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Copper-Catalyzed Tandem Radical Cyclization of 8-Ethynyl-1-naphthylamines for the Synthesis of 2*H*-benzo[*e*][1,2]thiazine 1,1-dioxides and its Fluorescence Properties

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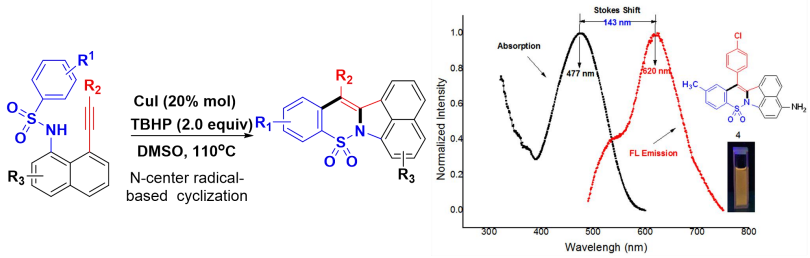
ABSTRACT: A copper-catalyzed radical cascade dehydrogenative cyclization of *N*-tosyl-8-ethynyl-1-naphthylamines under air is descried herein for the synthesis of thioazafluoranthenes. The reaction proceeds smoothly with a high efficiency and a broad reaction scope. The product is indeed a new fluorophore and its photophysical properties are also investigated. Based on the results, we are pleased to find that the Stokes shift of amino-linked thioazafluoranthenes in dilute tetrahydrofuran is determined to be 143 nm (4830 cm^{-1}).



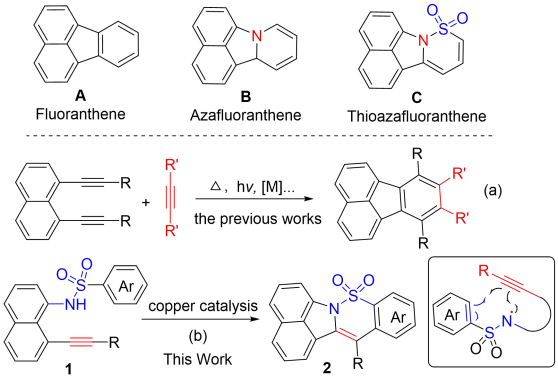
Introduction

Fluoranthene (structure A, Scheme 1) was a kind of important 6/5 ring system. Being always served as synthons for constructing many chemical Eulerean networks such as corannulene, fullerenes, and capped carbon tubes,[1] fluoranthene thus attracted growing interests of synthetic chemists with a wish to develop simple and efficient methodology towards this 6/5 ring system.[2] To the best of our knowledge, under thermal or photochemical conditions or in the presence of metal catalysts its synthetic methodologies from naphthalene and its derivatives represented the most straightforward protocols thus far.[3] For example, the use of rhodium catalysis enabled the synthesis of fluoranthene from 1,8-bis(phenylethynyl)-naphthalene with a high efficiency (Scheme 1, eq a).[3e] Recent advances suggested that introduction of heteoatom into fluoranthene could make a significant impact on their optoelectronic properties.[4] Particularly, its electrochemical, photophysical, and bowl-dynamic properties could be uniquely controlled when fluoranthene and its analogies were doped by nitrogen in indole core.[5] As such, tremendous efforts were made to develop novel and mild methods towards this azafluoranthene core (structure B, Scheme 1).[6]

On the other hand, the sulfonamide moiety always has a range of biological and medicinal applications.[7] With the sulfonamide structural core, 1,2-benzothiazine 1,1-dioxides (benzosultams) are the most important class of non-steroidal anti-inflammatory drugs.[8] Moreover, in a chemical context, introduction of sulphur atom into materials was an efficient strategy to improve its optoelectronic and sensing properties.[9] Therefore, in this paper we would like to disclose an efficient procedure for synthesizing sulphur/nitrogen-doped fluoranthenes (structure C, Scheme 1) under mild conditions.

To date, tandem radical reaction was well recognized as a powerful tool towards polycyclic architectures.[10] It was thus envisioned that a radical cascade reaction of *N*-tosyl-8-ethynyl-1-naphthylamines **1** could enabled the formation of sulphur/nitrogen-doped fluoranthenes **2**. In the past years, one of continuous interests in our group is focusing on *N*-center radical-based transformations.[11] For example, on basis of copper-catalyzed *N*-center radical-based 6-*endo-dig* cyclization of 2-alkynylbenzamide, we realized the formation of various isoquinoline-1-ones.[11a] In light of this result, the projected transformation of 8-ethynyl-1-naphthylamines **1** access to sulphur/nitrogen-doped fluoranthenes **2** was hypothesized to be triggered a formal *N*-center radical-based 5-*exo-dig* aza-cyclization[12] (scheme 1, eq b). The starting materials **1** were prepared from 8-iodo-1-naphthylamine.[13]

Scheme 1. Synthetic strategies of heteoatom-doped fluoranthenes

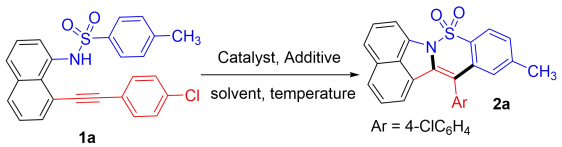


Results and Discussion

Under copper catalysis,[14] we initially tested the reaction of *N*-Tosyl-8-ethynyl-1-naphthylamines **1a** in the presence of CuI, $NaHCO_3$ and TBHP using CH_3CN as solvent under air at 110 °C for 12 h (Table 1, entry 1). To our delight, the desired product **2a** was obtained in 21% isolated yield as expected. This promising result indicated our above proposed hypothesis seemed reliable.

Screening solvents such as DMSO, DMF, DMAc or 1,4-dioxane, and DMSO was determined to be the optimal (Table 1, entries 2-5). Using 1,4-dioxane as the solvent, the reaction did not work at all (Table 1, entry 5). By changing the Cu catalyst to CuCl and CuBr, the reactions gave rise to inferior outcomes (Table 1, entries 6-7). The reaction became complex when the reaction employed copper acetate as catalyst (Table 1, entry 8). From the results on screening bases effects, no better yields were observed when the reactions with K_2CO_3 and Na_2CO_3 (Table 1, entries 9 and 10). A blank experiment without a base suggested the desired product **2a** was isolated in 78% yield (Table 1, entry 11). Subsequently, the optimal amount of TBHP was determined to be 2 equivalents (Table 1, entry 12). Using air and H_2O_2 as replacements of TBHP gave inferior yields (Table 1, entries 13-14). By decreasing the reaction temperature, the yield of **2a** was dropped (Table 1, entry 15). The improved yield was afforded by decreasing the amount of CuI to 0.2 equivalents while prolonging the reaction time to 18 hours (Table 1, entry 16). A blank reaction without copper salt did not provide the desired product **2a** (Table 1, entry 17). Furthermore, a 1 mmol scaled reaction was conducted, leading to desired product **2a** in 65% yield (278.9 mg, Table 1, entry 18). Thus, the optimal reaction conditions were established: running the mixture of *N*-Tosyl-8-ethynyl-1-naphthylamines, CuI and TBHP (1:0.2:2) in DMSO under air at 110 °C for 18 h.

Table 1. Optimization of the Reaction Conditions[a]

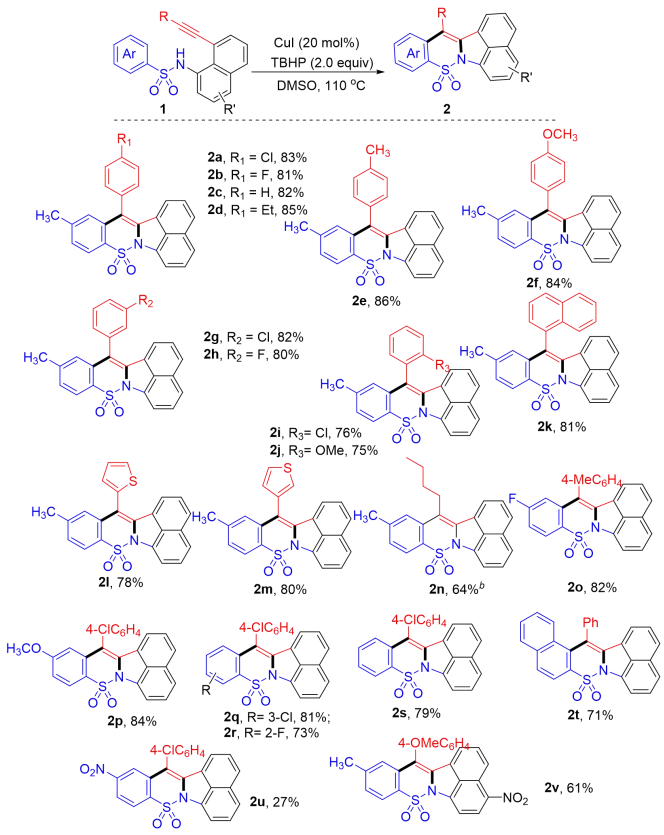


entry	[Cu] (equiv)	Sol.	Base	[O] (equiv)	Yields Of **2a**[a]
1	CuI (0.5)	MeCN	$NaHCO_3$	TBHP	21
2	CuI (0.5)	DMSO	$NaHCO_3$	TBHP	56
3	CuI (0.5)	DMF	$NaHCO_3$	TBHP	45
4	CuI (0.5)	DMAc	$NaHCO_3$	TBHP	46
5	CuI (0.5)	1,4-Dioxane	$NaHCO_3$	TBHP	nr
6	CuCl (0.5)	DMSO	$NaHCO_3$	TBHP	51
7	CuBr (0.5)	DMSO	$NaHCO_3$	TBHP	43
8	$Cu(OAc)_2$ (0.5)	DMSO	$NaHCO_3$	TBHP	trace
9	CuI (0.5)	DMSO	Na_2CO_3	TBHP	41
10	CuI (0.5)	DMSO	K_2CO_3	TBHP	40
11	CuI (0.5)	DMSO	-	TBHP	78
12	CuI (0.5)	DMSO	-	TBHP (2)	83
13	CuI (0.5)	DMSO	-	air	43
14	CuI (0.5)	DMSO	-	H_2O_2	12
15[b]	CuI (0.5)	DMSO	-	TBHP (2)	63
16[c]	CuI (0.2)	DMSO	-	TBHP (2)	83
17	CuI (0)	DMSO	-	TBHP (2)	nr
18[d]	CuI (0.2)	DMSO	-	TBHP (2)	65

[a] Reaction conditions: **1a** (0.1 mmol, 43.1 mg), [Cu], TBHP (1.5 equiv), and base (1.0 equiv) in 2 mL of solvent was stirred at 110 °C in air for 12 hours. [b] the reaction was conducted at 80 °C. [c] 18 hours. nr = no reaction. [d] 1 mmol scaled reaction was conducted.

With these optimal reaction conditions in hand, we then explored substituents effect on the alkynes in substrates (Scheme 2). Based on results, a variety of substituents was compatible in the reaction under standard conditions. For instance, arylethynyls substituted with electron-withdrawing groups such as -Cl and -F at the *para* position of aryl group proved to be efficient reaction partners, affording the corresponding products **2a** and **2b** in 83% and 81% yields, respectively. The introduction of electron donating groups such as $-CH_3$, -Et and -OMe at the *para* position produced the desired products **2d-2f** in improved yields. Good yields of the pentacyclic products **2g-2h** were obtained when *meta*-substituted phenylethynyls were employed. However, steric hindering effect made significant impact on the outcomes. For example, the substrates with *ortho*-Cl phenylacetylene and -methoxylphenylacetylene gave the products in lower yields. This cyclization method is also suitable to the reaction of naphthylacetylene-, 2-thiophenethyl- and 3-thiophenethyl-linked substrates. As expected, **2k**, **2l**, and **2m** were obtained in yields of 81%, 78%, and 80%, respectively. To our delight, when using the substrate with alkylethynyl, the reaction proceeded smoothly and gave the product **2n** in a 64% yield. In this report, the exact structures of these products were identified by diffraction of X-Ray (CCDC: 1992389 for **2m**).

Scheme 2. **The Influence of Substituents On The Alkynes** [a]



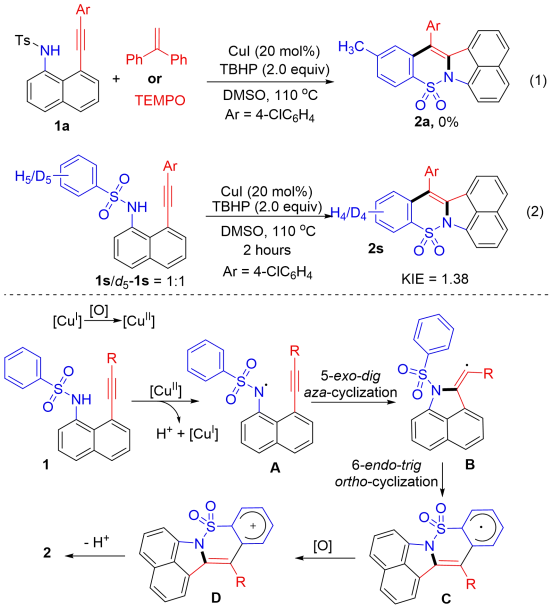
[a] Reaction conditions: **1** (0.1 mmol), CuI (0.02 mmol), TBHP (0.2 mmol) in DMSO (2.0 mL) was stirred under air for 18 hours. Yield of isolated product after column chromatography on silica gel. [b] The reaction time was 24 hours.

In order to understand the effect of substituents on the sulfonamides in the present reaction, the scope of substituted sulfonamides were subsequently examined. The *para* position of the aryl ring in arylsulfonamides could be replaced by an electron-withdrawing -F or an electron-donating $-OCH_3$, which both gave good yields. The reactions with *meta* and *ortho*-substituted sulfonamides also provided moderate to good yields. When there is no substituent on the benzenesulfonamide ring, **2s** was obtained

in 79% yield. 2-Naphthyl-linked sulfonamide was also compatible, leading to the desired product **2t** in 71% yield. When using *N*-(8-((4-chlorophenyl)ethynyl)naphthalen-1-yl)-4-nitrobenzene-sulfonamide as the substrate under standard conditions, the expected product **2u** could be obtained in 27% yield. It is probably due to the instability of radical intermediates in the presence of nitro group. Substituted naphthylamine had been tested in this reaction. When using *N*-(8-((4-methoxyphenyl)ethynyl)-4-nitronaphthalen-1-yl)-4-methylbenzenesulfonamide (**1v**) as the substrate, the expected product 13-(4-methoxyphenyl)-11-methyl-4-nitrobenzo[*cd*]benzo[5,6][1,2]thiazino[2,3-*a*]indole 8,8-dioxide (**2v**) could be obtained in 61% yield under the standard conditions. However, under standard conditions, the reactions of *N*-(8-((4-methoxyphenyl)ethynyl)naphthalen-1-yl)thiophene-2-sulfonamide or 4-methyl-*N*-(8-((trimethylsilyl)ethynyl)naphthalen-1-yl)benzenesulfon-amide or *N*-(8-ethynylnaphthalen-1-yl)-4-methylbenzenesulfonamide did not give desired products (please see ESI). The reaction of 4-methyl-*N*-(5-phenylpent-4-yn-1-yl)benzenesulfonamide did not take place under standard conditions, and starting material was recovered.

To gain insights into reaction mechanism, the control reactions and kinetic isotopic experiment were carried out under the standard conditions. By adding 4 equivalents of TEMPO or 1,1-diphenylethylene as radical scavengers under standard reaction conditions, the expected product **2a** was not observed (Scheme 3), and surprisingly, the corresponding radical was not trapped accordingly. We reasoned the use of radical scavengers retarded the formation of *tert*-butyloxygen radical from TBHP. The reaction of benzsulfonamide **1s** and deuterated benzsulfonamide **1s**-d_5 was also conducted. As expected, the value of the kinetic isotope effect (KIE) was 1.38. The KIE results indicated that the C-H bond cleavage step was not the rate-determining step in the formation of **1s**. Notably, a distinctive reaction pathway from that of our previous results was involved herein, although similar starting materials were employed.[15]

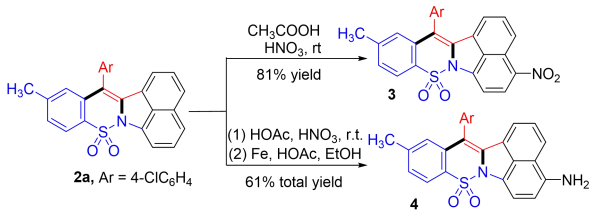
Scheme 3. The control experiments and Plausible Mechanism



Based on the aforementioned results, we postulated a plausible mechanism, as illustrated in Scheme 3. Initially, treated with *in situ* generated [Cu^{II}], a tosyl amide *N*-center radical **A** was produced with the removal of proton. The intermediate **A** then went through an intramolecular 5-*exo-dig aza*-cyclization to provide dihydrobenzo-[*c,d*]indole-fused 1,2-benzothiazine 1,1-dioxides vinyl radical **B**. Undergoing another radical 6-*endo-trig* dearomatization, the intermediate **B** was readily converted into polycyclic species **C**. Finally, oxidation and aromatization afforded the desired products **2**.

Structural elaboration of products **2** was also explored, and the results were presented in Scheme 4. Nitrated product **3** could be reached in an 81% yield at room temperature in the presence of HNO_3/HOAc. Moreover, the prepared nitrated product was able to be reduced *in situ* by Fe/HOAc to offer an aminated product **4** in a 61% total yield.

Scheme 4 Structural elaboration of product **2a**



During the experiments, we observed that these compounds emitted strong photoluminescence in dilute solutions as well as in solids (Figures 1 and 2). First of all, the effect of alkyne substituents on photophysical properties was investigated. The UV-vis absorption was measured in a $2*10^{-5}$ M concentration of tetrahydrofuran. The maximum absorption wavelengths for **2a**, **2e** and **2m** are around 406 nm without the apparent influence of the substituted groups (see ESI). **2a** and **2m** emitted bright blue light at about 480 nm with a large Stokes shift at about 74 nm (3800 cm^{-1}). With electron-donating group substitution, **2e** emitted light at 475 nm with a Stokes shift of 69 nm (3580 cm^{-1}). Next, we investigated the effect on photophysical properties of substituents on the aromatic ring adjacent to the sulfonamide. The absorption wavelengths of **2e** and **2o** were 406 and 408 nm (see ESI). **2e** emitted blue light at about 475 nm with a Stokes shift at about 69 nm, compared to **2o** which emitted bright light at about 482 nm with a large Stokes shift about 74 nm (3760 cm^{-1}).

Finally, the substituents effects of naphthalene ring on photophysical properties were investigated. Could be seen from the data, the substituent effect was apparent. Compounds **2a**, **3** and **4** absorbed light at about 406 nm, 439 nm and 477 nm (see ESI), respectively. Also the emission spectrum was done. The excitation wavelengths of **2a**, **3** and **4** were 480 nm, 505 nm and 620 nm. Based on the results, we found that Stokes shift of amino-linked 2*H*-benzo[*e*][1,2]thiazine 1,1-dioxides **4** in dilute tetrahydrofuran was identified to be 143 nm (4830 cm^{-1}).

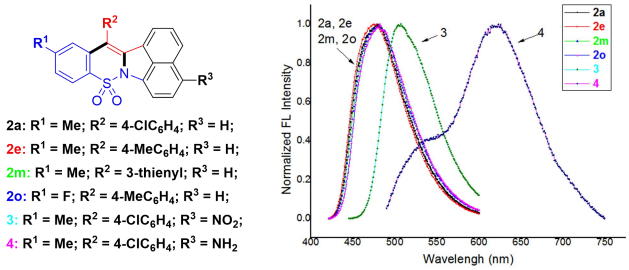


Figure 1 Fluorescence emission spectrum of **2a**, **2e** and **2m**

Besides, compounds **2a** had strong emission in solid. The emission wavelength of this compound was about 503 nm (Figure 2a). Before and after UV irradiation on **2a** was shown in Figure 2b.

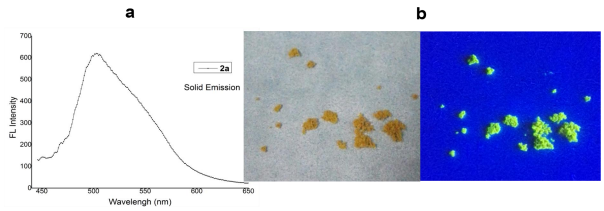


Figure 2 (a) Solid emission spectra of **2a**. (b) Images of compound **2a** under white light (left) and under UV light (365 nm) (right).

Conclusion

In conclusion, we have developed an efficient tandem radical pathway to prepare thio-azafluoranthenes from 8-alkynylnaphthalen-1-amines. The reactions were catalyzed by CuI, while TBHP was used as the oxidant. Moreover, this *thio*-azafluoranthene was indeed a new fluorophore and its photophysical properties were investigated. The largest Stokes shift in dilute tetrahydrofuran was determined to be 143 nm of compound **4**. Further studies on the synthetic application are currently ongoing.

Experimental Section

Unless stated otherwise, reactions were conducted in dried glassware. Commercially available reagents and solvents were used as received. 300-400 Mesh silica gel was used for flash column chromatography. Visualization on TLC was achieved by the use of UV light (254 nm). 400 MHz and 100 MHz were used for the record of ^{1}H NMR and ^{13}C NMR spectra. Chemical shifts (δ ppm) were reported in parts per million referring to either the internal standard of TMS or the residue of the deuterated solvents. Splitting pattern was described as follows: s for singlet, d for doublet, t for triplet, q for quartet, and m for multiplet. Coupling constants were reported in Hz. The high-resolution mass spectrum (HRMS) was performed on Waters Xevo G2-S QTof mass spectrometer. Absorption spectra were measured using UV-Vis spectrometer (Shimadzu, UV-2450). Emission spectra were recorded on a spectrofluorometer (Shimadzu, RF-5301PC) with a xenon lamp excitation source. All the substrates were synthesized with references to published literatures[13,16].

Typical Procedure for the synthesis of compound 1a:

8-iodonaphthalen-1-amine, *p*-chlorophenylacetylene (1.2 equiv), TEA (3.0 equiv), $PdCl_2(PPh_3)_2$ (5 mol%), and CuI (2 mol%) were added in flask under N_2 atmosphere. The mixture was stirred at room temperature. After reaction as indicated by TLC, filtration, evaporation under reduced pressure and purification by flash column chromatography provided 8-((4-chlorophenyl)ethynyl)naphthalen-1-amine in 82% yield. In the end, **1a** can be obtained in the presence of *p*-toluenesulfonyl chloride in 90% yield. All compounds are known in this paper as cited in Ref 13 and 16.

N-(8-((4-chlorophenyl)ethynyl)naphthalen-1-yl)benzenesulfonamide (1s-D5)

Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.89 (s, 1H), 7.82 (d, *J* = 7.5 Hz, 1H), 7.74 (d, *J* = 8.3 Hz, 3H), 7.63 (d, *J* = 7.1 Hz, 1H), 7.59 (d, *J* = 8.2 Hz, 1H), 7.44 – 7.40 (m, 3H), 7.33 (t, *J* = 7.7 Hz, 1H).

Typical Procedure for the synthesis of compound 2:

Substrate **1** (0.1 mmol) , CuI (0.2 equiv) and TBHP (2 equiv, 70% in water) were added to a test tube, and then DMSO (2.0 ml) was added. The mixture was stirred at 110 °C (oil bath) for 18 h (checked by TLC). After the substrate 1 was completely consumed, the reaction mixture was then cooled to room temperature, and quenched by adding 20 mL water and extracted with ethyl acetate (EA) (3*10 mL). After the organic layer was washed with saturated salt water, it was filtrated and concentrated under reduced pressure.The residue was purified by column chromatography to afford the desired product **2**.

13-(4-chlorophenyl)-11-methylbenzo[*cd*]benzo[5,6][1,2] thiazino[2,3-*a*]indole 8,8-dioxide (**2a**)

Yellow solid, 35.6 mg, 83%, eluent (PE:EA=10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.0 Hz, 1H), 7.82 – 7.76 (m, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.58 – 7.53 (m, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.36 – 7.30 (m, 2H), 6.84 (s, 1H), 6.31 (d, *J* = 7.3 Hz, 1H), 2.36 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.5, 137.3, 135.1, 134.5, 133.3, 132.1, 130.9, 130.8, 130.6, 129.0, 128.9, 128.9, 128.7, 128.5, 128.0, 127.8, 126.9, 126.7, 122.8, 121.6, 121.0, 109.4, 21.8; IR (neat) 3135, 1401, 820 cm^{-1}; HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{25}H_{17}ClNO_2S$: 430.0669; Found 430.0667.

13-(4-fluorophenyl)-11-methylbenzo[*cd*]benzo[5,6][1,2] thiazino[2,3-*a*]indole 8,8-dioxide (**2b**)

Yellow solid, 33.4 mg, 81%, eluent (PE:EA=10:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.0 Hz, 1H), 7.80 – 7.75 (m, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.57 – 7.52 (m, 2H), 7.47 – 7.40 (m, 2H), 7.40 – 7.27 (m, 4H), 6.85 (s, 1H), 6.25 (d, *J* = 7.3 Hz, 1H), 2.36 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.1 (J_{C-F} = 246.0 Hz), 143.4, 139.2, 137.3, 134.7, 132.5, 132.4, 130.9, 130.7 (J_{C-F} = 4.0 Hz), 128.9, 128.9, 128.7, 128.5, 128.0, 126.8, 126.8, 122.8, 121.5, 121.0, 117.5 (J_{C-F} = 22.0 Hz), 116.3, 109.3, 21.9. IR (neat) 3137, 1398, 818 cm^{-1}; HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{25}H_{17}FNO_2S$: 414.0964; Found 414.0962.

11-methyl-13-phenylbenzo[*cd*]benzo[5,6][1,2]thiazino[2,3-*a*]indole 8,8-dioxide (**2c**)

Yellow solid, 32.4 mg, 82%, eluent (PE:EA=10:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.1 Hz, 1H), 7.78 (dd, *J* = 5.9, 2.0 Hz, 1H), 7.72 – 7.58 (m, 4H), 7.58 – 7.50 (m, 2H), 7.45 (d, *J* = 6.4 Hz, 2H), 7.36 – 7.27 (m, 2H), 6.89 (s, 1H), 6.18 (d, *J* = 7.3 Hz, 1H), 2.35 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.3, 138.9, 137.4, 134.8, 131.1, 130.9, 130.5, 130.2, 128.9, 128.8, 128.8, 128.6, 128.4, 128.0, 127.0, 126.6, 122.7, 121.6, 120.9, 117.5, 112.0, 109.2, 21.8; IR (neat) 3136, 1403, 823 cm^{-1}; HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{25}H_{18}NO_2S$: 396.1058; Found 396.1059.

13-(4-ethylphenyl)-11-methylbenzo[*cd*]benzo[5,6][1,2] thiazino[2,3-*a*]indole 8,8-dioxide (**2d**)

Yellow solid, 35.9 mg, 85%, eluent (PE:EA=10:1).^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.0 Hz, 1H), 7.77 (dd, *J* = 5.9, 1.8 Hz, 1H), 7.68 (d, *J* = 8.1

Hz, 1H), 7.53 (d, *J* = 6.2 Hz, 2H), 7.48 (d, *J* = 7.8 Hz, 2H), 7.37 – 7.26 (m, 4H), 6.92 (s, 1H), 6.22 (d, *J* = 7.3 Hz, 1H), 2.85 (d, *J* = 7.6 Hz, 2H), 2.35 (s, 3H), 1.40 (t, *J* = 7.6 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 145.0, 143.3, 138.9, 137.4, 134.9, 131.9, 131.2, 130.9, 130.3, 129.6, 128.9, 128.8, 128.7, 128.3, 128.0, 127.0, 126.4, 122.6, 121.6, 120.8, 117.6, 109.1, 28.8, 21.8, 15.5; IR (neat) 3131, 1402, 820 cm^{-1}; HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{27}H_{22}NO_2S$: 424.1371; Found 424.1369.

11-methyl-13-(*p*-tolyl)benzo[*cd*]benzo[5,6][1,2] thiazino [2,3-*a*]indole 8,8-dioxide (**2e**)

Yellow solid, 35.2 mg, 86%, eluent (PE:EA=10:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.0 Hz, 1H), 7.80 – 7.73 (m, 1H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.57 – 7.49 (m, 2H), 7.46 (d, *J* = 7.7 Hz, 2H), 7.36 – 7.23 (m, 4H), 6.92 (s, 1H), 6.26 (d, *J* = 7.3 Hz, 1H), 2.55 (s, 3H), 2.34 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 143.3, 138.8, 138.7, 137.4, 134.9, 131.7, 131.2, 130.9, 130.9, 130.2, 128.9, 128.8, 128.7, 128.3, 128.0, 127.0, 126.5, 122.6, 121.7, 120.9, 117.6, 109.1, 21.8, 21.6; IR (neat) 3135, 1401, 817 cm^{-1}; HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{26}H_{20}NO_2S$: 420.1215; Found 420.1212.

13-(4-methoxyphenyl)-11-methylbenzo[*cd*]benzo[5,6][1,2] thiazino[2,3-*a*]indole 8,8-dioxide (**2f**)

Yellow solid, 35.7 mg, 84%, eluent (PE:EA=10:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 5.5 Hz, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.58 – 7.47 (m, 2H), 7.40 – 7.27 (m, 4H), 7.18 (d, *J* = 7.5 Hz, 2H), 6.92 (s, 1H), 6.31 (d, *J* = 7.1 Hz, 1H), 3.97 (s, 3H), 2.35 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 159.9, 143.3, 139.1, 137.4, 135.1, 131.7, 131.2, 130.9, 128.9, 128.8, 128.7, 128.3, 128.0, 127.0, 126.8, 126.5, 122.6, 121.7, 120.9, 117.2, 115.6, 109.1, 55.4, 21.8; IR (neat) 3134, 1401, 818 cm^{-1}; HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{26}H_{20}NO_3S$: 426.1164; Found 426.1161.

13-(3-chlorophenyl)-11-methylbenzo[*cd*]benzo[5,6][1,2] thiazino[2,3-*a*]indole 8,8-dioxide (**2g**)

Yellow solid, 35.2 mg, 82%, eluent (PE:EA=10:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 2.9 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.62 (d, *J* = 3.9 Hz, 2H), 7.55 (s, 2H), 7.48 (s, 1H), 7.40 – 7.29 (m, 3H), 6.84 (s, 1H), 6.27 (d, *J* = 7.3 Hz, 1H), 2.37 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 143.5, 141.8, 140.1, 137.2, 136.7, 136.0, 135.3, 134.7, 131.6, 130.9, 130.7, 129.3, 129.0, 128.9, 128.9, 128.6, 128.6, 126.9, 126.7, 122.8, 122.8, 121.7, 121.1, 109.4, 21.9; IR (neat) 3142, 1401, 807 cm^{-1}; HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{25}H_{17}ClNO_2S$: 430.0669; Found 430.0663.

13-(3-fluorophenyl)-11-methylbenzo[*cd*]benzo[5,6][1,2] thiazino[2,3-*a*]indole 8,8-dioxide (**2h**)

Yellow solid, 33.0 mg, 80%, eluent (PE:EA=10:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.1 Hz, 1H), 7.82 – 7.76 (m, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.70 – 7.60 (m, 1H), 7.58 – 7.51 (m, 2H), 7.38 – 7.28 (m, 3H), 7.28 – 7.23 (m, 1H), 7.19 (d, *J* = 9.0 Hz, 1H), 6.86 (s, 1H), 6.27 (d, *J* = 7.3 Hz, 1H), 2.37 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 164.0 (J_{C-F} = 248.0 Hz), 143.5, 139.0, 137.3, 137.0 (J_{C-F} = 8.0 Hz), 134.3, 132.0 (J_{C-F} = 8.0 Hz), 130.9, 130.7, 128.9, 128.6, 128.5, 127.9, 126.9, 126.7, 126.4 (J_{C-F} = 3.0 Hz), 122.8, 121.6, 121.1, 117.8, 117.6, 116.2, 116.0, 109.4, 21.9; IR (neat) 3140, 1400, 806 cm^{-1}; HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{25}H_{17}FNO_2S$: 414.0964; Found 414.0967.

13-(2-chlorophenyl)-11-methylbenzo[*cd*]benzo[5,6][1,2] thiazino[2,3-*a*]indole 8,8-dioxide (**2i**)

Yellow solid, 32.6 mg, 76%, eluent (PE:EA=10:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.1 Hz, 1H), 7.84 – 7.77 (m, 1H), 7.73 (d, *J* = 8.1 Hz, 2H), 7.63 – 7.53 (m, 4H), 7.52 – 7.44 (m, 1H), 7.37– 7.27 (m, 2H), 6.78 (s, 1H), 6.17 (d, *J* = 7.3 Hz, 1H), 2.37 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 143.5, 139.4, 137.4, 135.3, 133.6, 133.5, 132.5, 130.9, 130.9, 130.7, 130.6, 129.1, 128.9, 128.7, 128.6, 128.6, 127.9, 127.0, 126.3, 122.8, 121.2, 121.0, 114.5, 109.4, 21.9; IR (neat) 3138, 1401, 768 cm^{-1}; HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{25}H_{17}ClNO_2S$: 430.0669; Found 430.0666.

13-(2-methoxyphenyl)-11-methylbenzo[*cd*]benzo[5,6][1,2] thiazino[2,3-*a*]indole 8,8-dioxide (**2j**)

Yellow solid, 31.9 mg, 75%, eluent (PE:EA=10:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.0 Hz, 1H), 7.78 (dd, *J* = 6.1, 1.6 Hz, 1H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.65 – 7.57 (m, 1H), 7.56 – 7.48 (m, 2H), 7.36 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.33 – 7.26 (m, 2H), 7.26 – 7.15 (m, 2H), 6.87 (s, 1H), 6.25 (d, *J* = 7.3 Hz, 1H), 3.68 (s, 3H), 2.35 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 157.9, 143.2, 138.9, 137.5, 134.5, 132.1, 131.3, 130.9, 130.7, 129.0, 128.7, 128.3, 128.1, 126.7, 126.4, 123.2, 122.6, 122.2, 121.1, 120.7, 114.2, 112.1, 109.0, 55.8, 21.9; IR (neat) 3135, 1401, 771 cm^{-1}; HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{26}H_{20}NO_3S$: 426.1164; Found 426.1163.

11-methyl-13-(naphthalen-1-yl)benzo[*cd*]benzo[5,6][1,2] thiazino[2,3-*a*]indole 8,8-dioxide (**2k**)

Yellow solid, 36.0 mg, 81%, eluent (PE:EA=10:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.0 Hz, 2H), 8.03 (d, *J* = 8.2 Hz, 1H), 7.87 – 7.67 (m, 3H),7.66 – 7.57 (m, 2H), 7.57 – 7.47 (m, 3H), 7.38 – 7.29 (m, 2H), 7.09 (td, *J* = 8.1, 2.8 Hz, 1H), 6.74 (s, 1H), 5.79 (dd, *J* = 7.3, 2.6 Hz, 1H), 2.24 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 143.5, 139.7, 137.4, 134.9, 134.4, 132.2, 132.1, 130.9, 130.7, 129.5, 129.4, 128.9, 128.8, 128.6, 128.5, 128.5, 128.1, 127.2, 126.9, 126.8, 126.5, 126.5, 124.9, 122.6, 121.7, 121.0, 115.4, 109.3, 21.8; IR (neat) 3134, 1401, 771 cm^{-1}; HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{29}H_{20}NO_2S$: 446.1215; Found 446.1214.

11-methyl-13-(thiophen-2-yl)benzo[*cd*]benzo[5,6][1,2] thiazino[2,3-*a*]indole 8,8-dioxide (**2l**)

Orange solid, 31.3 mg, 78%, eluent (PE:EA=10:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.0 Hz, 1H), 7.83 – 7.73 (m, 2H), 7.68 (d, *J* = 5.2 Hz, 1H), 7.58 – 7.52 (m, 2H), 7.42 – 7.29

(m, 3H), 7.22 – 7.14 (m, 1H), 7.10 (s, 1H), 6.37 (d, J = 7.3 Hz, 1H), 2.40 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 151.1, 143.6, 141.0, 139.6, 137.6, 137.2, 135.2, 134.9, 130.8, 129.1, 129.0, 128.8, 128.5, 128.5, 128.3, 127.7, 127.2, 126.7, 122.6, 122.3, 121.2, 109.5, 21.9; IR (neat) 3129, 1401, 774 cm^{-1}; HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{23}H_{16}NO_2S_2$: 402.0622; Found 402.0623.

11-methyl-13-(thiophen-3-yl)benzo[*cd*]benzo[5,6][1,2] thiazino[2,3-*a*]indole 8,8-dioxide (**2m**)

Orange solid, 32.1 mg, 80%, eluent (PE:EA=10:1).^1H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.0 Hz, 1H), 7.81 – 7.74 (m, 1H), 7.73 – 7.65 (m, 2H), 7.58 – 7.48 (m, 2H), 7.44 (s, 1H), 7.33 (dd, J = 15.1, 7.4 Hz, 2H), 7.13 (d, J = 4.8 Hz, 1H), 6.97 (s, 1H), 6.35 (d, J = 7.3 Hz, 1H), 2.37 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 143.4, 139.4, 137.3, 134.7, 134.5, 130.9, 130.9, 129.0, 128.8, 128.5, 128.4, 128.1, 127.9, 126.8, 126.8, 125.8, 122.6, 121.5, 121.0, 112.0, 109.2, 21.9; IR (neat) 3128, 1401, 773 cm^{-1}; HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{23}H_{16}NO_2S_2$: 402.0622; Found 402.0625.

13-butyl-11-methylbenzo[*cd*]benzo[5,6][1,2]thiazino[2,3-*a*]indole 8,8-dioxide (**2n**)

Yellow solid, 24.0 mg, 64%, eluent (PE:EA=10:1).^1H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.0 Hz, 1H), 7.86 – 7.72 (m, 3H), 7.71 – 7.63 (m, 1H), 7.61 – 7.53 (m, 2H), 7.51 (s, 1H), 7.35 (d, J = 8.0 Hz, 1H), 3.16 – 3.06 (m, 2H), 2.54 (s, 3H), 1.74 (d, J = 6.9 Hz, 2H), 1.63 (dd, J = 14.6, 7.4 Hz, 2H), 1.11 – 1.02 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 143.3, 137.6, 134.3, 132.6, 131.3, 131.2, 129.2, 129.2, 128.9, 128.4, 128.3, 126.4, 125.0, 122.8, 121.4, 120.7, 117.7, 109.1, 29.7, 27.5, 23.1, 22.2, 14.1; IR (neat) 3466, 1747, 752 cm^{-1}; HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{23}H_{22}NO_2S$: 376.1371; Found 376.1373.

11-fluoro-13-(*p*-tolyl)benzo[*cd*]benzo[5,6][1,2]thiazino[2,3-*a*]indole 8,8-dioxide (**2o**)

Yellow solid, 33.8 mg, 82%, eluent (PE:EA=10:1).^1H NMR (400 MHz, $CDCl_3$) δ 8.17 (dd, J = 8.7, 5.3 Hz, 1H), 7.86 – 7.68 (m, 3H), 7.56 (d, J = 4.2 Hz, 3H), 7.46 (d, J = 7.7 Hz, 2H), 7.36 – 7.27 (m, 2H), 7.22 – 7.13 (m, 1H), 6.80 (dd, J = 10.3, 2.2 Hz, 1H), 6.34 (d, J = 7.3 Hz, 1H), 2.54 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 164.9 ($J_{C\text{-}F}$ = 252.0 Hz), 139.1, 137.1, 131.7, 131.1, 131.0, 130.8, 130.7, 130.1, 129.3, 128.9, 128.8, 128.7, 127.9, 127.1, 125.5 ($J_{C\text{-}F}$ = 10.0 Hz), 122.3, 121.2, 114.8 ($J_{C\text{-}F}$ = 23.0 Hz), 113.3, 113.1, 109.5, 21.5; IR (neat) 3134, 1401, 805 cm^{-1}; HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{25}H_{17}FNO_2S$: 414.0964; Found 414.0967.

13-(4-chlorophenyl)-11-methoxybenzo[*cd*]benzo[5,6][1,2] thiazino[2,3-*a*]indole 8,8-dioxide (**2p**)

Yellow solid, 37.4 mg, 84%, eluent (PE:EA=10:1).^1H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 8.8 Hz, 1H), 7.81 – 7.75 (m, 1H), 7.73 (d, J = 8.1 Hz, 1H), 7.64 (d, J = 8.3 Hz, 2H), 7.58 – 7.51 (m, 2H), 7.40 (d, J = 8.3 Hz, 2H), 7.33 (t, J = 7.8 Hz, 1H), 7.02 (dd, J = 8.8, 2.3 Hz, 1H), 6.48 (d, J = 2.3 Hz, 1H), 6.31 (d, J = 7.3 Hz, 1H), 3.76 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.7, 137.6, 137.2, 136.7, 135.1, 133.2, 132.1, 130.9, 130.7, 130.7, 128.9, 128.9, 127.9, 127.0, 124.9, 123.9, 121.8, 121.0, 115.8, 113.2, 111.4, 109.4, 55.6; IR (neat) 3137, 1401, 809 cm^{-1}; HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{25}H_{17}ClNO_3S$: 446.0618; Found 446.0619.

10-chloro-13-(4-chlorophenyl)benzo[*cd*]benzo[5,6][1,2] thiazino[2,3-*a*]indole 8,8-dioxide (**2q**)

Yellow solid, 36.4 mg, 81%, eluent (PE:EA=10:1).^1H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 7.5 Hz, 1H), 7.77 (d, J = 7.6 Hz, 2H), 7.65 – 7.51 (m, 5H), 7.50 – 7.41 (m, 3H), 7.35 (t, J = 7.7 Hz, 1H), 6.44 (d, J = 7.3 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 136.7, 136.5, 134.9, 134.2, 132.7, 132.5, 131.7, 131.2, 130.9, 130.6, 129.8, 129.3, 129.0, 129.0, 128.8, 128.7, 128.3, 127.6, 123.0, 122.0, 121.9, 110.6; IR (neat) 3135, 1401, 804 cm^{-1}; HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{24}H_{14}Cl_2NO_2S$: 450.0122; Found 450.0121.

13-(4-chlorophenyl)-9-fluorobenzo[*cd*]benzo[5,6][1,2] thiazino[2,3-*a*]indole 8,8-dioxide (**2r**)

Yellow solid, 31.6 mg, 73%, eluent (PE:EA=10:1).^1H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.78 (m, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.65 (d, J = 7.4 Hz, 2H), 7.60 – 7.52 (m, 2H), 7.48 (d, J = 6.0 Hz, 1H), 7.42 – 7.31 (m, 3H), 7.22 – 7.13 (m, 1H), 6.83 (d, J = 8.0 Hz, 1H), 6.30 (d, J = 7.1 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.6 ($J_{C\text{-}F}$ = 257.0 Hz), 137.1, 136.8, 135.3, 133.7, 133.6, 133.1, 132.1, 130.8, 130.8, 130.2, 129.0, 129.0, 127.5, 127.4, 122.4, 122.4, 122.1, 121.4, 115.1, 114.9, 109.9; IR (neat) 3132, 1401, 806 cm^{-1}; HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{24}H_{14}ClFNO_2S$: 434.0418; Found 434.0412.

13-(4-chlorophenyl)benzo[*cd*]benzo[5,6][1,2]thiazino[2,3-*a*]indole 8,8-dioxide (**2s**)

Yellow solid, 32.8 mg, 79%, eluent (PE:EA=10:1).^1H NMR (400 MHz, $CDCl_3$) δ 8.24 – 8.15 (m, 1H), 7.83 – 7.77 (m, 1H), 7.74 (d, J = 8.2 Hz, 1H), 7.65 (d, J = 8.4 Hz, 2H), 7.61 – 7.46 (m, 4H), 7.41 (d, J = 8.4 Hz, 2H), 7.38 – 7.30 (m, 1H), 7.12 – 7.04 (m, 1H), 6.35 (d, J = 7.3 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 137.2, 135.2, 134.5, 133.7, 133.2, 132.6, 132.1, 130.9, 130.7, 130.6, 128.9, 128.9, 128.0, 127.6, 127.3, 127.0, 126.5, 122.7, 121.7, 121.2, 116.1, 109.5; IR (neat) 3133, 1401, 805 cm^{-1}; HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{24}H_{15}ClNO_2S$: 416.0512; Found 416.0515.

15-phenylbenzo[*cd*]naphtho[1',2':5,6][1,2]thiazino[2,3-*a*]indole 7,7-dioxide (**2t**)

Yellow solid, 30.6 mg, 71%, eluent (PE:EA=10:1).^1H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 8.6 Hz, 1H), 7.97 (d, J = 8.6 Hz, 1H), 7.87 – 7.79 (m, 2H), 7.71 (d, J = 8.1 Hz, 1H), 7.67 – 7.62 (m, 3H), 7.59 – 7.54 (m, 5H), 7.48 – 7.41 (m, 1H), 7.28 (t, J = 7.8 Hz, 1H), 7.12 (t, J = 7.9 Hz, 1H), 6.39 (d, J = 7.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 140.4, 138.6, 136.8,

136.2, 131.9, 131.2, 130.9, 130.7, 130.5, 130.2, 129.8, 129.8, 129.2, 129.1, 129.0, 128.9, 128.6, 127.6, 127.4, 127.1, 126.7, 122.7, 121.7, 119.9, 118.2, 110.5; IR (neat) 3131, 1398, 803 cm^{-1}; HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{28}H_{18}NO_2S$: 432.1058; Found 432.1057.

13-(4-chlorophenyl)-11-nitrobenzo[*cd*]benzo[5,6][1,2] thiazino[2,3-*a*]indole 8,8-dioxide (**2u**)

Yellow solid, 12.4 mg, 27%, eluent (PE:EA=5:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J = 8.6 Hz, 1H), 8.30 (d, J = 8.7 Hz, 1H), 7.93 (s, 1H), 7.83 (d, J = 7.7 Hz, 2H), 7.71 (d, J = 8.1 Hz, 2H), 7.67 – 7.58 (m, 2H), 7.48 – 7.37 (m, 3H), 6.42 (d, J = 7.3 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 136.5, 136.3, 136.0, 135.5, 134.4, 131.9, 131.8, 131.1, 130.9, 130.0, 129.2, 129.0, 128.2, 124.6, 122.9, 122.8, 122.0, 121.4, 121.3, 115.1, 110.2, 105.0; IR (neat) 3130, 1401, 805 cm^{-1}; HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{24}H_{14}ClN_2O_4S$: 461.0363; Found 461.0361.

13-(4-methoxyphenyl)-11-methyl-4-nitrobenzo[*cd*]benzo [5,6][1,2]thiazino[2,3-*a*]indole 8,8-dioxide (**2v**)

Yellow solid, 28.7 mg, 61%, eluent (PE:EA=5:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.75 – 8.63 (m, 2H), 8.06 (d, J = 8.0 Hz, 1H), 7.78 (d, J = 8.3 Hz, 1H), 7.58 – 7.51 (m, 1H), 7.42 – 7.32 (m, 3H), 7.21 (d, J = 8.6 Hz, 2H), 6.96 (s, 1H), 6.39 (d, J = 7.4 Hz, 1H), 3.99 (s, 3H), 2.38 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.3, 144.1, 143.4, 139.2, 138.2, 134.5, 132.5, 131.2, 130.0, 129.7, 129.2, 128.9, 128.5, 127.8, 125.7, 124.8, 124.3, 123.0, 122.7, 120.0, 115.8, 107.0, 55.5, 21.9; IR (neat) 3132, 1400, 800 cm^{-1}; HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{26}H_{19}ClN_2O_5S$: 471.1015; Found 471.1017.

13-(4-chlorophenyl)-11-methyl-4-nitrobenzo[*cd*]benzo[5,6] [1,2]thiazino[2,3-*a*]indole 8,8-dioxide (**3**)

Yellow solid, 38.4 mg, 81%, eluent (PE:EA=5:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, J = 8.6 Hz, 1H), 8.68 (d, J = 8.5 Hz, 1H), 8.08 (d, J = 7.8 Hz, 1H), 7.81 (d, J = 8.4 Hz, 1H), 7.68 (d, J = 8.2 Hz, 2H), 7.58 (t, J = 8.0 Hz, 1H), 7.40 (d, J = 8.0 Hz, 3H), 6.87 (s, 1H), 6.38 (d, J = 7.3 Hz, 1H), 2.38 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 144.3, 136.4, 135.6, 132.6, 132.3, 131.6, 130.9, 130.5, 130.1, 129.7, 129.6, 129.5, 128.9, 127.4, 125.3, 124.5, 124.4, 123.6, 123.1, 122.8, 122.7, 107.3, 21.9; IR (neat) 3130, 1401, 779 cm^{-1}; HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{25}H_{16}ClN_2O_4S$: 475.0519; Found 475.0514.

4-amino-13-(4-chlorophenyl)-11-methylbenzo[*cd*]benzo[5,6] [1,2]thiazino[2,3-*a*]indole 8,8-dioxide (**4**)

Yellow solid, 27.1 mg, 61%, eluent (PE:EA=5:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.0 Hz, 1H), 7.75 – 7.60 (m, 3H), 7.56 (d, J = 7.9 Hz, 1H), 7.38 (d, J = 7.9 Hz, 2H), 7.35 – 7.20 (m, 2H), 6.87 – 6.70 (m, 2H), 6.29 (d, J = 7.4 Hz, 1H), 4.14 (s, 2H), 2.34 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 143.2, 139.3, 137.5, 134.9, 134.5, 133.5, 132.2, 131.1, 130.6, 129.4, 128.7, 128.3, 128.3, 127.7, 126.5, 122.6, 122.1, 122.0, 121.7, 115.6, 111.7, 110.5, 21.8; IR (neat) 3135, 1401, 724 cm^{-1}; HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{25}H_{18}ClN_2O_2S$: 445.0778; Found 445.0779.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures, compound characterization data (PDF), and FAIR Data are available as Supporting Information for Publication, and also includes the primary NMR FID files for compounds **2a**-**2v**, **3**, **4**, **1s**-D5 and **1s**-h. This material is available free of charge via the Internet at http://pubs.acs.org.;
X-ray crystal structures CCDC: 1992389 for **2m**

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Notes

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