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AIBN-Promoted Synthesis of Bibenzo[*b*][1,4]thiazines by the Condensation of 2,2′-Dithiodianiline with Methyl Aryl Ketones

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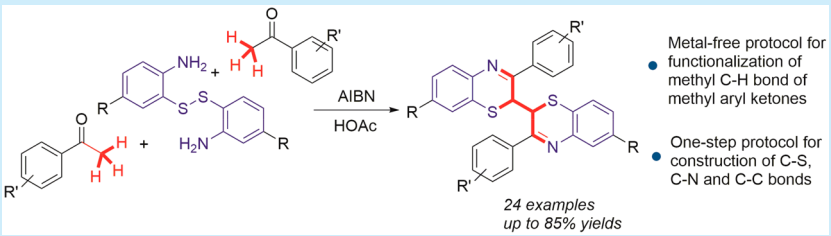
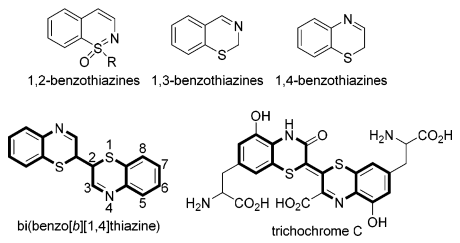
Supporting Information



ABSTRACT: A series of bibenzo[*b*][1,4]thiazines with various functional groups has been synthesized by a free-radical condensation reaction. Bibenzo[*b*][1,4]thiazines were obtained in moderate to good yield (up to 85%) through a one-step reaction of readily available 2,2′-dithiodianiline and methyl aryl ketones with AIBN as radical initiator in HOAc. Bibenzo[*b*][1,4]thiazines exhibit diversiform solid-state packing.

Benzothiazines are a class of heterocyclic compounds containing both nitrogen and sulfur in the six-membered thiazine ring, including benzo[*b*][1,2]thiazines,[1] benzo[*b*][1,3]-thiazines,[2] and benzo[*b*][1,4]thiazines[3] (Scheme 1). With their unique structure, benzo[*b*][1,4]thiazine derivatives have stimulated considerable interest in recent years due to their remarkable biological and pharmaceutical activities, such as antimalarial activity,[4] antimicrobial agents,[5] nervous system depressants,[6] anticancer properties,[7] and antagonists.[8] Additionally, benzo[*b*][1,4]thiazine is the major structural components of trichochrome C (Scheme 1) and more complex pheomelain pigments found in red hairs and feathers.[9] Recently, benzo[*b*][1,4]thiazines containing chromogenic systems have also been used to the visual detection of peroxides and proton switched "OR" logic gate.[10]

Scheme 1. Structure of Benzo[*b*]thiazines and Related Compounds



The earliest synthesis of benzo[*b*][1,4]thiazines was reported by Unger in the late 19th century.[11] Later on, it was found that the actual structure is bibenzo[*b*][1,4]thiazine due to the high instability of 2*H*-benzo[*b*][1,4]thiazine.[12] In light of the potential biological and dye chemistry applications, several synthesis methods of bibenzo[*b*][1,4]thiazine have been developed, including oxidative coupling of 3-phenyl-2*H*-1,4-benzothiazine with highly explosive picric acid under reflux,[10,13] anodic oxidation with low yield,[14] and the condensation of 2-aminothiophenol with 3-phenyl-5(4*H*)-isoxazolone,[15] α,α-dibromoacetophenone,[16] or 1,2-diaroylacetylene with silica-supported perchloric acid.[17] To the best of our knowledge, the synthesize of bibenzo[*b*][1,4]thiazine derivatives with readily available precursors is seldom reported. Herein, we report a serendipitously discovered method by an AIBN-promoted radical coupling of 2,2′-dithiodianiline with methyl aryl ketones.

The unexpected reaction was discovered while we were attempting the synthesis of a series of 2,2′-dithiodianiline-based Schiff base ligands. When 2,2′-dithiodianiline (**1a**, 1 equiv) was condensed with acetophenone (**2a**, 2.1 equiv) in HOAc (2 mL) at 80 °C, the target Schiff base was not obtained. Instead,

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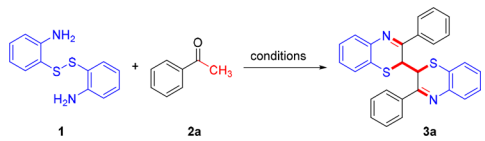
bibenzothiazine **3a** was isolated in 8% yield with most of the starting materials recovered (Table 1, entry 1). Inspired by a recently reported radical synthesis of benzo[*b*][1,4]thiazine[3g] and a widely used phenylthio radical precursor diphenyl disulfide/azobisisobutyronitrile (AIBN) system,[18] we hypothesized that this reaction might be promoted by radical initiators. Luckily, a simple addition of 5 mol % of AIBN as radical initiator improves the yield of **3a** to 42% while other conditions remain unchanged (Table 1, entry 2).

Table 1. Optimization of the Reaction Conditions[a,b]



1 2a 3a

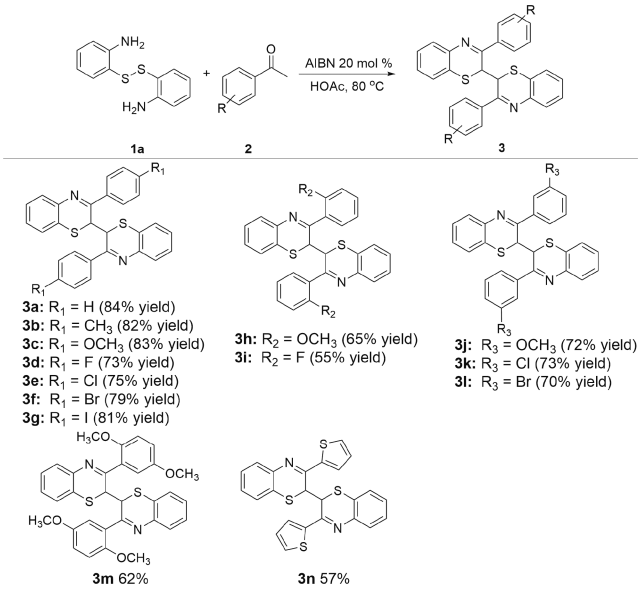
entry	catalyst (mol %)	time (h)	temp (°C)	yield[b] (%)
1		24	80	8
2	AIBN (5)	24	80	42
3	TBHP (5)	24	80	23
4	DDQ (5)	24	80	30
5	I_2 (5)	24	80	7
6	AIBN (10)	24	80	61[c]
7	AIBN (10)	24	80	58
8	AIBN (20)	24	80	84
9	AIBN (30)	24	80	81
10	AIBN (20)	24	40	57
11	AIBN (20)	24	100	76
12	AIBN (20)	18	80	80
13	AIBN (20)	24	80	82[d]
14	AIBN (20)	28	80	84

[a]Reaction condition: **1a** (0.25 mmol), **2a** (0.525 mmol), solvent (2 mL), 80 °C, 24 h. [b]Isolated yield based on **1a**. [c]The product is 2,2′-dithiodianilinium trifluoroacetate using CF_3CO_2H as solvent. [d]In the dark.

Since a radical initiator could dramatically increase the yield, we screened a series of other radical initiators, such as *tert*-butyl hydroperoxide (TBHP),[19] 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ),[20] and I_2.[21] It turns out that I_2 barely promotes this reaction, and TBHP and DDQ are less effective than AIBN (Table 1, entries 3−5). Metal ions have been shown to influence the synthesis of bibenzo[*b*][1,4]thiazine pigments in vitro and in vivo.[8b] We study the effect of inorganic copper salts as potential co-catalysts. However, in the presence of copper salts with a different counteranions, this reaction was almost completely inhibited (Table S1, entries 1−3). With AIBN as the best radical promoter, a variety of solvents such as chlorobenzene, ethanol, toluene, and *p*-xylene were further screened, and no reaction took place in these solvent systems (Table S1, entries 4−8). When CF_3CO_2H was employed as solvent, only 2,2′-dithiodianilinium trifluoroacetate was obtained in moderate yield (Table 1, entry 6, see the Supporting Information (SI) for its crystal structure[22]). Further optimization was carried out with the use of various amounts of AIBN (Table 1, entries 1 and 7−9), and we were glad to find that increasing the amount of AIBN from 5 to 20 mol % almost doubled the yield of **3a** (84% based on **1a**); however, the yield of **3a** is not further increased when the amount of AIBN is over 20 mol %. Next, we evaluated a range of different temperatures (Table 1, entries 8, 10, and 11) and found that 80 °C was the optimum temperature. In addition, this reaction is not light sensitive, and the yield is nearly the same under dark (Table 1, entry 13). Prolonging the reaction time to 28 h did not improve the yield (Table 1, entry 14). Ultimately, the optimized reaction conditions is **1a** (1 equiv), **2a** (2.1 equiv) and AIBN (20 mol %) in the HOAc (2 mL) at 80 °C for 24 h.

With the optimized reaction conditions in hand, the scope of this reaction was next explored, and the results are summarized in Scheme 2. First, various functional groups (−CH_3, −F, −Cl, −Br, −I) on the *para*-position of the benzene ring were examined. *p*-Methyl- or methoxy-substituted phenyl rings lead to the desired products (Scheme 2, **3b** and **3c**) in similar yields as for **3a**. The yields of **3d−g** with halogen on the *para*-position of acetophenones are slightly increased from 73 to 81% by when the substituents are changed from fluoro-, chloro-, bromo-, to iodo- (Scheme 2, **3d−g**). In addition, sterically hindered 2-methoxyacetophenone gives a lower yield compared to its *meta*- or *para*- counterparts **3j** and **3c**. Acetophenones with a halogen on the *ortho*- or *meta*-position are also successfully converted to the corresponding bibenzothiazines (Scheme 2, **3i**, **3k**, and **3l**). Furthermore, the dimethoxy-substituted acetophenone also yields the corresponding product **3m** in moderate yield (62%). Finally, 2-acetylthiophene[23] is chosen as a representative of heterocyclic ketones to further expand the substrate scope, and it worked smoothly under the standard conditions (Scheme 2, **3n**, 57% yield).

Scheme 2. Exploration of Substrate Scope of Methyl Aryl Ketones[a,b]



1a 2 3

[a]Reaction conditions: **1a** (0.25 mmol), **2** (0.525 mmol), AIBN (20 mol %), HOAc (2 mL) at 80 °C for 24 h. [b]Isolated yields.

The scope of this reaction was further explored by substituted dithiodianiline[24] with a different substituted acetophenone (Scheme 3). Dithiodianiline with the electron-withdrawing Cl− group or electron-donating Me− and MeO− groups could successfully condensate with acetophenones bearing *para*-substituted Me−, MeO−, Cl−, Br−, and I−. However, Cl-substituted dithiodianiline gives a slightly lower yield compared to its nonchloride counterparts.

Furthermore, we explored the gram-scale synthesis of compound **3a**. Gram-scale synthesis was successfully achieved (1.84 g of **3a**) with compromised yield (82%). Additionally,

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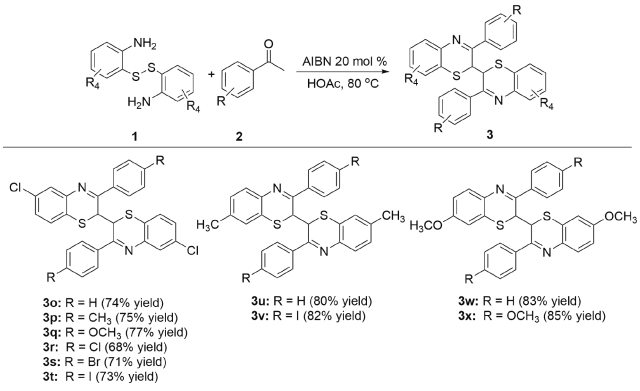
Scheme 3. Exploration of Substrate Scope of Dithiodianiline[a,b]



[a]Reaction conditions: **1** (0.25 mmol), **2** (0.525 mmol), AIBN (20 mol %), HOAc (2 mL) at 80 °C for 24 h. [b]Isolated yields.

halogenated arenes are important organic intermediates for the synthesis of useful compounds through the transition-metal-catalyzed cross-coupling reactions.[25] As an example, compound **3g** is coupled with phenylboronic acid by Suzuki−Miyaura reaction in 91% yield (SI).

The structures of bibenzothiazines were unambiguously confirmed by ^{1}H NMR, ^{13}C NMR, HRMS, and single-crystal X-ray diffraction analysis. All synthesized bibenzothiazines are mesomers with one set of proton or carbon signals appearing in their ^{1}H NMR or ^{13}C NMR. Protons attached to the newly formed C−C bond are singlets at around 4.0 ppm. As for compounds **3a−d**, **3h**, and **3n**, single crystals were grown and exhibit a similar core structure[22] (Figure 1 and SI). Their

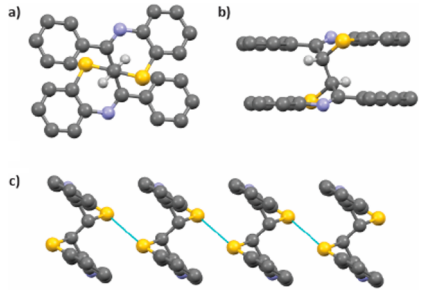


Figure 1. Crystal structure and solid-state packing of compound **3a**: (a) top view; (b) side view; (c) sulfur involved noncovalent interaction are shown in green lines.

single-crystal structures also show central symmetry with a staggered central carbon−carbon single bond, which agrees with their ^{1}H NMR and ^{13}C NMR analysis. Two benzothiazine units are linked by the newly formed C(2)−C(2′) single bond. The C(2)−C(2′) single bond in the fluoride-substituted compound **3d** is 1.569 Å, which the longest compared with the electron-donating substituted compounds, such as Me− and MeO− (1.532−1.544 Å). The angle of S(1)−C(2)−C(3) in the dihydrothiazine ring is quite similar, ranging from 106.35 to 108.16°. Because of the central symmetry in bibenzothiazines, the dihedral angle of S(1)−C(2)−C(2′)−S(1′) is 180° in all of the crystal structures, which avoids steric hindrance between two benzothiazines (Figure 1). Interestingly, the solid-state packing is very sensitive to the substituents. In compound **3a**, a one-dimensional molecular chain is formed by a double S···S interaction (3.527 Å) and 4-fold weak S···π interaction (3.486 Å). These chains are parallel to the *a*-axis and held together by C−H···N hydrogen bonding (2.718 Å), forming a herringbone structure. Compound **3b** forms a 4-fold C−H···S interaction (2.918 Å) with the surrounding molecules. Compound **3d** also forms a one-dimensional chain with a different molecular arrangement by 4-fold C−H···F hydrogen bonding (2.592 Å), and C−H···N bonds (2.692 Å) are formed between chains. For compounds **3c** and **3h**, the methoxyl group makes the solid-state assembly much more complex with multiple C−H···O, C−H···π, and π···π interactions. In compound **3h**, there is a 2D molecule layer form in the *bc* plane by 4-fold C−H···O (2.629 Å), C−H···π (2.864 Å), and double π···π (3.344 Å) between adjacent molecules. As in compound **3n**, an alternative brickwall layer is formed by the π···π interaction (3.302 Å) view along the *c*-axis, and different layers are packed together by C−H···N interactions (2.681 Å).

To gain insight into the mechanism of this reaction, three control experiments were designed and monitored by gas chromatography/mass spectrometer (GC−MS). First, 2,2,6,6-tetramethylpiperidin-1-oxy radical (TEMPO) was added to the reaction mixture to probe the radical nature of this reaction. As AIBN generates a large amount of isobutyronitrile radical during the reaction, we first chose the initial reaction conditions without AIBN as our model system. Without the addition of TEMPO, we observed imine **5**, benzothiazole **7a** and **7b**,[26] and 2*H*-1,4-benzothiazine **10** along with the starting materials (Figures S54−S58). Upon addition of 4.0 equiv of TEMPO, trapping product **11** was captured and intermediate **10** was oxidized by TEMPO to give compound **12** (Figures S59−S61). When the amount of TEMPO was increased to 10 equiv, the reaction was completely inhibited without detection of **10**. Second, oxygen plays an important role in the coupling of **10**.[10,12] When the reaction mixture was thoroughly degassed by freeze−pump−thaw cycles, the reaction was stopped at intermediate **10**. Intermediate **10** can be quantitatively converted to **3a** under our standard reaction conditions. Interestingly, the amount of oxygen needed by the dehydrogenation process could be provided by the oxygen dissolved in the solvent, which prevents overoxidation.[27] Finally, deuterated acetophenone was further employed to probe the reaction mechanism; we could observe the formation of deuterated **7a**, **7b**, and **10**, which provides additional evidence for paths A and B (Figures S62−S67).

Although the detailed mechanism of this condensation remains to be elucidated, a tentative mechanism is proposed (Scheme 4). Dithiodianiline **1a** could homolytic fission under heat to generate thiyl radical **4**, which was reversibly condensated with ketone **2a** to afford imine **5**. The thiyl radical in imine **5** could attack imine carbon through path A to give benzothiaole **7a** and **7b** in a trace amount. In path B, after tautomerization of imine **5**, the addition of thiyl radical to enamine could give intermediate **9**, which lost a hydrogen atom with the help of isobutyronitrile radical to generate key intermediate **10**. Finally, intermediate **10** could homocoupled to bibenzo[*b*][1,4]thiazine **3a**.[10]

In summary, we have developed an AIBN-mediated cascade condensation and radical-coupling strategy for the preparation of various 3,3′-bisarylbibenzo[*b*][1,4]thiazines involving multiple bond formation. This process could be easily scaled to gram-scale and is practical for the preparation of potential biologically and pharmaceutically useful organic compounds. Bisarylbibenzo[*b*][1,4]thiazine derivatives exhibit various solid-

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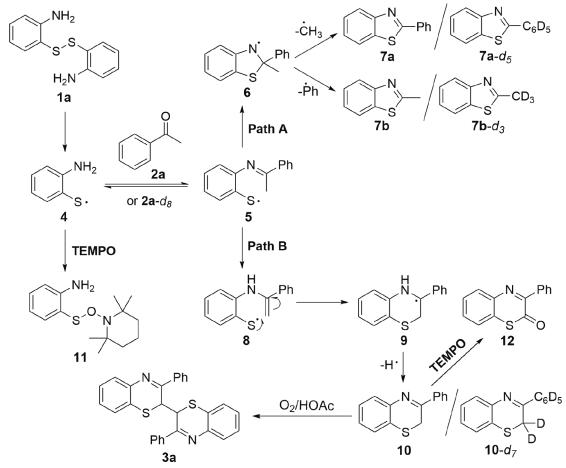
Scheme 4. Plausible Mechanism for the Formation of 3a



state assemblies, which were affected by subtle functional group difference.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b01238.

Full experimental procedures, characterization data, and NMR spectra (PDF)

Accession Codes

CCDC 1540959−1540965 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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