



Accepted Article

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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Adv. Synth. Catal. 10.1002/adsc.201901562

Link to VoR: http://dx.doi.org/10.1002/adsc.201901562

COMMUNICATION

DOI: 10.1002/adsc.201((will be filled in by the editorial staff))

cis-Selective Transfer Semihydrogenation of Alkynes by Merging Visible-Light Catalysis with Cobalt Catalysis

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Received: ((will be filled in by the editorial staff))

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201#######.((Please delete if not appropriate))

Abstract. Herein, the first example of visible-light-driven, cobalt-catalyzed transfer semihydrogenation of alkynes to alkenes is reported. It is carried out by using Ir[dF(CF₃)ppy]₂(dtbbpy)]PF₆ as photosensitizer, CoBr₂/n-Bu₃P as proton-reducing catalyst, and *i*-Pr₂NEt/AcOH as the hydrogen source. Under the established catalytic system, the semihydrogenation proceeds with Z as the major selectivity and with inhibition of over-reduction. Under mild reaction conditions, both internal and terminal alkynes, as well as reducible functional groups such as halogen, cyano, and ester, are tolerated. Preliminary mechanistic studies revealed the dual role of the photosensitizer in initiating the reaction via a singleelectron transfer process and controlling the stereoselectivity via an energy transfer process.

Keywords: Photoredox catalysis; Cobalt catalysis; Semihydrogenation; Alkynes

Olefins are essential structural units in many biologically active molecules.^[1] For example, resveratrol, an analogue of stilbene, demonstrates outstanding anti-oxidation, heart protection, and anticarcinogenic activities.^[2] Moreover, alkenes are widely used as building blocks in organic synthesis, which can be further modified into many other functional groups. Owing to the significant importance of alkenes, numerous methodologies, including the Wittig reaction,^[3] Horner–Wadsworth– Emmons reaction,^[4] Julia–Kocienski reaction,^[5] Peterson reaction,^[6] olefin metathesis,^[7] and crosscoupling reactions,^[8] have been developed to construct olefinic groups. In particular, transitionmetal-catalyzed semihydrogenation of alkynes represents one of the most efficient and straightforward approaches for alkene preparation.^[9] To date, several homogeneous catalytic systems have been developed for semihydrogenation of alkynes. The transition metals involved in these systems are Pd,^[10] Ru,^[11] Rh,^[12] Ir,^[13] V,^[14] Ni,^[15] Co,^[16] Cu,^[17]

Mn,^[18] and even Fe.^[19] Despite these significant achievements, many of the above mentioned procedures face limitations, such as lengthy synthesis process for catalysts, elevated reaction temperature, by-product formation due to over-reduction, and tedious operation of H₂ usage. Therefore, development of a simpler, milder, and safer protocol for selective semihydrogenation of alkynes is highly demanded and it remains a challenging task.^[9]

In recent years, visible-light-induced photoredox catalysis has attracted significant research attentiol. due to the environmentally friendly reaction procedures and the sustainability of visible light.^[20] Therefore, merging the visible-light catalysis with transition metal catalysis can provide a new opportunity to achieve the semihydrogenation of alkynes with high efficiency and simple procedure. To the best of our knowledge, this strategy has only been explored by Wu and co-workers, who developed a semihydrogenation protocol by employing eosin Y as the photocatalyst and colloidal Pd nanoparticles as hydrogenation catalyst.^[21]

Notably, metal hydride plays an important role in semihydrogenation transition metal-catalyzed reactions of alkynes. Among metal hydride species, Co-H has gained immense attention because it could be easily generated via single electron transfer (SET) process mediated by visible light, which have been well documented for the reactions such as water photolysis reactions,^[22] photocatalytic hydrogen evolution reactions,^[23] and recently developed photoredox-mediated coupling reaction.^[24] Inspired by these pioneering studies, we continued our longstanding interest in photoredox/cobalt (Co) catalytic system,^[25] and we speculated that the photochemical generated Co-H intermediate could be used for the semihydrogenation of alkynes, and there is no literature precedent of using the photoredox/Co catalytic system for semihydrogenation of alkynes.

We proposed that the reaction followed a mechanism described in Scheme 1. The excited



Scheme 1. Working hypothesis. $Co^{II} = (Cy_3P)_2CoBr_2$, $Ir^{III} = Ir[dF(CF_3)ppy]_2(dtbbpy)]PF_6$.

^{*}Ir[dF(CF₃)ppy]₂(dtbbpy)]PF₆ iridium catalyst $(E^{*IrIII/IrII} = +1.21 \text{ V vs SCE})^{[26]}$ could be reductively quenched by sacrificial reagent, such as *i*-Pr₂NEt (E^{i} $^{2\text{NEt} \bullet + / i - \text{Pr} 2\text{NEt}} = +0.78 \text{ V vs SCE}$, see SI), to afford Ir^{II} species. The Ir^{II} (E^{IrIII/IrII} = -1.37 V vs SCE)^[26] is capable of reducing the high-valent Co catalysts, such as $(Cy_3P)_2CoBr_2$ ($\breve{E}_{1/2}^{CoII/CoI} = -1.09$ V vs SCE, see SI) to Co^I species under visible-light irradiation.^[24a,24d] The generated Co^I species could react with a proton to form Co^{III}-H hydride,^[22-24] which subsequently undergoes hydrometalation with alkynes followed by protonation to form the semihydrogenation product and Co^{III} species. The Co^{III} could further accept an electron from Ir^{II} to form Co^{II} and thus close the Co Recently, visible-light-induced cvcle. photoisomerization of alkenes leading to stereodefined alkenes via energy transfer (EnT) was reported.^[27] Therefore, we expected that the excited *Ir^{III} could further catalyze the alkenes via EnT process to generate the final products in a stereoselective manner. It was further envisioned that the key advantage of such a photo-driven reaction would be milder reaction conditions, readily available catalyst, easy operations, and good tolerance of functionalities, including halides and other reducible groups. More importantly, it would provide a new route for reduction of other unsaturated compounds.

With these hypotheses in mind, the investigation of the photoredox/Co catalyzed semihydrogenation was thus initiated using 1,2-diphenylacetylene 1a as the model substrate. Herein, $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ was used as photosensitizer, CoBr₂ as cobalt catalyst, *i*-Pr₂NEt as electron donor, and CH₃CN as solvent with reaction mixture subjected to blue LED irradiation. First, various ligands were explored. To our delight, tri-alkyl phosphine ligands, such as Cy₃P and n-Bu₃P afforded the mixture of alkene products containing (Z)-stilbene 2a and (E)-stilbene 3a in 54 and 81% total yield respectively, with moderate stereoselectivity. Moreover, no over-reduction product 4a was observed (Table 1, entries 1 and 2). Other aryl containing phosphine ligands, such as Ph₃P and dppp did not show any desired products (entries 3 and 4). 4,4'-Di-tert-butyl bipyridine (dtbbpy) resulted in a slightly decreased yield of 78% with lower Z/E ratio (entry 5). When examining the influence of protic additives (entries 6-8), we found that AcOH further improved the yield up to 97% and the Z/E ratio up to 78:22; however, 3% of over-

reduction product 4a was also observed. Other photocatalysts, such as Ir[ppy]₂(dtbbpy)PF₆ and $Ir[ppy]_2(bpy)PF_6$ showed slight decrease of yield and selectivity with generation of alkane by-product (entries 9 and 10). $Ir(ppy)_3$ (E^{*IrIII/IrII} = +0.31 V vs SCE)^[28] showed no catalytic activity, which should be rationalized to its weaker oxidation ability (entry 11). Next, a survey of common organic solvents revealed that 1.4-dioxane provided the highest yield of >99% with the best Z/E ratio; nonetheless, no reaction occurred with CH₂Cl₂ (entries 12–17). Other reductants were also examined (entries 18-21). Among them, *i*-Pr₂NEt still exhibited the best performance. (Cy₃P)₂CoBr₂ as cobalt catalyst provided a low yield of 31% (entry 22). Noteworthy, the over-reduction of alkenes could be completely inhibited by selecting correct catalytic system and this phenomenon should be attributed to the rapid β hydride elimination after insertion of alkene into Co-H hydride.^[16a,29] Moreover, the control experiments demonstrated that photocatalyst, Co, ligand, and visible-light irradiation were essential for the effective occurrence of the reaction (entries 23-26). Finally, a simple and easily manipulated approach

Table 1. Optimization of the reaction conditions.^[a]

Ph-	Ph	blue LEDs PS (1 mol%) CoBr ₂ (5 mol%), I reductant (3.0 equipation of the solvent, ambient	₋igand (1: uiv), addit : temper a	5 mol%) ive (5.0 equiv) iture, 14 h	Ph Pl 2a	h ⁺ Ph 3;	Ph H H Ph + Ph H H a 4a	
entry	^[a] photos	ensitizer (PS)	ligand	reductant	additive	solven	2a : 3a : 4a	
1	Ir[dF(CF3)p	py]2(dtbbpy)PF6	Cy ₃ P	<i>i</i> -Pr ₂ NEt	-	t CH ₃ CN	34% : 20% : 0%	
2	Ir[dF(CF3)p	py] ₂ (dtbbpy)PF ₆	<i>n</i> −Bu ₃ P	<i>i</i> -Pr ₂ NEt	-	CH ₃ CN	54% : 27% : 0%	
3	Ir[dF(CF3)p	py] ₂ (dtbbpy)PF ₆	Ph ₃ P	<i>i</i> -Pr ₂ NEt	-	CH ₃ CN	no reaction	
4	Ir[dF(CF3)p	py] ₂ (dtbbpy)PF ₆	dppp	<i>i</i> -Pr ₂ NEt	-	CH₃CN	no reaction	-
5	Ir[dF(CF3)p	py] ₂ (dtbbpy)PF ₆	dtbbpy	<i>i</i> -Pr ₂ NEt	-	CH ₃ CN	50% : 28% : 0%	C
6	Ir[dF(CF3)p	py] ₂ (dtbbpy)PF ₆	<i>n</i> −Bu ₃ P	<i>i</i> -Pr ₂ NEt	H ₂ O	CH ₃ CN	41% : 29% : 0%	
7	Ir[dF(CF3)p	py] ₂ (dtbbpy)PF ₆	<i>n</i> −Bu ₃ P	<i>i</i> -Pr ₂ NEt	MeOH	CH ₃ CN	46% : 31% : 0%	
8	Ir[dF(CF3)p	py] ₂ (dtbbpy)PF ₆	<i>n</i> −Bu ₃ P	<i>i</i> -Pr ₂ NEt	AcOH	CH ₃ CN	76% : 21% : 3%	
9	Ir[ppy] ₂ (dtbbpy)PF ₆		<i>n</i> -Bu₃P	<i>i</i> -Pr ₂ NEt	AcOH	CH3CN	71% : 22% : 6%	d,
10	lr[ppy] ₂ (bpy)PF ₆		<i>n</i> −Bu ₃ P	<i>i</i> -Pr ₂ NEt	AcOH	CH ₃ CN	70% : 21% : 9%	
11	lr[ppy] ₃		<i>n</i> −Bu ₃ P	<i>i</i> -Pr ₂ NEt	AcOH	CH ₃ CN	no reaction	(
12	Ir[dF(CF3)ppy]2(dtbbpy)PF6		<i>n</i> −Bu ₃ P	<i>i</i> -Pr ₂ NEt	AcOH	CH_2CI_2	no reaction	
13	Ir[dF(CF3)ppy]2(dtbbpy)PF6		<i>n</i> −Bu ₃ P	<i>i</i> -Pr ₂ NEt	AcOH	DMF	63% : 19% : 0%	
14	Ir[dF(CF ₃)ppy] ₂ (dtbbpy)PF ₆		<i>n</i> −Bu ₃ P	<i>i</i> -Pr ₂ NEt	AcOH	DMSO	71% : 24% : 0%	L
15	Ir[dF(CF3)ppy]2(dtbbpy)PF6		<i>n</i> -Bu₃P	<i>i</i> -Pr ₂ NEt	AcOH	acetone	74% : 21% : 0%	
16	Ir[dF(CF3)p	py] ₂ (dtbbpy)PF ₆	<i>n</i> −Bu ₃ P	<i>i</i> -Pr ₂ NEt	AcOH	THF	75% : 22% : 0%	
17	Ir[dF(CF3)p	py] ₂ (dtbbpy)PF ₆	<i>n</i> −Bu ₃ P	<i>i</i> -Pr ₂ NEt	AcOH	dioxane	78% : 22% : 0%	
18	Ir[dF(CF3)p	py] ₂ (dtbbpy)PF ₆	<i>n</i> -Bu₃P	Et ₃ N	AcOH	dioxane	22% : 7% : 0%	ſ
19	Ir[dF(CF3)p	py] ₂ (dtbbpy)PF ₆	<i>n</i> −Bu ₃ P	TEOA	AcOH	dioxane	no reaction	
20	Ir[dF(CF3)p	py] ₂ (dtbbpy)PF ₆	<i>n</i> −Bu ₃ P	Hantzsch ester	AcOH	dioxane	56% : 25% : 0%	
21	Ir[dF(CF3)p	py] ₂ (dtbbpy)PF ₆	<i>n</i> −Bu ₃ P	PhSiH ₃	AcOH	dioxane	no reaction	
22 ^[b]	Ir[dF(CF3)p	py] ₂ (dtbbpy)PF ₆	-	<i>i</i> -Pr ₂ NEt	AcOH	dioxane	24%:7%:0%	
23		-	<i>n</i> −Bu ₃ P	<i>i</i> -Pr ₂ NEt	AcOH	dioxane	no reaction	
24	lr[dF(CF ₃)p	py] ₂ (dtbbpy)PF ₆	-	<i>i</i> -Pr ₂ NEt	AcOH	dioxane	no reaction	
25 ^[c]	Ir[dF(CF3)p	ppy] ₂ (dtbbpy)PF ₆	<i>n</i> −Bu ₃ P	<i>i</i> -Pr ₂ NEt	AcOH	dioxane	no reaction	
26 ^[d]	Ir[dF(CF3))p	py] ₂ (dtbbpy)PF ₆	<i>n</i> −Bu ₃ P	<i>i</i> -Pr ₂ NEt	AcOH	dioxane	no reaction	

Reaction conditions: ^[a] **1a** (0.2 mmol), PS (1 mol%), CoBr₂ (5 mol%), ligand (15 mol%), reductant (3.0 equiv.), additive (5.0 equiv.), solvent (2.0 mL), irradiation with blue LEDs for 14 h. After irradiation, the reaction mixture was filtered using a small pad of silica gel and ¹H NMR yield was reported using Cl₂CHCHCl₂ as an internal standard. ^[b] the Co catalyst is (Cy₃P)₂CoBr₂. ^[c] no CoBr₂. ^[d] in dark. involving the following reaction conditions: 1 mol% $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$, 5 mol% CoBr₂, 15 mol% *n*-Bu₃P, 3.0 equiv. *i*-Pr₂Net, and 5.0 equiv. AcOH in 1,4-dioxane solvent under blue LEDs irradiation for 14 h, was successfully established.

In order to test the generality of the photoredox/Co catalytic system, various internal alkynes were investigated (Table 2). Notably, diaryl alkynes either electron-donating bearing or electronwithdrawing groups on the phenyl ring (1a-11), reacted smoothly under the standard conditions and provided the desired products in excellent yields with moderate to good Z/E ratios (86-99% yield; 63/37-80/20 Z/E). Importantly, reducible functional groups such as halogen, cyano, and ester, survived under the standard conditions. Significantly, substrate containing thiophenyl (1m), which is believed to be a difficult substrate for hydrogenation due to its coordinating ability to metal centers, also exhibited excellent yields with acceptable chemo-selectivity (89%, 55/45 Z/E). The aryl-alkyl alkyne featuring a hydroxyl group **1n** was also found to be compatible with the reaction and afforded the alkenes in 97% yield with 72/28 Z/E selectivity. Strikingly, 6dodecyne 10, an example of typical dialkyl alkynes, exhibited an excellent yield of 95% with > 95/5 Z/E selectivity when dtbbpy was introduced as ligand and

Table 2. Substrate scope of internal alkynes.^[a]



Reaction conditions: ^[a] **1** (0.2 mmol), Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (1 mol.%), *n*-Bu₃P (15 mol.%), CoBr₂ (5 mol.%), *i*-Pr₂NEt (3.0 equiv.), AcOH (5.0 equiv.), dioxane (2.0 mL), irradiation with blue LEDs for 14 h, isolated yield was reported, Z/E ratio was determined by crude ¹H NMR. ^[b] dtbbpy as ligand, reaction time = 36 h. ^[c] acetone as solvent. ^[d] THF as solvent.

acetone as solvent with prolonged reaction time. Propargyl ether derivative **1p** could also react well to provide the corresponding Z-selective product in 72% yield.

Moreover, this reaction system was also extended to terminal alkynes (Table 3). Substituted aromatic terminal alkynes, such as **1q** and **1r**, smoothly underwent semihydrogenation and afforded the corresponding alkenes in 60% and 52% yield, respectively. Remarkably, this protocol also worked well on the complex bioactive steroids substrates such as ethisterone **1s** and ethinylestradiol **1t**, affording the desired products quantitatively.

Table 3. Substrate scope of terminal alkynes.^[a]



Reaction conditions: ^[a] **1** (0.2 mmol), Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (1 mol%), CoBr₂ (5 mol.%), *n*-Bu₃P (15 mol%), *i*-Pr₂NEt (3.0 equiv.), AcOH (5.0 equiv.), dioxane (2.0 mL), irradiation with blue LEDs for 14 h, isolated yield was reported. ^[b] reaction time = 7 h.

In order to obtain more information about the Z/E selectivity, several control experiments were further conducted (Scheme 2). Scheme 2 Eq. 1 illustrates that when (E)-stilbene **3a** was employed as the substrate under standard conditions, a large proportion of (E)stilbene 3a was isomerized to (Z)-stilbene 2a in a ratio of 78/22. Similar result was also observed in the absence of Co catalyst (Scheme 2, Eq. 2). Besides, when only $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ was present in the reaction system, (E)-stilbene **3a** could be partially isomerized to (Z)-stilbene 2a in a ratio of 62/38(Scheme 2, Eq. 3). Noteworthy, almost none of isomerization occurred in the absence of photosensitizer. (Scheme 2, Eq. 4). Moreover, when these experiments were conducted using (Z)-stilbene **2a** as the substrate, similar results of (Z)-major selectivity was obtained (Scheme S1). These investigations revealed the following conclusions: i) the Z/E selectivity was mainly determined by photosensitizer instead of Co catalyst; ii) *i*-Pr₂NEt and AcOH additives played an important role in deciding the Z/E selectivity;^[27a] and iii) the selectivity is in fact an equilibrium which is largely shifted to the Z-isomers. From above mentioned observation and literature reports,^[27] we believed that the triplet-



Scheme 2. Photoinduced alkenes isomerization.

triplet EnT process is responsible for the Z-major selectivity. Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ possesses a higher triplet energy ($E_T = 2.64 \text{ eV}$)^[26] than (Z)-stilbene **2a** ($E_T = 2.5 \text{ eV}$)^[30] and (E)-stilbene **3a** ($E_T = 2.2 \text{ eV}$)^[30], thus both (Z)- and (E)-stilbene could be excited to their triplet states, leading to the production of both isomers. Moreover, the corresponding (E)-isomer **2a** can more easily accept energy from the photosensitizer due to lower triplet states, and reversible isomerization shift to (Z)-major selectivity could occur. Thus, visible-light catalysis not only initiates the reaction, but also plays a crucial role in deciding the selectivity.

Further, for the comprehensive understanding of the reaction mechanism, the reaction was performed in the presence of the following three radical scavengers: 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO); 2,6-di-tert-butyl-4-methylphenol (BHT); and 9,10-dihydroanthracene (DHA) (Scheme 3, Eq. 1). When TEMPO was added to the solution, the yield of the reaction dropped to 20%; however, when BHT and DHA were added to the solution, respectively, the yields of the reaction were not affected. Considering that TEMPO may not solely act as a radical scavenger and may inhibit the reaction through another avenue,^[31] these experiments further demonstrated that free radical was not involved in the



Scheme 3. Control experiments.

reaction pathway.

In order to understand the role of AcOH, deuterium labeling experiment was conducted using AcOD as the external proton source. According to the crude ¹H NMR analysis, 38% of deuterium and 62% of hydrogen were contained in the corresponding alkenes, indicating that AcOH provides partial hydrogen to the alkynes (Scheme 3, Eq. 2, for details see SI). When the reaction was conducted without AcOH, the products were obtained in 60% yield, thus confirming the dual role of *i*-Pr₂NEt as electron donor and hydrogen donor for the catalytic transfer hydrogenation (Scheme 3, Eq. 3). Moreover, when the reaction was performed in dioxane-d⁸, D-labeled products were not obtained, thus excluding the possibilities of solvent acting as the hydrogen source (Scheme 3, Eq. 4).

Next, the luminescent quenching experiments were performed (Figure 1). 1a and CoBr₂ showed only slight quenching phenomena; however, *i*-Pr₂NEt displayed the most obvious quenching phenomenon, indicating that *i*-Pr₂NEt underwent an effective SET with excited ^{*}Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆. This result definitely supported the hypothesized mechanism depicted in Scheme 1. Moreover, $CoBr_2(n-Bu_3P)_2$ showed a slightly lower quenching rate with *i*-Pr₂NEt toward the excited photosensitizer *IrIII, which indicated the involvement of another plausible mechanism for the reaction (see Scheme S3). In this path, the excited photosensitizer $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ ($E^{IV/*III} = -0.89$ V vs. path, SCE^[26] is oxidatively quenched by $(n-Bu_3P)_2CoBr_2$ $(E^{CoII/CoI} = -0.89 \text{ V vs SCE}, \text{ see SI})$ via a SET to form the Ir^{VI} and Co^I species. The Ir^{IV} ($\dot{E}^{IV/III} = +1.69$ V vs SCE)^[26] subsequently abstracts an electron from *i*-Pr₂NEt ($E^{i-Pr_2NEt} = +0.78$ V vs SCE, see SI) to give *i*-Pr₂NEt radical cation and regenerate Ir^{III} to close the catalytic cycle. Then, Co^I follows the similar process as depicted in Scheme 1 to afford the final products.



Figure 1. Emission-quenching plots.

In summary, we successfully demonstrated the efficiency of photoredox/cobalt dual catalytic system in transfer semihydrogenation reaction of alkynes. This transformation occurred smoothly under blue LED irradiation at ambient temperature and tolerated both internal and external alkynes as well as various functional groups. *i*-Pr₂NEt and AcOH were proved to be the hydrogen source for the transfer hydrogenation. The advantages of the established protocol may inspire more extensive research on hydrogenation of alkynes.

Experimental Section

General procedure for the semihydrogenation of alkynes.

To a Schlenk tube containing a stirring bar was added $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6(0.002 mmol, 1 mol%), CoBr_2 (0.01 mmol, 5 mol%), alkynes$ **1**(0.20 mmol, 1.0 equiv.). Then*n*-Bu₃P (0.03 mmol, 15 mol%),*i*-Pr₂NEt (0.6 mmol, 3.0 equiv), AcOH (1.0 mmol, 5.0 equiv.), and 2.0 mL anhydrous 1,4-dioxane were added to the reaction tube via syringe under Ar atmosphere. The reaction mixture was stirred for 14 h under Blue LED irradiation at ambient temperature (the temperature range from 38 °C to 42 °C). Finally, the solvent was removed in vacuum and the residue was purified by column chromatography on silica gel to afford the desired products.

Acknowledgements

We acknowledge the National Natural Science Foundation of China (No. 21676131 and No. 21462019), the Science Foundation of Jiangxi Province (20143ACB20012), Jiangxi Science & Technology Normal University (2018BSQD024, Doctor Startup Fund) for financial support.

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