

Silver-catalyzed intramolecular oxidative decarboxylative C-H arylation reactions for synthesis of biaryl sultams

Junmin Chen,^{*a} Qihong Wang,^a Xiangkang Li,^{a,b} and Yongli Zhao^a

^aKey Laboratory of Functional Small Organic Molecules, Ministry of Education and College of Chemistry & Chemical Engineering, Jiangxi Normal University, Nanchang, Jiangxi 330022, China;

^bKey Laboratory of Organo-Pharmaceutical Chemistry of Jiangxi Province, Gannan Normal University, Ganzhou 341000, China

Email: jxnuchenjm@163.com

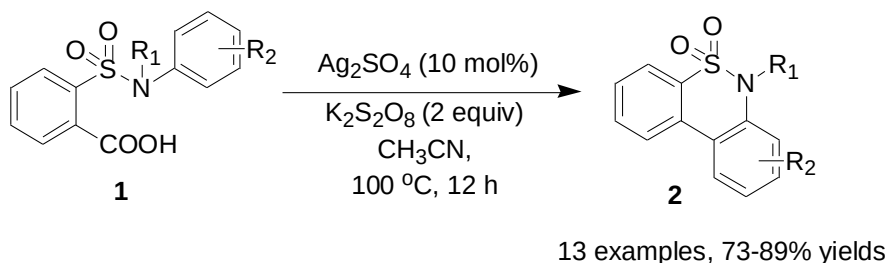
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Abstract

A mild, versatile and efficient method to form biaryl sultams through silver-catalyzed intramolecular oxidative decarboxylative C-H arylation reactions has been developed. The present protocol features a broad substrate scope and very good tolerance to different substituent groups with satisfactory yields, giving access to a wide range of biaryl sultam derivatives.



Keywords: silver-catalyzed; decarboxylative; C-H arylation; biaryl sultam

Introduction

The sulfonamides have been extensively used as pharmaceutical and agricultural agents because of their diverse biological properties.¹⁻⁵ Among them, sultams (cyclic sulfonamides) are important structural scaffolds. Thus the pharmaceutically relevant molecules **A**, **B** and **C** (**Figure 1**) have been found to exhibit broad inhibitory properties against a variety of enzymes as COX-2,⁶ HIV integrase,⁷ lipoxygenase,⁸ Calpain I,⁹ and MMP-2.¹⁰ Furthermore, biaryls embedded in cyclic sulfonamide (biaryl sultams) have emerged as privileged structures in drug discovery. For example, carbapenem derived biaryl sultam **D** provides for potent binding to the target penicillin binding proteins (PBPs).¹¹ The related quinolinederived biaryl sultam **E** plays an active role in the NF- κ B pathway, which has provided a favorable target for pharmacological intervention for chronic inflammation, neurodegenerative diseases, and certain types of cancer.⁶

As a consequence, a variety of strategies have been developed for the synthesis of sultams.¹²⁻¹⁷ However, it was less reported for the synthesis of biaryl based sultams. Recently, some methodologies have also been developed including intramolecular C-H arylation of the 2-halobenzenesulfonamides catalyzed by palladium or with the assistance of a single-electron-transfer pathway¹⁸⁻²¹ and intramolecular oxidative C-H amination of 2-phenylarylsulfonamides under metal-free conditions.²² In addition, palladium catalyzed intramolecular oxidative coupling (IOC) of two C(sp²)-H bonds was also developed for the synthesis of biaryl sultams.²³ Very recently, an alternative approach has been reported for the preparation of biaryl sultams using visible-light-promoted denitrogenative cyclization of 1,2,3,4-benzothiazine-1,1-dioxides.²⁴ Because of its significance in pharmaceutical development, the exploration of a novel and simple synthetic method for the construction of biaryl sultams would be highly desirable.

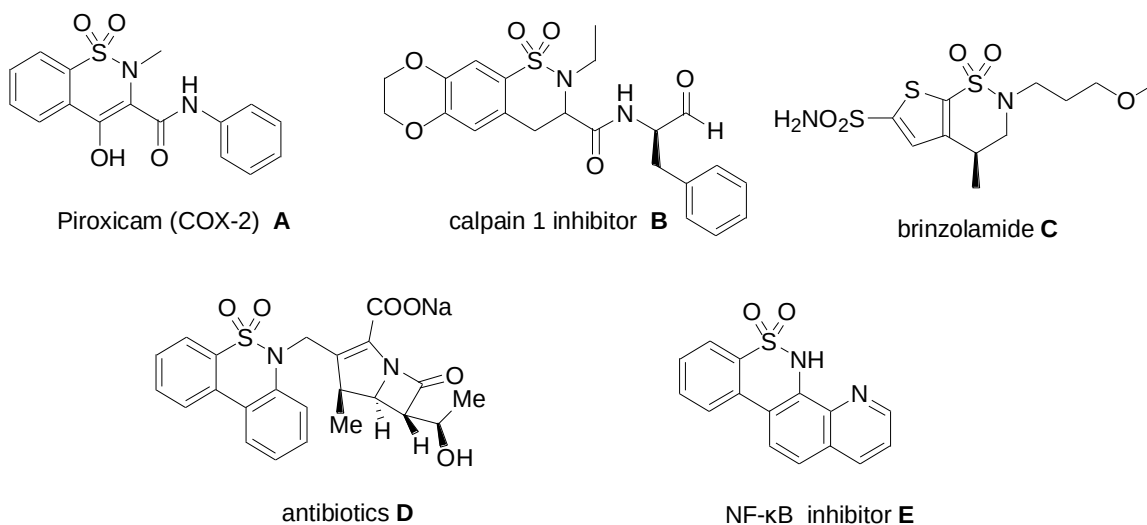


Figure 1

Transition-metal-catalyzed decarboxylative transformations of arenecarboxylic acids through extrusion of the traceless CO₂ have drawn considerable attention in the past decade.²⁵ Since the pioneering work of Myers and Gooßen, decarboxylative coupling of benzoic acids with aryl halides or triflates using Pd/Cu or Pd/Ag bimetallic catalyst systems have been extensively studied.²⁶⁻²⁸ Crabtree developed an elegant method for the synthesis of biaryl compounds *via* transition-metal-catalyzed decarboxylative C-H arylation reaction.²⁹ Subsequently, Larrosa,³⁰ Su,³¹ Greaney,³² and others³³⁻³⁶ reported palladium-catalyzed intramolecular and intermolecular decarboxylative arylation of activated heteroarenes for the synthesis of biaryl motifs. Notably,

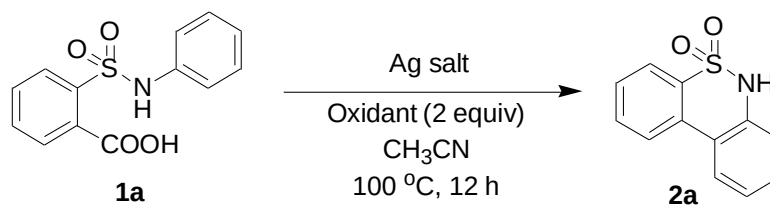
silver-catalyzed or visible-light-enabled decarboxylative transformations *via* aryl radical generation have also been successfully achieved.³⁷⁻³⁹

Inspired by recently elegant works on the intramolecular or intermolecular decarboxylative C-H arylation of (hetero)arenes with aromatic carboxylic acids.⁴⁰ In the course of our ongoing investigation on transition-metal-catalyzed C-H activation reactions to access sulfonamide derivatives.⁴¹ We report herein the first example of silver-catalyzed intramolecular oxidative decarboxylative C-H arylation for synthesis of biaryl sulfams.

Results and Discussion

Initially, we selected the intramolecular oxidative decarboxylative C-H arylation of 2-phenylsulfamoyl-benzoic acid **1a** as a model reaction for optimization studies (Table 1). To our delight, a 72% yield of the desired product **2a** was obtained when the reaction was conducted in CH₃CN at 100 °C for 12h in the presence of AgOAc (20 mol%) with K₂S₂O₈ (2 equiv) as an oxidant (Table 1, entry 1). And then, various oxidants were investigated, we found the yield of **2a** dropped to 37% (Table 1, entry 2) and 26% (Table 1, entry 3) when (NH₄)₂S₂O₈ and Cu(OAc)₂ was used, respectively. Surprisingly, No desired product could be detected using PhI(OAc)₂ as the oxidant (Table 1, entry 4). Subsequently, investigation of different silver catalysts for the reaction revealed that Ag₂SO₄ was superior, giving 89% yield (Table 1, entries 5-8). It is interesting to find that reducing the amount of catalyst loading from 20 to 10 mol % did not effect on the activity and gave the comparable yield (87%) (Table 1, entry 9). Whereas further reducing the amount of catalyst loading to 5% mol % only affords 64% yield (Table 1, entry 10). Temperature has a great impact on this reaction; the product **2a** was obtained in 76% yield at 80 °C (Table 1, entry 11). Control experiments revealed that no such coupling reaction occurred in the absence of the silver catalyst (Table 1, entry 12). Finally, the optimized reaction conditions were identified as follows: Ag₂SO₄ (10 mol %), and K₂S₂O₈ (2 equiv) in CH₃CN at 100 °C for 12 h under air.

Table 1. Optimization of reaction conditions



Entry ^a	Ag salt (mol%)	Oxidant	Yield ^b (%)
1	AgOAc (20)	K ₂ S ₂ O ₈	72
2	AgOAc (20)	(NH ₄) ₂ S ₂ O ₈	37
3	AgOAc (20)	Cu(OAc) ₂	26
4	AgOAc (20)	PhI(OAc) ₂	n.r
5	Ag ₂ CO ₃ (20)	K ₂ S ₂ O ₈	63
6	AgTFA (20)	K ₂ S ₂ O ₈	51
7	AgNO ₃ (20)	K ₂ S ₂ O ₈	53
8	Ag ₂ SO ₄ (20)	K ₂ S ₂ O ₈	89
9	Ag ₂ SO ₄ (10)	K ₂ S ₂ O ₈	87

Table 1. Continued

Entry a	Ag salt (mol%)	Oxidant	Yield b (%)
10	Ag ₂ SO ₄ (5)	K ₂ S ₂ O ₈	64
11 ^c	Ag ₂ SO ₄ (10)	K ₂ S ₂ O ₈	76
12	\	K ₂ S ₂ O ₈	n.r

^a Reaction conditions: **1a** (0.2 mmol), Ag salt (0.02 mmol), oxidant (0.4 mmol), and CH₃CN (1.0 mL), heated at 100 °C for 12 h under air.

^b Isolated yields.

^c at 80 °C.

With the optimized reaction conditions in hand, we then evaluated the influence of the aniline moiety bearing various substituents on the reactivity and regioselectivity (Table 2). The electronic nature of the substituents seemed to have a little effect on the product yields, for example, substrate **1** with a electron-donating *para*-methyl or chloro group on the N-aryl ring afforded the biaryl sultams **2b-c** in 83% or 82% yield, respectively (Table 2, entries 2,3), while the slightly higher yield (87%) was obtained for **2d** containing an electron-withdrawing *para*-CF₃ group (Table 2, entry 4). As for substrates **1e-g** bearing a *meta*-group, such as chloro, fluoro or methoxyl, Cyclisation only occurs regioselectively on the less hindered position and the desired biaryl sultams **2e-g** were obtained in good yields (Table 2, entries 5-7). It should be noted that *ortho*-chloro or *ortho*-methoxyl substituted substrates **1g**, **1h**, and **1i** worked well to generate the corresponding desired products **2g-i** in excellent yields without the cleavage of the C-Cl bond even though aryl halides are well-known to participate in Pd-catalyzed decarboxylative coupling reactions (Table 2, entries 8-10). Thus, these halogens can provide the opportunity for further transition metal catalyzed syntheses, thereby broadening the diversity of the products. Furthermore, methyl protected amino group substrates **1k** and **1l** also provided the desired products **2k** and **2l** in very high yield (Table 2, entries 11,12). Notably, heteroaromatic thiophene on the acid moiety **1m** was also successfully employed to provide the corresponding biaryl sultam **2m** in good yield (Table 2, entry 13).

Table 2. Silver-catalyzed intramolecular oxidative decarboxylative C-H arylation

Entry ^a	Substrate 1	Product 2	Yield ^b (%)
1	 1a	 2a	89

Table 2. Continued

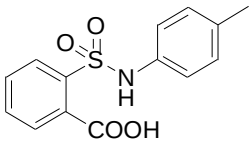
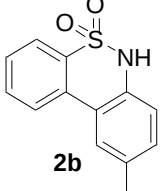
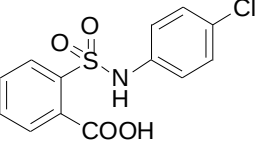
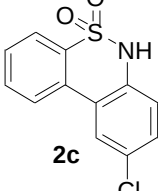
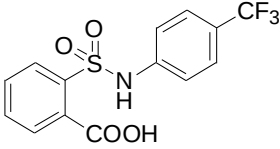
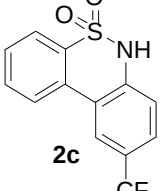
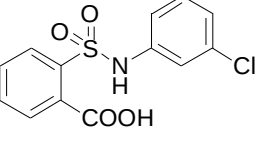
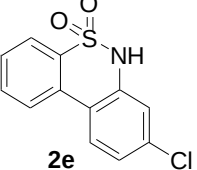
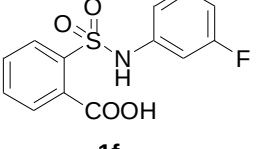
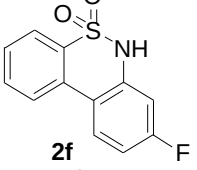
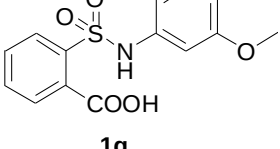
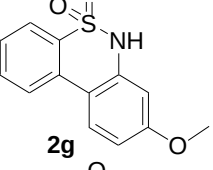
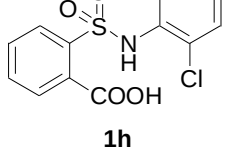
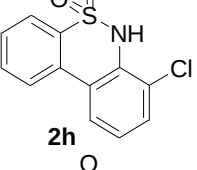
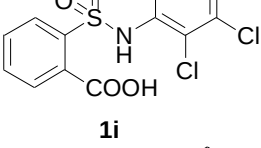
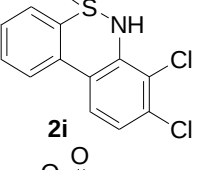
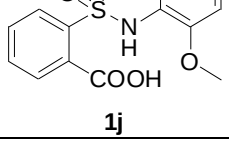
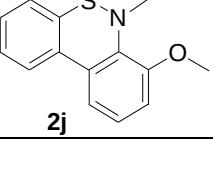
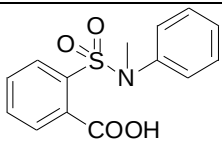
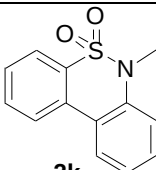
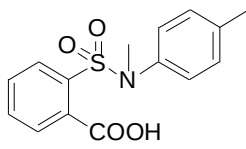
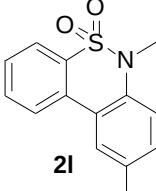
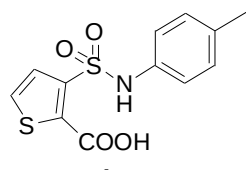
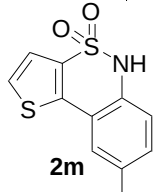
Entry ^a	Substrate 1	Product 2	Yield ^b (%)
2	 1b	 2b	83
3	 1c	 2c	82
4	 1d	 2c	87
5	 1e	 2e	79
6	 1f	 2f	84
7	 1g	 2g	75
8	 1h	 2h	83
9	 1i	 2i	86
10	 1j	 2j	74

Table 2. Continued

Entry ^a	Substrate 1	Product 2	Yield ^b (%)
11	 1k	 2k	82
12	 1l	 2l	77
13	 1m	 2m	73

^a Reaction conditions: **1** (0.2 mmol), Ag₂SO₄ (0.02 mmol), K₂S₂O₈ (0.4 mmol), and CH₃CN (1.0 mL), heated at 100 °C for 12 h under air.

^b Isolated yields.

Conclusions

In summary, we have developed a novel and efficient protocol for the synthesis of biaryl sultams *via* silver-catalyzed intramolecular oxidative decarboxylative C-H arylation. The reaction proceeds under mild conditions without the use of expensive transition metals or ligands. Many functional groups are tolerated, giving access to a wide range of biaryl sultam derivatives. The cyclization was proposed to proceed *via* a radical mechanism. Further investigations to the reaction mechanism and utilization of this catalyzed system in other biaryl based heterocyclic compounds are currently in progress.

Experimental Section

General. All reactions were carried out under air atmosphere in oven-dried glassware with magnetic stirring. Unless otherwise specified, all other reagents and solvents were purchased from Energy Chemical, Alfa Aesar or J&K Chemical Company and used without any further purification. TLC information was recorded on GF-254 (Qingdao Haiyang Chemical Co., Ltd. P. R. China) plates. Purification of reaction products was carried out by flash chromatography using Silica gel (200-300 mesh, Qingdao Haiyang Chemical Co. Ltd. P. R. China). All products were recorded using Bruker Avance-400 instruments, calibrated to TMS as the internal reference (0.00 ppm for ¹H NMR spectra and 100.00 ppm for ¹³C NMR spectra). High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer using ESI (electrospray ionization). Melting points were measured uncorrected.

Silver-catalyzed intramolecular oxidative decarboxylative C-H arylation

An oven-dried 10 mL Schlenk tube was charged with **1** (0.20 mmol), Ag₂SO₄ (6.22 mg, 0.02 mmol, 10 mol %), K₂S₂O₈ (108 mg, 0.4 mmol, 2 equiv), and CH₃CN (1 mL). It was then closed with a Teflon-lined cap and kept for stirring at 100 °C (preheated oil bath temperature) for 12 h. After the mixture cooled to room temperature, the reaction mixture was filtered through a short pad of Celite; the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/EtOAc to afford the desired product **2**.

6H-dibenzo[c,e][1,2]thiazine 5,5-dioxide (2a)²³ White solid, isolated yield 89% (41 mg); mp: 195-196 °C; ¹H NMR (400 MHz, *d*₆-DMSO): δ 8.42 (d, *J* = 8.0 Hz, 1H), 8.23 (d, *J* = 8.0 Hz, 1H), 8.16-8.08 (m, 4H), 8.06-7.84 (m, 2H). ¹³C NMR (100 MHz, *d*₆-DMSO): δ 158.36, 136.92, 136.69, 136.00, 133.29, 130.43, 129.79, 127.60, 127.56, 126.82, 126.16, 122.36.

6H-dibenzo[c,e][1,2]thiazine 5,5-dioxide (2a)²³ White solid, isolated yield 89% (41 mg); mp: 195-196 °C; ¹H NMR (400 MHz, *d*₆-DMSO): δ 8.42 (d, *J* = 8.0 Hz, 1H), 8.23 (d, *J* = 8.0 Hz, 1H), 8.16-8.08 (m, 4H), 8.06-7.84 (m, 2H). ¹³C NMR (100 MHz, *d*₆-DMSO): δ 158.36, 136.92, 136.69, 136.00, 133.29, 130.43, 129.79, 127.60, 127.56, 126.82, 126.16, 122.36.

9-Methyl-6H-dibenzo[c,e][1,2]thiazine 5,5-Dioxide (2b)⁴² White solid, isolated yield 82% (40 mg); mp: 217-218 °C; ¹H NMR (400 MHz, *d*₆-DMSO): δ 8.15 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.94-7.86 (m, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 2.43 (s, 3H). ¹³C NMR (100 MHz, *d*₆-DMSO): δ 158.52, 140.51, 137.71, 135.01, 134.40, 130.62, 128.66, 127.32, 125.83, 125.61, 121.25, 21.34.

9-chloro-6H-dibenzo[c,e][1,2]thiazine 5,5-Dioxide (2c) White solid, isolated yield 85% (43 mg); mp: 156-158 °C; ¹H NMR (400 MHz, *d*₆-DMSO): δ 8.43 (d, *J* = 4.0 Hz, 1H), 8.24 (d, *J* = 8.0 Hz, 1H), 8.18-8.08 (m, 2H), 7.77-7.73 (m, 2H), 7.66-7.63 (m, 2H). ¹³C NMR (100 MHz, *d*₆-DMSO): δ 158, 136.99, 136.58, 135.90, 131.25, 130.56, 128.01, 126.86, 126.04, 122.34. HRMS (ESI) *m/z* calcd for C₁₂H₉ClNO₂S (M+H)⁺ 266.0043, found 266.0045.

9-(trifluoromethyl)-6H-dibenzo[c,e][1,2]thiazine 5,5-Dioxide (2d)⁴² White solid, isolated yield 87% (52 mg); mp: 234-235 °C; ¹H NMR (400 MHz, *d*₆-DMSO): δ 8.47 (d, *J* = 8.0 Hz, 1H), 8.27 (d, *J* = 8.0 Hz, 1H), 8.20-7.07 (m, 4H), 7.89 (d, *J* = 8.0 Hz, 1H). ¹³C NMR (100 MHz, *d*₆-DMSO): δ 158.36, 136.89, 136.69, 136.01, 133.28, 130.76, 130.44, 129.81, 127.60, 127.67, 126.15, 125.57, 122.85, 122.37.

8-(chloro)-6H-dibenzo[c,e][1,2]thiazine 5,5-Dioxide (2e) White solid, isolated yield 79% (42 mg); mp: 155-157 °C; ¹H NMR (400 MHz, *d*₆-DMSO): δ 8.42 (d, *J* = 8.0 Hz, 1H), 8.23 (d, *J* = 8.0 Hz, 1H), 8.16-8.08 (m, 4H), 8.07-7.84 (m, 2H). ¹³C NMR (100 MHz, *d*₆-DMSO): δ 158.36, 136.92, 136.69, 136.00, 133.29, 130.43, 129.79, 127.60, 127.56, 125.82, 125.16, 122.36. HRMS (ESI) *m/z* C₁₂H₉ClNO₂S (M+H)⁺ 266.0043, found 266.0045.

8-(fluoro)-6H-dibenzo[c,e][1,2]thiazine 5,5-Dioxide (2f) White solid, isolated yield 84% (42 mg); mp: 152-154 °C; ¹H NMR (400 MHz, *d*₆-DMSO): δ 8.28 (d, *J* = 8.0 Hz, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 8.02-7.92 (m, 2H), 7.60-7.54 (m, 1H), 7.41-7.32 (m, 3H). ¹³C NMR (100 MHz, *d*₆-DMSO): δ 167.42 (d, *J* = 244 Hz), 163.11, 141.53 (d, *J* = 32 Hz), 140.69, 136.79, 135.37, 131.55, 130.81, 130.26, 127.09, 122.50 (d, *J* = 21 Hz), 121.46 (d, *J* = 25 Hz). HRMS (ESI) *m/z* calcd for C₁₂H₉O₂NFS: 250.0333; found: 250.0330.

8-methoxy-6H-dibenzo[c,e][1,2]thiazine 5,5-Dioxide (2g)²⁴ White solid, isolated yield 71% (64 mg); mp: 86-88 °C; ¹H NMR (400 MHz, *d*₆-DMSO): δ 8.44 (d, *J* = 8.0 Hz, 1H), 8.24 (d, *J* = 8.0 Hz, 1H), 8.19-8.09 (m, 2H), 7.52-7.48 (m, 2H), 7.24-7.21 (m, 2H), 3.90 (s, 1H). ¹³C NMR (100 MHz, *d*₆-DMSO): δ 158.44, 137.08, 136.53, 135.85, 131.14, 130.10, 126.85, 125.98, 122.26, 121.36, 116.24, 115.19, 56.03.

7-chloro-6H-dibenzo[c,e][1,2]thiazine 5,5-Dioxide (2h) White solid, isolated yield 83% (43 mg); mp: 141-143 °C; ¹H NMR (400 MHz, *d*₆-DMSO): δ 8.45 (d, *J* = 8.0 Hz, 1H), 8.25 (d, *J* = 8.0 Hz, 1H), 8.18-8.07 (m, 2H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.72-7.62 (m, 3H). ¹³C NMR (100 MHz, *d*₆-DMSO): δ 157.78, 137.51, 136.89, 136.11, 134.63,

133.20, 132.95, 131.37, 129.26, 126.26, 122.61. HRMS (ESI) m/z calcd for $C_{12}H_9ClNO_2S$ ($M+H$)⁺ 266.0043, found 266.0044.

7,8-(dichloro)-6H-dibenzo[c,e][1,2]thiazine 5,5-Dioxide (2i) White solid, isolated yield 86% (52 mg); mp: 219--221 °C; ¹H NMR (400 MHz, *d*₆-DMSO): δ 8.46 (d, *J* = 8.0 Hz, 1H), 8.26 (d, *J* = 8.0 Hz, 1H), 8.19-8.08 (m, 2H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.73-7.63 (m, 2H), ¹³C NMR (100 MHz, *d*₆-DMSO): δ 157.64, 137.48, 136.98, 136.18, 133.83, 133.71, 133.37, 131.78, 129.82, 126.36, 125.19, 122.69. HRMS (ESI) m/z calcd for $C_{12}H_8Cl_2NO_2S$ ($M+H$)⁺ 299.9654, found 299.9651.

7-methoxy-6H-dibenzo[c,e][1,2]thiazine 5,5-Dioxide (2j)²⁴ White solid, isolated yield 74% (39 mg); mp: 211-213 °C; ¹H NMR (400 MHz, *d*₆-DMSO): δ 8.37 (d, *J* = 8.0 Hz, 1H), 8.20 (d, *J* = 4.0 Hz, 1H), 8.12-8.06 (m, 2H), 7.61 (s, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.17 (q, *J* = 4.0 Hz, 1H), 3.77 (s, 3H), ¹³C NMR (100 MHz, *d*₆-DMSO): δ 157.15, 137.67, 136.58, 135.88, 132.93, 131.64, 126.55, 125.98, 122.40, 121.54, 116.70, 113.79, 56.64. HRMS (ESI) m/z calcd for $C_{13}H_{12}O_3NS$ ($M+H$)⁺ 262.0532; found: 262.0534.

5-Methylphenanthridin-6(5H)-one (2k)⁴³ White solid, isolated yield 82% (35 mg); mp: mp 79-81 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.93 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 1H), 7.12-7.18 (m, 2H), ¹³C NMR (100 MHz, CDCl₃): δ 139.52, 134.27, 132.27, 130.45, 128.24, 125.52, 125.44, 124.69, 124.01, 122.51, 119.43, 32.77

6,9-Dimethyl-6H-dibenzo[c,e][1,2]thiazine 5,5-dioxide (2l)⁴⁴ White solid, isolated yield 82% (43mg); mp: 185-187 °C; ¹H NMR (400 MHz, *d*₆-DMSO): δ 7.93 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 1H), 7.12-7.18 (m, 2H), ¹³C NMR (100 MHz, *d*₆-DMSO): δ 139.52, 134.27, 132.27, 130.45, 128.24, 125.52, 125.44, 124.69, 124.01, 122.51, 119.43, 32.77.

8-Methyl-5H-1,4-dithia-5-aza-cyclopenta[a]naphthalene 4,4-dioxide (2m) White solid, isolated yield 73% (37mg); mp: 158-160 °C; ¹H NMR (400 MHz, *d*₆-DMSO): δ 8.47 (d, *J* = 4.0 Hz, 1H), 7.94-7.92 (m, 1H), 7.43-7.38 (m, 3H), 2.40 (s, 3H), ¹³C NMR (100 MHz, *d*₆-DMSO): δ 140.48, 134.06, 131.74, 130.37, 129.62, 129.58, 128.18, 128.08, 127.74, 125.80, 21.34. HRMS (ESI) m/z calcd for $C_{11}H_{10}NO_2S_2$ ($M+H$)⁺ 252.0154, found 252.0148.

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Supplementary Material

¹H and ¹³C NMR spectra of products **2** can be found in the online Supplementary Material.

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