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ARTICLE

## Successive Cu/Pd Transmetalation Relay Catalysis in Stereoselective Synthesis of Tetraarylethenes

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Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

A new and efficient strategy for the synthesis of tetraaryl-substituted olefins has been developed. With a Cu/Pd-catalyzed isomerization/insertion/oxidative coupling cascade reaction of cyclopropene with internal alkyne, a wide variety of *cis*-tetrasubstituted olefins were synthesized in good yields as single stereoisomers. The photophysical properties of these novel tetraarylethenes were fully characterized and proved to be good AIE (aggregation-induced emission) luminogens. Experimental studies and theoretical calculation indicated that Cu(I) and Pd(II) were the actual catalysts. A novel deprotonative Cu-catalyzed cyclopropene cycloisomerization and subsequent successive Cu/Pd transmetalation relay mechanism was proposed for the discovered reaction.

### Introduction

Multimetallic cooperative catalysis has recently been developed to achieve exquisite one-pot cascade reactions, which require multiple reaction steps with the traditional one-catalyst one-reaction approach.<sup>1</sup> This multi-catalyst cascade concept, represents one of the most efficient synthetic methodologies in terms of environmental benignness, atom-economy and also step-economy. More importantly, with the synergistic cooperation of different catalytic species, potentially unprecedented transformations with single metal catalyst could be achieved. However, it is still a challenge for the rational design of multimetallic catalysts to achieve programmed activation of the reactants toward the expected products, rather than the undesired side reactions.<sup>2</sup> Recently we utilized transmetalation as a key strategy to bridge two catalytic cycles and developed an efficient copper-palladium transmetalation relay catalysis for the synthesis of tetrasubstituted furan derivatives from cyclopropenes.<sup>3</sup> Cyclopropene went through copper catalyzed cycloisomerization forming furanyl copper intermediate **M**<sub>1</sub>, and subsequent transmetalation to palladium generating the key furanyl palladium intermediate **M**<sub>2</sub>, which underwent Heck, carbonylation, or dimerization reaction

generating the tetrasubstituted furan and bifuran derivatives. In this Tandem Metal Relay Catalysis (TMRC) strategy, two different metals, i.e. copper and palladium, allow the activation and further functionalization of cyclopropenes in one pot. Herein, we present our recent efforts on the stereoselective synthesis of tetraarylethenes with an unprecedented successive double Cu/Pd relay catalysis.

Tetrasubstituted olefins are privileged scaffold presented in biological important drugs such as Tamoxifen or Vioxx, and natural products such as Nileprost analogues.<sup>4</sup> The congested nature of the tetrasubstituted double bond make tetrasubstituted olefins very useful molecules applied in material research such as molecular motors and liquid crystals.<sup>5</sup> More importantly, tetraarylethene showed an unusual photophysical phenomenon of aggregation-induced emission (AIE) that is non-emissive or low-emissive in solution, but induced to emit efficiently by aggregate formation in the solid state.<sup>6,7</sup> However most organic chromophores are highly emissive in solution but weakly luminescent in the solid state due to the ubiquitous aggregation-caused quenching (ACQ) effect.<sup>8</sup> Because organic light-emitting materials are often used in solid state, for example, as thin films in the fabrication of organic light-emitting diodes (OLEDs), the development of AIE active functional materials is very important. Recently the tetraphenylethene (TPE) type molecules have been widely applied in fluorescence sensors for ion and pH, fluorescent light-up bioprobes for analytical sensing and optical imaging, and multistimuli-responsive nanomaterials.<sup>9</sup>

The regio- and stereoselective synthesis of tetraarylethenes is still one of the most challenging subjects in organic synthesis (Scheme 1).<sup>10</sup> For the construction of double bonds, Wittig olefination and olefin metathesis remain the most important and

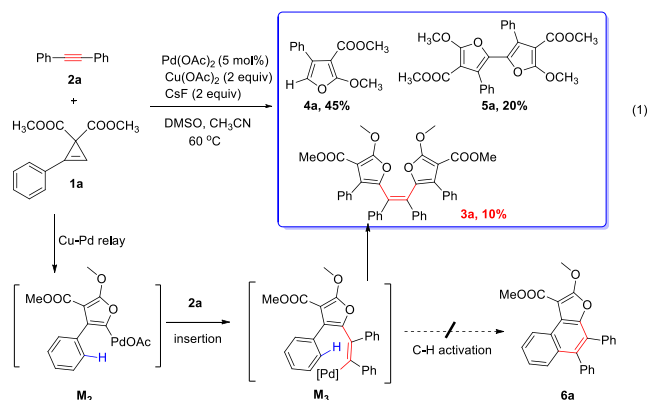
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† Electronic Supplementary Information (ESI) available: Detailed experimental procedures and analytical data. See DOI: 10.1039/x0xx00000x

general approaches. However, it is very difficult to apply these methods in the construction of steric hindered tetraarylethene. McMurry reaction,<sup>11</sup> in which two aromatic ketones are coupled to alkenes in the presence of titanium chloride and reducing reagent, were utilized by Tang and others as a major approach for the synthesis of tetraarylethenes as the AIE luminogens. Under this condition, mixtures of E/Z isomers are generally obtained. The regio- and stereoselectivity problem became the most challenging problems for the synthesis of tetraarylethene because of the similarity of different aromatic substituents. In 2003, Larock reported a palladium-catalyzed three-component cross-coupling reaction of an aryl iodide, an internal alkyne, and an arylboronic acid for the efficient synthesis of tetraarylethene.<sup>12</sup> Itami and Yoshida took use of vinyl 2-pyrimidyl sulfide as a key template, sequentially installed four different aromatics onto the double bond through two Heck reactions and another two palladium-catalyzed cross-coupling reactions.<sup>13</sup> These two methods demonstrated the brilliant applications of transition-metal catalyzed cross-coupling reactions between aromatic iodides and organometallic reagents.<sup>14</sup> In this article, we report the synthesis of tetraarylethenes with an unprecedented Cu/Pd-catalyzed isomerization/insertion/oxidative coupling cascade reaction of cyclopropene and internal alkyne. The obtained tetraarylethenes embedded with two *cis*-furan rings represent a new type of AIE luminogens. The X-ray crystal structures, optical properties and structure-function relationships of these tetraarylethenes were also discussed. After detailed theoretical calculations and experimental mechanism study, an unprecedented successive double Cu/Pd transmetalation relay reaction mechanism was uncovered.



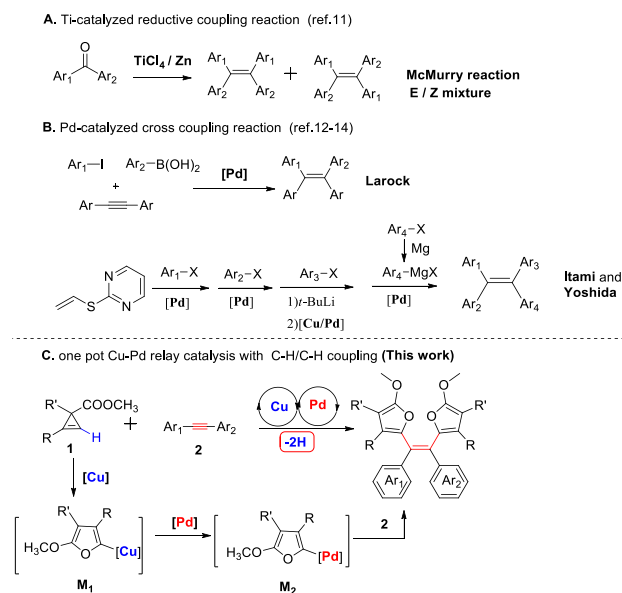
Scheme 2. Initial observation of the formation of tetraarylethene.

## Results and discussion

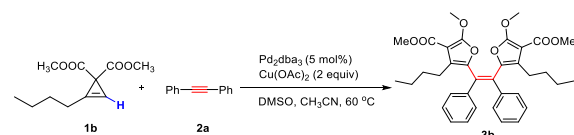
### Initial studies and reaction optimization

We began our study with the reaction of cyclopropene<sup>15</sup> **1a** with diphenylacetylene **2a** in the presence of copper and palladium catalysts (Scheme 2). It was anticipated that the furanyl palladium **M<sub>2</sub>** was formed through Cu/Pd relay process, followed by the insertion to the triple bond and intramolecular C-H activation to form the tricyclic aromatics **6a**. However, in the complicated reaction mixture, two major byproducts, trisubstituted furan **4a** and bifuran **5a** were isolated in 45% and 20% yield respectively. Moreover, another new compound was isolated in less than 10% yield. To our great surprise, it is not the expected tricyclic product **6a**, but the tetraarylethene **3a** with two *cis* tetrasubstituted furan rings. This unexpected result prompted us to develop a general synthetic method to the challenging tetraarylethene. The alkyl substituted cyclopropene **1b** was also amenable to this reaction (Table 1), and the isolated yellow solid tetraarylethene **3b** showed a very bright color under irradiation of 365 nm.

Then we started to optimize the reaction conditions (Table 1, For details, see SI). We noticed that the base is crucial for this transformation. No desired product was observed without base (entry 1). A detailed screening of different bases found that Cs<sub>2</sub>CO<sub>3</sub> was the best choice (entries 2-5). Removal of the DMSO additive or running the reaction in DMSO solvent both decreased the yield (entries 6,7). Then different palladium catalysts, ligands were examined. When different phosphine or amino acid were introduced as the ligand, the yield of **3b** all decreased (entries 8-10). The best conditions found consisted of performing the reaction in the presence of 5 mol% Pd<sub>2</sub>(dba)<sub>3</sub> and one equivalent of Cs<sub>2</sub>CO<sub>3</sub> at 60 °C. Under these conditions the target product **3b** was isolated in 72% yield when slightly excess amount of cyclopropene **1b** was used (entry 14). Very importantly, only the *cis*-isomer was observed in this reaction. Only trisubstituted furan was formed in the presence of copper without palladium catalyst (entry 15). No product was formed with only palladium catalyst (entry 16).



Scheme 1. Synthesis of tetraarylethene.

**Table 1** Optimization of reaction conditions<sup>a</sup>

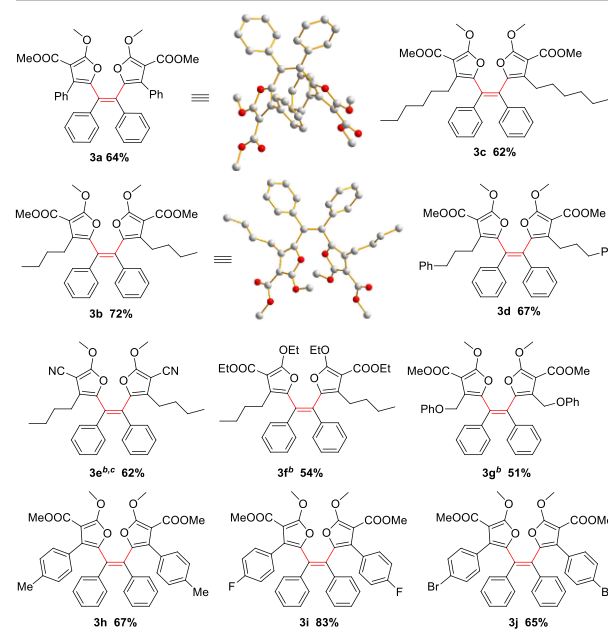
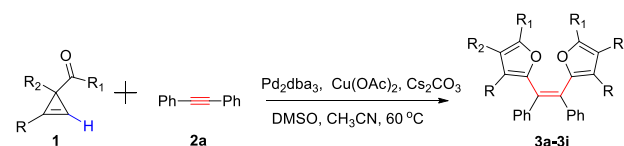
Entry	Catalyst	Ligand	Base	Yield/% <sup>b</sup>
1	Pd(OAc) <sub>2</sub>		/	< 5
2	Pd(OAc) <sub>2</sub>		CsF	20
3	Pd(OAc) <sub>2</sub>		KF	8
4	Pd(OAc) <sub>2</sub>		Cs <sub>2</sub> CO <sub>3</sub>	55
5	Pd(OAc) <sub>2</sub>		Et <sub>3</sub> N	10
6 <sup>c</sup>	Pd(OAc) <sub>2</sub>		Cs <sub>2</sub> CO <sub>3</sub>	8
7 <sup>d</sup>	Pd(OAc) <sub>2</sub>		Cs <sub>2</sub> CO <sub>3</sub>	20
8	Pd(OAc) <sub>2</sub>	DPEphos	Cs <sub>2</sub> CO <sub>3</sub>	28
9	Pd(OAc) <sub>2</sub>	PCy <sub>3</sub>	Cs <sub>2</sub> CO <sub>3</sub>	20
10	Pd(OAc) <sub>2</sub>	Boc-Pro	Cs <sub>2</sub> CO <sub>3</sub>	22
11	PdCl <sub>2</sub>		Cs <sub>2</sub> CO <sub>3</sub>	12
12	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>		Cs <sub>2</sub> CO <sub>3</sub>	37
13	Pd <sub>2</sub> (dba) <sub>3</sub>		Cs <sub>2</sub> CO <sub>3</sub>	42
14 <sup>e</sup>	Pd <sub>2</sub> (dba) <sub>3</sub>		Cs <sub>2</sub> CO <sub>3</sub>	72
15	/		Cs <sub>2</sub> CO <sub>3</sub>	0
16 <sup>f</sup>	Pd <sub>2</sub> (dba) <sub>3</sub>		Cs <sub>2</sub> CO <sub>3</sub>	0

<sup>a</sup> Reaction conditions: Cyclopropene **1b** (0.2 mmol), Diphenylacetylene **2a** (0.1 mmol), catalyst (5 % mol), oxidant (0.2 mmol), base (0.1 mmol), DMSO (0.6 mmol), CH<sub>3</sub>CN (1 mL), 60 °C. <sup>b</sup> Isolated yield. <sup>c</sup> Without DMSO. <sup>d</sup> DMSO (1 mL) as the solvent. <sup>e</sup> Cyclopropene **1b** (0.25 mmol). <sup>f</sup> Without Cu(OAc)<sub>2</sub>. DPEphos = Bis(2-diphenylphosphinophenyl)ether; Boc-Pro = N-(tert-Butoxycarbonyl)-L-proline

### Substrate Scope

With the optimized reaction conditions established, the scope of various cyclopropenes was firstly investigated (Table 2). Both aliphatic cyclopropenes and aromatic cyclopropenes generated the corresponding *cis* products in good yields (**3a-3j**). The structure of **3a** and **3b** were confirmed by the X-ray crystallography.<sup>16</sup> Different ester groups, other electron-withdrawing group such as CN, phenol group on the alkyl chain, were well tolerated in this reaction (**3e-3g**). Cyclopropenes with different substituents on the phenyl ring such as Br, F and methyl were also amenable to this transformation, giving corresponding products in 68-83% yields (**3h-3j**).

Then we investigated the scope of various disubstituted acetylenes (Table 3). Not only symmetric diaryl alkynes, but also asymmetric alkynes are all suitable for this transformation, and a large variety of different tetraarylethenes were prepared in moderate to good yields. A series of functional groups such as F, Br, CH<sub>3</sub>, OCH<sub>3</sub>, CF<sub>3</sub>, CN, were all tolerated under this reaction condition, thus allowing further functionalization if need be (**3k-3s**). Electro-deficient internal alkyne with an ester, ketone, or amide group also reacted efficiently to furnish the *cis* tetrasubstituted alkenes as the single isomer in moderate yields (**3t-3w**). The structure of **3w** was also confirmed by single crystal X-ray analysis. To our delight, 1,4-diphenylbuta-1,3-diyne also reacted smoothly to give the corresponding *cis* tetrasubstituted olefin with an alkyne substituent in respectable

**Table 2.** Scope of Cyclopropenes<sup>a</sup>

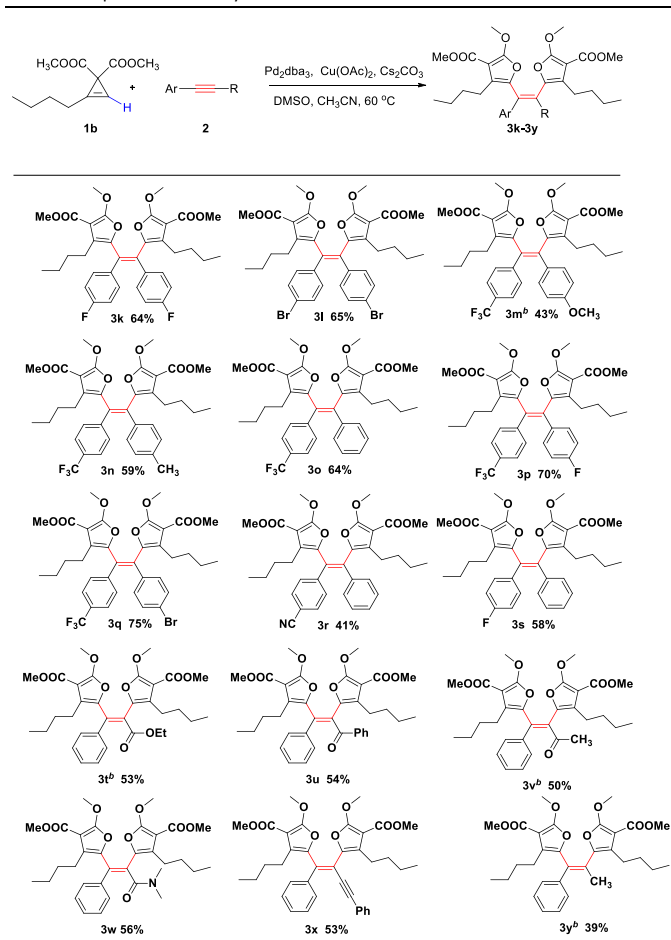
<sup>a</sup> Reaction conditions: Cyclopropene **1a-1j** (0.25 mmol), Diphenylacetylene **2a** (0.1 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (5 % mol), Cu(OAc)<sub>2</sub> (0.2 mmol), Cs<sub>2</sub>CO<sub>3</sub> (0.1 mmol), DMSO (0.6 mmol), CH<sub>3</sub>CN (1 mL), 60 °C. <sup>b</sup> Pd<sub>2</sub>(dba)<sub>3</sub> (10 % mol).

53% yield (**3x**). The internal alkyne with one alkyl group is more challenging for this reaction, and the produced *cis* tetrasubstituted olefin was isolated in 39% with 10 mol% catalyst loading (**3y**). Thus this new reaction displayed high functional group tolerance and proved to be a general method for the synthesis of tetraarylethene derivatives.

### Photophysical property study

Organic molecules bearing heteroaryls are making significant contributions in organic materials. The unprecedented *cis*-difuryl tetrasubstituted alkenes prompted us to investigate their photophysical properties. As indicated in Table 4, they all display an absorption at 369-390 nm in THF solution, which are greatly red shifted compared with TPE at 299 nm<sup>17</sup> (For absorption and fluorescence spectra, see SI). In the fluorescence spectra, they exhibited cyan to green emission at 492-510 nm with very low quantum yields (0.47-0.77%). The most interestingly compounds are the alkyl substituted products (**3b**, **3o**, **3w**). The fluorescence quantum yields (Φ<sub>F</sub>) of these compounds in the aggregation state are 9.69%, 3.00%, 5.07%, respectively, which are much higher than those in solution. In contrast, compound **3a** synthesized from the phenyl substituted cyclopropene **1a**, showed a very weak emission in solution, and almost no emission in solid state. These differences could be explained by their crystal structures and packing mode of



**Table 3.** Scope of Internal Alkynes<sup>a</sup>

<sup>a</sup> Reaction conditions: Cyclopropene **1b** (0.25 mmol), alkyne (0.1 mmol),  $\text{Pd}_2(\text{dba})_3$  (5 mol),  $\text{Cu}(\text{OAc})_2$  (0.2 mmol),  $\text{Cs}_2\text{CO}_3$  (0.1 mmol),  $\text{DMSO}$  (0.6 mmol),  $\text{CH}_3\text{CN}$  (1 mL),  $60^\circ\text{C}$ .  
<sup>b</sup>  $\text{Pd}_2(\text{dba})_3$  (10 mol).

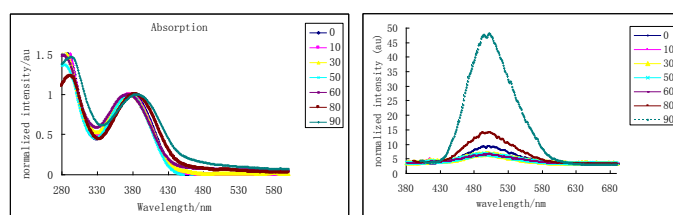
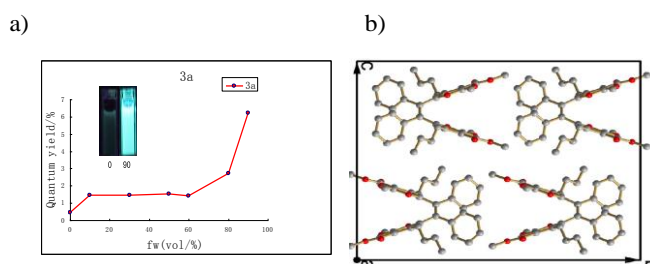
compounds **3a**, **3b**, and **3w**. For compound **3b** and **3w**, the butyl group serves an important handle to inhibit the possible intramolecular  $\pi$ - $\pi$  interactions. At the same time, the intermolecular  $\text{CH}\cdots\text{O}$  interaction makes the whole molecular pack into a relative rigid structure. For example, compound **3b** takes a very interesting head-to-tail packing mode (Fig. 2b). For compound **3a**, there is an obvious intramolecular  $\pi$ - $\pi$  stacking between the phenyl group on one furan ring and the other furan ring. The distance between them is only 3.74 Å. This intramolecular interaction may attribute to their non-emission in solid state.

To further study if these compounds are really AIE active, we chose THF/ $\text{H}_2\text{O}$  system to examine their photophysical properties, since these compounds are very soluble in THF, but completely insoluble in water. With increased fraction of water, the absorption of **3b** in THF was almost the same (Fig. 1),

**Table 4.** Optophysics Data of the Tetraarylethenes

Compound	$\lambda_{\text{abs}}/\text{nm}^a$	$\lambda_{\text{em}}/\text{nm}^b$ (in THF)	$\lambda_{\text{em}}/\text{nm}^b$ (solid)	$\Phi_{\text{F}}$ (in THF) <sup>c</sup>	$\Phi_{\text{F, solid}}^d$
<b>3a</b>	390	492	/	/	/
<b>3b</b>	379	500	501	0.47	9.69
<b>3o</b>	369	510	521	0.53	3.00
<b>3w</b>	390	495	514	0.77	5.07

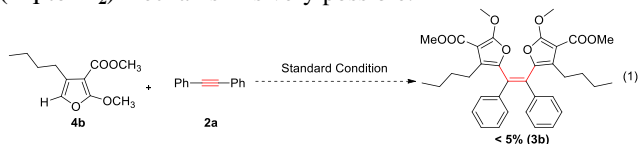
<sup>a</sup>Only the longest absorption maxima are shown. <sup>b</sup>Excited at the longest absorption maxima. <sup>c</sup>Calculated using fluorescein as standard. <sup>d</sup>Absolute quantum yield determined by a calibrated integrating sphere system.

**Fig. 1** Absorption (left) and fluorescence (right) spectra of **3b** in THF/water with different fraction of water (fw %).**Fig. 2** a) Variations of fluorescence quantum yields of **3b** with water fractions in THF/water mixtures. b) Head to tail packing of **3b** in solid state.

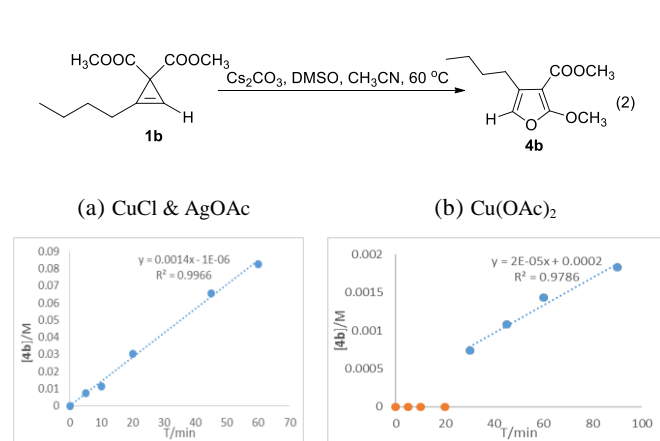
but the fluorescence of **3b** strengthened gradually. When the water fraction increased to 90%, the quantum yield increased by 45 times relative to its pure THF solution (Fig. 2a). These compounds represent a new type of AIE luminogens and could be potentially utilized as optoelectronic materials.

### Mechanism Discussion

Then we started to explore the reaction mechanism. Trisubstituted furan **4b** could not react with **2a** to form the product under standard condition, indicating furan is not the reaction intermediate (eqn (1)). Thus a stepwise reaction is not likely and furanyl copper to furanyl palladium transmetalation ( $\text{M}_1$  to  $\text{M}_2$ ) mechanism is very possible.



The first step of this transformation is the copper catalyzed cycloisomerization to form furanyl copper intermediate  $\text{M}_1$ . Importantly, we noticed that the reaction rate of Cu(I) catalyzed cyclopropene isomerization was much faster than that of

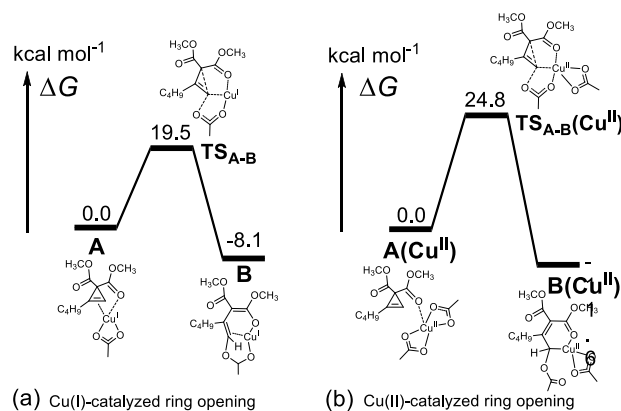


**Fig. 3** Kinetic study of Cu(I) and Cu(II) catalyzed cycloisomerization of cyclopropene.

Cu(II).<sup>18</sup> Then we carried the kinetic study of the first step reaction (Figure 3). The in situ formed CuOAc catalyzed the isomerization reaction efficiently and completed in less than 1 hour, but the reaction catalyzed by Cu(OAc)<sub>2</sub> was much slower and there is an obvious induction period of about 30 minutes. These data indicated that Cu(I) might be the actual catalyst and Cu(II) could be reduced to Cu(I) to catalyze this reaction by base, Pd(0), or even solvents.<sup>19,2c</sup>

Since only Pd(0) and Cu(II) were used in this reaction and Pd(II) is required in the transmetalation step, the redox reaction between Pd(0) and Cu(II) possibly led to Pd(II) and Cu(I) simultaneously. Then we investigated the redox reaction of Cu(II) and Pd(0) in the presence or absence of Cs<sub>2</sub>CO<sub>3</sub> by X-Ray photoelectron spectroscopy (for details, see SI). Pd<sub>2</sub>dba<sub>3</sub> and Cu(OAc)<sub>2</sub> were reacted under N<sub>2</sub> atmosphere at 60 °C for 30 min, after removal of the solvent, the obtained black solid were subjected to the XPS analysis. From the copper spectra, binding energy of Cu2p<sub>3/2</sub> was 932.0 eV and Cu2p<sub>1/2</sub> was 954.1 eV, which were the typical binding energy for Cu(I) species.<sup>20</sup> At the same time, Pd(II) species were observed with the binding energy of 338.4 eV (Pd3d<sub>5/2</sub>) and 343.6 eV (Pd3d<sub>3/2</sub>). In addition, in the reaction without a base, palladium black was also observed (336.4 eV for Pd3d<sub>5/2</sub> and 341.8 eV for Pd3d<sub>3/2</sub>),<sup>20b</sup> but no palladium black formation was observed in the reaction with Cs<sub>2</sub>CO<sub>3</sub>. These results also highlighted the importance of the base in the standard reactions.

The above mechanistic experiments imply that Cu(II) is not likely to be the actual catalyst in cyclopropene cycloisomerization, and it needs to be transformed to the actual catalyst, most likely Cu(I), before reaction occur. To investigate the origin of this advantage of Cu(I) over Cu(II) in cyclopropene cycloisomerization at the molecular level, we further directly compared the reactivity of Cu(I) and Cu(II) employing computational density functional theory (DFT) modelings. The first step of cyclopropene cycloisomerization is the cyclopropene ring opening by breaking the corresponding C-C bond. As shown in Fig. 4, we discovered that Cu(I) catalyst CuOAc is kinetically more reactive in cyclopropene ring opening than Cu(II) catalyst



**Fig. 4** Comparison between DFT calculations of (a) Cu(I)-catalyzed cyclopropene ring opening and (b) Cu(II)-catalyzed cyclopropene ring opening.

Cu(OAc)<sub>2</sub>, by having a substantially lower ring opening barrier by 5.3 kcal mol<sup>-1</sup> from Cu(I)-cyclopropene reactant complex **A** to ring-opened Cu(I) enolate **B** through transition state **TSA-B**. Thus the experimental implication of actual Cu(I) catalyst is supported by the DFT modeling. Inspecting the transition states and products of ring opening processes as shown in Fig. 5, which constitute the lowest energy reaction profiles for both Cu(I) and Cu(II) systems resulting from our extensive reaction pathway search,<sup>21</sup> it is notable that during the C-C cleavage, the acetate ligand of Cu catalyst migrates from Cu to C2 position. This mechanistic feature of cyclopropene ring opening is consistent with the very recent computational study by Xia et al. on mechanism of cyclopropene cycloisomerization to produce trisubstituted furan catalyzed by CuI catalyst.<sup>22</sup> However, as shown below, the subsequent mechanism after ring opening to generate furanyl copper intermediate **M**<sub>1</sub> in this work is completely different from that of producing trisubstituted furan found before.<sup>22</sup>

From DFT theoretical modeling, the detailed reaction pathway to generate furanyl copper intermediate **M**<sub>1</sub> from cyclopropene-Cu(I) complex **A** is depicted in Fig. 6. After cyclopropene ring opening occurs to form intermediate **B**, we discovered that the added carbonate base took part in the reaction by abstracting the proton from the C2 position of **B** via transition state **TSB-C** merely with a reaction barrier of 16.1 kcal mol<sup>-1</sup>. Thus, one important deprotonative role played by the carbonate base (Cs<sub>2</sub>CO<sub>3</sub>), which is the key additive in the reaction, is discovered from our DFT calculations. Without this pivotal deprotonation process, as in the case of CuI catalyzed cyclopropene cycloisomerization found by Xia et al.,<sup>22</sup> furan rather than furanyl copper intermediate **M**<sub>1</sub> is found to be generated directly from intermediate **B**, through a very high-lying transition state (23.6 kcal mol<sup>-1</sup> higher than **TSB-C**) of O-attack at C2 position. Recalling that furan has been ruled out experimentally to act as an intermediate in the reactions (eqn (1)), deprotonation of **B** is crucial for the formation of furanyl copper intermediate **M**<sub>1</sub>. After this deprotonation by added base, alkenyl copper intermediate **C** is generated and subsequent cyclization by O-attack of C2 position to form **M**<sub>1</sub> can be accomplished through a second-order saddle point **TS(2)**<sub>C-M</sub>.<sup>23</sup>

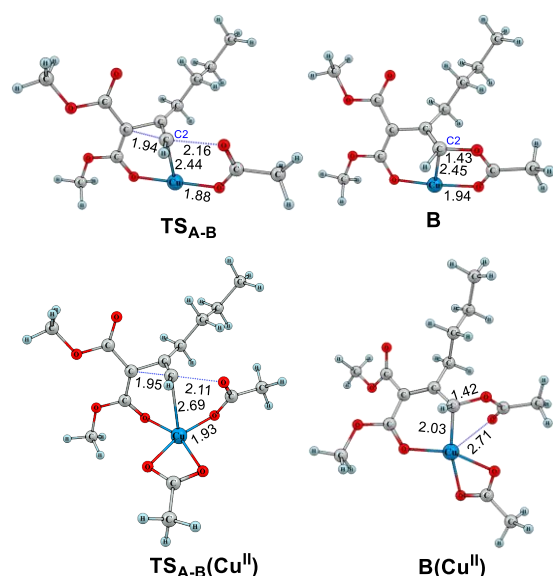


Fig. 5. DFT optimized structures of transition state and intermediate in cyclopropene ring opening mechanism shown in Fig. 4 for Cu(I) and Cu(II) catalytic systems.

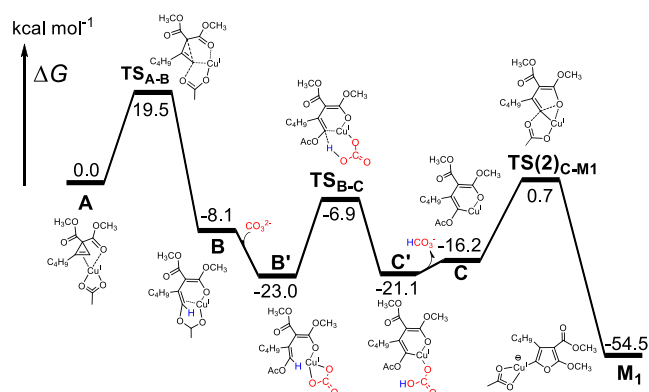


Fig. 6. DFT calculated reaction profile from cyclopropene-Cu(I) complex A to key furanyl copper intermediate  $M_1$

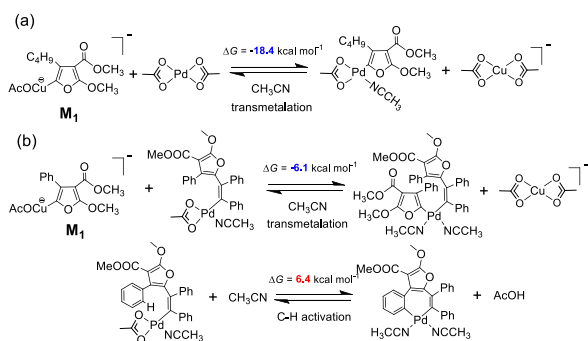


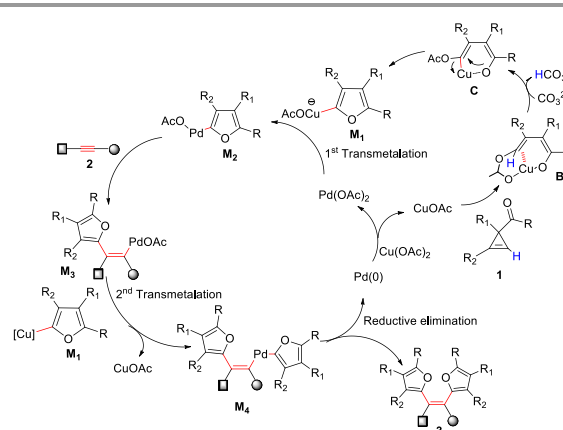
Fig. 7. DFT calculated free energy driving forces of (a) first transmetalation, and (b) second transmetalation in comparison of C-H activation.

on potential energy surface by overcoming a barrier of 16.9 kcal mol<sup>-1</sup>. Generally, the relatively low calculated reaction barriers below 20 kcal mol<sup>-1</sup> in this reaction mechanism of  $M_1$  formation shown in Fig. 6 is consistent with the experimentally observed fast reaction rate at mild reaction condition (60 °C).

After furanyl copper intermediate  $M_1$  is produced, transmetalations are possible. To explore whether

transmetalations are thermodynamically feasible, we calculated thermodynamic free energy driving forces of first and second transmetalations. The results of which are depicted in Fig. 7. We can see that the first and second transmetalations from Cu site of  $M_1$  to Pd catalytic center are all thermodynamically feasible processes, with the former transmetalation bearing relatively larger thermodynamic driving force. Importantly, as shown in Fig. 7b, compared with alternative aromatic C-H activation, the second transmetalation is more favorable thermodynamically. This explains well why C-H activation was not observed in our experiments (Scheme 2).

Based on these results and our previous reactions, a plausible Cu/Pd relay catalyzed cross-coupling reaction was proposed in Scheme 3. Cu(OAc)<sub>2</sub> reacted with Pd<sub>2</sub>dba<sub>3</sub> to form Pd(II), while itself was reduced to CuOAc. Cyclopropene reacted with CuOAc through the ring opening reaction to get the ring-opened Cu(I) enolate intermediate **B**. With the help of base (stronger and more beneficial CO<sub>3</sub><sup>2-</sup>, or weaker AcO<sup>-</sup>) in the reaction system, deprotonation process occurs to generate alkenyl copper intermediate **C**. Subsequent cyclization by O-attack generates the furanyl copper intermediate  $M_1$ . It was transmetalated to Pd(II) catalyst, generating key furanyl palladium  $M_2$ , which went through *cis* alkyne insertion to form the alkenyl palladium  $M_3$ , followed by second Cu/Pd transmetalation with  $M_1$  and the subsequent reductive elimination to afford the final products **3** and Pd(0). Finally a redox reaction between Pd(0) and Cu(II) would lead to both Pd(II) catalyst regeneration and more Cu(I) catalyst, all participating into next catalytic cycle. Importantly, the cyclopropene cycloisomerization mechanism revealed in this work is characterized by deprotonation after cyclopropene ring opening, and was found optimal for generation of furanyl copper intermediate  $M_1$ , while differently the mechanism without deprotonation as recently proposed by Xia et al. is suitable for producing trisubstituted furan, but can not cope with the generation of furanyl copper intermediate  $M_1$  necessitated in this study as well as in our previous work.<sup>3</sup>



Scheme 3. Proposed mechanism of tetraarylethenes production involving Cu/Pd transmetalation relay catalysis based on experiments and theoretical modeling results.



## Conclusions

In summary, a new Cu/Pd-catalyzed reaction between cyclopropene and internal alkyne has been successfully developed. Different from many other transition-metal catalyzed C-H activation reactions, this oxidative insertion coupling reaction proceeded under very mild conditions. Based on experimental and computational studies, Cu(I) and Pd(II) were identified as the actual catalysts, and a novel deprotonative Cu-catalyzed cyclopropene cycloisomerization mechanism was proposed for the discovered reaction. The subsequent thermodynamically favored Cu/Pd transmetalations afford the carbon-palladium bond, which is the major reason for the mildness of the reaction. The successive double transmetalation relay is the most important feature of this reaction. A wide variety of tetrasubstituted alkenes, especially tetraarylethenes with two *cis* tetrasubstituted furans, were prepared conveniently, efficiently, and stereoselectively by this one-pot cascade reaction. The photophysical properties of these novel tetraarylethenes were fully characterized and these tetraarylethenes proved to be good AIE luminogens. This new type of tetraarylethenes will potentially have more applications as the AIE active materials, and we believe this synthetic method should serve as a new powerful tool for the synthesis of highly functionalized tetrasubstituted alkenes.

## Acknowledgements

We are grateful for the fundamental research and subject construction funds of Shandong University (No 2014JC008, 104.205.2.5) and National Natural Science Foundation of China (Nos. 21290194, 21221002 and 21473215). We thank Prof. Dr. Di Sun for the analysis of X-ray structure.

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