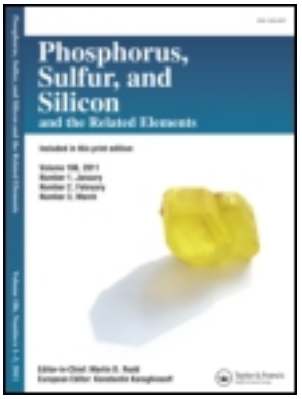

Phosphorus, Sulfur, and Silicon and the Related Elements

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Microwave-Assisted Direct Synthesis of 4H-1,2,4-Benzothiadiazine 1,1-Dioxide Derivatives

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MICROWAVE-ASSISTED DIRECT SYNTHESIS OF 4*H*-1,2,4-BENZOTHIADIAZINE 1,1-DIOXIDE DERIVATIVES

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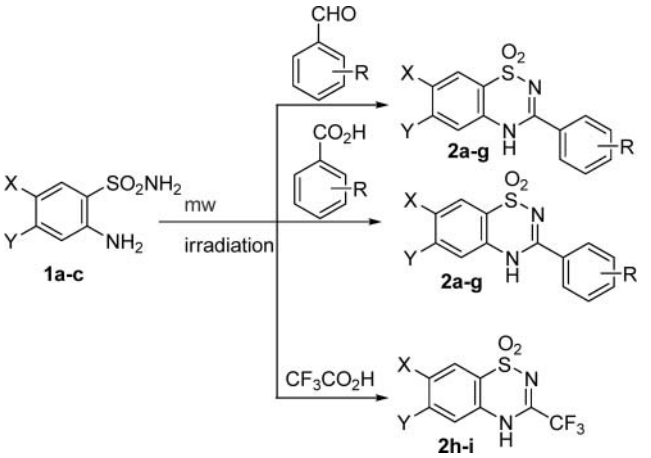
GRAPHICAL ABSTRACT



Abstract *We describe a rapid and convenient methodology for the preparation of diverse 3-aryl and 3-trifluoromethyl 4H-1,2,4-benzothiadiazine-1,1-dioxides in a one-pot microwave-promoted reaction between 2-aminobenzenesulfonamides and benzaldehydes, trifluoroacetic acid or benzoic acids.*

Keywords 1,2,4-Benzothiadiazines; sodium hydrogen sulfite; microwave irradiation; 2-aminobenzenesulfonamides; trifluoroacetic acid; benzoic acids

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INTRODUCTION

Microwave-assisted organic synthesis is a highly useful tool and a continuously growing area over the last years, with a wide application to the synthesis of heterocyclic compounds.[1] Its use provides diminished reaction times, usually increased yields, as well as reproducible results facilitating the rapid development of new reactions.[2] 1,2,4-Benzothiadiazines have attracted the scientific community for over 50 years, mainly because of their interesting biological activities, which include diuretic,[3] antihypertensive,[4] α_1-adrenoceptor antagonists,[5] KATP channel activators,[6] and anticancer;[7] however, their preparation through microwave-assisted synthesis has not been well explored[8] a remarkable difference when compared with their isoster analogs 4-quinazolinones.[9] Classical synthesis of 3-substituted alkyl and aryl 1,2,4-benzothiadiazine-1,1-dioxides includes their preparation by condensation of a 2-aminobenzenesulfonamide with an alkyl-orthoformate[10,11] and a two-step procedure that involves the preparation of a 2-acylaminobenzenesulfonamide intermediate with reactive carboxylic acid derivatives followed by a cyclodehydration promoted by heating with base.[11,12] Other much less common procedures are the direct cyclocondensation with amidines at elevated temperatures,[13] and the cyclodehydrogenation with some aldehydes in the presence of sodium hydrogen sulfite.[14] Recently, an iron-catalyzed ($FeCl_3$) method for the cascade synthesis of 1,2,4-benzothiadiazine-1,1-dioxides has been reported.[15] We have described the preparation and biological evaluation of novel 3,4-dihydro-2*H*-1,2,4-benzothiadiazine-1,1-dioxide derivatives[16] and explored the preparation of 3-trifluoromethyl-*4H*-1,2,4-benzothiadiazines by the promoted direct condensation of 2-aminobenzenesulfonamides with trifluoroacetic acid (TFA) using polyphosphoric acid trimethylsilyl ester (PPSE).[17]

RESULTS AND DISCUSSION

Intrigued by our previously obtained results concerning to the lacking of the 3,4 double-bond direct generation for desired 2*H*-1,2,4-benzothiadiazines by the attempted cyclodehydrogenation reaction of 2-aminobenzenesulfonamides with substituted benzaldehydes using sodium hydrogen sulfite,[16] we now decided to explore such reactions under microwave irradiation as well as the direct condensation–cyclodehydration between 2-aminobenzenesulfonamides and carboxylic acids (Figure 1). Initially, we started to optimize the conditions for the direct preparation of the 3-aryl-4*H*-1,2,4-benzothiadiazine-1,1-dioxide **2a** using a microwave-promoted cyclodehydrogenation reaction between 2-aminobenzenesulfonamide **1a** and benzaldehyde (Table 1). As seen, it was necessary to use an irradiation time of 17 min and 2.5 equivalents of sodium hydrogen sulfite to complete the full conversion to desired 4*H*-1,2,4-benzothiadiazine **2a** in 85% yield (entry 5), instead of the 3,4-dihydro analog **3c** (entries 1–4). Once optimized, we proceed to prepare a set of seven 4*H*-1,2,4-benzothiadiazines (**2a–g)** in good to excellent yields (80%–92%, Table 2, Method A). Different electron-donating and electron-withdrawing groups located at *meta and para* positions of the 3-aryl ring were employed giving good results; even with an *ortho*–chloro substituent (**2g**), the reaction worked satisfactorily. Knowing the reaction is thought to pass through the 3,4-dihydro intermediate before oxidation to the 4*H*-1,2,4-benzothiadiazine,[14] we proceeded to test the microwave-promoted direct conversion of the isolated dihydro analog **3a** into the 4*H*-1,2,4-benzothiadiazine **2c** (Tables 3 and 4), finding the required conditions to fulfill the conversion in almost quantitative yield to be 1.2 equivalents of sodium hydrogen sulfite and an irradiation time of 7 min. A possible mechanism

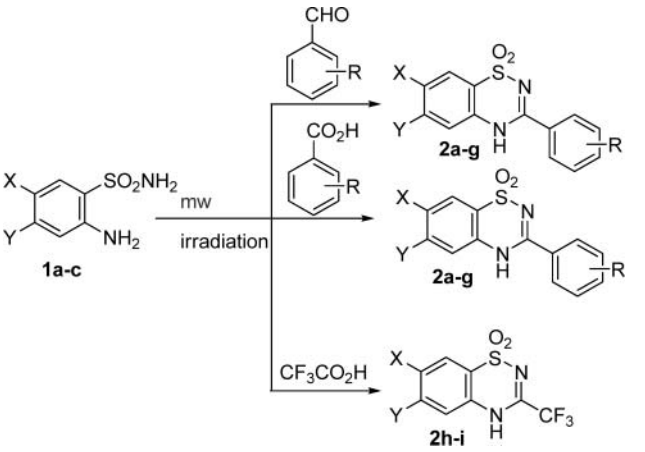


Figure 1 Preparation of 4*H*-1,2,4-benzothiadiazine 1,1-dioxide derivatives from 2-aminobenzenesulfonamides by microwave irradiation.

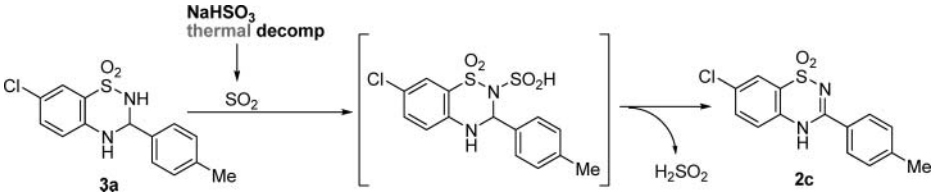
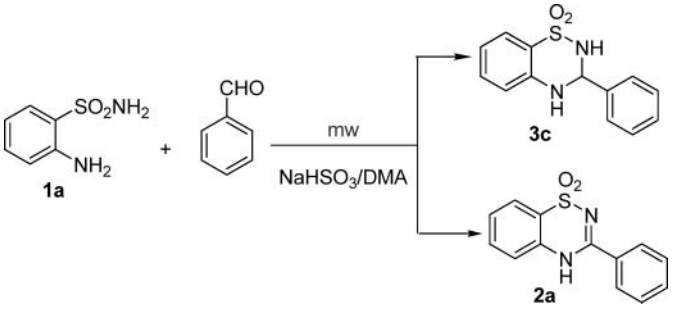


Figure 2 A proposed mechanism for the dehydrogenation step to form desired 4*H*-1,2,4-benzothiadiazines.

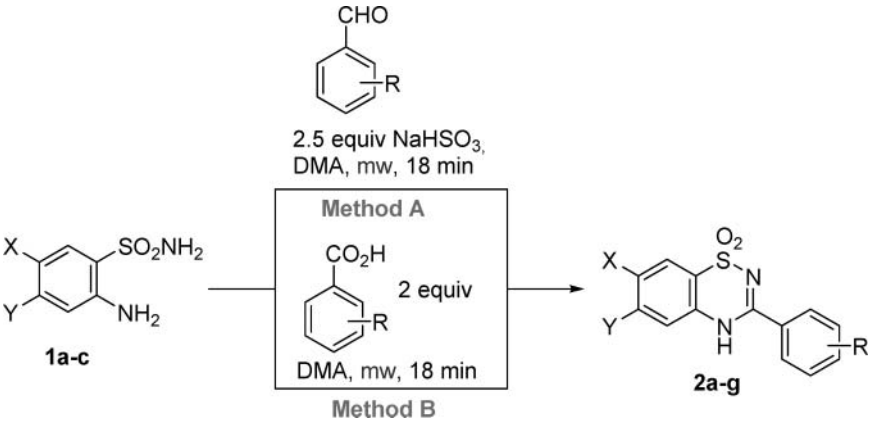
Table 1 Optimization conditions for the microwave-promoted synthesis of 4*H*-1,2,4-benzothiadiazine-1,1-dioxides from 2-aminobenzenesulfonamides and benzaldehydes using sodium hydrogen sulfite



Entry	1a (equivalent): $NaHSO_3$ (equivalent)	Time (min)	Yield (%)[a]
1	1:1	8	3c (30)
2	1:1.5	8	3c (43)
3	1:2	8	3c (65)
4	1:2	12	3c (80)
5	1:2.5	17	2a (85)

[a]Yields of isolated products. Compound **2a** was only detected in entry 5.

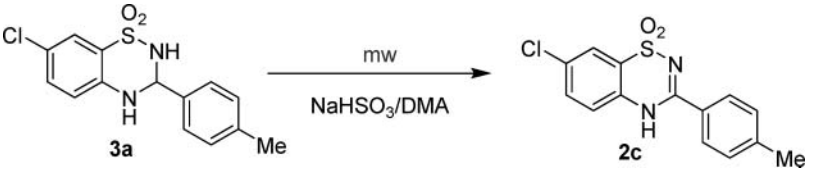
Table 2 One-pot microwave-promoted synthesis of 4*H*-1,2,4-benzothiadiazine-1,1-dioxides from 2-aminobenzenesulfonamides and benzaldehydes using sodium hydrogen sulfite (Method A) or benzoic acids (Method B)



Compounds	X	Y	R	Method A yield (%)	Method B yield (%)[a]	Mp (°C) (Lit. mp)
2a	H	H	H	85	90	300–302 (302–303)[19]
2b	H	H	4′-Me	80	93	337–339 (334–336)[20]
2c	Cl	H	4′-Me	85	87	335–337
2d	Cl	H	4′-Cl	90	93	285–287
2e	Cl	H	3′-F	92	–	339–340
2f	Br	H	3′-Me	82	86	190–192
2g	Cl	Cl	2′-Cl	85	80	271–272

[a]10N hydrochloric acid (5% mol) was added to the irradiated reaction mixture.

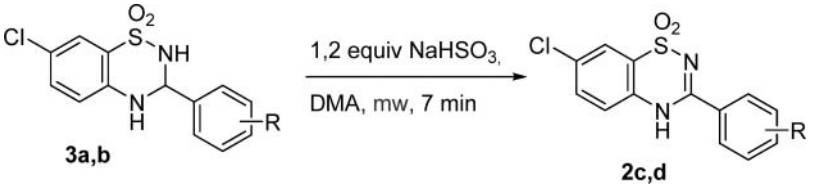
Table 3 Optimization conditions for the microwave-promoted dehydrogenation of 3-aryl-3,4-dihydro-1,2,4-benzothiadiazine-1,1-dioxides to 3-aryl-4*H*-1,2,4-benzothiadiazine-1,1-dioxides using sodium hydrogen sulfite



Entry	3b (equivalent): $NaHSO_3$ (equivalent)	Time (min)	Yield (%)[a]
1	1:0.5	2	b
2	1:0.5	4	b
3	1:1	3	b
4	1:1.2	3	**3a** (60):**2c** (38)[c]
5	1:1.2	7	**2c** (99)

[a]Yields of isolated products.[b]Only compound **3a** could be detected (^{1}H NMR).[c]Following separation using column chromatography.

Table 4 Direct-microwave-promoted dehydrogenation of 3-aryl-3,4-dihydro-1,2,4-benzothiadiazine-1,1-dioxides to 3-aryl-4*H*-1,2,4-benzothiadiazine-1,1-dioxides using sodium hydrogen sulfite

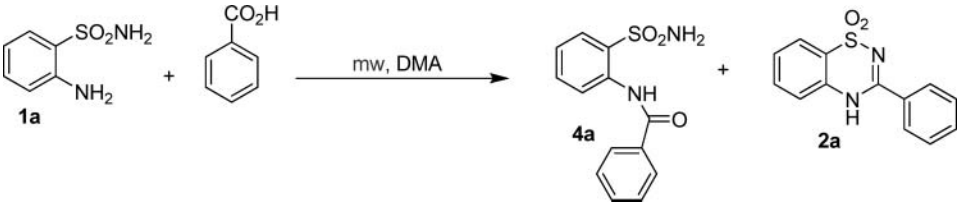


Compounds	R	Yield (%)	Mp (°C)
2c	4′-Me	99	335–337
2d	4′-Cl	98	285–287

for this reaction is given (Figure 2), where the decomposition of sodium hydrogen sulfite under heating generates sulfur dioxide,[18] which forms an adduct with the nitrogen atom of the sulfonamide on the dihydro intermediate, and then eliminates hyposulfurous acid to produce the 3,4 double bond of desired 4*H*-1,2,4-benzothiadiazines.

Turning our attention to a direct condensation–cyclodehydration reaction between 2-aminobenzenesulfonamides with carboxylic acids, we tried to avoid the classical synthesis that includes the isolation of a 2-acylaminobenzenesulfonamide key intermediate before alkaline cyclization,[11,12] doing a microwave irradiation of 2-aminobenzenesulfonamides with benzoic acid (Table 2, Method B) and TFA (Table 7). Optimization experiments gave interesting results when a 10N hydrochloric acid solution (5% mol) was added as a catalyst to rise up the yields to 90% with an irradiation time of 18 min and 2 equivalents of the benzoic acid (entry 6, Table 5); thus, a series of 4*H*-1,2,4-benzothiadiazine-1,1-dioxides (**2a–d, 2f–g**) were prepared by using these conditions in good yields (Table 2, Method B). Finally, guided

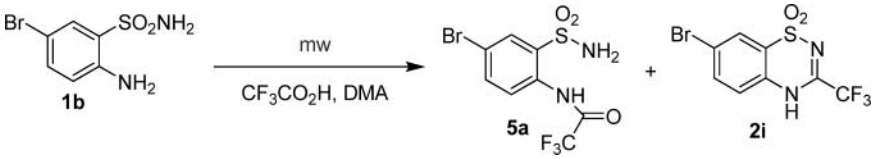
Table 5 Optimization conditions for the microwave-promoted synthesis of 3-aryl-4*H*-1,2,4-benzothiadiazine-1,1-dioxides from 2-aminobenzenesulfonamides and benzoic acids



Entry	1a: benzoic acid	Time (min)	Yield (%)[a]
1	1:1	6	**4a** (65)
2	1:1.2	6	**4a** (70)
3	1:1.3	9	**4a** (60)[20]: **2a** (30)
4	1:1.5	9	**4a** (40): **2a** (50)
5	1:1.5[b]	18	**2a** (80)
6	1:2[b]	18	**2a** (90)

[a]Yields of isolated products.[b]10N hydrochloric acid (5% mol) was added to the irradiated reaction mixture.

Table 6 Optimization conditions for the microwave-promoted synthesis of 3-trifluoromethyl-4*H*-1,2,4-benzothiadiazine-1,1-dioxides from 2-aminobenzenesulfonamides and TFA

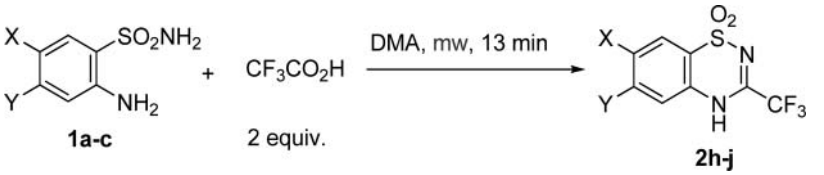


Entry	1b (equivalent): CF_3CO_2H (equivalent)	Time (min)	Yield (%)[a]
1	1:1	2	**5a** (40)
2	1:1	4	**5a** (39)
3	1:2	6	**5a** (45)
4	1:2	9	**5a** (34)[17]: **2i** (43)
5	1:2.5	13	**2i** (56)

[a]Yields of isolated products.

by our previous experience in the synthesis of 3-trifluomethyl-1,2,4-benzohiadiazine-1,1-dioxide derivatives by a PPSE-promoted trifluoroacetylation–cyclodehydration reaction of anilines with TFA,[16] we extended the above methodology to the preparation of 3-trifluoromethyl-1,2,4-benzothiadiazine-1,1-dioxides **2h–j**, requiring an irradiation time of 13 min (13 irradiation sets of 1 min each) and 2.5 equivalents of TFA to perform this reaction (Table 6), giving the desired heterocyclic compounds only in moderate yields (Table 7). Assigned 4*H*-isomeric form of prepared 1,2,4-benzothiadiazines was confirmed by NOESY NMR experiments, by the observation of an spatial correlation between the nitrogen H-4 and the ring H-5 hydrogen atoms of these compounds in hexadeuterated dimethylsulfoxide solutions. Due to the importance of trifluoromethyl-substituted heterocyclic compounds,[21,22] an extension of this reaction using other trifluoroacetyl intermediates will also be explored for the preparation of new trifluoromethyl heterocycles.

Table 7 One-pot microwave-promoted synthesis of 3-trifluoromethyl-4*H*-1,2,4-benzothiadiazine-1,1-dioxides from 2-aminobenzenesulfonamides and TFA



Compounds	X	Y	Yield (%)	Mp (°C) (Lit. mp)
2h	Cl	H	53	245–246
2i	Br	H	56	230–232 (230–232)[17]
2j	Cl	Cl	60	270–272

CONCLUSION

We have developed a rapid and convenient methodology for the preparation of different 3-aryl and 3-trifluoromethyl 4*H*-1,2,4-benzothiadiazine-1,1-dioxides in a one-pot microwave-promoted reaction from readily available starting materials, such as 2-aminobenzenesulfonamides, benzoic acids, and TFA. High yields of desired 2-aryl 4*H*-1,2,4-benzothiadiazines were obtained for their preparation from 2-aminobenzenesulfonamides and benzaldehydes or benzoic acids under the developed protocols, but moderate yields were obtained for 3-trifluoromethyl-4*H*-1,2,4-benzothiadiazines.

EXPERIMENTAL

Melting points were determined in a Fischer–Johns micro hot-stage apparatus and were uncorrected. Microwave irradiation was made using a GoldStar microwave domestic oven, model MA-690M (600-W power, 2450-MHz, and cycled irradiation multimode employs a time-slicing method, where the maximum power is applied for time intervals that are proportional to the power which the user sets on the controller); the reactions were performed in a 10-mL-capped conical flask that was put into a teflon cylinder container (5 cm diameter × 15 cm height). NMR spectra were obtained on a JEOL Eclipse Plus (^{1}H NMR spectra were recorded at 400 MHz, ^{13}C NMR at 100 MHz, and ^{19}F NMR spectra at 376 MHz) and Bruker Avance-500 (500 MHz, NOESY experiments) spectrometers in hexadeuterated dimethylsulfoxide (DMSO-d_6). Chemical shifts (δ) are given in ppm versus tetramethylsilane (TMS) (^{1}H NMR, ^{13}C NMR) or $CFCl_3$ (^{19}F NMR) used as internal references. Coupling constants are given in hertz. The IR spectra were recorded as KBr discs using an FTIR Nicolet Magna Spectrometer. Elemental analyses of new synthesized compounds were performed on a Perkin Elmer 2400 CHN analyzer; results fell in the range of ±0.4% of the required theoretical values. Silica gel plates ALUGRAM® SIL G/UV254 (Macherey-Nagel GmbH & Co., Germany) were used for TLC testing. Reagents were obtained from Aldrich (Milwaukee, MI, USA) or Merck (Darmstadt, Germany) and used without further purification. 2-Aminobenzenesulfonamides **1a–d** were easily obtained from substituted anilines as reported.[23] All products were obtained in high purity as indicated by TLC, ^{1}H NMR, and elemental analysis.

General Procedure for the Preparation of 3-Aryl-4H-1,2,4-Benzothiadiazine-1,1-Dioxides 2a–g from 2-Aminobenzenesulfonamides and Benzaldehydes Using Sodium Hydrogen Sulfite (Method A)

A mixture of the corresponding 2-aminobenzenesulfonamide **1a–d** (16 mg; 0.062 mmol), appropriate substituted benzaldehyde (0.093 mmol), sodium hydrogen sulfite (29 mg; 0.155 mmol), and dimethylacetamide (0.5 mL) was microwave-irradiated at several stages (2–3 min each) to complete the indicated time. An initial microwave-promoted preheating of 30 s (70% power) was needed in all cases, followed by seven irradiation steps of 2–3 min each (90% power). The reaction was followed by TLC until the starting 5-bromo-aminobenzenesulfonamide was consumed. After being cooled to room temperature, an amount of ice water was added to the resulting mixture to precipitate the products that were then filtered and washed three times with cool water and dried in vacuo to give compounds **2a–g**.

7-Chloro-3-(4-methylphenyl)-4*H*-1,2,4-benzothiadiazine-1,1-dioxide (2c): Beige solid, mp 335 °C–337 °C. ^{1}H NMR: δ 11.68 (s, 1H, NH), 7.77 (d, 2H, ArH, $J = 8.1$ Hz, H3′, H5′), 7.62 (d, 1H, ArH, $J = 2.2$ Hz, H8), 7.40 (d, 1H, ArH, $J = 8.8$ Hz, H6), 7.29 (dd, 1H, ArH, $J = 2.2$ Hz, $J = 8.8$ Hz, H5), 7.11 (d, 2H, ArH, $J = 8.1$ Hz, H2′, H6′), 2.22 (s, 3H, CH_3); ^{13}C NMR: δ 143.7, 134.5, 132.8, 130.9, 129.3, 128.9, 128.5, 123.3, 120.2, 118.6, 21.5; IR (KBr, cm^{-1}) υ: 3310 (NH), 1360 (SO_2), 1156 (SO_2); Anal. Calcd. for $C_{14}H_{11}ClN_2O_2S$; C, 54.81; H, 3.61; N, 9.13. Found: C, 54.58; H, 3.74; N, 9.25.

7-Chloro-3-(4-chlorophenyl)-4*H*-1,2,4-benzothiadiazine-1,1-dioxide (2d): Brown solid, mp 285 °C–287 °C. ^{1}H NMR: δ 11.71 (s, 1H, NH), 7.46 (d, 1H, ArH, $J = 8.1$ Hz, H3′, H5′), 7.18 (d, 1H, ArH, $J = 2.0$ Hz, H8), 7.00 (m, 2H, ArH), 6.95 (d, 2H, ArH, $J = 8.1$ Hz, H2′,6′); ^{13}C NMR: δ 153.7, 138.5, 134.1, 132.8, 130.7, 129.9, 129.7, 128.6, 122.6, 122.3, 120.3; IR (KBr, cm^{-1}) υ: 3315 (NH), 1360 (SO_2), 1158 (SO_2); Anal. Calcd. for $C_{13}H_8Cl_2N_2O_2S$; C, 47.72; H, 2.46; N, 8.56. Found: C, 47.93; H, 2.52; N, 8.45.

7-Chloro-3-(3-fluorophenyl)-4*H*-1,2,4-benzothiadiazine-1,1-dioxide (2e): Brown solid, mp 339 °C–340 °C. ^{1}H NMR: δ 11.76 (s, 1H, NH), 7.64 (m, 3H, ArH), 7.28 (m, 3H, ArH), 7.08 (m, 1H, ArH); ^{13}C NMR: δ 154.6, 134.2, 133.0, 131.4, 130.5 (d, $J = 8.4$ Hz), 124.4, 123.5, 122.9, 120.2, 119.9 (d, $J = 20.6$ Hz), 116.1, 115.5. ^{19}F NMR: δ −111.5; IR (KBr, cm^{-1}) υ: 3316 (NH), 1368 (SO_2), 1167 (SO_2); Anal. Calcd. for $C_{13}H_8ClFN_2O_2S$; C, 50.25; H, 2.60; N, 9.02. Found: C, 50.08; H, 2.73; N, 8.89.

7-Bromo-3-(3-methylphenyl)-4*H*-1,2,4-benzothiadiazine-1,1-dioxide (2f): Beige solid, mp 190 °C–192 °C. ^{1}H NMR: δ 12.29 (s, 1H, NH), 8.01 (d, 1H, ArH, $J = 2.0$ Hz), 7.93 (dd, 1H, $J = 2.0$ Hz, $J = 8.8$ Hz), 7.86 (s, 1H, ArH), 7.60 (d, 1H, ArH, $J = 8.8$ Hz), 7.51 (d, 2H, ArH, $J = 8.8$ Hz, H2′, H6′), 7.53 (bs, 2H, ArH), 2.44 (s, 3H, CH_3).;^{13}C NMR: δ 155.6, 139.0, 136.6, 135.4, 134.2, 132.2, 129.4, 129.2, 126.1, 125.9, 123.4, 121.6, 118.3, 21.5; IR (KBr, cm^{-1}) υ: 3314 (NH), 1354 (SO_2), 1165 (SO_2); Anal. Calcd. for $C_{14}H_{11}BrN_2O_2S$; C, 47.88; H, 3.16; N, 7.98. Found: C, 47.99; H, 3.25; N, 7.86.

6,7-Dichloro-3-(2-chlorophenyl)-4*H*-1,2,4-benzothiadiazine-1,1-dioxide (2g): Brown solid, mp 271 °C–272 °C. ^{1}H NMR: δ 11.84 (s, 1H, NH), 8.29 (s, 1H, ArH), 8.60 (s, 1H, ArH), 8.50 (d, 1H, ArH, $J = 8.1$ Hz), 8.25 (dd, 1H, ArH, $J = 8.1$ Hz, $J = 7.8$ Hz), 7.86 (d, 1H, ArH, $J = 8.1$ Hz), 7,78 (t, 1H, ArH, $J = 7.7$ Hz, $J = 7.7$ Hz); IR (KBr, cm^{-1}) υ: 3312 (NH), 1366 (SO_2), 1162 (SO_2); Anal. Calcd. for $C_{13}H_7Cl_3N_2O_2S$; C, 43.18; H, 1.95; N, 7.75. Found: C, 43.09; H, 1.90; N, 7.71.

General Procedure for the Preparation of 3-Aryl-4H-1,2,4-Benzothiadiazine-1,1-Dioxides 2a–d and f–g from 2-Aminobenzenesulfonamides and Benzoic Acid (Method B)

A mixture of the corresponding 2-aminobenzenesulfonamide **1a–d** (16 mg; 0.062 mmol), appropriate substituted benzoic acid (0.124 mmol), 5% mol of hydrochloric acid (10N solution), and dimethylacetamide (1 mL) was microwave-irradiated at several stages (3 min each) to complete the indicated time. An initial microwave-promoted preheating of 30 s (50% power) was needed in all cases, followed by six irradiation steps of 3 min each (90% power). The reaction was followed by TLC until the starting 5-bromo-2-aminobenzenesulfonamide was consumed. After being cooled to room temperature, an amount of ice water was added to the resulting mixture to precipitate the products that were then filtered and washed three times with cool water and dried in vacuo to give compounds **2a–d** and **f–g**.

General Procedure for the Preparation of 3-Aryl-4H-1,2,4-Benzothiadiazine-1,1-Dioxides 2c–d from 3,4-Dihidro-2H-1,2,4-Benzotiadiazine-1,1-Dioxides

A solution of substituted 3,4-dihydro-2*H*-1,2,4-benzothiadiazine-1,1-dióxide **3a,b** (20 mg, 0.062 mmol) and sodium hydrogen sulfite (10 mg, 0.093 mmol) in dimethylacetamide (0.5 mL) was microwave-irradiated at several stages (2–3 min each) to complete the indicated time (7 min). An initial microwave-promoted preheating of 30 s (70% power) was needed in all cases, followed by several irradiation steps of 2–3 min (90% power). The reaction was followed by TLC until the starting 3,4-dihydro-2*H*-benzothiadiazine-1,1-dioxide was consumed. After being cooled to room temperature, an amount of ice water was added to the resulting mixture to precipitate the products that were then filtered and washed three times with cool water and dried in vacuo to give title pure compounds **2c–d** in almost quantitative yield.

General Procedure for the Preparation of 3-Trifluoromethyl-4H-1,2,4-Benzothiadiazine-1,1-Dioxides 2h–j from 2-Aminobenzenesulfonamides and TFA

A mixture of the corresponding 2-aminobenzenesulfonamide **1b–d** (16 mg; 0.062 mmol), TFA (0.124 mmol), and dimethylacetamide (1 mL) was microwave-irradiated at several stages (3 min each) to complete the indicated time. An initial microwave-promoted preheating of 30 s (40% power) was needed in all cases, followed by 13 irradiation steps of 1 min each (80% power). The reaction was followed by TLC until the starting 2-aminobenzenesulfonamide was consumed. After being cooled to room temperature, an amount of ice water was added to the resulting mixture to precipitate the products that were then filtered and washed three times with cool water and dried in vacuo to give compounds **2h–j**.

7-Chloro-3-trifluoromethyl-4*H*-1,2,4-benzothiadiazine-1,1-dioxide (2h): Brown solid, mp 245 °C–246 °C. ^{1}H NMR: δ 11.81 (bs, 1H, NH), 7.88 (d, 1H, ArH, $J = 2.5$ Hz, H8), 7.77 (dd, 1H, ArH, $J = 2.5$ Hz, $J = 8.9$ Hz, H6), 7.36 (d, 1H, ArH, $J = 8.9$ Hz, H5); ^{13}C NMR: δ 148.5 (d, $J = 36.7$ Hz), 139.8, 136.3, 125.7, 125.5, 124.6, 118.4. ^{19}F NMR: δ −77.0; IR (KBr, cm^{-1}) υ: 3278 (NH), 1369 (SO_2), 1168 (SO_2); Anal. Calcd. for $C_8H_4ClF_3N_2O_2S$; C, 33.76; H, 1.42; N, 9.84. Found: C, 33.68; H, 1.39; N, 9.89.

6,7-Dichloro-3-trifluoromethyl-4*H*-1,2,4-benzothiadiazine-1,1-dioxide (2j): Brown solid, mp 270 °C–272 °C. ^{1}H NMR: δ 13.26 (s, 1H, NH), 7.76 (s, 1H, ArH), 7.59 (s,1H, ArH); ^{13}C NMR: δ 175.1, 147.8 (d, $J = 36.7$ Hz), 137.8, 133.5, 131.6, 125.6, 121.6, 120.9; ^{19}F NMR: δ −71.2; IR (KBr, cm^{-1}) υ: 3263 (NH), 1363 (SO_2), 1160 (SO_2); Anal. Calcd. for $C_8H_3Cl_2F_3N_2O_2S$; C, 30.11; H, 0.95; N, 8.78. Found: C, 30.09; H, 0.92; N, 8.71.

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