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

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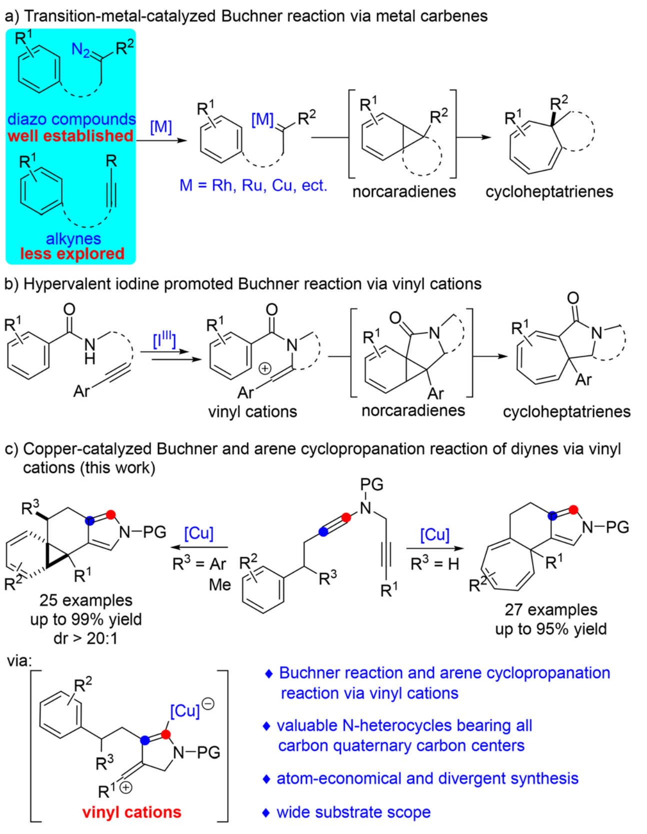
The Buchner reaction, as an exclusive category of expansive dearomatization, represents a powerful approach for the construction of valuable functionalized cycloheptatrienes in a direct manner from readily available aromatic precursors. However, the traditional Buchner reaction almost relies on using 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 carbenes[4] 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 coworkers 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 alkynes[7] 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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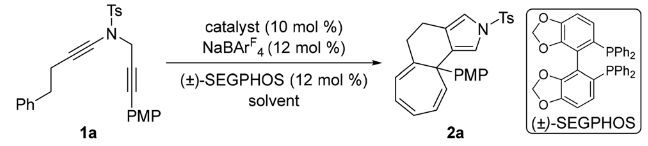
advances (Scheme 1a), these protocols are almost limited to noble-metal catalysts, and they are not atom-economical synthesis. Therefore, the exploration of novel approaches for the non-noble-metal-catalyzed Buchner reaction from alkynes, especially in an atom-economical manner, is highly desirable.

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 enantioenriched 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 $Cu(MeCN)_4PF_6$ (10 mol%) as a catalyst, $NaBAr^F_4$ (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 CH_2Cl_2, DCE and THF (Table 1, entries 2–4), and CH_2Cl_2 was found to be the optimal solvent with 80% yield (Table 1, entry 2). Then, various typical copper catalysts, such as $Cu(MeCN)_4BF_4$, CuOTf, CuCl, CuBr, $Cu(OTf)_2$ and $CuCl_2$, 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 $NaBAr^F_4$ (Table 1, entries 11–13).

Table 1 Optimization of reaction conditions[a]

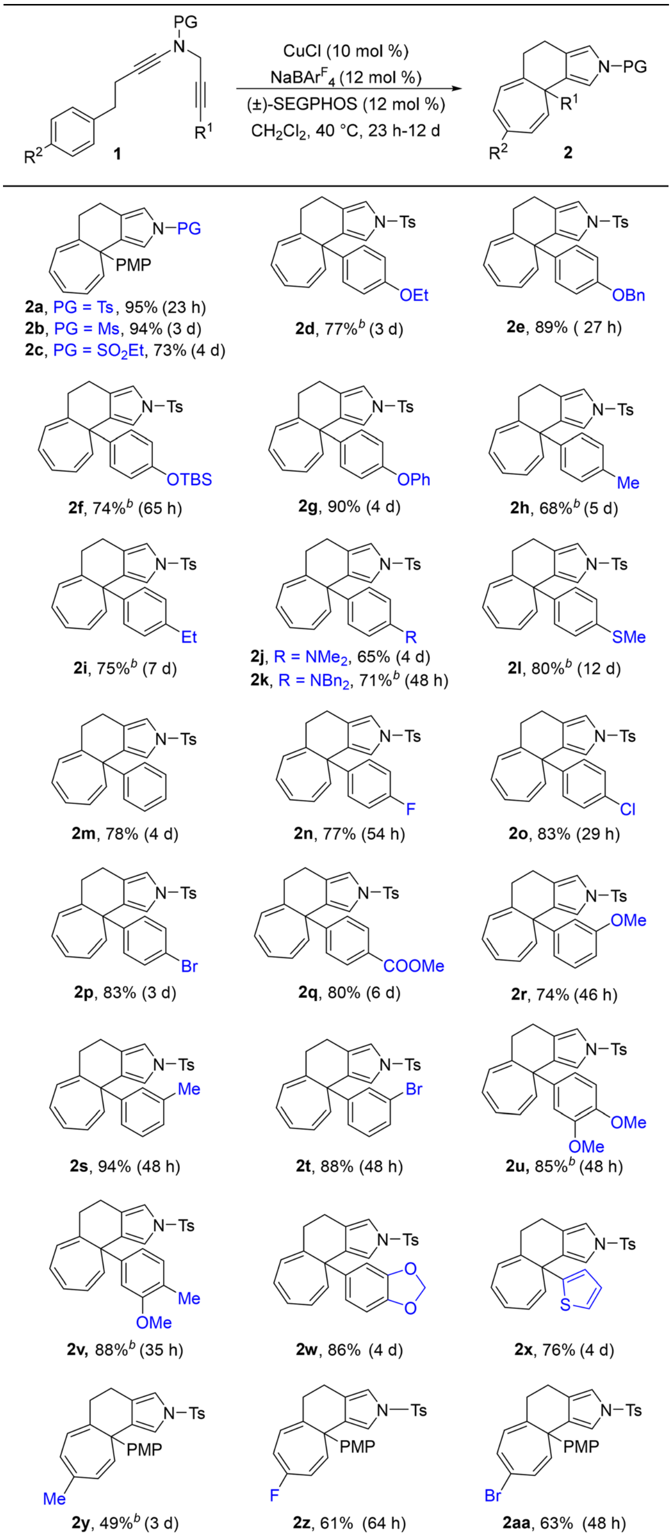


Entry	Catalyst	Reaction conditions	Yield[b] (%)
1	$Cu(MeCN)_4PF_6$	Toluene, rt, 23 h	76
2	$Cu(MeCN)_4PF_6$	CH_2Cl_2, rt, 23 h	80
3	$Cu(MeCN)_4PF_6$	DCE, rt, 23 h	58
4	$Cu(MeCN)_4PF_6$	THF, rt, 23 h	<5
5	$Cu(MeCN)_4BF_4$	CH_2Cl_2, rt, 23 h	10
6	CuOTf	CH_2Cl_2, rt, 23 h	<5
7	**CuCl**	**CH_2Cl_2, 40 °C, 4 d**	**84**
8	CuBr	CH_2Cl_2, rt, 23 h	70
9	$Cu(OTf)_2$	CH_2Cl_2, rt, 23 h	20
10	$CuCl_2$	CH_2Cl_2, rt, 4 d	<5
11[c]	CuCl	CH_2Cl_2, 40 °C, 4 d	67
12[d]	CuCl	CH_2Cl_2, 40 °C, 4 d	<5
13[c,d]	CuCl	CH_2Cl_2, 40 °C, 4 d	68

[a] Reaction conditions: **1** (0.05 mmol), catalyst (0.005 mmol), (±)-SEGPHOS (0.006 mmol), $NaBAr^F_4$ (0.006 mmol), solvent (1 mL), PMP = 4-methoxyphenyl, $NaBAr^F_4$ = 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 $NaBAr^F_4$.

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 SO_2Et, providing the corresponding cycloheptatriene-fused pyrroles **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 NMe_2, NBn_2, 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 CO_2Me) 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]



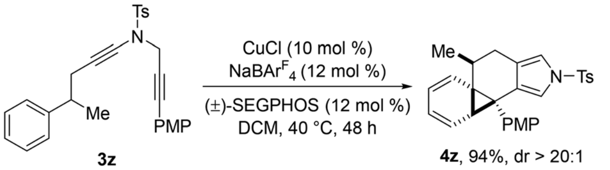
2a, PG = Ts, 95% (23 h)
2b, PG = Ms, 94% (3 d)
2c, PG = SO_2Et, 73% (4 d)
2d, 77%[b] (3 d)
2e, 89% (27 h)
2f, 74%[b] (65 h)
2g, 90% (4 d)
2h, 68%[b] (5 d)
2i, 75%[b] (7 d)
2j, R = NMe_2, 65% (4 d)
2k, R = NBn_2, 71%[b] (48 h)
2l, 80%[b] (12 d)
2m, 78% (4 d)
2n, 77% (54 h)
2o, 83% (29 h)
2p, 83% (3 d)
2q, 80% (6 d)
2r, 74% (46 h)
2s, 94% (48 h)
2t, 88% (48 h)
2u, 85%[b] (48 h)
2v, 88%[b] (35 h)
2w, 86% (4 d)
2x, 76% (4 d)
2y, 49%[b] (3 d)
2z, 61% (64 h)
2aa, 63% (48 h)

[a] **1** (0.2 mmol), CuCl (0.02 mmol), (±)-SEGPHOS (0.024 mmol), $NaBAr^F_4$ (0.024 mmol), CH_2Cl_2 (2 mL), 40 °C, 23 h–12 d; yields are those for the isolated products. [b] $Cu(MeCN)_4PF_6$ 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 desymmetrization[13] and dearomatization[14] 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, $NaBAr^F_4$ (12 mol%) as an additive and BINAP (12 mol%) as a ligand in CH_2Cl_2. 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 SO_2-2-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)).



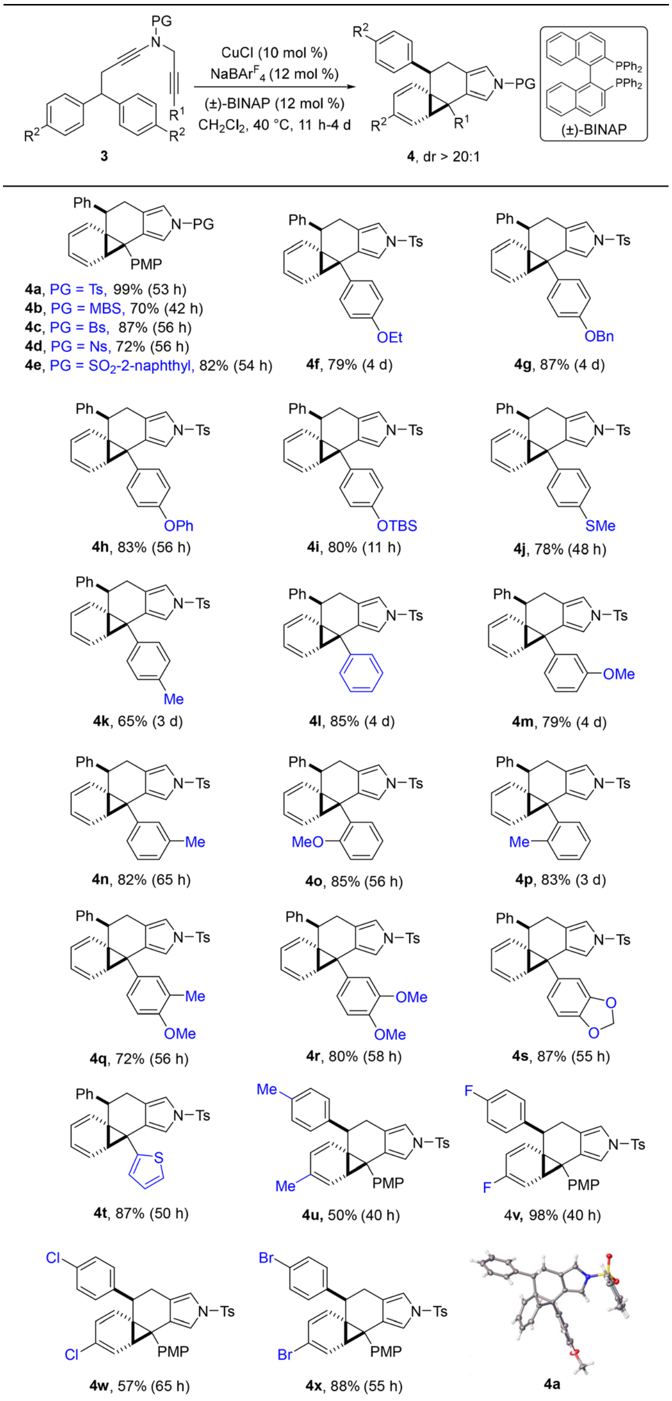
3z

4z, 94%, dr > 20:1

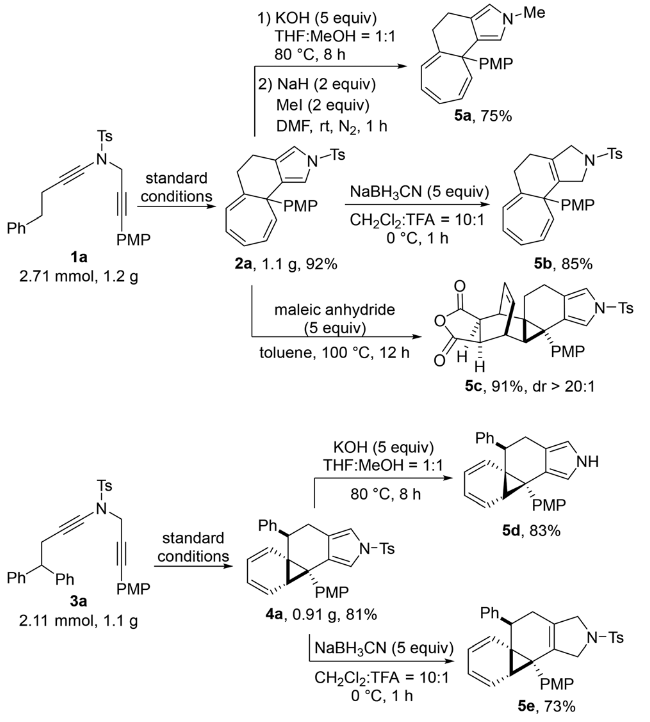
(1)

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]



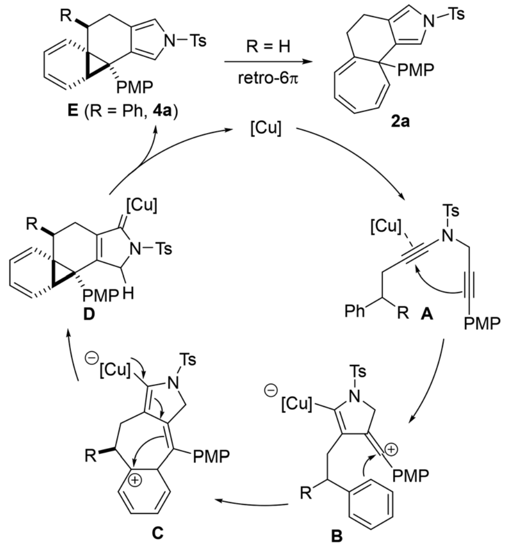
[a] **3** (0.2 mmol), CuCl (0.02 mmol), (±)-BINAP (0.024 mmol), $NaBAr^F_4$ (0.024 mmol), CH_2Cl_2 (2 mL), 40 °C, 11 h–4 d; yields are those for the isolated products.



Scheme 2 Gram-scale synthesis and synthetic transformations.

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 desired **5a** in 75% yield in 2 steps. Then, the treatment of **2a** with $NaBH_3CN$ 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, 6π-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 $NaBH_3CN$ 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-6π 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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15 CCDC 2410274† (**4a**) contains the supplementary crystallographic data for this paper.