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Reductive C-C Coupling by Desulfurizing Gold-Catalyzed Photoreactions

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ABSTRACT: [Au$_2$(μ-dppm)$_2$]Cl$_2$-mediated photocatalysis reactions are usually initiated by UVA light, herein, an unreported system which using blue LEDs as excitation light source was found. The red shift of the absorption wavelength originates from the combination of [Au$_2$(μ-dppm)$_2$]Cl$_2$ and ligand (Ph$_3$P or mercaptan). Based on this finding, a gold-catalyzed reductive desulfurizing C-C coupling of electrophilic radicals and styrenes mediated by blue-LEDs is presented, a coupling which cannot be efficiently accessed by previously reported methods. This mild and highly efficient C-C bond formation strategy uses mercaptans both as electron-deficient alkyl radical precursor as well as the hydrogen source. Two examples of amino acids have also been modified by using this strategy. Moreover, this methodology could be applied in polymer synthesis. Gram scale synthesis and mechanistic insights into this transformation are also presented. **KEYWORDS:** *photoreaction, gold catalysis, radical C-C coupling, desulfurization, blue LEDs*

Photochemistry has become one of the most dynamic and powerful manifolds in today's synthetic chemistry as it offers the opportunity to induce radical chemistry under extremely mild conditions.[1-7] During the last years, our group has dedicated considerable effort to develop novel methodologies relying on light-driven processes.[8-16] Based on our's[8,9] and other group's studies,[5,17] the binuclear bis(diphosphine) complex [Au$_2$(μ-dppm)$_2$]Cl$_2$ (dppm = bis(diphenylphosphino)-methane) has gradually proven to be very useful in photocatalysis. However, the requirement of UVA light as the light source (Scheme 1, 1a) inherently prevents its application, especially for selectivity studies and the invention of new reactions. Interestingly, the combination of [Au$_2$(μ-dppm)$_2$]Cl$_2$ with a ligand (Ph$_3$P or mercaptan) provides a bathochromic shift on UV-vis absorptions (see SI), this means a novel species is generated. Subsequently, after irradiation with blue LEDs, if oxygen is not excluded, Ph$_3$P is oxidized by O$_2$, or under an atmosphere of dinitrogen, by 4-iodoanisole in the presence of substochiometric amount of [Au$_2$(μ-dppm)$_2$]Cl$_2$ (Scheme 1, 2a and SI). In addition, disulfide and desulfurization products are produced by irradiating the mixture of [Au$_2$(μ-dppm)$_2$]Cl$_2$ and mercaptans (stoichiometric experiment, see SI), hypothetically forming a thiyl radical by going through ligand to metal charge transfer (S→Au) process.[18-21] These new findings inspired us that the combination of Ph$_3$P or mercaptan with [Au$_2$(μ-dppm)$_2$]Cl$_2$ would not only form a new species which can absorb blue light but also offer the possibility for a use in photocatalysis. Based on our new findings and previous studies on mercaptans,[22] we envisaged that mercaptans could act as the precursor of alkyl radical and hydrogen donating group which would possibly further react with alkenes to form a C-C bond. The strategy of combining desulfurization and C-C coupling has only been reported once before,[23] by forming thioimidoyl radicals through re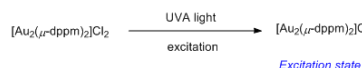acting *t*BuNC with thiols and AIBN as radical initiator. However, that report shows only 12 examples, and a large excess of alkenes has to be used (aliphatic olefins, 10.0 eqs) at 80 °C.

Traditionally, alkyl radicals are generated by reduction alkyl halides, the radical initiator or hydrogen atom donor required for a subsequent C-C coupling is toxic (organotin compounds),[24] potentially explosive (AIBN and peroxides), or pyrophoric (trialkylboranes).[25] With the rapid development of metal-based photocatalysts in the last decade,[1-7] a large number of reactions involving alkyl radical have been reported.[26-33] However, reductive electron-deficient alkyl radical addition with styrenes is rare, probably, because stable benzyl radical which has been formed by radical addition on styrene is readily oxidized to a benzyl cation, followed by a β-H elimination to form styrene products, or nucleophilic trapping by methanol or halogen anions. Although in some cases, the reductive addition can proceed by introducing an excess of a hydrogen donating reagent, such NEt$_3$, DIPEA, NMP, Hantzsch ester or formic acid, the reaction is still limited to aliphatic alkenes. One distinct example was reported by Qing's group,[34] under the same reaction conditions, for aliphatic alkenes, reductive radical addition products were produced. However, only alkenyl products were formed for reaction with styrenes. The only strategy by using phosphorus ylide as the precursor of an (alkoxycarbonyl)methyl radical species[35] has been reported recently. This reaction is a distinct pre-functionalization strategy which needs several equivalent of substrates and additives, only low yields are obtained (43%) and the substrate scope is limited to ester substituents. Furthermore, our attempts to utilize common α-bromo esters to react with styrene by following reported photocatalysis methodologies (Scheme 1, 1b) all failed to yield the desired product. Given that, we now provide a novel and convenient methodology using mercaptans as both electron-deficient alkyl radical precursor and hydrogen source, catalyzed by a dimeric
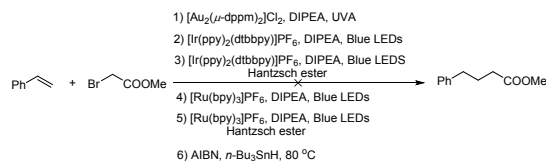
gold complex to achieve a reductive radical addition with styrenes under blue LEDs light (Scheme 1, 2b).

1) Previous studies

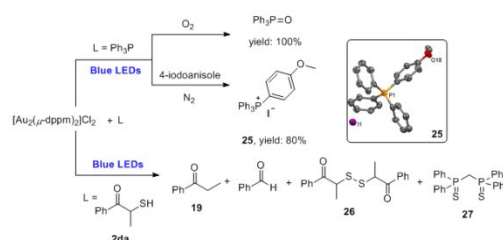 a) Traditional way for activating photocatalyst $[Au_2(\mu\text{-dppm})_2]Cl_2$

$$[Au_2(\mu\text{-dppm})_2]Cl_2 \xrightarrow[\text{excitation}]{\text{UVA light}} [Au_2(\mu\text{-dppm})_2]Cl_2^*$$

Excitation state

  b) Attempts to react methyl bromoacetate with styrene

Ph + Br—COOMe →
1) $[Au_2(\mu\text{-dppm})_2]Cl_2$, DIPEA, UVA
2) $[Ir(ppy)_2(dtbbpy)]PF_6$, DIPEA, Blue LEDs
3) $[Ir(ppy)_2(dtbbpy)]PF_6$, DIPEA, Blue LEDS Hantzsch ester
4) $[Ru(bpy)_3]PF_6$, DIPEA, Blue LEDs
5) $[Ru(bpy)_3]PF_6$, DIPEA, Blue LEDs Hantzsch ester
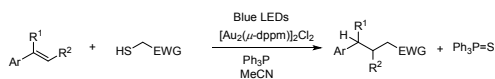6) AIBN, n-Bu$_3$SnH, 80 °C
→ Ph—COOMe

2) Our new concepts

  a) Shift the light source from traditional UVA light to Blue LEDs

  b) Reductive C-C coupling by desulfurizing gold-catalyzed photoreactions

Scheme 1. Previous studies and our new concepts

In our initial experiments indeed C-C coupling method could be achieved in 92% isolated yield by using styrene and methyl thioglycolate as coupling partners, Ph_3P as the phosphorous source, in the presence of $[Au_2(\mu\text{-dppm})_2]Cl_2$, MeCN by exposure to blue LED lights (Table 1, entry 1). Control experiments indicated that none or only traces of desulfurizing C-C coupling product **3aa** were produced in the absence of either phosphorous source, blue led or photocatalyst (entry 2-7). Without light (entry 3, 5, 7), no C-C coupling product was formed after heating at 55 °C for 24 h, which excludes the possibility of a thermal reaction (e.g. warming by light). The use of other photosensitizers of $[Ir(ppy)_2(dtbbpy)]PF_6$, $[Ru(bpy)_3](PF_6)_2$, Eosin Y, or Mes-Acr-Me$^+$BF$_4^-$ instead of the $[Au_2(\mu\text{-dppm})_2]Cl_2$ resulted in lower yields or no desired product (entry 8-11). Furthermore, decreased yields were obtained with other phosphine sources (entry 12).
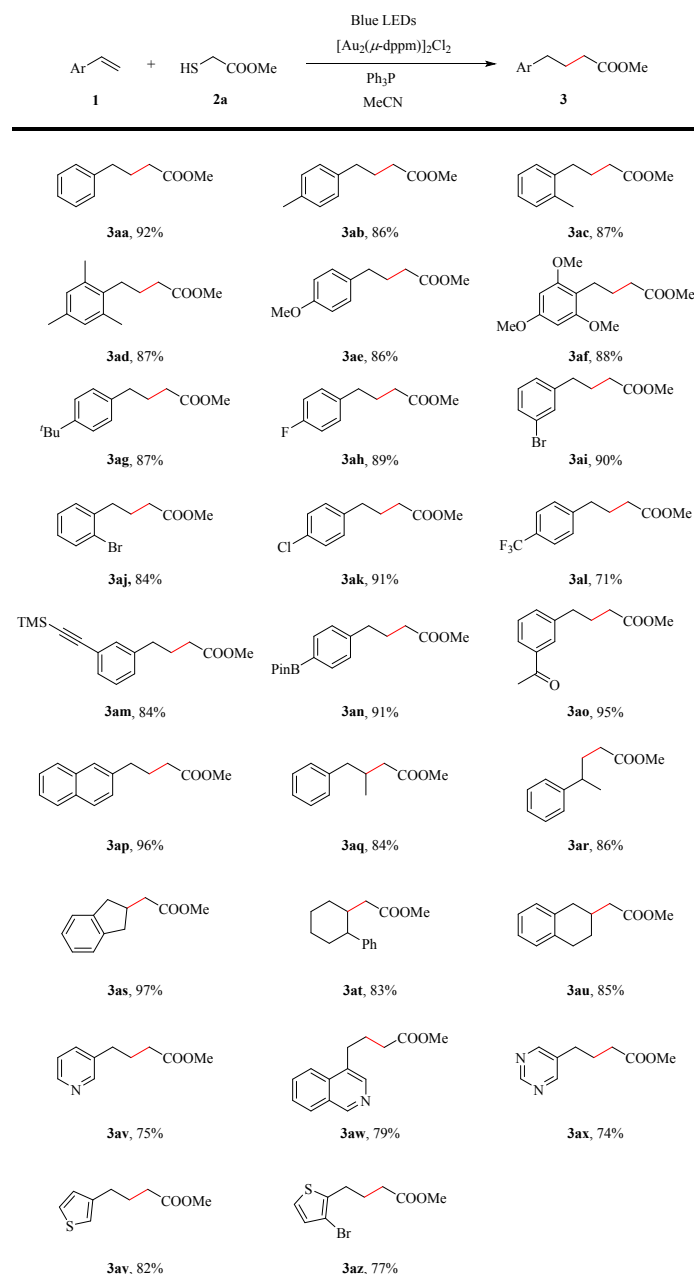
Table 1. Initial Studies and control experiments[a]

Ph (1a) + HS—COOMe (2a) →[Photocatalyst, Phosphine, MeCN, Blue LED] Ph—COOMe (3aa)

Entry	1a	2a	Phosphine	Blue LED	Photocatalyst	3aa[b]
1	+	+	Ph₃P	+	$[Au_2(\mu\text{-dppm})_2]Cl_2$	92%
2	+	+	-	+	$[Au_2(\mu\text{-dppm})_2]Cl_2$	trace
3	+	+	Ph₃P	-	$[Au_2(\mu\text{-dppm})_2]Cl_2$	- (-)*
4	+	+	Ph₃P	+	-	trace
5	+	+	Ph₃P	-	-	- (-)*
6	+	+	-	+	-	-
7	+	+	-	-	$[Au_2(\mu\text{-dppm})_2]Cl_2$	- (-)*
8	+	+	Ph₃P	+	$[Ir(ppy)_2(dtbbpy)]PF_6$	64%
9	+	+	Ph₃P	+	$[Ru(bpy)_3](PF_6)_2$	3%
10	+	+	Ph₃P	+	Eosin Y	20%
11	+	+	Ph₃P	+	Mes-Acr-Me⁺BF₄⁻	-
12	+	+	dppm	+	$[Au_2(\mu\text{-dppm})_2]Cl_2$	82%

[a]Reactions were run with 1.0 mL of the mixture of styrene (1.0 eq) and mercaptan (1.2 eqs) in MeCN (0.2 M), photocatalyst (2.5 mol %), phosphorous (1.3 eqs) for 24 h. [b]Yield determined by ¹H NMR analysis using 1,3,5-trimethoxybenzene as the internal standard. *Heating at 55 °C if no reaction without light.

With optimized conditions in hand, we next determined the generality of the styrene components in this desulfurizing C-C coupling reaction. As shown in Table 2, electron-rich styrenes containing one or several alkyl or methoxy groups performed well (**3ab-3ag**, 86-88% yield). A diverse array of electron-withdrawing substituents (halogens, trifluoromethyl, boronic esters and ketones) in the o-, m- or p-position of the styrene derivatives (**3ah-3al**, **3am-3ao**) gave the corresponding desulfurized C-C coupling products in 71-95% yield. The TMS-protected alkynyl styrene and 2-vinylnaphthalene substrates were also coupled with high efficiency (**3am** and **3ap**, 84% and 96% yield). Multi-substituted and cyclic styrene derivatives also readily underwent this C-C coupling (**3aq-3au**, 83-97% yield). Even heteroaromatic coupling partners, which are notoriously problematic for many photoredox coupling technologies, performed well under these reaction conditions (**3av-3az**, 74-82% yield).
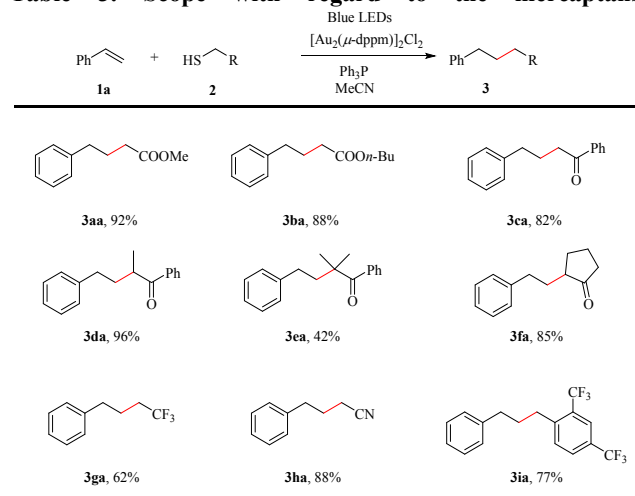
Table 2. Scope with regard to the styrene substrates[a]

Reaction scheme: Ar–CH=CH₂ (1) + HS–CH₂COOMe (2a) → [Blue LEDs, [Au₂(μ-dppm)]₂Cl₂, Ph₃P, MeCN] → Ar–CH₂CH₂–COOMe (3)

3aa, 92% **3ab**, 86% **3ac**, 87%

3ad, 87% **3ae**, 86% **3af**, 88%

3ag, 87% **3ah**, 89% **3ai**, 90%

3aj, 84% **3ak**, 91% **3al**, 71%

3am, 84% **3an**, 91% **3ao**, 95%

3ap, 96% **3aq**, 84% **3ar**, 86%

3as, 97% **3at**, 83% **3au**, 85%

3av, 75% **3aw**, 79% **3ax**, 74%

3ay, 82% **3az**, 77%

[a]Isolated yields. Performed with photocatalyst (2.5 mol%), styrene (1.0 eq), mercaptan (1.2 eqs), Ph₃P (1.3 eqs), in MeCN (0.2 M) for 24-36 h. See Supporting Information.

We next investigated the scope with regard to the mercaptans. As shown in Table 3, α-mercaptyl ketones containing alkyl or phenyl groups, both provided 88% and 82% yield (**3ba** and **3ca**). Moreover, a secondary mercaptan also reacted efficiency under these conditions (**3da**, 96% yield). A tertiary mercaptan was also tolerated, albeit in slightly diminished yield (**3ea**, 42% yield). A cyclic mercaptan was also shown to be a competent substrate (**3fa**, 85% yield). For α-mercaptyl-trifluoroethane and -nitrile can also couple with styrene to obtain the desired product in good yield (**3ga**-**3ha**, 62-88% yield). Trifluoromethyl-substituted benzyl mercaptan generated the desulfurized C-C coupling product in 77% yield (**3ia**).

Table 3. Scope with regard to the mercaptans[a]

Reaction scheme: Ph–CH=CH₂ (1a) + HS–R (2) → [Blue LEDs, [Au₂(μ-dppm)]₂Cl₂, Ph₃P, MeCN] → Ph–CH₂CH₂–R (3)

3aa, 92% **3ba**, 88% **3ca**, 82%

3da, 96% **3ea**, 42% **3fa**, 85%

3ga, 62% **3ha**, 88% **3ia**, 77%

[a]Isolated yields. Performed with photocatalyst (2.5 mol%), styrene (1.0 eq), mercaptan (1.2 eqs), Ph₃P (1.3 eqs), in MeCN (0.2 M) for 24-36 h. See Supporting Information.

With unactivated alkenes the major product is simple desulfuration, with 4-phenylbut-1-ene only 22% of C-C coupling are observed.

Furthermore, this methodology has been successfully applied in the modification of small amino acids fragments (Scheme 2a). Both linear amino acid **4** with free NH group and protected proline substrate **6** has been converted to **5** and **7** in 78% and 83% yield, respectively. This application could provide the possibility of using this novel methodology in the modification of peptides. Our gram scale synthesis also worked very well by extending the reaction time with 0.25 mol% of [Au₂(μ-dppm)₂]Cl₂ (Scheme 2b).

a) Modification of amino acids derivatives

(1)

(2)
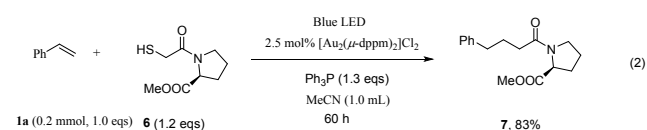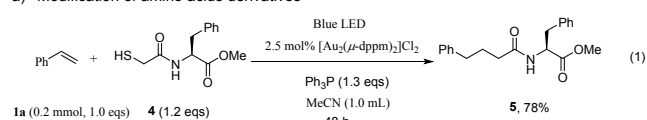
b) Gram scale synthesis
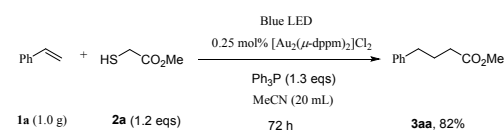
Scheme 2. Modification of amino acids derivatives and gram scale synthesis.

We further demonstrated the application of this desulfurized C-C coupling methodology by the synthesis of polymer **13** (Scheme 3). The attempt to react both monomer **8** and **10** with **2a** and **1a**, respectively, are both working well. Polymer **13** has been successfully synthesized by using this strategy with the number-average weight (Mn) is 6735 g mol⁻¹, and the polydispersity (Đ) is 1.5.

1)

8 (0.2 mmol, 1.0 eq)   **2a**, 2.2 eqs   Blue LEDs 2.5 mol% [Au$_2$(μ-dppm)$_2$]Cl$_2$ Ph$_3$P (2.4 eqs)   MeCN (1.0 mL)   36 h   **9**, 81%

2)

1a (0.2 mmol, 1.0 eq)   **10**, 0.6 eq   Blue LEDs 2.5 mol% [Au$_2$(μ-dppm)$_2$]Cl$_2$ Ph$_3$P (1.4 eqs)   MeCN (1.0 mL)   36 h   **11**, 55%   +   **12**, 38%

3)

8 (0.2 mmol, 1.0 eq)   **10**, 1.0 eq   Blue LEDs 2.5 mol% [Au$_2$(μ-dppm)$_2$]Cl$_2$ Ph$_3$P (2.4 eqs)   MeCN (1.0 mL)   60 h   **13**

M_n = 6.735E+3 g/mol
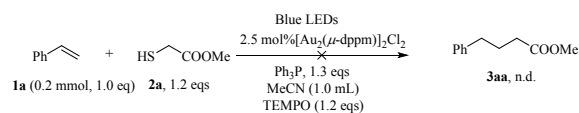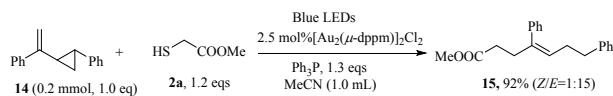D = 1.472E+0
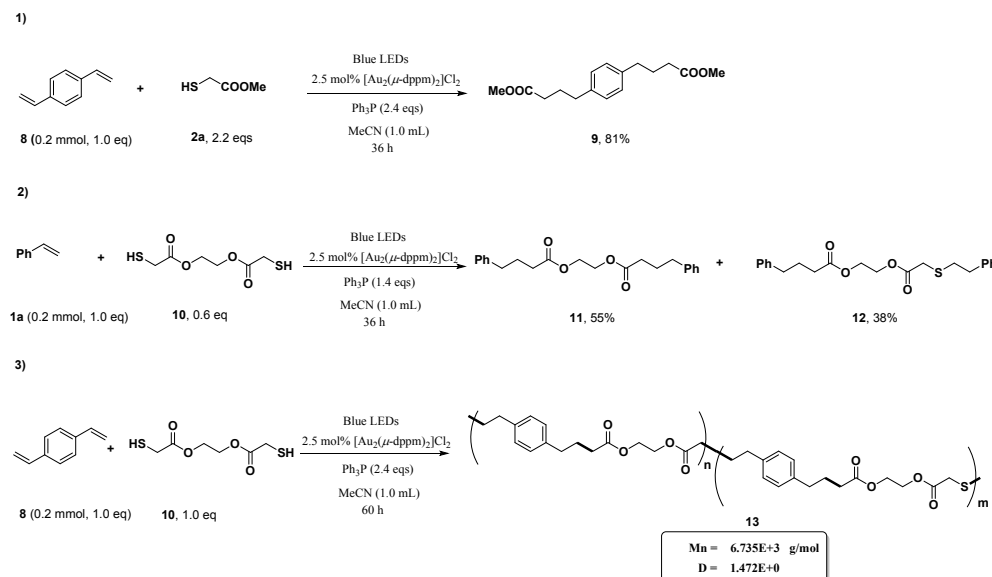
Scheme 3. Application for polymer synthesis.

Concerning the mechanism, an inhibition experiment has been performed by adding TEMPO as radical inhibitor, no desired product was detected (Scheme 4a). Moreover, the reaction of 1-phenyl-2-(1-phenylethenyl)cyclopropane **14** was also examined (Scheme 4b), the desulfurized C-C coupling product **15** was obtained in 92% yield through a ring-opening process of the cyclopropane unit, thus we presumed that a radical process is operative. Deuterium experiments have been performed, which indicated that thiol was not the only hydrogen source (see SI). The hydrogen would also come from the water contained in the solvent without deteriorating the yield of desulfurized C-C coupling which means this reaction can be performed in water solution (see SI). Control experiments showed that thiol addition and the desulfurized products were also detected (Scheme 4c). Quantum yield (Φ = 19.5%) (See SI) has been measured to certify that the photocatalyst is regenerated during the reaction. However radical chain propagation could also be involved in this reaction based on our control experiment that this reaction is also performed well in the condition of AIBN as initiator at 80 °C (see SI). More details of fundamental mechanism studies can be found in our supporting information.
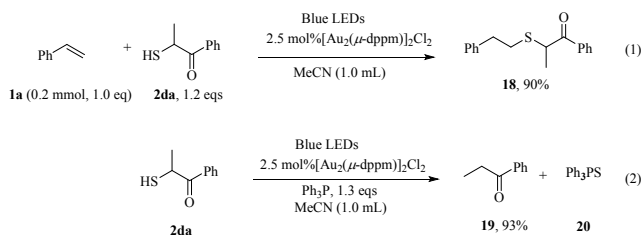
a) Inhibition experiment

1a (0.2 mmol, 1.0 eq)   **2a**, 1.2 eqs   Blue LEDs 2.5 mol%[Au$_2$(μ-dppm)]$_2$Cl$_2$ Ph$_3$P, 1.3 eqs   MeCN (1.0 mL)   TEMPO (1.2 eqs)   **3aa**, n.d.

b) Radical clock reaction

14 (0.2 mmol, 1.0 eq)   **2a**, 1.2 eqs   Blue LEDs 2.5 mol%[Au$_2$(μ-dppm)]$_2$Cl$_2$ Ph$_3$P, 1.3 eqs   MeCN (1.0 mL)   **15**, 92% (Z/E=1:15)

c) Control experiments

1a (0.2 mmol, 1.0 eq)   **2da**, 1.2 eqs   Blue LEDs 2.5 mol%[Au$_2$(μ-dppm)]$_2$Cl$_2$ MeCN (1.0 mL)   **18**, 90%   (1)

2da   Blue LEDs 2.5 mol%[Au$_2$(μ-dppm)]$_2$Cl$_2$ Ph$_3$P, 1.3 eqs   MeCN (1.0 mL)   **19**, 93%   +   Ph$_3$PS   **20**   (2)

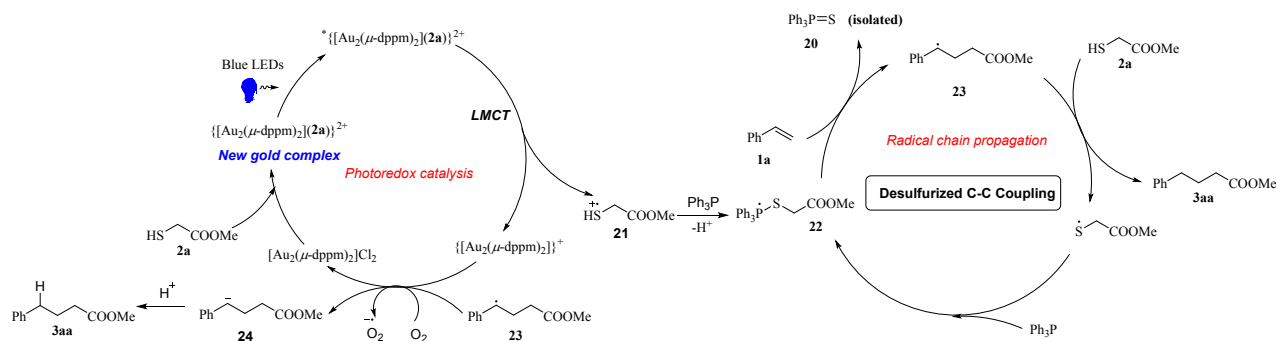**Scheme 4. Mechanistic experiments.**

Figure 1. Proposed mechanism

Based on previous studies[18-22, 42-44] and our experiments, a possible mechanism is shown in Figure 1. This desulfurizing C-C-coupling photoreaction is catalyzed by the combination of [Au$_2$(μ-dppm)$_2$]Cl$_2$ with mercaptan to form a three-

coordinated gold complex[36-39] or the combination of [Au$_2$(μ-dppm)$_2$]Cl$_2$, Ph$_3$P and mercaptan which would act as the photosensitizer. Upon irradiation with Blue LEDs, intermediate **21** is formed by going through the process of

LMCT,[20,40] this radical cation further reacts with Ph_3P and generates a phosphoranyl radical **22**, which by going through a β-scission and radical addition to styrene, provides an alkyl radical **23**. The alkyl radical further abstracts a hydrogen atom from the thiol (S-H BDE = 87.2 Kcal/mol),[41] generating the desulfurized C-C coupling product **3aa** and a thiol radical. The reduced gold catalyst would be converted to the original $[Au_2(\mu\text{-dppm})_2]^{2+}$ species either by reducing radical **23** to the anion **24** or by being oxidized by a trace amount of O_2

In conclusion, the combination of $[Au2(\mu\text{-dppm})2]Cl2$ with ligand ($Ph3P$ or mercaptan) exhibited the possibility for new reaction inventions under blue LEDs lights. Moreover a highly efficient C-C coupling by a desulfurizing gold-catalyzed radical reaction has been explored under blue LEDs using inexpensive, air-stable $Ph3P$ as the phosphorous source. This method can be a crucial foundation for studying C-C coupling by desulfurizing under mild and water-soluble reaction environment in both organic synthetic chemistry, bioorganic chemistry and also shows new options for polymer synthesis

ASSOCIATED CONTENT

Accession Code
CCDC 1907518 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures/.

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Notes
The authors declare no competing financial interest.

Supporting Information.
The supporting information is available free of charge via the Internet at http://pubs.acs.org.
Experimental procedures and compound characterization (PDF)

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Blue LEDs

[Au$_2$(μ-dppm)]$_2$Cl$_2$

Ph$_3$P

MeCN

40 examples
42-97% yields