Preparation of 3,4-Dihydro-2,1-benzothiazine 2,2-Dioxide Skeleton from *N*-Methyl 2-(Aryl)ethanesulfonamides with (Diacetoxyiodo)arenes

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It is well-known that sulfonamides have enormous potential as pharmaceutical and agricultural agents due to their biological activities,[1] and cyclic sulfonamides (sultams) are important as chiral auxiliaries.[2] Among them, 3,4-dihydro-2,1-benzothiazine 2,2-dioxide derivatives (benzosultams) have potent biological activities such as lipoxygenase inhibition and as drugs for treating heart diseases (Figure 1). Therefore, active studies for the synthetic development of benzothiazine derivatives have been carried out.[1a,3] Today, three methods for the construction of 3,4-dihydro-2,1-benzothiazine 2,2-dioxide skeleton are known, i.e., the cyclization of 2-(*o*-aminophenyl)ethanesulfonic acid,[4a] the cyclization of *N*-benzyl-*N*-methanesulfonyl(*o*-chloromethyl)aniline,[4b] and the cyclization of *N*-phenylsulfamoylacetic acid and subsequent reduction of the carbonyl group.[4c] However, these methods require many steps, and the yields of the cyclized products are not good. We have also been interested in the new synthetic study of such benzothiazine derivatives. Here, as part of our program to develop the synthetic use of hypervalent iodine compounds for organic synthesis,[5] we would like to report a new preparative method of 3,4-dihydro-2,1-benzothiazine 2,2-dioxides from *N*-alkyl 2-(aryl)ethanesulfonamides with (diacetoxyiodo)arenes under photochemical conditions.

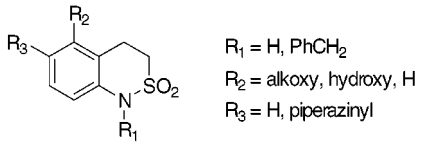
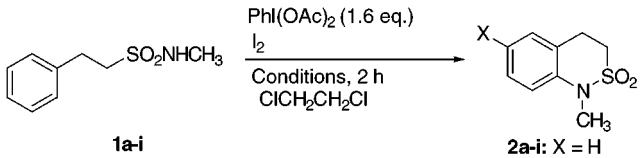


Figure 1. 3,4-Dihydro-2,1-benzothiazine 2,2-dioxide derivatives.

Table 1. Formation of 3,4-Dihydro-2,1-benzothiazine 2,2-Dioxide with PhI(OAc)$_2$/I$_2$ System



1a-i **2a-i:** X = H **3a-i:** X = I

	conditions			yields (%)	
entry	light	*T* (°C)	I$_2$ (equiv)	**2a-i**	**3a-i**
1	dark	20−30	1.0	0	0
2	W-*hν*	20−30	0	0	0
3	fluorescent lighting	20−30[a]	1.0	0	85
4	Hg-*hν*	20−30	1.0	13	66
5	W-*hν*	0−5	1.0	63	18
6	W-*hν*	20−30	1.0	6	89
7	W-*hν*	55−65	1.0	46	41
8	W-*hν*	20−30	0.1	95	0
9	W-*hν*	20−30[b]	1.0	0	0

[a] Reaction for 5 h. [b] In the presence of TEMPO (1.0 equiv).

At first, photochemical treatment of *N*-methyl 2-(phenyl)ethanesulfonamide with (diacetoxyiodo)benzene (1.6 equiv) in the presence of iodine (1.0 equiv) was carried out at room temperature as shown in Table 1. Here, the cyclization reaction did not proceed at all under dark conditions (entry 1) or without iodine (entry 2). Under fluorescent lighting, the formation of 3,4-dihydro-6-iodo-2,1-benzothiazine 2,2-dioxide **3a-i** was observed in 85% yield (entry 3). Under irradiation with a high-pressure mercury lamp (Hg-*hν*), 3,4-dihydro-2,1-benzothiazine 2,2-dioxide **2a-i** and the iodo compound **3a-i** were obtained in 13% and 66% yields, respectively (entry 4). However, the best yield of compound **3a-i** was obtained when the irradiation reaction was carried out with a tungsten lamp in the range of 20−30 °C (W-*hν*, entry 6), while the reaction was completely inhibited by the addition of a 2,2,6,6-tetramethyl-1-piperidinyloxy free radical (TEMPO, entry 9). Moreover, the addition of a catalytic amount of iodine (0.1 equiv) gave the compound **2a-i** alone in good yield (entry 8). Thus, the formation of compounds **2a-i** and **3a-ii** can be controlled by the amount of iodine.

The effect of (diacetoxyiodo)arenes for the present cyclyzation was examined as shown in Table 2. (Diacetoxyiodo)benzene gave the compound **3a-i** in 89% yield (entry 2), while, 2,6-diphenyl-1-(diacetoxyiodo)benzene

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† Graduate School of Science and Technology.
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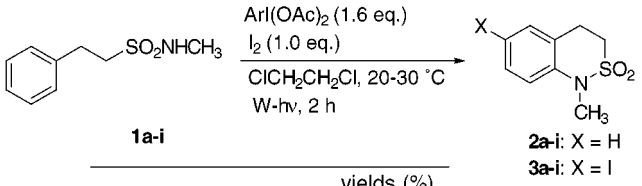
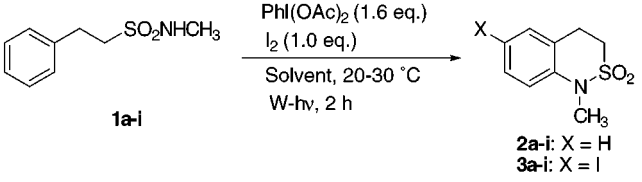
Table 2. Effect of (Diacetoxyiodo)arenes



entry	Ar	yields (%) 2a-i	3a-i
1	CH_3O–	39	48
2		6	89
3	Cl–	13	63
4	Ph, Ph	63	21

Table 3. Effect of Solvents



entry	solvent	yields (%) 2a-i	3a-i
1	$ClCH_2CH_2Cl$	6	89
2	AcOEt	81[a]	10
3	THF	0[b]	0
4	EtOH	0[c]	0

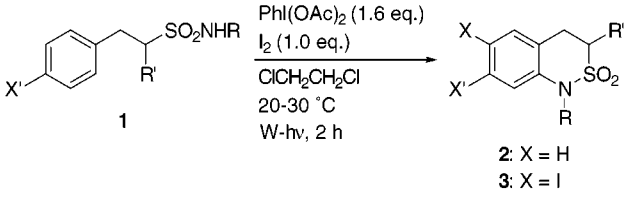
[a] Reaction for 40 min. [b] Starting amide was recovered in 55% yield. [c] Reaction at 55−65 °C. Starting amide was recovered in 88% yield.

gave compound **2a-i** as a major product under the same conditions.

Furthermore, the solvent effect in the present cyclization was examined as shown in Table 3. Here, an interesting solvent effect was observed. Under the same conditions, 1,2-dichloroethane gave compound **3a-i** as a major product (entry 1), while ethyl acetate gave the compound **2a-i** as a major product (entry 2). This result probably comes from the solvation of acetyl hypoiodite species or (diacetoxyiodo)benzene/iodine complex by ethyl acetate, which reduces the electrophilicity of the iodonium species. This is the second control for the formation of compounds **2a-i** and **3a-i**. THF and ethanol did not give the cyclized products due to their α-hydrogen abstraction by the formed sulfonamidyl radical.

On the basis of the above results, the formation of 3,4-dihydro-2,1-benzothiazine 2,2-dioxides with other *N*-alkyl 2-(aryl)ethanesulfonamides under the best conditions was carried out as shown in Table 4. Here, with respect to the effect of the *N*-alkyl groups, *N*-methyl (**a**), *N*-ethyl (**b**), and *N*-benzyl (**d**) groups gave the cyclized compound **2** or **3** in good yields (entries 1, 2, and 4). Utilization of the *N*-benzyl group is very useful for the easy deprotection (debenzylation) after the cyclization. However, the same treatment with 2-phenylethanesulfonamide, without an *N*-alkyl group, did not give the corresponding cyclized product at all. Moreover, an electronic effect on

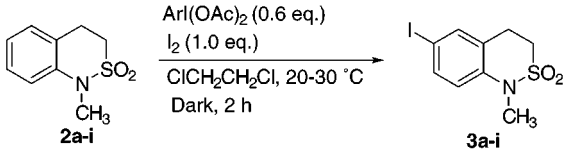
Table 4. Formation of 3,4-Dihydro-2,1-benzothiazine 2,2-Dioxides with Other *N*-Alkyl 2-(Aryl)ethanesulfonamides



entry	1	R	R′	X′	yields (%) 2	3
1	**1a-i**	CH_3	H	H	6	89
2	**1b-i**	CH_3CH_2	H	H	0	89
3	**1c-i**	$CH_3(CH_2)_5$	H	H	27	0
4	**1d-i**	$PhCH_2$	H	H	36	54
5	**1a-ii**	CH_3	CH_3	H	18	77
6	**1a-ii**	CH_3	CH_3	H	0	97[a]
7	**1a-iii**	CH_3	H	CH_3	0	92
8	**1a-iii**	CH_3	H	CH_3	0	94[a]
9	**1a-iv**	CH_3	H	F	26	60
10	**1a-v**	CH_3	H	Cl	34	49

[a] Reaction at 55−65 °C.

Table 5. Iodination of 3,4-Dihydro-2,1-benzothiazine 2,2-Dioxide



entry	Ar	yields (%) 2a-i	3a-i
1	CH_3O–	28	65
2		22	69
3	Cl–	44	51

the aromatic group in compounds **1** was observed. Thus, by the introduction of halogen groups on the aromatic ring, the decrease of compound **3** and the increase of compound **2** were observed due to the reduction of electron density on the aromatic ring toward the iodonium species.

Here, the compound **3** is formed via the iodination of the formed compound **2** by hypoiodite species. Thus, compound **2a-i** was easily iodinated under the same conditions to give compound **3a-i** as shown in Table 5. Today, the iodination of aromatics by a (diacetoxyiodo)-benzene/iodine system is well-known.[6]

N-Methyl 2-(α-naphthyl)ethanesulfonamide **6** and *N*-methyl 1-methyl-2-(*β*-naphthyl)ethanesulfonamide **8** gave the corresponding 3,4-dihydro-2,1-naphthothiazine 2,2-dioxides in good yields, under the same conditions.

When the present cyclization was carried out with *N*-methyl 3-(phenyl)propanesulfonamide, *N*-methyl 3-phenyl-1,3-propanesultam was obtained in 60% yield (entry 4 in Table 6) via the Hofmann−Löffler−Freytag-

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Scheme 1. Formation of 3,4-Dihydro-2,1-naphthothiazine 2,2-Dioxides

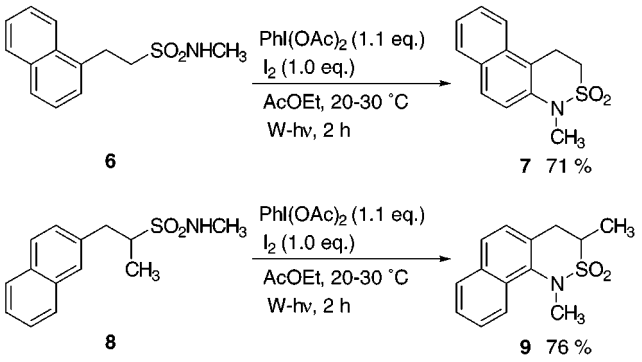
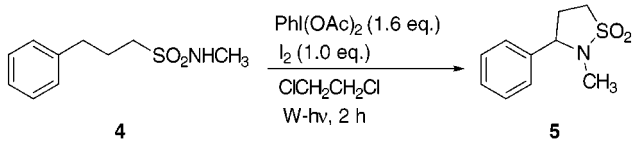


Table 6. Hofmann−Löffler−Freytag-Type Reaction



entry	*T* (°C)	additive	yield (%)
1	0	none	41
2	20−30	none	46
3	55−65	none	43
4	20−30	K_2CO_3	60

type reaction. *N*-Methyl 4-(phenyl)butanesulfonamide gave also *N*-methyl 4-phenyl-1,4-butanesultam in 21% yield, together with many byproducts. *N*-Methyl phenylmethanesulfonamide did not give the cyclized products under any conditions, and the starting sulfonamide was recovered quantitatively.

On the basis of these results, a reasonable reaction pathway of 3,4-dihydro-2,1-benzothiazine 2,2-dioxides is shown in Scheme 2. Here, the formation of intermediate **B** was observed by NMR under dark conditions, and the compound **2a-i** is easily iodinated to give compound **3a-i** under the present reaction conditions.

Finally, *N*-benzyl 3,4-dihydro-2,1-benzothiazine 2,2-dioxide was easily debenzylated to give free benzo-2,1-thiazine 2,2-dioxide in 91% yield by treatment with palladium hydroxide.[4b]

In conclusion, the present radical cyclization reactions are very useful for the preparation of 3,4-dihydro-2,1-benzothiazine 2,2-dioxide skeleton, which bears potent biological activity, from 2-(aryl)ethanesulfonamides in high yields.

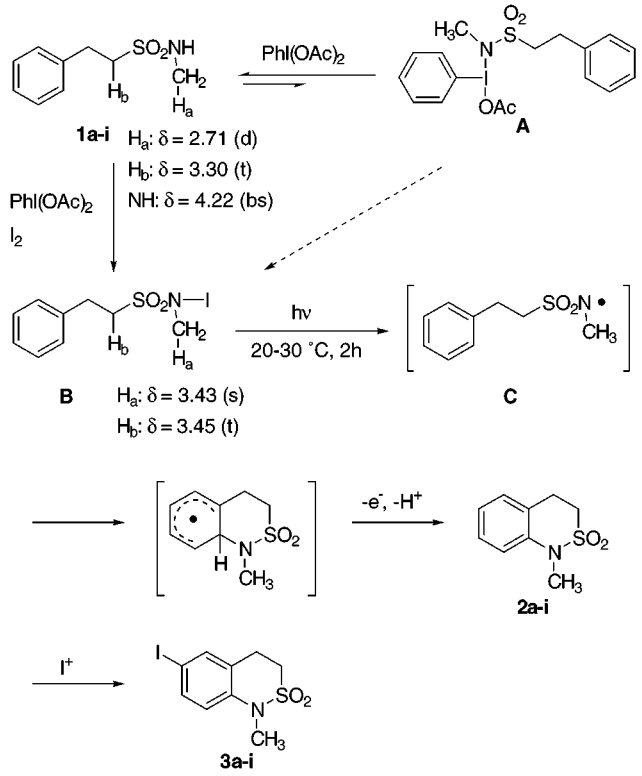
Experimental Section

General Methods. Melting points were determined on an electrothermal apparatus in open capillary tubes and are uncorrected. ^{1}H NMR spectra were recorded on 400 and 500 MHz spectrometers, and ^{13}C NMR spectra were recorded on 100 and 125 MHz spectrometers. Chemical shifts are reported as ppm downfield from tetramethylsilane (TMS) in δ units. Mass spectra were measured with QMS (EI), and high-resolution mass spectra (HRMS) were measured with a 110A mass spectrometer. Silica gel C-200 was used for column chromatography, Kieselgel 60 F254 (Merck) was used for TLC, and Wakogel B-5F was used for pTLC.

Materials. (Diacetoxyiodo)benzene is commercially available. The other (diacetoxyiodo)arenes were prepared by oxidation of the corresponding iodoarenes based on the literature method.[7]

(7) Mckillop, A.; Kemp, D. *Tetrahedron* **1989**, *45*, 3299.

Scheme 2. Plausible Reaction Mechanism



Most sulfonamides were prepared by the reaction of sulfonyl chlorides with alkylamines. Sulfonyl chlorides were prepared from the corresponding sodium sulfonates, which were prepared from the reaction of alkyl bromides and sodium sulfite.[8]

General Procedure for the Conversion of Sulfonamides to the Corresponding 3,4-Dihydro-2,1-benzothiazine 2,2-Dioxide. (Diacetoxyiodo)arene (0.8 mmol) and iodine (0.5 mmol) were added to a solution of sulfonamide (0.5 mmol) in 1,2-dichloroethane (5 mL). The mixture was irradiated with a tungsten lamp (500 W) at 20−30 °C (or irradiated with fluorescent lighting at room temperature) for 2 h under an argon atmosphere. After the reaction, the mixture was poured into a saturated aqueous sodium sulfite solution and extracted with chloroform three times. The organic layer was dried over sodium sulfate. After removal of the solvent under reduced pressure, the residue was chromatographed by preparative TLC (pTLC) on silica gel using a mixture of hexane, ethyl acetate, and chloroform (6:3:1) as an eluent.

***N*-Methyl-3,4-dihydro-2,1-benzothiazine 2,2-dioxide (2a-i):** mp 77.0−79.0 °C; IR (KBr) 2980, 2940, 1580, 1490, 1330, 1170 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.30 (s, 3H), 3.33 (t, J = 6.9 Hz, 2H), 3.44 (t, J = 6.9 Hz, 2H), 6.96 (dd, J = 8.0, 1.0 Hz, 1H), 7.05 (t,d J = 7.6, 1.0 Hz, 1H), 7.16 (dd, J = 7.6, 1.2 Hz, 1H), 7.27 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.90 (s), 31.97(p), 45.55 (s), 117.47 (t), 122.82 (q), 123.14 (t), 127.88 (t), 129.30 (t), 141.14 (q); MS (EI) M^+ 197. Anal. Calcd for $C_9H_{11}NO_2S$: C, 54.80; H, 5.62; N, 7.10. Found: C, 54.74; H, 5.52; N, 7.07.

***N*-Methyl-6-iodo-3,4-dihydro-2,1-benzothiazine 2,2-dioxide (3a-i)**: mp 139.0−141.0 °C; IR (KBr) 2940, 1590, 1560, 1320, 1100 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.26 (s, 3H), 3.32 (t, J = 7.1 Hz, 2H), 3.40 (t, J = 7.1 Hz, 2H), 6.70 (d, J = 8.8 Hz 1H), 7.49 (d, J = 2.0 Hz 1H), 7.55 (dd, J = 8.8, 2.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.51 (s), 31.74 (p), 45.27 (s), 86.24 (q), 119.16 (t), 125.03 (q), 136.73 (t), 137.89 (t), 141.06 (q); MS (EI) M^+ 323. Anal. Calcd for $C_9H_{10}INO_2S$: C, 33.45; H, 3.12; N, 4.33. Found: C, 33.55; H, 3.06; N, 4.27.

***N*-Ethyl-6-iodo-3,4-dihydro-2,1-benzothiazine 2,2-dioxide (3b-i)**: oil; IR (neat) 3000, 2950, 1580, 1320, 1140 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 (t, J = 7.1 Hz, 3H), 3.27 (t, J = 7.1 Hz, 2H), 3.41 (t, J = 7.1 Hz, 2H), 3.89 (q, J = 7.1 Hz, 2H),

(8) Rudolph, A. A.; William, D. H. *J. Am. Chem. Soc.* **1981**, *103*, 1525.

6.75 (d, J = 8.7 Hz, 1H), 7.50 (d, J = 1.9 Hz, 1H) 7.55 (dd, J = 8.7, 1.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.01 (p), 27.66 (s), 41.52 (s), 45.87 (s), 86.20 (q), 119.88 (t), 125.54 (q), 136.62 (t), 138.22 (t), 139.59 (q); MS (EI) M^+ 337. Anal. Calcd for $C_{10}H_{12}INO_2S$: C, 35.62; H, 3.59; N, 4.15. Found: C, 35.86; H, 3.50; N, 4.14.

***N*-Hexyl-3,4-dihydro-2,1-benzothiazine 2,2-dioxide (2c-i)**: oil; IR (neat) 3080, 2960, 2930, 2860, 1600, 1580, 1490, 1450, 1330, 1160 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 7.0 Hz, 3H), 1.28−1.39 (m, 6H), 1.67−1.75 (m, 2H), 3.29 (t, J = 6.8 Hz, 2H), 3.43 (t, J = 6.8 Hz, 2H), 3.79 (t, J = 7.7 Hz, 2H), 6.98 (dd, J = 8.5, 1.0 Hz, 1H), 7.03 (td, J = 7.6, 1.0 Hz, 1H), 7.16 (dd, J = 7.6, 1.1 Hz, 1H), 7.23−7.27 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.94 (p), 22.51 (s), 26.39 (s), 28.06 (s), 28.66 (s), 31.32 (s), 46.09 (s), 46.60 (s), 118.09 (t), 123.07 (t), 123.15 (q), 127.76 (t), 129.59 (t), 139.92 (q); MS (EI) M^+ 267.

***N*-Benzyl-3,4-dihydro-2,1-benzothiazine 2,2-dioxide (2d-i)**: mp 71.0−73.0 °C; IR (KBr) 3030, 2930, 1600, 1580, 1500, 1460, 1330, 1160 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.27 (t J = 6.9 Hz, 2H), 3.46 (t, J = 6.9 Hz, 2H), 5.01 (s, 2H), 6.90 (dd, J = 9.0, 1.4 Hz, 1H), 7.02 (td, J = 7.5, 1.2 Hz, 1H), 7.13−7.17 (m, 2H), 7.25−7.37 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.16 (s), 45.92 (s), 51.11 (s), 119.09 (t), 123.05 (q), 123.46 (t), 127.09 (t), 127.63 (t), 127.81 (t), 128.79 (t), 129.51 (t), 136.57 (q), 140.26 (q); MS (EI) M^+ 273. Anal. Calcd for $C_{15}H_{15}NO_2S$: C, 65.91; H, 5.53; N, 5.12. Found: C, 65.78; H, 5.53; N, 5.02.

***N*-Benzyl-6-iodo-3,4-dihydro-2,1-benzothiazine 2,2-dioxide (3d-i)**: mp 148.0−149.0 °C; IR (KBr) 3020, 2940, 1580, 1560, 1480, 1450, 1320, 1300, 1160, 1130 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.25 (t, J = 6.9 Hz, 2H), 3.41 (t, J = 6.9 Hz, 2H), 4.98 (s, 2H), 6.63 (d, J = 8.8 Hz, 1H), 7.26−7.36 (m, 5H), 7.42 (dd, J = 8.8, 2.1 Hz, 1H), 7.47 (d, J = 2.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.73 (s), 45.63 (s), 50.70 (s), 86.72 (q), 120.75 (t), 125.33 (q), 127.02 (t), 127.80 (t), 128.89 (t), 136.02 (q), 136.63 (t), 138.11 (t), 140.12 (q); MS (EI) M^+ 399. Anal. Calcd for $C_{15}H_{14}INO_2S$: C, 45.12; H, 3.53; N, 3.51. Found: C, 45.08; H, 3.53; N, 3.52.

1,3-Dimethyl-3,4-dihydro-2,1-benzothiazine 2,2-dioxide (2a-ii): oil; IR (neat) 3020, 2980, 1600, 1580, 1320, 1150 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.46 (d, J = 6.6 Hz, 3H), 3.16−3.23 (m, 1H), 3.34 (s, 3H), 3.36−3.48 (m, 2H), 6.94 (dd, J = 7.8, 1.0 Hz, 1H), 7.03 (td, J = 7.8, 1.0 Hz, 1H), 7.13 (dd, J = 7.8, 1.4 Hz, 1H), 7.26 (td, J = 7.8, 1.4 Hz,1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.50 (p), 31.95 (p), 35.72 (s), 50.67 (t), 116.84 (t), 122.13 (q), 122.86 (t), 127.70 (t), 129.55 (t), 140.71 (q); MS (EI) M^+ 211. Anal. Calcd for $C_{10}H_{13}NO_2S$: C, 56.85; H, 6.20; N, 6.63. Found: C, 56.86; H, 6.20; N, 6.74.

1,3-Dimethyl-6-iodo-3,4-dihydro-2,1-benzothiazine 2,2-dioxide (3a-ii): mp 110.0−112.0 °C; IR (KBr) 2980, 1480, 1460, 1320, 1150 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.45 (d, J = 6.6 Hz, 3H), 3.11−3.19 (m, 1H), 3.30 (s, 3H), 3.34−3.43 (m, 2H), 6.68 (d, J = 8.6 Hz, 1H), 7.45 (d, J = 1.9 Hz, 1H), 7.55 (dd, J = 8.6, 1.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.54 (p), 31.78 (p), 35.29 (s), 50.55 (t), 85.96 (q), 118.62 (t), 124.42 (q), 136.61 (t), 138.18 (t), 140.73 (q); MS (EI) M^+ 337. Anal. Calcd for $C_{10}H_{12}INO_2S$: C, 35.62; H, 3.59; N, 4.15. Found: C, 35.77; H, 3.63; N, 4.32.

***N*-Methyl-6-iodo-7-methyl-3,4-dihydro-2,1-benzothiazine 2,2-dioxide (3a-iii):** mp 138.0−139.0 °C; IR (KBr) 3000, 2940, 1600, 1550, 1330, 1160 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.41 (s, 3H), 3.27 (s, 3H), 3.30 (t, J = 6.8 Hz, 2H), 3.38 (t, J = 6.8 Hz, 2H), 6.82 (s, 1H), 7.57 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.95 (s), 27.89 (p), 31.86 (p), 45.31 (s), 93.21 (q), 118.45 (t), 122.07 (q), 139.06 (t), 141.07 (q), 141.31 (q); MS (EI) M^+ 337. Anal. Calcd for $C_{10}H_{12}INO_2S$: C, 35.62; H, 3.59; N, 4.15. Found: C, 35.67; H, 3.45; N, 3.99.

***N*-Methyl-7-fluoro-3,4-dihydro-2,1-benzothiazine 2,2-dioxide (2a-iv):** mp 67.0−68.0 °C; IR (KBr) 3000, 2950, 1620, 1590, 1510, 1320, 1300, 1210, 1170, 1140 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.28 (s, 3H), 3.34 (ddd, J = 7.5, 6.3, 1.3 Hz, 2H), 3.43 (ddd, J = 7.5, 6.3, 1.3 Hz, 2H), 6.66 (dd, J = 10.8, 2.4 Hz, 1H), 6.75 (td, J = 8.2, 2.4 Hz, 1H), 7.10−7.13 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.36 (s), 31.21 (p), 45.68 (s), 104.34 (t, J_{C-F} = 26.5 Hz), 109.68 (t, J_{C-F} = 21.5 Hz), 118.05 (q, J_{C-F} = 4.2 Hz), 130.67 (t, J_{C-F} = 9.1 Hz), 142.43 (q, J_{C-F} = 9.9 Hz), 162.30 (q, J_{C-F} = 245.6 Hz); MS (EI) M^+ 215. Anal. Calcd for $C_9H_{10}FNO_2S$: C, 50.22; H, 4.68; N, 6.51. Found: C, 50.03; H, 4.70; N, 6.50.

***N*-Methyl-7-fluoro-6-iodo-3,4-dihydro-2,1-benzothiazine 2,2-dioxide (3a-iv):** mp 115.0−117.0 °C; IR (KBr) 3000, 2940, 1600, 1570, 1490, 1330, 1160, 1130 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.27 (s, 3H), 3.34 (t, J = 6.6 Hz, 2H), 3.41 (t, J = 6.6 Hz, 2H), 6.66 (d, J_{H-F} = 9.6 Hz, 1H), 7.51 (d, J_{H-F} = 6.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.94 (s), 31.01 (p), 45.41 (s), 72.55 (q, J_{C-F} = 26.3 Hz), 104.36 (t, J_{C-F} = 27.9 Hz), 120.15 (q, J_{C-F} = 3.3 Hz), 139.20 (t, J_{C-F} = 6.6, 2.5 Hz), 142.83 (q, J_{C-F} = 9.0 Hz), 161.17 (q, J_{C-F} = 244.5 Hz); HRMS (EI) found M^+ 340.9362, calcd for $C_9H_9FINO_2S$ M 340.9383.

***N*-Methyl-7-chloro-3,4-dihydro-2,1-benzothiazine 2,2-dioxide (2a-v):** mp 93.0−94.0 °C; IR (KBr) 3080, 2940, 1600, 1490, 1330, 1160 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.29 (s, 3H), 3.34 (ddd, J = 8.2, 5.6, 1.4 Hz, 2H), 3.43 (t, J = 8.2, 5.6, 1.4 Hz, 2H), 6.93 (d, J = 2.1 Hz, 1H), 7.02 (dd, J = 8.2, 2.1 Hz, 1H), 7.09 (d, J = 8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.53 (s), 31.42 (p), 45.52 (s), 117.10 (t), 120.89 (q), 122.96 (t), 130.45 (t), 133.65 (q), 142.11 (q); MS (EI) M^+ 231. Anal. Calcd for $C_9H_{10}ClNO_2S$: C, 46.65; H, 4.35; N, 6.05. Found: C, 46.60; H, 4.29; N, 5.94.

***N*-Methyl-7-chloro-6-iodo-3,4-dihydro-2,1-benzothiazine 2,2-dioxide (3a-v):** mp 141.0−142.0 °C; IR (KBr) 2980, 2940, 1580, 1550, 1460, 1330, 1160, 1130 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.26 (s, 3H), 3.33 (t, J = 6.8 Hz, 2H), 3.40 (t, J = 6.8 Hz, 2H), 7.01 (s, 1H), 7.61 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.01 (s), 31.15 (p), 45.32 (s), 89.59 (q), 117.33 (t), 122.74 (q), 137.90 (q), 140.13 (t), 142.30 (q); MS (EI) M^+ 357. Anal. Calcd for $C_9H_9ClINO_2S$: C, 30.23; H, 2.54; N, 3.92. Found: C, 30.30; H, 2.49; N, 3.83.

***N*-Methyl-3-phenyl-1,3-propanesultam (5):** mp 87.0−88.0 °C; IR (KBr) 3040, 2960, 2880, 1500, 1460, 1300, 1140, 1120, cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.22−2.34 (m, 1H), 2.52 (s, 3H), 2.59−2.69 (m, 1H), 3.21 (ddd, J = 13.0, 8.6, 8.3 Hz, 1H), 3.39 (ddd, J = 13.0, 8.9, 4.1 Hz, 1H), 4.13 (dd, J = 6.7, 5.3 Hz, 1H), 7.34−7.43 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.80 (p), 29.14 (s), 46.33 (s), 64.11 (t), 126.81 (t), 128.69 (t), 129.14 (t), 139.20 (q); MS (EI) M^+ 211. Anal. Calcd for $C_{10}H_{13}NO_2S$: C, 56.85; H, 6.20; N, 6.63. Found: C, 56.80; H, 6.14; N, 6.61.

***N*-Methyl-3,4-dihydro-2,1-naphthothiazine 2,2-dioxide (7):** mp 190.0−191.0 °C; IR (KBr) 3060, 2940, 1620, 1600, 1510, 1470, 1330, 1160, cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.40 (s, 3H), 3.41 (t, J = 7.1 Hz, 2H), 3.76 (t, J = 7.1 Hz, 2H), 7.21 (d, J = 9.7 Hz, 1H), 7.46 (ddd, J = 7.9, 7.0, 1.0 Hz, 1H), 7.55 (ddd, J = 8.5, 7.0, 1.4 Hz, 1H), 7.77 (d, J = 9.7 Hz, 1H), 7.80 (dd, J = 7.9, 1.4 Hz, 1H), 7.88 (dd, J = 8.5, 1.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.24 (s), 35.77 (p), 43.30 (s), 117.26 (q), 119.72 (t), 122.30 (t), 125.27 (t), 127.34 (t), 128.62 (t), 128.99 (t), 130.21 (q), 131.71 (q), 139.07 (q); MS (EI) M^+ 247. Anal. Calcd for $C_{13}H_{13}NO_2S$: C, 35.62; H, 3.59; N, 4.15. Found: C, 35.86; H, 3.50; N, 4.14.

***N*-Methyl-3,4-dihydro-2,1-naphthothiazine 2,2-dioxide (9):** mp 147.0−148.0 °C; IR (KBr) 3060, 2980, 2940, 1600, 1570, 1340, 1160 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.57 (d, J = 6.4 Hz, 3H), 3.19 (dd, J = 17.1, 11.6 Hz, 1H), 3.31 (s, 3H), 3.44−3.58 (m, 2H), 7.17 (d, J = 8.5 Hz, 1H), 7.49 (ddd, J = 8.0, 6.9, 1.1 Hz, 1H) 7.56 (ddd, J = 8.3, 6.9, 1.3 Hz, 1H), 7.65 (d, J = 8.5 Hz, 1H), 7.81 (dd, J = 8.0, 1.3 Hz, 1H), 8.07 (dd, J = 8.3, 1.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.29 (p), 36.93 (s), 42.06 (p), 46.26 (t), 122.70 (t), 124.86 (q), 126.21 (t), 126.32 (t), 126.83 (t), 126.93 (t), 128.25 (t), 128.96 (q), 133.32 (q), 138.02 (q); MS (EI) M^+ 261. Anal. Calcd for $C_{14}H_{15}NO_2S$: C, 64.34; H, 5.79; N, 5.36. Found: C, 64.17; H, 5.77; N, 5.43.

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