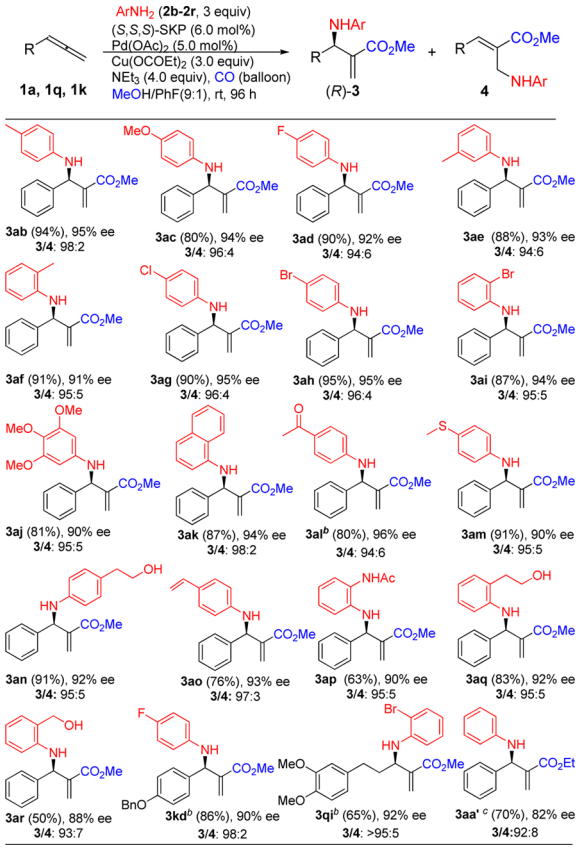
tivities (87−94% ee) irrespective of whether an aromatic (**1a−k**) or aliphatic (**1l−p**) substituent is tethered to the terminus of the allene. Allenes bearing alkyl substituents at the ortho, meta, or para position of the phenyl terminus gave the corresponding products (**3ba**, **3ea**, **3fa**) in similar yields and selectivities, and functional groups such as *tert*-butyldimethylsilyloxy (TBSO) (**3pa**) and halides (**3da**, **3ga**, **3ha**, **3ia**) were well-tolerated in the catalysis. It is noteworthy that the present SKP/Pd(II)-catalyzed process effectively overcomes some intrinsic limitations of the aforementioned SKP/Pd(0)-catalyzed allylic amination route to products **3**, wherein the presence of both 1-aryl and 2-CO_2Et groups in the allylic acetate substrate was found to be crucial for the reactivity and hence the products were confined to **3** bearing a β-aryl group.[11,12] Finally, the absolute configuration of **3ha** was established to be *R* by single-crystal X-ray diffraction analysis.

A survey of various arylamines (**2a−r**) in the reactions with several terminal allenes (**1a**, **1k**, and **1q**), CO, and MeOH was also performed (Table 3). Substituents on the arylamines seemed to have no impact on the SKP/Pd$(OAc)_2$ catalysis, as both electron-rich and electron-poor arylamines were compatible with the procedure, and a broad functional group tolerance was observed in the reaction. The reactions of arylamines bearing F, Cl, Br, acyl, MeO, MeS, hydroxyalkyl, or vinyl substituents proceeded smoothly under conditions B or A, providing the corresponding products **3ab−ar**, **3qi**, and **3aa′** in good yields (up to 95%) with high B/L ratios (>92:8) and excellent ee values (up to 96%). Notably, product **3kd** as a synthetic intermediate for the chiral drug ezetimibe was obtained in good yield with high regioselectivity (98:2) and enantioselectivity (90% ee) using conditions A. Preliminary studies on reactions involving other types of amines and allenes afforded less satisfactory results (see the Supporting Information (SI)), suggesting a large space for future development.

The synthetic utility of the methodology was exemplified in the asymmetric construction of **9**, a useful cycloheptene-fused chiral β-lactam.[18] As shown in Scheme 2, (*R*)-**3pa**, obtained in 80% yield with 92% ee from a gram-scale synthesis using the present protocol (see the SI), was treated with $Sn[N(SiMe_3)_2]_2$ to give silyl-protected β-lactam **5**. Deprotection of **5** using tetrabutylammonium fluoride (TBAF) afforded alcohol **6**, which upon Swern oxidation furnished aldehyde **7**. Wittig methylenation afforded β-lactam **8** with two terminal alkene groups, which underwent ring-closing metathesis with the second-generation Grubbs catalyst[19] to give β-lactam **9** in an overall yield of 50% over five steps with 93% ee.

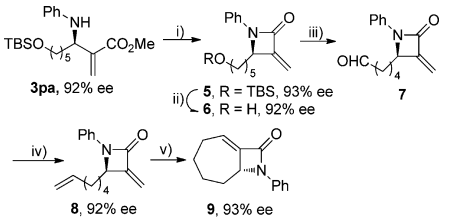
While the exact mechanism of the title catalysis is not clear at this stage, the results from a series of comparative studies (for details, see the SI) seem to be consistent with the proposed catalytic cycle shown in Scheme 3. Herein the catalysis is likely to be initiated by *trans*-[(SKP)(AcO)Pd−COOMe] species **B** generated via exchange of OAc in [(SKP)Pd$(OAc)_2$] (**A**) with a methoxy group followed by carbonyl insertion. Methoxycarbonylpalladation of allene **1a** by intermediate **B** followed by intramolecular rearrangement would give phosphonium−Pd(II) species **C**, which is the same key intermediate as in the mechanism for SKP/Pd(0)-catalyzed allylic amination of MBH acetates reported previously by our group.[12] The subsequent ligand exchange of intermediate **C** with the amido from aniline is expected to be fast under basic conditions, affording amido−Pd(II) species **D**. Reductive elimination of **D** followed by intramolecular Pd-assisted phosphonium dissociation would then furnish the product **3aa**, with concomitant release of (SKP)Pd(0) species **E**. Oxidation of **E** by a Cu(II) salt regenerates the active Pd(II) species **A**, thus accomplishing the catalytic cycle. It is noteworthy that there are clear distinctions between the courses to intermediate **C** for the SKP/Pd(II)-catalyzed methoxycarbonylative amination of allenes and the SKP/Pd(0)-catalyzed allylic amination of MBH acetates. Control experiments using a Hg(0) test suggested that Pd(0) reoxidation tends to be sluggish in the catalytic cycle and that a

Table 3. Substrate Scope of Arylamines[a]



[a]Unless otherwise noted, the reactions were performed under conditions B. Data in parentheses are the yields of isolated **3**. In each case, the branched/linear (**3**/**4**) ratio was determined by ^1H NMR analysis of the crude product, while the ee value for **3** was determined by chiral HPLC. [b]Reactions were conducted under conditions A. [c]The reaction was conducted under conditions B using EtOH instead of MeOH.

Scheme 2. Synthetic Transformation of (*R*)-3pa into β-Lactam 9[a]



[a]Reagents and conditions: (i) $Sn[N(SiMe_3)_2]_2$, toluene, reflux, 12 h, 93%; (ii) *n*-Bu_4NF, 0 °C to rt, 6 h, 95%; (iii) SO_3·Pyr, DMSO, NEt_3, CH_2Cl_2, 0 °C to rt, 8 h, 88%; (iv) Ph_3PMeBr, *n*-BuLi, THF, 0 °C to rt, 10 h, 80%; (v) second-generation Grubbs catalyst, *n*-hexane, 55 °C, 6 h, 79%.

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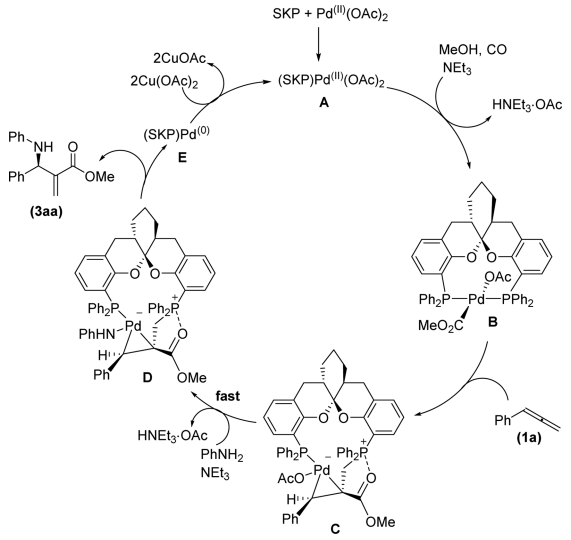
Scheme 3. A Plausible Mechanism



significant fraction of Pd species lie dormant as Pd(0) in the system, which may account for the relatively high catalyst loading needed in the Pd(II) catalysis.

In conclusion, we have developed the first highly chemo-, regio-, and enantioselective alkoxycarbonylation−amination cascade process of terminal allenes with arylamines, carbon monoxide, and methanol via oxidative SKP/Pd(II) catalysis with a Cu(II) salt as the oxidant, affording a range of β-arylamine-α-methylenecarboxylic acid derivatives in good yields with excellent regio- and enantioselectivities (B/L > 92:8, up to 96% ee) with a broad substrate scope. Preliminary mechanistic studies suggested that the reaction is likely to proceed through alkoxylcarbonylpalladation of the allene followed by an amination process. The synthetic utility of the protocol is exemplified by the asymmetric construction of a cycloheptene-fused chiral β-lactam. We anticipate that the strategy of the present Pd-catalyzed cascade process may find wider applications in the efficient synthesis of multifunctional compounds starting from simple olefinic molecules.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b07764.

Synthetic procedures, characterization, and additional data (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*wzsioc@sioc.ac.cn

*kding@mail.sioc.ac.cn

Notes

The authors declare no competing financial interest.

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