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Palladium-catalyzed enantioselective rearrangement of dienyl cyclopropanes†

Qi Xu,‡ Chuan-Jun Lu, ID ‡ Chang-Qiu Guo, Jia Feng and Ren-Rong Liu ID *

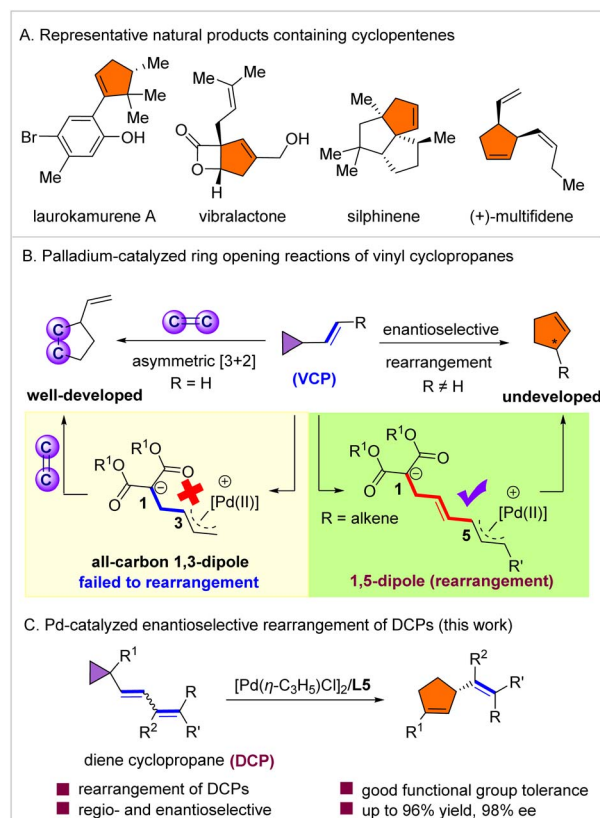
Vinyl cyclopropanes (VCPs) are among the most useful three-carbon building blocks in organic synthesis. They are commonly used as dienophiles in a range of cycloaddition reactions. However, VCP rearrangement has not received much attention since its discovery in 1959. In particular, the enantioselective rearrangement of VCP is synthetically challenging. Herein, we report the first palladium-catalyzed regio- and enantioselective rearrangement of VCPs (dienyl or trienyl cyclopropanes) for the construction of functionalized cyclopentene units in high yields and with excellent enantioselectivities and 100% atom economy. The utility of the current protocol was highlighted by a gram-scale experiment. Moreover, the methodology provides a platform for accessing synthetically useful molecules containing cyclopentanes or cyclopentenenes.

Introduction

Chiral five-membered carbocycles are ubiquitous structural motifs in a myriad of biologically active natural products and pharmaceuticals,^{1–4} such as laurokamurene A, vibrallactone, silphinene and (+)-multifidene (Scheme 1A). In addition, they also serve as intermediates in various total syntheses of unnatural and natural products.^{5,6} However, in contrast to six-membered carbocycles, which can be readily accessed *via* asymmetric Diels–Alder reactions, chiral 5-membered all-carbon rings are difficult to synthesize. Thus, the development of enantioselective and flexible synthetic routes to these frameworks is highly warranted.

Vinyl cyclopropanes are among the most useful three-carbon building blocks in organic synthesis.^{7–10} They are well known to generate a dipole, which allows for their application in a range of cycloaddition reactions with unsaturated compounds.^{11–16} Among these, the palladium-catalyzed asymmetric [3 + 2] annulation of VCPs with activated alkenes is by far one of the most studied transformations, providing a powerful approach to optically active cyclopentane derivatives (Scheme 1B).¹⁷ In 2011, Trost and co-workers achieved the first palladium-catalyzed enantioselective synthesis of chiral cyclopentanes *via* [3 + 2] annulation of vinyl cyclopropanes.¹⁸ Since then, significant advancements have been made in this field using activated alkenes.^{19–28} On the other hand, VCPs are also known

to undergo rearrangement to afford cyclopentenenes.²⁹ However, compared with cycloaddition, VCP rearrangement has been largely overlooked since its discovery in 1959 due to the



Scheme 1 Representative natural products containing cyclopentenenes and asymmetric reactions of vinyl cyclopropanes.

College of Chemistry and Chemical Engineering, Qingdao University, Qingdao, 266071, P. R. China. E-mail: renrongliu@qdu.edu.cn

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‡ These authors contributed equally to this work.



necessity for harsh conditions (normally proceeds at 300–500 °C).^{30–35} Only a handful of studies have been reported regarding VCP rearrangement under mild conditions catalyzed by transition metals such as Rh,^{36–39} Pd,^{40–42} Ni,^{43–45} and Cu,^{46–48} that proceed *via* coordination of the metal catalyst to the vinyl substituent of VCP. Nevertheless, the direct enantioselective rearrangement of VCP has remained a formidable challenge and the development of strategies for achieving this objective is highly desirable. Inspired by the recently reported palladium-catalyzed asymmetric functionalization of dienes,^{49–54} we herein report the first palladium-catalyzed enantioselective isomerization of dienyl cyclopropanes (activated VCPs) under mild conditions (Scheme 1C) for the formation of chiral cyclopentene derivatives, which are otherwise challenging to synthesize.

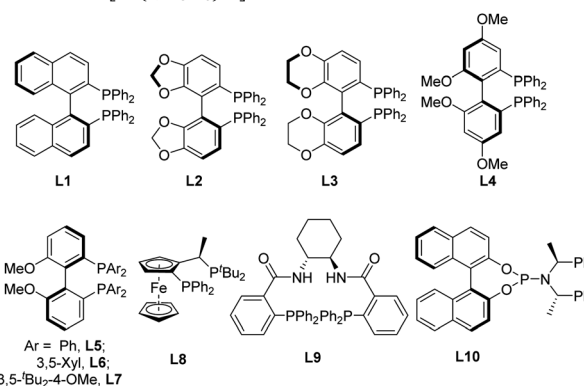
Results and discussion

We initiated our investigation using **1a** as a model substrate. Substrate **1a** was obtained as a *Z/E* mixture in high yield *via* the Wittig reaction (see ESI† for details). Selective rearrangement of dienyl cyclopropane **1a** was initially attempted using Pd(OAc)₂ (5 mol%), (*S*)-BINAP (**L1**) (7.5 mol%) in toluene at 80 °C, affording 5-membered cyclopentene derivative **2a** in 75% yield and with 83% ee as a single *E*-isomer (Table 1, entry 1). The use of Pd(dba)₂ instead of Pd(OAc)₂ delivered comparable results (entry 2), while a slightly higher yield was observed by employing [Pd(η-C₃H₅)Cl]₂ as the catalyst (entry 3). After screening several other solvents, including THF, dioxane and DMF (entries 4–6), it was found that toluene remained the best choice. Various phosphine ligands were then screened to improve the ee of **2a** (entries 7–15). In general, palladium complexes with electron-rich phosphine ligands afforded good results for this rearrangement. The use of (*S*)-SEGPHOS (**L2**) as the ligand improved the enantioselectivity significantly to 94% (entry 7). Comparable results (94% yield, 94% ee) were obtained when the reaction was performed with (*R*)-MeO-BIPHEP (**L5**) as the ligand (entry 10). (*S*)-SYNPHOS (**L3**) and (*S*)-GARPHOS (**L4**) displayed comparable activities, both affording product **2a** in 87% yield and with 88% and 90% ee, respectively (entries 8–9). Interestingly, the use of highly electron-donating (*R*)-DTBM-BIPHEP (**L7**) or (*R,S*)-JOSIPHOS (**L8**), sharply reduced the yields and enantioselectivities (entries 12–13). The use of palladium/Trost ligand (**L9**) or palladium/Feringa ligand (**L10**) complexes failed to give any desired rearrangement product (entries 14–15). The enantioselectivity could not be further enhanced by lowering the reaction temperature to 60 °C (entry 16). Although the rearrangement proceeded smoothly at room temperature, the yield was moderate (entry 17). Increasing the concentration of **1a** to 0.2 M decreased the yield of **2a** to 87% without affecting the enantioselectivity (entry 18). Halving the catalyst loading did not significantly affect the results, with the enantioselectivity remaining unchanged and the yield was slightly lower (entry 19).

After establishing the optimal reaction conditions, we explored the scope of the rearrangement reaction. As shown in Scheme 2, the dienylsubstituent R was first examined. Most of

Table 1 Optimization of conditions for dienyl cyclopropanes^a

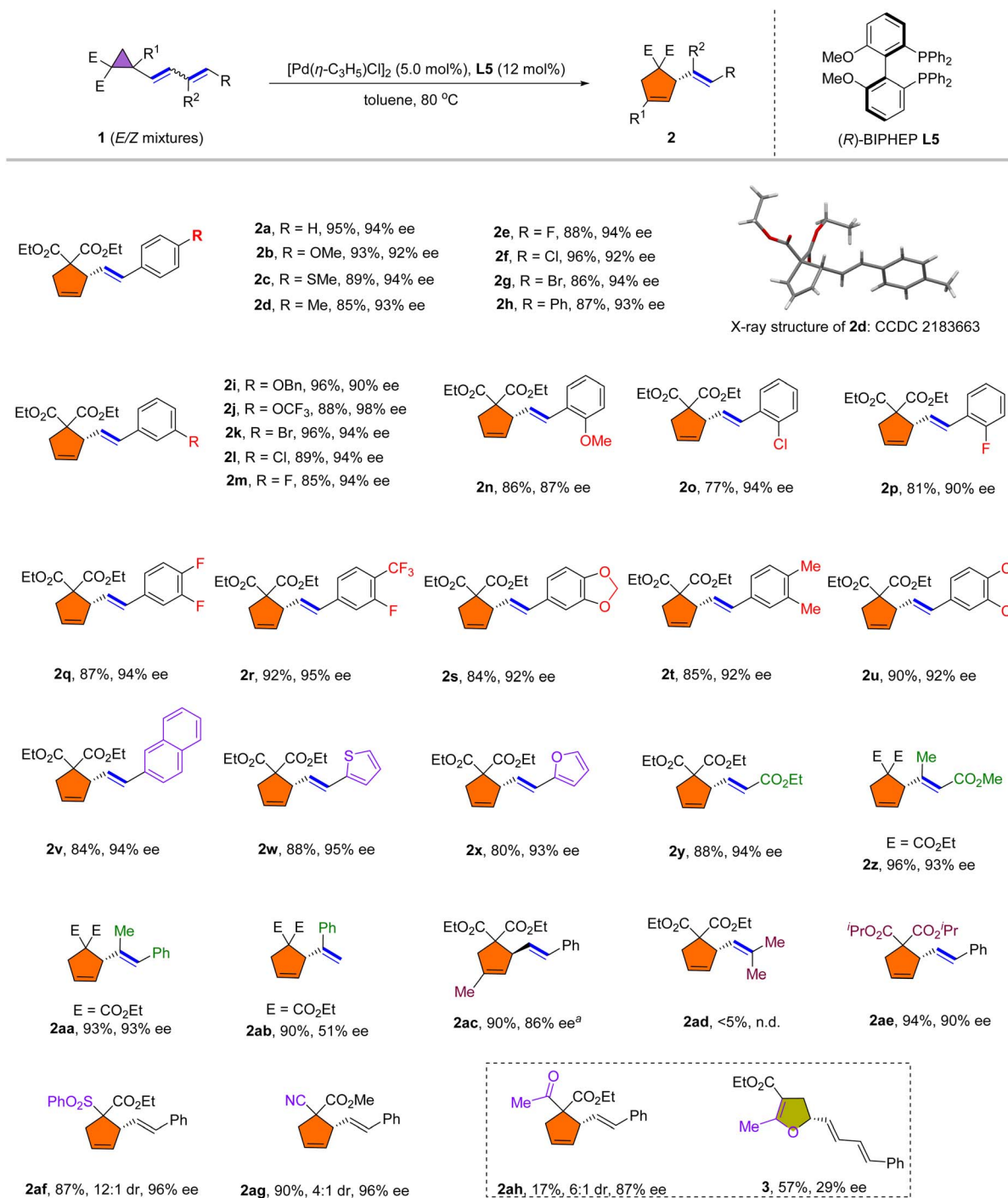
Entry	L*	[Pd]	Solvent	Yield ^b (%)	ee ^c (%)
1	L1	Pd(OAc) ₂	Toluene	75	83
2	L1	Pd(dba) ₂	Toluene	77	83
3	L1	[Pd(η-C ₃ H ₅)Cl] ₂	Toluene	85	83
4	L1	[Pd(η-C ₃ H ₅)Cl] ₂	THF	80	82
5	L1	[Pd(η-C ₃ H ₅)Cl] ₂	Dioxane	84	80
6	L1	[Pd(η-C ₃ H ₅)Cl] ₂	DMF	82	62
7	L2	[Pd(η-C ₃ H ₅)Cl] ₂	Toluene	91	94
8	L3	[Pd(η-C ₃ H ₅)Cl] ₂	Toluene	87	88
9	L4	[Pd(η-C ₃ H ₅)Cl] ₂	Toluene	87	90
10	L5	[Pd(η-C ₃ H ₅)Cl] ₂	Toluene	94	94
11	L6	[Pd(η-C ₃ H ₅)Cl] ₂	Toluene	89	90
12	L7	[Pd(η-C ₃ H ₅)Cl] ₂	Toluene	50	42
13	L8	[Pd(η-C ₃ H ₅)Cl] ₂	Toluene	20	40
14	L9	[Pd(η-C ₃ H ₅)Cl] ₂	Toluene	<5%	—
15	L10	[Pd(η-C ₃ H ₅)Cl] ₂	Toluene	<5%	—
16 ^d	L5	[Pd(η-C ₃ H ₅)Cl] ₂	Toluene	75	94
17 ^e	L5	[Pd(η-C ₃ H ₅)Cl] ₂	Toluene	45	95
18 ^f	L5	[Pd(η-C ₃ H ₅)Cl] ₂	Toluene	87	93
19 ^g	L5	[Pd(η-C ₃ H ₅)Cl] ₂	Toluene	83	94



^a Reaction conditions: **1a** (0.1 mmol, *E/Z* mixtures), [Pd] (5.0 mol%), and ligand (12 mol%) in toluene (1.0 mL) at 80 °C for 3 h. ^b Isolated yield. ^c Determined by chiral HPLC. ^d Reaction performed at 60 °C. ^e Reaction performed at 25 °C for 20 h. ^f Reaction performed with 0.2 M concentration of **1a**. ^g [Pd(η-C₃H₅)Cl]₂ (2.5 mol%), ligand (6 mol%), reaction time: 10 h.

the tested *para*- and *meta*-substituted aromatic dienyl cyclopropanes (**1a–1m**) underwent the rearrangement smoothly to afford vinylcyclopentene adducts **2a–2m** in 85–96% yield and with 90–98% ee. It is noteworthy that in all cases, the *E/Z* mixtures of dienyl cyclopropanes **1** afforded pure *E*-isomers. The absolute configuration was confirmed based on single crystal X-ray analysis of **2d** (CCDC 2183663). Substrates bearing halogens, including fluorine (**2e**, **2m**), chlorine (**2f**, **2l**) and bromine (**2g**, **2k**), were rearranged smoothly in good yields and with high ees. 3,4-Disubstituted aromatic dienes were also well tolerated (**2q–2u**). It is worth noting that ortho-substituted aromatic dienes also rearranged to give good yields and high enantioselectivities (**2n–2p**). The inclusion of 2-naphthyl (**1v**),





Scheme 2 Scope of dienylic cyclopropanes, reaction conditions: **1** (0.1 mmol, *E/Z* mixtures), $[Pd(\eta-C_3H_5)Cl]_2$ (5.0 mol%), **L5** (12 mol%), in toluene (1.0 mL) at 80 °C for 3–5 h. ^a **L2** was used as the ligand instead of **L5**.

thienyl (**1w**) and furyl (**1x**) functionalities on the diene was successful, affording products **2v–2x** in 80–88% yield and 93–95% ee. Importantly, we found that ester-substituted dienes **1y–1z** rearranged satisfactorily into cyclopentene **2y** and **2z**. Moreover, 1,2-disubstituted dienylic cyclopropane **1aa** was also applicable in this rearrangement reaction to afford **2aa** in high yield and with good enantioselectivity (93% ee). However, 1,1-disubstituted dienylic cyclopropane **1ad** failed to undergo the

rearrangement. Furthermore, the terminal dienylic cyclopropane **1ab** afforded **2ab** in 90% yield with a moderate ee, which may be caused by the reduced steric hindrance of terminal olefin during rearrangement. The cyclopropane substituents (*R*¹, *E*) were examined next. Dienylic cyclopropane **1ac**, bearing geminal methyl and dienylic groups, reacted favorably under the reaction conditions to afford **2ac** in 90% yield and with 86% ee. In addition, changing the substituents on the ester functional

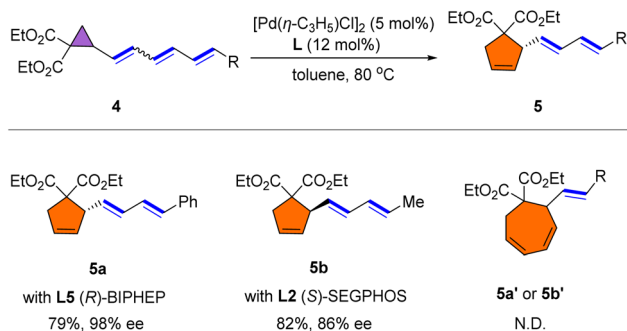


groups had little effect on this rearrangement reaction (**2ae**). Other electron-withdrawing substituents, such as CN or SO₂Ph substituted vinyl cyclopropanes were also suitable for this rearrangement reaction to afford **2af** and **2ag** in high yields with good enantioselectivities. Interestingly, rearrangement of acetyl substituted cyclopropane under the standard conditions afforded the corresponding Cloke–Wilson type vinyl-dihydrofuran **3** in 57% yield with 29% ee, while **2ah** was achieved in 17% yield with 87% ee.

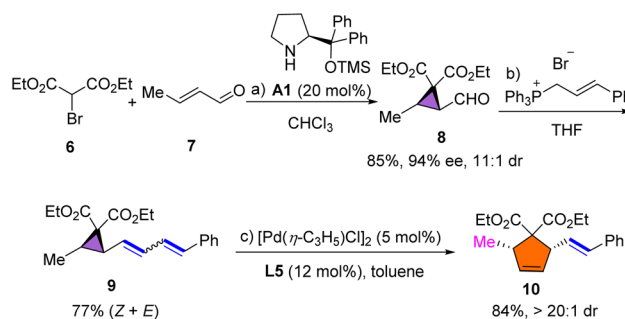
To further verify the universality of the reaction, we examined the rearrangement of triene cyclopropane substrates (Scheme 3). To our delight, the rearrangement occurred smoothly to afford **5a** and **5b** with 98% ee and 86% ee, respectively. The regiochemistry is intriguing in that a five-membered-ring product was again observed, even in the case of triene rearrangement, while seven-membered-ring formation did not occur.

Polysubstituted cyclopentane units are widely distributed in pharmaceuticals and biologically active compounds; thus, we envisaged the synthesis of polysubstituted cyclopentane using the developed rearrangement. As shown in Scheme 4, 2-formylcyclopropane **8** was synthesized in 85% yield with 94% ee and 11:1 dr *via* a one-pot organocatalytic domino Michael/ α -alkylation using bromomalonate **6** and crotonaldehyde **7**.⁵⁵ The subsequent Wittig reaction afforded dienyl cyclopropane substrate **9** in 77% yield. Under the standard conditions, polysubstituted cyclopentene **10** was formed in high yield and with excellent diastereoselectivity. The configuration of **10** was assigned to be *cis* *via* H–H NOESY analysis (see the ESI†).

A gram-scale reaction of **1a** was performed by decreasing the loading of [Pd(η -C₃H₅)Cl]₂ and L5, delivering **2a** in 83% yield and with comparable enantioselectivity to that of the small-scale reaction (Scheme 5A). The synthetic importance of this dienyl cyclopropane-vinylcyclopentene rearrangement was further highlighted by several transformations of representative compound **2a** (Scheme 5B). Reduction of the alkene groups of **2a** proceeded smoothly under Pd/C-catalyzed hydrogenation to provide **11** in 90% yield and with 93% ee. Compound **2a** was selectively converted to functionalized cyclopentene **12** through epoxidation using *m*-CPBA in moderate yield. Reduction of the ester group using LiAlH₄ proceeded smoothly to afford diol **13** in 70% yield. Subsequently, **2a** was decarboxylated employing the Krapcho reaction to deliver **14** in 82% yield.



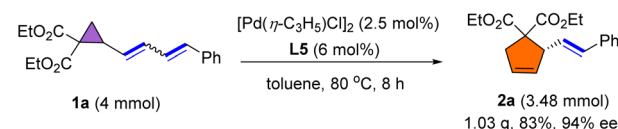
Scheme 3 Reaction conditions: **3** (0.1 mmol), [Pd(η -C₃H₅)Cl]₂ (5.0 mol%), L (12 mol%), in toluene (1.0 mL) at 80 °C for 3 h.



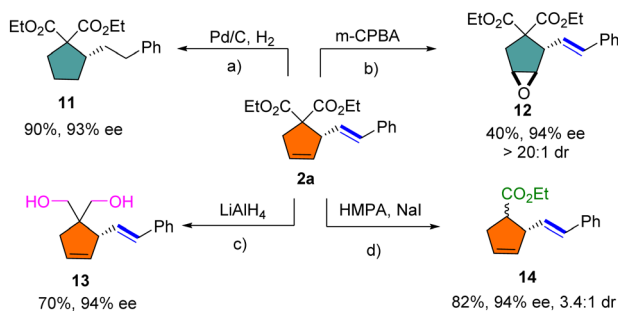
Scheme 4 Reaction conditions: ^a **6** (0.5 mmol), **7** (0.6 mmol), A1 (20 mol%), Et₃N (0.5 mmol), CHCl₃ (2.0 mL), 85% yield. ^b **8** (0.33 mmol), cinnamyltriphenylphosphonium (0.3 mmol), *n*-BuLi (0.33 mmol), in THF (2.0 mL) at 0 °C for 5 h, 77% yield. ^c **9** (0.1 mmol), [Pd(η -C₃H₅)Cl]₂ (5.0 mol%), L5 (12 mol%), in toluene (1.0 mL) at 100 °C for 24 h, 84% yield, > 20:1 dr.

To better understand the mechanism of the rearrangement, several control experiments were conducted. As shown in Scheme 6A, pure *E*-**1a** and *Z*-**1a** were subjected to the standard conditions used in Scheme 2, providing the product *E*-**2a** in 92% and with 94% ee, and in 88% and with 94% ee, respectively (eqn (1) and (2)), suggesting that isomerization occurred during the rearrangement of dienyl cyclopropane. However, when vinyl cyclopropane **15** was reacted under the standard conditions, the VCP decomposed and rearrangement product **16** was not detected. A plausible mechanism for the rearrangement is shown in Scheme 6B. Initially, coordination of the double bond of **1a** to the palladium complex forms intermediate **A**. Subsequent oxidative addition of cyclopropane leads to the formation of the *syn,syn*- η^3 -allyl palladium complex **B**, which affords the

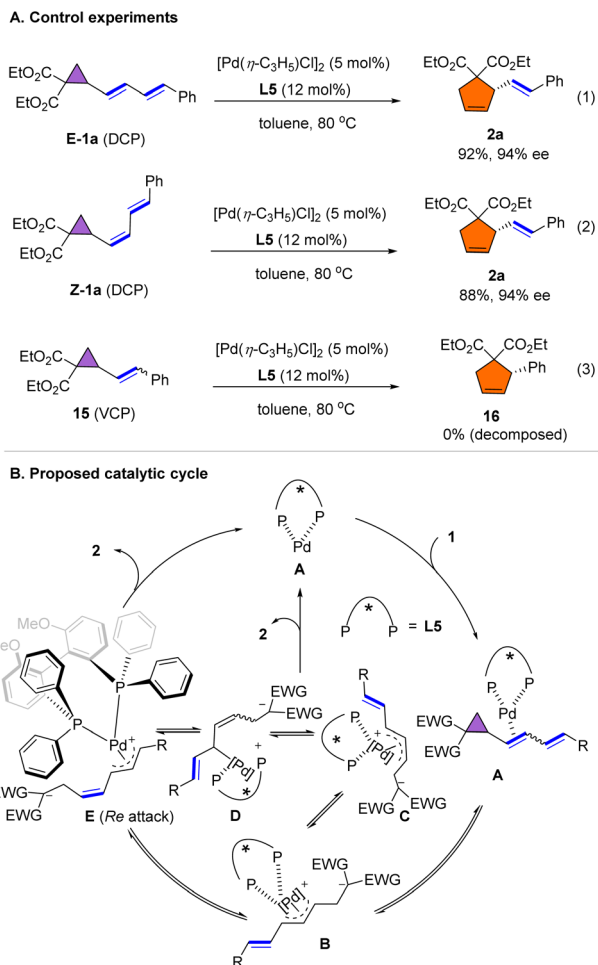
A. Gram-scale reaction



B. Derivatization of 2a



Scheme 5 Gram-scale reaction and derivatization of **2a**, reaction conditions: ^a **2a** (0.1 mmol), Pd/C (20 mol%), H₂ (balloon), MeOH (1.0 mL) at RT for 12 h, 90% yield. ^b **2a** (0.1 mmol), *m*-CPBA (0.2 mmol), NaHCO₃ (0.12 mmol), in DCM (1.0 mL) at 0 °C for 10 min, then RT for 24 h, 40% yield. ^c **2a** (0.1 mmol), LiAlH₄ (0.28 mmol), in THF (1.0 mL) at 0 °C for 12 h, 70% yield. ^d **2a** (0.1 mmol), NaI (0.14 mmol), in HMPA (0.2 mL) at 110 °C for 24 h, 82% yield, 3.4:1 dr.



Scheme 6 Control experiments and proposed catalytic cycle.

anti,syn- η^3 -allyl intermediate C. Dynamic equilibration of C into *syn,syn*- η^3 -allyl complex E through π - σ - π (C–D–E) isomerization triggers the formation of cyclopentene product 2 via a Re attack on the Pd- π -allyl moiety. However, we couldn't exclude another reaction pathway that proceed via initial coordination of palladium to the distal alkene, followed by the formation of the η -allyl complex accompanied by alkene migration and cyclopropane ring opening to give D.

Conclusions

In conclusion, we have developed a mild and efficient palladium-catalyzed enantioselective rearrangement of dienyl or trienyl cyclopropanes. A broad range of functionalized vinylcyclopentene derivatives were conveniently constructed in high yields and with excellent regioselectivities and enantioselectivities. The utility of the current protocol was highlighted by a successful gram-scale experiment. Furthermore, the developed method provides a platform for constructing synthetically useful molecules containing cyclopentanes or cyclopentenes. To the best of our knowledge, the reported palladium-catalyzed enantioselective ring expansion is unprecedented.

Data availability

Experimental data associated with this article can be found in the ESI.†

Author contributions

R. R. L. conceived, designed, and originated this project. Q. X., C. J. L., C. Q. G and J. F. performed the experiments, obtained all spectroscopic data, and analysed the results. R. R. L. and C. J. L. co-wrote the manuscript. All authors analysed the data, discussed the results and contributed to the relevant discussion.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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