SCIENCE CHINA
Chemistry

•ARTICLES•

November 2020 Vol.63 No.11: 1652–1658
https://doi.org/10.1007/s11426-020-9811-6

Visible-light-induced regioselective cross-dehydrogenative coupling of 2-isothiocyanatonaphthalenes with amines using molecular oxygen

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Received May 13, 2020; accepted July 2, 2020; published online August 3, 2020

An efficient and eco-friendly protocol for the construction of naphtho[2,1-*d*]thiazol-2-amines through visible-light photoredox-catalyzed C(sp^2)–H/S–H cross-dehydrogenative coupling reactions between 2-isothiocyanatonaphthalenes and amines was established. In this reaction, the new C–N and C–S bonds are formed simultaneously in a single step. This new method provides a straightforward approach for constructing valuable sulfur-containing compounds.

visible light, cross-dehydrogenative coupling, C–S bond, synthetic methods, metal-free

Citation: Gan Z, Li G, Yang X, Yan Q, Xu G, Li G, Jiang YY, Yang D. Visible-light-induced regioselective cross-dehydrogenative coupling of 2-isothiocyanatonaphthalenes with amines using molecular oxygen. *Sci China Chem*, 2020, 63: 1652–1658, https://doi.org/10.1007/s11426-020-9811-6

1 Introduction

Organosulfur compounds pervasively exist in bioactive natural products, pharmaceuticals, organic photoelectric materials and flavor compounds [1]. In 2011, sulfur-containing drugs accounted for 20% of the top 200 retail drugs in the USA [2]. Thus, designing efficient and environmentally friendly approaches for the formation of C–S bonds remains a fundamentally important goal for the synthetic community [3]. The classical approaches for the synthesis of C–S bonds are the transition-metal-catalyzed cross-coupling of aryl halides, arylboronic acids or pseudo-halides with disulfides or thiols [4]. From an organic synthesis perspective, sulfenylation reaction using cross-dehydrogenative coupling (CDC) method is one of the most efficient and straightforward strategies for the formation of C–S bonds due to its high atom economy and low number of synthetic steps [5]. However, a detailed literature search revealed that this synthetic strategy for the C–S bond formation is limited when compared to the forming reaction of C–N, C–O or C–C bonds [6]. This might be due to the facile over-oxidation of sulfur-containing compounds under oxidative conditions. Therefore, it is highly desirable to develop more economical, efficient, and practical CDC strategies for constructing C–S bonds under mild conditions [7].

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2-Aminobenzothiazole and its derivatives are important sulfur-containing structural motifs in many pharmaceuticals and agrochemicals and possess excellent biological and medicinal activities, including antitumor, anticonvulsant, anti-inflammatory, anti-infective, HIV-1 protease inhibition, neuroprotective and antimicrobia [8]. Consequently, the development of efficient and green synthetic strategies to access 2-aminobenzothiazole and its derivatives remains one of the most attractive research areas in organic and pharmaceutical chemistry. Generally, the 2-aminobenzothiazoles forming pathway involves the following methods: (1) transition-metal-catalyzed direct oxidative coupling of benzothiazoles with amines [9]; (2) base or transition-metal promoted coupling of 2-halobenzothiazoles with amines [10]; (3) transition-metal-catalyzed cascade condensation and cyclization of 2-haloanilines with isothiocyanates [11]; and (4) cyclization of *N*-aryl thioureas through transition-metal-catalyzed intramolecular C–S bond formation [12]. Despite successes with this approach, these methods have certain drawbacks, including unavailable precursors, toxic metal salt catalysts, and harsh reaction conditions. In 2017, Lei and co-workers [13] demonstrated an environmentally friendly electrochemical reaction protocol for the synthesis of 2-aminobenzothiazoles through the direct coupling of aryl isothiocyanates with aliphatic amines. In 2017, Fan and Zhang *et al*. [14] also developed an elegant approach to 2-aminobenzothiazoles *via* iodine-catalyzed cascade reactions of isothiocyanatobenzenes with primary or secondary amines. However, these elegant reactions still have several drawbacks that limit potential applications: (1) the amines mainly focused on secondary aliphatic amines. Primary aliphatic amines and aryl amines were not compatible in Lei's work; (2) toxic chlorobenzene used as the solvent; and (3) high reaction temperature. Therefore, the development of a facile and novel method that can complement existing synthetic methods while meeting requirements of sustainable and green chemistry remains an ongoing challenge.

Visible light photoredox catalysis is a versatile, powerful and environmentally friendly synthetic tool and has attracted extensive attention in the field of synthetic chemistry [15]. Visible-light induced oxidation is an ideal choice for C–H/S–H cross-dehydrogenative coupling (CDC) sulfenylation reactions [16]. However, studies on the synthesis of 2-aminobenzothiazoles based on light-induced transformation have not been reported. As part of our continuing studies of photochemical reactions in green organic synthesis and photochemical reactions [17], herein, we report an efficient and simple visible-light-induced Eosin Y-catalyzed method for the synthesis of 2-aminobenzothiazoles through the direct coupling of 2-isothiocyanatonaphthalenes and amines using molecular oxygen as the green oxidant at room temperature (Scheme 1).

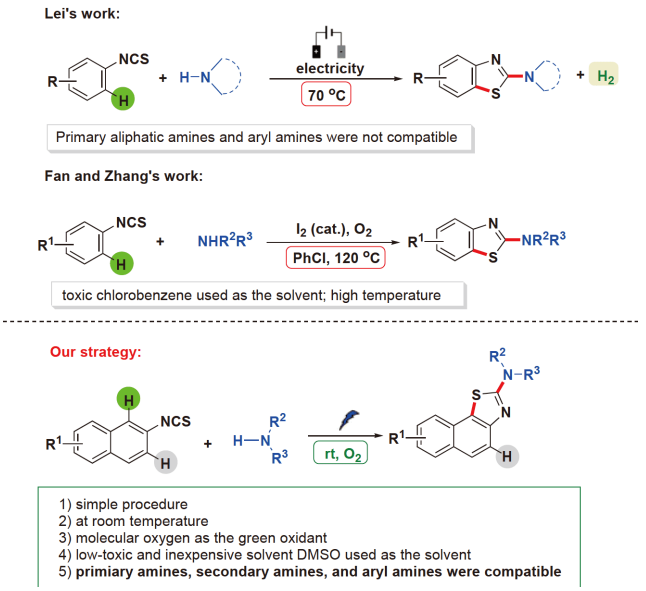
2 Experimental

2.1 General information

All reagents and solvents were obtained from commercial suppliers and used without further purification. The photocatalysts were purchased from Sigma Aldrich (USA). Flash chromatography was performed on silica gel (200–300 mesh). ^{1}H and ^{13}C NMR data were recorded at 500 and 125 MHz on a BRUKER 500 spectrometer (Germany). Chemical shifts (δ) are expressed in parts per million (ppm), coupling constants (J) are in Hz. Proton and carbon magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded using tetramethylsilane (TMS) as the internal standard in DMSO-d_6 or in $CDCl_3$. Mass analyses and high resolution mass spectrometry (HRMS) were obtained by electrospray ionization (ESI) on a time of flight (TOF) mass analyzer. All diffraction data were obtained on a Bruker Smart Apex CCD diffractometer equipped with graphite-monochromated Mo Kα radiation. UV-visible spectroscopy of reaction solution was recorded on a PERSEE TU-1901 UV-visible spectrophotometer (China). The fluorescence emission intensity of reaction solution was recorded on a F-4600 spectrofluorimeter. The reactor was 3.0 cm from 12 W Blue LED.

2.2 General procedure for the synthesis of 3 or 4

A 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with **1** (0.2 mmol), **2** (0.3 mmol), and Eosin Y (1 mol%). The tube was evacuated twice and backfilled with



Scheme 1 Recent strategies for the synthesis of 2-aminobenzothiazoles (color online).

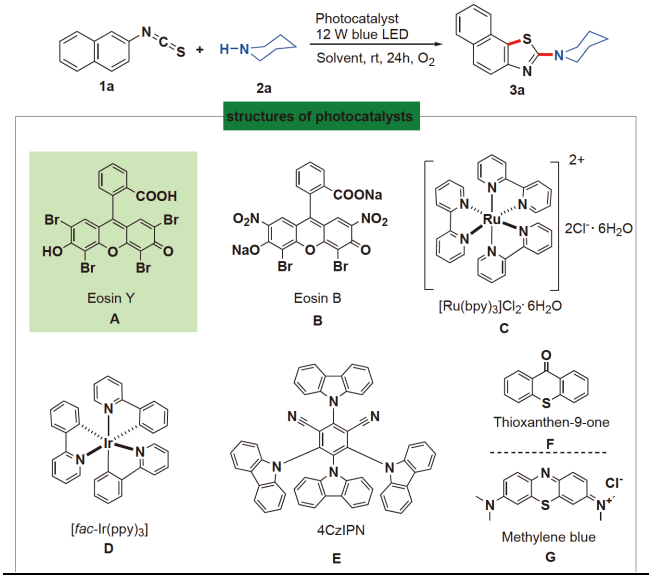
oxygen, and 2 mL dimethyl sulfoxide (DMSO) was added to the tube under oxygen atmosphere. The tube was sealed with an oxygen balloon and then the mixture was allowed to stir at room temperature with the irradiation of a 12 W blue LED for 24 h. After completion of the reaction, the solvent was removed with the aid of a rotary evaporator. The residue was purified by column chromatography on silica gel using the petroleum ether/ethyl acetate as eluent to provide the desired products **3** or **4**.

3 Results and discussion

We initially chose 2-isothiocyanatonaphthalene (**1a**) and piperidine (**2a**) as model substrates to investigate the optimal reaction conditions, including the solvents and photocatalysts, under an oxygen atmosphere and visible light irradiation using a 12 W blue LED. As shown in Table 1, six solvents (CH_3CN, H_2O, toluene, 1,4-dioxane, EtOH, and DMSO) were screened using Eosin Y (**A**) as the photocatalyst at room temperature, and DMSO afforded the highest yield (92%) (entries 1–6, Table 1). Subsequently, seven photoredox catalysts were tested in DMSO. Among these photocatalysts investigated, Eosin Y was proven to be the most effective for obtaining the desired product 2-(piperidin-1-yl)naphtho[2,1-*d*]thiazole (**3a**) in 92% yield (entries 6–12, Table 1). Notably, none of the desired oxidative cyclization product **3a** was detected under a nitrogen atmosphere, and instead a 92% yield of nucleophilic addition product *N*-(naphthalen-2-yl)piperidine-1-carbothioamide was obtained (entry 13, Table 1). In addition, when the reaction was performed under air atmosphere, it gave a lower yield (entry 14, Table 1). Furthermore, none of the desired product **3a** was detected in the absence of a photoredox catalyst (entry 15, Table 1). In addition, control experiments showed that no oxidative cyclization conversion could be induced by increasing the reaction temperature in the absence of light irradiation (entries 16 and 17, Table 1).

After establishing the optimized reaction conditions, we then evaluated the substrate scope of this reaction using different 2-isothiocyanatonaphthalene derivatives and aliphatic amines (Scheme 2). To our delight, a variety of aliphatic amines reacted smoothly with 2-isothiocyanatonaphthalenes, affording the corresponding naphtho[2,1-*d*]thiazol-2-amines in good to excellent yields. Notably, primary aliphatic amines showed good reactivity in this photocatalytic system, while these primary amines were not well tolerated in the electrocatalytic system (**3g**, **3i**, **3j**, **3r**, and **3t**). Dicyclohexylamine which has large steric bulk also participated well in the reaction, giving a high yield (**3f** and **3q**). The bioactive amines methyl alaninate and *cis*-2-Boc-hexahydropyrrolo[3,4-*c*]pyrrole showed good reactivity affording the corresponding products in good yield, so this method

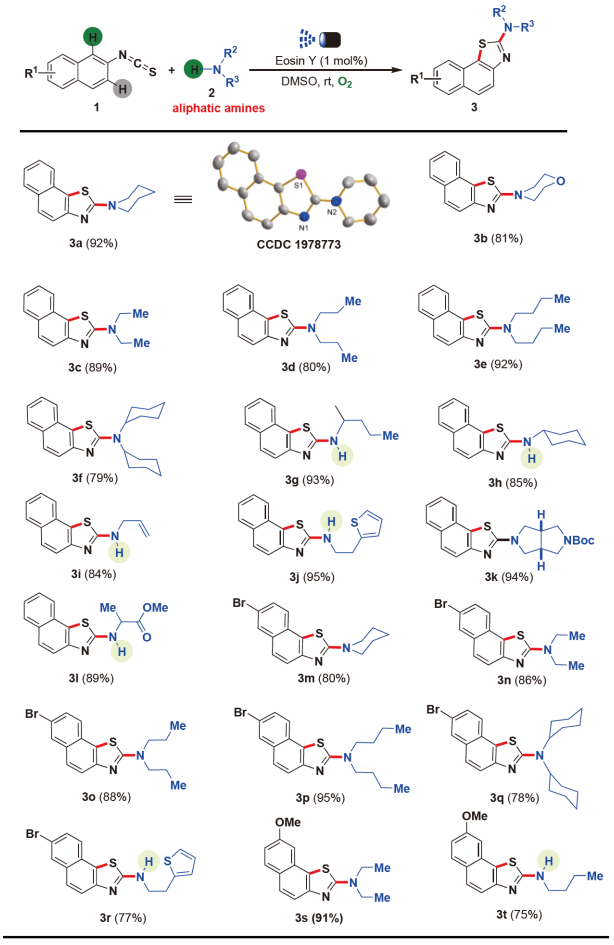
Table 1 Optimization of the reaction conditions[a)]



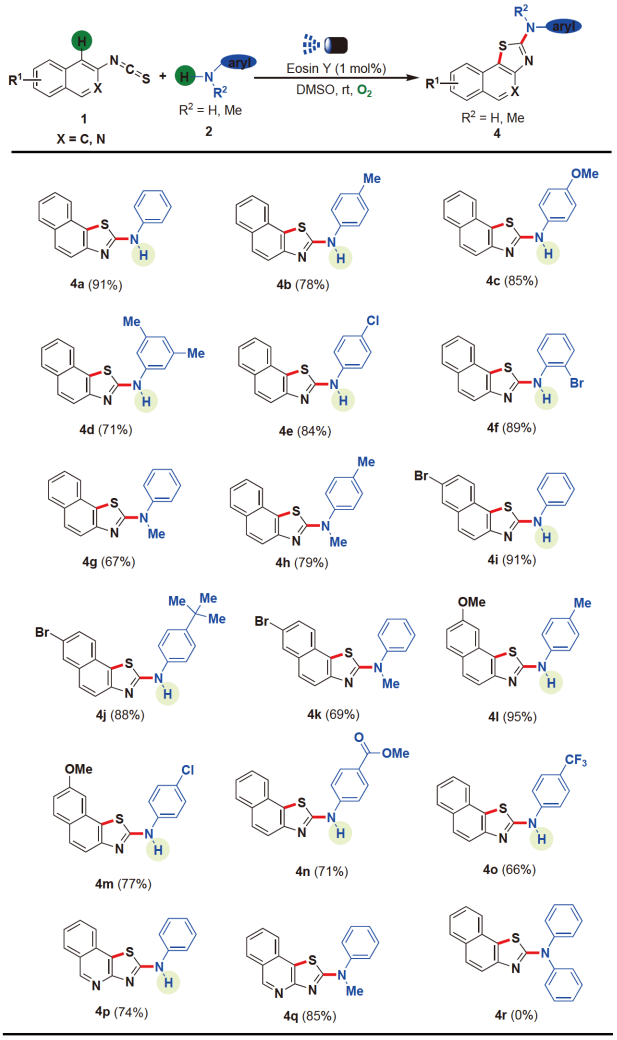
Entry	Photoredox catalyst	Solvent	Yield (%)[b)]
1	A	CH_3CN	51
2	A	H_2O	42
3	A	Toluene	67
4	A	1,4-Dioxane	56
5	A	EtOH	47
6	A	DMSO	92
7	B	DMSO	64
8	C	DMSO	37
9	D	DMSO	41
10	E	DMSO	73
11	F	DMSO	43
12	G	DMSO	0
13	A	DMSO	0[c)]
14	A	DMSO	53[d)]
15	None	DMSO	0
16	A	DMSO	0[e)]
17	A	DMSO	0[f)]

a) Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), photocatalyst (1.0 mmol%), solvent (2 mL), temperature (rt, ~25 °C), time (24 h). b) Isolated yield. c) Under a nitrogen atmosphere (extrusion of air). d) In air. e) At 40 °C, no light. f) At 60 °C, no light.

provides a new strategy for constructing bioactive heterocycles (**3k** and **3l**). 2-(Thiophen-2-yl)ethan-1-amine was tolerated in this transformation, affording the desired products in 95% and 77% yield (**3j** and **3r**), respectively. Next, aryl amines were screened to further demonstrate the substrate scope in this photochemical process (Scheme 3). We were pleased to find that both primary and secondary aromatic amines successfully afforded the corresponding cyclization products with high to excellent yields (**4a**–**4l**). The electron-effect of the substituted groups in aryl amines including electron-rich, -deficient, and -neutral groups did not



Scheme 2 Substrate scope of 2-isothiocyanatonaphthalenes with aliphatic amines. Reaction conditions: under an oxygen atmosphere, 2-isothiocyanatonaphthalenes **1** (0.2 mmol), aliphatic amines **2** (0.3 mmol), DMSO (2.0 mL), 12 W blue LED, temperature (rt, ~25 °C), reaction time (24 h). Isolated yield (color online).

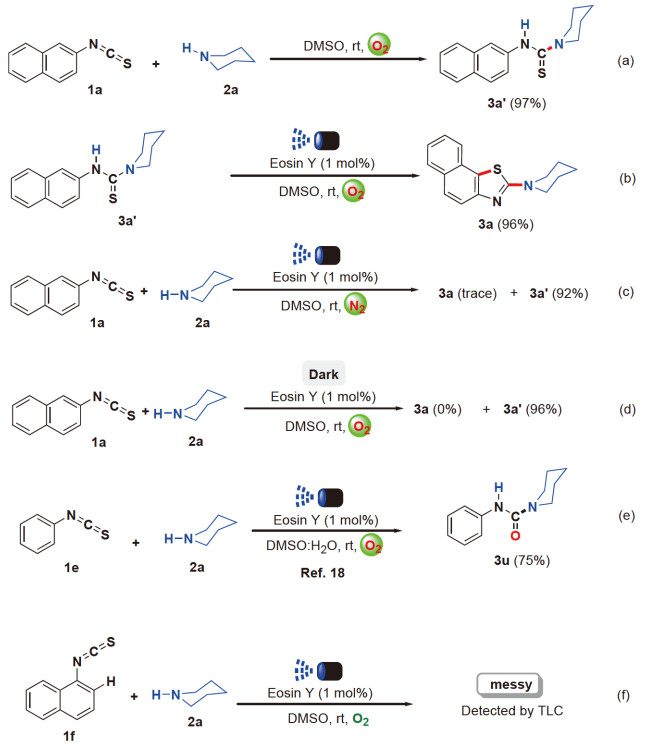


Scheme 3 Substrate scope of 2-isothiocyanatonaphthalenes with aryl amines. Reaction conditions: under an oxygen atmosphere, 2-isothiocyanatonaphthalenes **1** (0.2 mmol), aryl amines **2** (0.3 mmol), DMSO (2.0 mL),12 W blue LED, temperature (rt, ~25 °C), reaction time (24 h). Isolated yield (color online).

display evidently difference of reactivity. To our delight, 3-isothiocyanatoisoquinoline was also compatible under the standard conditions and the desired products were generated in good yields (**4p** and **4q**). Finally, diphenylamine was investigated under the standard conditions. Unfortunately, no oxidative cyclization product was observed (**4r**), and only a trace amount of the thiourea was produced. The visible-light promoted regioselective C(sp^2)–H/S–H cross-dehydrogenative reactions could tolerate some functional groups such as methyl, trifluoromethyl, ether, ester, C–Cl bond, and C–Br bond, leaving ample room for further modification.

To gain mechanistic insights into this novel oxidative cyclization pathway, some preliminary control experiments were performed (Scheme 4). When the direct coupling of 2-isothiocyanatonaphthalene (**1a**) with piperidine (**2a**) was performed in the absence of Eosin Y, the nucleophilic addition product **3a′** was obtained in 97% yield (Scheme 4(a)). In addition, the treatment of **3a′** under the standard conditions afforded **3a** in 96% yield, suggesting that **3a′** may be an intermediate in the photocatalytic transformation (Scheme 4 (b)). Furthermore, the treatment of 2-isothiocyanatonaphthalene (**1a**) with piperidine (**2a**) under a nitrogen atmosphere was examined. As expected, only a trace amount of the desired product **3a** was observed along with the nucleophilic addition product **3a′** (92% yield), which reveals that oxygen is crucial for this reaction (Scheme 4(c)). It should also be noted that only nucleophilic addition product **3a′** was obtained in the absence of light (Scheme 4(d)). Finally, the treatment of 1-isothiocyanatonaphthalene (**1f**) with piperidine (**2a**) under the standard conditions gave a messy thin layer chromatography (TLC), and only a trace amount of **1f** was recovered (Scheme 4(f)).

In order to obtain more information about the mechanism, Stern-Volmer fluorescence quenching experiments of Eosin



Scheme 4 Control experiments (color online).

Y with *N*-(naphthalen-2-yl)piperidine-1-carbothioamide (**3a′**) were performed. As shown in Figure 1, the 572 nm fluorescence launched by Eosin Y was observed when it was excited at 510 nm, and the addition of **3a′** dramatically decreased the fluorescence intensity. In addition, the non-linear

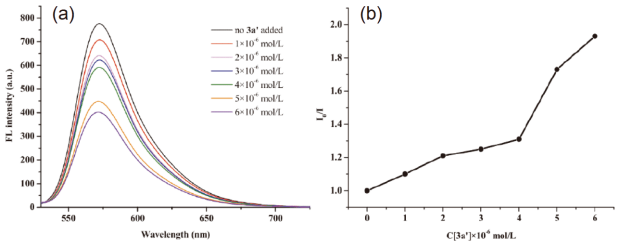


Figure 1 (a) Quenching of the Eosin Y fuorescence emission in the presence of **3a′**. (b) Stern-Volmer plots (color online).

Stern-Volmer fluorescence quenching plots presumably indicated a single electron transfer between Eosin Y's excited state and **3a′**.

The cyclization reaction in our proposed mechanism and the potential competitive oxidative desulfurization (Scheme 4(e)) [18] were investigated using DFT calculations to explore the origin of the selectivity (Figure 2) (see Supporting Information for computational details). The hydrogen abstraction of **3a″** by excited Eosin Y and oxygen to generate the radical **6′** is exergonic by 4.0 kcal/mol. From **6′**, α-cyclization can proceed *via* **TS1** to afford the intermediate **7′**, which cause an energy increase of only 3.3 kcal/mol. Then electron transfer occurs to give the cation **8′**, from which facile deprotonation by a hydroperoxide anion can proceed *via* **TS2** to generate the product **3b** with an overall energy barrier of 11.7 kcal/mol. The aromatization makes the deprotonation highly exergonic by about 60 kcal/mol. By contrast, β-cyclization *via* **TS3** affords the less stable radical intermediate **9′** and the subsquent electron transfer makes the

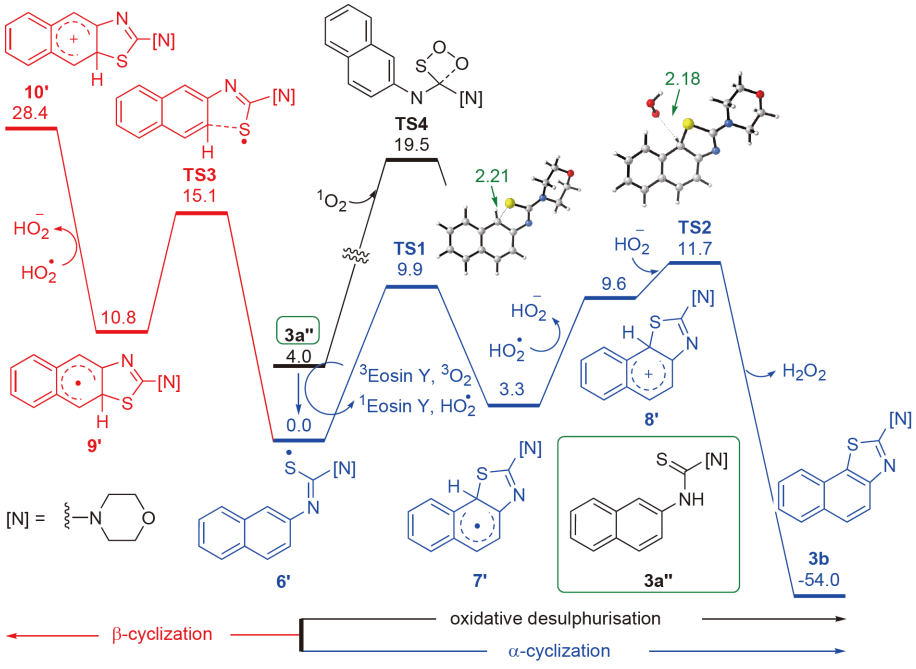
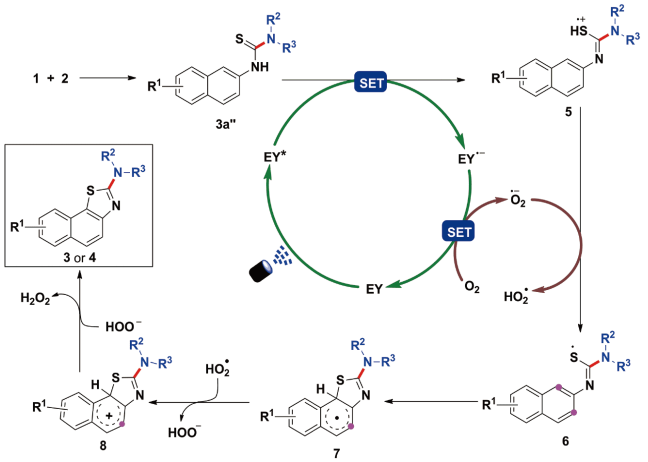


Figure 2 DFT-computed free-energy profile for the most favorable pathway (color online).

overall pathway endergonic by 28.4 kcal/mol, indicating that this pathway is less feasible than α-cyclization. The calculated different thermodynamics is easily understandable according to resonance structures of the radical/cationic intermediates (Figure S7, Supporting Information online). On the other hand, the oxidative desulfurization of **3a″** is less favorable than the α-cyclization by 7.8 kcal/mol but the oxidative desulphurisation of the *N*-phenylthiourea derivative is more favorable than the cyclization pathway by 1.6 kcal/mol (Figure S8). These results are consistent with the different selectivity observed in the aerobic transformations of isothiocyanatobenzene and 2-isothiocyanatonaphthalene (Scheme 4(e)) [18]. We found that the elementary energy barriers of the oxidative desulfurization and the deprotonation of the cationic cyclization intermediates are similar in both reactions. By contrast, the relative energies of the radical/cationic intermediates in the cyclization pathway differ significantly, indicating that the stability of the radical/cationic intermediates is the key factor of controlling the selectivity.

Based on these preliminary experimental results, a reasonable mechanism was proposed, shown in Scheme 5. First, the photocatalyst Eosin Y was excited by visible light irradiation, leading to the excited species Eosin Y*. Then Eosin Y* reacted with the intermediate **3a″**, gengerated *in situ* from addition of **1** and **2**, to form the radical cation **5** and the Eosin $Y^{\bullet-}$ radical anion. The oxidation of Eosin $Y^{\bullet-}$ by oxygen afforded the ground state Eosin Y and $O_2^{\bullet-}$. Subsequently, the radical cation **5** was deprotonated by $O_2^{\bullet-}$, leading to the thiyl radical **6**. The thiyl radical **6** then underwent regioselective intramolecular radical addition to generate the carbon radical **7**, which could be further transformed into the intermediate **8** through single electron transfer (SET) with $HO_2^{\bullet}$. Finally, the superoxide anion reacted with intermediate **8** to give the desired cyclization products **3** or **4**.



Scheme 5 Possible reaction pathway (color online).

4 Conclusions

To summarize, we have successfully developed the first visible-light photoredox-catalyzed cross-dehydrogenative coupling reactions between 2-isothiocyanatonaphthalenes and amines leading to naphtho[2,1-*d*]thiazol-2-amines. The corresponding oxidative cyclization products were obtained in good to excellent yield. The developed method can offer the following advantages: (1) diverse amines were tolerated; (2) easy workup procedure; (3) low-toxic and inexpensive DMSO as the solvent; (4) oxygen as the green oxidant; (5) at room temperature. The advantages of this developed method meet the requirements of green and sustainable synthetic chemistry and provide a straightforward approach to construct valuable sulfur-containing compounds.

Acknowledgements This work was supported by the National Natural Science Foundation of China (21302110, 21702119), the Natural Science Foundation of Shandong Province (ZR2016JL012, ZR2017QB001), the Scientific Research Foundation of Qingdao University of Science and Technology, the Natural Science Foundation of Liaoning Province (20180550882) and the Program for Creative Talents in University of Liaoning Province.

Conflict of interest The authors declare no conflict of interest.

Supporting information The supporting information is available online at http://chem.scichina.com and http://link.springer.com/journal/11426. The supporting materials are published as submitted, without typesetting or editing. The responsibility for scientific accuracy and content remains entirely with the authors.

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