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Ion-supported PhI-catalyzed cyclization of *N*-methoxy-2-arylethanesulfonamides with *m*CPBA

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ABSTRACT

The ion-supported PhI-catalyzed cyclization of *N*-methoxy-2-arylethanesulfonamides with *m*CPBA was carried out to form the corresponding *N*-methoxy-3,4-dihydro-2,1-benzothiazine-2,2-dioxides in moderate to good yields in 2,2,2-trifluoroethanol. Here, reactive hypervalent iodine compounds, that is, ion-supported [(hydroxy)(tosyloxy)iodo]benzenes, were formed in situ and reacted with *N*-methoxy-2-arylethanesulfonamides to form the corresponding *N*-methoxy-3,4-dihydro-2,1-benzothiazine-2,2-dioxides in an electrophilic manner on the aromatic ring. Moreover, ion-supported PhI could be efficiently reused to provide the products in good yields. The same ion-supported PhI-catalyzed cyclization of *N*-methoxy-3-phenylpropionamide and *N*-methoxy-4-phenylbutyramide with *m*CPBA was carried out to form the corresponding *N*-methoxy benzolactams in moderate yields in 2,2,2-trifluoroethanol.

It is well known that sulfonamides possess biological activities.[1] Cyclic sulfonamides (sultams), in particular, are important as therapeutic compounds[2] and chiral auxiliaries.[3] Among them, 3,4-dihydro-2,1-benzothiazine-2,2-dioxides (benzosultams) have potent biological activities, such as lipoxygenase inhibitory activity and are used as drugs for treating heart diseases. This is precisely the reason why much attention has been given to the synthesis of the 3,4-dihydro-2,1-benzothiazine-2,2-dioxide skeleton.[4] Today, four established methods for the construction of the 3,4-dihydro-2,1-benzothiazine-2,2-dioxide skeleton are known, that is, cyclization of *N*-benzyl-*N*-methanesulfonyl(*o*-chloromethyl)aniline with NaH,[5a] pyrolysis of β-arylethanesulfonyl azides,[5b] cyclization of *N*-phenylsulfamoylacetic acid with PPA and subsequent reduction of the carbonyl group,[5c] and cyclization of 2-(*o*-aminophenyl)ethanesulfonic acid with $POCl_3$.[5d] However, these methods require multiple steps from commercially available materials and quite acidic or basic conditions. Moreover, the yields of the cyclized products are generally low. In our laboratory, novel methods for the preparation of heterocyclic compounds with hypervalent iodine reagents under photolytic conditions with a tungsten lamp have been studied to realize reactions that proceed under mild conditions with clean transformation and low toxicity.[6] Previously, we reported a new method for preparing *N*-methyl-3,4-dihydro-2,1-benzothiazine-2,2-dioxide via a radical pathway that involved reaction of *N*-methyl-2-arylethanesulfonamides with (diacetoxyiodo)arenes in the presence of molecular iodine under photochemical conditions.[7] Using this method, *N*-methyl-3,4-dihydro-2,1-benzothiazine-2,2-dioxide derivatives were obtained in high yields. However, the demethylation to free NH group from the *N*-methyl group was very difficult. On the other hand, the cyclization of *N*-methoxy-3-arylpropionamide with [bis(trifluoroacetoxy)iodo]benzene is known to form benzolactams via *N*-acylnitrenium ions.[8] Recently, we have reported the preparation of the *N*-methoxy-3,4-dihydro-2,1-benzothiazine-2,2-dioxide skeleton via an ionic pathway with [(hydroxy)(tosyloxy)iodo]arenes.[9] The PhI-catalyzed α-acetoxylation of ketones with *m*-chloroperbenzoic acid (*m*CPBA) and related reactions were reported, and recently, the PhI-catalyzed spirocyclization of *N*-methoxy-3-arylpropanamides with *m*CPBA in 2,2,2-trifluoroethanol to give *N*-fused spirolactams was reported.[10] We also reported the direct one-pot preparation of various [(hydroxy)(sulfonyloxy)iodo]arenes from iodoarenes with *m*CPBA and sulfonic acids at room temperature,[11] the PhI-catalyzed α-tosyloxylation of ketones with *m*CPBA and *p*-toluenesulfonic acid,[12] the efficient conversion of ketones into α-tosyloxyketones with *m*CPBA and *p*-toluenesulfonic acid in the presence of a catalytic amount of ion-supported PhI in [emim]OTs.[13] More recently, we have reported PhI-catalyzed cyclization of *N*-methoxy-2-arylethanesulfonamides with *m*CPBA in 2,2,2-trifluoroethanol to form the corresponding *N*-methoxy-3,4-dihydro-2,1-benzothiazine-2,2-dioxides in moderate to good yields.[14] However, in this method, iodobenzene, which showed the best reactivity among iodobenzene, *p*-iodotoluene, *p*-chloroiodobenzene, *p*-iodoanisole, and poly(4-iodostyrene), could not be recovered efficiently because of its low boiling point and therefore, iodobenzene could

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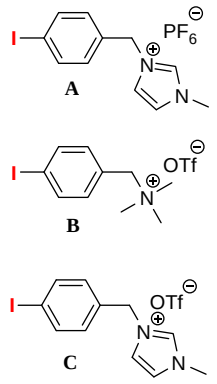


Figure 1. Ion-supported Ph**I A**–**C**.

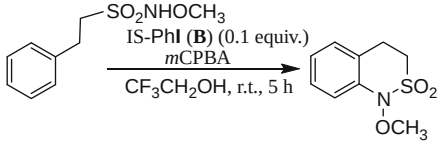
not be reused. Here, as part of our study of the Ph**I**-catalyzed synthesis with *m*CPBA, we would like to report the ion-supported Ph**I**-catalyzed preparation of *N*-methoxy-3,4-dihydro-2,1-benzothiazine-2,2-dioxides from *N*-methoxy-2-arylethanesulfonamides with *m*CPBA in 2,2,2-trifluoroethanol and its related reactions.

First, we prepared three novel ion-supported Ph**I** catalysts, that is, 1-methyl-3-(4′-iodobenzyl)imidazolium phosphoruspentafluoride (**A**), (4-iodobenzyl)trimethylammonium trifluoromethanesulfonate (**B**), and 1-methyl-3-(4′-iodobenzyl)imidazolium trifluoromethanesulfonate (**C**), based on our previous study (Fig. 1).[13] When *m*CPBA was added to *N*-methoxy-2-phenylethanesulfonamide in the presence of ion-supported Ph**I A** and *p*-toluenesulfonic acid monohydrate in [emim]OTs or [bmpy]NTf_2, *N*-methoxy-3,4-dihydro-2,1-benzothiazine-2,2-dioxide was formed in moderate to low yields, as shown in Table 1 (entries 1–4). In the absence of ion-supported Ph**I A**, *N*-methoxy-3,4-dihydro-2,1-benzothiazine-2,2-dioxide was not formed at all and the starting material was recovered quantitatively. The best result was obtained when 0.1 equiv of ion-supported Ph**I A** and 1.1 equiv of *m*CPBA were used in 2,2,2-trifluoroethanol, without *p*-toluenesulfonic acid monohydrate (entry 6). It is known that acidic 2,2,2-trifluoroethanol (pK_a 12.4)[15] is the best solvent for the oxidative cyclization with hypervalent iodines.[10d,14] As shown in entries 1–7, ion-supported Ph**I A** acts as a catalyst. Under optimal conditions, ion-supported Ph**I B** was used for the same preparation of *N*-methoxy-3,4-dihydro-2,1-benzothiazine-2,2-dioxide from *N*-methoxy-2-phenylethanesulfonamide and entry 7 showed the best result (Table 2).

Based on these results, *N*-methoxy-2-arylethanesulfonamides bearing a *p*-substituent on the aromatic ring, such as *p*-methyl, *p*-fluoro, *p*-chloro, *p*-bromo, and *p*-chloromethyl, were treated with *m*CPBA in the presence of ion-supported Ph**I A**–**C** in 2,2,2-trifluoroethanol, and the corresponding *N*-methoxy-3,4-dihydro-2,1-benzothiazine-2,2-dioxides were obtained in good to moderate yields for *p*-methyl, *p*-chloro, *p*-bromo, and *p*-chloromethyl compounds, as shown in Table 3. Ion-supported Ph**I A** and **B** showed better reactivity than ion-supported Ph**I C**.[16] On the other hand, when *N*-methoxy-2-(4′-methoxyphenyl)ethanesulfonamide was treated with ion-supported Ph**I A** and **B** in the presence of *m*CPBA under the same conditions, the corresponding spiro-sultam **I** was obtained as a sole product (entry 7). Finally, *N*-methoxy-3,4-dihydro-2,1-benzothiazine-2,2-dioxide was easily reduced to provide *N*-free 3,4-dihydro-2,1-benzothiazine-2,2-dioxide quantitatively at room temperature by treatment with samarium diiodide in THF as shown in Scheme 1.[17] Then, recyclic use of ion-supported Ph**I A**, **B**, and **C** for the preparation of *N*-methoxy-3,4-dihydro-2,1-benzothiazine-2,2-dioxide from *N*-methoxy-2-phenylethanesulfonamide with *m*CPBA was carried out and the results are shown in Table 4. The results indicate that ion-supported Ph**I B** could be efficiently reused to provide the products in good yields until the 4th time, among ion-supported Ph**I A**, **B**, and **C**.

The present method could be used to prepare benzolactams in moderate yields with ion-supported Ph**I A** from *N*-methoxy 3-phenylpropionamide and *N*-methoxy 4-phenylbutyramide, as shown

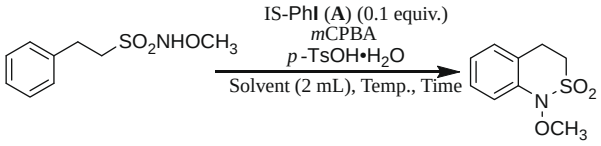
Table 2
Ion-supported Ph**I** (**B**)-catalyzed cyclization of *N*-methoxy-2-phenylethanesulfonamide



Entry	CF_3CH_2OH (mL)	*m*CPBA (equiv)	Yield (%)
1	2	1.0	67
2	2	1.1	73
3	5	1.1	38 (45)[a]
4	1	1.1	80
5	1	1.3	80
6	1	1.5	82
7	0.5	1.1	82
8[b]	0.5	1.1	68

[a] Yield of starting material.
[b] Reaction temperature was 40 °C.

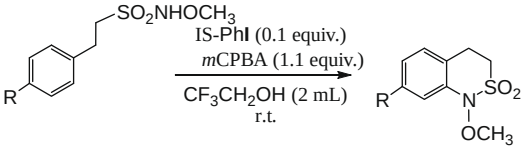
Table 1
Ion-supported Ph**I** (**A**)-catalyzed cyclization of *N*-methoxy-2-phenylethanesulfonamide



Entry	*m*CPBA (equiv)	*p*-TsOH·H_2O (equiv)	Temp	Solvent	Time (h)	Yield (%)
1	3.0	3.0	rt	[emim]OTs	8	44
2	3.0	3.0	rt	[emim]OTs	24	52
3	3.0	3.0	50 °C	[emim]OTs	24	29
4	3.0	3.0	rt	[bmpy]NTf_2	24	17
5	3.0	0	rt	CF_3CH_2OH	5	87
6	1.1	0	rt	CF_3CH_2OH	5	93
7	1.1	0	rt	CF_3CH_2OH	2	67

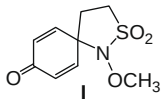
[emim]OTs: 1-Ethyl-3-methylimidazolium tosylate.
[bmpy]NTf_2: Butylmethylpyrrolidinium bis(trifluoromethanesulfonyl)imidate.

Table 3
Ion-supported Ph**I**-catalyzed preparation of benzosultams

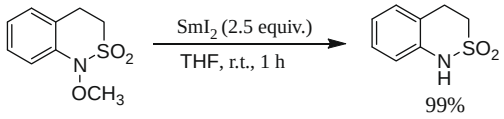


Entry	R	Time (h)	Yields (%)		
			A	**B**[a]	**C**
1	H	5	93	82	72
2	CH_3	5	37	58	—
3	F	24	35	31	—
4	Cl	5	55	62	—
5	Br	5	85	72	—
6	CH_2Cl	5	89	76	—
7	CH_3O	5	70[b]	71[b]	—

[a] CF_3CH_2OH (0.5 mL) was used.
[b] Yield of spiro compound **I**.

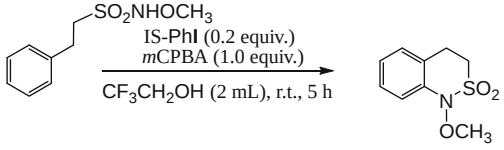


I



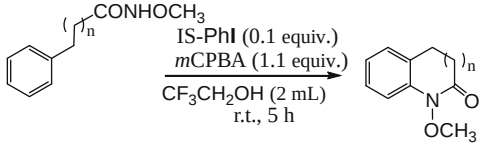
Scheme 1.

Table 4
Recyclic use of ion-supported Ph**I** (**A**)–(**C**)



Recycle	Yields (%)		
	A	**B**[a]	**C**
0	84	80	82
1	84	84	48
2	37	82	20
3	<1	79	0
4	—	60	—

[a] CF_3CH_2OH (0.5 mL) was used.



IS-Ph **I**	**A**	**B**[a]
n = 1	60%	38%
n = 2	51%	37%

[a] CF_3CH_2OH (0.5 mL) was used.

Scheme 2. Ion-supported Ph**I**-catalyzed preparation of benzolactams.

in Scheme 2. Here, ion-supported Ph**I A** gave the products in better yields than ion-supported Ph**I B**.

In conclusion, the ion-supported Ph**I**-catalyzed preparation of *N*-methoxy-3,4-dihydro-2,1-benzothiazine-2,2-dioxides by the reaction of *N*-methoxy-2-arylethanesulfonamides with *m*CPBA in 2,2,2-trifluoroethanol proceeded efficiently depending on the substituent on the aromatic ring, and *p*-toluenesulfonic acid monohydrate was not required when 2,2,2-trifluoroethanol was used. The advantages of ion-supported Ph**I**-catalyzed preparation of benzosultams are that the extraction of the reaction mixture with ether, washing the ether extract with aq Na_2SO_3, and subsequent removal of the solvent provided the product with high purity (over 90%), even if the yield of benzosultams was not high. Moreover, ion-supported Ph**I B** could be efficiently reused to provide the products in good yields. Finally, the *N*-methoxy group could be easily and quantitatively reduced to the corresponding *N*-free 3,4-dihydro-2,1-benzothiazine-2,2-dioxides with samarium diiodide.

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References and notes

1. (a) Hanson, P. R.; Probst, D. A.; Robinson, R. E.; Yau, M. *Tetrahedron Lett.* **1999**, *40*, 4761; (b) Rough, W. R.; II Gwaltney, S. L.; Cheng, J.; Scheidt, K. A.; McKerrow, J. H.; Hansell, E. *J. Am. Chem. Soc.* **1998**, *120*, 10994; (c) Moree, W. J.; van der Marel, G. A.; Liskamp, R. M. *J. J. Org. Chem.* **1995**, *60*, 5157; (d) Gennari, C.; Nestler, H. P.; Salom, B.; Still, W. C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1765; (e) Gennari, C.; Salom, B.; Potenza, D.; Williams, A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2067; (f) Moree, W. J.; van Gent, L. C.; van der Marel, G. A.; Liskamp, R. M. J. *Tetrahedron* **1993**, *49*, 1133; (g) Moree, W. J.; van der Marel, G. A.; Liskamp, R. M. *Tetrahedron Lett.* **1991**, *32*, 409; (h) Zecchini, G. P.; Paradisi, M. P.; Torrini, I.; Lucente, G.; Gavuzzo, E.; Mazza, F.; Pochetti, G. *Tetrahedron Lett.* **1991**, *32*, 6779.
2. (a) Hayashi, S.; Ueki, H.; Sako, Y.; Ashunura, T.; Hayashi, K.; Takase, K. *Kumamoto. Pharm. Bull.* **1962**, *5*, 51; (b) Friebel, H.; Sommer, S. *Deut. Med. Wochschr.* **1960**, *85*, 2192; (c) Flugel, F.; Bente, D.; Itil, T. *Deut. Med. Wochschr.* **1960**, *85*, 2199.
3. (a) Ahn, K. H.; Ham, C.; Kim, S.-K.; Cho, C.-W. *J. Org. Chem.* **1997**, *62*, 7047; (b) Oppolzer, W.; Kingma, A. J.; Pillai, S. K. *Tetrahedron Lett.* **1991**, *32*, 4893; (c) Oppolzer, W.; Wills, M.; Starkemann, C.; Bernardinelli, G. *Tetrahedron Lett.* **1990**, *31*, 4117; (d) Oppolzer, W.; Wills, M.; Kelly, M. J.; Signer, M.; Blagg, J. *Tetrahedron Lett.* **1990**, *31*, 5015; (e) Oppolzer, W.; Rodriguez, I.; Starkemann, C.; Walther, E. *Tetrahedron Lett.* **1990**, *31*, 5019.
4. (a) Harmata, M.; Kahraman, M. *J. Org. Chem.* **1998**, *63*, 6845; (b) *Chem. Abstr.* **1992**, *117*, 748 (131207e, WO 9205164).; (c) *Chem. Abstr.* **1990**, *112*, 585 (35887e, JP 0161470).; (d) *Chem. Abstr.* **1985**, *102*, 605 (78901p, JP59164786).; (e) Cecchetti, V.; Fravolini, A.; Schiaffella, F. *J. Heterocycl. Chem.* **1982**, *19*, 1045; (f) Kaiser, E. M.; Knutson, P. L. A. *J. Org. Chem.* **1975**, *40*, 1342.
5. (a) Blondet, D.; Pascal, J.-C. *Tetrahedron Lett.* **1994**, *35*, 2911; (b) Abra, R. A.; Holcomb, W. D. *J. Am. Chem. Soc.* **1975**, *97*, 676; (c) Loev, B.; Kormendy, M. F.; Snader, K. M. *J. Org. Chem.* **1966**, *31*, 3531; (d) Loev, B.; Kormendy, M. F. *J. Org. Chem.* **1965**, *30*, 3163.
6. (a) Katohgi, M.; Togo, H.; Yamaguchi, K.; Yokoyama, M. *Tetrahedron* **1999**, *55*, 14885; (b) Muraki, T.; Togo, H.; Yokoyama, M. *J. Org. Chem.* **1999**, *64*, 2883; (c) Togo, H.; Hoshina, Y.; Muraki, T.; Nakayama, H.; Yokoyama, M. *J. Org. Chem.* **1998**, *63*, 5193; (d) Togo, H.; Muraki, T.; Hoshina, Y.; Yamaguchi, K.; Yokoyama, M. *J. Chem. Soc., Perkin Trans. 1* **1997**, 787.
7. Togo, H.; Harada, Y.; Yokoyama, M. *J. Org. Chem.* **2000**, *65*, 926.
8. (a) Kikugawa, Y.; Kawase, M. *Chem. Lett.* **1990**, 581; (b) Amano, Y.; Nishiyama, S. *Tetrahedron Lett.* **2006**, *47*, 6505.
9. Misu, Y.; Togo, H. *Org. Biomol. Chem.* **2003**, *1*, 1342.
10. Review: (a) Ochiai, M.; Miyamoto, K. *Eur. J. Org. Chem.* **2008**, 4229; Papers: (b) Ochiai, M.; Takeuchi, Y.; Katayama, T.; Sueda, T.; Miyamoto, K. *J. Am. Chem. Soc.* **2005**, *127*, 12244; (c) Dohi, T.; Maruyama, A.; Yoshimura, M.; Morimoto, K.; Tohma, H.; Kita, Y. *Angew. Chem., Int. Ed.* **2005**, *44*, 6193; (d) Dohi, T.; Maruyama, A.; Minamitsuji, Y.; Takenaga, N.; Kita, Y. *Chem. Commun.* **2007**, 1224.
11. Yamamoto, Y.; Togo, H. *Synlett* **2005**, 2486.
12. (a) Yamamoto, Y.; Togo, H. *Synlett* **2006**, 798; (b) Yamamoto, Y.; Kawano, Y.; Toy, P. H.; Togo, H. *Tetrahedron* **2007**, *63*, 4680.
13. Akiike, J.; Yamamoto, Y.; Togo, H. *Synlett* **2007**, 2168.
14. Moroda, M.; Togo, H. *Synthesis* **2008**, 1257.
15. Detar, D. F. *J. Am. Chem. Soc.* **1982**, *104*, 7205.

16. *General procedure for preparation of 1-methoxy-3,4-dihydro-2,1-benzothiazine 2,2-dioxides with ion-supported PhI*: To a solution of *N*-methoxy-2-arylethanesulfonamide (0.5 mmol) and ion-supported Ph**I** (0.05 mmol) in CF_3CH_2OH (2 mL or 0.5 mL) was added *m*CPBA (0.55 mmol). The mixture was stirred for 5 h at rt under an argon atmosphere. After removal of the solvent, the residue was extracted with Et_2O three times (20 mL × 3). The ether solution was washed with aq Na_2SO_3 and dried over Na_2SO_4. After filtration, removal of the solvent provided the residual benzosultam (purity, over 90%). If it is necessary, the residue was subjected to preparative TLC (silica gel; hexane: EtOAc = 3: 1).

General procedure for recyclic use of ion-supported PhI: To a solution of *N*-methoxy-2-phenylethanesulfonamide (0.5 mmol) and ion-supported Ph**I** (0.05 mmol) in CF_3CH_2OH (2 mL or 0.5 mL) was added *m*CPBA (0.55 mmol). The mixture was stirred for 5 h at rt under an argon atmosphere. After removal of the solvent, the residue was extracted with Et_2O three times (20 mL × 3). The ether solution was washed with aq Na_2SO_3 and dried over Na_2SO_4. After filtration, removal of the solvent provided the residual benzosultam (purity, over 90%). On the other hand, the residue of ion-supported Ph**I** was reused for the next reaction after drying by a vacuum pump for 1 h at rt.

N-Methoxy-3,4-dihydro-2,1-benzothiazine-2,2-dioxide: mp 104.0–106.0 °C; IR (KBr) 3000, 2950, 2815, 1580, 1480, 1360, 1170 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 3.42 (t, *J* = 6.4 Hz, 2H), 3.50 (td, *J* = 6.4, 1.5 Hz, 2H), 4.08 (s, 3H), 7.20–7.23 (m, 1H), 7.31–7.34 (m, 2H), 7.36–7.40 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 27.86 (s), 40.20 (s), 65.57 (p), 126.72 (q), 127.88 (t), 128.03 (t), 128.90 (t), 129.41 (t), 141.88 (q); MS (EI) M^+ 213. Anal. Calcd for $C_9H_{11}NO_3S$: C, 50.69; H, 5.20; N, 6.57. Found: C, 50.76; H, 5.32; N, 6.58.

N-Methoxy-7-methyl-3,4-dihydro-2,1-benzothiazine-2,2-dioxide: mp 119.0–121.0 °C; IR (KBr) 3000, 2950, 2815, 1620, 1500, 1360, 1170 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 2.36 (s, 3H), 3.36 (t, *J* = 6.6 Hz, 2H), 3.47 (t, *J* = 6.6 Hz, 2H), 4.07 (s, 3H), 7.08 (d, *J* = 7.9 Hz, 1H), 7.12 (d, *J* = 7.9 Hz, 1H), 7.18 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 20.99 (p), 27.56 (s), 40.20 (s), 65.68 (p), 123.61 (q), 128.27 (t), 129.32 (t), 130.07 (t), 138.22 (q), 141.63 (q); MS (EI) M^+ 227. Anal. Calcd for $C_{10}H_{13}NO_3S$: C, 52.85; H, 5.77; N, 6.16. Found: C, 52.80; H, 5.69; N, 6.14.

N-Methoxy-7-chloromethyl-3,4-dihydro-2,1-benzothiazine-2,2-dioxide: mp 120.0–122.5 °C; IR (paraffin oil) 1360, 1280, 1236, 1170 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 3.40 (t, *J* = 6.5 Hz, 2H), 3.49 (t, *J* = 6.5 Hz, 2H), 4.09 (s, 3H), 4.58 (s, 2H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.34 (dd, *J* = 8.0, 1.9 Hz, 1H), 7.39 (d, *J* = 1.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 27.61 (s), 40.11 (s), 44.92 (s), 65.69 (p), 126.69 (q), 127.44 (t), 128.80 (t), 129.84 (t), 137.59 (q), 141.96 (q); MS (FAB) $(M+1)^+$ = 261. Anal. Calcd for $C_{10}H_{12}ClNO_3S{\cdot}1/5H_2O$: C, 45.44; H, 4.69; N, 5.30. Found: C, 45.44; H, 4.62; N, 5.24.

N-Methoxy-7-bromo-3,4-dihydro-2,1-benzothiazine-2,2-dioxide: mp 138.0–139.5 °C; IR (paraffin oil) 1360, 1292, 1167 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 3.35 (t, *J* = 6.6 Hz, 2H), 3.48 (t, *J* = 6.6 Hz, 2H), 4.08 (s, 3H), 7.08 (d, *J* = 8.4 Hz, 1H), 7.42 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.52 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 27.50 (s), 40.24 (s), 65.86 (p), 120.94 (q), 125.51 (q), 130.00 (t), 130.73 (t), 131.71 (t), 142.94 (q); MS (FAB) $(M+1)^+$ = 291. Anal. Calcd for $C_9H_{10}BrNO_3S$: C, 37.00; H, 3.45; N, 4.79. Found: C, 36.87; H, 3.43; N, 4.75.

N-Methoxy-7-chloro-3,4-dihydro-2,1-benzothiazine-2,2-dioxide: mp 123.0–125.0 °C; IR (KBr) 3000, 2950, 2815, 1600, 1480, 1360, 1160 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 3.37 (t, *J* = 6.5 Hz, 2H), 3.48 (t, *J* = 6.5 Hz, 2H), 4.08 (s, 3H), 7.14 (d, *J* = 8.2 Hz, 1H), 7.27 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.36 (d, *J* = 2.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 27.55 (s), 40.42 (s), 65.95 (p), 125.08 (q), 127.14 (t), 128.92 (t), 130.60 (t), 133.53 (q), 142.90 (q); MS (EI) M^+ 247. Anal. Calcd for $C_9H_{10}ClNO_3S$: C, 43.64; H, 4.07; N, 5.65. Found: C, 43.39; H, 4.08; N, 5.52.

N-Methoxy-7-fluoro-3,4-dihydro-2,1-benzothiazine-2,2-dioxide: mp 76.0–78.0 °C; IR (KBr) 3000, 2950, 2820, 1600, 1490, 1360, 1170 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 3.37 (t, *J* = 6.4 Hz, 2H), 3.47 (t, *J* = 6.4 Hz, 2H), 4.08 (s, 3H), 7.02 (td, *J* = 8.5, 2.7 Hz, 1H), 7.08 (dd, *J* = 8.9, 2.7 Hz, 1H), 7.17 (dd, *J* = 8.5, 5.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 27.22 (s), 40.48 (s), 65.83 (p), 113.52 (t, J_{C-F} = 23.8 Hz), 115.96 (t, J_{C-F} = 22.1 Hz), 122.14 (q, J_{C-F} = 4.2 Hz), 130.72 (t, J_{C-F} = 8.2 Hz), 142.84 (q, J_{C-F} = 9.8 Hz), 161.64 (q, J_{C-F} = 247.5 Hz); MS (EI) M^+ 231. Anal. Calcd for $C_9H_{10}FNO_3S$: C, 46.75; H, 4.36; N, 6.06. Found: C, 46.94; H, 4.41; N, 5.89.

1-Methoxy-3,4-dihydroquinolin-2(1H)-one: Oil. IR (neat): 2936, 1697, 1354, 1332, 1267, 1192, 1065 cm^{-1}. ^1H NMR ($CDCl_3$, TMS): δ = 7.15–7.32 (m, 3H), 7.05 (td, *J* = 7.3, 1.4 Hz, 1H), 3.93 (s, 3H) 2.92 (t, *J* = 7.4.Hz, 2H), 2.71(t, *J* = 7.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS): δ = 165.7, 137.8, 127.7, 124.3, 123.6, 62.5, 31.5, 24.8. HRMS (FAB): *m*/*z* calcd for $C_{10}H_{11}NO_2$ (M): 177.0790; found: 177.0785.

1-Methoxy-4,5-dihydro-1H-benzo[b]azepin-2(3H)-one: Oil. IR (neat): 2935, 1690, 1457, 1358, 1329, 1244, 1038 cm^{-1}. ^1H NMR ($CDCl_3$, TMS): δ = 7.44 (d, *J* = 7.8 Hz, 1H), 7.31–7.39 (m, 1H), 7.21–7.25 (m, 2H), 3.79 (s, 3H), 2.78 (t, *J* = 7.1 Hz, 2H), 2.17–2.34 (m, 4H). ^{13}C NMR ($CDCl_3$, TMS): δ = 168.5, 139.3, 134.2, 129.2, 127.7, 127.2, 121.9, 62.1, 32.7, 30.2, 28.5. HRMS (FAB): *m*/*z* calcd for $C_{11}H_{14}NO_2$ (M+H): 192.1025; found: 192.1012.

1-Methoxy-2,2-dioxo-2λ⁶-thia-1-aza-spiro[4.5]deca-6,9-dien-8-one: mp 133.0–135.0 °C. IR (KBr) 2980, 2950, 2830, 1680, 1610, 1400, 1330, 1160 cm^{-1}. ^1H NMR ($CDCl_3$, TMS): δ = 2.44 (t, *J* = 7.9 Hz, 2H), 3.44 (t, *J* = 7.9 Hz, 2H), 3.81 (s, 3H), 6.39 (d, *J* = 10.4 Hz, 2H), 7.05 (d, *J* = 10.4 Hz, 2H), Anal Calcd for $C_9H_{11}NO_4S$: C, 47.15; H, 4.84; N, 6.11. Found: C, 47.16; H, 4.68; N, 6.07.

1-Methyl-3-(4′-Iodobenzyl)imidazolium Phosphoruspenta-fluoride (**A**): mp 99–100 °C. IR (nujol): 1440, 1380, 1160, 840, 820, 750, 560 cm^{-1}. ^1H NMR (400 MHz, acetone-d_6): δ = 3.95 (s, 3H), 5.45 (s, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 7.63 (d, *J* = 3.4 Hz, 1H), 7.66 (d, *J* = 3.4 Hz, 1H), 7.70 (d, *J* = 8.5 Hz, 2H), 9.00 (s, 1H). E. A Calcd for $C_{11}H_{12}F_6IN_2P$: C, 29.75; H, 2.72; N, 6.31. Found: C, 29.88; H, 2.49; N, 6.28.

(4-Iodobenzyl)trimethylammonium trifluoromethanesulfonate (**B**): mp 138.5–143.0 °C. IR (Nujol): 3034, 1479, 1464, 1261, 1230, 1150, 1034, 645, 517 cm^{-1}. ^1H NMR ($CDCl_3$, TMS): δ = 7.80 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 4.60 (s, 2H), 3.16 (s, 9H). E. A Calcd for $C_{11}H_{15}F_3INO_3S{\cdot}1/20CF_3SO_3Ag$: C, 30.30; H, 3.45; N, 3.20. Found: C, 30.37; H, 3.15; N, 3.19.

17. *3,4-Dihydro-2,1-benzothiazine-2,2-dioxide*: To a THF (8 mL) solution of Sm (2.5 mmol) was added a THF (2 mL) solution of 1,2-diiodoethane (2.5 mmol) at room temperature under argon atmosphere. After being stirred for 2 h, *N*-methoxy 3,4-dihydro-2,1-benzothiazine-2,2-dioxide (1 mmol) was added, and the obtained mixture was stirred for one hour at room temperature. Then, water (20 mL) was added to the reaction mixture and the mixture was extracted with chloroform (10 mL × 3). The organic layer was dried over Na_2SO_4. After filtration, removal of the solvent provided the product in an almost pure state in 99% yield. Mp 150.0–152.0 °C. ^1H NMR (400 MHz, $CDCl_3$) δ = 3.32 (t, *J* = 6.9 Hz, 2H), 3.49 (t, *J* = 6.9 Hz, 2H), 6.45 (s, 1H), 6.75 (dd, *J* = 8.1 and 1.1 Hz, 1H), 7.05 (td, *J* = 7.5 and 1.1 Hz, 1H), 7.17–7.23 (m, 2H).