Chemical Science

ROYAL SOCIETY OF CHEMISTRY

EDGE ARTICLE

View Article Online
View Journal | View Issue

Open Access Article. Published on 16 1446. Downloaded on 08/10/47 06:48:10 .
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

Check for updates

Cite this: *Chem. Sci.*, 2025, **16**, 10951

All publication charges for this article have been paid for by the Royal Society of Chemistry

Received 31st March 2025
Accepted 13th May 2025

DOI: 10.1039/d5sc02421h

rsc.li/chemical-science

Copper-catalyzed asymmetric carbonylative hydroallylation of vinylarenes†

Sufang Shao,‡[ab] Yang Yuan,‡[a] Alban Schmoll[a] and Xiao-Feng Wu *[abc]

We describe a novel and efficient copper-catalyzed carbonylative hydroallylation of vinylarenes, providing a direct route to chiral α,β-unsaturated ketones, which are important compounds in organic synthesis and bioactive molecules. The method employs readily accessible vinylarenes and allylic phosphates, utilizing carbon monoxide as the carbonyl source under mild reaction conditions. The reaction demonstrates a broad substrate scope, including diverse vinylarenes with various functional groups, as well as vinylarenes derived from natural products. Additionally, all four stereoisomers of a chiral allylic alcohol were prepared by employing this strategy, showcasing its versatility in stereodivergent synthesis.

Introduction

α,β-Unsaturated carbonyl compounds are important intermediates in organic chemistry, extensively used in synthetic transformations and the production of fine and commodity chemicals.[1] Traditionally, these compounds have been prepared through methods such as the Horner–Wadsworth–Emmons reaction,[2] aldol condensation,[3] Knoevenagel condensation,[4] and Saegusa oxidation.[5] More recently, alternative methods, including dehydrogenation reactions,[6] coupling reactions,[7] and other strategies,[8] have also been developed for the synthesis of α,β-unsaturated carbonyl compounds. However, most of these methods require a pre-existing carbonyl group in the reactant, which somewhat limits the substrate scope. Consequently, developing practical and efficient methods for their synthesis is still important and desired.

Carbonylation, a process that introduces carbon monoxide (CO) into molecules, has become one of the most direct and efficient methods for synthesizing carbonyl compounds.[9] Among these, α,β-unsaturated ketones are important intermediates in organic synthesis, widely utilized in various transformations such as Michael addition,[10] Baylis–Hillman reaction,[11] epoxidation,[12] Simmons–Smith reaction,[13] Diels–Alder reaction,[14] hydrogenation,[15] hydroalkoxylation,[16] and aldol addition.[17] Additionally, they serve as key structural elements in numerous drug molecules and bioactive compounds (Fig. 1a).[18] In contrast to other α,β-unsaturated derivatives, such as α,β-unsaturated amides and α,β-

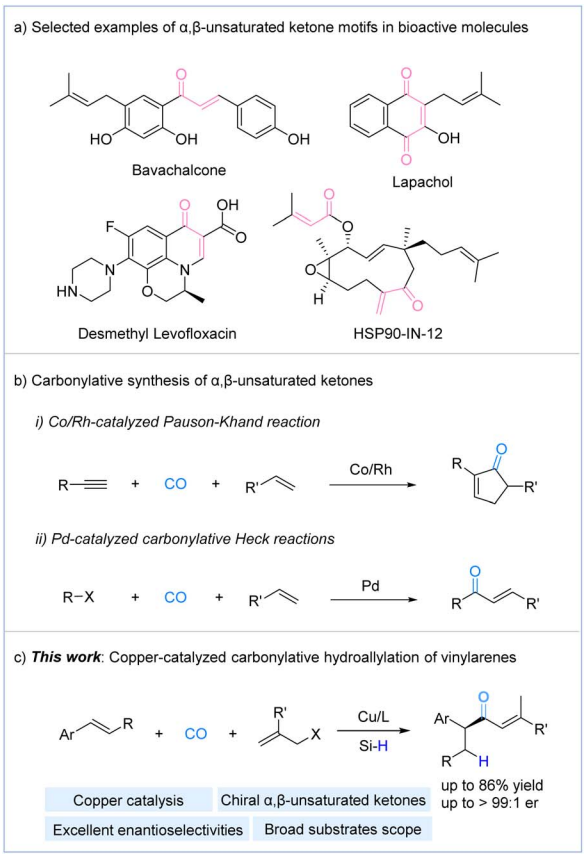


Fig. 1 (a) Selected examples of α,β-unsaturated ketone motifs in bioactive molecules; (b) carbonylative synthesis of α,β-unsaturated ketones; (c) this work: copper-catalyzed carbonylative hydroallylation of vinylarenes.

[a]Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P. R. China. E-mail: xwu2020@dicp.ac.cn

[b]Leibniz-Institut für Katalyse, Rostock 18059, Germany

[c]State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin, 300071, China

† Electronic supplementary information (ESI) available: General comments, general procedures, analytic data and NMR spectra. CCDC 2413898. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d5sc02421h

‡ They contribute equally to this work.

© 2025 The Author(s). Published by the Royal Society of Chemistry

Open Access Article. Published on 16 1446. Downloaded on 08/10/47 06:48:10 .
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

unsaturated esters, the carbonylative synthesis of α,β-unsaturated ketones remains relatively challenging and underdeveloped, primarily due to the generally lower reactivity of carbon-based nucleophiles.[19] The two most important carbonylative methods for synthesizing α,β-unsaturated ketones are the Pauson–Khand reaction[20] and carbonylative Heck reactions[21] (Fig. 1b). In addition, Mankad and co-workers presented a copper-catalyzed four-component coupling reaction of alkynes, alkyl halides, B_2pin_2, and CO enables modular synthesis of β-borylated tetrasubstituted enones.[22] Alexanian group reported a cobalt-catalyzed stereospecific carbonylative coupling of alkyl tosylates and dienes producing enantioenriched enones.[23]

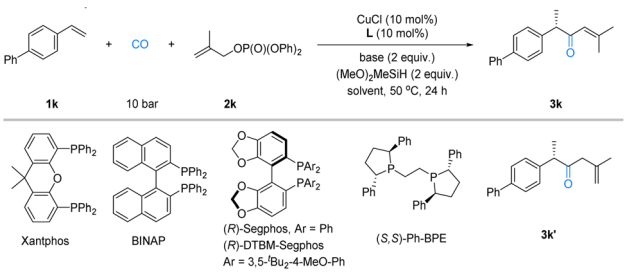
Recently, our group developed copper-catalyzed hydroaminocarbonylation of alkenes with hydroxylamine electrophiles to provide α-chiral amides, β-chiral amides, and γ-chiral amides.[24] Given the rapid advancements in copper-catalyzed enantioselective hydrofunctionalization and allylic substitution reactions in recent years,[25] as well as our ongoing interest in carbonylation reactions, we hypothesized that a similar approach could be employed to construct enantioenriched α,β-unsaturated ketones using a suitable allylic agent. Herein, we report a copper-catalyzed carbonylative hydroallylation of vinylarenes with allylic electrophiles, using carbon monoxide (CO) as the carbonyl source under mild conditions. This approach provides a highly efficient strategy for the synthesis of valuable chiral α,β-unsaturated ketones with good functional group tolerance (Fig. 1c).

Results and discussion

In the initial phase of our research, we studied the reaction of vinylarene (**1k**) with 2-methylallyl diphenyl phosphate (**2k**) in THF at 50 °C under 10 bar CO, using $(MeO)_2MeSiH$ as the hydrogen source. Xantphos was used as the ligand, and various bases were screened. The results showed that LiOMe, NaO^{t}Bu, and CsF produced trace amounts of the desired product **3k** (Table 1, entries 1, 3 and 4). However, using LiO^{t}Bu as the base improved the yield slightly (Table 1, entry 2). Subsequently, with LiO^{t}Bu showing the most promise, we evaluated different ligands. BINAP, (*R*)-Segphos, and (*R*)-DTBM-Segphos exhibited similar low reactivity to Xantphos, yielding very low yields of the product (entries 5–7). The use of (*S*,*S*)-Ph-BPE as the ligand significantly improved the yield to 44% with 84 : 16 enantiomeric ratio (entry 8). The examination of the solvent effects revealed that 1,2-dichloroethane (DCE) was the optimal choice, affording the product in 89% yield and high enantioselectivity (entry 9). Despite this, DCE led to the formation of side product **3k′** (9% yield), which posed a considerable challenge to the purification and isolation. This problem was resolved by employing a mixed solvent system of DCE and 1,4-dioxane, which yielded a single product **3k** in 84% isolated yield with 92 : 8 enantiomeric ratio (Table 1, entry 12).

After establishing the optimal conditions for the carbonylative hydroallylation reaction, an extensive investigation into the substrate scope of olefins was conducted. The results,

Table 1 Optimization of the reaction conditions[a]



Entry	Ligand	Base	Solvent	Yield (%)	er
1	Xantphos	LiOMe	THF	Trace	—
2	Xantphos	LiO^{t}Bu	THF	<10	—
3	Xantphos	NaO^{t}Bu	THF	Trace	—
4	Xantphos	CsF	THF	0	—
5	BINAP	LiO^{t}Bu	THF	<10	—
6	(*R*)-Segphos	LiO^{t}Bu	THF	<10	—
7	(*R*)-DTBM-Segphos	LiO^{t}Bu	THF	13	—
8	(*S*,*S*)-Ph-BPE	LiO^{t}Bu	THF	44	84 : 16
9	(*S*,*S*)-Ph-BPE	LiO^{t}Bu	PhMe	54	89 : 11
10	(*S*,*S*)-Ph-BPE	LiO^{t}Bu	Dioxane	75	92 : 8
11	(*S*,*S*)-Ph-BPE	LiO^{t}Bu	DCE	89[c]	93 : 7
12	(*S*,*S*)-Ph-BPE	LiO^{t}Bu	Dioxane : DCE = 1 : 1	88 (84)[b]	92 : 8

[a] Reaction conditions: **1a** (0.1 mmol), **1b** (0.2 mmol), CuCl (10 mol%), **L** (10 mol%), base (2.0 equiv.), $(MeO)_2MeSiH$ (2.0 equiv.) and CO (10 bar) in solvent (1 mL) at 50 °C for 24 h. Yields are determined by GC-FID with *n*-hexadecane as the internal standard, enantiomeric ratios were determined by chiral HPLC. [b] Isolated yield. [c] Mixed with 9% yield of **3k′**.

 © 2025 The Author(s). Published by the Royal Society of Chemistry

Open Access Article. Published on 16 1446. Downloaded on 08/10/47 06:48:10 .
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

summarized in the Fig. 2, demonstrate that a wide variety of aryl olefins can produce the corresponding α,β-unsaturated ketones with excellent yields (up to 84%) and enantiomeric ratios (up to >99 : 1 er). Specifically, variations in the position of alkyl substituents on the aromatic ring had a negligible effect on reaction outcomes, as evident in examples (**3a–3d**, 69–78% yield, 92 : 8–96 : 4 er). Substrates with electron-donating groups on the aromatic ring (**3e**, **3i**, **3j**) exhibited improvements in both yield and enantioselectivity, achieving yields of up to 83% and enantiomeric ratios of >99 : 1 er. Halogen-substituted olefins (**3f–3h**) afforded the desired products with slightly lower enantioselectivity, as shown by yields of 66–84% and er values of 84 : 16–96 : 4. Notably, internal aryl olefins, such as **3n** and **3o**, were well-tolerated, achieving enantiomeric ratios of up to >99 : 1 er. Olefins containing heteroatoms (N, O) exhibited excellent reactivity and stereoselectivity, with yields ranging from 64% to 86% and er values of up to >99 : 1 (**3p–3u**). Furthermore, natural product-derived olefins were explored. Substrates derived from furfuryl alcohol (**3v**), nerol (**3w**), myrtenol (**3x**), and diacetone fructose (**3y**) produced the desired products in high yields. It should be noted that when 4-vinylphenyl acetate was used as the substrate, only **3z** can be detected and isolated in 27% yield with 95 : 5 er. The absolute configuration of **3z** was determined to be *S* through X-ray crystallographic analysis.

Then, we investigated the scope of electrophilic reagents. Allyl phosphates with various substituents at the 2-position, including aryl, benzyl, and related groups, were compatible with the reaction. These substrates produced the desired α,β-unsaturated ketones (**3aa–3af**) with yields up to 81% and enantiomeric ratios of up to 99 : 1 er. α-Methylstyrene, (*E*)-stilbene, and

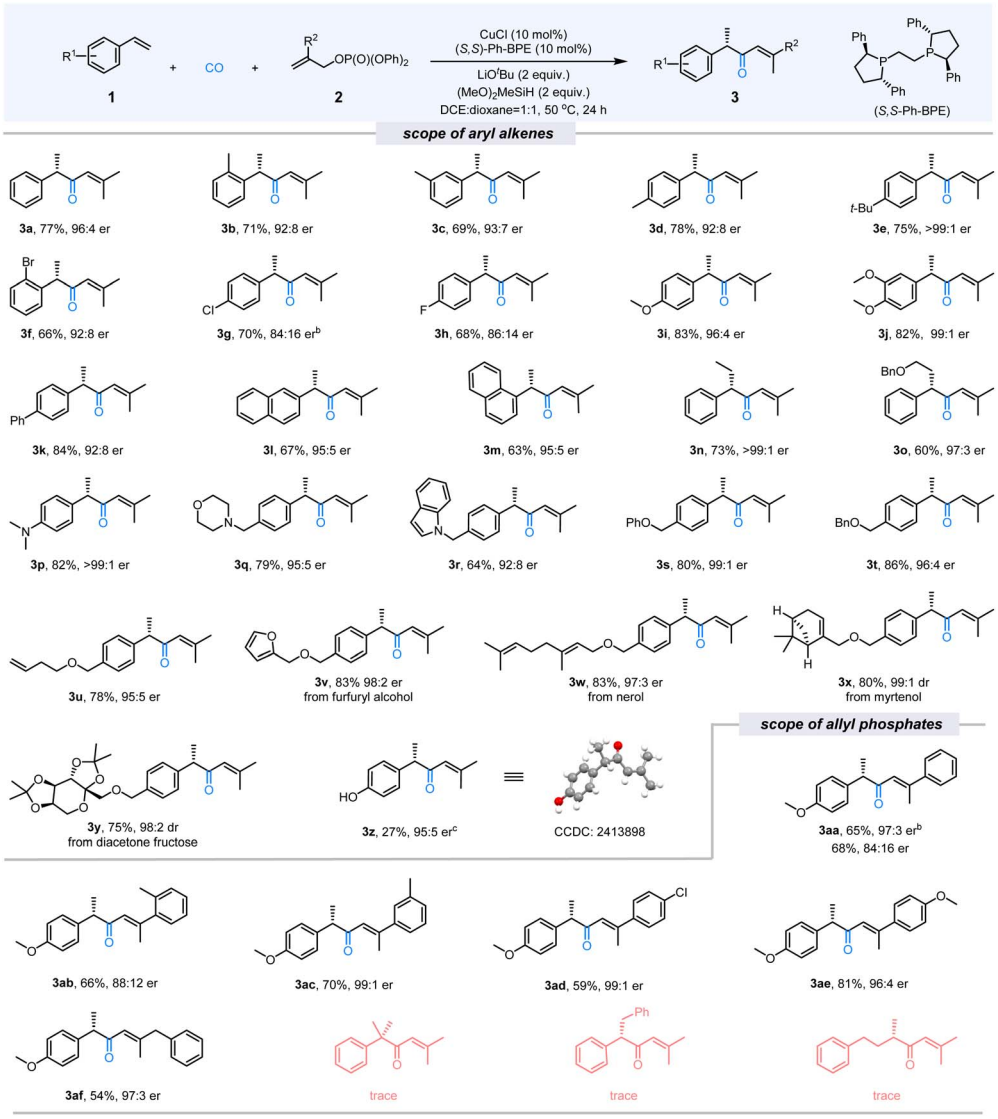


Fig. 2 Substrate scope.[a] [a]Reaction conditions: **1** (0.1 mmol), **2** (0.2 mmol), CuCl (10 mol%), (*S*,*S*)-Ph-BPE (10 mol%), LiO^{t}Bu (2.0 equiv.), (MeO)$_2$MeSiH (2 equiv.) and CO (10 bar) in DCE (0.5 mL) and 1,4-dioxane (0.5 mL) at 50 °C for 24 h; [b]30 °C for 48 h; [c]The reactant of the reaction was 4-vinylphenyl acetate, and only product **3z** can be detected and isolated. Enantiomeric ratios and diastereomeric ratios were determined by chiral HPLC.

Open Access Article. Published on 16 1446. Downloaded on 08/10/47 06:48:10 .
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

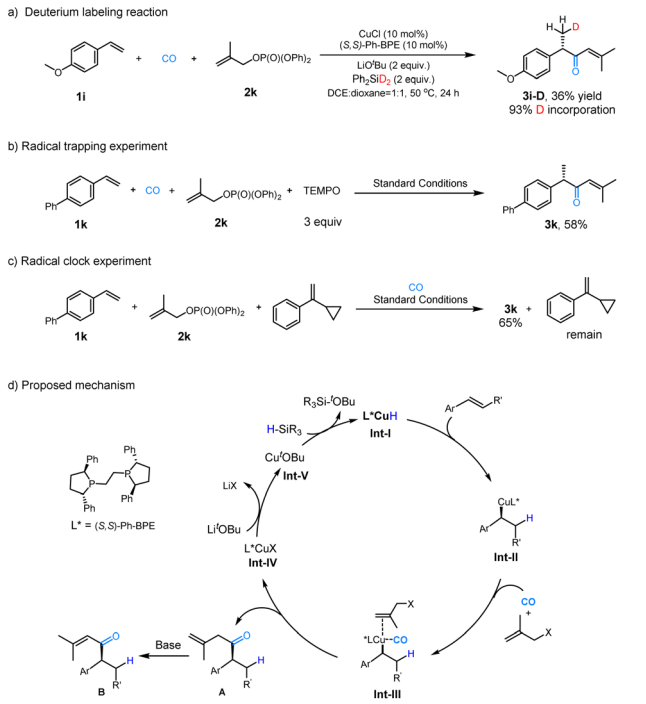


Fig. 3 Mechanism investigation experiments and proposed mechanism. Standard conditions: CuCl (10 mol%), (*S*,*S*)-Ph-BPE (10 mol%), LiO^{t}Bu (2.0 equiv.), $(MeO)_2MeSiH$ (2 equiv.) and CO (10 bar) in DCE (0.5 mL) and 1,4-dioxane (0.5 mL) at 50 °C for 24 h.

4-phenyl-1-butene were also subjected to the reaction under standard conditions, unfortunately, no desired ketone products can be detected.

To gain deeper insight into the reaction pathway, a series of experiments was conducted. First, deuterated diphenylsilane was synthesized, and a deuterium-labelling experiment was performed under standard conditions. Using Ph_2SiD_2 as the hydrogen source, product **3i-D** was obtained 36% yield, and 93% deuterium incorporation was observed at the β-position (Fig. 3a). To investigate whether the reaction proceeds through a radical-based mechanism, two experiments were conducted. First, TEMPO (3 equiv.) was employed as a radical trapping reagents, and the product **3k** was obtained in 58% yield, indicating that the reaction was not significantly inhibited. Next, a radical clock experiment was performed using (1-cyclopropylvinyl)benzene as an additional substrate. In this case, the desired product **3k** was formed in 68% yield, and (1-cyclopropylvinyl)benzene remained intact. These results indicate that no radical intermediates were involved, suggesting that the reaction likely proceeds through a non-radical pathway (Fig. 3b and c).

Based on the experimental results presented above and previous literature,[25,26] we proposed the following plausible reaction mechanism (Fig. 3d). The cycle begins with the insertion of olefin into the key catalyst L*CuH **Int-I**, generating an enantiomerically enriched intermediate, **Int-II**. Subsequently, CO and the allyl electrophilic reagent coordinate with **Int-II**, leading to the formation of intermediate **Int-III**. Following this, CO insertion, S_N2'-allylic substitution, and reductive elimination occur, affording product **A**, which undergoes isomerization to form the final α,β-unsaturated ketone (see ESI†). Finally, in the presence of a metal alkoxide and hydrosilane, **Int-IV** facilitates the regeneration of LCuH, completing the catalytic cycle.

In biological systems, the chiral environment plays a crucial role, as drugs with different stereochemical configurations can exhibit varying therapeutic efficacies or cause adverse reactions. Despite many advances in the field of asymmetric catalytic reactions, the construction of multiple consecutive chiral centers continues to be a challenge.[27] Therefore, we wondered whether we could identify reaction conditions suitable for the stereodivergent construction of all four stereoisomers of **5**. Initially, following literature precedent,[28] we subjected racemic **3j** to reduction using the $Cu(OAc)_2$/DTBM-Segphos catalytic system, obtaining racemic **5** in 81% isolated yield (Fig. 4a). Next, we prepared α,β-unsaturated ketones (*R*)-**3j** and (*S*)-**3j** by using (*R*,*R*)-**L1** and (*S*,*S*)-**L1** as the ligands, respectively. Notably, by

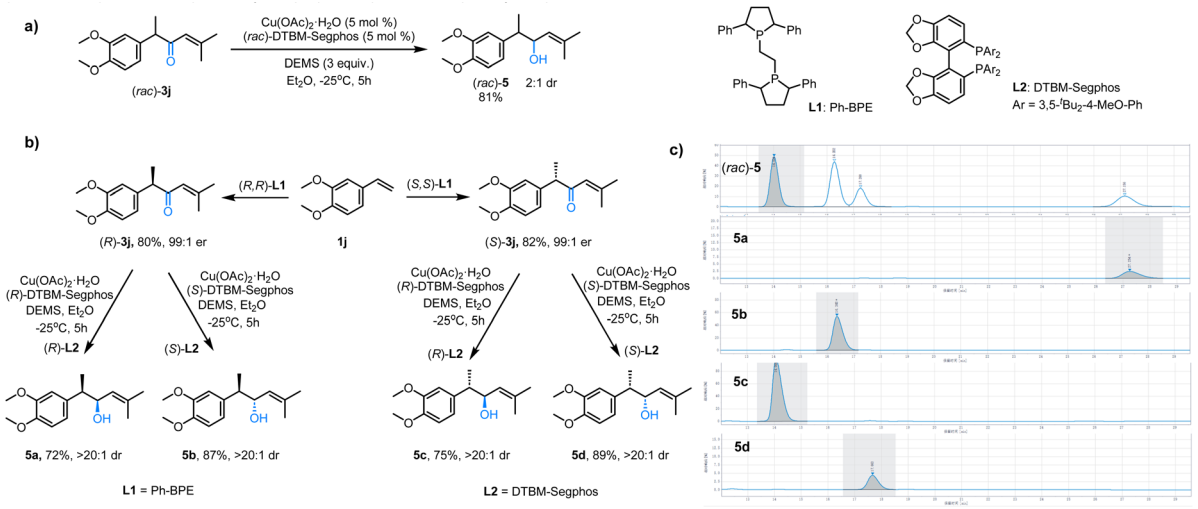


Fig. 4 (a and b) Synthesis of all stereoisomeric chiral alcohols; (c) HPLC traces of all stereoisomeric chiral alcohols.

 © 2025 The Author(s). Published by the Royal Society of Chemistry

Open Access Article. Published on 16 1446. Downloaded on 08/10/47 06:48:10 .
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

subjecting (*R*)-**3j** and (*S*)-**3j** to the reaction under the specified conditions with (*R*)-**L2** or (*S*)-**L2**-based catalysts, all four stereoisomeric chiral alcohols (**5a–5d**) were obtained in high yields (72–89%) with excellent enantioselectivities (>20 : 1 dr),as confirmed by the HPLC traces in Fig. 4c.

Conclusions

In conclusion, we have developed an efficient copper-catalyzed carbonylative hydroallylation methodology for the enantioselective synthesis of α,β-unsaturated ketones. This approach utilizes mild reaction conditions, demonstrating high functional group tolerance and excellent enantioselectivity across a broad substrate scope. Moreover, the stereodivergent construction of all four stereoisomers of a chiral allylic alcohol was achieved, highlighting the method's versatility for synthesizing potential multiple contiguous stereocentres biologically relevant molecules in organic and medicinal chemistry.

Data availability

The data supporting this article have been included as part of the ESI.†

Author contributions

XW and YY directed the project and revised the manuscript. SS performed most of the experiments and prepared the manuscript. AS supported in substrates preparation.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We appreciate the financial support provided by National Key R&D Program of China (2023YFA1507500), National Natural Science Foundation of China (22302198) and the International Partnership Program of the Chinese Academy of Sciences (Grant No. 028GJHZ2023045FN).

Notes and references

1 (*a*) L. V. Reddy, V. Kumar, R. Sagar and A. K. Shaw, *Chem. Rev.*, 2013, **113**, 3605–3631; (*b*) M. Schroeder, M. Mathys, N. Ehrensperger and M. Büchel, *Chem. Biodiversity*, 2014, **11**, 1651–1673; (*c*) J. W. Choi, B. K. Jang, N. C. Cho, J. H. Park, S. K. Yeon, E. J. Ju, Y. S. Lee, G. Han, A. N. Pae, D. J. Kim and K. D. Park, *Bioorg. Med. Chem.*, 2015, **23**, 6486–6496; (*d*) R. Buffa, P. Sedova, I. Basarabova, M. Moravcova, L. Wolfova, T. Bobula and V. Velebny, *Carbohydr. Polym.*, 2015, **134**, 293–299; (*e*) B. Hu, T. X. Liu, P. Zhang, Q. Liu, J. Bi, L. Shi, Z. Zhang and G. Zhang, *Org. Lett.*, 2018, **20**, 4801–4805.

2 (*a*) L. Horner, H. Hoffmann and H. G. Wippel, *Chem. Ber.*, 1958, **91**, 61–63; (*b*) W. S. Wadsworth and W. D. Emmons, *J. Am. Chem. Soc.*, 1961, **83**, 1733–1738.

3 F. A. Carey and R. J. Sundberg, *Advanced Organic Chemistry: Part B: Reactions and Synthesis*, Springer, 3rd edn, 1993, pp. 65–137.

4 E. Knoevenagel, *Ber. Dtsch. Chem. Ges.*, 1898, **31**, 2596–2619.

5 Y. Ito, T. Hirao and T. Saegusa, *J. Org. Chem.*, 1978, **43**, 1011–1013.

6 (*a*) K. Nicolaou, Y.-L. Zhong and P. Baran, *J. Am. Chem. Soc.*, 2000, **122**, 7596–7597; (*b*) M. A. Bigi and M. C. White, *J. Am. Chem. Soc.*, 2013, **135**, 7831–7834; (*c*) M.-M. Wang, X.-S. Ning, J.-P. Qu and Y.-B. Kang, *ACS Catal.*, 2017, **7**, 4000–4003.

7 (*a*) T. S. Jiang and J. H. Li, *Chem. Commun.*, 2009, 7236–7238; (*b*) J. Wang, C. Liu, J. Yuan and A. Lei, *Angew. Chem., Int. Ed.*, 2013, **52**, 2256–2259.

8 (*a*) S. Mandal, S. Mahato and C. K. Jana, *Org. Lett.*, 2015, **17**, 3762–3765; (*b*) D. Kaiser, L. F. Veiros and N. Maulide, *Adv. Synth. Catal.*, 2017, **359**, 64–77.

9 (*a*) W. Bertleff, M. Roeper and X. Sava. Carbonylation, *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, 2007; (*b*) Q. Liu, H. Zhang and A. Lei, *Angew. Chem., Int. Ed.*, 2011, **50**, 10788–11079; (*c*) J.-B. Peng, H.-Q. Geng and X.-F. Wu, *Chem*, 2019, **5**, 526–552.

10 H. Pellissier, *Adv. Synth. Catal.*, 2015, **357**, 2745–2780.

11 J. Karabline-Kuks, P. Ramesh and M. Portnoy, *Adv. Synth. Catal.*, 2016, **358**, 3541–3554.

12 M. Bougauchi, S. Watanabe, T. Arai, H. Sasai and M. Shibasaki, *J. Am. Chem. Soc.*, 1997, **119**, 2329–2330.

13 L. Pontini, J. A. Leitch and D. L. Browne, *Green Chem.*, 2023, **25**, 4319–4325.

14 A. B. Northrup and D. W. MacMillan, *J. Am. Chem. Soc.*, 2002, **124**, 2458–2460.

15 N. J. A. Martin and B. List, *J. Am. Chem. Soc.*, 2006, **128**, 13368–13369.

16 J.-J. Yun, M.-L. Zhi, W.-X. Shi, X.-Q. Chu, Z.-L. Shen and T.-P. Loh, *Adv. Synth. Catal.*, 2018, **360**, 2632–2637.

17 S. Crotti, G. Belletti, N. Di Iorio, E. Marotta, A. Mazzanti, P. Righi and G. Bencivenni, *RSC Adv.*, 2018, **8**, 33451–33458.

18 (*a*) Z. Nowakowska, *Eur. J. Med. Chem.*, 2007, **42**, 125–137; (*b*) D. Kumar, N. M. Kumar, K. Akamatsu, E. Kusaka, H. Harada and T. Ito, *Bioorg. Med. Chem. Lett.*, 2010, **20**, 3916–3919; (*c*) R. G. Damazio, A. P. Zanatta, L. H. Cazarolli, L. D. Chiaradia, A. Mascarello, R. J. Nunes, R. A. Yunes and F. R. M. B. Silva, *Eur. J. Med. Chem.*, 2010, **45**, 1332–1337; (*d*) N. K. Sahu, S. S. Balbhadra, J. Choudhary and D. V. Kohli, *Curr. Med. Chem.*, 2012, **19**, 209–255.

19 S. Zhang, H. Neumann and M. Beller, *Chem. Soc. Rev.*, 2020, **49**, 3187–3210.

20 (*a*) I. U. Khand, G. R. Knox, P. L. Pauson, W. E. Watts and M. I. Foreman, *J. Chem. Soc., Perkin Trans. 1*, 1973, 977–981; (*b*) O. Geis and H.-G. Schmalz, *Angew. Chem., Int. Ed.*, 1998, **37**, 911–914; (*c*) J. Blanco-Urgoiti, L. AÇorbe, L. PØrez-Serrano, G. Domínguez and J. PØrez-Castells, *Chem. Soc. Rev.*, 2004, **33**, 32–42; (*d*) E. Cristóbal-Lecina, A. R. Costantino, A. Grabulosa, A. Riera and X. Verdaguer, *Organometallics*, 2015, **34**, 4989–4993.

Open Access Article. Published on 16 1446. Downloaded on 08/10/47 06:48:10 .
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

21 (*a*) X.-F. Wu, H. Neumann, A. Spannenberg, T. Schulz, H. Jiao and M. Beller, *J. Am. Chem. Soc.*, 2010, **132**, 14596–14602; (*b*) X.-F. Wu, H. Neumann and M. Beller, *Angew. Chem., Int. Ed.*, 2010, **49**, 5284–5288; (*c*) X.-F. Wu, H. Neumann and M. Beller, *Angew. Chem., Int. Ed.*, 2010, **122**, 5412–5416; (*d*) X.-F. Wu, H. Neumann and M. Beller, *Chem. Soc. Rev.*, 2011, **40**, 4986–5009.

22 L.-J. Cheng and N. P. Mankad, *Angew. Chem., Int. Ed.*, 2018, **57**, 10328–10332.

23 B. T. Sargent and E. J. Alexanian, *J. Am. Chem. Soc.*, 2017, **139**, 12438–12440.

24 (*a*) Y. Yuan, F.-P. Wu, C. Schünemann, J. Holz, P. C. J. Kamer and X.-F. Wu, *Angew. Chem., Int. Ed.*, 2020, **59**, 22441–22445; (*b*) Y. Yuan, F. Zhao and X.-F. Wu, *Chem. Sci.*, 2021, **12**, 12676–12681; (*c*) Y. Yuan, Y. Zhang, W. Li, Y. Zhao and X.-F. Wu, *Angew. Chem., Int. Ed.*, 2023, **62**, e202309993; (*d*) Y. Yuan, Y. Zhang and X.-F. Wu, *Nat. Commun.*, 2024, **15**, 6705–6712.

25 (*a*) Y.-M. Wang and S. L. Buchwald, *J. Am. Chem. Soc.*, 2016, **138**, 5024–5027; (*b*) R. Y. Liu and S. L. Buchwald, *Acc. Chem. Res.*, 2020, **53**, 1229–1243; (*c*) S. Krautwald and E. M. Carreira, *J. Am. Chem. Soc.*, 2017, **139**, 5627–5639; (*d*) Z.-Y. Yi, H. Xu, X. Chang, Y. Dang, X.-Q. Dong and C.-J. Wang, *ACS Catal.*, 2024, **14**, 14058–14068.

26 N. Kim, J. T. Han, D. H. Ryu and J. Yun, *Org. Lett.*, 2017, **19**, 6144–6147.

27 S.-L. Shi, Z. L. Wong and S. L. Buchwald, *Nature*, 2016, **532**, 353–356.

28 R. Moser, Ž. V. Bošković, C. S. Crowe and B. H. Lipshutz, *J. Am. Chem. Soc.*, 2010, **132**, 7852–7853.

 © 2025 The Author(s). Published by the Royal Society of Chemistry