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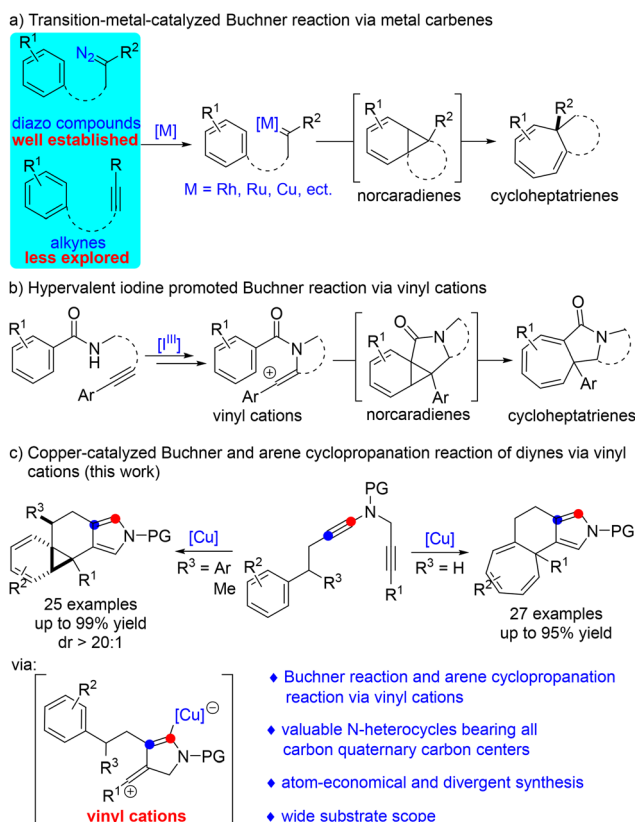
Copper-catalyzed Buchner reaction and phenyl cyclopropanation through diyne cyclization†

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The Buchner reaction, as an exclusive category of expansive dearomatization, represents a powerful approach for the construction of valuable functionalized cycloheptatrienes in a direct manner from readily available aromatic precursors. However, the traditional Buchner reaction almost relies on using explosive diazo compounds as carbene precursors. Herein, we disclose a copper-catalyzed Buchner reaction through diyne cyclization, and bicycle-fused cycloheptatrienes bearing all carbon quaternary stereogenic centers are obtained in moderate to excellent yields with a broad substrate scope. In addition, norcaradiene derivatives can also be selectively produced by substrate control through a phenyl cyclopropanation reaction, thus constituting a copper-catalyzed controllable cyclization of diynes.

The Buchner reaction, since its discovery in 1885 by Buchner and Curtius,¹ has become a feasible protocol for the straightforward synthesis of valuable functionalized cycloheptatrienes from ubiquitous aromatic precursors.² In addition, norcaradiene, as an arene cyclopropanation intermediate in the Buchner reaction, has also been extensively employed to synthesize versatile cyclopropane derivatives.³ In the past decades, transition-metal-catalyzed reactions *via* metal carbenes⁴ have proven to be the most important method to realize the Buchner reaction. However, most of the transition-metal-catalyzed Buchner reactions have to rely on the use of explosive diazo compounds as carbene precursors (Scheme 1a),⁵ which strictly restrain their further synthetic applications. By comparison, the Buchner reaction based on alkynes *via* a non-diazo approach was far less explored (Scheme 1a). In 2014, Panek and co-workers first reported the Buchner reaction based on alkynes *via* a rhodium-catalyzed nitrene-alkyne cycloaddition.^{6a} Such a similar strategy was nicely exploited by Zhang^{6b} and Huang^{6c} respectively *via* a gold-catalyzed intermolecular oxidation of

alkynes. In 2021, the first example of the asymmetric Buchner reaction based on alkynes⁷ was demonstrated by Nemoto and Harada *via* a non-diazo approach.^{7a} Despite these significant



Scheme 1 Buchner reaction via metal carbenes or vinyl cations.

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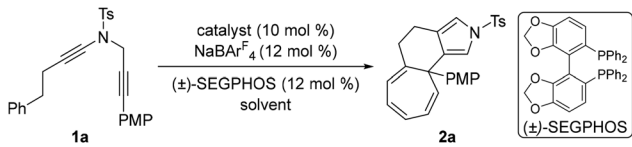
advances (Scheme 1a), these protocols are almost limited to noble-metal catalysts, and they are not atom-economical synthesis. Therefore, the exploration of novel approaches for the non-noble-metal-catalyzed Buchner reaction from alkynes, especially in an atom-economical manner, is highly desirable.

The vinyl cation, as a prominent intermediate in organic synthesis, has attracted widespread interest for its unique carbene-like reactivity in recent years.⁸ On the basis of this, in 2022, Zhang and co-workers first disclosed a hypervalent iodine-promoted Buchner reaction *via* a vinyl cation (Scheme 1b).⁹ In the past several years, our group has established a unique copper-catalyzed cyclization of diynes for the generation of vinyl cations. By using this methodology, a variety of valuable asymmetric conversions have been developed through the remote control of enantioselectivity, enabling the divergent synthesis of enantio-enriched N-heterocycles.¹⁰ Inspired by the above results and by our recent study on developing ynamide chemistry for heterocycle synthesis,¹¹ we envisaged that vinyl cations, generated from copper-catalyzed diyne cyclization, could react with intramolecular arene moieties, delivering the corresponding dearomatized products (Scheme 1c). Very recently, our group also reported an asymmetric Buchner reaction and arene cyclopropanation *via* a copper-catalyzed controllable cyclization of diynes.¹² However, in this protocol, the diyne substrates were limited to phenyl-fused diynes for the Buchner reaction and only naphthyl-substituted diynes were suitable for arene cyclopropanation. Herein, we disclose a Buchner reaction and phenyl cyclopropanation *via* a copper-catalyzed cyclization of phenyl linked diynes, furnishing a series of valuable bicycle-fused cycloheptatrienes and norcaradienes bearing all carbon quaternary carbon centers in generally moderate to excellent yields with a wide substrate scope.

We started our investigations by using the phenethyl-substituted *N*-propargyl ynamide **1a** as the model substrate using the copper-catalyzed method for the Buchner reaction (Table 1). To our delight, the desired cycloheptatriene **2a** bearing an all carbon quaternary carbon center could be readily prepared in 76% yield by employing Cu(MeCN)₄PF₆ (10 mol%) as a catalyst, NaBAR₄^F (12 mol%) as an additive and (±)-SEGPHOS (12 mol%) as a ligand in toluene (Table 1, entry 1). Stimulated by this primary attempt, we next screened several typical solvents such as CH₂Cl₂, DCE and THF (Table 1, entries 2–4), and CH₂Cl₂ was found to be the optimal solvent with 80% yield (Table 1, entry 2). Then, various typical copper catalysts, such as Cu(MeCN)₄BF₄, CuOTf, CuCl, CuBr, Cu(OTf)₂ and CuCl₂, were also evaluated (Table 1, entries 5–10). We were pleased to find that the use of CuCl as a catalyst led to a slightly increased yield, and the anticipated cycloheptatriene **2a** was delivered in 84% yield (Table 1, entry 7). Finally, significantly decreased yields of **2a** were detected in the absence of a ligand and NaBAR₄^F (Table 1, entries 11–13).

Having established the optimized reaction conditions (Table 1, entry 7), we next sought to explore the scope of this Buchner reaction. As shown in Table 2, we initially investigated the scope of different *N*-protecting groups of *N*-propargyl ynamides. Apart from the Ts-protected ynamide, the reaction also proceeded smoothly with alkyl sulfonyl groups, such as Ms and SO₂Et, providing the corresponding cycloheptatriene-fused pyr-

Table 1 Optimization of reaction conditions^a

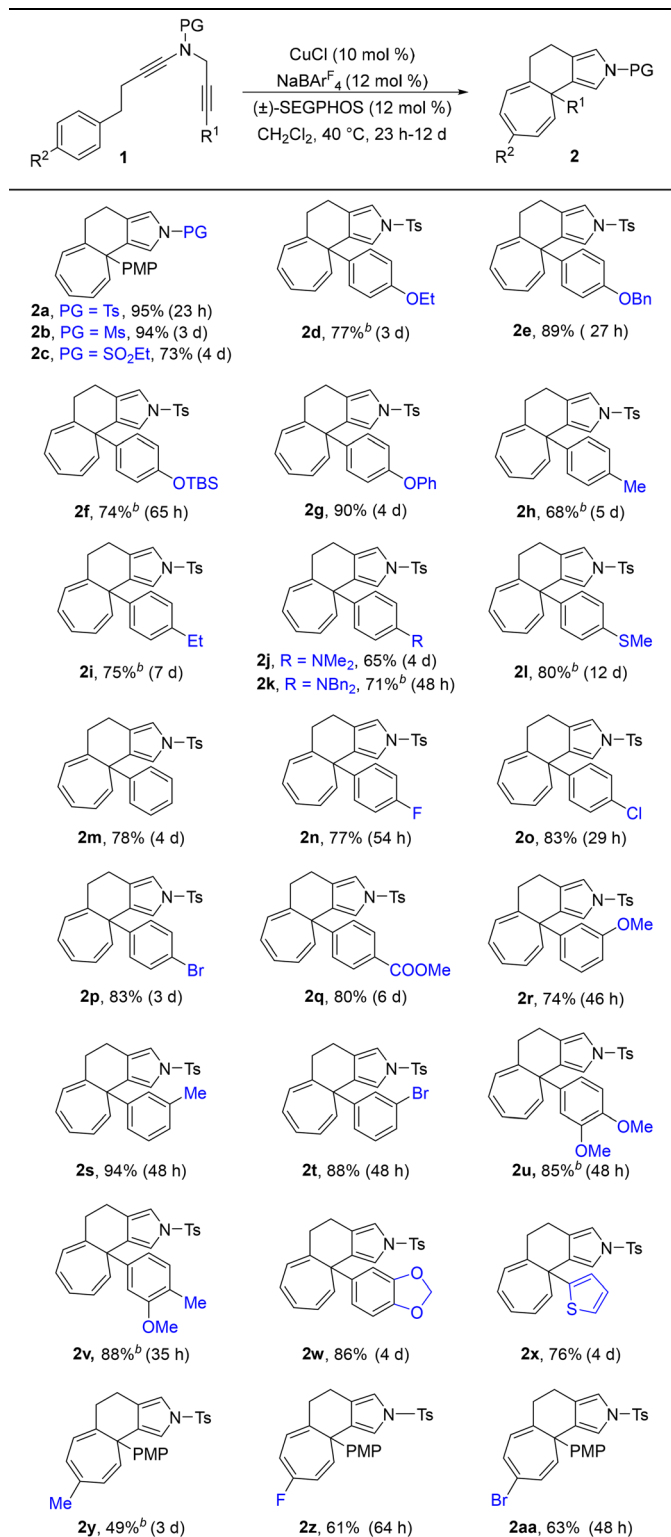


Entry	Catalyst	Reaction conditions	Yield ^b (%)
1	Cu(MeCN) ₄ PF ₆	Toluene, rt, 23 h	76
2	Cu(MeCN) ₄ PF ₆	CH ₂ Cl ₂ , rt, 23 h	80
3	Cu(MeCN) ₄ PF ₆	DCE, rt, 23 h	58
4	Cu(MeCN) ₄ PF ₆	THF, rt, 23 h	<5
5	Cu(MeCN) ₄ BF ₄	CH ₂ Cl ₂ , rt, 23 h	10
6	CuOTf	CH ₂ Cl ₂ , rt, 23 h	<5
7	CuCl	CH₂Cl₂, 40 °C, 4 d	84
8	CuBr	CH ₂ Cl ₂ , rt, 23 h	70
9	Cu(OTf) ₂	CH ₂ Cl ₂ , rt, 23 h	20
10	CuCl ₂	CH ₂ Cl ₂ , rt, 4 d	<5
11 ^c	CuCl	CH ₂ Cl ₂ , 40 °C, 4 d	67
12 ^d	CuCl	CH ₂ Cl ₂ , 40 °C, 4 d	<5
13 ^{c,d}	CuCl	CH ₂ Cl ₂ , 40 °C, 4 d	68

^a Reaction conditions: **1** (0.05 mmol), catalyst (0.005 mmol), (±)-SEGPHOS (0.006 mmol), NaBAR₄^F (0.006 mmol), solvent (1 mL), PMP = 4-methoxyphenyl, NaBAR₄^F = sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate. ^b Measured by ¹H NMR using diethyl phthalate as an internal standard. ^c Without a ligand. ^d Without NaBAR₄^F.

roles **2b** and **2c** in good yields. Then, we changed PMP to other O-containing electron-donating groups (EDGs). For instance, different O-containing arylsubstituted *N*-propargyl ynamides encompassing functional groups (*e.g.* ethyl, benzyl, silyl, and phenyl) were suitable substrates for this tandem cyclization, affording the desired cycloheptatrienes **2d–2g** in 74–90% yields. In addition, the Me- and Et-substituted diynes **1h** and **1i** could react smoothly in this protocol, and the cyclic products **2h** and **2i** were produced in 68% and 75% yields, respectively. Subsequently, other heteroatom-containing EDGs, such as NMe₂, NBn₂, and SMe, were also applicable for this reaction to deliver the desired cycloheptatriene-fused pyrroles **2j–2l** in moderate to good yields. The simple phenyl-substituted cycloheptatriene **2m** could be readily prepared from diyne **1m** as well. In particular, we were surprised to find that *N*-propargyl ynamides bearing electron-withdrawing groups (EWGs) on the aryl ring (*e.g.* F, Cl, Br, and CO₂Me) could participate in this transformation as well, giving rise to **2n–2q** in 77–83% yields. It is worth noting that EWG-substituted diynes were incompatible in the asymmetric Buchner reaction previously reported by our group.¹³ Furthermore, various substitutions at the *meta*-position of the phenyl ring had little effect on this protocol, delivering the related cycloheptatrienes **2r–2t** in 74–94% yields. Besides the mono-substituted aryl groups, di-substituted aromatic groups were also readily tolerated, leading to products **2u–2w** in excellent yields. Heteroaryl-substituted *N*-propargyl ynamide **1x** was proved to be the applicable substrate in this reaction, providing the anticipated product **2x** in 76% yield. Finally, substitutions at the phenyl of the phenethyl moiety were studied. It was found that *para*-substitutions including both electron-donating and electron-withdrawing groups worked efficiently,



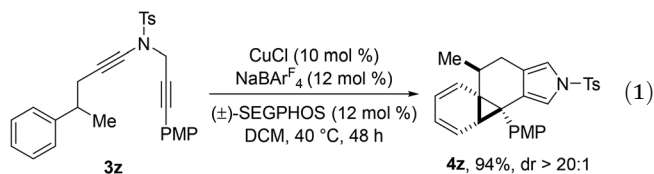
Table 2 Reaction scope for the formation of cycloheptatriene-fused pyrroles **2**^a

^a **1** (0.2 mmol), CuCl (0.02 mmol), (±)-SEGPHOS (0.024 mmol), NaBAR₄ (0.024 mmol), CH₂Cl₂ (2 mL), 40 °C, 23 h-12 d; yields are those for the isolated products. ^b Cu(MeCN)₄PF₆ was used as a catalyst, rt.

and the corresponding cycloheptatriene products **2y–2aa** were obtained with receivable yields. We also attempted to realize this asymmetric Buchner reaction by using various chiral ligands. However, only low enantioselectivities were obtained at this stage (for details, see the ESI†).

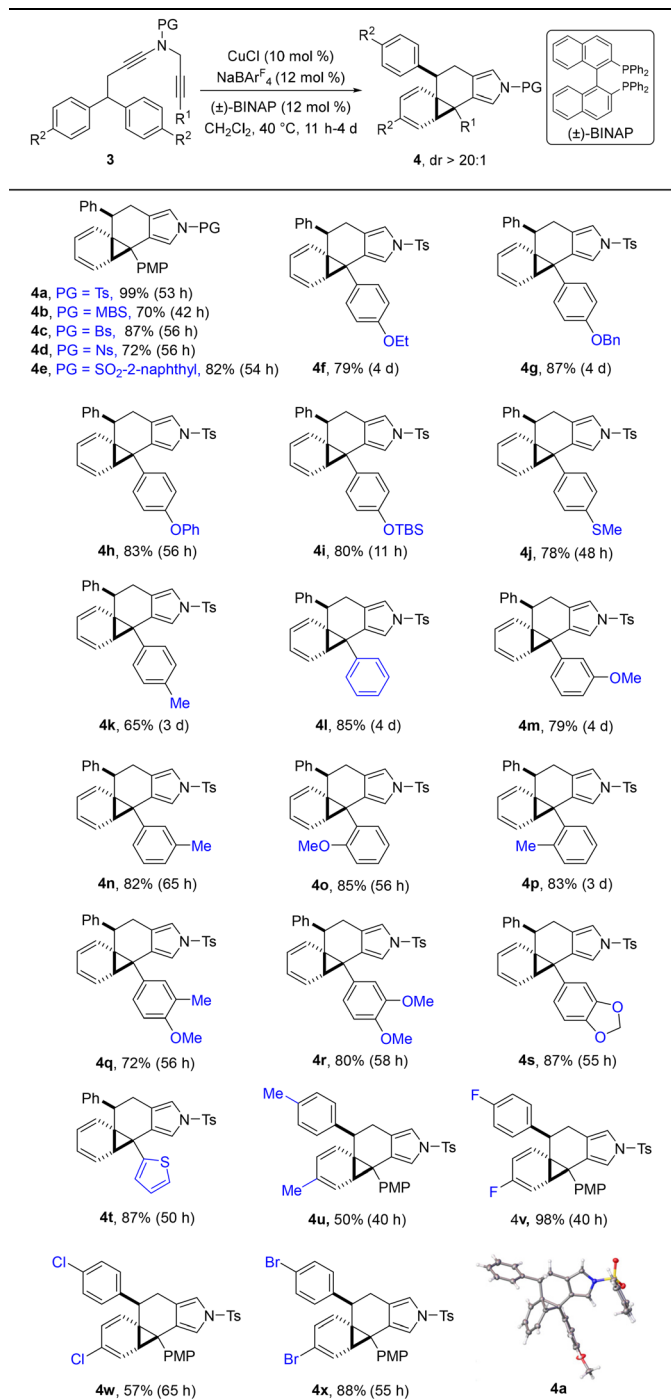
Intriguingly, during the substrate scope study of the above Buchner reaction, it was found that when the diphenyl-substituted diynes **3** were used as substrates, only the phenyl cyclopropanation products **4** were obtained and no seven-membered Buchner cyclization products were isolated. Notably, the desymmetrization¹³ and dearomatization¹⁴ processes were simultaneous in this phenyl cyclopropanation. After the optimization study (for details, see the ESI†), we confirmed the optimized reaction conditions as follows: CuCl (10 mol%) as a catalyst, NaBAR₄ (12 mol%) as an additive and BINAP (12 mol%) as a ligand in CH₂Cl₂. The substrate scope for the synthesis of norcaradiene-derived pyrroles was then examined. As depicted in Table 3, this phenyl cyclopropanation was remarkably tolerant of various *N*-protected ynamides, including Ts, MBS, Bs, Ns, and SO₂-2-naphthyl, affording the corresponding norcaradienes **4a–4e** in 70–99% yields. Moreover, this dearomatization process readily accommodated substitutions at different positions of the phenyl ring with a variety of electron-rich substituents such as Me, OMe, OEt, OBn, OPh, OTBS, and SMe, enabling the assembly of the expected norcaradiene-derived pyrroles **4f–4p** in generally good yields. Then, the reaction was also extended to di-substituted diynes **3q–3s**, enabling an approach for the synthesis of the anticipated norcaradienes **4q–4s** in 72–87% yields. Next, the thienyl-substituted *N*-propargyl ynamide **3t** performed well in this phenyl cyclopropanation, and the corresponding product **4t** was isolated in 87% yield. Ultimately, further modifications of the substituents (R substituent) of diphenyl groups with electron-rich and electron-deficient substituents encompassing 4-Me, 4-F, 4-Cl and 4-Br were also tolerated to furnish the desired norcaradiene derived pyrroles **4u–4x** in moderate to excellent yields. However, the reaction of 3-fluorophenyl-substituted diyne **3y** under the standard conditions only gave a complex mixture. Of note, excellent diastereoselectivities (dr > 20 : 1) were achieved in all cases. The enantioselective phenyl cyclopropanation was also demonstrated, but only low enantioselectivities were detected by employing various chiral ligands (for details, see the ESI†). The relative configuration of product **4a** was confirmed by X-ray crystallographic analysis.¹⁵

Interestingly, it was found that the treatment of phenyl and methyl substituted diyne **3z** under the standard reaction conditions afforded the cyclopropanation product **4z** as a single product in 94% yield (eqn (1)).



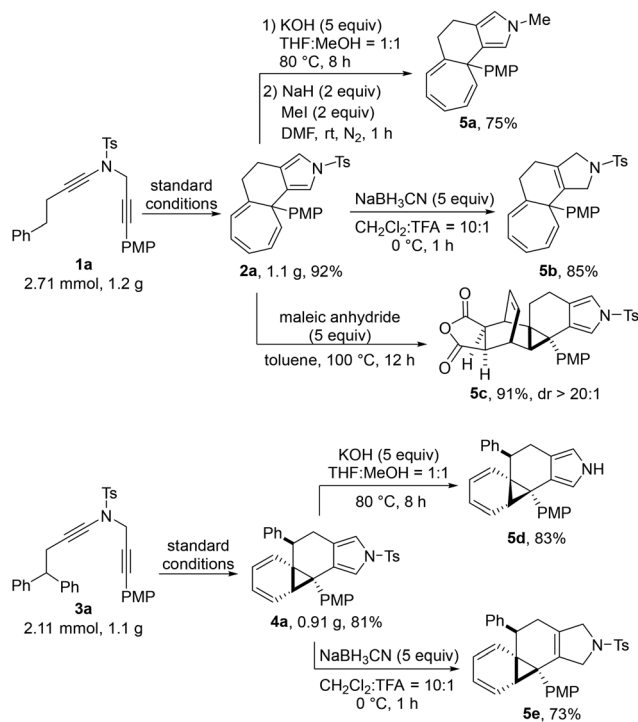
Gram-scale synthesis and further synthetic applications of the as-synthesized cycloheptatriene **2a** and norcaradiene **4a**



Table 3 Reaction scope for the formation of norcaradiene-derived pyrroles **4**^a

^a **3** (0.2 mmol), CuCl (0.02 mmol), (±)-BINAP (0.024 mmol), NaBARF₄ (0.024 mmol), CH₂Cl₂ (2 mL), 40 °C, 11 h-4 d; yields are those for the isolated products.

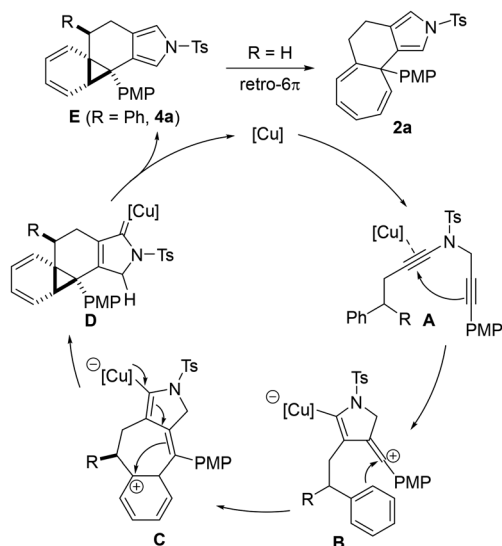
were then investigated, as shown in Scheme 2. First, the cycloheptatriene-derived pyrrole **2a** could be prepared on a gram scale in 92% yield under the standard conditions. The protecting group of **2a** could be efficiently removed by treatment with KOH, followed by protection with the Me group to form the

**Scheme 2** Gram-scale synthesis and synthetic transformations.

desired **5a** in 75% yield in 2 steps. Then, the treatment of **2a** with NaBH₃CN as the reductant led to the tricyclic dihydropyrrole **5b** in a good yield. Interestingly, **2a** could undergo the Diels–Alder reaction with maleic anhydride to furnish the polycyclic bridged product **5c** with an excellent yield and diastereoselectivity. Of note, 6 π -electrocyclization of **2a** occurred first to form norcaradiene at a high temperature, followed by the subsequent Diels–Alder reaction of norcaradiene with maleic anhydride to produce **5c**. In addition, the Ts group in the norcaradiene-derived pyrrole **4a** could be readily removed under basic conditions to produce the unprotected pyrrole **5d** in 83% yield. Finally, reduction of **4a** with NaBH₃CN led to the norcaradiene-derived dihydropyrrole **5e** in a good yield.

Based on our previous research studies,^{10,13} a plausible mechanism for this copper-catalyzed controllable Buchner reaction and phenyl cyclopropanation was proposed and is presented in Scheme 3. First, the coordination of copper complexes with diyne **1a** or **3a** forms complex **A**, which induces an intramolecular cyclization to afford the vinyl cation intermediate containing alkenyl copper species **B**. Subsequently, the vinyl cation is trapped by the phenyl group *via* an intramolecular nucleophilic attack to provide the phenyl cation intermediate **C**, which undergoes further intramolecular cyclization to generate the copper carbene **D**. Then, intermediate **D** undergoes a formal [1,4]-H shift and demetallation to produce norcaradiene **E** with the regeneration of the copper catalyst. When the R substitution is phenyl, only the phenyl cyclopropanation product **4a** is achieved. Alternatively, cycloheptatriene **2a** is delivered selectively *via* a retro-6 π electro-ring opening





Scheme 3 Plausible catalytic cycle for the copper-catalyzed controllable Buchner reaction and arene cyclopropanation.

when the R substitution is hydrogen. For this unique chemoselectivity, we assumed that when the R substitution is aryl or methyl, the steric-hindrance effect may hinder the ring opening of cyclopropanes to give the 7-membered ring products.

In conclusion, we have developed an efficient copper-catalyzed controllable Buchner reaction and phenyl cyclopropanation of phenyl or diphenyl tethered diynes, providing a series of valuable bicycle-fused cycloheptatrienes and norcaradienes bearing all carbon quaternary carbon centers in generally moderate to excellent yields with a wide substrate scope under mild reaction conditions. In particular, the diynes can tolerate various EWGs on the aryl ring in the Buchner reaction, and a desymmetrization/dearomatization process is involved in the phenyl cyclopropanation. Further investigation of catalytic asymmetric cyclization of these diynes is undergoing in our laboratory.

Data availability

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

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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References

- 1 E. Buchner and T. Curtius, Ueber die Einwirkung von Diazoessigäther auf aromatische Kohlenwasserstoffe, *Ber. Dtsch. Chem. Ges.*, 1885, **18**, 2377.
- 2 For selected reviews on the Buchner reaction, see: (a) C.-Y. Shi, G.-Y. Zhu, Y. Xu, M.-Y. Teng and L.-W. Ye, Recent Advances in Catalytic Asymmetric Buchner Reaction, *Chin. Chem. Lett.*, 2023, **34**, 108441; (b) G. Ma, K.-F. Wei, M. Song, Y.-L. Dang, Y. Yue, B. Han, H. Su and W.-B. Shen, Recent Advances in Transition-metal-catalyzed Buchner Reaction of Alkynes, *Org. Biomol. Chem.*, 2023, **21**, 5150; (c) S. E. Reisman, R. R. Nani and S. Levin, Buchner and Beyond: Arene Cyclopropanation as Applied to Natural Product Total Synthesis, *Synlett*, 2011, 2437.
- 3 For selected examples of the arene cyclopropanation reaction, see: (a) F. Guan, R. Zhou, X. Ren, Z. Guo, C. Wang and C.-Y. Zhou, Asymmetric Dearomative Cyclopropanation of Naphthalenes to Construct Polycyclic Compounds, *Chem. Sci.*, 2022, **13**, 13015; (b) N. Otog, B. Gantogos, I. Fujisawa and S. Iwasa, Highly Enantioselective Synthesis of Norcaradiene Derivatives from Naphthyl Diazoacetamides Using a Ru(II)-Pheox Complex, *Chem. Commun.*, 2022, **58**, 12325; (c) S. Zhao, X.-X. Chen, N. Gao, M. Qian and X. Chen, Visible-Light-Mediated Cyclopropanation Reactions of 3-Diazoindoles with Arenes, *J. Org. Chem.*, 2021, **86**, 7131; (d) K. L. Smith, C. L. Padgett, W. D. Mackay and J. S. Johnson, *J. Am. Chem. Soc.*, 2020, **142**, 6449; (e) R. R. Nani and S. E. Reisman, Catalytic Asymmetric Dearomative Synthesis of Complex Cyclohexanes via a Highly Regio- and Stereoselective Arene Cyclopropanation Using α -Cyanodiazoacetates, *J. Am. Chem. Soc.*, 2013, **135**, 7304; (f) M. P. Doyle, D. G. Ene, D. C. Forbes and T. H. Pillow, Chemoselectivity and Enantiocontrol in Catalytic Intramolecular Metal Carbene Reactions of Diazo Acetates Linked to Reactive Functional Groups by Naphthalene-1,8-Dimethanol, *Chem. Commun.*, 1999, 1691.
- 4 For recent selected reviews on the transition-metal-catalyzed reaction *via* metal carbenes, see: (a) Y. Chen and S. Zhu, Recent Advances in Metal Carbene-Induced Semipinacol Rearrangements, *Chem. Commun.*, 2024, **60**, 11253; (b) T. R. Roose, D. S. Verdoorn, P. Mampuy, E. Ruijter, B. U. W. Maes, R. V. A. Orru and T. R. Roose, Transition Metal-Catalysed Carbene- And Nitrene Transfer To Carbon Monoxide and Isocyanides, *Chem. Soc. Rev.*, 2022, **51**, 5842; (c) X. Qi and Y. Lan, Recent Advances in Theoretical Studies on Transition-Metal-Catalyzed Carbene Transformations, *Acc. Chem. Res.*, 2021, **54**, 2905; (d) T. Wang and A. S. K. Hashmi, 1,2-Migrations onto Gold Carbene Centers, *Chem. Rev.*, 2021, **121**, 8948; (e) L.-W. Ye, X.-Q. Zhu, R. L. Sahani, Y. Xu, P.-C. Qian and R.-S. Liu, Nitrene Transfer and Carbene Transfer in Gold Catalysis,



- Chem. Rev.*, 2021, **121**, 9039; (f) S. W. Roh, K. Choi and C. Lee, Transition Metal Vinylidene- and Allenylidene-Mediated Catalysis in Organic Synthesis, *Chem. Rev.*, 2019, **119**, 4293.
- 5 For recent selected examples of the Buchner reaction by using diazo compounds as carbene precursors, see: (a) B. Darses, P. Maldivi, C. Philouze, P. Dauban and J.-F. Poisson, Asymmetric Intramolecular Buchner Reaction: From High Stereoselectivity to Coexistence of Norcaradiene, Cycloheptatriene, and an Intermediate form in the Solid State, *Org. Lett.*, 2021, **23**, 300; (b) Q. Zeng, K. Dong, C. Pei, S. Dong, W. Hu, L. Qiu and X. Xu, Divergent Construction of Macrocyclic Alkynes via Catalytic Metal Carbene C(sp²)-H Insertion and the Buchner Reaction, *ACS Catal.*, 2019, **9**, 10773; (c) T. Hoshi, E. Ota, Y. Inokuma and J. Yamaguchi, Asymmetric Synthesis of a 5,7-Fused Ring System Enabled by an Intramolecular Buchner Reaction with Chiral Rhodium Catalyst, *Org. Lett.*, 2019, **21**, 10081; (d) N. P. T. Thanh, M. Tone, H. Inoue, I. Fujisawa and S. Iwasa, Highly Stereoselective Intramolecular Buchner Reaction of Diazoacetamides Catalyzed by a Ru(II)-Pheox Complex, *Chem. Commun.*, 2019, **55**, 13398; (e) H. Nakayama, S. Harada, M. Kono and T. Nemoto, Chemoselective Asymmetric Intramolecular Dearomatization of Phenols with α -Diazoacetamides Catalyzed by Silver Phosphate, *J. Am. Chem. Soc.*, 2017, **139**, 10188; (f) H. Wang, C.-Y. Zhou and C.-M. Che, Cobalt-Porphyrin-Catalyzed Intramolecular Buchner Reaction and Arene Cyclopropanation of in situ Generated Alkyl Diazomethanes, *Adv. Synth. Catal.*, 2017, **359**, 2253; (g) G. S. Fleming and A. B. Beeler, Regioselective and Enantioselective Intermolecular Buchner Ring Expansions in Flow, *Org. Lett.*, 2017, **19**, 5268; (h) X. Xu, X. Wang, P. Z. Zavalij and M. P. Doyle, Straightforward Access to the [3.2.2]Nonatriene Structural Framework via Intramolecular Cyclopropanation/Buchner Reaction/Cope Rearrangement Cascade, *Org. Lett.*, 2015, **17**, 790; (i) Z. Liu, H. Tan, L. Wang, T. Fu, Y. Xia, Y. Zhang and J. Wang, Transition-Metal-Free Intramolecular Carbene Aromatic Substitution/Buchner Reaction: Synthesis of Fluorenes and [6,5,7]Benzofused Rings, *Angew. Chem., Int. Ed.*, 2015, **54**, 3056; (j) X. C. Wang, Q. M. Abrahams, P. J. Zavalij and M. P. Doyle, Highly Regio- and Stereoselective Dirhodium Vinylcarbene Induced Nitrene Cycloaddition with Subsequent Cascade Carbenoid Aromatic Cycloaddition/N-O Cleavage and Rearrangement, *Angew. Chem., Int. Ed.*, 2012, **51**, 5907; (k) P. Panne and J. M. Fox, Rh-Catalyzed Intermolecular Reactions of Alkynes with α -Diazoesters that Possess β -Hydrogens: Ligand-Based Control over Divergent Pathways, *J. Am. Chem. Soc.*, 2007, **129**, 22; (l) B. R. Galan, M. Gembicky, P. M. Dominiak, J. B. Keister and S. T. Diver, Carbon Monoxide-Promoted Carbene Insertion into the Aryl Substituent of an N-Heterocyclic Carbene Ligand: Buchner Reaction in a Ruthenium Carbene Complex, *J. Am. Chem. Soc.*, 2005, **127**, 15702.
- 6 (a) R. A. Brawn, K. Zhu and J. S. Panek, Rhodium(II)-Catalyzed Alkyne Amination of Homopropargylic Sulfamate Esters: Stereoselective Synthesis of Functionalized Norcaradienes by Arene Cyclopropanation, *Org. Lett.*, 2014, **16**, 74; (b) K. Ji and L. Zhang, Cyclopropanation of Benzene Rings by Oxidatively Generated α -Oxo Gold Carbene: One-Pot Access to Tetrahydropyranone-Fused Cycloheptatrienes from Propargyl Benzyl Ethers, *Adv. Synth. Catal.*, 2018, **360**, 647; (c) J. Xia, J. Liu, Y. Yu, J. Zhang and X. Huang, Divergent Access to Polycyclic N-Heterocyclic Compounds through Büchner-Type Dearomatization Enabled Cycloisomerization of Diynamides under Gold Catalysis, *Org. Lett.*, 2022, **24**, 4298.
- 7 (a) T. Ito, S. Harada, H. Homma, H. Takenaka, S. Hirose and T. Nemoto, Asymmetric Intramolecular Dearomatization of Nonactivated Arenes with Ynamides for Rapid Assembly of Fused Ring System under Silver Catalysis, *J. Am. Chem. Soc.*, 2021, **143**, 604; (b) D. Zhu, T. Cao, K. Chen and S. Zhu, Rh₂(II)-Catalyzed Enantioselective Intramolecular Buchner Reaction and Aromatic Substitution of Donor-Donor Carbenes, *Chem. Sci.*, 2022, **13**, 1992.
- 8 For selected reviews on vinyl cations, see: (a) X.-J. Liu, Y. Xu, C. Tang, P.-C. Qian and L.-W. Ye, Unactivated C(sp³)-H Functionalization via Vinyl Cations, *Sci. China: Chem.*, 2022, **65**, 20; (b) M. Niggemann and S. Gao, Are Vinyl Cations Finally Coming of Age?, *Angew. Chem., Int. Ed.*, 2018, **57**, 16942. For selected examples, see: (c) A. Ahrens, J. Schwarz, D. M. Lustosa, R. Pourkaveh, M. Hoffmann, F. Rominger, M. Rudolph, A. Dreuw and A. S. K. Hashmi, Synthesis of Fulvene Vinyl Ethers by Gold Catalysis, *Chem. - Eur. J.*, 2020, **26**, 5280; (d) S. Tavakkolifard, K. Sekine, L. Reichert, M. Ebrahimi, K. Museridz, E. Michel, F. Rominger, R. Babaahmadi, A. Ariafard, B. F. Yates, M. Rudolph and A. S. K. Hashmi, Gold-Catalyzed Regiospecific Annulation of Unsymmetrically Substituted 1,5-Diynes for the Precise Synthesis of Bispentalenes, *Chem. - Eur. J.*, 2019, **25**, 12180; (e) T. Wurm, J. Bucher, S. B. Duckworth, M. Rudolph, F. Rominger and A. S. K. Hashmi, On the Gold-Catalyzed Generation of Vinyl Cations from 1,5-Diynes, *Angew. Chem., Int. Ed.*, 2017, **56**, 3364.
- 9 D.-F. Yuan, Z.-C. Wang, R.-S. Geng, G.-Y. Ren, J. S. Wright, S.-F. Ni, M. Li, L.-R. Wen and L.-B. Zhang, Hypervalent Iodine Promoted the Synthesis of Cycloheptatrienes and Cyclopropanes, *Chem. Sci.*, 2022, **13**, 478.
- 10 (a) F.-L. Hong, Z.-S. Wang, D.-D. Wei, T.-Y. Zhai, G.-C. Deng, X. Lu, R.-S. Liu and L.-W. Ye, Generation of Donor/Donor Copper Carbenes through Copper-Catalyzed Diyne Cyclization: Enantioselective and Divergent Synthesis of Chiral Polycyclic Pyrroles, *J. Am. Chem. Soc.*, 2019, **141**, 16961; (b) F.-L. Hong, Y.-B. Chen, S.-H. Ye, G.-Y. Zhu, X.-Q. Zhu, X. Lu, R.-S. Liu and L.-W. Ye, Copper-Catalyzed Asymmetric Reaction of Alkenyl Diynes with Styrenes by Formal [3 + 2] Cycloaddition via Cu-Containing All-Carbon 1,3-Dipoles: Access to Chiral Pyrrole-Fused



- Bridged [2.2.1]Skeletons, *J. Am. Chem. Soc.*, 2020, **142**, 7618; (c) X.-Q. Zhu, P. Hong, Y.-X. Zheng, Y.-Y. Zhen, F.-L. Hong, X. Lu and L.-W. Ye, Copper-Catalyzed Asymmetric Cyclization of Alkenyl Dienes: Method Development and New Mechanistic Insights, *Chem. Sci.*, 2021, **12**, 9466; (d) F.-L. Hong, C.-Y. Shi, P. Hong, T.-Y. Zhai, X.-Q. Zhu, X. Lu and L.-W. Ye, Copper-Catalyzed Asymmetric Diyne Cyclization via [1,2]-Stevens-Type Rearrangement for the Synthesis of Chiral Chromeno[3,4-*c*]pyrroles, *Angew. Chem., Int. Ed.*, 2022, **61**, e202115554; (e) L.-J. Qi, C.-T. Li, Z.-Q. Huang, J.-T. Jiang, X.-Q. Zhu, X. Lu and L.-W. Ye, Enantioselective Copper-Catalyzed Formal [2 + 1] and [4 + 1] Annulations of Dienes with Ketones via Carbonyl Ylides, *Angew. Chem., Int. Ed.*, 2022, **61**, e202210637; (f) J.-J. Zhou, Y.-N. Meng, L.-G. Liu, Y.-X. Liu, Z. Xu, X. Lu, B. Zhou and L.-W. Ye, Copper-Catalyzed Enantioselective Diyne Cyclization via C(sp²)-O Bond Cleavage, *Chem. Sci.*, 2023, **14**, 3493; (g) Y.-B. Chen, L.-G. Liu, C.-M. Chen, Y.-X. Liu, B. Zhou, X. Lu, Z. Xu and L.-W. Ye, Construction of Axially Chiral Arylpyrroles via Atroposelective Diyne Cyclization, *Angew. Chem., Int. Ed.*, 2023, **62**, e202303670; (h) C.-T. Li, L.-J. Qi, L.-G. Liu, C. Ge, X. Lu, L.-W. Ye and B. Zhou, Asymmetric Formal C-C Bond Insertion into Aldehydes via Copper-Catalyzed Diyne Cyclization, *Nat. Commun.*, 2023, **14**, 7058; (i) H.-J. Xu, C.-T. Li, C.-M. Chen, J. Chen, X.-Q. Zhu, B. Zhou and L.-W. Ye, Copper-Catalyzed Formal [4 + 1] Annulation of *N*-Propargyl Ynamides with Diketones, *Org. Chem. Front.*, 2023, **10**, 203; (j) Y.-B. Chen, L.-G. Liu, Z.-Q. Wang, R. Chang, X. Lu, B. Zhou and L.-W. Ye, Enantioselective Functionalization of Unactivated C(sp³)-H Bonds through Copper-Catalyzed Diyne Cyclization by Kinetic Resolution, *Nat. Commun.*, 2024, **15**, 2232; (k) F.-S. Li, X.-Y. Zou, T.-Q. Hu, Q. Sun, Z. Xu, B. Zhou and L.-W. Ye, Asymmetric One-Carbon Ring Expansion of Diverse *N*-Heterocycles via Copper-Catalyzed Diyne Cyclization, *Sci. Adv.*, 2024, **10**, eadq7767; (l) H.-H. Chen, Y.-B. Chen, J.-Z. Gao, L.-W. Ye and B. Zhou, Copper-Catalyzed Enantioselective Dehydro-Diels-Alder Reaction: Atom-Economical Synthesis of Axially Chiral Carbazoles, *Angew. Chem., Int. Ed.*, 2024, **63**, e202411709; (m) B. Prabagar, R. K. Mallick, R. Prasad, V. Gandon and A. K. Sahoo, Umpolung Reactivity of Ynamides: An Unconventional [1,3]-Sulfonyl and [1,5]-Sulfinyl Migration Cascade, *Angew. Chem., Int. Ed.*, 2019, **58**, 2365; (n) S. Dutta, R. K. Mallick, R. Prasad, V. Gandon and A. K. Sahoo, Alkyne Versus Ynamide Reactivity: Regioselective Radical Cyclization of Yne-Ynamides, *Angew. Chem., Int. Ed.*, 2019, **58**, 2289.
- 11 For recent selected reviews on ynamide chemistry, see: (a) L. Hu and J. Zhao, Ynamide Coupling Reagents: Origin and Advances, *Acc. Chem. Res.*, 2024, **57**, 855; (b) Y.-C. Hu, Y. Zhao, B. Wan and Q.-A. Chen, Reactivity of Ynamides in Catalytic Intermolecular Annulations, *Chem. Soc. Rev.*, 2021, **50**, 2582; (c) C. C. Lynch, A. Sripada and C. Wolf, Asymmetric Synthesis with Ynamides: Unique Reaction Control, Chemical Diversity and Applications, *Chem. Soc. Rev.*, 2020, **49**, 8543; (d) Y.-B. Chen, P.-C. Qian and L.-W. Ye, Brønsted Acid-Mediated Reactions of Ynamides, *Chem. Soc. Rev.*, 2020, **49**, 8897; (e) F.-L. Hong and L.-W. Ye, Transition Metal-Catalyzed Tandem Reactions of Ynamides for Divergent *N*-Heterocycle Synthesis, *Acc. Chem. Res.*, 2020, **53**, 2003; (f) J. Luo, G.-S. Chen, S.-J. Chen, J.-S. Yu, Z.-D. Li and Y.-L. Liu, Exploiting Remarkable Reactivities of Ynamides: Opportunities in Designing Catalytic Enantioselective Reactions, *ACS Catal.*, 2020, **10**, 13978; (g) B. Zhou, T.-D. Tan, X.-Q. Zhu, M. Shang and L.-W. Ye, Reversal of Regioselectivity in Ynamide Chemistry, *ACS Catal.*, 2019, **9**, 6393; (h) G. Evans, C. Theunissen and M. Lecomte, Ynamides: Powerful and Versatile Reagents for Chemical Synthesis, *Aldrichimica Acta*, 2015, **48**, 59; (i) X.-N. Wang, H.-S. Yeom, L.-C. He, S. Fang, Z.-X. Ma, B. L. Kedrowski and R. P. Hsung, Ynamides in Ring Forming Transformations, *Acc. Chem. Res.*, 2014, **47**, 560; (j) S. Shandilya, M. P. Gogoi, S. Dutta and A. K. Sahoo, Gold-catalyzed transformation of ynamides, *Chem. Rec.*, 2021, **21**, 4123; (k) B. Prabagar, N. Ghosh and A. K. Sahoo, Cyclization and Cycloisomerization of π -Tethered Ynamides: An Expedient Synthetic Method to Construct Carbo- and Heterocycles, *Synlett*, 2017, 2539.
- 12 Y.-X. Zheng, L.-G. Liu, T.-Q. Hu, X. Li, Z. Xu, X. Hong, X. Lu, B. Zhou and L.-W. Ye, Asymmetric Buchner Reaction and Arene Cyclopropanation via Copper-Catalyzed Controllable Cyclization of Dienes, *Nat. Commun.*, 2024, **15**, 9227.
- 13 For recent selected reviews on the desymmetrization reaction, see: (a) X.-P. Zeng, Z.-Y. Cao, Y.-H. Wang, F. Zhou and J. Zhou, Catalytic Enantioselective Desymmetrization Reactions to All-Carbon Quaternary Stereocenters, *Chem. Rev.*, 2016, **116**, 7330; (b) A. Borissov, T. Q. Davies, S. R. Ellis, T. A. Fleming, M. S. W. Richardson and D. J. Dixon, Organocatalytic Enantioselective Desymmetrisation, *Chem. Soc. Rev.*, 2016, **45**, 5474; (c) M.-Y. Teng, T. Han, E.-H. Huang and L.-W. Ye, Research Progress on Enantioselective Desymmetrization Reactions Involving Metal Carbenes, *Chin. J. Org. Chem.*, 2022, **42**, 3295; (d) Y. Xu, T.-Y. Zhai, Z. Xu and L.-W. Ye, Recent Advances towards Organocatalytic Enantioselective Desymmetrizing Reactions, *Trends Chem.*, 2022, **4**, 191; (e) Y. Zhang, H. Cai, X. Gan and Z. Jin, *N*-Heterocyclic Carbene-Catalyzed Enantioselective (dynamic) Kinetic Resolutions and Desymmetrizations, *Sci. China: Chem.*, 2024, **67**, 482.
- 14 For selected reviews on the dearomatization reaction of arenes, see: (a) W. C. Wertjes, E. H. Southgate and D. Sarlah, Recent Advances in Chemical Dearomatization of Nonactivated Arenes, *Chem. Soc. Rev.*, 2018, **47**, 7996; (b) A. R. Pape, K. P. Kaliappan and E. P. Kündig, Transition-Metal-Mediated Dearomatization Reactions, *Chem. Rev.*, 2000, **100**, 2917.
- 15 CCDC 2410274† (4a) contains the supplementary crystallographic data for this paper.

