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Asymmetric bifunctionalization of allenes with aryl iodides and amino acids enabled by chiral aldehyde/palladium combined catalysis†

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Even though catalytic asymmetric bifunctionalization of allenes has been extensively studied, almost all of the reported examples have been achieved in a two-component manner. In this study, we report a highly efficient asymmetric bifunctionalization of allenes with iodohydrocarbons and NH_2-unprotected amino acid esters. The adopted chiral aldehyde/palladium combined catalytic system precisely governs the chemoselectivity, regioselectivity, and stereoselectivity of this three-component reaction. A wide range of substituted aryl iodides, allenes and amino acid esters can well participate in this reaction and deliver structurally diverse α,α-disubstituted α-amino acid esters with excellent experimental outcomes. One of the resulting products is utilized for the total synthesis of the molecule (*S*,*R*)-VPC01091.

Introduction

Following Burton and Pechmann's significant synthesis of allene compounds in 1887,[1] allene swiftly emerged as a pivotal building block for the construction of allylic molecules due to its remarkable reactivity and versatile nature.[2–9] Subsequently, extensive efforts have been dedicated to the development of allene-involved hydrofunctionalization[10–18] and bifunctionalization[19–25] reactions, profoundly enriching the field of allene chemistry. However, the corresponding asymmetric functionalization of allenes was conspicuously absent at the close of the last century.[26] In particular, investigations into the catalytic asymmetric hydrofunctionalization of allenes commenced in 2003 with Trost and colleagues' disclosure of a palladium-catalyzed hydroalkylation reaction of alkoxylallenes with Meldrum's acids and azlactones.[27] Through this reaction modality, numerous asymmetric reactions for the synthesis of chiral allylic compounds, encompassing alcohols, amines, aldehydes, ketones, amino acids, and beyond, have been developed.[28–39]

The catalytic asymmetric bifunctionalization of allenes fully exploits the multiple reactivity offered by the adjacent C–C double bonds of allenes. Following the groundbreaking work on a palladium-catalyzed enantioselective carboannulation of allenes with *ortho*-substituted aryl halides as reported by Larock *et al.*,[40] this transformation has been extensively explored for the fabrication of intricately structured chiral molecules. However, the majority of these reactions have taken place in a two-component fashion through combining two of the required three reaction sites—namely, the allene, the halide, and the nucleophile—within a single substrate (Fig. 1a).[41–49] Undoubtedly, dispersing the three reaction sites among individual substrates, or in other words, developing a multicomponent reaction, could significantly expand the range of substrates amenable to this bifunctionalization reaction. In fact, as early as 1998, Hiroi *et al.* had realized this concept with a palladium-catalyzed asymmetric reaction involving racemic allene, iodobenzene, and malonate carbanion (Fig. 1b).[50,51] However, this work represented the sole successful example that can achieve the catalytic enantioselective bifunctionalization of allenes in a three-component manner. The complexity of regulating the reaction sequences, regioselectivity, and stereoselectivity has been a key factor contributing to this situation. Consequently, the creation of highly efficient multicomponent reactions involving an allene, an electrophile, and a nucleophile through asymmetric catalysis presents a captivating and challenging endeavor for synthetic chemists.

Drawing from the pioneering work unveiled by Hiroi,[50] and building on our investigation of the catalytic asymmetric allylation of NH_2-unprotected amino acids with various allylation reagents,[52,53] we envisioned a three-component reaction involving allenes, halohydrocarbons, and amino acid esters, facilitated by the synergy of chiral aldehyde/palladium combined catalysis (Fig. 1c).[54–56] This process would yield enantioenriched α,α-disubstituted nonproteinogenic amino acid derivatives with distinctive structures.[57–63] To our

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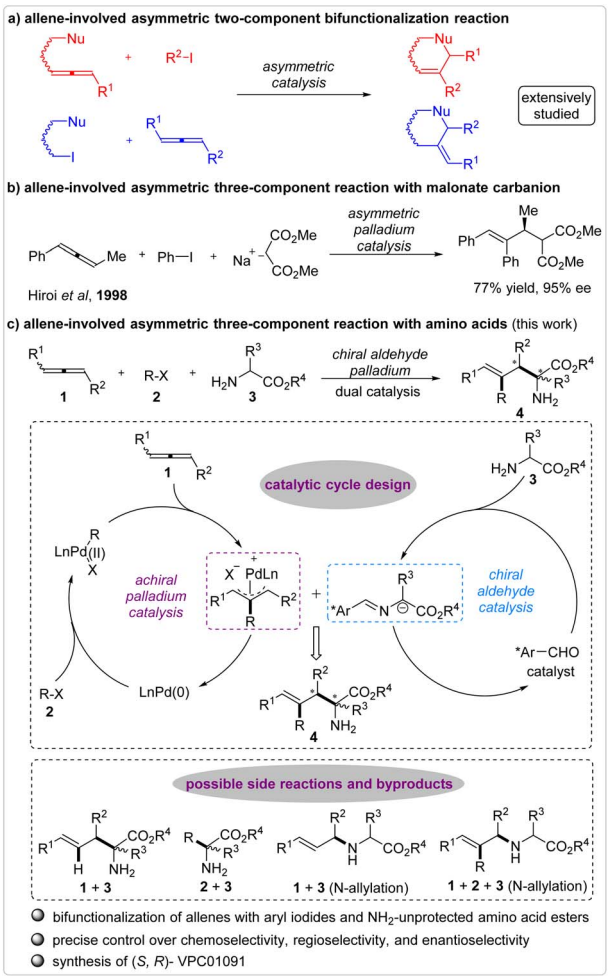


Fig. 1 The catalytic asymmetric bifunctionalization of allene.

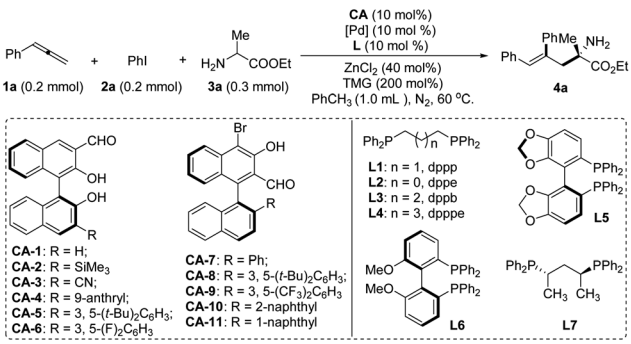
knowledge, the catalytic asymmetric bifunctionalization of allenes has never been employed for the construction of chiral amino acid derivatives. In our proposed reaction, the palladium catalytic cycle commences with the oxidation addition of Pd(0) to a halohydrocarbon, forming a weakly nucleophilic carbon–Pd(II) intermediate. Subsequent addition of this intermediate to an allene generates an active electrophilic π-allyl palladium species for the ensuing coupling process. The chiral aldehyde catalyst plays a pivotal role in the generation of nucleophilic carbanion intermediates from amino acid esters. However, significant challenges are evident in this reaction. Apart from the aforementioned complexities associated with controlling the reaction sequences, regioselectivity, and stereoselectivity, the chemoselectivity of N-allylation and C-allylation further complicates this reaction. Here, we documented our efforts to investigate this catalytic asymmetric three-component reaction, yielding a diverse range of optically active nonproteinogenic α-amino acid esters while precisely controlling the corresponding chemoselectivity, regioselectivity, and enantioselectivity. Furthermore, leveraging this methodology, one of the stereoisomer of VPC01091 was succinctly synthesized.

Results and discussion

Optimization of reaction conditions

Our investigation commenced with the assessment of the reaction involving allene **1a**, iodobenzene **2a**, and amino acid ester **3a**, under the influence of a combined catalytic system employing chiral aldehyde **CA-1** and palladium $Pd(PPh_3)_4$. The introduction of the Lewis acid $ZnCl_2$ and base TMG (1,1,3,3-tetramethylguanidine) expedited the processes of Schiff base formation and deprotonation. As anticipated, the desired product **4a** was yielded at an 83% yield and 81% ee. Encouraged by these outcomes, a comprehensive catalyst screening and optimization of reaction conditions were conducted. Chiral aldehyde catalyst screening revealed that **CA-1** and **CA-5** delivered comparable yields and enantioselectivities (Table 1, entries 1 and 5). With **CA-1** as the organocatalyst, a variety of achiral

Table 1 Optimization of reaction conditions[a]



Entry	CA	[Pd]	L	y^a (%)	ee^b (%)
1	**CA-1**	$Pd(PPh_3)_4$	**L1**	83	81
2	**CA-2**	$Pd(PPh_3)_4$	**L1**	39	28
3	**CA-3**	$Pd(PPh_3)_4$	**L1**	34	12
4	**CA-4**	$Pd(PPh_3)_4$	**L1**	71	20
5	**CA-5**	$Pd(PPh_3)_4$	**L1**	81	80
6	**CA-6**	$Pd(PPh_3)_4$	**L1**	74	68
7	**CA-7**	$Pd(PPh_3)_4$	**L1**	34	70
8	**CA-8**	$Pd(PPh_3)_4$	**L1**	19	95
9	**CA-9**	$Pd(PPh_3)_4$	**L1**	32	96
10	**CA-10**	$Pd(PPh_3)_4$	**L1**	28	89
11	**CA-11**	$Pd(PPh_3)_4$	**L1**	16	84
12	**CA-1**	$Pd(PPh_3)_4$	**L2**	24	62
13	**CA-1**	$Pd(PPh_3)_4$	**L3**	19	50
14	**CA-1**	$Pd(PPh_3)_4$	**L4**	10	32
15	**CA-1**	$Pd(PPh_3)_4$	**L5**	19	56
16	**CA-1**	$Pd(PPh_3)_4$	**L6**	34	34
17	**CA-1**	$Pd(PPh_3)_4$	**L7**	67	86
18	*ent*-**CA-1**	$Pd(PPh_3)_4$	**L7**	21	−29
19[c]	**CA-1**	$Pd(PPh_3)_4$	**L1**	70	90
20[c]	**CA-5**	$Pd(PPh_3)_4$	**L1**	80	90
21[c]	**CA-5**	$Pd(dppe)_2$	**L1**	52	84
22[c,d]	**CA-5**	$[Pd(C_3H_5)Cl]_2$	**L1**	93	89
23[c,d,e]	**CA-5**	$[Pd(C_3H_5)Cl]_2$	**L1**	83	90
24[c,d,e,f]	**CA-5**	$[Pd(C_3H_5)Cl]_2$	**L1**	89	90

[a] Yields of isolated products. [b] Determined by chiral HPLC. [c] Using TDMAIP as the base. [d] With 5 mol% palladium. [e] At 55 °C. [f] With 1.5 mL toluene. TDMAIP = tris(dimethylamino)iminophosphorane.

and chiral ligands for palladium catalysis was evaluated, establishing that the achiral ligand dppp produced optimal results (Table 1, entry 1). Subsequent assessments of Lewis acids and reaction solvents failed to yield improved experimental outcomes (see ESI†). Upon substituting the base TMG with TDMAIP, product **4a** was obtained with a 90% ee (Table 1, entry 19). To enhance the corresponding yields, chiral aldehyde catalysts were reassessed with the introduction of the base TDMAIP, revealing that the utilization of **CA-5** yielded product **4a** at an 80% yield and 90% ee (Table 1, entry 20). Additionally, palladium sources were scrutinized, with $[Pd(C_3H_5)Cl]_2$ yielding superior results compared to $Pd(PPh_3)_4$ (Table 1, entry 22). Lowering the reaction temperature and diluting the reactant concentration led to the production of product **4a** at an 89% yield and 90% ee (Table 1, entry 24). Based on these findings, the optimal reaction conditions for this three-component asymmetric reaction were determined.

The substrate scopes

After establishing the optimal reaction conditions, we proceeded to examine the substrate scope of this reaction. Initially, various amino acid esters were utilized as reaction partners with allene **1a** and iodobenzene **2a** (Fig. 2). The results indicated that amino acid esters containing saturated alkyls performed well in this reaction, yielding the corresponding products **4a–4e** with excellent yields and enantioselectivities. Ethyl esters generated from methionine and α-allyl α-amino acid also exhibited good reactivity in this reaction, producing products **4f** and **4g** with favorable experimental outcomes. Subsequently, phenylalanines, homophenylalanine, glutamic acid and lysine-derived amino acid esters were employed as reactants, all of which led to the formation of the respective products with good-to-excellent yields and excellent enantioselectivities (Fig. 2, **4h–4t**). Glycine ethyl ester could participate in this reaction, but no enantioselective bias was observed in the product (Fig. 2, **4u**).

Subsequently, a variety of aryl and alkenyl iodides were examined (Fig. 3a). Phenyl iodides comprising of *ortho*-, *meta*-, or *para*-substituted phenyl groups demonstrated good participation in this reaction, resulting in the corresponding products with good-to-excellent yields and high-to-excellent enantioselectivities (Fig. 3, **5a–5n**). Similar experimental outcomes were observed when phenyl iodides containing two substituents were utilized as reactants (Fig. 3, **5o–5t**). Other aryl iodides, such as 2-iodothiophene, 2-iodonaphthalene, and 2-iodo-9*H*-fluorene,

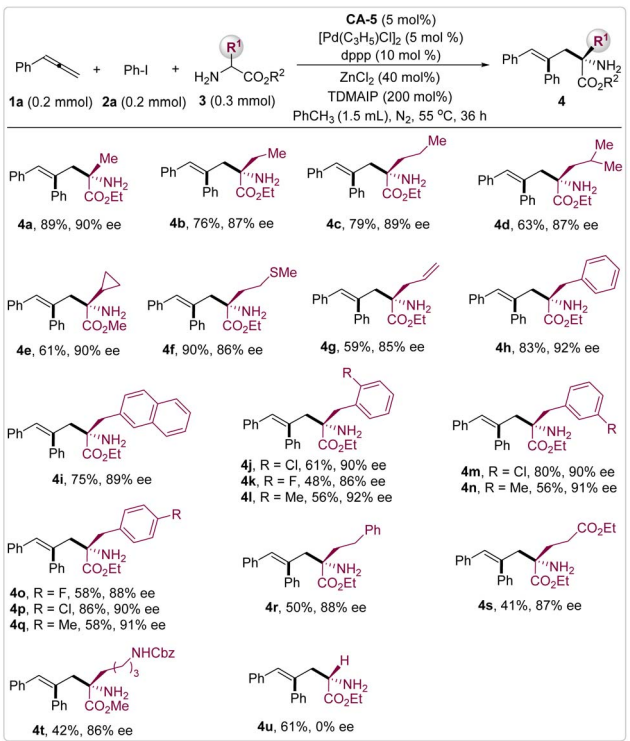


Fig. 2 Substrate scope of amino acid esters.

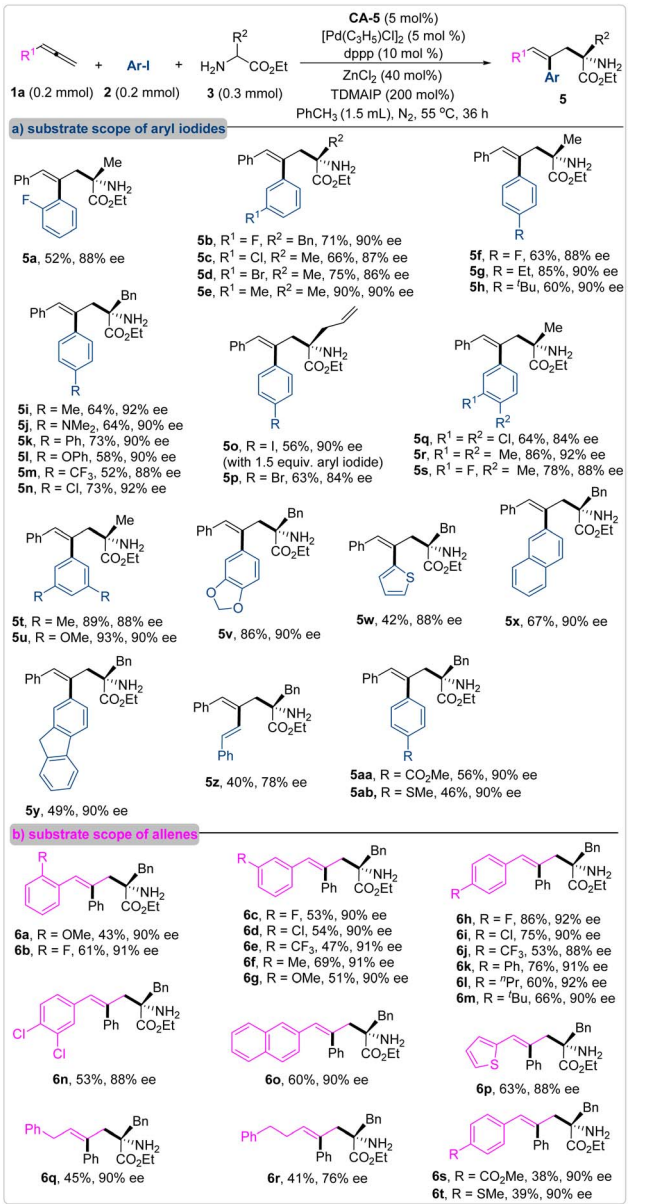


Fig. 3 Substrate scope of aryl iodides and allenes.

acted as good reaction partners with allene **1a** and phenylalanine ethyl ester **3b**, producing the corresponding products **5u–5w** with good yields and excellent enantioselectivities. The reactivity of alkenyl iodide substrates was also examined, however, low yield was observed. For instance, (*E*)-(2-iodovinyl) benzene could partake in this reaction but the corresponding product **5z** was only yielded in 40% with 78% ee. Aryl iodides bearing polar groups such as ester and thioether also exhibited good reactivity in this reaction, leading to products **5aa** and **5ab** in good yields and excellent enantioselectivities.

We then investigated the substrate scope of substituted allenes in reaction with iodobenzene **2a** and phenylalanine ethyl ester **3b** (Fig. 3b). Our findings indicated that allenes bearing substituted phenyl groups performed well in this reaction. For instance, all phenyl allenes containing *ortho*-, *meta*-, or *para*-substituents displayed good reactivity, producing the corresponding products **6a–6n** with good-to-excellent yields and excellent enantioselectivities. Positive experimental outcomes were also observed for 2-naphthyl- and 2-thienyl-substituted allenes (Fig. 3, **6o–6p**). In comparison, the reactivity of alkyl-substituted allenes notably decreased, with buta-2,3-dien-1-ylbenzene and penta-3,4-dien-1-ylbenzene generating the corresponding products in yields of 45% and 41%, respectively (Fig. 3, **6q** and **6r**). Additionally, the enantioselectivity produced by penta-3,4-dien-1-ylbenzene was lower than that of other allenes. Aryl-substituted allenes bearing polar groups including ester and thioether could participate in this reaction, giving products **6s** and **6t** in moderate yields and excellent enantioselectivities.

Mechanism studies

In order to determine the *E*/*Z* conformation of the C=C bond and the absolute configuration of the chiral carbon center, the product **4a** was transformed into the chiral oxazolinone **8** for the preparation of a single crystal (see the ESI†). The X-ray crystal analysis of **8** revealed that the alkene unit adopts a *Z*-conformation and the absolute configuration of the chiral carbon center is *S*. Consequently, the stereocenters of **4a** were deduced to be (*Z*,*S*). Considering the (*Z*,*S*) stereocenters induced by the combined chiral aldehyde/palladium catalytic system and our previous studies on the mechanism of the same catalytic system that enabled asymmetric allylation and benzylation reactions,[64,65] potential catalytic cycles and transition states were proposed as follows. Under the chiral aldehyde catalysis, the chiral aldehyde condensed with amino acid ester **3a** and then coordinated with Lewis acid $ZnCl_2$ to form the Zn-Schiff base complex **I**. Upon deprotonation by the base, this Schiff base converted into the active nucleophilic intermediate enolate **II**. In the palladium catalysis, iodobenzene **2a** underwent oxidative addition to generate the corresponding nucleophilic carbon-Pd(II) intermediate. Upon addition of this intermediate to allene **1a**, the active electrophilic π-allyl palladium species **III** was produced. Through a ligand exchange process, the enolate **II** and the π-allyl palladium **III** fused together to form the potential transition state **IV**, wherein the enolate provided its *si*-face to attack the π-allyl palladium species, leading to the formation of the Schiff base **V** and releasing Pd(0). The chiral aldehyde catalytic cycle concluded with the hydrolysis or amine exchange of the Schiff base **V** with **3a** (Fig. 4).

Synthetic applications

VPC01091 contains four stereoisomers and some of the them could be converted into the potent S1P3 antagonists and S1P1 receptor agonists.[66] The molecular structure of VPC01091 is characterized by a 1,3-disubstituted cyclopentanamine with nonadjacent quaternary–tertiary carbon centers. Several asymmetric synthetic routes have been developed for the synthesis of this compound.[67–70] Typically, compound **11** has been identified as one of the most commonly employed building blocks for the production of VPC01091, and the core five-membered carbon ring of **11** was typically constructed *via* olefin metathesis. Building upon this established synthetic strategy, as well as the three-component asymmetric allylation reaction we disclosed here, we hypothesized that the catalytic product **5o** could serve as a promising chiral building block for the synthesis of optically active (*S*,*R*)-VPC01091. Notably, the simultaneous introduction of an allylic unit and the establishment of a chiral quaternary carbon center allowed for the streamlining of the entire synthetic pathway.

With this idea in mind, we initiated an exploration of this novel synthetic pathway (Scheme 1). After protecting the amino group of **5o**, an olefin metathesis reaction was performed utilizing the second-generation Grubb's catalyst, resulting in the formation of iodine-substituted amino acid ester **10** with a total yield of 66% (two steps). Subsequently, the coupling reaction of compound **10** with octylboronic acid furnished product **11** with a high yield (80%). Then, the ester group and the C=C bonds of compound **11** were successively reduced, leading to the generation of the pivotal chiral building block **13** with favorable yields. Adhering to the established deprotecting strategy in literature,[70] the (*S*,*R*)-VPC01091 was successfully prepared. Notably, commencing from easily accessible starting materials, the total synthesis of (*S*,*R*)-VPC01091 was achieved within 7 steps, which represented the most concise synthesis

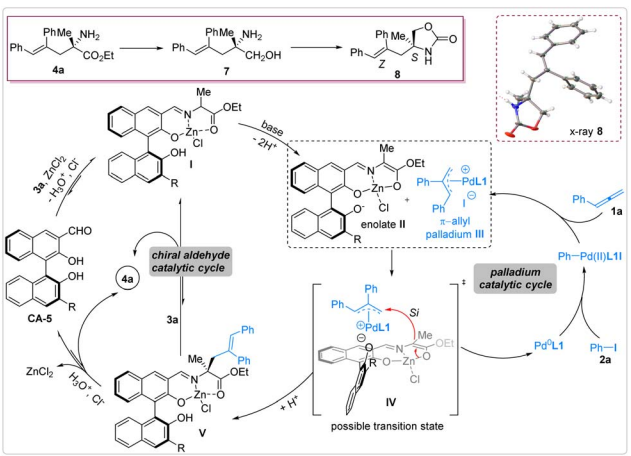
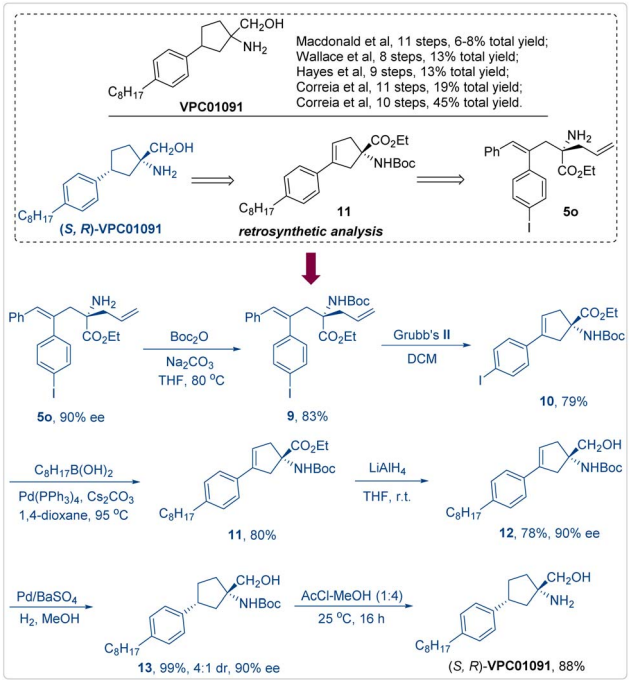


Fig. 4 Proposed catalytic cycles and transition state.



Scheme 1 The total synthesis of (*S*,*R*)-VPC01091.

route at present. Furthermore, by altering the absolute configuration of the chiral catalyst, the synthesis of other stereoisomers of VPC01091 is anticipated to be accomplished. The utilization of mild reaction conditions in this synthetic pathway rendered it favorable for a potential large-scale synthesis.

Conclusions

In conclusion, we have described a highly efficient catalytic asymmetric three-component reaction involving allenes, aryl iodides and NH_2-unprotected amino acid esters. The employed chiral aldehyde/palladium combining catalytic system precisely governed the chemoselectivity, regioselectivity and enantioselectivity. A wide range of allenes, aryl iodides and NH_2-unprotected amino acid esters could participate in this reaction well and afford corresponding optically active nonproteinogenic α-amino acid esters with exceptional experimental outcomes. A reasonable transition state was proposed to illustrate the observed stereoselective control results. This method could be used for the synthesis of the key chiral intermediate leading to a potential S1P3 antagonist and S1P1 receptor agonist.

Data availability

All data supporting the findings of this study are available within the article and its ESI† file.

Author contributions

W. W. and G. Q. X. conceived this project. Z. H.; W. Y. Y.; L. Z. X. and L. J. L. carried out the experiments. W. Z. L. and C. T. performed the HRMS analysis. G. Q. X. wrote the manuscript. All authors discussed the results.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1 B. S. Burton and H. v. Pechmann, *Ber. Dtsch. Chem. Ges.*, 1887, **20**, 145–149.
2 S. Yu and S. Ma, *Angew. Chem., Int. Ed.*, 2012, **51**, 3074–3112.
3 R. Blieck, M. Taillefer and F. Monnier, *Chem. Rev.*, 2020, **120**, 13545–13598.
4 P. Koschker and B. Breit, *Acc. Chem. Res.*, 2016, **49**, 1524–1536.
5 Y. Yamamoto, M. Al-Masum and N. Asao, *J. Am. Chem. Soc.*, 1994, **116**, 6019–6020.
6 B. M. Trost and D. L. Van Vranken, *Chem. Rev.*, 1996, **96**, 395–422.
7 J. F. Hartwig and L. M. Stanley, *Acc. Chem. Res.*, 2010, **43**, 1461–1475.
8 I. Shimizu and J. Tsuji, *Chem. Lett.*, 1984, **13**, 233–236.
9 B. M. Trost and M. L. Crawley, *Chem. Rev.*, 2003, **103**, 2921–2944.
10 B. M. Trost, J. Xie and J. D. Sieber, *J. Am. Chem. Soc.*, 2011, **133**, 20611–20622.
11 H. Zhou, Z. Wei, J. Zhang, H. Yang, C. Xia and G. Jiang, *Angew. Chem., Int. Ed.*, 2017, **56**, 1077–1081.
12 H. Zhou, Y. Wang, L. Zhang, M. Cai and S. Luo, *J. Am. Chem. Soc.*, 2017, **139**, 3631–3634.
13 Z. Yang and J. Wang, *Angew. Chem., Int. Ed.*, 2021, **60**, 27288–27292.
14 M. Zhu, Q. Zhang and W. Zi, *Angew. Chem., Int. Ed.*, 2021, **60**, 6545–6552.
15 W. Chai, B. Guo, Q. Zhang and W. Zi, *Chem. Catal.*, 2022, **2**, 1428–1439.
16 T. M. Beck and B. Breit, *Angew. Chem., Int. Ed.*, 2017, **56**, 1903–1907.
17 J. D. Osborne, H. E. Randell-Sly, G. S. Currie, A. R. Cowley and M. C. Willis, *J. Am. Chem. Soc.*, 2008, **130**, 17232–17233.
18 J.-L. Xu, Z.-Y. Xu, Z.-L. Wang, W.-W. Ma, X.-Y. Sun, Y. Fu and Y.-H. Xu, *J. Am. Chem. Soc.*, 2022, **144**, 5535–5542.
19 S. Ma, Z. Shi and S. Wu, *Tetrahedron: Asymmetry*, 2001, **12**, 193–195.
20 X. Xie and S. Ma, *Chem. Commun.*, 2013, **49**, 5693–5695.
21 M. Li, A. Hawkins, D. M. Barber, P. Bultinck, W. Herrebout and D. J. Dixon, *Chem. Commun.*, 2013, **49**, 5265–5267.
22 H. Luo, Z. Yang, W. Lin, Y. Zheng and S. Ma, *Chem. Sci.*, 2018, **9**, 1964–1969.

23 H. Li, I. Khan, Q. Li and Y. J. Zhang, *Org. Lett.*, 2022, **24**, 2081–2086.
24 Q.-W. Shen, W. Wen and Q.-X. Guo, *Org. Lett.*, 2023, **25**, 3163–3167.
25 S. Inuki, A. Iwata, S. Oishi, N. Fujii and H. Ohno, *J. Org. Chem.*, 2011, **76**, 2072–2083.
26 B. M. Trost, A. B. C. Simas, B. Plietker, C. Jäkel and J. Xie, *Chem.–Eur. J.*, 2005, **11**, 7075–7082.
27 B. M. Trost, C. Jäkel and B. Plietker, *J. Am. Chem. Soc.*, 2003, **125**, 4438–4439.
28 W. Lim, J. Kim and Y. H. Rhee, *J. Am. Chem. Soc.*, 2014, **136**, 13618–13621.
29 S. Ganss and B. Breit, *Angew. Chem., Int. Ed.*, 2016, **55**, 9738–9742.
30 P. Steib and B. Breit, *Angew. Chem., Int. Ed.*, 2018, **57**, 6572–6576.
31 H. Kim and Y. H. Rhee, *J. Am. Chem. Soc.*, 2012, **134**, 4011–4014.
32 H. Kim, W. Lim, D. Im, D.-g. Kim and Y. H. Rhee, *Angew. Chem., Int. Ed.*, 2012, **51**, 12055–12058.
33 S. H. Jang, H. W. Kim, W. Jeong, D. Moon and Y. H. Rhee, *Org. Lett.*, 2018, **20**, 1248–1251.
34 R. Zimmer, C. U. Dinesh, E. Nandanan and F. A. Khan, *Chem. Rev.*, 2000, **100**, 3067–3126.
35 G. Helmchen and A. Pfaltz, *Acc. Chem. Res.*, 2000, **33**, 336–345.
36 J. D. Weaver, A. Recio III, A. J. Grenning and J. A. Tunge, *Chem. Rev.*, 2011, **111**, 1846–1913.
37 S. Biswas, M. M. Parsutkar, S. M. Jing, V. V. Pagar, J. H. Herbort and T. V. RajanBabu, *Acc. Chem. Res.*, 2021, **54**, 4545–4564.
38 G. Li, X. Huo, X. Jiang and W. Zhang, *Chem. Soc. Rev.*, 2020, **49**, 2060–2118.
39 J. Le Bras and J. Muzart, *Chem. Soc. Rev.*, 2014, **43**, 3003–3040.
40 R. C. Larock, N. G. Berrios-Pena and C. A. Fried, *J. Org. Chem.*, 1991, **56**, 2615–2617.
41 J. M. Zenner and R. C. Larock, *J. Org. Chem.*, 1999, **64**, 7312–7322.
42 Q. Yang, X. Jiang and S. Ma, *Chem.–Eur. J.*, 2007, **13**, 9310–9316.
43 W. Shu, Q. Yang, G. Jia and S. Ma, *Tetrahedron*, 2008, **64**, 11159–11166.
44 W. Shu, Q. Yu and S. Ma, *Adv. Synth. Catal.*, 2009, **351**, 2807–2810.
45 P. Renzi, E. Azzi, E. Bessone, G. Ghigo, S. Parisotto, F. Pellegrino and A. Deagostino, *Org. Chem. Front.*, 2022, **9**, 906–916.
46 F. Yan, H. Liang, J. Song, J. Cui, Q. Liu, S. Liu, P. Wang, Y. Dong and H. Liu, *Org. Lett.*, 2017, **19**, 86–89.
47 R. Grigg, S. McCaffrey, V. Sridharan, C. W. G. Fishwick, C. Kilner, S. Korn, K. Bailey and J. Blacker, *Tetrahedron*, 2006, **62**, 12159–12171.
48 R. Grigg and V. Sridharan, *J. Organomet. Chem.*, 1999, **576**, 65–87.
49 R. C. Larock and J. M. Zenner, *J. Org. Chem.*, 1995, **60**, 482–483.
50 K. Hiroi, F. Kato and A. Yamagata, *Chem. Lett.*, 1998, **27**, 397–398.
51 F. Kato and K. Hiroi, *Chem. Pharm. Bull.*, 2004, **52**, 95–103.
52 J.-H. Liu, Q. Zhou, Y. Lin, Z.-L. Wu, T. Cai, W. Wen, Y.-M. Huang and Q.-X. Guo, *ACS Catal.*, 2023, **13**, 6013–6022.
53 H. Zhang, W. Wen, Z.-X. Lu, Z.-L. Wu, T. Cai and Q.-X. Guo, *Org. Lett.*, 2024, **26**, 153–159.
54 W. Wen and Q.-X. Guo, *Synthesis*, 2023, **55**, 719–732.
55 W. Wen and Q.-X. Guo, *Acc. Chem. Res.*, 2024, **57**, 776–794.
56 Z. Su, B. Tan, H. He, K. Chen, S. Chen, H. Lei, T.-G. Chen, S.-F. Ni and Z. Li, *Angew. Chem., Int. Ed.*, 2024, e202402038.
57 D. Ma, K. Ding, H. Tian, B. Wang and D. Cheng, *Tetrahedron: Asymmetry*, 2002, **13**, 961–969.
58 H. Bräuner-Osborne, J. Egebjerg, E. Ø. Nielsen, U. Madsen and P. Krogsgaard-Larsen, *J. Med. Chem.*, 2000, **43**, 2609–2645.
59 X. Huo, J. Zhang, J. Fu, R. He and W. Zhang, *J. Am. Chem. Soc.*, 2018, **140**, 2080–2084.
60 L. Wei, S.-M. Xu, Q. Zhu, C. Che and C.-J. Wang, *Angew. Chem., Int. Ed.*, 2017, **56**, 12312–12316.
61 T. Kanayama, K. Yoshida, H. Miyabe and Y. Takemoto, *Angew. Chem., Int. Ed.*, 2003, **42**, 2054–2056.
62 T. Kanayama, K. Yoshida, H. Miyabe, T. Kimachi and Y. Takemoto, *J. Org. Chem.*, 2003, **68**, 6197–6201.
63 R. He, X. Huo, L. Zhao, F. Wang, L. Jiang, J. Liao and W. Zhang, *J. Am. Chem. Soc.*, 2020, **142**, 8097–8103.
64 J.-H. Liu, W. Wen, J. Liao, Q.-W. Shen, Y. Lin, Z.-L. Wu, T. Cai and Q.-X. Guo, *Nat. Commun.*, 2022, **13**, 2509.
65 L. Chen, M.-J. Luo, F. Zhu, W. Wen and Q.-X. Guo, *J. Am. Chem. Soc.*, 2019, **141**, 5159–5163.
66 R. Zhu, A. H. Snyder, Y. Kharel, L. Schaffter, Q. Sun, P. C. Kennedy, K. R. Lynch and T. L. Macdonald, *J. Med. Chem.*, 2007, **50**, 6428–6435.
67 V. C. de Oliveira, J. M. de Oliveira, V. H. Menezes da Silva, I. U. Khan and C. R. D. Correia, *Adv. Synth. Catal.*, 2020, **362**, 3395–3406.
68 G. A. Wallace, T. D. Gordon, M. E. Hayes, D. B. Konopacki, S. R. Fix-Stenzel, X. Zhang, P. Grongsaard, K. P. Cusack, L. M. Schaffter, R. F. Henry and R. H. Stoffel, *J. Org. Chem.*, 2009, **74**, 4886–4889.
69 S. R. Fix-Stenzel, M. E. Hayes, X. Zhang, G. A. Wallace, P. Grongsaard, L. M. Schaffter, S. M. Hannick, T. S. Franczyk, R. H. Stoffel and K. P. Cusack, *Tetrahedron Lett.*, 2009, **50**, 4081–4083.
70 I. U. Khan, S. Kattela, A. Hassan and C. R. D. Correia, *Org. Biomol. Chem.*, 2016, **14**, 9476–9480.