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Potassium Hydroxide/Dimethyl Sulfoxide Superbase-Promoted Transition Metal-Free Synthesis of 2-Substituted Benzothiophenes under Visible Light

Li Gao,[a] Bin Chang,[a] Wenzhao Qiu,[a] Lele Wang,[a] Xianzhi Fu,[a]
and Rusheng Yuan[a,]*

[a] State Key Laboratory of Photocatalysis on Energy and Environment, College of Chemistry, Fuzhou University, Fuzhou 350002, People's Republic of China
E-mail: yuanrs@fzu.edu.cn

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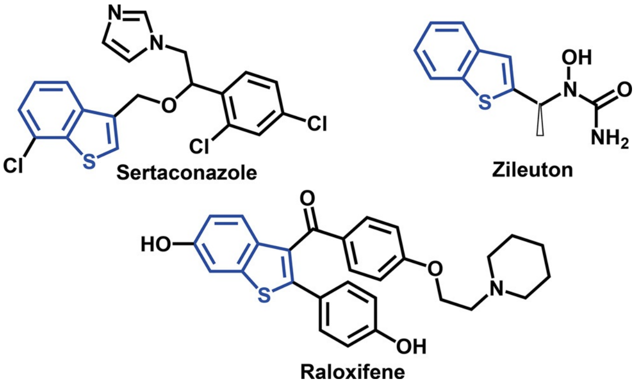
Abstract: A potassium hydroxide/dimethyl sulfoxide (KOH/DMSO) superbase-promoted method for the synthesis of 2-substituted benzothiophenes has been developed *via* photoinduced intermolecular annulation of 2-halothioanisoles with terminal alkynes at ambient temperature. The present protocol uses commercially available 2-halothioanisoles as substrates and visible light as energy force, which offers a wide range of benzothiophenes regioselectively in moderate to good yields. Such a facile and effective transformation will provide an environment-friendly approach to the synthesis of benzothiophene derivatives.

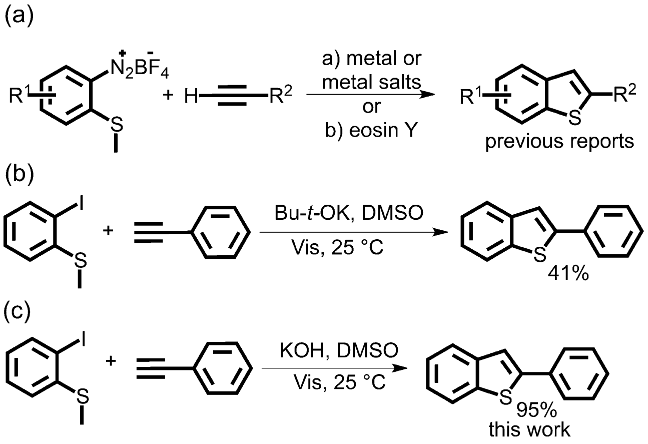
Keywords: aryl radicals; benzothiophenes; photoinduced reaction; potassium hydroxide/dimethyl sulfoxide (KOH/DMSO) superbase; transition metal-free conditions

Benzothiophene is an important sulfur-containing heterocyclic compound that is widely used as a building block for the synthesis of larger, usually bioactive structures.[1] Its substituted derivatives occupy a unique place in medicinal chemistry because they have promising antibacterial, antifungal and antitumour activities.[2] Raloxifene,[3] zileuton[4] and sertaconazole[5] are examples of commercial drugs containing a benzothiophene core (Scheme 1). This has given rise to a great interest in the synthesis of benzothiophene derivatives in recent years.[6] Among a variety of synthetic methodologies to construct the benzothiophene ring, cyclization reactions are much more preferable due to the existence of plentiful starting materials meeting the demand of atom economy. However, the cyclization reactions usually involve transition metals such as Pd,[7] Au[8] and Cu[9] as catalysts which have detrimental effects in pharmaceutical applications. Thus, it would be desirable to develop transition metal-free, efficient and facile methodologies for their synthesis from readily available starting materials.



Scheme 1. Three typical drugs containing a benzothiophene moiety.

As early as 1985, the Zanardi group first reported the reaction of *o*-methylthioarendiazonium tetrafluoroborates with alkynes catalyzed by fresh copper or metal salts to achieve 2-benzothiophenes selectively.[10] In 2012, the König group reported a visible light photocatalytic synthesis of benzothiophenes catalyzed by eosin Y using similar reaction substrates.[11] Both reactions (Scheme 2a) employed rather reactive diazo compounds to generate aryl radicals and the reactions proceeded *via* a free radical route under mild conditions. However, the instability and commercially unavailability of the *o*-methylthioarendiazonium tetrafluoroborates largely limit its practicality. In recent decades, transition metal-free processes have been developed to construct biaryl



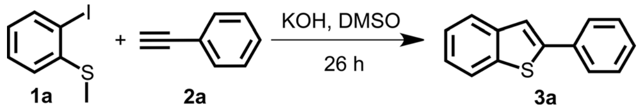
Scheme 2. Intermolecular cyclization reactions to construct the benzothiophene ring.

structures by utilizing a metal *tert*-butoxide, typically Bu-*t*-OK, as the key promoter.[12] In 2013, the Rossi group demonstrated that Bu-*t*-OK/DMSO is able to mediate biaryl formation under visible light irradiation.[13] Our group also described the synthesis of biaryls using a photosensitive complex of Bu-*t*-OK and nitrogenous heterocyclic ligands *via* visible light excitation.[14] It should be noted that these arylation reactions proceeded *via* a base-promoted aryl radical route in which aryl halides were successfully converted into the aryl radical intermediates. Hence, if terminal alkynes and commercially available 2-halothioanisoles instead of diazo compounds were used as the reaction substrates, we believed that an efficient visible light responsive system such as Bu-*t*-OK/DMSO could also promote the synthesis of 2-benzothiophenes in a similar aryl radical process.

Interestingly, the reaction of 2-iodothioanisole and phenylacetylene successfully gave the target 2-phenylbenzothiophene with a yield of 41% in the presence of Bu-*t*-OK/DMSO using visible light excitation (Scheme 2b). In an optimization of the reaction conditions, it was found that KOH/DMSO superbase can be used to prepare 2-phenylbenzothiophene in an unexpectedly high yield of up to 95% under visible light irradiation (Scheme 2c). Both Bu-*t*-OK/DMSO and KOH/DMSO are superbase systems which have been well studied by Trofimov.[15] The KOH/DMSO suspension is a two-phase equilibrium system and has outstanding performance as a promoter in synthetic chemistry.[16] However, most of KOH/DMSO superbase-promoted reactions proceeded under thermal conditions. Particularly, no example was found using visible light for the KOH/DMSO superbase-promoted reactions. For the first time, KOH/DMSO is used to promote the synthesis of benzothiophenes under visible light.

To explore the role of visible light in the cyclization reaction of 2-iodothioanisole and phenylacetylene using KOH/DMSO, a series of control experiments was conducted under visible light irradiation (Table 1 and Supporting Information, Figure S1). Under dark conditions, the above reaction gave 2-phenylbenzothiophene (**3a**) in only 13% yield at 25 °C (Table 1, entry 1), which was decreased greatly compared with the use of visible light irradiation (entry 15). This indicates that visible light irradiation should be essential to promote the reaction in high efficiency. To further study the effect of temperature on the reaction yield, a low temperature (~15 °C) under visible light irradiation was also used and the target product **3a** was obtained in 76% yield (entry 2). In the absence of visible light, the yield of **3a** increased with increasing reaction temperature, but only a 66% yield was obtained even at 120 °C (entries 3–7). Besides, the unwanted self-dimerization and self-trimerization of phenylacetylene appeared seriously during this heating process. From these results, it is evident that visible light irradiation plays a more significant role than temperature and promotes the formation of 2-phenylbenzothiophene in high efficiency under mild conditions when a thermal effect (at 25 °C) was partially involved in the cyclization reaction of 2-iodothioanisole and phenylacetylene. Upon irradiation of visible light with a shorter wavelength or a higher intensity, an improved yield of the desired product **3a** can be ob-

Table 1. Effects of the visible light-induced features on the reaction system.[a]



Entry	Wavelength [nm]	Irradiation intensity [mW·cm^{-2}]	*T* [°C]	Yield [%][b]
1	dark	0	25	13
2	420–780	1000	15	76
3	dark	0	40	18
4	dark	0	60	38
5	dark	0	80	56
6	dark	0	100	66
7	dark	0	120	66
8	420	100	25	43
9	450	100	25	36
10	500	100	25	32
11	420–780	200	25	39
12	420–780	400	25	51
13	420–780	600	25	60
14	420–780	800	25	70
15	420–780	1000	25	95

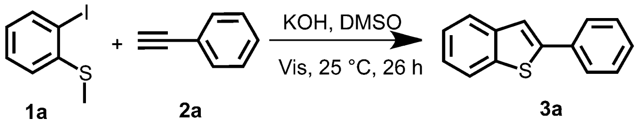
[a] *General reaction conditions:* **1a** (0.5 mmol), **2a** (6.5 equiv.), KOH (1.25 equiv.) and DMSO (2.0 mL) in a sealed tube under an N_2 atmosphere. The reaction time was 26 h and the reaction temperature was controlled by a circulation condensate device.

[b] Yields were determined by ^1H NMR analysis.

served (entries 8–15), suggesting that the cyclization reaction is a typical photoinduced reaction. When 2-iodothioanisole (brown liquid) was added into the KOH/DMSO (colorless) two-phase system, a new orange-red substance was formed at the solid-liquid interface. After the addition of 2-iodothioanisole, the UV-Vis spectrum of the mixed solution exhibited an absorption in the visible region (450 to 500 nm) (Supporting Information, Figure S2). This indicates a formation of a visible light-responsive complex intermediate between 2-iodothioanisole and KOH/DMSO.

Effects of different amounts of KOH and phenylacetylene, reaction time, different bases and solvents on the yield of **3a** were elucidated to optimize the reaction conditions. An increasing amount of KOH or phenylacetylene resulted in a growing yield of the desired product **3a** (Table 2, entries 2–8). When a mixture of 2-iodothioanisole (1.25 equivalents), phenylacetylene (6.5 equivalents) and DMSO (2 mL) was stirred for 26 h under visible light, 2-phenylbenzothiophene was obtained in almost quantitative yield (up to 95%) (Table 2, entry 1). It is found that the initial yield of 2-phenylbenzothiophene **3a** is maintained at a constant value of 30% from 2 h to 14 h and later accelerated up to 95% at 26 h (entries 9–12 and entry 1). This suggested the existence of an induction period in the cyclization reaction of 2-iodothioanisole and phenylacetylene, which is in accord with the common characteristics of radical reactions.[17] As a substitute for DMSO (entries 13–16), similar polar solvents such as CH_3CN and DMF could also promote the reaction in moderate yields while other solvents such as toluene, alcohol and tetrahydrofuran (THF) were not good. Also, other bases were screened to replace KOH. Similar to KOH, NaOH showed extremely high activity (94%) (entry 17). Given that NaOH is more readily subject to deliquescence than KOH, KOH is determined to be the optimal reaction promoter. Bu-*t*-OK could also afford the desired product in moderate yield (entry 18), but no obvious yield was observed for reaction employing K_2CO_3 (entry 19). KOH is indispensable in the cyclization reaction because no reactivity was found in the absence of KOH (entry 20).

Table 2. Optimization of the reaction conditions.[a]



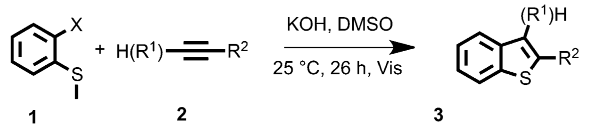
Entry	Reaction conditions	Yield [%][b]
1	standard conditions	95
2	KOH (0.308 equiv.)	67
3	KOH (0.625 equiv.)	86
4	**2a** (1.5 equiv.)	33
5	**2a** (2.5 equiv.)	56
6	**2a** (3.5 equiv.)	68
7	**2a** (4.5 equiv.)	76
8	**2a** (5.5 equiv.)	87
9	irradiation for 2 h	30
10	irradiation for 8 h	30
11	irradiation for 14 h	30
12	irradiation for 20 h	73
13	toluene in place of DMSO	5
14	CH_3CH_2OH or THF in place of DMSO	trace
15	CH_3CN in place of DMSO	38
16	DMF in place of DMSO	54
17	NaOH in place of KOH	94
18	Bu-*t*-OK in place of KOH	41
19	K_2CO_3 in place of KOH	trace
20	without KOH	trace

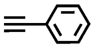
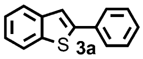
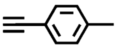
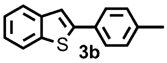
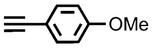
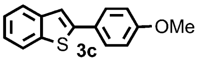
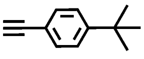
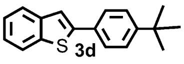
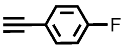
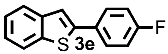
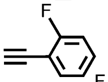
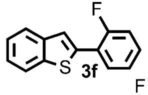
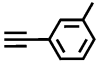
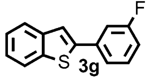
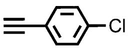
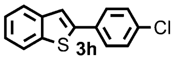
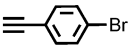
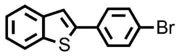
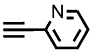
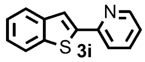
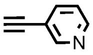
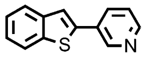
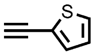
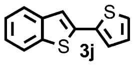
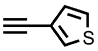
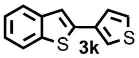
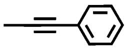
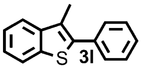
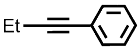
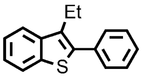
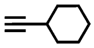
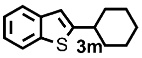
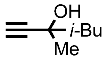
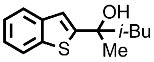
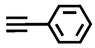
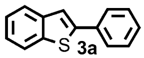
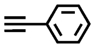
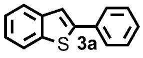
[a] *Standard reaction conditions:* **1a** (0.5 mmol), **2a** (6.5 equiv.), KOH (1.25 equiv.) and DMSO (2.0 mL) in a sealed tube under an N_2 atmosphere. The reaction was irradiated by xenon lamp ($420\ nm < \lambda < 780\ nm$, $1\ W\cdot cm^{-2}$) for 26 h and the reaction temperature was kept at 25 °C by means of a circulation condensate device.

[b] Yields were determined by ^1H NMR analysis.

Under the optimized conditions, the cyclization reactions of 2-halothioanisoles and various alkynes were examined to explore potential applications of this method (Table 3). The introduction of both electron-donating and electron-withdrawing groups into the phenyl ring of phenylacetylene afforded the corresponding products in moderate to good isolated yields (entries 2–7), except for 4-chlorophenylacetylene and 4-bromophenylacetylene with rather low yields (entries 8 and 9). For fluorophenylacetylene, the transformation is sensitive to steric effects, and the yield of the corresponding products for *o*-, *m*- and *p*-substituted substrates increased progressively (entries 5–7). Acetylenes containing heterocycles such as pyridyl and thienyl groups were found to be suitable substrates, resulting in the corresponding products in good isolated yields (entries 10–13), except for 3-ethynylpyridine (entry 11). In addition, non-terminal alkynes were tested, but the desired products were obtained in inferior yields, probably due to the steric hindrance of non-terminal alkynes (entries 14 and 15). Acetylenes bearing non-aromatic groups exhibited much lower yields (entries 16 and 17). It should be noted that the phenylacetylenes containing strong electron-withdrawing substituents such as formyl, nitro and cyano on the phenyl ring did not lead to the desired products at all. Compared to 2-iodothioanisole (**1a**), more inert 2-bromothioanisole (**1b**) and 2-chlorothioanisole (**1c**) could also provide 2-phenylbenzothiophene in 39% and 29% yield, respectively (entries 18 and 19). These above results indicate that the proposed method should exhibit good tolerance to a diverse range of functional groups, providing great potential in the synthesis of benzothiophene derivatives.

Table 3. Intermolecular cyclization of 2-halothioanisole and alkynes.[a]



Entry	Alkyne	Product	Yield [%][b]
1		 3a	73
2		 3b	61
3		 3c OMe	45
4		 3d	59
5		 3e	63
6		 3f	20
7		 3g	59
8		 3h	8
9[c]			<5
10		 3i	67
11[c]			<5
12		 3j	42
13		 3k	61
14		 3l	9
15[c]			trace
16		 3m	15
17[c]			<5
18[d]		 3a	39
19[e]		 3a	29

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[a] *General reaction conditions:* X = I, **1** = **1a** (0.5 mmol), **2** (6.5 equiv.), KOH (1.25 equiv.) and DMSO (2.0 mL) in a sealed tube under an N_2 atmosphere. The reaction was irradiated by xenon lamp ($420\,nm < \lambda < 780\,nm$, $1\,W\cdot cm^{-2}$) for 26 h and the reaction temperature was kept at 25 °C by means of a circulation condensate device.

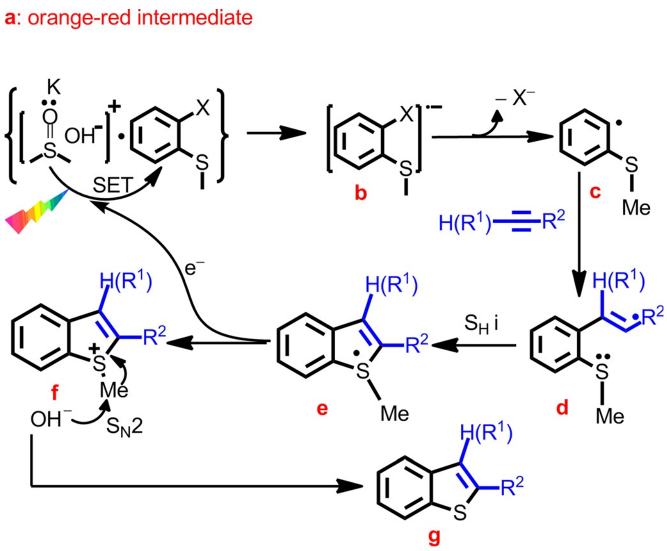
[b] Isolated yield by SiO_2 column chromatography.

[c] Detected by GC-MS.

[d] **1** = **1b**, X = Br.

[e] **1** = **1c**, X = Cl.

Based on our experimental results and previous reports,[10,11,13] we think that the KOH/DMSO-promoted cyclization reaction of 2-halothioanisoles and alkynes is a radical chain reaction (Scheme 3) that was initiated by a visible-light responsive single electron transfer (SET) process. It is evident that the addition of a typical radical scavenger TEMPO (2,2,6,6-tetramethylpiperidine 1-oxyl) or electron acceptor BQ (benzoquinone) inhibited the reaction to a large extent (Supporting Information, Table S1). The new orange-red complex (**a**) at the solid-liquid interface results from the interaction of KOH/DMSO superbase and 2-halothioanisole, which is visible-light responsive. Under visible light irradiation, KOH/DMSO superbase can transfer a single electron to 2-halothioanisole (SET process) to produce the corresponding aryl radical anion (**b**) which is prone to dissociate into an aryl radical (**c**) and a halogen anion. With the utility of *N-tert*-butyl-α-phenylnitrone (PBN) as the trapping agent, the electron spin resonance (ESR) spectrum of the irradiated orange-red mixture shows a typical triplet of doublets with the hyperfine splitting constants of about $\alpha_N = 13.7$ and $\alpha_H = 4.0$ (Figure 1) that can be assigned to the aryl radical-PBN adduct.[18] Also, the generation of I^- was confirmed by the high-resolution mass spectrum of the irradiated solution of KOH/DMSO and 2-iodothioanisole (Supporting Information, Figure S3). So it is reasonable that 2-iodothioanisole receives a single electron from KOH/DMSO. The addition reaction of aryl radical (**c**) with alkyne generates vinyl radical (**d**) which undergoes intramolecular homolytic substitution (S_Hi process) to give the sulfuranyl radical (**e**). After the radical (**e**) offers a single electron back to KOH/DMSO, the electron transfer cycle is accomplished while cation (**f**) is formed. Finally, cation (**f**) loses a methyl cation in a bimolecular



Scheme 3. Conceivable radical reaction pathway.

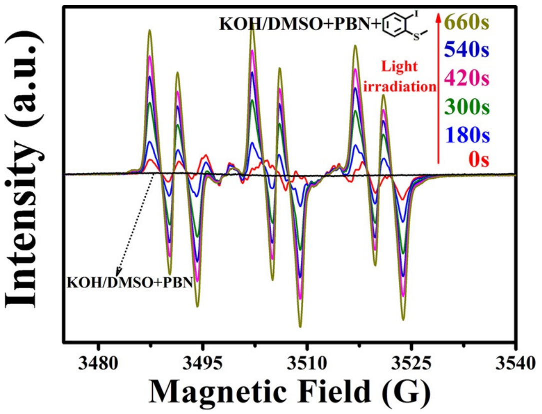


Figure 1. ESR spectra recorded at different light irradiation times for the solution of KOH/DMSO, PBN and 2-iodothioanisole.

nucleophilic substitution (S_N2 process) in the presence of OH^- to afford the benzothiophene derivative (**g**).

It is well known that KOH/DMSO is a superbase with its pK_a at 30–32, which has the ability to dehydrohalogenate aryl halides for the formation of aryne intermediates.[16i,j] If the cyclization reaction proceeds *via* the aryne mechanism, the reaction using 3-bromothioanisole as the substrate should also go as well as that using 2-iodothioanisole because the same aryne intermediate could be generated in both KOH/DMSO superbase-promoted reactions and then it is added to phenylacetylene to produce 2-phenylbenzothiophene. Instead, no 2-phenylbenzothiophene was found with use of 3-bromothioanisole (Supporting Information, Scheme S1). The aryne mechanism could thus be preliminarily excluded.

In conclusion, we have developed a novel route for the transition metal-free synthesis of 2-benzothiophenes using KOH/DMSO superbase under visible light irradiation. This reaction not only can use commercially available 2-halothioanisole to replace diazonium salts as substrates, but also provides good yields and high regioselectivity for the desired benzothiophene derivatives. An aryl radical pathway induced by a visible light-driven SET process is involved in the cyclization of 2-halothioanisole and alkynes. This inexpensive and environment-friendly KOH/DMSO system displays good functional group tolerance and stable reaction activity, and provides a facile and efficient access to the synthesis of benzothiophene derivatives.

Experimental Section

General Remarks

All reagents and solvents are commercially available and were used without further purification. All reactions were carried out in dry tube reactors under an N_2 atmosphere protection with a circulating cooling device to maintain a constant temperature. The visible light ($\lambda > 420$ nm) irradiation upon the tube reactor was provided by a 300 W xenon lamp (PLS-SXE300C, Beijing Perfect Light Co.) equipped with an IR-cutoff filter ($\lambda < 780$ nm). The irradiance spectrum and incident light energy on the suspension were measured with a spectroradiometer (International Light Technologies Model ILT950). The illuminated area was estimated to be about 1 cm^2 corresponding to the cross-section of the columned tube. The resulting mixture after being stirred for a certain time was preliminarily analyzed by GC-MS (Hewlett–Packard HP 5973) with the injection temperature at 350 °C and a flame ionization detector using an HP-5 5% phenyl methyl siloxane column (30 m × 0.32 mm × 0.5 μm). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer and Bruker Avance 75 MHz spectrometer, respectively, in $CDCl_3$ solution using TMS or solvent signal peak as a standard. Visualization was performed with single wavelength ultra-violet light ($\lambda = 240$ nm or 365 nm). The electron spin resonance (ESR) experiments were conducted according to the following procedures. All chemicals were first thoroughly mixed and then the liquid portion was sucked by a capillary tube. One end of it was plugged with plasticine and the capillary tube was then placed into a quartz tube and sealed. All these procedures were performed in an N_2-filled glovebox. The quartz tube was irradiated with a xenon lamp and the spectra were recorded *in situ* with a Bruker A300 operating in the X-band at room temperature.

Typical Procedure for Photoreactions

The addition of reagents was accomplished in the N_2-filled glovebox. The reaction was carried out in a 10-mL glass tube reactor with a magnetic stirrer and KOH (1.25 equivalents, pulverized), 2-halothioanisole (1 equivalent) and alkyne (6.5 equivalent) were mixed in dry DMSO (2 mL). The tube reactor was sealed and immersed in a transparent vessel with jacket connected to a circulating cooling water source controlled by a thermostatic apparatus (maintaining the temperature at 25 °C), and then was irradiated with visible light at a certain light intensity. After 26 h of irradiation, the reaction mixture was quenched by 1 M aqueous HCl and extracted with diethyl ether. The organic layer was washed with saturated aqueous NaCl (3 × 25 mL) and the aqueous layer was washed with diethyl ether (3 × 25 mL). The organic layers were combined, dried over Na_2SO_4 and concentrated under vacuum distillation. The ^{1}H NMR yield was determined by using pyrazine as an internal with its single signal peak at 8.61 ppm in $CDCl_3$. The crude products were purified by SiO_2 column chromatography using petroleum ether as an eluent to finally obtain white solids benzo[*b*]thiophene derivatives.

Typical Procedure for Thermal Reactions

The procedures for thermal reactions of 2-iodothioanisole and phenylacetylene and the separation of the products are similar to those for the photoreactions while the reaction temperature was controlled by a heating jacket.

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