ORGANIC CHEMISTRY
FRONTIERS

RESEARCH ARTICLE

View Article Online
View Journal

Check for updates

**Cite this:** DOI: 10.1039/d4qo00188e

# Palladium-catalysed α and β C–H allylation of aryl alkenes†

Yilei Liao,‡[a] Xiandie Zhang,‡[a] Xiaoli Li,[a] Xiuying Liu,[a] Jiakai Chen,[a] Chao Shen,*[b] Rui He,[d] Guofu Zhong *[a,c] and Jian Zhang *[a,d]

Received 29th January 2024,
Accepted 17th April 2024

DOI: 10.1039/d4qo00188e

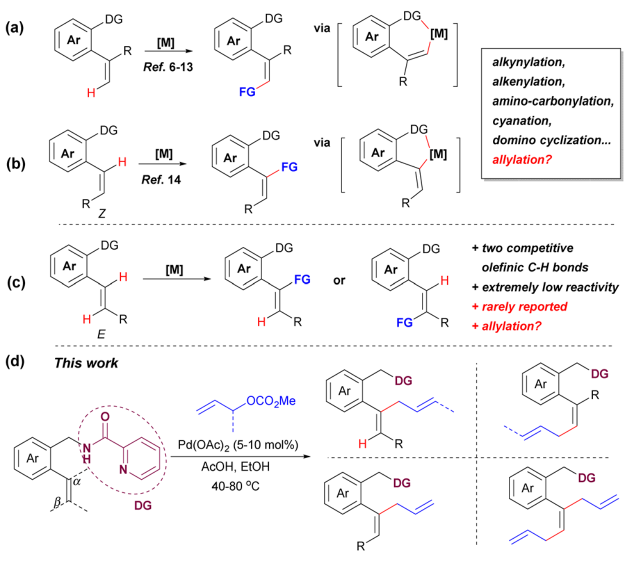
rsc.li/frontiers-organic

Remarkable progress has been made on chelation-assisted α and β C–H functionalization of aryl alkenes; however, there is no report on C–H allylation reactions. This work focuses on the first α and β C–H allylation of aryl alkenes using allyl carbonates to produce linear and branched 1,4-dienes enabled by chelation-assistance of pyridine-2-carboxamide, simply performed with $Pd(OAc)_2$/AcOH in ethanol. This operationally simple protocol exhibited wide functionality tolerance and broad substrate scope and enabled successful gram-scaled preparation.

## Introduction

Chelation-assisted C–H functionalization represents a powerful strategy toward structural complexity from simple raw feedstocks. Among them, olefinic C–H functionalization has attracted remarkable attentions, which provide regio- and stereo-selective synthesis of olefinic derivatives such as 1,3-dienes, 1,4-dienes, and eneynes.[1–3] These chelation-assisted alkenyl C–H functionalizations proceed by *endo*- or *exo*-metallocycle intermediates, generally using 1,1-disubstituted alkenes[2] and disubstituted *Z*-alkenes[3] as the substrates, with the other possible reaction sites blocked (Scheme 1a). To the best of our knowledge, although C–H functionalization of *Z*-alkenes by *exo*-metallocycle has shown remarkable progress,[3] chelation-assisted α C–H functionalization of *E*-alkenes (including *E*-styrenes) bearing two competitive C–H bonds through *exo*-cyclometallation remains unexplored.

Aryl alkenes are widely occurring and show extensive applications in material and pharmaceutical science.[4] Significant progress has been made on chelation-assisted olefinic C–H functionalization of aryl alkenes.[5–13] The well-defined one is the β C–H functionalization of aryl alkenes by *endo*-metallocycles, including C–H alkynylation, alkenylation, cyanation and amino-carbonylation (Scheme 1a).[6–13] However, α C–H functionalization of aryl alkenes has attracted very limited attention, and the reported methods not only restricted to C–H alkenylation reactions but also employed only (*Z*)-configurated aryl alkenes[14] or plain styrenes (Scheme 1b).[12a] For example, Engle[14a] and our group[14b] simultaneously reported on (asymmetric) α C–H alkenylation of aryl alkenes, affording (axially chiral) aryl dienes. In stark contrast, α C–H functionalization of *E*-aryl alkenes is rarely reported due to the more difficult



Scheme 1 Chelation-assisted α and β C–H allylation of aryl alkenes.

---

[a] *College of Material, Chemistry and Chemical Engineering, Key Laboratory of Organosilicon Chemistry and Material Technology, Ministry of Education, Hangzhou Normal University, Hangzhou, 311121 Zhejiang, China. E-mail: zhangjian@hznu.edu.cn*

[b] *Key Laboratory of Pollution Exposure and Health Intervention of Zhejiang Province, College of Biology and Environmental Engineering, Zhejiang Shuren University, Hangzhou 310015, P. R. China. E-mail: shenchaozju@zjsru.edu.cn*

[c] *Department of Chemistry, Eastern Institute of Technology, Ningbo 315200, Zhejiang, China. E-mail: gzhong@eitech.edu.cn*

[d] *Department of Stomatology, The Affiliated Hospital of Hangzhou Normal University, Hangzhou Normal University, Hangzhou310015, Zhejiang, China*

† Electronic supplementary information (ESI) available: Experimental procedures, characterization data, NMR spectra. See DOI: **https://doi.org/10.1039/d4qo00188e**

‡ These authors contributed equally to this work.

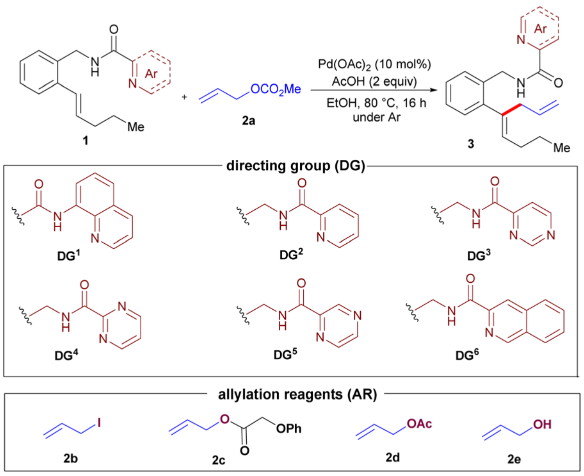
*exo*-cyclometallation and the existence of two competitive C–H bonds.[15] Moreover, although remarkable progress has been made on olefinic C–H allylation of simple alkenes,[16] there is no report on α or β C–H allylation of aryl alkenes (Scheme 1a–c).

Development of α C–H allylation of (*E*)- and (*Z*) configurated styrenes is highly desirable not only for the synthetic diversity to giving skipped diene products with complementary *E*/*Z* selectivity but also for providing in-depth mechanistic insight into C–H cyclometallation.[1–3] With our ongoing interest in olefinic C–H functionalization,[2i–o,3e–f,14b,15] herein, we report on the first chelation-assisted α and β C–H allylation of various styrenes, affording linear and branched skipped dienes and even triene in excellent *E*/*Z* ratio selectivity (Scheme 1d).

## Results and discussion

Based on our previous reports,[12a,15] we herein turned to examine the C–H allylation of *trans*-styrene bearing a *N*,*N* bidentate-chelation directing group (**DG**$^{1-6}$). Although styrene **1** bearing Daugulis's 8-aminoquinoline (**DG**$^{1}$)[17] led to no reaction with allyl carbonate **2a** (Table 1, entry 1), the substrate bearing pyridine-2-carboxamide (**DG**$^{2}$)[18] afforded α C–H allylation product **3a** in 77% yield, simply in the presence of 10 mol% $Pd(OAc)_2$ and 2.0 equivalent AcOH in EtOH at 80 °C (entry 2). Aryl alkene bearing pyrimidine-4-carboxamide (**DG**$^{3}$) led to comparable results (entry 3). Other nitrogen heterocycle carboxamide such as pyrimidine-2-carboxamide (**DG**$^{4}$), pyrazinamide (**DG**$^{5}$) and isoquinoline-3-carboxamide (**DG**$^{6}$) were also examined, demonstrating that **DG**$^{2}$ was the best one (entries 4–6). Using PivOH instead of AcOH led to a 63% yield (entry 7). The reaction without carboxylic acid only afforded a trace product, exhibiting a carboxylate-assisted C–H activation event (entry 8). The reaction was unsuccessful using $H_2O$ as a solvent, however, $H_2O$/MeOH still led to a 53% yield to demonstrate its robustness (entries 9 and 10). Some other allylation reagents (**AR**) were also examined in such C–H allylation reactions. While allyl iodide **2b** and allyl alcohol **2e** afforded no reaction, allyl carboxylates **2c** and **2d** gave moderate yields (entries 11–14).

**Table 1** Evaluation and optimization of the reaction[a,b]



| Entry | DG | AR | Additive | Yield[b] (%) |
|---|---|---|---|---|
| 1 | **1** | **2a** | AcOH | 0 |
| 2 | **2** | **2a** | **AcOH** | 77 |
| 3 | **3** | **2a** | AcOH | 73 |
| 4 | **4** | **2a** | AcOH | 31 |
| 5 | **5** | **2a** | AcOH | 65 |
| 6 | **6** | **2a** | AcOH | 46 |
| 7 | **2** | **2a** | PivOH | 63 |
| 8 | **2** | **2a** | — | <5 |
| 9[c] | **2** | **2a** | AcOH | <5 |
| 10[d] | **2** | **2a** | AcOH | 53 |
| 11 | **2** | **2b** | AcOH | 0 |
| 12 | **2** | **2c** | AcOH | 52 |
| 13 | **2** | **2d** | AcOH | 51 |
| 14 | **2** | **2e** | AcOH | 0 |

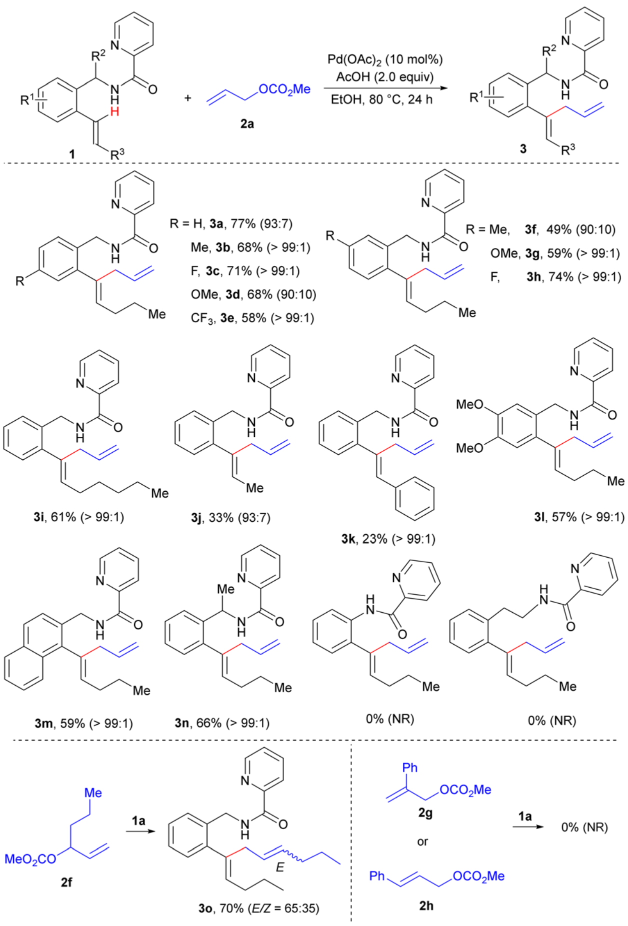
[a] Reaction conditions: **1** (0.15 mmol, 1 equiv.), **2a** (0.6 mmol, 4 equiv.), $Pd(OAc)_2$ (10 mol%), AcOH (2 equiv.), in EtOH (0.1 M) at 80 °C, for 24 h. [b] *E*/*Z* ratios of the isomer given in parentheses were determined by $^1H$ NMR analysis. [c] Using $H_2O$ as a solvent. [d] Using MeOH/$H_2O$ as a solvent.

With the optimized conditions in hand, C–H allylation between various *trans*-styrenes **1** and allyl carbonates **2** were examined (Table 2). *meta*- and *para*-Substitutes such as F, OMe, $CF_3$, and Me were all well tolerated, affording aryl 1,4-dienes in 49–77% yields (**3a–3h**). Styrene bearing longer aliphatic chains such as pentyl afforded **3i** in 59% yield. However, changing propyl to methyl and phenyl groups decreased the product yield to 33% (**3j**) and 23% (**3k**), respectively. Substrates bearing dimethoxy phenyl and naphthyl also gave **3l** and **3m** in good yields. Secondary amine-derived amide still converted well to give **3n** in 66% yield. Unfortunately, neither aniline nor phenylethylamine derivatives showed reactivity, exhibiting the difficult formation of five- and seven-membered palladacycle. Notably, branched allyl carbonate **2f** also reacted well to give rise to **3o** in 70% yield with 65 : 35 *E*/*Z* ratio selectivity. However, other allyl carbonates from 2-phenyl prop-2-en-1-ol (**2g**) and cinnamyl alcohol (**2h**) exhibited no reactivity.

After that, we turned to examine the β C–H allylation of aryl alkenes **4** also bearing pyridine-2-carboxamide (**DG**$^{2}$) (Table 3). Under the optimal conditions, styrenes bearing F, $CF_3$ and OMe were converted smoothly to afford 1,4-dienes **5a–5d** in 51–76% yields. Notably, branched allyl carbonate **2f** reacted well to give diene product **5e** in 83% yield. Aryl alkenes **4** bearing phenyl or ethyl at the α position reacted successfully to afford **5f** and **5g** in 74% and 65% yields, respectively, with excellent *E*/*Z* ratio selectivity.

Next, we investigated the reaction of *Z*-configurated aryl alkene **6** and plain styrene **8** under optimal conditions. While *Z*-styrene gave rise to α C–H allylation product **7** in 66% yield with 93 : 7 *E*/*Z* ratio selectivity (Scheme 2a), plain styrene **8** afforded triene product **9** in 51% yield with >99 : 1 *E*/*Z* ratio selectivity (Scheme 2b).[19]

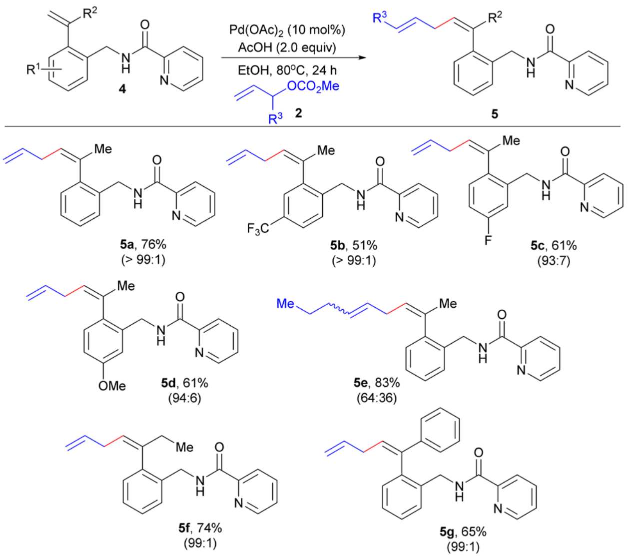
**Table 2** Pd-catalysed α C–H allylation of *E*-styrenes[a,b]



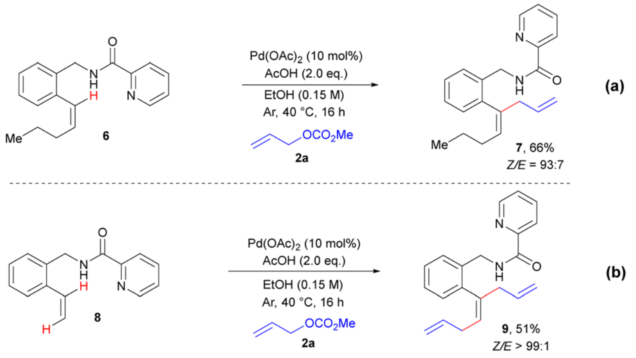
[a] Reactions conditions: **1** (0.15 mmol, 1 equiv.), **2** (0.6 mmol, 4 equiv.), $Pd(OAc)_2$ (10 mol%), AcOH (2 equiv.), in EtOH (0.1 M) at 80 °C, for 24 h. [b] Isolated yields; *E*/*Z* ratios of the isomers given in parentheses were determined by $^1$H NMR analysis.

To explore the mechanism of this C–H allylation of styrenes, controlled reactions were performed as described in Scheme 3. If *E*-styrene **1a** was subjected to the optimal conditions with EtOD (0.1 M), 97% deuterium incorporation was observed with 81% recovery, exhibiting the α C–H activation to be facile and reversible (Scheme 3a). If the same reaction was conducted in the presence of allyl carbonate **2a**, 38% product yield and 50% recovery of **1a** without deuterium incorporation were observed, which demonstrated a much faster olefin insertion to outcompete the C–H activation step (Scheme 3b). Allylation product **3a** was obtained in 38% yield with 0% deuterium incorporation, exhibiting a direct **2a** insertion followed by liberation of $CO_2$ and MeOH.[3f,16] An intermolecular competition experiment between **6** and **1a** was conducted to give the product **7** in 40% yield and **3a** in trace amount, exhibiting a much higher reactivity of *Z*-styrene to outcompete *E*-styrene, also exhibiting a more difficult formation of *exo*-metallocycle with *E*-alkenes (Scheme 3c).[15] Aliphatic *E*-alkene **10** was also examined, and only a trace product was detected under optimal conditions (Scheme 3d). Benzyl amide **11** led to no aromatic C–H allylation, exhibiting the difficult formation of five-membered palladacycle (Scheme 3e).[20]

**Table 3** Pd-catalysed β C–H allylation of styrenes[a,b]



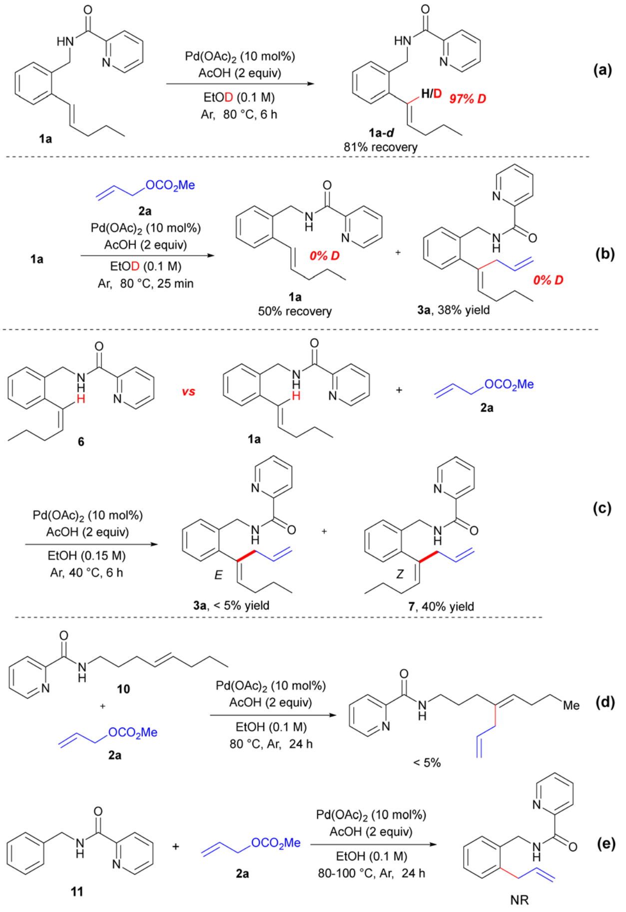
[a] Reactions conditions: **4** (0.15 mmol, 1 equiv.), **2** (0.6 mmol, 4 equiv.), $Pd(OAc)_2$ (10 mol%), AcOH (2 equiv.), in EtOH (0.1 M) at 80 °C, for 24 h. [b] Isolated yields; *Z*/*E* ratios of the isomers given in parentheses were determined by $^1$H NMR analysis.



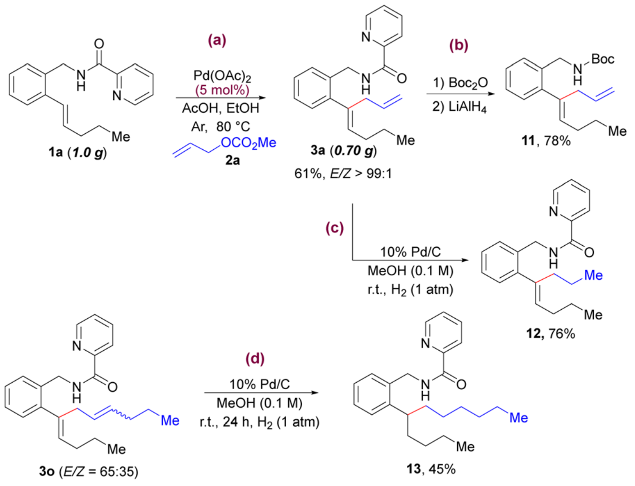
**Scheme 2** α and β C–H allylation of *Z*- and plain styrenes.

Gram-scaled preparation of **3a** was successful using 5 mol% $Pd(OAc)_2$ to demonstrate the robustness and practicality of this method (Scheme 4a). The directing group was readily removed by N-Boc protection followed by reduction with $LiAlH_4$, providing NHBoc benzylamine **11** in 78% yield (Scheme 4b). Terminal alkene of 1,4-diene **3a** was selectively reduced to give alkene **12** in 76% yield by using 10% Pd/C under hydrogen (1 atm) (Scheme 4c). Notably, two olefin moieties in **3o** were completely reduced to afford branched alkane **13** in 45% yield (Scheme 4d).

Based on previous reports[16] and experiment results, a plausible catalytic cycle is proposed in Scheme 5. Coordination between the substrate and metal occurred to give a π-olefin palladium complex **I**, which then formed a six-membered pal-

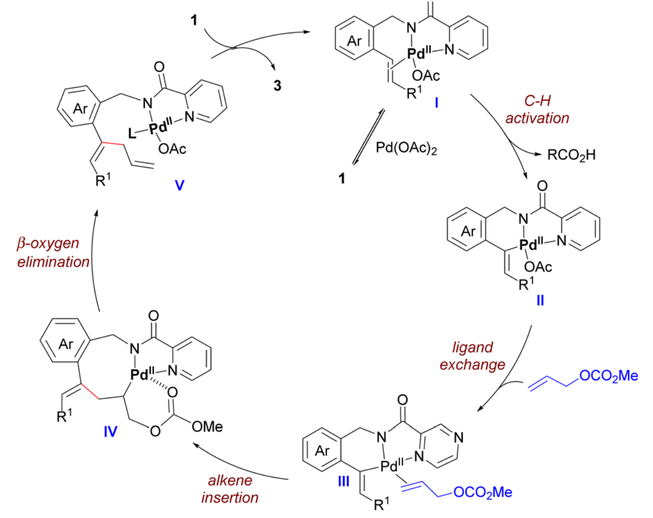


**Scheme 3** Controlled experiments.



**Scheme 4** Gram-scaled synthesis and derivation.

ladacycle **II** by a reversible α-C–H activation. Ligand exchange by allyl carbonate coordination and alkene insertion took place to afford an eight-membered palladacycle **IV**. Finally, β-oxygen elimination occurred to produce aryl 1,4-diene **3**.



**Scheme 5** Proposed mechanism.

## Conclusions

In conclusion, we have developed *N*,*N*-bidentate-chelation assisted α and β C–H allylation of *E*- and *Z*-configurated aryl alkenes, as well as α-substituted styrenes and plain styrenes, producing linear and branched 1,4-dienes and 1,4,7-triene with excellent *Z*/*E* ratio selectivity. The operationally simple protocol showed a broad substrate scope and enabled gram-scaled preparation. This method is anticipated to exhibit wide applications in multifarious organic synthesis.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

We gratefully acknowledge the National Natural Science Foundation of China (NSFC) (No. 22278103, 21502037, 21672048 and 81570989), Natural Science Foundation of Zhejiang Province (ZJNSF) (LY19B020006), Major Project of Hangzhou Health Science and Technology Plan (Z20200046), and Key Subject of Stomatology in Hangzhou for financial support.

## References

1 (*a*) X.-J. Shang and Z.-Q. Liu, Transition metal-catalyzed $C_{vinyl}$–$C_{vinyl}$ bond formation via double $C_{vinyl}$–H bond activation, *Chem. Soc. Rev.*, 2013, **42**, 3253–3260; (*b*) K. Wang, F.-D. Hu, Y. Zhang and J.-B. Wang, Directing group-assisted transition-metal-catalyzed vinylic C-H bond functionali-

zation, *Sci. China: Chem.*, 2015, **58**, 1252–1265; (*c*) D. A. Colby, A. S. Tsai, R. G. Bergman and J. A. Ellman, Rhodium catalyzed chelation-assisted C–H bond functionalization reactions, *Acc. Chem. Res.*, 2012, **45**, 814–825; (*d*) J. Zhang, X.-N. Lu, C. Shen, L.-Y. Xu, L.-Y. Ding and G.-F. Zhong, Recent advances in chelation-assisted site- and stereoselective alkenyl C–H functionalization, *Chem. Soc. Rev.*, 2021, **50**, 3263–3314; (*e*) M.-Z. Lu, J. Goh, M. Maraswami, Z.-H. Jia, J.-S. Tian and T.-P. Loh, Recent advances in alkenyl sp$^2$ C–H and C–F bond functionalizations: scope, mechanism, and applications, *Chem. Rev.*, 2022, **122**, 17479–17646.

2 (*a*) T. Besset, N. Kuhl, F. W. Patureau and F. Glorius, RhIII-catalyzed oxidative olefination of vinylic C–H bonds: efficient and selective access to di-unsaturated α-amino acid derivatives and other linear 1,3-butadienes, *Chem. – Eur. J.*, 2011, **17**, 7167–7171; (*b*) Q.-J. Liang, C. Yang, F.-F. Meng, B. Jiang, Y.-H. Xu and T.-P. Loh, Chelation versus non-chelation control in the stereoselective alkenyl sp$^2$ C–H bond functionalization reaction, *Angew. Chem., Int. Ed.*, 2017, **56**, 5091–5095; (*c*) X.-H. Hu, J. Zhang, X.-F. Yang, Y.-H. Xu and T.-P. Loh, Stereo- and Chemoselective Cross-Coupling between Two Electron Deficient Acrylates: An Efficient Route to (*Z*,*E*)-Muconate Derivatives, *J. Am. Chem. Soc.*, 2015, **137**, 3169–3172; (*d*) B. Jiang, M. Zhao, S.-S. Li, Y.-H. Xu and T.-P. Loh, Macrolide synthesis through intramolecular oxidative cross-coupling of alkenes, *Angew. Chem., Int. Ed.*, 2018, **57**, 555–559; (*e*) X.-H. Hu, X.-F. Yang and T.-P. Loh, Selective alkenylation and hydroalkenylation of enol phosphates through direct C–H functionalization, *Angew. Chem., Int. Ed.*, 2015, **54**, 15535–15539; (*f*) Y. Aihara and N. Chatani, Nickel-catalyzed direct alkylation of C–H bonds in benzamides and acrylamides with functionalized alkyl halides via bidentate-chelation assistance, *J. Am. Chem. Soc.*, 2013, **135**, 5308–5311; (*g*) F. Mo and G.-B. Dong, Regioselective ketone α-alkylation with simple olefins via dual activation, *Science*, 2014, **345**, 68–72; (*h*) D. Xing and G.-B. Dong, Branched-selective intermolecular ketone α-alkylation with unactivated alkenes via an enamide directing strategy, *J. Am. Chem. Soc.*, 2017, **139**, 13664–13667; (*i*) F.-F. Li, C.-B. Yu, J. Zhang and G.-F. Zhong, Olefination of electron-deficient alkenes with allyl acetate: stereo- and regioselective access to (2*Z*,4*E*)-dienamides, *Org. Lett.*, 2016, **18**, 4582–4585; (*j*) C.-B. Yu, F.-F. Li, J. Zhang and G.-F. Zhong, A direct cross-coupling reaction of electron-deficient alkenes using an oxidizing directing group, *Chem. Commun.*, 2017, **53**, 533–536; (*k*) C.-B. Yu, J. Zhang and G.-F. Zhong, One step synthesis of γ-alkylidenebutenolides from simple vinyl carboxylic acids and alkenes, *Chem. Commun.*, 2017, **53**, 9902–9905; (*l*) T.-Y. Li, J. Zhang, C.-B. Yu, X.-N. Lu, L.-Q. Xu and G.-F. Zhong, Ruthenium-catalyzed olefinic C–H alkenylation of enol-carbamates: highly stereo-selective synthesis of (*Z*,*Z*) and (*Z*,*E*)-butadienes, *Chem. Commun.*, 2017, **53**, 12926–12929; (*m*) K.-K. Meng, J. Zhang, F.-F. Li, Z.-W. Lin, K. Zhang and G.-F. Zhong, Amide directed cross-coupling between alkenes and alkynes: a region- and stereoselective approach to substituted (2*Z*,4*Z*)-dienamides, *Org. Lett.*, 2017, **19**, 2498–2501; (*n*) L.-Y. Xu, K.-K. Meng, J. Zhang, Y.-L. Sun, X.-N. Lu, T.-Y. Li, Y. Jiang and G.-F. Zhong, Iridium-catalyzed alkenyl C–H allylation using conjugated dienes, *Chem. Commun.*, 2019, **55**, 9757–9760; (*o*) K.-K. Meng, Y.-L. Sun, J. Zhang, K.-Y. Zhang, X.-H. Ji, L.-Y. Ding and G.-F. Zhong, Iridium-catalyzed cross-coupling reactions of alkenes by hydrogen transfer, *Org. Lett.*, 2019, **21**, 8219–8224.

3 (*a*) M.-Y. Liu, P.-S. Yang, M. K. Karunananda, Y.-Y. Wang, P. Liu and K. M. Engle, C(alkenyl)–H activation via six-membered palladacycles: catalytic 1,3-diene synthesis, *J. Am. Chem. Soc.*, 2018, **140**, 5805–5813; (*b*) B. S. Schreib and E. M. Carreira, Palladium-catalyzed regioselective C–H iodination of unactivated alkenes, *J. Am. Chem. Soc.*, 2019, **141**, 8758–8763; (*c*) B. S. Schreib, M. Fadel and E. M. Carreira, Palladium-catalyzed C–H alkynylation of unactivated alkenes, *Angew. Chem., Int. Ed.*, 2020, **59**, 7818–7822; (*d*) B. S. Schreib, M. Son, F. A. Aouane, M.-H. Baik and E. M. Carreira, Allene C(sp$^2$)–H activation and alkenylation catalyzed by palladium, *J. Am. Chem. Soc.*, 2021, **143**, 21705–21712; (*e*) K.-K. Meng, T.-Y. Li, C.-B. Yu, C. Shen, J. Zhang and G.-F. Zhong, Geminal group-directed olefinic C-H functionalization via four- to eight-membered exo-metallocycles, *Nat. Commun.*, 2019, **10**, 5109; (*f*) C. Shen, X.-N. Lu, J. Zhang, L.-Y. Ding, Y.-L. Sun and G.-F. Zhong, Bidentate auxiliary-directed alkenyl C–H allylation via exo-palladacycles: synthesis of branched 1,4-dienes, *Chem. Commun.*, 2019, **55**, 13582–13585; (*g*) B.-Y. Han, B. Li, L.-P. Qi, P. Yang, G. He and G. Chen, Construction of cyclophane-braced peptide macrocycles via palladium-catalyzed picolinamide-directed intramolecular C(sp$^2$)–H arylation, *Org. Lett.*, 2020, **22**, 6879–6883; (*h*) H.-C. Tsai, Y.-H. Huang and C.-M. Chou, Rapid access to ortho-alkylated vinylarenes from aromatic acids by dearomatization and tandem decarboxylative C–H olefination/rearomatization, *Org. Lett.*, 2018, **20**, 1328–1332; (*i*) Y.-C. Wang, Y.-H. Huang, H.-C. Tsai, R. S. Basha and C.-M. Chou, Palladium-catalyzed proaromatic C(alkenyl)–H olefination: synthesis of densely functionalized 1,3-dienes, *Org. Lett.*, 2020, **22**, 6765–6770; (*j*) Z. Wu, N. Fatuzzo and G. Dong, Distal alkenyl C–H functionalization via the palladium/norbornene cooperative catalysis, *J. Am. Chem. Soc.*, 2020, **142**, 2715–2720.

4 (*a*) B. A. Vaughan, M. S. Webster-Gardiner, T. R. Cundari and T. B. Gunnoe, A rhodium catalyst for single-step styrene production from benzene and ethylene, *Science*, 2015, **348**, 421–424; (*b*) A. S. Jadhav, Y. A. Pankhade, R. Hazra and R. V. Anand, 1,6-Hydroolefination and Cascade Cyclization of *p*-Quinone Methides with Styrenes: Total Synthesis of (±)-Isopaucifloral F, *J. Org. Chem.*, 2018, **83**, 10107–10119; (*c*) Y. Huang and T. Hayashi, Chiral Diene Ligands in Asymmetric Catalysis, *Chem. Rev.*, 2022, **122**, 14346–14404.

5 Y.-H. Zhu, Y.-L. Liao, S.-Q. Jin, L.-Y. Ding, G. Zhong and J. Zhang, Functionality-Directed Regio- and Enantio-Selective Olefinic C–H Functionalization of Aryl Alkenes, *Chem. Rec.*, 2023, e202300012.

6 Arylation: (*a*) L. Ilies, S. Asako and E. Nakamura, Iron-Catalyzed Stereospecific Activation of Olefinic C-H Bonds with Grignard Reagent for Synthesis of Substituted Olefins, *J. Am. Chem. Soc.*, 2011, **133**, 7672–7675; (*b*) D. Zell, S. Warratz, D. Gelman, S. J. Garden and L. Ackermann, Single-Component Phosphinous Acid Ruthenium(II) Catalysts for Versatile C-H Activation by Metal-Ligand Cooperation, *Chem. – Eur. J.*, 2016, **22**, 1248–1252.

7 Alkylation: (*a*) Y. Li, X.-S. Zhang, Q.-L. Zhu and Z.-J. Shi, Olefinic C–H Bond Addition to Aryl Aldehyde and Its N-Sulfonylimine via Rh Catalysis, *Org. Lett.*, 2012, **14**, 4498–4501; (*b*) B.-W. Zhou, Y.-Y. Hu and C.-Y. Wang, Manganese-Catalyzed Direct Nucleophilic C(sp$^2$)–H Addition to Aldehydes and Nitriles, *Angew. Chem., Int. Ed.*, 2015, **54**, 13659–13663.

8 Cyanation: M. Chaitanya and P. Anbarasan, Rhodium-Catalyzed Cyanation of C(sp$^2$)–H Bond of Alkenes, *Org. Lett.*, 2015, **17**, 3766–3769.

9 Cyclization: (*a*) D.-B. Zhao, J. H. Kim, L. Stegemann, C. A. Strassert and F. Glorius, Cobalt(III)-Catalyzed Directed C–H Coupling with Diazo Compounds: Straightforward Access towards Extended π-Systems, *Angew. Chem., Int. Ed.*, 2015, **54**, 4508–4511, (*Angew. Chem.*, 2015, **127**, 4591–4594); (*b*) C. Aïssa, K. Y. T. Ho, D. J. Tetlow and M. Pin-Nó, Diastereoselective Carbocyclization of 1,6-Heptadienes Triggered by Rhodium-Catalyzed Activation of an Olefinic C-H Bond†, *Angew. Chem., Int. Ed.*, 2014, **53**, 4209–4212, (*Angew. Chem.*, 2014, **126**, 4293–4296); (*c*) A. Seoane, N. Casanova, N. Quiñones, J. L. Mascareñas and M. Gulías, Straightforward Assembly of Benzoxepines by Means of a Rhodium(III)-Catalyzed C–H Functionalization of o-Vinylphenols, *J. Am. Chem. Soc.*, 2014, **136**, 834–837; (*d*) A. Seoane, N. Casanova, N. Quiñones, J. L. Mascareñas and M. Gulías, Rhodium(III)-Catalyzed Dearomatizing (3 + 2) Annulation of 2-Alkenylphenols and Alkynes, *J. Am. Chem. Soc.*, 2014, **136**, 7607–7610; (*e*) L. Guo, F.-Y. Zhang, W.-M. Hu, L. Li and Y.-X. Jia, Palladium-catalyzed synthesis of benzofurans via C–H activation/oxidation tandem reaction and its application to the synthesis of decursivine and serotobenine†, *Chem. Commun.*, 2014, **50**, 3299–3302; (*f*) N. Casanova, A. Seoane, J. L. Mascareñas and M. Gulías, Rhodium-Catalyzed (5 + 1) Annulations Between 2-Alkenylphenols and Allenes: A Practical Entry to 2,2-Disubstituted 2H-Chromenes, *Angew. Chem., Int. Ed.*, 2015, **54**, 2374–2377; (*g*) N. Casanova, K. P. Del Rio, R. García-Fandiño, J. L. Mascareñas and M. Gulías, Palladium(II)-Catalyzed Annulation between ortho-Alkenylphenols and Allenes. Key Role of the Metal Geometry in Determining the Reaction Outcome, *ACS Catal.*, 2016, **6**, 3349–3353; (*h*) R. Kuppusamy, K. Muralirajan and C.-H. Cheng, Cobalt (III)-Catalyzed [5 + 1] Annulation for 2H-Chromenes Synthesis via Vinylic C–H Activation and Intramolecular Nucleophilic Addition, *ACS Catal.*, 2016, **6**, 3909–3913; (*i*) M. Font, B. Cendón, A. Seoane, J. L. Mascareñas and M. Gulías, Rhodium(III)-Catalyzed Annulation of 2-Alkenyl Anilides with Alkynes through C–H Activation: Direct Access to 2-Substituted Indolines, *Angew. Chem., Int. Ed.*, 2018, **57**, 8255–8259; (*j*) R.-X. Yu, D.-J. Li and F.-L. Zeng, Palladium-Catalyzed Sequential Vinylic C–H Arylation/Amination of 2-Vinylanilines with Aryl boronic Acids: Access to 2-Arylindoles, *J. Org. Chem.*, 2018, **83**, 323–329; P. Chen, J. Nan, Y. Hu, Q. Ma and Y.-M. Ma, RuII-Catalyzed/NH$_2$-Assisted Selective Alkenyl C–H [5 + 1] Annulation of Alkenylanilines with Sulfoxonium Ylides to Quinolines, *Org. Lett.*, 2019, **21**, 4812–4815; (*k*) A. Seoane, C. Comanescu, N. Casanova, R. García-Fandiño, X. Diz, J. L. Mascareñas and M. Gulías, Rhodium-Catalyzed Annulation of ortho-Alkenyl Anilides with Alkynes: Formation of Unexpected Naphthalene Adducts, *Angew. Chem., Int. Ed.*, 2019, **58**, 1700–1704.

10 Aminocarbonylation: (*a*) J. Li and L. Ackermann, Cobalt(III)-Catalyzed Aryl and Alkenyl C–H Aminocarbonylation with Isocyanates and Acyl Azides†, *Angew. Chem., Int. Ed.*, 2015, **54**, 8551–8554, (*Angew. Chem.*, 2015, **127**, 8671–8674); (*b*) W. Hou, B. Zhou, Y.-X. Yang, H.-J. Feng and Y.-C. Li, Rh (III)-Catalyzed Addition of Alkenyl C–H Bond to Isocyanates and Intramolecular Cyclization: Direct Synthesis 5-Ylidenepyrrol-2(5H)-ones, *Org. Lett.*, 2013, **15**, 1814–1817.

11 Alkynylation: P. Finkbeiner, U. Kloeckner and B. J. Nachtsheim, OH-Directed Alkynylation of 2-Vinylphenols with Ethynyl Benziodoxolones: A Fast Access to Terminal 1,3-Enynes, *Angew. Chem., Int. Ed.*, 2015, **54**, 4949–4952.

12 Alkenylation: (*a*) C. Shen, Y.-H. Zhu, S.-Q. Jin, K.-J. Xu, S.-X. Luo, L.-X. Xu, G.-F. Zhong, L.-J. Zhong and J. Zhang, Regio- and stereo-selective olefinic C–H functionalization of aryl alkenes in ethanol, *Org. Chem. Front.*, 2022, **9**, 989–994; (*b*) L. Jin, P. Zhang, Y. Li, X. Yu and B.-F. Shi, Atroposelective Synthesis of Conjugated Diene-Based Axially Chiral Styrenes via Pd(II)-Catalyzed Thioether-Directed Alkenyl C–H Olefination, *J. Am. Chem. Soc.*, 2021, **143**, 12335–12344; (*c*) C. Shen, Y.-H. Zhu, W.-Z. Shen, S.-Q. Jin, G.-F. Zhong, S.-X. Luo, L.-X. Xu, L.-J. Zhong and J. Zhang, Access to axially chiral aryl 1,3-dienes by transient group directed asymmetric C–H alkenylations, *Org. Chem. Front.*, 2022, **9**, 2109–2115; (*d*) D.-T. Dai, M.-W. Yang, Z.-Y. Chen, Z.-L. Wang and Y.-H. Xu, Chelation-Controlled Stereospecific Cross-Coupling Reaction between Alkenes for Atroposelective Synthesis of Axially Chiral Conjugated Dienes, *Org. Lett.*, 2022, **24**, 1979–1984.

13 Carboxylation: K. Sasano, J. Takaya and N. Iwasawa, Palladium(II)-Catalyzed Direct Carboxylation of Alkenyl C–H Bonds with CO$_2$, *J. Am. Chem. Soc.*, 2013, **135**, 10954–10957.

14 (*a*) M.-Y. Liu, J.-T. Sun, T. G. Erbay, H.-Q. Ni, R. Martín-Montero, P. Liu and K. M. Engle, PdII-Catalyzed C(alkenyl)–H Activation Facilitated by a Transient Directing

Group, *Angew. Chem., Int. Ed.*, 2022, **61**, e202203624; (*b*) C. Shen, Y.-H. Zhu, W.-Z. Shen, S.-Q. Jin, L.-J. Zhong, S.-X. Luo, L.-X. Xu, G.-F. Zhong and J. Zhang, Construction of axial chirality by asymmetric alpha C–H alkenylation of aryl alkenes†, *Org. Chem. Front.*, 2022, **9**, 4834–4839.

15 Very recently, our group reported a sequential α-/β-C–H alkenylation of trans-styrenes using alkenes and alkynes to afford polyenes, see: Y. Zhu, Y. Wang, W. Shen, X. Chen, Q. Liu, L. Yang, G. Zhong and J. Zhang, Stereoselective Synthesis of Complex Polyenes through Sequential α-/β-C–H Functionalization of trans-Styrenes, *Angew. Chem., Int. Ed.*, 2024, **63**, e2023152.

16 (*a*) C. Feng, D.-M. Feng and T.-P. Loh, Rhodium(III)-catalyzed C–H allylation of electron-deficient alkenes with allyl acetates, *Chem. Commun.*, 2015, **51**, 342–345; (*b*) D.-G. Yu, T. Gensch, F. Azambuja, S. Vásquez-Céspedes and F. Glorius, Co(III)-Catalyzed C–H Activation/Formal SN-Type Reactions: Selective and Efficient Cyanation, Halogenation, and Allylation, *J. Am. Chem. Soc.*, 2014, **136**, 17722–17725; (*c*) S.-S. Zhang, J.-Q. Wu, Y.-X. Lao, X.-G. Liu, Y. Liu, W.-X. Lv, D.-H. Tan, Y.-F. Zeng and H.-G. Wang, Mild Rhodium(III)-Catalyzed C–H Allylation with 4-Vinyl-1,3-dioxolan-2-ones: Direct and Stereoselective Synthesis of (E)-Allylic Alcohols, *Org. Lett.*, 2014, **16**, 6412–6415; (*d*) Y. Kuninobu, K. Ohta and K. Takai, Rhenium-catalyzed allylation of C–H bonds of benzoic and acrylic acids, *Chem. Commun.*, 2011, **47**, 10791–10793; (*e*) X.-W. Wu and H.-T. Ji, Ruthenium-Catalyzed C–H Allylation of Alkenes with Allyl Alcohols via C–H Bond Activation in Aqueous Solution, *J. Org. Chem.*, 2018, **83**, 12094–12102; (*f*) H. He, W.-B. Liu, L.-X. Dai and S.-L. You, Ir-Catalyzed Cross-Coupling of Styrene Derivatives with Allylic Carbonates: Free Amine Assisted Vinyl C–H Bond Activation, *J. Am. Chem. Soc.*, 2009, **131**, 8346–8347; (*g*) C. Shen, X.-N. Lu, J. Zhang, L.-Y. Ding, Y.-L. Sun and G.-F. Zhong, Bidentate auxiliary-directed alkenyl C–H allylation via exo-palladacycles: synthesis of branched 1,4-dienes, *Chem. Commun.*, 2019, **55**, 13582–13585.

17 (*a*) V. G. Zaitsev, D. Shabashov and O. Daugulis, Highly Regioselective Arylation of sp$^3$ C–H Bonds Catalyzed by Palladium Acetate, *J. Am. Chem. Soc.*, 2005, **127**, 13154; (*b*) A. Deb, S. Bag, R. Kancherla and D. Maiti, Palladium Catalyzed Aryl C–H Olefination with Unactivated, Aliphatic Alkenes, *J. Am. Chem. Soc.*, 2014, **136**, 13602.

18 (*a*) Y. Gao, M.-F. Zhang, C.-Y. Wang, Z. Yang, X.-Q. Huang, R.-K. Feng and C.-Z. Qi, Cobalt(II)-catalyzed hydroarylation of 1,3-diynes and internal alkynes with picolinamides promoted by alcohol, *Chem. Commun.*, 2020, **56**, 14231–14234; (*b*) A. M. Martínez, J. Echavarren, I. Alonso, N. Rodríguez, R. G. Arrayás and J. C. Carretero, RhI/RhIII catalyst-controlled divergent aryl/heteroaryl C–H bond functionalization of picolinamides with alkynes, *Chem. Sci.*, 2015, **6**, 5802–5814; (*c*) Y.-S. Zhao, G. He, W. A. Nack and G. Chen, Palladium-Catalyzed Alkenylation and Alkynylation of ortho-C(sp$^2$)–H Bonds of Benzylamine Picolinamides, *Org. Lett.*, 2012, **14**, 2948–2951; (*d*) X.-N. Wang, S.-T. Tao, L.-T. Xu, C. Zhang, L.-X. Meng, X.-J. Zhang and D.-W. Ma, Pd-Catalyzed Dimethylation of Tyrosine-Derived Picolinamide for Synthesis of (S)-N-Boc-2,6-dimethyltyrosine and Its Analogues, *Org. Lett.*, 2017, **19**, 246–249; (*e*) P. Liu, J. Han, Q. Wang, Z.-B. Huang, D.-Q. Shi, R.-S. Zeng and Y.-S. Zhao, Palladium(II)-catalyzed Sequential ortho-olefination of β-arylethamines with assistance of oxalyl amide, *RSC Adv.*, 2015, **5**, 60646–60649; (*f*) P. Singh, A. Dalal and S. A. Babu, Palladium(II)-Catalyzed Sp$^3$/Sp$^2$ γ- and δ-C-H Functionalization of Aryl Amines using 5-Methylisoxazole-3-Carboxamide as Directing Group, *Asian J. Org. Chem.*, 2019, **8**, 877–886; (*g*) B.-B. Zhan, Y. Li, J.-W. Xu, X.-L. Nie, J. Fan, L. Jin and B.-F. Shi, Site-Selective δ-C(sp$^3$)–H Alkylation of Amino Acids and Peptides with Maleimides via a Six-Membered Palladacycle, *Angew. Chem., Int. Ed.*, 2018, **57**, 5858–5862; (*h*) N. Bisht, P. Singh and S. A. Babu, Pd(II)-Catalyzed, Picolinamide-Aided γ-(sp2)-C–H Functionalization of Racemic and Enantiopure α-Methylbenzylamine and Phenylglycinol Scaffolds, *Synthesis*, 2022, **54**, 4059–4094; (*i*) R. Parella and S. A. Babu, Pd(II)-Catalyzed, Picolinamide-Assisted, Z-Selective γ-Arylation of Allylamines To Construct Z-Cinnamylamines, *J. Org. Chem.*, 2017, **82**, 6550–6567; (*j*) R. Parella and S. A. Babu, Pd(OAc)$^2$-C atalyzed, AgOAc-Promoted Z Selective Directed β-Arylation of Acrylamide Systems and Stereoselective Construction of Z-Cinnamamide Scaffolds, *J. Org. Chem.*, 2015, **80**, 12379–12396; (*k*) X.-Z. Cheng, Z. Chen, Y.-D. Gao, F.-T. Xue and C. Jiang, Aminoquinoline-assisted vinylic C–H arylation of unsubstituted acrylamide for the selective synthesis of Z olefins, *Org. Biomol. Chem.*, 2016, **14**, 3298–3306.

19 1,4-Diene was not obtained herein, and this is because 1,4-diene from allylation of **8** is more reactive than **8** to undergo the second allylation to give triene.

20 All of the substrates in Tables 2 and 3 and Scheme 2 afforded no aromatic C–H allylation, exhibiting excellent regio selectivity.