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Regio- and Redox Divergent Hydrated Ring Expansion of Butafulvenes

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By providing highly functionalized building blocks in an efficient approach, catalytic hydration of alkenes plays a significant role in fundamental chemical transformations and pharmaceutical synthesis. However, hydration reactions have predominantly involved addition reactions of water and alkenes double bond. Herein, we developed a regio- and redox divergent hydrated ring expansion protocol of butafulvenes. With the aid of Pd^{II} or acid catalysis, various highly functionalized and unsaturated cyclopentanone derivatives could be obtained in high regioselectivities under oxidative or redox neutral conditions. Isotope labeling experiments suggest that the carbonylic oxygen atom of target product is derived from water. In addition, the unsaturated cyclopentanone intermediate could undergo divergent transformations and serve as a key molecule to create skeletal editing compounds of butafulvenes via one-pot protocol, which highlights the potential applications of this strategy.

Introduction

The direct conversion of alkenes with water, named hydration process, is a fundamental reaction utilized in chemical industry and pharmaceutical synthesis.[1] The past decades have witnessed substantial achievements in the selective hydration of simple olefins (Figure 1a).[2] Under oxidative or redox neutral condition, alcohol or carbonyl compounds have been efficiently delivered through hydrations.[3] Despite extensive research spanning decades, hydration reactions have predominantly involved addition reactions of water onto alkenes double bond. However, the catalytic hydration of benzenoids–a kind of special "conjugated triene" in form, still lags far behind due to the existence of 6e π-system and aromatic property. As a four-membered cyclic isomer of benzene, unsubstituted butafulvene also features a triple conjugated C=C bond with elevated ring strain. Very recently, our group reported a hydrated [3 + 2] cyclotelomerization of butafulvenes to create contiguous fully substituted carbon backbone (Figure 1b).[4] Given the importance of hydration and our continuing interest on the transformation of butafulvenes,[4,5] we wondered how to develop new chemistry between water and butafulvenes.

Methylenecyclobutanes (MCBs) are highly strained molecules, which serve as unique structural motif in bioactive products and organic synthesis.[6] Meanwhile, hydrated ring expansion of MCBs has emerged as an intriguing tool for the step-economic construction of cyclopentanone compounds (Figure 1c). Using stoichiometric oxidants, hydrated ring expansion reactions of MCBs could yield rearranged ketones.[7] In addition, Matsuda group reported a Rh-catalyzed carbon monoxide insertion of MCBs for forming cyclopentanones under high pressure condition.[8] Hence, developing a new approach for the construction of more highly substituted and functionalized cyclopentanones through hydration is still highly desirable. Using butafulvenes as a synthon, we herein successfully executed a regio- and redox divergent hydrated ring expansion protocol for constructing unsaturated cyclopentanones, which could undergo divergent transformations and skeletal editings (Figure 1d).

Results and Discussion

Initially, unsymmetric butafulvene (**1a**) was chosen as the model substrate to optimize the reaction (Table 1). Under the previous Wacker conditions of Wahl group, only a small amount of the unsaturated cyclopentanone product **2a** (2% yield) was observed (entry 1).[7b] Subsequent evaluation of the Pd(II) precatalysts revealed that $Pd(OAc)_2$ exhibited superior catalytic performance (entries 2–4). Impressively, the yield of **2a** was boosted to 50% with the use of $AgNO_2$ as additive (entry 5). Compared with ^{t}BuONO, the reaction efficacies of alternative oxidants were profoundly inferior (see the Supporting Information, Tables S1 for details). These results suggest that ^{t}BuONO plays a pivotal role in re-oxidation of the accumulating Pd^0 within this catalytic system.[9] Further screening of solvents showed that this reaction only proceeded in protic solvents and the yield of **2a** could be further increased to 60% in mixed solvents of MeOH/DCM by improving the solubility of butafulvene **1a** (entries 6–9, see the Supporting Information, Tables S2 for details). To our delight, with increasing the amount of ^{t}BuONO to 3.0 equiv. (entries 10), the yield of the target product

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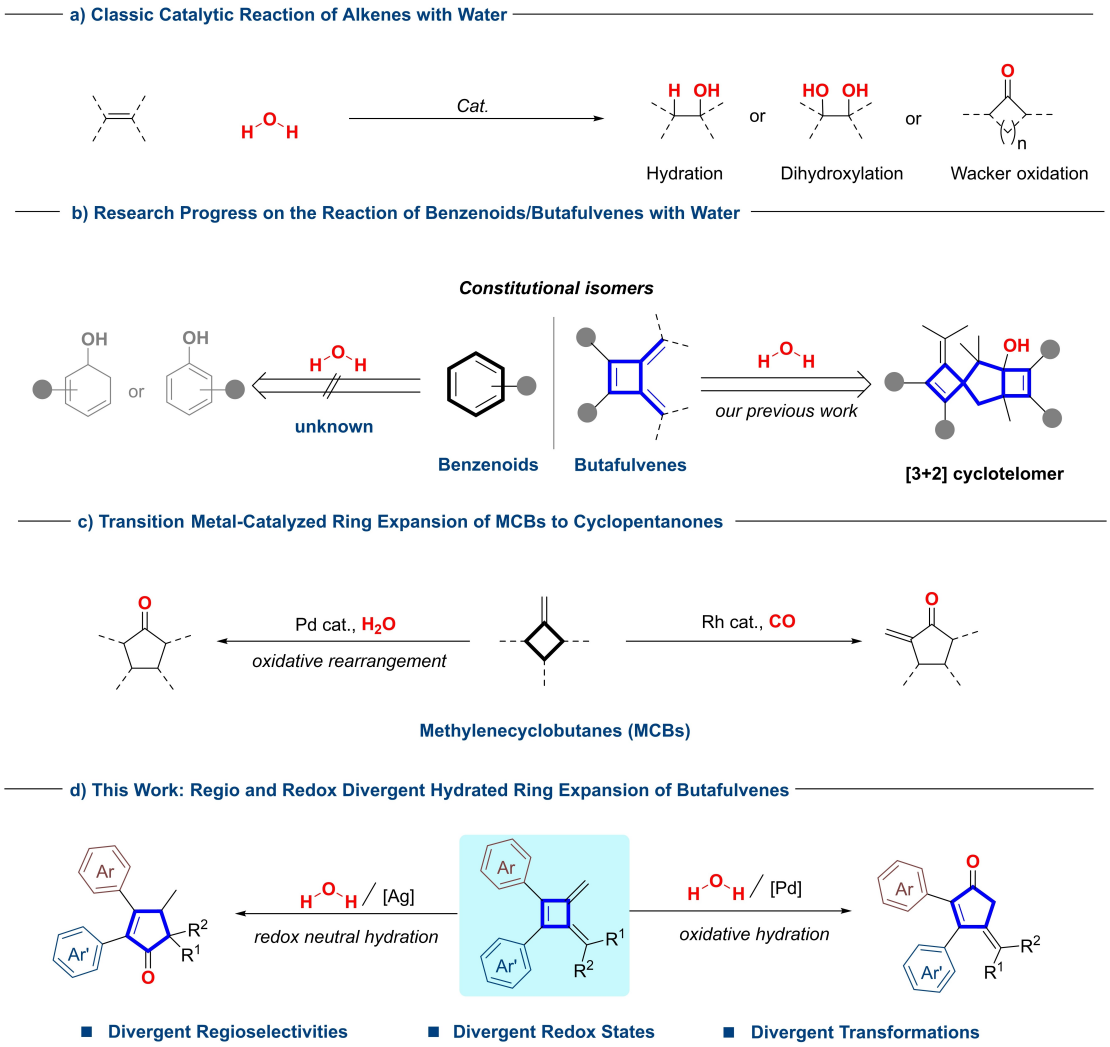


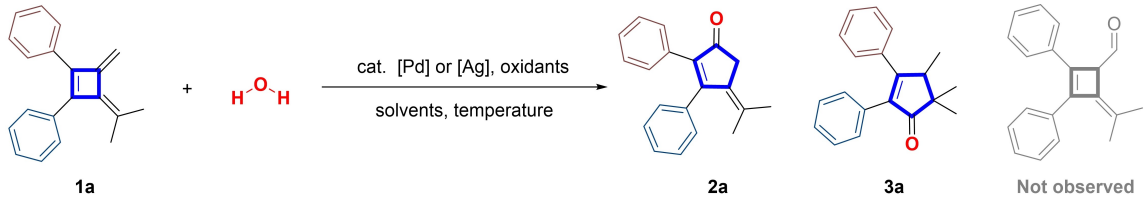
Figure 1. Catalytic hydration of alkenes and regiodivergent hydrated ring expansion of butafulvenes.

2a could be substantially improved to 90% (84% isolated yield). The use of other nitrite sources and different amount of water gave lower yields (see the Supporting Information, Tables S3 and S4 for details). Screening of other Ag salts gave moderate yields (entries 11–12). In absence of Pd catalyst, an unexpected regioisomer product **3a** was generated in 72% yield with increasing reaction temperature (entry 13 vs 12). Subsequent screening excluded chloroform, yielding minimal progress (see the Supporting Information, Tables S5 for details). No improvement on the yield of **3a** was observed using other Ag salts (entries 14–15). Upon extending reaction time to 24 h, the yield of target product **3a** was increased to 76% (entry 16). Throughout this exploration, the production of aldehyde side product was entirely absent, indicating that the reaction can selectively generate the desired unsaturated cyclopentanone product. The structures of **2a** and **3a** were further confirmed by single-crystal X-ray crystallography (CCDC: 2356647 and 2383215).

With the optimized conditions in hand, the substrate scope for this Pd-catalyzed hydrated ring expansion of substituted butafulvenes was evaluated (Figure 2). The substituted butafulvenes bearing alkyl groups at the *para* position of phenyl motif, afforded the products **2b–2d** in 50–75% yields. Replacing alkyl with halogen groups, the substituted butafulvenes were amenable under the optimized condition, giving target products in good yields (**2e–2f**). The presence of strong electron-withdrawing groups, such as Ac and CF_3, still delivered the desired products **2g** and **2h**, respectively. When introducing a phenyl at the *para* position of the benzene ring, a highly aryl substituted ring expansion product **2i** could be obtained in 76% yield. The reaction of substrates with alkyl and halogen substituents at *meta* position of phenyl motif all proceeded smoothly to afford the desired products (**2j–2l**, 66–72% yields). Steric hindered *ortho*-methyl and naphthyl substituted butafulvenes were also tolerated well under the standard conditions to give the target products **2m** and **2n** in 64% and 69%, respectively.

Subsequently, substituent effect on the below aromatic ring of unsymmetric butafulvenes **4** was investigated (Figure 3). The presence of alkyl groups, such as methyl, ethyl, *tert*-butyl at *para* position of phenyl motif were all tolerated to give the products in decent yields (**5a–5c**). Substrates possessing

Table 1. Optimization of Reaction Conditions.



1a **2a** **3a** Not observed

Entry	[Pd]	[Ag]	Temperature	Solvents[a]	**2a** (%)	**3a** (%)
1	$PdCl_2(MeCN)_2$	–	rt	MeOH	2	nd
2	$Pd(BF_4)_2(MeCN)_4$	–	rt	MeOH	11	nd
3	$Pd(TFA)_2$	–	rt	MeOH	19	nd
4	$Pd(OAc)_2$	–	rt	MeOH	26	nd
5	$Pd(OAc)_2$	$AgNO_2$	rt	MeOH	50	nd
6	$Pd(OAc)_2$	$AgNO_2$	rt	EtOH	22	nd
7	$Pd(OAc)_2$	$AgNO_2$	rt	DCM	nd	nd
8	$Pd(OAc)_2$	$AgNO_2$	rt	MeCN	nd	nd
9	$Pd(OAc)_2$	$AgNO_2$	rt	MeOH/DCM (4:1)	60	nd
10[c]	$Pd(OAc)_2$	$AgNO_2$	rt	MeOH/DCM (4:1)	90 (84)[b]	nd
11[c]	$Pd(OAc)_2$	$AgNO_3$	rt	MeOH/DCM (4:1)	57	nd
12[c]	$Pd(OAc)_2$	$AgClO_4$	rt	MeOH/DCM (4:1)	60	nd
13[d]	–	$AgClO_4$	120 °C	$CHCl_3$	nd	72
14[d]	–	Ag(OTf)	120 °C	$CHCl_3$	nd	64
15[d]	–	$AgNTf_2$	120 °C	$CHCl_3$	nd	46
16[e]	–	$AgClO_4$	120 °C	$CHCl_3$	nd	76 (78)[b]

Standard condition: **1a** (0.10 mmol), H_2O (3.0 mmol), [Pd] (10 mol%) or [Ag] (10 mol%), ^{t}BuONO (0.20 mmol), solvent (1.0 mL), temperature, 12 h. Yields were determined by GC-FID using 1,3,5-trimethoxybenzene as the internal standard. [a] Water content of $CHCl_3$ = 0.91 mmol/mL. [b] Isolated yield. [c] Using of ^{t}BuONO was 0.3 mmol. [d] Reaction time was 16 h without additional H_2O and ^{t}BuONO, $CHCl_3$ (0.5 mL) was used. [e] Reaction time was 24 h without additional H_2O and ^{t}BuONO; $CHCl_3$ (0.5 mL) was used. nd: no detection; rt: room temperature.

halides were also compatible under current standard reaction conditions (**4d**–**4e**). The presence of strong electron-withdrawing group performed well, affording desired products (**5f**–**5g**) in 87% and 68% yield, respectively. The aryl group such as phenyl was also evaluated and provided the unsaturated cyclopentanone **5h** in 70% yield. Substitution of methyl or halogen at *meta* positions of phenyl motif for butafulvenes gave the target products in 65–79% yield (**5i**–**5k**). Steric hindrance exerted minimal effect on the reaction, affording target products **5l** and **5m** smoothly. The substrate with the 1,3-benzodioxole motif also underwent the current reaction to give the product **5n** in 72% yield. This protocol also worked well when long-chain alkyl groups (**5o**–**5p**) were introduced onto the exocyclic double bond of butafulvenes **3**. The replacing methyl with bulky cyclohexyl and tetrahydropyran groups on butafulvenes showed no significant effect on the yields of this ring expansion reaction (**5q**–**5r**).

Next, the generality of acid-catalyzed hydrated ring expansion was explored (Figure 4). Initially, an investigation of substrate scope on butafulvenes **1** was conducted. Unsymmetric butafulvenes **1** bearing methyl group at the *para* position of phenyl motif, afforded the products **3b** in 75% yield. Replacing methyl with other alkyl groups, such as ethyl (**3c**) and *tert*-butyl (**3d**), the substituted butafulvenes were amenable under the standard condition. The reaction of substrates with halogen substituents at the *para* and *meta* positions all proceeded smoothly to afford the desired products in 59–66% yields (**3e**–**3h**). Biphenyl substituted butafulvene was also tolerated to give the highly aryl substituted unsaturated cyclopentanone **3i** in moderate yield. Then, substitutions at unsymmetric butafulvenes **4** were evaluated. The *para*-substituted butafulvenes **4** bearing various alkyl and halogen groups performed well to deliver the products (**3j**–**3n**) in 49–65% yields. The presence of electron-withdrawing groups, such as Ac and CF_3, still gave the desired products in moderate yields (**3o**–**3p**). Substrates possessing *meta*-substituents were also compatible under current standard reaction conditions (**3q**–**3r**). The reaction with alkyl-substituted butafulvene failed to yield the corresponding product (**3s**).

Corresponding control experiments were carried out to shed light on mechanistic insights for Pd-catalyzed hydrated ring expansion (Figure 5). A mixture of butafulvene **1a**, $Pd(OAc)_2$ (10 mol%), $AgNO_2$ (10 mol%), ^{t}BuONO (3.0 eq.) and H_2O (30 eq.) in MeOH/DCM mixed solvent were stirred for 12 h, and the desired product **2a** was obtained in 90% yield (Figure 5a, entry 1). No conversion was found in the absence of $Pd(OAc)_2$, indicating its indispensable role (Figure 5a, entry 2). Without the addition of ^{t}BuONO, only minimal target product **2a** was

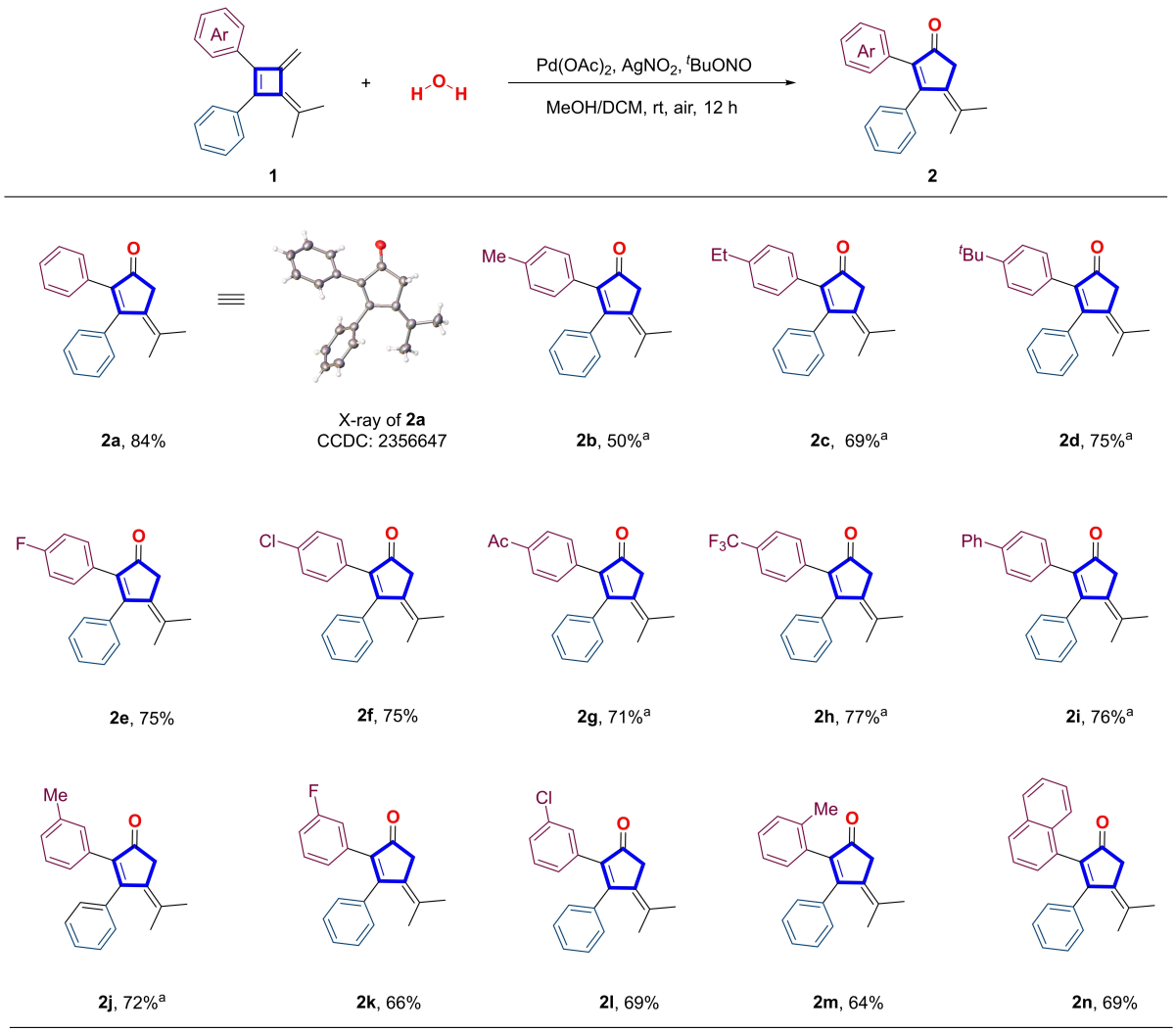


Figure 2. Substrate scope for Pd-catalyzed hydrated ring expansion of unsymmetric butafulvenes **1**. Conditions: **1** (0.20 mmol), H_2O (6.0 mmol), $Pd(OAc)_2$ (10 mol%), $AgNO_2$ (10 mol%), ^tBuONO (0.60 mmol), MeOH/DCM (1.6 mL/0.4 mL), rt, 12 h. [a]$Pd(OAc)_2$ (15 mol%).

produced, indicating ^tBuONO acts as the terminal oxidant in this process (Figure 5a, entry 3). Furthermore, a significant decrease on the yield of **2a** was observed without $AgNO_2$ or under a nitrogen atmosphere (Figure 5a, entries 4–5). The addition of catalytic amount of silver salts could slightly improve the yields of **2a**. It supported the role of silver salt in facilitating the transformation of NO into NO_2 (see the Supporting Information, Figure S1 for details). These results reveal that oxygen and $AgNO_2$ probably facilitate the re-oxidation of Pd^0. As expected, the target product **2a** was rarely detected without the addition of water (Figure 5a, entry 6). Subsequently, an isotopic labeling experiment was conducted to determine the origin of oxygen atom on **2a**. When additional $H_2{}^{18}O$ (98 atom% ^{18}O) was added to the reaction system under a nitrogen atmosphere, 30% yield of **2a** with 89%^{18}O-labeled incorporation was obtained (Figure 5 a, entry 7, see the Supporting Information, Figure S2 for details).

Based on the mechanistic investigations and previous works,[10] a proposed mechanism is shown in Figure 5b. Initially, butafulvene **1a** coordinates with $Pd^{II}(OAc)_2$ to form intermediate **A**. A subsequent hydroxypalladation of intermediate **A** and H_2O generates the Pd^{II} complex **B**, which may undergo two reaction pathways. One reaction route involves the initial formation of the Pd^{II} species **C** via β-carbon elimination from the Pd^{II} complex **B**. Then, the following intramolecular migratory insertion of the Pd^{II} species **C** generates the intermediate **D**. It proceeds through direct β-H elimination to form the target product **2a** and release H-Pd^{II}-OAc. A subsequent reductive elimination produces Pd^0. Finally, the catalytically active $Pd^{II}(OAc)_2$ is regenerated by the oxidation of Pd^0 with NO_2,[11] which is in situ generated from the oxidation of NO with molecular oxygen and $AgNO_2$. An alternative approach involves the oxidation of the Pd^{II} complex **B** to form a Pd^{IV} species **E**. A subsequent semipinacol rearrangement yields the target product **2a** and regenerates $Pd^{II}(OAc)_2$.

To understand another regioselective pathway for acid-catalyzed hydrated ring expansion, various control experiments were conducted (Figure 5c). Using both Ag(OTf) and the corresponding conjugate acid TfOH respectively, the target product **3a** were obtained in moderate yield with detecting the

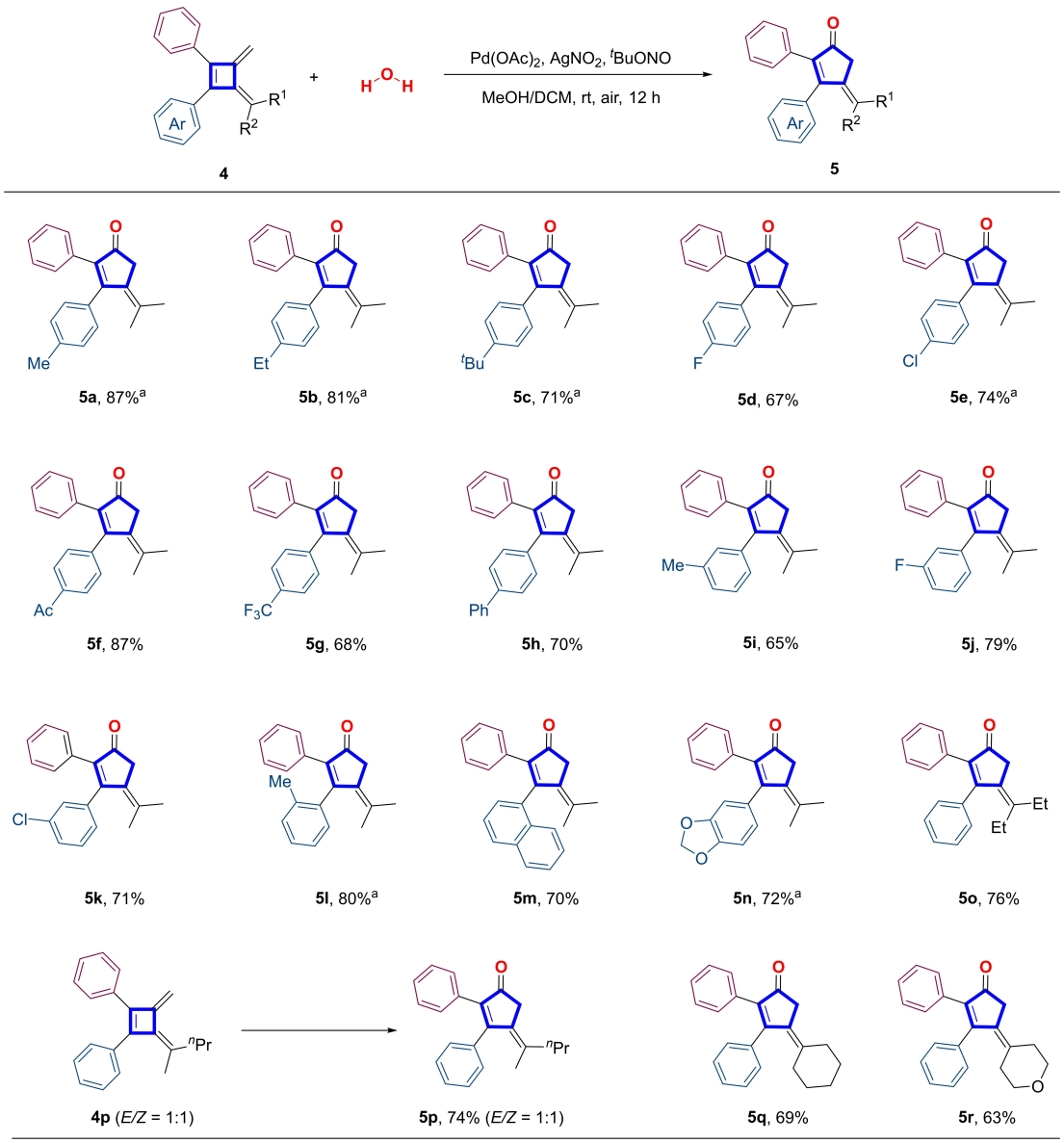


Figure 3. Substrate scope for Pd-catalyzed hydrated ring expansion of unsymmetric butafulvenes **4**. Conditions: **4** (0.20 mmol), H_2O (6.0 mmol), $Pd(OAc)_2$ (10 mol%), $AgNO_2$ (10 mol%), ^tBuONO (0.60 mmol), MeOH/DCM (1.6 mL/0.4 mL), room temperature, 12 h. [a]$Pd(OAc)_2$ (15 mol%).

ring-opening side product **6a** (Figure 5c, entries 1–2). When an extra amount of H_2O (1.0 eq.) was added, a significant decrease on the yield of **3a** was observed. Meanwhile, it increased the formation of side product **6a** (Figure 5c, entries 3–4). These results indicate that the addition of excess water could lead to the formation of byproduct **6a**. Hence, an increase in temperature was required to improve the reaction rate. As expected, no reaction occurred by adding 50 mg 4 Å molecular sieve (Figure 5c, entry 5). Then, an isotopic labeling experiment was conducted to determine the origin of oxygen atom on **3a**. When an external $H_2{}^{18}O$ (98 atom% ^{18}O) was added to the reaction system, 44% yield of **3a** with 37%^{18}O-labeled incorporation was obtained (Figure 5d-I, see the Supporting Information, Figures S3 for details). Furthermore, a possible intermediate exploration experiment was conducted (Figure 5d-II). Cyclobutanol **7** failed to yield target product **3a** under the standard conditions.

Taking the above results together, a plausible mechanism is proposed as outlined (Figure 5e). First, $AgClO_4$ generates proton acid catalyst in situ. Chloroform undergoes photolysis with oxygen to form phosgene, which is then hydrolyzed to deliver hydrogen chloride.[12] Hydrogen chloride reacts reversibly with silver perchlorate, yielding perchloric acid for continuous reaction. Under proton acid catalysis, butafulvene **1a** is protonated to form a carbon cation intermediate **F**, which then undergoes hydrated 1,4-addition to give the alcohol **G**. Continuous hydration occurs on the intermediate **G** to provide the vicinal diol **H**, which go through a final pinacol rearrangement to deliver the target product **3a**.

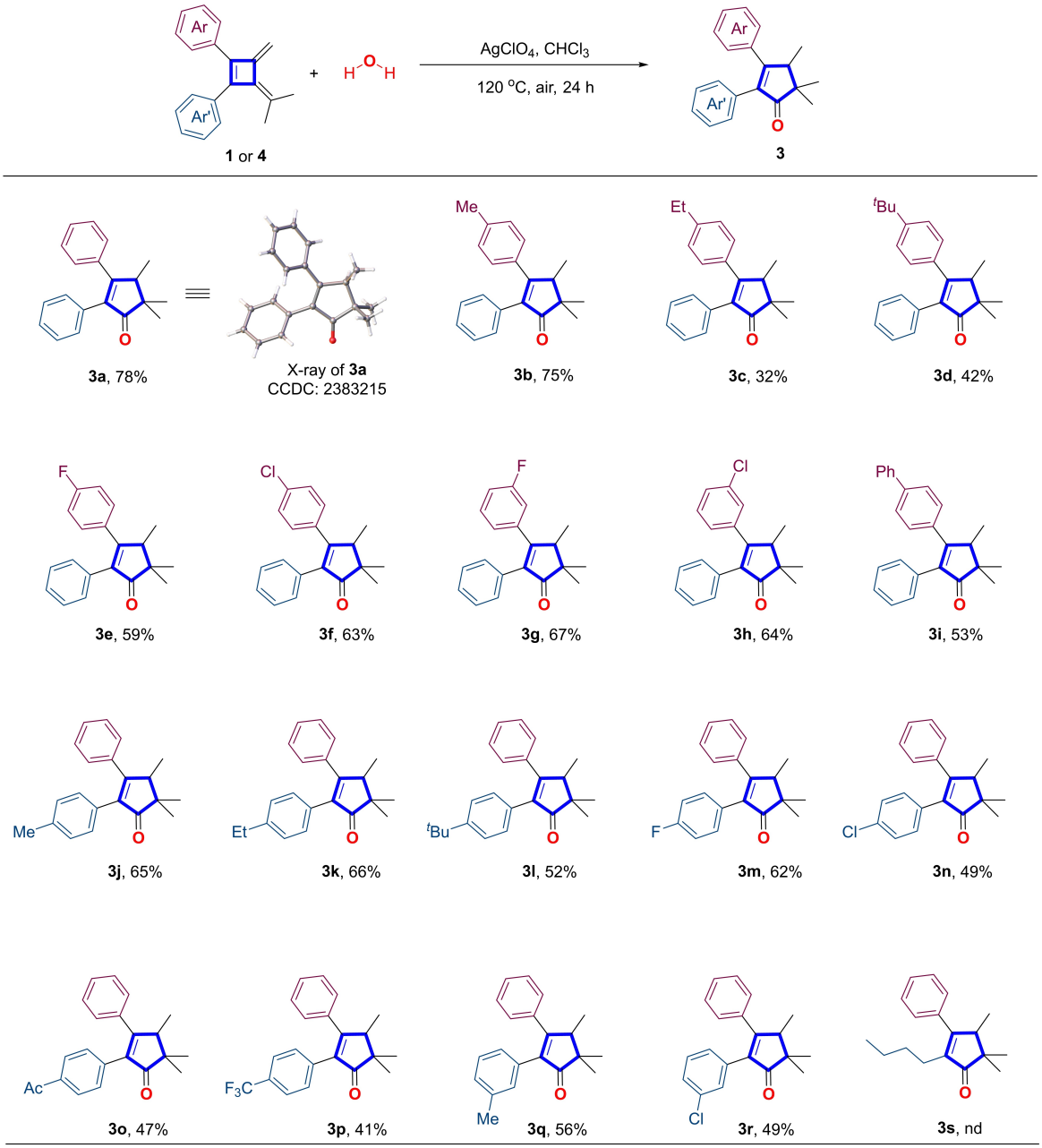


Figure 4. Substrate scope for acid-catalyzed hydrated ring expansion of unsymmetric butafulvenes **1** or **4**. Conditions: **1** or **4** (0.20 mmol), $AgClO_4$ (15 mol%), $CHCl_3$ (1.0 mL), 120 °C, 24 h. Water content of $CHCl_3$ = 0.91 mmol/mL.

To further demonstrate the synthetic utility of this regioselectively hydrated ring expansion protocol, scale-up experiment and divergent transformations were carried out. As shown in Figure 6a, the target product **2a** was successfully isolated in 0.85 g with 77% yield under the standard condition. Through regulating the amounts of benzyl bromide and ^{t}BuOK, the carbonyl α-position of **2a** could be selectively mono- or di-benzylated to yield compounds **8** and **9** with the yields of 90% and 60%, respectively. C–Se bond formation from cross-coupling on **2a** with PhSeSePh could proceed smoothly to afford product **10** in 58% yield.[13] In the presence of allylmagnesium bromide, the nucleophilic addition and dehydration of **2a** efficiently delivered the allyl cyclopentadiene **11** in 71% yield.[14] On the other hand, the epoxidation reaction of exocyclic double bond also proceeded smoothly with *m*-CPBA to give epoxide **12** in 96% yield.[15] In addition, subjecting **2a** to osmium-catalyzed dihydroxylation delivered diol product **13** in good yield.[16] Meanwhile, the regioisomer **3a** (0.67 g) have been isolated in a scale up preparation with 61% yield (Figure 6b). With the aid of strong base, an interesting carbon–carbon double bond isomerization of conjugated enone **3a** occurred to afford unconjugated cyclopentanone **14**. Moreover, a regioselective benzylation has been demonstrated to create more substituted and unconjugated cyclopentanone **15** in the

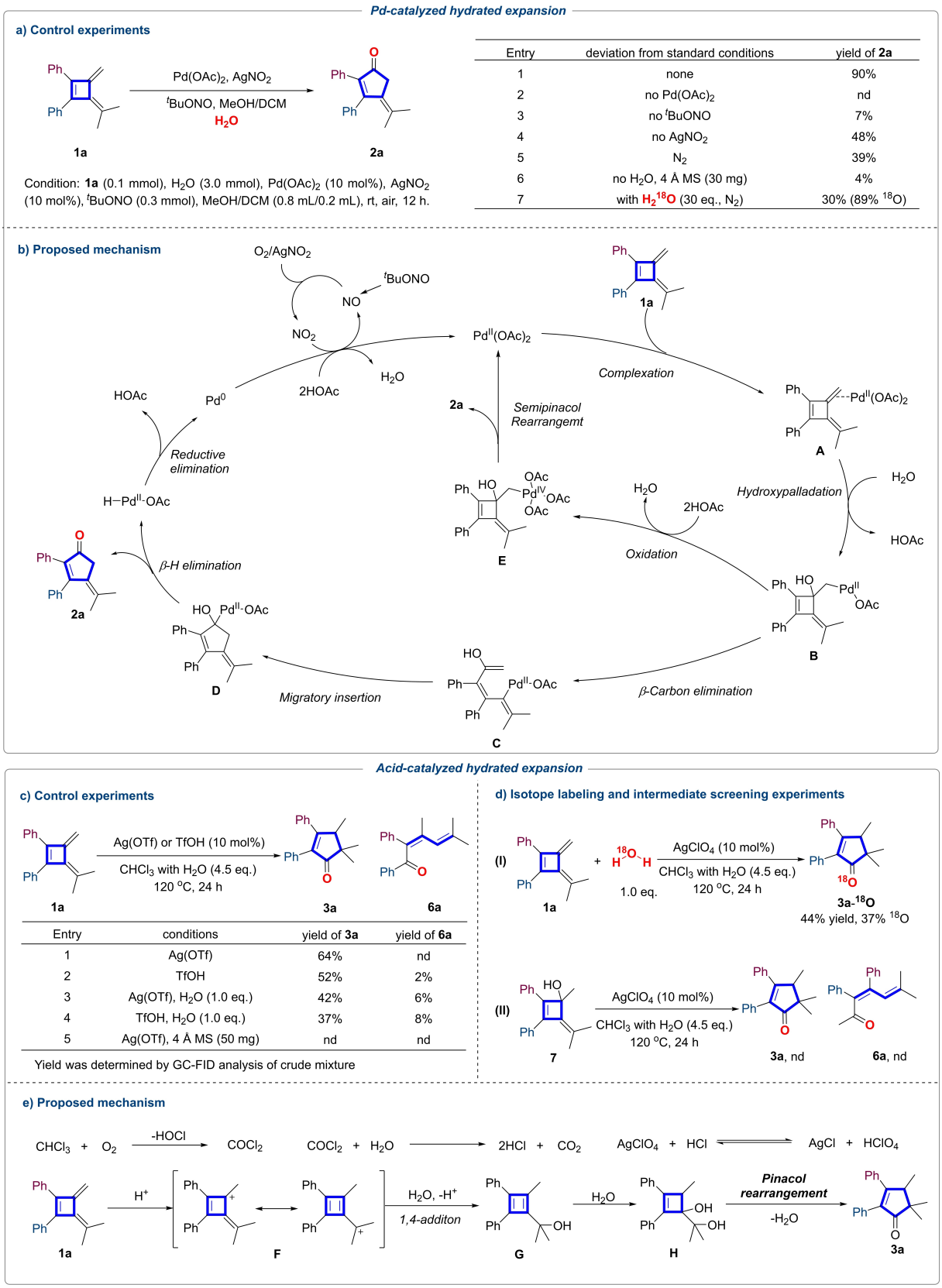


Figure 5. Mechanistic studies and proposed mechanism.

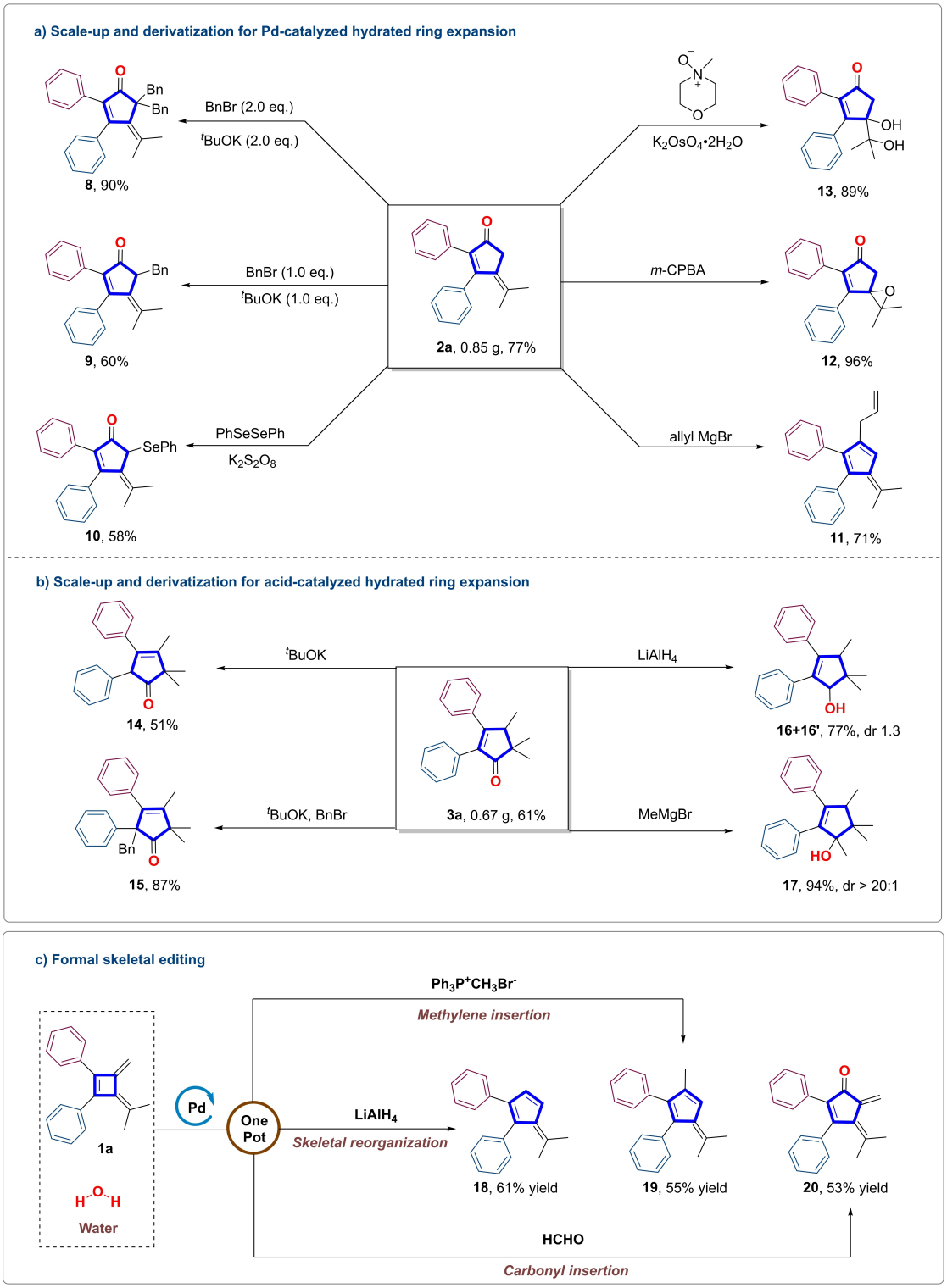


Figure 6. Scale-up reaction and divergent transformations.

presence of benzyl bromide and ^{t}BuOK. In addition, the reactions of **3a** with methylmagnesium[14] and $LiAlH_4$[17] were carried out to provide the unsaturated tertiary and quaternary alcohols **16** and **17** in 77% and 94% yield, respectively.

Skeletal editing reactions have emerged as a powerful method for the conversion of readily available molecules into more complex structures, which are difficult to access through conventional strategies.[18] Taking advantages of the unsaturated cyclopentanone intermediates under Pd catalysis, three types of formal skeletal editing of butafulvenes have been demonstrated via one-pot process (Figure 6c). The skeletal reorganization of butafulvene **1a** to cyclopentadiene **18** was

achieved through the reductive dehydration of the intermediate **2a** with $LiAlH_4$.[17] Through Witting reaction and further tautomerism manipulation, a methylene insertion product **19** of butafulvene was obtained in 55% yield.[19] Additionally, **2a** could undergo condensation with formaldehyde to form the carbonyl insertion product **20** of butafulvene.[20]

Conclusions

In summary, we have developed a regio- and redox divergent hydrated ring expansion protocol of butafulvenes for constructing highly substituted unsaturated cyclopentanone derivatives. Moreover, various unsaturated cyclopentanones could be accessed with good functional group tolerance under the hydration process. Isotope labeling experiments showed that the carbonylic oxygen atom of target product is derived from water. The synthetic utilities of the unsaturated cyclopentanone products were demonstrated in a scale-up experiment and divergent transformations. Formal skeletal editing through one-pot protocol enabled the skeletal reorganization, methylene insertion, and carbonyl insertion of butafulvenes. Further applications of this hydrated strategy are underway in our laboratory.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Butafulvene · Hydration · Ring expansion · Pd catalysis · Acid catalysis

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