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纳米 Cu-$CuFe_2O_4$ 在乙醇中催化选择性还原 α,β,γ,δ-不饱和羰基化合物

从屹康 曾祥华*
(嘉兴学院生物与化学工程学院 浙江嘉兴 314001)

摘要 纳米 Cu-$CuFe_2O_4$ 通过质子去硼策略能高效催化 α,β,γ,δ-不饱和酮、酯和腈酯发生 1,4-还原. 与已报道的方法相比, 该方法具有以乙醇溶剂为氢源、催化剂量低(0.5 mol%)、催化剂可循环使用等优点. 同时, 研究了该催化体系的克级规模反应和反应机理. 此外, 也研究了还原产物(*E*)-γ,δ-不饱和羰基化合物的应用, 如可转化生成 3-丁烯-1-醇、3-丁烯-1-胺、γ-酮酸、环醚和环硝基酮.

关键词 α,β,γ,δ-不饱和羰基化合物; 纳米 Cu-$CuFe_2O_4$; 化学选择性; 1,4-还原

Nano Cu-$CuFe_2O_4$-Catalyzed Selective Reduction of α,β,γ,δ-Unsaturated Carbonyls in Alcohol Medium

Cong, Yikang Zeng, Xianghua*
(*College of Biological, Chemical Science and Engineering, Jiaxing University, Jiaxing, Zhejiang 314001*)

Abstract An efficient Cu-$CuFe_2O_4$ nanoparticle-catalyzed protodeboronation strategy has been developed for the chemoselective 1,4-reduction of α,β,γ,δ-unsaturated ketones, carboxylic ester and cyano-ester. This protocol has the advantageous of the use of alcohol as hydrogen source and solvent, low catalyst loading (0.5 mol%), and excellent catalyst recyclability. Additionally, the Cu-$CuFe_2O_4$ catalyst has shown excellent performance in gram-scale reactions. Furthermore, the catalytic mechanism has also been discussed. The reactivity of (*E*)-γ,δ-unsaturated carbonyl products, an important class of γ,δ-unsaturated alkenes, enables easy access to 3-buten-1-ols, 3-buten-1-amines, γ-keto acids, cyclic ethers, and cyclic nitrones.

Keywords α,β,γ,δ-unsaturated carbonyls; nano Cu-$CuFe_2O_4$; chemoselective; 1,4-reduction

1 Introduction

The selective reduction of a functional group in the presence of a number of other reducible functional groups has long been a problem that organic chemists have struggled to resolve.[1] The chemoselective 1,4-reduction of α,β-unsaturated carbonyl compounds is well-established.[2] In contrast, very limited knowledge is available regarding the selective reduction of highly activated α,β,γ,δ-unsaturated carbonyl compounds.[3] This is due to the presence of three reducible positions (*e.g.*, 1,2-, 1,4-, and 1,6-reduction), often resulting in mixtures of multi-reduced products under reductive conditions. To the best of our knowledge, there are only two general reports concerning regarding the 1,4-reduction of α,β,γ,δ-unsaturated alkenes, previously divulged by Ranu *et al.*[4] (Scheme 1a) and Song *et al.*[5] (Scheme 1b). However, these methods suffer from a number of disadvantages, such as low yields, the need for high temperatures, low efficiency and the use of toxic solvents. The γ,δ-unsaturated alkenes are important intermediates and building blocks for the construction of other valuable fine chemicals,[6] and therefore, the development of a highly efficient catalyst for the environmentally benign reduction of α,β,γ,δ-unsaturated alkenes into γ,δ-unsaturated alkenes is thus highly desirable.

In recent, there is an explosive growth in the use of nanoparticles as highly reactive catalysts,[7] with the size and shape of various metal nanoparticles giving rise to their improved catalytic performance over traditionally employed catalysts.[8] Incorporation of metal nanoparticles in magnetic materials has recently gained attraction because a combination of magnetic materials and metal nanoparticles provides synergistically useful performance and stability.[9] In addition, they possess the added benefit of being separable by means of an external magnet after completion of the reaction. Au,[10] Cu,[11] Pt,[12] Pd,[13] Ru[14] and Rh[15]

* Corresponding author. E-mail: xianghuazeng@zjxu.edu.cn
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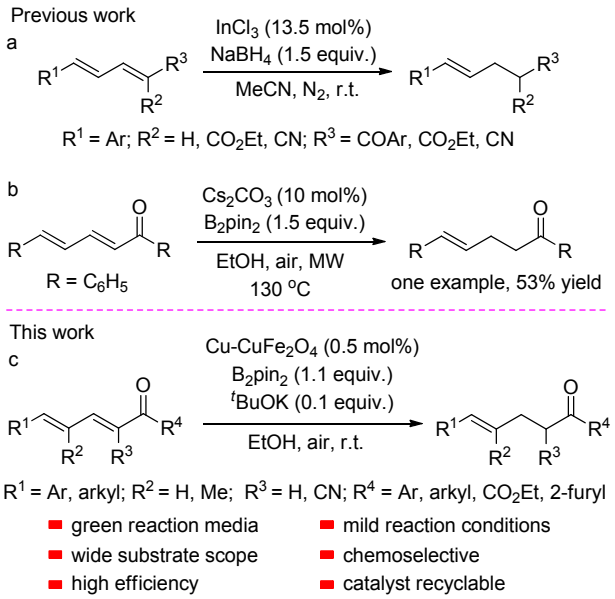


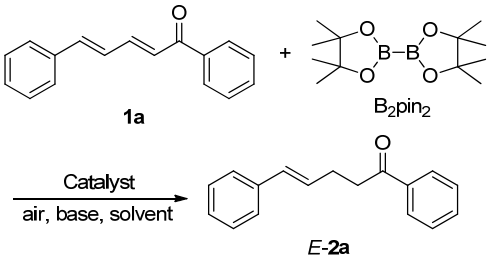
Scheme 1 1,4-Reduction of *α*,*β*,*γ*,*δ*-unsaturated alkenes

nanoparticles have been incorporated into a magnetic materials for use as catalysts in several transformations. In particular, iron-oxide nanoparticles (NPs) such as MFe_2O_4 (M＝Mn, Fe, Co, Ni, Cu), Fe_3O_4 and Fe_2O_3, have been widely used as solid magnetic supports.[16] As a part of our continuous efforts in the field of nano-catalysis, the catalytic activity of Cu(0) incorporated into $CuFe_2O_4$ NPs for the hydroboration of alkynes and protodeboronation of ynones have been demonstrated.[17] Herein, we reveal the activity of the same Cu-$CuFe_2O_4$ NPs catalyst toward the 1,4-reduction of *α*,*β*,*γ*,*δ*-unsaturated carbonyls with bis(pinacolato)diboron (B_2pin_2), employing an environmentally benign and inexpensive alcohol as a hydrogen donor and solvent (Scheme 1c).)

2 Results and discussion

For our initial studies, reactions of commercially available B_2pin_2 and micro Cu powder with *α*,*β*,*γ*,*δ*-unsaturated ketone **1a** in the presence of sodium methoxide, resulted in the formation of product **2a** in 12% isolated yield (Table 1, Entry 1). Encouraged by this result, this reaction using our reported Cu-$CuFe_2O_4$ NPs in place of micro Cu powder was then tested. Gratifyingly, **2a** could be obtained in 87% yield using this catalyst (Table 1, Entry 2). The use of $CuFe_2O_4$ NPs significantly reduced the yield of product **2a** and no reaction occurred in the absence of catalyst (Table 1, Entries 3 and 4). From these results, it can be concluded that the Cu(0) NPs incorporated into $CuFe_2O_4$ provide improved catalytic performance. When *t*-BuOK was used in place of sodium methoxide, the desired product **2a** was obtained in 94% yield (Table 1, Entry 5). Upon further optimization concerning the equivalents of base, catalyst loading, solvent and reaction time (Table 1, Entries 6～10), the final optimized reaction conditions were able to afford the desired product in 95% yield in only 4 h (Table 1, Entry 7).

Table 1 Screening of reaction conditions[a]



Entry	Catalyst	Solvent	Base	*t*/h	Yield[b]/%
1	Micro Cu powder	EtOH	MeONa	6	12
2	Nano Cu-$CuFe_2O_4$	EtOH	MeONa	6	87
3	Nano $CuFe_2O_4$	EtOH	MeONa	6	28
4	—	EtOH	MeONa	6	0
5	Nano Cu-$CuFe_2O_4$	EtOH	*t*-BuOK	6	94
6	Nano Cu-$CuFe_2O_4$	MeOH	*t*-BuOK	6	92
7	Nano Cu-$CuFe_2O_4$	EtOH	*t*-BuOK	4	95
8	Nano Cu-$CuFe_2O_4$	EtOH	*t*-BuOK	2	86
9[c]	Nano Cu-$CuFe_2O_4$	EtOH	*t*-BuOK	4	70
10[d]	Nano Cu-$CuFe_2O_4$	EtOH	*t*-BuOK	4	79

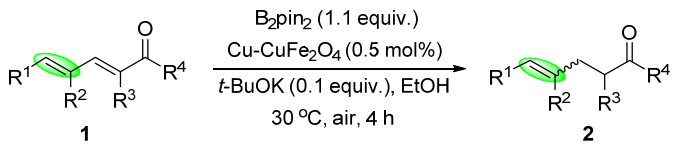
[a] Unless otherwise noted, the reactions were carried out with **1a** (0.2 mmol), B_2pin_2 (0.21 mmol), catalyst (0.5 mol%), base (0.1 equiv.), solvent (2 mL), 30 ℃, under air. [b] Isolated yield. [c] 5 mol% of base. [d] 0.25 mol% of catalyst.

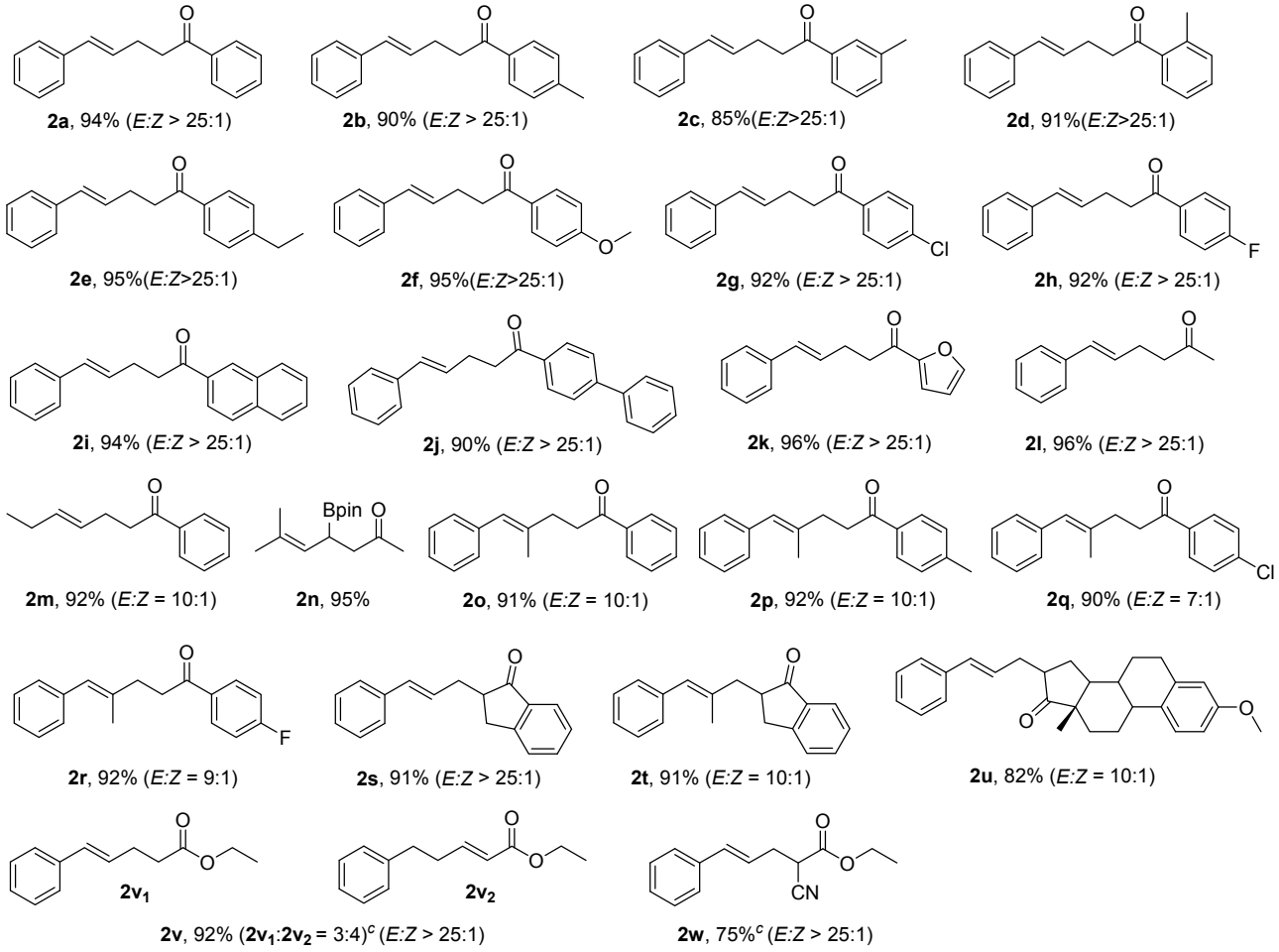
Next, the substrate scope of *α*,*β*,*γ*,*δ*-unsaturated compounds was investigated. Firstly, the different aryl group-substituted *α*,*β*,*γ*,*δ*-unsaturated ketones were surveyed. As shown in Table 2, good to excellent *E*/*Z* selectivity and yield were maintained across a range of ketones with varying electronic demand at the carbonyl position (**2a**～**2n**). Particular attentions should be paid to compounds containing alkyl group substituted at the *δ*-position (**2m** and **2n**), since in these cases, the corresponding products were obtained with either moderate *E*/*Z* selectivity (*E*/*Z*＝10∶1) or as the *β*-boration addition adduct. The amenability of sterically demanding *α*,*β*,*γ*,*δ*-unsaturated ketones to the catalytic conditions was also examined. Fortunately, the desired products bearing amethyl or methylene group substituted at the *γ*-position (**2o**～**2r**) and *α*-position (**2s**～**2u**) were obtained with good to excellent regioselectivity. The *α*,*β*,*γ*,*δ*-unsaturated carboxylic ester (**2s**) also reacted highly regioselectively. However, in this case, both 1,4-reduction and 1,6-reduction occured. Additionally, *α*,*β*,*γ*,*δ*-unsaturated cyano-ester (**2t**) was also examined and interestingly, only the 1,4-reduced product was obtained in 75% yield and with a high *E*/*Z* selectivity of ＞25∶1.

Based on the *β*-boration addition of (*E*)-6-methylhepta-3,5-dien-2-one (**1n**), the utility of this methodology was further explored by applying our catalytic conditions to the reduction of natural products (Scheme 2). To our delight, irisone was successfully reduced to give their corresponding derivatives in 95% yield.

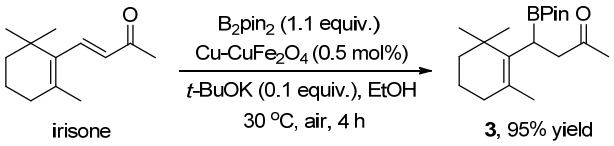
To further illustrate the synthetic utility of our reaction, we carried out the reduction of *α*,*β*,*γ*,*δ*-unsaturated carbonyl products **1a** on a gram scale. The corresponding *γ*,*δ*-unsaturated ketone **2a** was obtained in 80% isolated yield

Table 2 $\alpha,\beta,\gamma,\delta$-Unsaturated carbonyl scope[a,b]





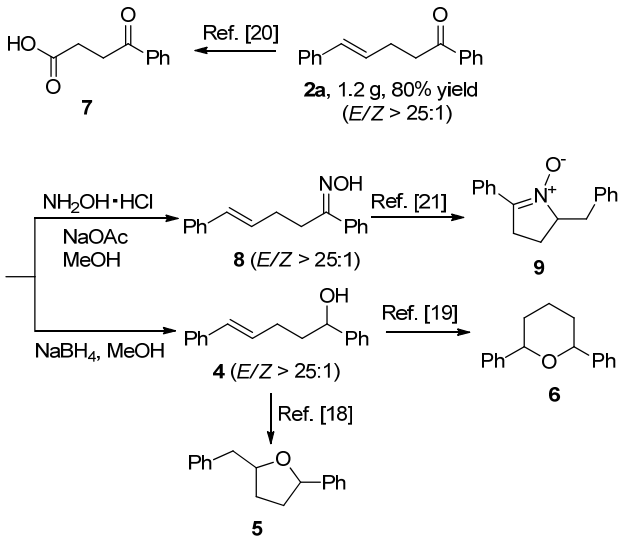
[a] Reaction conditions: **2** (0.2 mmol), $B_2(Pin)_2$ (0.22 mmol), EtOH (2 mL), KO^{t}Bu (0.02 mmol), and Cu-$CuFe_2O_4$ (0.6 mg, 0.5 mol%) at 30 ℃ under air for 4 h. The values in parentheses are the *E*/*Z* ratios detected by ^{1}H NMR spectroscopy. [b] Isolated yield. [c] 60 ℃.



Scheme 2 Cu-$CuFe_2O_4$-catalyzed the borylation reaction of natural products

(Scheme 3). The γ,δ-unsaturated ketone was then successfully transformed into three structurally distinct synthons: (1) selective reduction of the ketone group under the reducing conditions gave the unsaturated alcohol **4** which was widely used for the synthesis of cyclic ethers **5**[18] and **6**[19] via intramolecular hydroalkoxylation; (2) selective oxidation of the carbon-carbon double bond under the oxidizing conditions gave the γ-keto acids **7**[20] which could be further elaborated to other compounds by an amidation reaction; (3) condensation of the ketone with hydroxylamine hydrochloride afforded the oxime **8** which could be used to prepare cyclic nitrone **9**.[21] It should be noted that nearly all of the cinnamaldehydes and ketones employed in the synthesis of $\alpha,\beta,\gamma,\delta$-unsaturated carbonyl compounds (Table 2) are commercially available, further demonstrating the advantages of directly employing $\alpha,\beta,\gamma,\delta$-unsaturated carbonyl compounds in this 1,4-reduction reaction.

In our experiment, the magnetic $CuFe_2O_4$ composite with stabilized copper nanoparticles could be readily removed from the reaction mixture and recovered by simple filtration. The Cu-$CuFe_2O_4$ NPs may act as a heterogeneous catalyst in this reaction. To prove this hypothesis, the recyclability of Cu-$CuFe_2O_4$ NPs was tested in the reaction of **1a** with B_2Pin_2. Remarkably, the catalyst maintained excellent activity, even after being used in six cycles, as shown in Figure 1. In each cycle, the recovered copper nanoparticles were washed with ethyl acetate and ethanol, then dried and



Scheme 3 Gram-scale experiment and synthetic applications

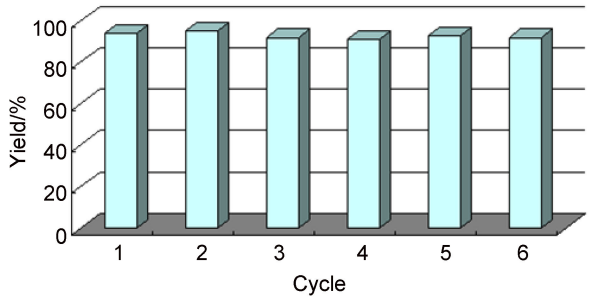
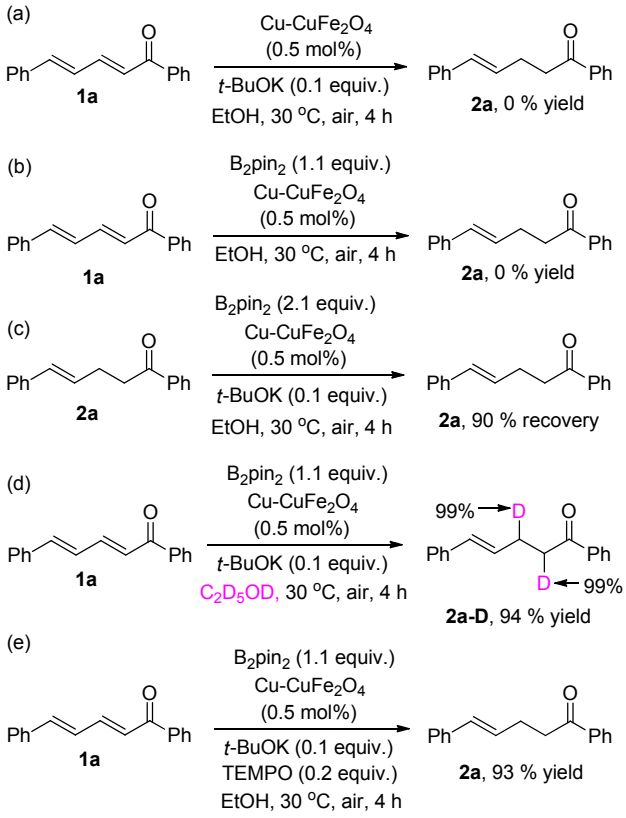


Figure 1 Recyclability of the Cu-$CuFe_2O_4$ NPs catalyst

reused for subsequent reactions without further activation. The transmission electron microscopy (TEM) and X-ray diffraction (XRD) images of the fresh and sixth recycled catalysts indicated that little morphological change had occurred. In addition, the color of the final reaction solution did not change, which indicated that the catalyst had not been oxidized.[22] Furthermore, inductively coupled plasma mass spectrometry (ICP-MS) analysis showed that the amount of Cu(0) lost to leaching was 0.021% after one catalytic circle. These results indicated that the Cu-$CuFe_2O_4$ NPs acted as a highly active heterogeneous catalyst for the 1,4-reduction of *α*,*β*,*γ*,*δ*-unsaturated carbonyl compounds. The methodology possesses several advantages, such as easy recovery of the catalyst, being operational simple and the fact that the catalyst can be recycled multiple times without losing activity.

To investigate the key factors affecting the whole protodeboronation process, several control experiments were also conducted. No reaction occurred when B_2pin_2 and base were removed from the reaction system, respectively (Schemes 4a and 4b). Notably, the protodeboronation product **2a** was still obtained in 90% yield when the amount of B_2pin_2 was increased to 2.1 equiv. (Scheme 4c). This proves that the system exhibits high chemical selectivity. A deuterium labeling experiment was carried out in ethanol-d_6 solvent under the standard conditions (Scheme 4d), and the product was isolated and analyzed by NMR spectroscopy. The result revealed that deuterium was incorporated at the *α*-position and *β*-position of the reduced product with 99% ratio, clearly demonstrating that the solvent serves as the hydrogen source for this protodeboronation system. The reaction was not inhibited by adding 0.2 equiv. 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) (**4e**).

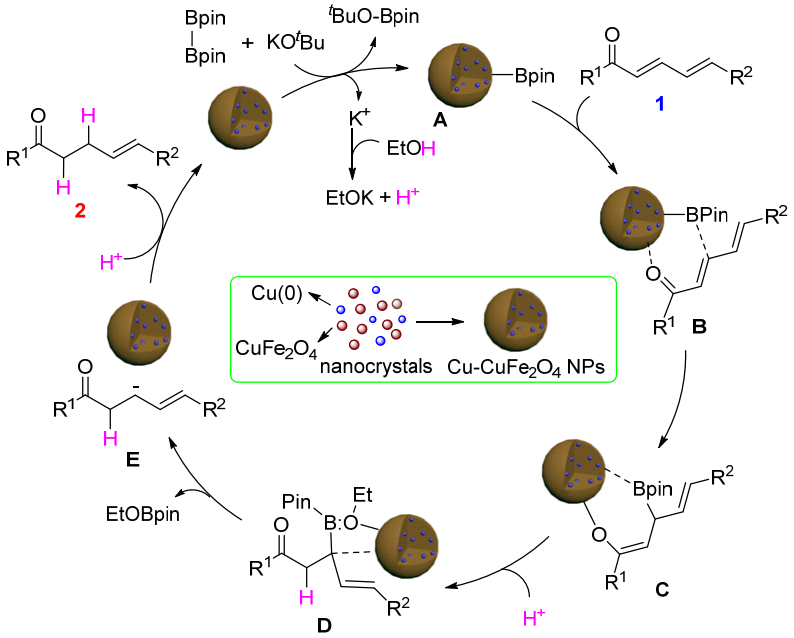


Scheme 4 Control and hydrogen isotope labelling experiments

According to previous literature reports[23] and our experimental results, a plausible mechanism is described in Scheme 5. The catalytic cycle is initiated by reaction of Cu-$CuFe_2O_4$ with B_2Pin_2 in the presence of KO^{t}Bu, forming key intermediate **A**, K^+ can react with EtOH to generate H^+ and EtOK. Intermediate **A**, through adsorption of the *α*,*β*,*γ*,*δ*-unsaturated compounds, gives intermediate **B**. Subsequent boron addition occurs via a six-membered cyclic transition states to afford **C**,[23c] which is protonated by H^+ to give *β*-boration addition species **D**.[5] Then the boron group of **D** is removed leading to the formation of the negatively charged species **E**.[24] Finally, **E** is further protonated by the remaining H^+ to give the reduced product **2** together with the nano Cu-$CuFe_2O_4$ catalyst.

3 Conclusions

In summary, an efficient methodology for the Cu-$CuFe_2O_4$ NPs catalyzed the boron 1,4-reduction of *α*,*β*,*γ*,*δ*-unsaturated carbonyl compounds in an alcohol medium under mild condition has been developed. This methodol-



Scheme 5 Possible mechanism

ogy tolerates a broad substrate scope and gives the desired products in good yields (up to 96% yield) and with high chemoselectivities (*E*/*Z* up to ＞25∶1). This new synthetic method is operationally simple and scalable, and the obtained *γ*,*δ*-unsaturated ketone products can be readily derivatized. Remarkably, the Cu-$CuFe_2O_4$ NPs could be easily recovered and reused at least six times with only a slight decrease in catalytic activity. Furthermore, the mechanistic studies concerning catalyst activation and intermediate formation have been discussed.

4 Experimental section

4.1 Materials

The chemicals used in this study were purchased from Energy Chemicals Co. Ltd. (Shanghai, P. R. China). The solvents used in this study were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, P. R. China). All chemicals and solvents were used directly without any purification. Preparation of the catalyst was according to our previous report.[17]

4.2 General procedure for the reduction of *α*,*β*,*γ*,*δ*-unsaturated carbonyls

CH_3CH_2OH (2 mL), *α*,*β*,*γ*,*δ*-unsaturated carbonyls (0.2 mmol), B_2Pin_2 (56 mg, 0.22 mmol), potassium *t*-butoxide (2.3 mg, 0.02 mmol) and Cu-$CuFe_2O_4$ nanoparticles (0.6 mg, 0.5 mol%) were added to a Schlenk tube under air atmosphere. The mixture was then stirred at 30 ℃ for 4 h. Next, H_2O (2 mL) was added into the mixture. Then the mixture was extracted with CH_2Cl_2 (3 mL, three times). The combined organic phase was dried over anhydrous $MgSO_4$ and concentrated, and the residue was purified by column chromatography using petroleum ether/ethyl acetate (*V*/*V*＝30/1) as an eluent. Evaporation of the volatiles under vacuum resulted in the corresponding product.

4.3 General procedure for catalyst recycling

(2*E*,4*E*)-1,5-Diphenylpenta-2,4-dien-1-one (**1a**, 20 mmol), B_2Pin_2 (22 mmol), Cu-$CuFe_2O_4$ nanoparticles (12 mg, 0.5 mol%), *t*-BuOK (10 mol%), ethanol (30 mL), under air at room temperature for 12 h. In each run, after reaction, the catalyst was separated by filtration, washed thoroughly with ethyl acetate, water, ethanol and dried by vacuum. Then, the dried catalyst was used further, without any purification or reactivation. The filtrate was evaporated under vacuum, and the residue was purified by column chromatography.

(*E*)-1,5-Diphenylpent-4-en-1-one (**2a**):[25] Light yellow oil (44.4 mg, 94% yield, *E*∶*Z*＞25∶1). ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.97～7.99 (m, 2H), 7.56～7.57 (m, 1H), 7.45～7.49 (m, 2H), 7.20～7.36 (m, 5H), 6.47 (d, *J*＝16.0 Hz, 1H), 6.26～6.34 (m, 1H), 3.14～3.18 (m, 2H), 2.64～2.69 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 199.3, 137.4, 136.9, 133.1, 130.8, 129.1, 128.61, 128.5, 128.0, 127.1, 126.0, 38.3, 27.5.

(*E*)-5-Phenyl-1-(p-tolyl)pent-4-en-1-one (**2b**):[26] Light yellow oil (45.0 mg, 90% yield, *E*∶*Z*＞25∶1). ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.87～7.89 (m, 2H), 7.27～7.35 (m, 6H), 7.18～7.21 (m, 1H), 6.57 (d, *J*＝15.6 Hz, 1H), 6.26～6.33 (m, 1H), 3.11～3.15 (m, 2H), 2.62～2.67 (m, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 199.0, 143.8, 137.5, 134.4, 130.7, 129.3, 129.3, 128.5, 128.2, 127.0, 126.0, 38.1, 27.6, 21.7.

(*E*)-5-Phenyl-1-(m-tolyl)pent-4-en-1-one (**2c**): Light yellow oil (42.6 mg, 85% yield, *E*∶*Z*＞25∶1). ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.87～7.89 (m, 2H), 7.27～7.35 (m, 6H), 7.18～7.21 (m, 1H), 6.57 (d, *J*＝15.6 Hz, 1H), 6.26～6.33 (m, 1H), 3.11～3.15 (m, 2H), 2.62～2.67 (m, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 199.6, 138.4, 137.5, 136.9, 133.8, 130.7, 129.2, 128.6, 128.5, 127.0, 126.0,

125.3, 38.3, 27.5, 21.4. HRMS (ESI) calcd for $C_{18}H_{18}ONa$ $[M+Na]^+$: 273.1250, found 273.1247.

(*E*)-5-Phenyl-1-(o-tolyl)pent-4-en-1-one (**2d**): Light yellow oil (45.6 mg, 91% yield, *E*∶*Z*>25∶1). ^1H NMR (400 MHz, $CDCl_3$) *δ*: 7.64～7.66 (m, 1H), 7.24～7.32 (m, 8H), 6.44 (d, *J*=16.0 Hz, 1H), 6.23～6.31 (m, 1H), 3.06～3.10 (m, 2H), 2.60～2.66 (m, 2H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 203.6, 138.0, 137.9, 137.4, 132.0, 131.3, 130.8, 129.0, 128.5, 128.4, 127.1, 126.0, 125.7, 41.1, 27.7, 21.3. HRMS (ESI) calcd for $C_{18}H_{18}ONa$ $[M+Na]^+$: 273.1250, found 273.1252.

(*E*)-1-(4-Ethylphenyl)-5-phenylpent-4-en-1-one (**2e**): Light yellow oil (50.2 mg, 95% yield, *E*∶*Z*>25∶1). ^1H NMR (400 MHz, $CDCl_3$) *δ*: 7.90～7.92 (m, 2H), 7.27～7.35 (m, 6H), 7.19～7.21 (m, 1H), 6.46 (d, *J*=16.0 Hz, 1H), 6.26～6.33 (m, 1H), 3.12～3.15 (m, 2H), 2.62～2.74 (m, 4H), 1.26 (t, *J*=7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 199.0, 150.0, 137.5, 134.6, 130.7, 129.3, 128.5, 128.3, 128.1, 127.0, 126.0, 38.2, 29.0, 27.6, 15.3. HRMS (ESI) calcd for $C_{19}H_{20}ONa$ $[M+Na]^+$: 287.1406, found 287.1405.

(E)-1-(4-Methoxyphenyl)-5-phenylpent-4-en-1-one (**2f**):[25] Light yellow oil (50.5 mg, 95% yield, *E*∶*Z*>25∶1). ^1H NMR (400 MHz, $CDCl_3$) *δ*: 7.95～7.98 (m, 2H), 7.27～7.35 (m, 4H), 6.64 (d, *J*=9.2 Hz, 2H), 6.46 (d, *J*=16.0 Hz, 1H), 6.26～6.33 (m, 1H), 3.87 (s, 3H), 3.08～3.12 (m, 2H), 2.62～2.67 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 198.0, 163.4, 137.5, 130.6, 130.3, 130.0, 129.3, 128.5, 127.0, 126.0, 113.7, 55.5, 37.9, 27.7.

(*E*)-1-(4-Chlorophenyl)-5-phenylpent-4-en-1-one (**2g**):[25] Light yellow solid (49.7 mg, 92% yield, *E*∶*Z*>25∶1). m.p. 51.0～52.1 ℃; ^1H NMR (400 MHz, $CDCl_3$) *δ*: 7.91～7.93 (m, 2H), 7.43～7.47 (m, 2H), 7.18～7.35 (m, 4H), 7.02～7.17 (m, 1H), 6.46 (d, *J*=16.0 Hz, 1H), 6.24～6.31 (m, 1H), 3.11～3.14 (m, 2H), 2.62～2.67 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 198.1, 145.3, 142.4, 139.5, 137.3, 135.1, 130.9, 129.8, 129.5, 128.9, 128.9, 128.8, 128.5, 127.3, 127.1, 126.0, 38.3, 27.4.

(*E*)-1-(4-Fluorophenyl)-5-phenylpent-4-en-1-one (**2h**): Light yellow oil (46.7 mg, 92% yield, *E*∶*Z*>25∶1). ^1H NMR (400 MHz, $CDCl_3$) *δ*: 7.99～8.02 (m, 2H), 7.27～7.35 (m, 4H), 7.11～7.16 (m, 3H), 6.46 (d, *J*=16.0 Hz, 1H), 6.24～6.32 (m, 1H), 3.13 (t, *J*=7.2 Hz, 2H), 2.65 (q, *J*=7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 197.7, 167.0, 164.4, 137.6, 133.3, 130.9, 130.7, 130.6, 128.9, 128.5, 127.1, 126.0, 115.8, 115.6, 38.2, 27.5. HRMS (ESI) calcd for $C_{17}H_{15}OFNa$ $[M+Na]^+$: 277.0999, found 277.0997.

(E)-1-(Naphthalen-2-yl)-5-phenylpent-4-en-1-one (**2i**):[25] White solid (53.8 mg, 94% yield, *E*∶*Z*>25∶1). m.p. 62.0～63.4 ℃; ^1H NMR (400 MHz, $CDCl_3$) *δ*: 8.50 (s, 1H), 8.05～8.05 (m, 1H), 7.96～7.98 (m, 2H), 7.87～7.92 (m, 2H), 7.56～7.61 (m, 2H), 7.25～7.37 (m, 5H), 6.50 (d, *J*=16.0 Hz, 1H), 6.31～6.38 (m, 1H), 3.28～3.32 (m, 2H), 2.70～2.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 199.3, 137.4, 135.6, 134.2, 132.5, 130.8, 129.7, 129.6, 129.2, 128.5, 128.5, 128.5, 127.8, 127.1, 126.8, 126.0, 123.9, 38.4, 27.7.

(*E*)-1-(4-Chlorophenyl)-4-methyl-5-phenylpent-4-en-1-one (**2j**): White solid (53.1 mg, 85% yield, *E*∶*Z*>25∶1). m.p. 57.5～58.3 ℃; ^1H NMR (400 MHz, $CDCl_3$) *δ*: 8.05～8.07 (m, 2H), 7.69～7.71 (m, 2H), 7.62～7.64 (m, 2H), 7.28～7.50 (m, 8H), 6.49 (d, *J*=15.6 Hz, 1H), 6.28～6.36 (m, 1H), 3.17～3.21 (m, 2H), 2.66～2.72 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 198.9, 145.7, 139.9, 137.4, 135.6, 130.8, 129.1, 128.9, 128.6, 128.5, 128.2, 127.3, 127.1, 126.0, 38.3, 27.6. HRMS (ESI) calcd for $C_{23}H_{20}ONa$ $[M+Na]^+$: 335.1406, found 335.1405.

(*E*)-1-(Furan-2-yl)-5-phenylpent-4-en-1-one (**2k**): Light yellow oil (43.4 mg, 96% yield, *E*∶*Z*>25∶1). ^1H NMR (400 MHz, $CDCl_3$) *δ*: 7.58～7.59 (m, 1H), 7.28～7.32 (m, 4H), 7.20～7.21 (m, 2H), 6.53～6.54 (m, 1H), 6.45 (d, *J*=15.6 Hz, 1H), 6.22～6.30 (m, 1H), 3.01 (t, *J*=7.6 Hz, 2H), 2.61～2.66 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 188.6, 152.7, 146.3, 137.4, 130.9, 128.8, 128.5, 127.1, 126.0, 117.1, 112.2, 38.1, 27.4. HRMS (ESI) calcd for $C_{15}H_{14}O_2Na$ $[M+Na]^+$: 249.0886, found 249.0884.

(*E*)-6-Phenylhex-5-en-2-one (**2l**): Light yellow oil (33.5 mg, 96% yield, *E*∶*Z*>25∶1). ^1H NMR (400 MHz, $CDCl_3$) *δ*: 7.26～7.34 (m, 4H), 7.18～7.22 (m, 1H), 6.40 (d, *J*=15.6 Hz, 1H), 6.15～6.23 (m, 1H), 2.60～2.63 (m, 2H), 2.45～2.51 (m, 2H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 208.1, 137.3, 130.7, 128.8, 128.5, 127.1, 126.0, 43.2, 30.1, 27.1. HRMS (ESI) calcd for $C_{12}H_{14}ONa$ $[M+Na]^+$: 197.0937, found 197.0935.

(*E*)-1-Phenylhept-4-en-1-one (**2m**): Light yellow oil (34.6 mg, 92% yield, *E*∶*Z*=10∶1). ^1H NMR (400 MHz, $CDCl_3$) *δ*: 7.95～7.97 (m, 2H), 7.53～7.57 (m, 1H), 7.45～7.47 (m, 2H), 5.37～5.55 (m, 2H), 3.01～3.05 (m, 2H), 2.40～2.48 (m, 2H), 1.98～2.09 (m, 2H), 0.95 (t, *J*=7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 199.9, 137.0, 133.1, 132.9, 128.5, 128.0, 127.5, 38.6, 27.2, 25.5, 13.8. HRMS (ESI) calcd for $C_{13}H_{16}ONa$ $[M+Na]^+$: 211.1093, found 211.1089.

6-Methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-5-en-2-one (**2n**): Colorless oil (37.9 mg, 95% yield). ^1H NMR (400 MHz, $CDCl_3$) *δ*: 4.98 (d, *J*=13.6 Hz, 2H), 2.60～2.63 (m, 2H), 2.17～2.19 (m, 1H), 2.10 (s, 3H), 1.67 (s, 3H), 1.62 (s, 3H), 1.22 (s, 6H), 1.19 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 208.9, 132.0, 123.0, 83.0, 46.2, 29.5, 25.8, 24.6, 24.5, 18.0. HRMS (ESI) calcd for $C_{14}H_{25}O_3BNa$ $[M+Na]^+$: 275.1789, found 275.1786.

(*E*)-4-Methyl-1,5-diphenylpent-4-en-1-one (**2o**): Light yellow oil (46.0 mg, 91% yield, *E*∶*Z*=10∶1). ^1H NMR (400 MHz, $CDCl_3$) *δ*: 7.99～8.01 (m, 2H), 7.56～7.58 (m, 1H), 7.46～7.50 (m, 2H), 7.30～7.34 (m, 2H), 7.19～7.24 (m, 3H), 6.33 (s, 1H), 3.19～3.23 (m, 2H), 2.60～2.64 (m, 2H), 1.92 (d, *J*=0.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 199.8, 138.2, 137.6, 137.0, 133.1, 128.8, 128.6, 128.1, 128.0, 126.0, 125.5, 37.3, 34.9, 18.0. HRMS (ESI) calcd for $C_{18}H_{18}ONa$ $[M+Na]^+$: 273.1250, found 273.1254.

(*E*)-4-Methyl-5-phenyl-1-(p-tolyl)pent-4-en-1-one (**2p**): Light yellow oil (48.6 mg, 92% yield, *E*∶*Z*=10∶1). ^1H NMR (400 MHz, $CDCl_3$) *δ*: 7.89～7.91 (m, 2H), 7.19～

7.33 (m, 7H), 6.33 (s, 1H), 3.15～3.19 (m, 2H), 2.55～2.63 (m, 2H), 2.42 (s, 3H), 1.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 199.5, 143.8, 138.2, 137.8, 134.4, 129.3, 128.81, 128.2, 128.0, 126.0, 125.4, 37.2, 35.0, 21.7, 18.0. HRMS (ESI) calcd for $C_{19}H_{20}ONa$ $[M+Na]^+$: 287.1406, found 287.1405.

(*E*)-1-(4-Chlorophenyl)-4-methyl-5-phenylpent-4-en-1-one (**2q**): Light yellow oil (51.2 mg, 90% yield, *E* : *Z*=7 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92～7.94 (m, 2H), 7.44～7.46 (m, 2H), 7.30～7.34 (m, 2H), 7.20～7.23 (m, 2H), 6.32 (s, 1H), 3.15～3.19 (m, 2H), 2.58～2.62 (m, 2H), 1.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 198.5, 139.5, 138.1, 137.4, 135.2, 129.5, 128.9, 128.9, 128.8, 128.5, 128.3, 128.1, 126.1, 125.6, 37.3, 34.8, 18.0. HRMS (ESI) calcd for $C_{18}H_{17}OClNa$ $[M+Na]^+$: 307.0860, found 307.0859.

(*E*)-1-(4-Fluorophenyl)-4-methyl-5-phenylpent-4-en-1-one (**2r**): Light yellow oil (49.3 mg, 92% yield, *E* : *Z*=9 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.00～8.04 (m, 2H), 7.30～7.33 (m, 2H), 7.12～7.23 (m, 5H), 6.32 (s, 1H), 3.15～3.19 (m, 2H), 2.59～2.62 (m, 2H), 1.91 (d, *J*=0.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 198.2, 167.0, 164.4, 138.1, 137.5, 133.3, 130.7, 130.6, 128.8, 128.1, 126.1, 125.6, 115.8, 115.6, 37.3, 34.9, 18.0. HRMS (ESI) calcd for $C_{18}H_{17}OFNa$ $[M+Na]^+$: 291.1156, found 291.1151.

2-Cinnamyl-2,3-dihydro-1*H*-inden-1-one (**2s**): Light yellow oil (45.6 mg, 91% yield, *E* : *Z*>25 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.76～7.78 (m, 1H), 7.57～7.60 (m, 1H), 7.44～7.46 (m, 1H), 7.20～7.39 (m, 6H), 6.48 (d, *J*=15.6 Hz, 1H), 6.17～6.24 (m, 1H), 3.28～3.35 (m, 1H), 2.72～2.92 (m, 3H), 2.39～2.47 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 208.1, 153.7, 137.2, 136.6, 134.8, 132.2, 128.5, 127.4, 127.2, 126.6, 126.1, 123.9, 47.1, 34.8, 32.1. HRMS (ESI) calcd for $C_{18}H_{16}ONa$ $[M+Na]^+$: 271.1093, found 271.1089.

(*E*)-2-(2-Methyl-3-phenylallyl)-2,3-dihydro-1*H*-inden-1-one (**2t**): Light yellow oil (45.1 mg, 86% yield, *E* : *Z*=10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77～7.79 (m, 1H), 7.58～7.60 (m, 1H), 7.45～7.47 (m, 1H), 7.31～7.40 (m, 3H), 7.21～7.26 (m, 3H), 6.34 (s, 1H), 3.26～3.30 (m, 1H), 2.91～2.96 (m, 3H), 2.19～2.23 (m, 1H), 1.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 208.4, 153.7, 138.0, 136.6, 134.8, 128.9, 128.1, 127.4, 126.9, 126.3, 126.2, 124.0, 45.8, 42.5, 32.2, 17.6. HRMS (ESI) calcd for $C_{19}H_{18}ONa$ $[M+Na]^+$: 285.1250, found 285.1247.

(13*S*)-16-Cinnamyl-3-methoxy-13-methyl-7,8,9,11,12,13,15,16-octahydro-6*H*-cyclopenta[a]phenanthren-17(14*H*)-one (**2u**): Light yellow solid (65.6 mg, 82% yield, *E* : *Z*=10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49～7.51 (m, 1H), 7.17～7.39 (m, 6H), 6.95 (s, 1H), 6.71～6.73 (m, 1H), 6.64～6.66 (m, 1H), 3.78～3.79 (m, 3H), 2.87～2.93 (m, 2H), 2.76～2.80 (m, 1H), 2.39～2.51 (m, 5H), 1.19～2.05 (m, 3H), 1.39～1.59 (m, 5H), 0.95 (s, 1H), 0.85～0.87 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 208.8, 157.5, 141.1, 140.9, 137.8, 137.7, 135.7, 132.1, 128.8, 128.4, 128.4, 127.1, 126.3, 126.1, 124.6, 113.9, 111.5, 55.2, 48.3, 47.8, 44.0, 37.8, 34.6, 31.7, 31.6, 29.6, 26.7, 26.1, 25.9, 14.3. HRMS (ESI) calcd for $C_{28}H_{32}O_2Na$ $[M+Na]^+$: 423.2295, found 423.2293.

(*E*)-Ethyl 5-phenylpent-4-enoate (**2v**): Colorless oil (16.3 mg, 40% yield, *E* : *Z*>25 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27～7.35 (m, 3H), 7.17～7.22 (m, 2H), 6.43 (d, *J*=16.0 Hz, 1H), 6.19～6.24 (m, 1H), 4.12～4.41 (m, 2H), 3.38～3.43 (m, 1H), 2.76～2.78 (m, 1H), 2.48～2.55 (m, 2H), 1.24～1.30 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.9, 140.8, 130.9, 128.5, 127.1, 126.1, 126.0, 121.8, 60.2, 34.3, 28.3, 14.3. HRMS (ESI) calcd for $C_{13}H_{16}O_2Na$ $[M+Na]^+$: 227.1043, found 227.1041.

(*E*)-Ethyl 2-cyano-5-phenylpent-4-enoate (**2w**):[26] Colorless oil (34.4 mg, 75% yield, *E* : *Z*>25 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.26～7.37 (m, 5H), 6.58 (d, *J*=16.0 Hz, 1H), 6.14～6.21 (m, 1H), 6.27 (q, *J*=7.2 Hz, 2H), 3.61～3.64 (m, 1H), 2.83～2.87 (m, 2H), 1.31 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.5, 136.2, 135.0, 128.6, 128.0, 126.4, 122.4, 116.1, 45.8, 63.0, 37.9, 33.3, 14.0.

(*E*)-Ethyl 2-cyano-5-phenylpent-4-enoate (**3**): Colorless oil (60.8 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.02～3.09 (m, 1H), 2.25～2.29 (m, 1H), 2.16～2.22 (m, 1H), 2.10 (s, 3H), 1.83～1.86 (m, 2H), 1.56 (s, 1H), 1.37～1.41 (m, 4H), 1.17 (s, 6H), 1.13 (s, 6H), 1.02 (s, 3H), 0.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 208.8, 138.0, 127.4, 82.9, 45.9, 39.9, 36.1, 33.4, 30.0, 28.5, 27.6, 24.6, 24.5, 21.4, 19.5. HRMS (ESI) calcd for $C_{19}H_{33}BO_3Na$ $[M+Na]^+$: 343.2415, found 343.2417.

(*E*)-1,5-Diphenylpent-4-en-1-ol (**4**):[6] Colorless oil (41.0 mg, 85% yield, *E* : *Z*>25 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28～7.38 (m, 8H), 7.13～7.22 (m, 2H), 6.41 (d, *J*=16.0 Hz, 1H), 6.22～6.27 (m, 1H), 4.73～4.76 (m, 1H), 3.35～3.39 (m, 1H), 2.29～2.31 (m, 2H), 1.90～1.99 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.6, 137.6, 133.2, 130.4, 130.0, 128.5, 128.49, 128.5, 127.6, 126.9, 125.9, 125.9, 74.0, 38.5, 29.3.

4-Oxo-4-phenylbutanoic acid (**7**):[20] White solid (27.0 mg, 75% yield). m.p. 117.0～118.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96～7.98 (m, 2H), 7.55～7.58 (m, 1H), 7.44～7.48 (m, 2H), 3.29～3.32 (m, 2H), 2.79～2.82 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 197.8, 179.0, 136.3, 133.3, 128.6, 128.0, 33.1, 28.1.

(4*E*)-1,5-Diphenylpent-4-en-1-one oxime (**8**):[21] White solid (34.0 mg, 67% yield, *E* : *Z*>25 : 1). m.p. 115.3～116.6 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.68 (s, 1H), 7.62～7.64 (m, 2H), 7.40～7.40 (m, 3H), 7.19～7.39 (m, 5H), 6.42 (d, *J*=15.6 Hz, 1H), 6.21～6.28 (m, 1H), 2.98～3.02 (m, 2H), 2.48～2.53 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.2, 137.5, 130.5, 129.3, 129.3, 128.6, 128.5, 127.0, 126.4, 126.0, 29.7, 26.1.

Supporting Information Full experimental details, TEM images, XRD spectrums, photographs of before reaction and after reaction of B_2Pin_2 and **1a**, ^{1}H NMR spectrum of deuterium-labeling experiments, and ^{1}H NMR and ^{13}C NMR spectra for all compounds. The Supporting Infor-

mation is available free of charge via the Internet at http://sioc-journal.cn/.

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(Li, L.; Fan, Y.)

