

Article

Efficient Synthesis of Eight-Membered Cyclic Diaryl Sulfides via an Aryne Reaction with 2-Methylenebenzothiophene-3-Ones

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Abstract: In this study, we develop a concise and efficient synthetic strategy for the construction of eight-membered cyclic diaryl sulfides by undertaking [3+2] cycloaddition, 1,2-hydrogen shift, and C(sp²)-S bond cleavage steps on 2-methylenebenzothiophene-3-ones with aryne, using TBAT as the fluorine source. This transformation proceeds well under mild conditions and affords the target products in high to excellent yields (up to 93% yields). The process provides a practical route to achieving sulfur-containing medium-sized heterocycles.

Keywords: aryne; [3+2] cycloaddition; eight-membered cyclic diaryl sulfides; 2-methylenebenzothiophene-3-ones

1. Introduction

Sulfur-containing heterocycles are prominent structural motifs, which constitute the core structure of a significant number of natural products [1–5], pharmaceuticals [6–11], functional materials [12–17], and active biological molecules [18–22]. For instance, as shown in Scheme 1, diltiazem (calcium channel blocker) is used in the treatment of hypertension and angina [23,24]. Raloxifene is a widely recognized therapeutic agent for the treatment of osteoporosis [25]; Zaltoprofen is a non-steroidal anti-inflammatory drug [26–28]; and DNTT is a well-known organic thin-film transistor [29,30]. Additionally, thiolactomycin exhibits interesting antibacterial activity [31–33]. Compound A was found to be an effective inhibitor of stomach secretion [34], compound B showed anti-tumor activity [35], and compound C exhibited anti-ischemic activity [36]. As a result, many efforts have been devoted to the construction of sulfur-containing heterocycles [37–52]. Notably, there has been far less research focused on efficient methods for the synthesis of sulfur-containing benzo-fused eight-membered heterocycles. Likely due to unfavorable entropic and enthalpic constraints [53,54], the construction of these eight-membered heterocycles is a challenge.

A survey of the relevant literature revealed that only several very limited examples have been reported. In 1987, Hellwinkel reported the connection of the head and tail of a sulfide using Dieckmann cyclization for the synthesis of benzo-fused eight-membered cyclic sulfides [55]. Biehl reported the synthesis of benzene-fused eight-membered rings containing nitrogen and sulfur via a benzyne ring closure reaction [56]. Foubelo reported the cyclisation of sulfanyl alcohol under acidic conditions to yield the eight-membered sulfur-containing heterocycle [57]. Jiang reported straightforward protocols for diarylannulated sulfide construction through S-I exchange [58,59]. Asai reported using the thio-alkylation of thiosalicylic acid and then intramolecular Friedel–Crafts acylation to synthesize diaryl sulfide [60]. In 2019, Chen's and Meng's groups reported the construction



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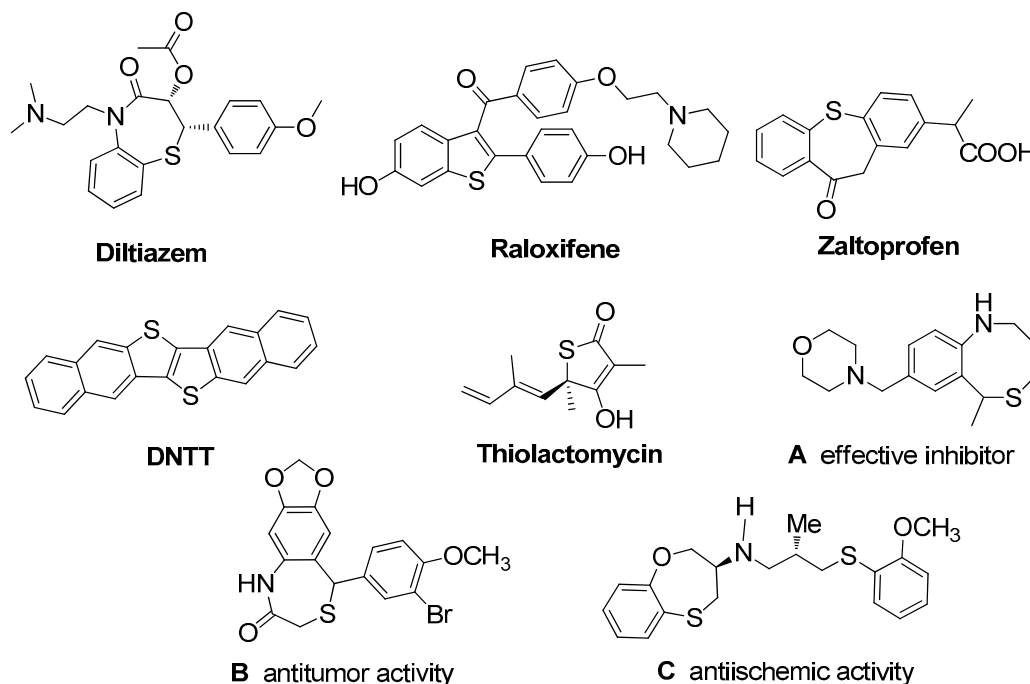
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of benzo-fused eight-membered cyclic sulfides via the domino reaction of arynes and methylenebenzothiopheneones with CsF as the fluorine source [61,62]. When unsubstituted methylenebenzothiopheneone reacted with an unsubstituted aryne precursor, only a 31% yield was obtained. In other cases, there is no substrate scope of the reaction with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate as the benzyne precursor. Reddy reported using copper (I)-catalyzed interrupted click-sulfonylation of *O*-/*N*-propargyl benzyl thiosulfonates with organic azides to construct triazole-fused eight-membered heterocycles [63]. Despite some efforts made in the past, the synthetic chemistry of sulfur-containing benzo-fused eight-membered heterocycles still suffers from considerable limitations, such as low yields and narrow substrate scope.



Scheme 1. Representative examples of sulfur-containing heterocycles.

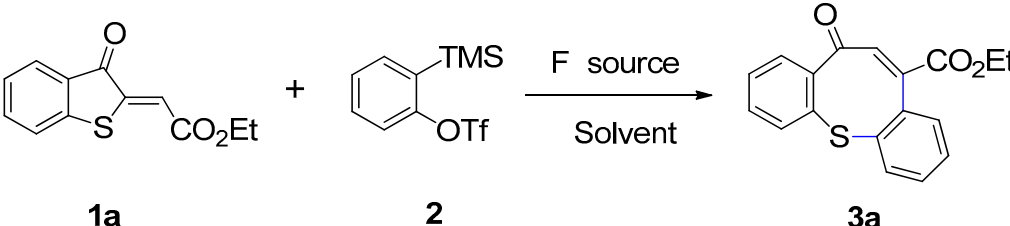
Considering the importance of eight-membered cyclic diaryl sulfides, we here report undertaking the [3+2] cycloaddition, 1,2-hydrogen shift and C(sp²)-S bond cleavage of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate and 2-methylenebenzothiophene-3-ones with TBAT as fluorine source for the preparation of eight-membered cyclic diaryl sulfides.

2. Results and Discussion

In our initial attempts, we commenced with the reaction of 2-methylenebenzothiophene-3-one (**1a**) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (unsubstituted aryne precursor) (**2**) for the exploration of the optimal reaction conditions. As shown in Table 1, first, the reaction was conducted with CsF as the fluorine source in ethyl acetate at 30 °C. Regrettably, only a trace amount of the anticipated product (**3a**) was obtained (Table 1, entry 1). Various solvents were screened (Table 1, entries 2–7). Similarly, only a trace amount of desired product (**3a**) was generated with THF, CH₂Cl₂, and EtOH (Table 1, entries 2–4). When the solvent was toluene, the desired product (**3a**) was not obtained (Table 1, entry 5). Fortunately, a significant improvement was noted when acetone was used as the solvent, resulting in 33% yield of the product (Table 1, entry 6). Further experimentation revealed that CH₃CN was an optimal solvent, affording a 52% yield (Table 1, entry 7). Subsequently, the screening of different fluorine sources for the reaction was carried out. A yield of only 16% was generated when using KF as fluorine source (Table 1, entry 8). When using NaF

or TBAF, trace amounts of the desired product (**3a**) were obtained (Table 1, entries 9 and 10). Gratifyingly, when TBAT was employed as the fluorine source, a remarkable 92% yield of product **3a** was achieved (Table 1, entry 11). The effect of the additive 18-crown-6 was also evaluated, and the yield of **3a** was substantially reduced to 73% (Table 1, entry 12). Then, further evaluations of the effect of temperature revealed that, when the reaction was carried out at 60 °C, no distinct change was detected (91% yield, Table 1, entry 15). At other temperatures, the reaction decreased yields (77% and 84% yields, Table 1, entries 13 and 14). Finally, the equivalent of TBAT was screened. Further increases in the equivalence of TBAT and **2** did not improve the yield of **3a** (Table 1, entries 16 and 17).

Table 1. Optimization of the reaction conditions ^a.

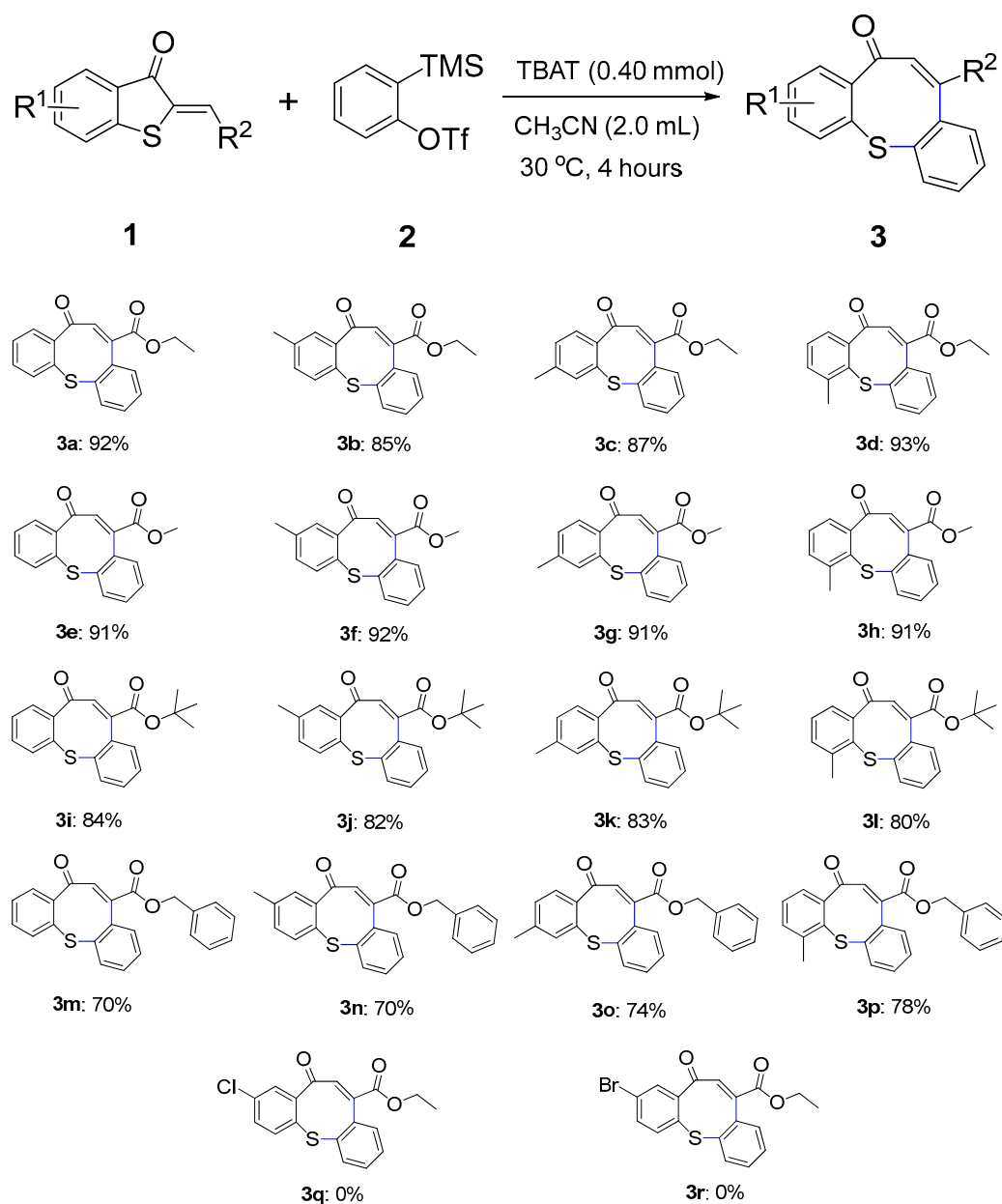
				
1a	2	3a		
Entry	Solvent	F Source	T (°C)	Yield (%) ^b
1	EtOAc	CsF	30	Trace
2	THF	CsF	30	Trace
3	CH ₂ Cl ₂	CsF	30	Trace
4	EtOH	CsF	30	Trace
5	Toluene	CsF	30	N.R. ^c
6	Acetone	CsF	30	33
7	CH ₃ CN	CsF	30	52
8	CH ₃ CN	KF	30	16
9	CH ₃ CN	NaF	30	Trace
10	CH ₃ CN	TBAF	30	Trace
11	CH ₃ CN	TBAT	30	92
12 ^d	CH ₃ CN	TBAT	30	73
13	CH ₃ CN	TBAT	40	77
14	CH ₃ CN	TBAT	50	84
15	CH ₃ CN	TBAT	60	91
16 ^e	CH ₃ CN	TBAT	30	92
17 ^f	CH ₃ CN	TBAT	30	87

^a Unless otherwise noted, the reaction was carried out with **1a** (0.05 mmol), **2** (0.10 mmol, 2.0 equiv.) and the fluorine source (0.10 mmol, 2.0 equiv.) in a solvent (0.50 mL) at the indicated temperature for 4 h. ^b Isolated yield after flash chromatography on silica gel. ^c N.R. = no reaction. ^d 2.0 equiv. of 18-crown-6 was added. ^e 3.0 equiv. of TBAT and 3.0 equiv. of **2** were used. ^f 4.0 equiv. of TBAT and 4.0 equiv. of **2** were used. THF = tetrahydrofuran. TBAT = tetrabutylammonium difluorotriphenylsilicate. TBAF = tetrabutylammonium fluoride.

Thus, the optimal reaction conditions were found to be 1.0 equiv. of 2-methylenebenzothiophene-3-one **1a**, 2.0 equiv. of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2**, and 2.0 equiv. of TBAT in 0.5 mL of CH₃CN at 30 °C for 4 h.

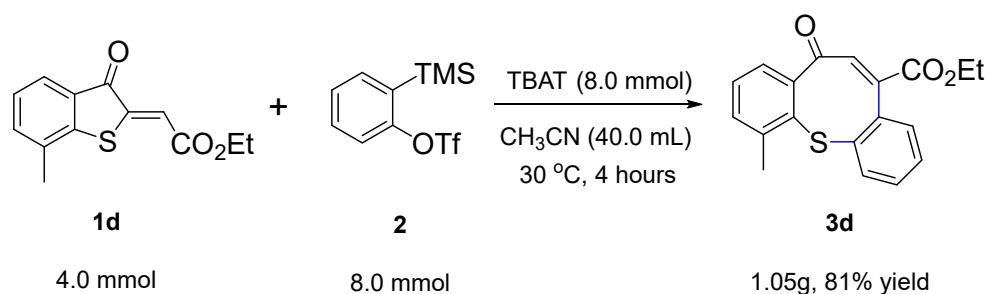
With the optimal reaction conditions established, we further explored the substrate range of 2-methylenebenzothiophene-3-ones **1** (Scheme 2). First, we investigated the substrates with R² = CO₂Et. When the methyl group was substituted at the C5 or C6 positions, the corresponding products **3b** and **3c** were obtained in 85% and 87% yields, respectively. Product **3d** was obtained in 93% yield when the methyl substitution was located at the C7 position. Next, when the R² group of substrate **1** was changed from CO₂Et to CO₂Me, substrates that had a C5-, C6-, or C7-substituent phenyl ring with a methyl group were also subjected to general reaction conditions, producing the compounds **3e–3h** in excellent yields (91–92% yields). When the ester moiety of substrate **1** changes to sterically hindered CO₂^tBu, the reaction of the substrate-bearing methyl group at the

C5–C7 positions of the phenyl ring resulted in 80–84% yields of products **3i–3l**. In addition, substrates with benzyl on the ester moiety were well tolerated and afforded products **3m–3p** in high yields (70–78% yields). Unfortunately, when the substituents on the benzene ring were electron-withdrawing groups (Cl or Br), the desired products could not be generated.



Scheme 2. Substrate scope for the domino reaction between various 2-methylenebenzothiophene-3-ones **1** and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2**. Reaction conditions: **1** (0.20 mmol), **2** (0.40 mmol), and TBAT (0.40 mmol) in CH₃CN (2.0 mL) at 30 °C; isolated yields.

Furthermore, to demonstrate the applicability of this reaction, we carried out a gram-scale experiment under optimized conditions. As shown in Scheme 3, when using 4.0 mmol (0.99 g) of methylenebenzothiophene-one **1d** for cycloaddition, the reaction still proceeded well, producing **3d** with a yield of 81% (1.05 g).



Scheme 3. Scale-up reaction.

3. Conclusions

In summary, a variety of eight-membered cyclic diaryl sulfides were effectively synthesized. Utilizing TBAT as the fluorine source, the [3+2] cycloaddition of 2-methylenebenzothiophene-3-ones with aryne, following a 1,2-hydrogen shift and C-S bond cleavage, proceeded smoothly to afford the target products in high to excellent yields (70–93% yields). The reaction could be conducted on a gram scale. Our laboratory is undertaking further investigations of the potential of using arynes to construct sulfur-containing heterocycles.

4. Materials and Methods

The ^1H and ^{13}C NMR spectra of all compounds were recorded on a Bruker 400 advance III spectrometer (^1H = 400 MHz and ^{13}C = 101 MHz) (Bruker corporation) at room temperature (25 $^\circ\text{C}$) using CDCl_3 (Adamas-Beta, Shanghai, China) as the solvent. The processing of NMR spectra was performed using *MestReNova* Software (version 14.2.1-27684; Mestrelab Research, 2021). The chemical shifts were recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), coupling constants (Hz), and integration. The melting points were determined using Melting-Point Apparatus (HUAZHI HMX-1B, Fujian, China). HRMS data were acquired using a Thermo Scientific Q Exactive Plus Quadrupole-Orbitrap mass spectrometer (Thermo Fisher Scientific, Bremen, Germany) equipped with a Heated Electrospray Ionization (HESI) source. Flash chromatography was performed using silica gel (Qingdao Haiyang chemical corporation, Qingdao, China). Thin-layer chromatography (TLC): Huanghai HSGF254, Yantai, China. ^1H and ^{13}C -NMR spectra of compounds **3a–3p** are in Supplementary Materials.

General procedure for the synthesis of **3**:

In a test tube, **2** (0.40 mmol) was added to a solution of **1** (0.20 mmol) and TBAT (0.40 mmol) in CH_3CN (2.0 mL). The mixture was stirred at 30 $^\circ\text{C}$ for 4 h. After the reaction was complete (monitored by TLC), the solvent was removed under reduced pressure, and the residue was purified via column chromatography to afford the pure product **3** (ethyl acetate: petroleum ether = 1:20).

Ethyl (*E*)-5-oxo-5*H*-dibenzo[*b,g*]thiocine-7-carboxylate (**3a**):

Yellow solid (57.2 mg, 92% yield), mp 134–136 $^\circ\text{C}$, R_f = 0.68 (Ethyl acetate: Petroleum ether = 1:5). ^1H NMR (400 MHz, CDCl_3) δ 7.82–7.73 (m, 1H), 7.71–7.61 (m, 2H), 7.56–7.36 (m, 4H), 7.34–7.25 (m, 2H), 4.37–4.26 (m, 2H), 1.33 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 195.93, 165.17, 140.96, 140.81, 139.57, 136.48, 136.41, 135.96, 132.76, 132.58, 131.99, 131.57, 130.08, 129.84, 129.58, 127.51, 61.87, 14.21. HRMS (ESI): m/z calcd for $\text{C}_{18}\text{H}_{14}\text{O}_3\text{S}$ [$\text{M} + \text{H}$] $^+$: 311.0736, found: 311.0736.

Ethyl (*E*)-3-methyl-5-oxo-5*H*-dibenzo[*b,g*]thiocine-7-carboxylate (**3b**):

Yellow solid (55.2 mg, 85% yield), mp 134–135 $^\circ\text{C}$, R_f = 0.64 (Ethyl acetate: Petroleum ether = 1:5). ^1H NMR (400 MHz, CDCl_3) δ 7.76–7.62 (m, 2H), 7.58–7.46 (m, 2H), 7.44–7.37 (m,

2H), 7.29–7.24 (m, 1H), 7.29–7.24 (m, 1H), 4.36–4.27 (m, 2H), 2.39 (s, 3H), 1.33 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 195.32, 165.30, 143.98, 140.96, 140.68, 139.72, 136.30, 135.45, 134.05, 132.89, 132.67, 131.74, 129.95, 129.87, 129.48, 128.51, 61.83, 21.37, 14.22. HRMS (ESI): m/z calcd for $\text{C}_{19}\text{H}_{16}\text{O}_3\text{S}$ $[\text{M} + \text{H}]^+$: 325.0893, found: 325.0894.

Ethyl (*E*)-2-methyl-5-oxo-5*H*-dibenzo[*b,g*]thiocine-7-carboxylate (**3c**):

Yellow solid (56.5 mg, 87% yield), $R_f = 0.64$ (Ethyl acetate: Petroleum ether = 1:5). ^1H NMR (400 MHz, CDCl_3) δ 7.72–7.52 (m, 2H), 7.50–7.38 (m, 2H), 7.37–7.25 (m, 2H), 7.21–7.15 (m, 1H), 7.08–7.00 (m, 1H), 4.30–4.16 (m, 2H), 2.31 (s, 3H), 1.25 (t, $J = 7.1$ Hz, 3H). HRMS (ESI): m/z calcd for $\text{C}_{19}\text{H}_{16}\text{O}_3\text{S}$ $[\text{M} + \text{H}]^+$: 325.0893, found: 325.0892.

Ethyl (*E*)-1-methyl-5-oxo-5*H*-dibenzo[*b,g*]thiocine-7-carboxylate (**3d**):

Yellow solid (60.3 mg, 93% yield), mp 143–144 °C, $R_f = 0.64$ (Ethyl acetate: Petroleum ether = 1:5). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.66–7.59 (m, 1H), 7.58–7.48 (m, 2H), 7.46–7.33 (m, 3H), 7.28–7.23 (m, 1H), 7.18 (t, $J = 7.6$ Hz, 1H), 4.38–4.26 (m, 2H), 2.61 (s, 3H), 1.33 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 196.72, 165.06, 141.78, 140.77, 140.20, 138.46, 137.13, 136.85, 136.20, 134.14, 132.35, 130.17, 129.68, 129.57, 129.34, 126.49, 61.79, 21.47, 14.24. HRMS (ESI): m/z calcd for $\text{C}_{19}\text{H}_{16}\text{O}_3\text{S}$ $[\text{M} + \text{H}]^+$: 325.0893, found: 325.0893.

Methyl (*E*)-5-oxo-5*H*-dibenzo[*b,g*]thiocine-7-carboxylate (**3e**):

Light yellow solid (53.7 mg, 91% yield), mp 146–147 °C, $R_f = 0.66$ (Ethyl acetate: Petroleum ether = 1:5). ^1H NMR (400 MHz, CDCl_3) δ 7.79–7.72 (m, 1H), 7.71–7.65 (m, 2H), 7.50 (d, $J = 7.7$ Hz, 1H), 7.46–7.40 (m, 3H), 7.34–7.26 (m, 2H), 3.86 (s, 3H). HRMS (ESI): m/z calcd for $\text{C}_{17}\text{H}_{12}\text{O}_3\text{S}$ $[\text{M} + \text{H}]^+$: 297.0580, found: 297.0584.

Methyl (*E*)-3-methyl-5-oxo-5*H*-dibenzo[*b,g*]thiocine-7-carboxylate (**3f**):

Light yellow solid (57.1 mg, 92% yield), mp 159–161 °C, $R_f = 0.62$ (Ethyl acetate: Petroleum ether = 1:5). ^1H NMR (400 MHz, CDCl_3) δ 7.73–7.65 (m, 1H), 7.63–7.52 (m, 2H), 7.51–7.34 (m, 3H), 7.30–7.24 (m, 2H), 3.85 (s, 3H), 2.33 (s, 3H). HRMS (ESI): m/z calcd for $\text{C}_{18}\text{H}_{14}\text{O}_3\text{S}$ $[\text{M} + \text{H}]^+$: 311.0736, found: 311.0736.

Methyl (*E*)-2-methyl-5-oxo-5*H*-dibenzo[*b,g*]thiocine-7-carboxylate (**3g**):

Orange waxy solid (56.6 mg, 91% yield), $R_f = 0.62$ (Ethyl acetate: Petroleum ether = 1:5). ^1H NMR (400 MHz, CDCl_3) δ 7.69 (t, $J = 7.3$ Hz, 2H), 7.53–7.37 (m, 4H), 7.30–7.24 (m, 1H), 7.13 (d, $J = 7.8$ Hz, 1H), 3.85 (s, 3H), 2.34 (s, 3H). HRMS (ESI): m/z calcd for $\text{C}_{18}\text{H}_{14}\text{O}_3\text{S}$ $[\text{M} + \text{H}]^+$: 311.0736, found: 311.0736.

Methyl (*E*)-1-methyl-5-oxo-5*H*-dibenzo[*b,g*]thiocine-7-carboxylate (**3h**):

Light yellow solid (56.6 mg, 91% yield), mp 128–129 °C, $R_f = 0.62$ (Ethyl acetate: Petroleum ether = 1:5). ^1H NMR (400 MHz, CDCl_3) δ 7.65–7.61 (m, 1H), 7.58–7.49 (m, 2H), 7.47–7.31 (m, 3H), 7.30–7.24 (m, 1H), 7.19 (t, $J = 7.6$ Hz, 1H), 3.86 (s, 3H), 2.61 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 196.57, 165.56, 141.66, 140.72, 140.52, 138.49, 137.08, 136.87, 135.92, 134.17, 132.39, 130.22, 129.63, 129.36, 126.51, 52.75, 29.73, 21.48. HRMS (ESI): m/z calcd for $\text{C}_{18}\text{H}_{14}\text{O}_3\text{S}$ $[\text{M} + \text{H}]^+$: 311.0736, found: 311.0740.

tert-Butyl (*E*)-5-oxo-5*H*-dibenzo[*b,g*]thiocine-7-carboxylate (**3i**):

Green oil (57.0 mg, 84% yield), $R_f = 0.73$ (Ethyl acetate: Petroleum ether = 1:5). ^1H NMR (400 MHz, CDCl_3) δ 7.73–7.65 (m, 1H), 7.64–7.56 (m, 2H), 7.46–7.40 (m, 1H), 7.39–7.29 (m, 2H), 7.26–7.15 (m, 3H), 1.46 (s, 9H). HRMS (ESI): m/z calcd for $\text{C}_{20}\text{H}_{18}\text{O}_3\text{S}$ $[\text{M} + \text{H}]^+$: 339.1049, found: 339.1052.

tert-Butyl (*E*)-3-methyl-5-oxo-5*H*-dibenzo[*b,g*]thiocine-7-carboxylate (**3j**):

Orange solid (58.0 mg, 82% yield), mp 113–115 °C, $R_f = 0.75$ (Ethyl acetate: Petroleum ether = 1:5). ^1H NMR (400 MHz, CDCl_3) δ 7.70–7.63 (m, 1H), 7.62–7.53 (m, 2H), 7.52–7.45 (m, 1H), 7.42–7.31 (m, 2H), 7.27–7.24 (m, 2H), 2.33 (s, 3H), 1.53 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 196.30, 164.32, 141.00, 138.68, 137.83, 137.64, 137.15, 136.39, 136.16, 133.63, 133.03, 132.11, 131.95, 129.95, 129.73, 129.32, 82.28, 28.05, 20.76. HRMS (ESI): m/z calcd for $\text{C}_{21}\text{H}_{20}\text{O}_3\text{S}$ $[\text{M} + \text{H}]^+$: 353.1206, found: 353.1207.

tert-Butyl (*E*)-2-methyl-5-oxo-5*H*-dibenzo[*b,g*]thiocine-7-carboxylate (**3k**):

Bright yellow waxy solid (58.7 mg, 83% yield), $R_f = 0.71$ (Ethyl acetate: Petroleum ether = 1:5). ^1H NMR (400 MHz, CDCl_3) δ 7.72–7.64 (m, 2H), 7.54–7.47 (m, 2H), 7.42–7.36 (m, 1H), 7.34 (s, 1H), 7.28–7.24 (m, 1H), 7.14–7.11 (m, 1H), 2.39 (s, 3H), 1.53 (s, 9H). HRMS (ESI): m/z calcd for $\text{C}_{21}\text{H}_{20}\text{O}_3\text{S}$ $[\text{M} + \text{H}]^+$: 353.1206, found: 353.1206.

tert-Butyl (*E*)-1-methyl-5-oxo-5*H*-dibenzo[*b,g*]thiocine-7-carboxylate (**3l**):

Orange waxy solid (56.5 mg, 80% yield), $R_f = 0.72$ (Ethyl acetate: Petroleum ether = 1:5). ^1H NMR (400 MHz, CDCl_3) δ 7.62 (d, $J = 7.8$ Hz, 1H), 7.53 (t, $J = 8.4$ Hz, 2H), 7.43–7.35 (m, 2H), 7.30 (s, 1H), 7.26 (s, 1H), 7.19 (t, $J = 7.6$ Hz, 1H), 2.62 (s, 3H), 1.54 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 197.09, 164.13, 142.07, 140.86, 139.29, 138.39, 137.55, 137.20, 136.77, 134.03, 132.28, 129.99, 129.77, 129.36, 129.28, 126.39, 82.25, 28.07, 21.44. HRMS (ESI): m/z calcd for $\text{C}_{21}\text{H}_{20}\text{O}_3\text{S}$ $[\text{M} + \text{Na}]^+$: 375.1025, found: 375.1025.

Benzyl (*E*)-5-oxo-5*H*-dibenzo[*b,g*]thiocine-7-carboxylate (**3m**):

Orange waxy solid (52.0 mg, 70% yield), $R_f = 0.64$ (Ethyl acetate: Petroleum ether = 1:5). ^1H NMR (400 MHz, CDCl_3) δ 7.75 (d, $J = 7.8$ Hz, 1H), 7.68 (t, $J = 7.0$ Hz, 2H), 7.51 (d, $J = 7.7$ Hz, 1H), 7.48–7.14 (m, 10H), 5.36–5.24 (m, 2H). HRMS (ESI): m/z calcd for $\text{C}_{23}\text{H}_{16}\text{O}_3\text{S}$ $[\text{M} + \text{H}]^+$: 373.0893, found: 373.0894.

Benzyl (*E*)-3-methyl-5-oxo-5*H*-dibenzo[*b,g*]thiocine-7-carboxylate (**3n**):

Orange waxy solid (54.4 mg, 70% yield), $R_f = 0.62$ (Ethyl acetate: Petroleum ether = 1:5). ^1H NMR (400 MHz, CDCl_3) δ 7.68 (d, $J = 7.8$ Hz, 1H), 7.63–7.54 (m, 2H), 7.52–7.44 (m, 2H), 7.42–7.30 (m, 6H), 7.28–7.18 (m, 2H), 5.35–5.24 (m, 2H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 195.78, 165.12, 140.56, 140.03, 137.76, 137.71, 136.28, 135.52, 133.76, 133.19, 132.17, 132.00, 129.94, 129.85, 129.61, 128.63, 128.38, 128.15, 67.43, 20.78. HRMS (ESI): m/z calcd for $\text{C}_{24}\text{H}_{18}\text{O}_3\text{S}$ $[\text{M} + \text{H}]^+$: 387.1049, found: 387.1052.

Benzyl (*E*)-2-methyl-5-oxo-5*H*-dibenzo[*b,g*]thiocine-7-carboxylate (**3o**):

Light yellow waxy solid (57.4 mg, 74% yield), $R_f = 0.62$ (Ethyl acetate: Petroleum ether = 1:5). ^1H NMR (400 MHz, CDCl_3) δ 7.73–7.53 (m, 2H), 7.53–7.45 (m, 2H), 7.43–7.22 (m, 8H), 7.12 (d, $J = 7.9$ Hz, 1H), 5.34–5.24 (m, 2H), 2.33 (d, $J = 41.6$ Hz, 3H). HRMS (ESI): m/z calcd for $\text{C}_{24}\text{H}_{18}\text{O}_3\text{S}$ $[\text{M} + \text{H}]^+$: 387.1049, found: 387.1049.

Benzyl (*E*)-1-methyl-5-oxo-5*H*-dibenzo[*b,g*]thiocine-7-carboxylate (**3p**):

Orange waxy solid (60.6 mg, 78% yield), $R_f = 0.62$ (Ethyl acetate: Petroleum ether = 1:5). ^1H NMR (400 MHz, CDCl_3) δ 7.62 (d, $J = 7.8$ Hz, 1H), 7.53 (d, $J = 7.9$ Hz, 2H), 7.46–7.30 (m, 8H), 7.29–7.23 (m, 1H), 7.17 (t, $J = 7.6$ Hz, 1H), 5.30 (d, $J = 7.2$ Hz, 2H), 2.61 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 196.59, 164.90, 141.62, 140.76, 140.66, 138.48, 137.08, 136.90, 135.91, 135.52, 134.18, 132.41, 130.21, 129.69, 129.66, 129.35, 128.65, 128.41, 128.21, 126.50, 67.42, 21.48. HRMS (ESI): m/z calcd for $\text{C}_{24}\text{H}_{18}\text{O}_3\text{S}$ $[\text{M} + \text{H}]^+$: 387.1049, found: 387.1051.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/reactions6020035/s1>, ^1H and ^{13}C -NMR spectra of compounds **3a–3p**.

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