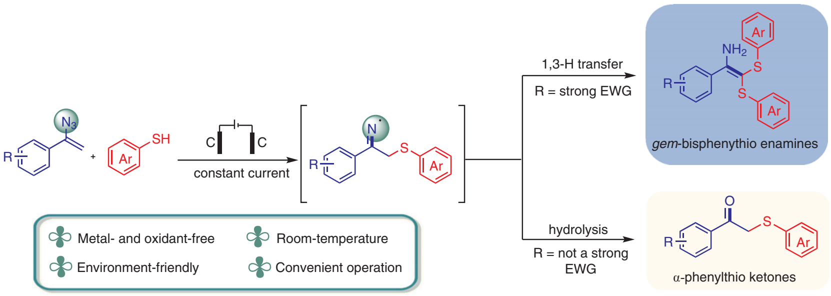
# Electrocatalytic Synthesis of *gem*-Bisarylthio Enamines and α-Phenylthio Ketones via a Radical Process under Mild Conditions

**Yong-Zhou Pan**
**Shi-Yan Cheng**
**Qian-Yu Li**
**Hai-Tao Tang**
**Ying-Ming Pan**
**Xiu-Jin Meng***
**Zu-Yu Mo***

State Key Laboratory for Chemistry and Molecular Engineering of Medicinal Resources, School of Chemistry and Pharmaceutical Sciences, Guangxi Normal University, Guilin 541004, P. R. of China
18877380547@163.com
mengxiujin@163.com

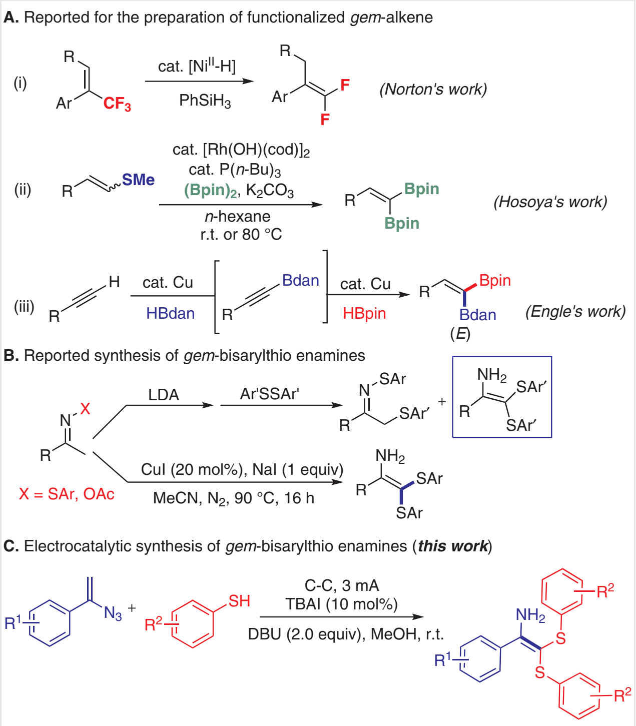


Received: 16.10.2020
Accepted after revision: 11.12.2020
Published online: 11.12.2020
DOI: 10.1055/a-1335-7902; Art ID: st-2020-r0554-l

**Abstract** The novel method for the synthesis of *gem*-bisarylthio enamines and α-phenylthio ketones was developed via the coupling of α-substituted vinyl azides with thiols in the presence of tetrabutylammonium iodide (TBAI) as a redox catalyst and electrolyte at room temperature. Electronic properties were crucial in the generated products. This protocol features metal- and oxidant-free materials, broad tolerance of substrates, and mild reaction conditions.

**Key words** electrocatalytic, vinyl azides, thiophenols, *gem*-bisarylthio enamines, metal-free

A multisubstituted alkene is an important structural motif frequently found in functional materials and bioactive compounds. To efficiently prepare multisubstituted alkenes, various stereoselective synthetic methods have been developed. *gem*-Dialkenes are important and useful building blocks for chemo- and regioselective synthesis of multisubstituted alkenes.[1] Therefore, much attention has been paid to the preparation of functionalized *gem*-dialkenes. For example, Norton[2] reported a method for the synthesis of *gem*-difluoroalkenes *via* the nickel hydride catalyzed hydrodefluorination of $CF_3$ alkenes (Scheme 1A, path i). The rhodium-catalyzed desulfanylative *gem*-diborylation of 2-arylvinyl sulfides for the synthesis of (2,2-diborylvinyl)arenes was also reported (Scheme 1A, path ii).[3] In addition, Engle *et al.*[4] recently performed a copper-catalyzed diboration of terminal alkynes for the preparation of *E*-selective 1,1-diborylalkenes(Scheme 1A, path iii). However, the *gem*-bisphenylthio enamine has been reported rarely over the past decades. Up to now, only two reports have discussed the synthesis of this kind of *gem*-bisphenylthio enamine (Scheme 1B). In 1980, Davis *et al.*[5] first disclosed this *gem*-bisphenylthio enamine as a byproduct when they treated sulfenimine with lithium diisopropylamide (LDA). Recently, Zhang et al.[6] reported a copper-catalyzed oxidative cross-coupling of oxime acetates with diaryl disulfides leading to a unique class of *gem*-bisarylthio enamines. However, these methods involved a strong base and multistep reaction, long reaction time, inert atmosphere, and metal catalysts. Therefore, it is still a challenge to develop a mild method to construct *gem*-bisphenylthio enamines α-substituted vinyl azides,[7] a special subclass of vinyl azides that are active and outstanding synthons, which display



**Scheme 1** Reactions of organic azides

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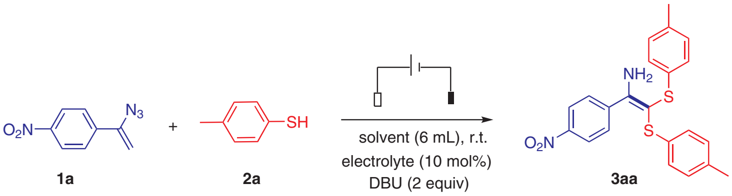
distinct and unique chemical reactivities from other organic azides, such as alkyl azides and aryl azides, and can act as radical acceptors,[8] nucleophile acceptors,[9] electrophile acceptors,[10] 2*H*-azirine, vinylnitrene precursors,[11] enamine-type nucleophiles,[12] and 1,3-dipoles.[13] Generally, α-substituted vinyl azides can be attacked by other radicals to generate imine radical,[8,14] which likely undergo hydrolysis and afford ketones,[15] or 1,3-H transfer and deliver enamines[16] or intramolecular cyclization and furnish N-heterocycles.[17]

Organic electrochemistry, which employs electrons as reagents to achieve redox reactions, is a green and benign tool for generating radicals.[18] In 2019, Xu's group[19] disclosed an efficient strategy for the synthesis of enaminones via an imine radical process which was generated from the addition of a carbonyl radical to vinyl azide under electrochemical conditions. Since the introduction of an electron-withdrawing radical, the imine radical then underwent 1,3-H migration and gave the enamine compounds. In addition, Terent'ev and co-workers[20] also described a similar work. Very recently, our group[21] reported a radical cyclization cascade for the synthesis of sulfide imidazopyridines via an imine radical intermediate under electrochemical conditions. However, employing vinyl azide and mercaptan as raw materials for the synthesis of *gem*-bisphenylthio enamine through the electrochemical conditions has not been reported. We herein describe an efficient electrochemical method of achieving *gem*-bisphenylthio enamine from vinyl azides and thiophenols (Scheme 1C).

In our initial studies, 1-(1-azidovinyl)-4-nitrobenzene (**1a**) and 4-methylbenzenethiol (**2a**) were selected as model substrates to optimize the reaction conditions in an undivided cell equipped with a graphite rod cathode and a platinum anode under the constant current of 3 mA with a mixed solvent of MeCN/MeOH (v/v = 1:1) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a base. The target product 1-(4-nitrophenyl)-2,2-bis(*p*-tolylthio)ethenamine (**3aa**) was obtained in 24% yield (Table 1, entry 1). Subsequently, we investigated the effect of electrolytes, solvents, and electrodes in this reaction (Table 1). When another iodine salt, TBAI, was used as electrolyte, the desired product **3aa** was produced in a much-improved yield of 62% (entry 2). Two noniodized salts were investigated. Only the trace target product **3aa** was detected when $n$-$Bu_4NBF_4$ was used as an electrolyte (entry 3). The desired product **3aa** was generated in 50% yield when $n$-$Bu_4NPF_6$ was employed as an electrolyte (entry 4). After screening the different solvents, namely, MeCN/MeOH, MeOH/$H_2O$ (v/v = 10:1), and MeOH, we found that MeOH was the best choice, yielding 75% (en-

**Table 1** Optimization of Reaction Conditions[a,b]



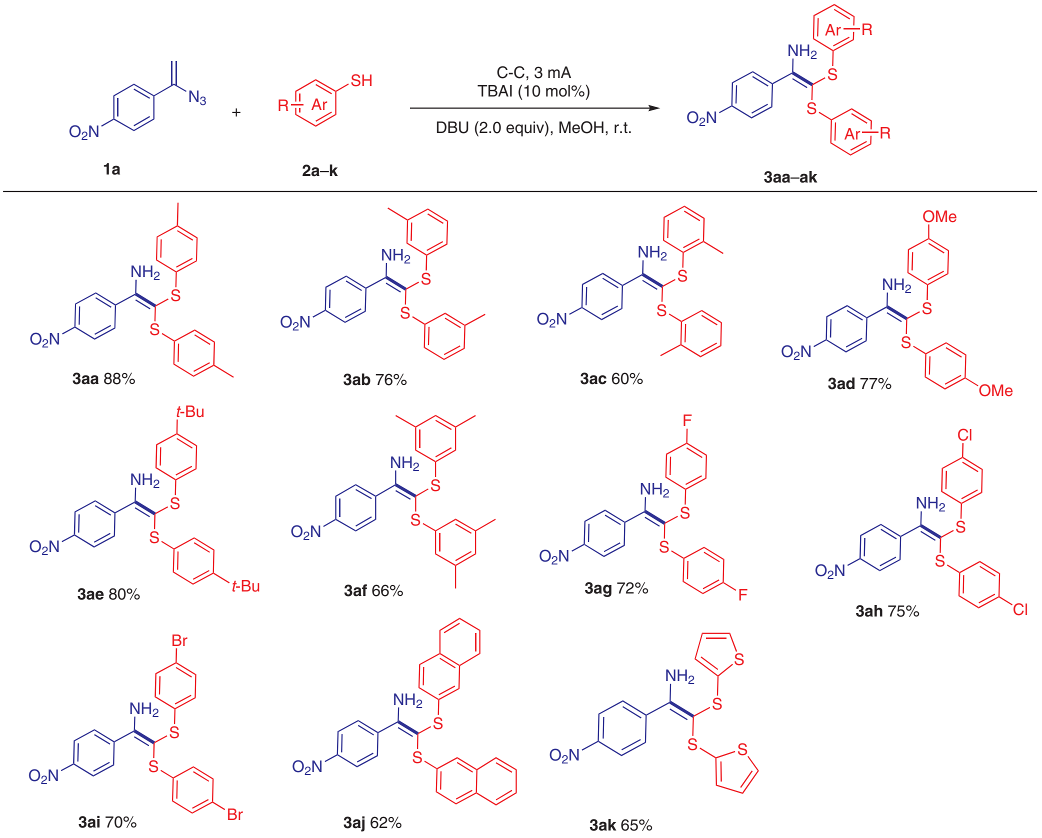
| Entry | Electrolyte | Solvent | Electrode | Yield (%)[b] |
|---|---|---|---|---|
| 1 | $NH_4I$ | MeCN/MeOH[c] | Pt (+)\|C (–) | 24 |
| 2 | TBAI | MeCN/MeOH | Pt (+)\|C (–) | 62 |
| 3 | $n$-$Bu_4NBF_4$ | MeCN/MeOH | Pt (+)\|C (–) | trace |
| 4 | $n$-$Bu_4NPF_6$ | MeCN/MeOH | Pt (+)\|C (–) | 50 |
| 5 | TBAI | MeOH/$H_2O$[d] | Pt (+)\|C (–) | 52 |
| 6 | TBAI | MeOH | Pt (+)\|C (–) | 75 |
| 7 | TBAI | MeOH | Pt (+)\|Pt (–) | 60 |
| 8 | TBAI | MeOH | C (+)\|C (–) | 88 |
| 9[e] | TBAI | MeOH | C (+)\|C (–) | 48 |
| 10[f] | TBAI | MeOH | C (+)\|C (–) | NR |
| 11[g] | TBAI | MeOH | C (+)\|C (–) | 87 |

[a] Reaction conditions: undivided cell with a Pt plate anode (1 cm × 1 cm) and graphite rod cathode, constant current = 3 mA, **1a** (0.3 mmol, 1 equiv), **2a** (0.72 mmol, 2.4 equiv), DBU (0.6 mmol, 2.0 equiv), TBAI (10 mol %), and solvent (6 mL) under air atmosphere at room temperature for 1 h.
[b] Isolated yields; NR = no reaction.
[c] MeCN/MeOH (v/v = 1:1).
[d] MeOH/$H_2O$ (v/v = 10:1).
[e] Constant current = 5 mA.
[f] Without electricity.
[g] Under Ar atmosphere.

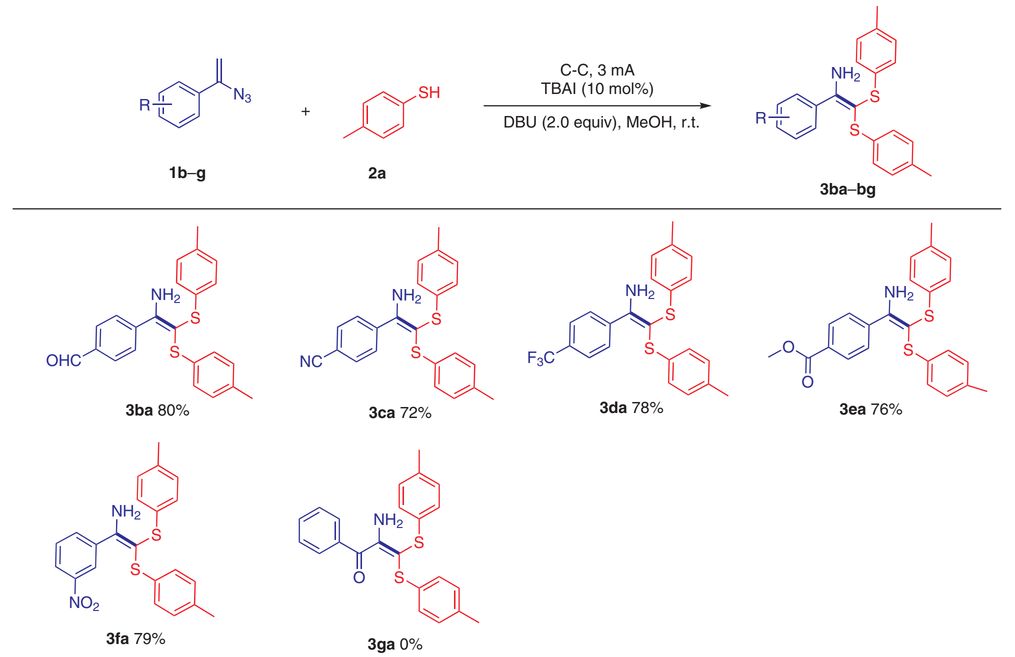
try 6). Different electrodes as an anode or a cathode were also tested. When platinum was used as an anode and cathode, the target product **3aa** was given in a reduced yield of 60% (entry 7). When graphite rod was employed as both an anode and a cathode, the target product **3aa** was afforded in the highest yield of 88% (entry 8). We also investigated the effect of current on the yield of the product. When we increased the current to 5 mA, the yield of the target product **3aa** was markedly decreased (entry 9). The target product **3aa** was not observed in the absence of electricity (entry 10). When this reaction was conducted in an inert atmosphere (Ar), the yield of the target product **3aa** was not markedly improved (entry 11). Various bases, including inorganic bases, such as $K_2CO_3$, 2,6-lutidine, and 4-dimethylamino- pyridine, were examined. DBU was found as the optimal base (Table S1, entries 12–14). In summary, we found that an 88% isolated yield of the target product **3aa** could be furnished at a constant current of 3.0 mA in MeOH with 10% TBAI as an electrolyte, DBU as a base, and graphite rod as an anode and cathode at room temperature (entry 8).

Under optimal electrolytic conditions, we then screened the scope of various thiophenols **2** under the standard conditions (Scheme 2). Most of the thiophenols could react with 1-(1-azidovinyl)-4-nitrobenzene (**1a**) and produce the desired products containing the enamine skeleton **3aa**–**ak**. We found that substituents at the *para* position with electron-withdrawing groups (F, Cl, and Br) and electron-donating groups (*t*-Bu, OMe, Me) could be well tolerated in this process and provided the corresponding products in moderate to good yields (**3aa**–**ai**). The *para*, *ortho*, and *meta* substituents were proceeded smoothly to yield the desired products in good yields (**3ab**,**ac**). However, the *para* substituents delivered the highest yield (**3aa**, 88%), the *meta* substituents afforded the second-highest yield (**3ab**, 76%), and the *ortho* substituents produced a much lower yield (**3ac**, 60%), which might be due to the steric properties of the substrate. A dimethyl substrate was compatible with this reaction and generated the expected product with a yield of 66% (**3af**). 1-Naphthyl mercaptan (2-naphthalenethiol) and heterocyclic thiophenols were well tolerated under the standard conditions and delivered the final products with yields of 62% and 65%, respectively (**3aj** and **3ak**).

Subsequently, the scope of α-substituted vinyl azides was comprehensively explored (Scheme 3). Conventionally, a diverse range of α-substituted vinyl azides with different substituents (R = strong electron-withdrawing groups) on



**Scheme 2** Substrate scope of thiophenols **2**. *Reagents and conditions*: graphite rod as an anode and cathode, an undivided cell, a constant current of 3.0 mA, **1a** (0.3 mmol, 1 equiv), **2** (0.72 mmol, 2.4 equiv), TBAI (10 mol %), DBU (0.6 mmol, 2.0 equiv), and solvent (6 mL) under air atmosphere at room temperature for 1 h. Isolated yields are given.



**Scheme 3** Scope for vinyl azides **1** with a strong electron-withdrawing group. *Reagents and conditions*: graphite rod as an anode and cathode, an undivided cell, a constant current of 3.0 mA, **1** (0.3 mmol, 1 equiv), **2a** (0.72 mmol, 2.4 equiv), TBAI (10 mol %), DBU (0.6 mmol, 2.0 equiv), and solvent (6 mL) under air atmosphere at room temperature for 1 h. Isolated yields are given.

the benzene ring were found to be well tolerated in this reaction and yielded the desired products. For example, electron-withdrawing groups, such as CHO, CN, CF$_3$, and CO$_2$Me, on the benzene ring at the *para* position were well tolerated under the standard conditions and generated the expected products (**3ba**–**ea**) in good yields (72–80%). When the electron-withdrawing group was at the *meta* position, this process could undergo smoothly and furnish the desired product **3fa** in satisfactory yields of 79%. However, 2-azido-1-phenylprop-2-en-1-one (**1g**) was found to be incompatible under these optimized electrolytic conditions, and the expected product was not detected.

When the substituent was no strong electron-withdrawing group (R = MeO, Me, *t*-Bu, Et, Cl) on the benzene ring of different α-substituted vinyl azides, a series of α-phenylthio ketones (**4aa**–**ag**) were generated in moderate to excellent yields under the optimized electrolytic conditions (Scheme 4). The main reason may be that dithiolated enamine is a product of high electron-cloud density, so it needs an electron-withdrawing group to stabilize it. When no substituent was present on the benzene ring of the α-substituted vinyl azide, the corresponding α-phenylthio ketone (**4ah**) was obtained in 86% yield. Polycyclic vinyl azide could also react with *p*-methylphenylene mercaptan to form the corresponding ketone with 83% yield (**4ai**). In addition, an α-substituted vinyl azide bearing a heterocyclic ring formed smoothly and gave the desired product (**4aj**) in 88% yield. Finally, alkyl azides such as (2-azidoallyl)benzene were compatible with the standard conditions and afforded the α-phenylthio ketone (**4ak**) in 80% yield. Unfortunately, this method cannot be applied to aliphatic vinyl azides and thiols.

To gain further understanding of the reaction mechanism, we performed some control experiments. First, the reaction of 1-(1-azidovinyl)-4-nitrobenzene (**1a**) and 4-methylbenzenethiol (**2a**) was conducted under the optimized reaction conditions without a constant current. The corresponding *gem*-bisphenylthio enamine product **3aa** also failed to be detected (Scheme 5a). In addition, a reaction was conducted in the presence of molecular iodine, in which the enamine **3aa** was observed only in trace amount (Scheme 5b). At last, we also did free-radical-trapping experiments, the TEMPO-trapped radicals I, II, and III were detected with an HRMS spectrometer (Scheme 5c). The results indicated that a radical process might be involved in this transformation.

To confirm this hypothesis, we subsequently carried out a radical-trapping experiment, which was monitored through EPR spectroscopy. In Figure 1, when 3.0 equivalents 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) were used as radical-spin-trapping agents under standard reaction conditions, a strong radical signal was detected (red line in Figure 1). The radical signal belonged to the thiyl radical ($g$ = 2.0067, $A_N$ = 14.06, $A_H$ = 12.92) by comparing with the simulated EPR spectrum (black line in Figure 1). Consequently, the above EPR results verified that a radical process was involved in this transformation.

A cyclic voltammetry experiment was also conducted to gain further insights into this transformation. As shown in the left of Figure 2, 1-(1-azidovinyl)-4-nitrobenzene (**1a**) showed an oxidation peak at 1.68 V (curve b), whereas the first oxidation peak of 4-methylbenzenethiol (**2a**) was at 1.40 V (curve c). These experimental data indicated that 4-methylbenzenethiol (**2a**) was earlier oxidated than 1-(1-azidovinyl)-4-nitrobenzene (**1a**). As shown in the right of Figure 2, when 4-methylbenzenethiol (**2a**) was added to the mixture of $LiClO_4$ and TBAI, the current increased distinctly (curve e), indicating that TBAI played a catalyst role in this reaction.

Subsequently, the thiyl radical **A** attacked the C=C bonds of the vinyl azides **1** and provided the intermediate **B** and the imine radical intermediate **C** furnished with the rapid exit of the molecular $N_2$ (Scheme 6). The imine radical intermediate **C** might undergo two completely different reaction paths (paths a and b). When R¹ was a strong electron-

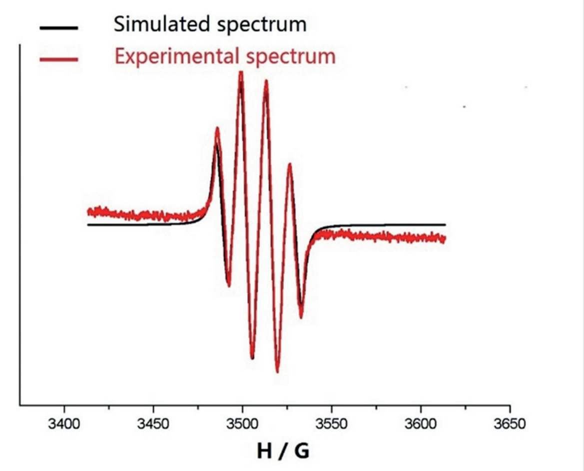


**Figure 1** Simulated (black line) and experimental (red line) EPR spectra of the trapped radical intermediates

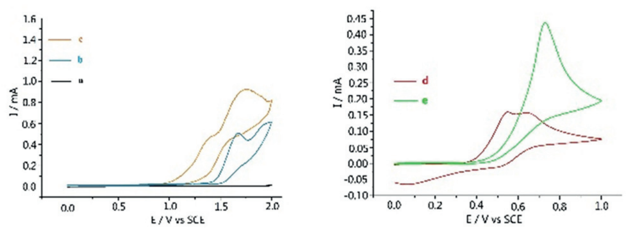
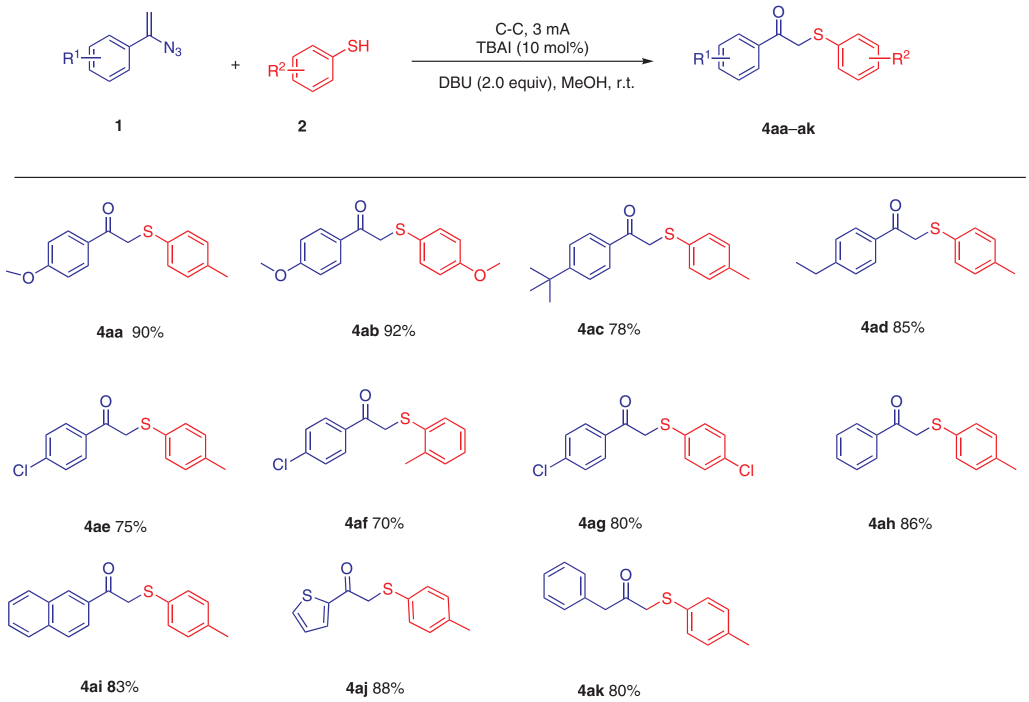
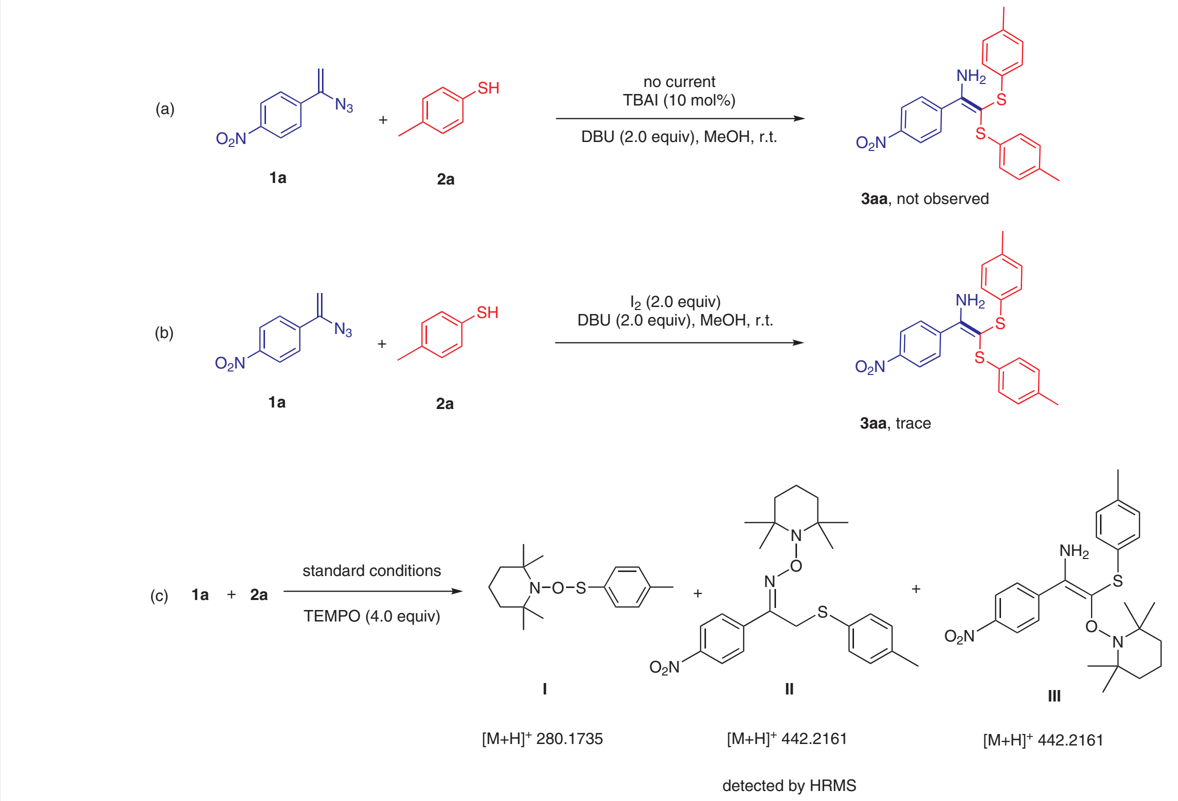


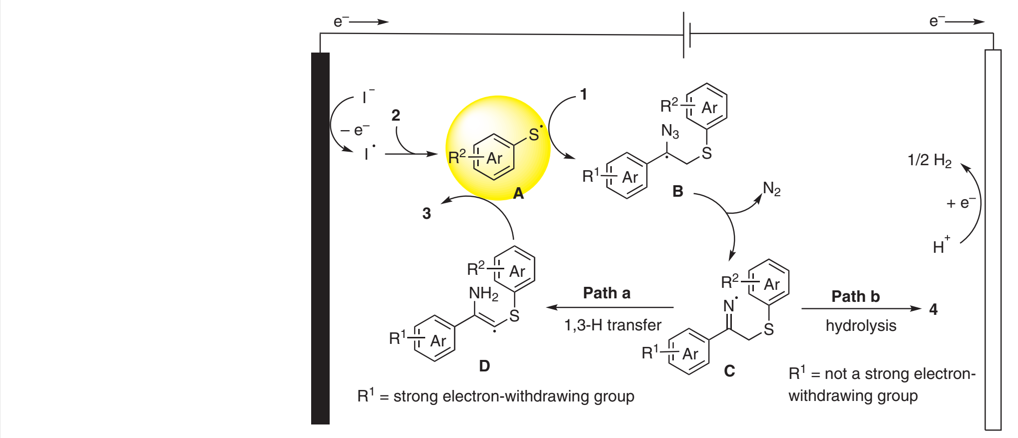
**Figure 2** Cyclic voltammograms of reactants and their mixtures in 0.1 M $LiClO_4/CH_3OH$ by using a glassy carbon disk (3 mm diameter) as a working counter and a Pt disk and Ag/AgCl (in saturated KCl solution) as reference electrodes at a scan rate of 100 mV/s: (a) background, (b) $LiClO_4$ (0.1 mmol/L) + **1a** (10 mmol/L), and (c) $LiClO_4$ (0.1 mmol/L) + **2a** (10 mmol/L), (d) $LiClO_4$ (0.1 mmol/L) + TBAI (10 mmol/L), and (e) $LiClO_4$ (0.1 mmol/L) + TBAI (10 mmol/L) + **2a** (10 mmol/L).



**Scheme 4** Scope for vinyl azides **1** with no strong electron-withdrawing group. *Reagents and conditions*: graphite rod as an anode and cathode, an undivided cell, a constant current of 3.0 mA, **1** (0.3 mmol, 1 equiv), **2** (0.36 mmol, 1.2 equiv), TBAI (10 mol %), DBU (0.6 mmol, 2.0 equiv), and solvent (6 mL) under air atmosphere at room temperature for 1 h. Isolated yields are given.



**Scheme 5** Control experiments



**Scheme 6** Plausible mechanism

withdrawing group, the imine radical intermediate **C** might undergo 1,3-H transfer and generate a **D** radical. Generally speaking, direct 1,3-H transfer is forbidden. This process requires the help of water in the air.[22] It is worth mentioning that if too much water is added, it would promote the hydrolysis process and reduce the yield of **3aa**. Finally, another thiyl radical coupled with the intermediate **D** offered the target products **3**. By contrast, when $R^1$ was not a strong electron-withdrawing group, the imine radical intermediate **C** might experience hydrolysis and deliver the α-phenylthio ketone **4**.[23]

In conclusion, we developed an efficient and convenient strategy for the straightforward construction of a series of *gem*-bisarylthio enamines and α-phenylthio ketones.[24,25] The notable features of this electrochemical approach are wide substrate scope, convenient operation, and a catalytic amount of inexpensive electrolyte requirement. In comparison with the reported metal catalysts or strong base conditions for the synthesis of *gem*-bisarylthio enamines, our present reaction conditions are mild, green, and environmentally friendly without the use of metals, oxidants, or harsh reaction conditions. Further investigations on their applications will be carried out by our group in the future.

## Funding Information

We thank the National Natural Science Foundation of China (22061003), the Natural Science Foundation of Guangxi Province (2019GXNSFAA245027), Bagui Scholars Program of Guangxi Zhuang Autonomous Region (2016A13), and the Special Fund for Distinguished Experts in Guangxi of China for financial support.

## Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/a-1335-7902.

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(24) **General Procedure for the Synthesis of *gem*-Bisphenylthio Enamine 3aa**
The azide **1a** (0.3 mmol), thiophenol **2a** (0.75 mmol), DBU (0.6 mmol), and TBAI (0.03 mmol) were placed in a 10 mL three-necked round-bottomed flask. The flask was equipped with a

condenser and graphite rod as cathode and anode. MeOH (6.0 mL) was added. The electrolysis was carried out under air atmosphere at room temperature using a constant current of 3 mA until complete consumption of the substrate (monitored by TLC, about 1 h). The reaction mixture was concentrated, and the residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether to give the product **3aa**.

(25) **Analytical Data for Compound 3aa**
88% yield; yellow solid; mp 94.1–95.4 °C. Analytical TLC on silica gel. $R_f$ = 0.48 (hexane/ether; 6.1). $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.19 (d, *J* = 8.4 Hz, 2 H), 7.66 (d, *J* = 8.4 Hz, 2 H), 7.22–7.17 (m, 2 H), 7.14–7.04 (m, 6 H), 5.04 (s, 2 H), 2.33 (s, 3 H), 2.31 (s, 3 H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 158.0, 148.1, 143.8, 136.0, 135.3, 134.7, 131.8, 129.9, 129.7, 129.1, 127.8, 126.5, 123.5, 91.0, 21.0, 21.0. HRMS (ESI): *m/z* calcd for $C_{22}H_{21}N_2O_2S_2$ $[M + H]^+$: 409.1039; found: 409.1036.