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The Zeolite ZSM-5-SO_3H as an Efficient Mild Heterogeneous Catalyst for the Synthesis of 1,2,5-Thiadiazolidines, 1,2,6-Thiadiazines, and Benzo[d][1,2,7] thiadiazepines Under Microwave-assisted Solvent-free Conditions

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ABSTRACT Three series of compounds namely,1,2,5-thiadiazolidine-3,4(*H*)-dione-1,1-dioxydes, 1,2,6-thiadiazine-3,5(*H*)-dione-1,1-dioxydes, and benzo[d][1,2,7]thiadiazepine-1,5(*2H*)-dione-3,3-dioxydes have been synthesized by the acylation of *N*,*N*'-disubstituted symmetric sulfamides with oxalyl chloride, malonyl chloride, and phthaloyl chloride, respectively. These compounds were prepared under conventional and microwave-assisted solvent-free reaction conditions using the zeolite ZSM-5-SO_3H as catalyst.

KEYWORDS Microwave, ZSM-5-SO_3H, Thiadiazolidine, Thiadiazine, Benzothiadiazepine.

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INTRODUCTION

Thiadiazolidine, thiadiazine, and benzothiadiazepine [**Figure 1**] have attracted much attention as an important class of sulfur and nitrogen-containing heterocycles with a wide spectrum of biological activity and synthetic utilities.[1,2] These compounds are widely known in the literature us enzymes inhibitors, especially serine proteases,[3] γ-secretases,[4] and transcriptase.[5,6] In addition, numerous benzothiadiazepine hydroxamates derivatives can be used as selective tumor necrosis factor-α converting enzyme inhibitors.[7] Thus, the development of the chemistry and the synthetic methods for the preparation of thiadiazolidine, thiadiazine, and benzothiadiazepine-based compounds are important targets.[8] Numerous methods have been reported, which include the use of microwave-promoted solvent-free and mild heterogeneous catalyst.[9]

During recent years, the application of microwave heating technology has become a powerful mode of activation in organic synthesis. This eco-friendly technique has been used as an efficient and non-polluting methodology for the synthesis of heterocyclic compounds with high purity and in better yields.[10,11]

As an extension of our aim on the discovery of new eco-friendly chemical synthesis,[12] we report herein a green protocol for the synthesis of five-, six-, and seven-membered heterocyclic derivatives, namely, thiadiazolidines, thiadiazines, and thiadiazepines, respectively, using ZSM-5-SO_3H[13-15] as a mild heterogeneous catalyst under microwave solvent-free conditions.

RESULTS AND DISCUSSION

The synthesis of starting materials, *N*,*N*'-disubstituted symmetric sulfamides **1a-1f** by the reaction of sulfuryl chloride (SO_2Cl_2) with an excess of the corresponding primary amine in methylene chloride has been reported previously.[16,17] These sulfamides were successfully used as versatile precursors for the generation of various heterocycles (1,2,5-thiadiazolidine, 1,2,6-thiadiazine, and

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benzothiadiazepine) through double acylation condensation with different acylating agents under mild heterogeneous and microwave solvent-free conditions.

The classical preparation of sulfur-containing heterocycles **2a-2f**, **3a-3b**, and **4a-4c** usually involves the double acylation condensation of *N,N'*-disubstituted symmetric sulfamides **1a-1f** with an acylating agent (oxalyl chloride, malonyl chloride, or phthaloyl chloride) in benzene or dichloromethane under basic conditions (triethylamine [TEA] or 4-Dimethyl amino pyridine [DMAP]).[18,19] The results of conventional reactions [**Table 1**] show that all heterocyclic products were obtained in yields ranged from 63 to 81%. The double acylation pathways are shown in **Scheme 1**.

To develop an innovative and reliable protocol for the preparation of mentioned heterocyclic systems (thiadiazolidine, thiadiazine, and benzothiadiazepine), we carried out the double acylation under microwave-assisted solvent-free conditions in combination with heterogeneous solid catalyst ZSM-5-SO_3H. A mixture of sulfamide, ZSM-5-SO_3H, and acylating agent was stirred under solvent-free conditions to produce the corresponding heterocycle in high yields. Detailed procedure for the synthesis of ZSM-5-SO_3H is included in the experimental section according to the reported method.[13-15] The experimental results of microwave-assisted solvent-free acylation are shown in **Table 1**.

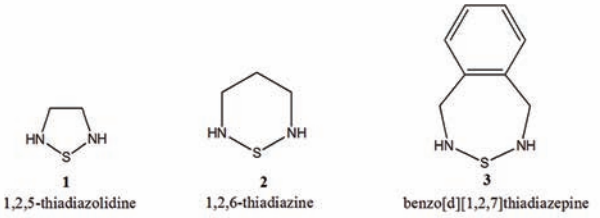
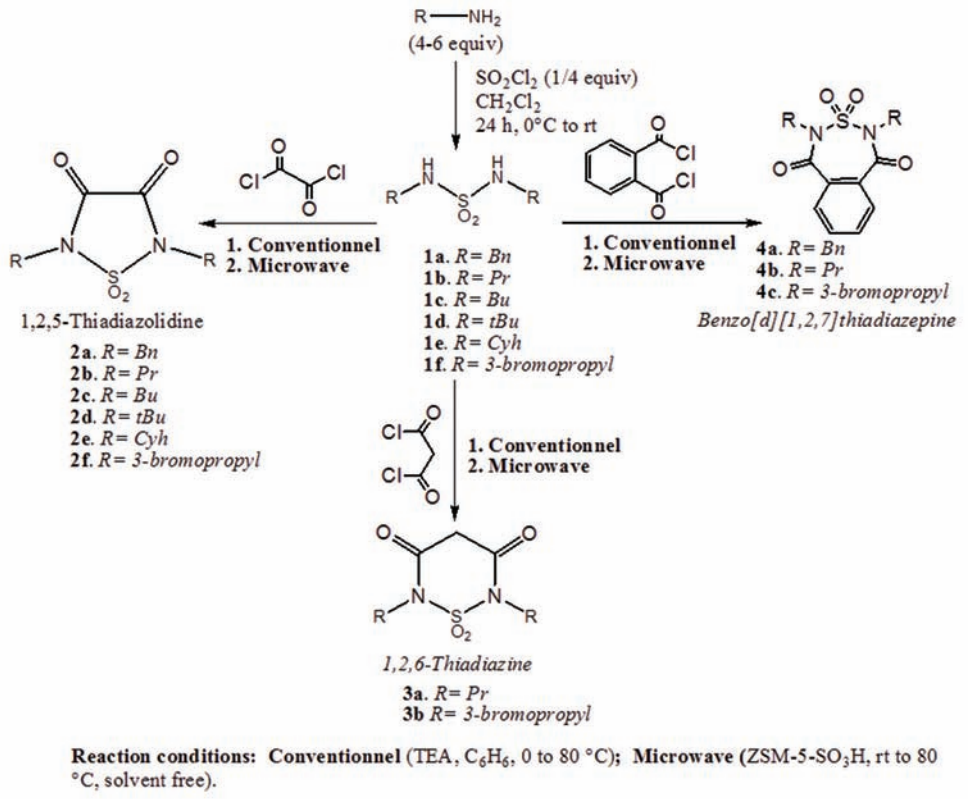


Figure 1: Structures of thiadiazolidine, thiadiazine, and benzothiadiazepine

To illustrate the advantages of using ZSM-5-SO_3H under solvent-free conditions, this method is compared with conventional heating. As **Table 1** demonstrates, using microwave-assisted solvent-free with solid catalyst, the double acylation proceeded smoothly at 80°C in excellent yields (>85%) within 20 min.

The efficient approach under microwave solvent-free conditions can provide an environmentally benign reaction with many advantages, including selectivity, easier work-up, economical, shorter reaction time, and better yields.[20]

The structure of the synthesized compounds was confirmed by analysis of elemental and spectral data (IR, ^{1}H-NMR, and mass). The FT-IR spectra confirm that the desired products of acylation were obtained by the appearance of strong absorption bands at $\bar{\upsilon}$ = 1700 cm^{-1} corresponding to C=O groups. In addition, all IR spectra showed a characteristic band over 1140 and $\bar{\upsilon}$ = 1300 cm^{-1} corresponding to a sulfonyl (SO_2) group. Another evidence is the appearance of the absorption band at 1600 cm^{-1}, corresponding to the aromatic ring stretch for all benzothiadiazepine derivatives **4a-4c**. The ^{1}H-NMR of benzothiadiazepine **4a-4c** revealed signals at 7.60 ppm assigned to aromatic ring protons. In addition, the ^{1}H NMR spectra of thiadizines derivatives **3a-3b** revealed the apparition of methylene protons at 3.96



Scheme 1: Synthetic routes to 1,2,5-thiadiazolidines, 1,2,6-thiadiazines, and benzothiadiazepines

Table 1: Reaction times and yields for the synthesis of 1,2,5-Thiadiazolidines, 1,2,6-thiadiazines, and benzothiadiazepines

Comp. no	R	Rea. T (min)	Microwave-solvent free ZSM-5-SO_3H			Conventional			
			Yield (%)	Temp. (°C)	MW watt	Yield (%)	Rea. T (h)	base	Solvent
2a	*Benzyl*	20	91	80	240	82	3	TEA	C_6H_6
2b	*Propyl*	20	94	80	240	75	4	TEA	C_6H_6
2c	*Butyl*	20	89	80	240	80	4	TEA	CH_2Cl_2
2d	*t-Butyl*	20	97	80	240	76	3	TEA	C_6H_6
2e	*Cyclohexyl*	20	85	80	240	63	4	TEA	C_6H_6
2f	*3-bromopropyl*	20	90	80	240	75	4	TEA	C_6H_6
3a	*Propyl*	20	91	80	240	76	4	DMAP	C_6H_6
3b	*3-bromopropyl*	20	92	80	240	81	4	TEA	C_6H_6
4a	*Benzyl*	15	93	80	240	81	4	TEA	C_6H_6
4b	*Propyl*	20	90	80	240	77	4	DMAP	C_6H_6
4c	*3-bromopropyl*	20	91	80	240	82	4	TEA	C_6H_6

and 3.93 ppm, respectively. Furthermore, the mass spectra of all heterocyclic products showed peaks at *m/z* = [M+1] corresponding to the molecular mass of ions $[M+H]^+$.

Experimental

^{1}H NMR spectra were recorded on a Bruker Avance spectrometer at 300 MHz and 75 MHz, respectively. The chemical shifts δ (ppm) were measured in $CDCl_3$ relative to tetramethylsilane, which served as the internal standard (δ = 0) for ^{1}H NMR. Infrared spectra were recorded on a Bruker Vector 22 FT-IR spectrometer. The mass spectral data were recorded using an HP 5989A instrument at 70 eV. Melting points (Mp) were determined in open capillary tubes using an Electrothermal 9200 apparatus and are uncorrected. The microwave-assisted reactions were carried out using a CEM Discover synthesis reactor. The catalyst ZSM-5-SO_3H was prepared following the procedure previously reported.[13-15]

General procedure for the synthesis of *N,N*-bis sulfonamides 1a-1f

Compounds **1a-1f** were prepared as described in previously published protocols.[16,17] The reaction was performed by the dropwise addition of a solution of sulfuryl chloride (1 equiv) in 20 mL of CH_2Cl_2 to a solution of the corresponding amine (4–6 equiv) in 50 mL of CH_2Cl_2 at 0°C in darkness. Gas evolution was observed during sulfuryl chloride addition. The reaction mixture was warmed to room temperature (r.t), stirred for 24 h, and monitored by thin-layer chromatography (TLC) (SiO_2). The crude product was washed with HCl (2 N, 2 × 20 mL) and water (2 × 30 mL) and dried over Na_2SO_4. The solution was filtered and concentrated under reduced pressure to yield a yellow solid as the crude product. Column chromatography (CH_2Cl_2: MeOH = 95:5) afforded the *N, N*'-dialkylsulfamide in moderate yields.

N,N'-Dibenzylsulfamide (1a)[12]

This compound was prepared according to the above general procedure using a solution of benzylamine (6 equiv) in CH_2Cl_2 and SO_2Cl_2 (1 equiv) in CH_2Cl_2. Compound **1a** was obtained as a white solid in 59% yield. R_f = 0.36 (SiO_2, CH_2Cl_2); Mp: 182–183°C (reported 180–182°C); IR (KBr, $\bar{\upsilon}$ cm^{-1}): 3277 (NH), 3088, 3065, 3034 (CH-Ar), 1350 and 1143 (SO_2); ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 4.17 (d, 4H, CH_2), 4.37 (t broad, *2H*, NH), 7.28–7.34 (m, 10H, Ar-H); LRMS (CI)): 277 M^+, 199, 91.

N,N'-Dipropylsulfamide (1b)[12]

Compound **1b** was obtained as a white solid in 60% yield. R_f = 0.45 (SiO_2, CH_2Cl_2:MeOH = 95:5); Mp: 64–65°C (reported: 62–63°C); IR (KBr, $\bar{\upsilon}$ cm^{-1}): 3280 (NH), 1333 and 1150 (SO_2); ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 0.95 (t, J = 7.2 Hz, 6H, CH_3), 1.57 (sext, J = J' = 7.1 Hz, 4H, β-CH_2), 2.99 (q, 4H, *α*-CH_2), 4.27 (t broad, *2H*, NH); ^{13}C NMR ($CDCl_3$): 11.26 (*γ*-C), 22.89 (β-C), 44.95 (*α*-C); LRMS (CI): 181 M^+.

N,N'-Dibutylsulfamide (1c)

Compound **1c** was obtained as a white solid in 58% yield. R_f = 0.36 [(SiO_2, CH_2Cl_2))]; Mp: 126–127°C (described 126.5°C). IR (KBr, $\bar{\upsilon}$ cm^{-1}): 3281 (NH), 1314 and 1145 (SO_2). ^{1}HNMR ($CDCl_3$): 4.33 (t broad, *2H*, NH), 3.04 (m, 4H, *α*-CH_2), 1.54 (m, 4H, β-CH_2), 1.38 (m, 4H, *γ*-CH2), 0.93 (t, J = 7.1 Hz, 6H, CH_3). ^{13}C NMR ($CDCl_3$): 43.2 (*α*-C), 31.7 (β-C), 20.11 (*γ*-C), 13.88 (CH_3). LRMS (CI): 209 $[M+H]^+$.

N,N'-Di(t-butyl)sulfamide (1d)

Compound **1d** was obtained as a white solid in 60% yield. R_f = 0.62 [SiO_2, CH_2Cl_2/MeOH (95:5)]; Mp: 140–142°C. IR (KBr, $\bar{\upsilon}$ cm^{-1}): 3303 (NH), 1368 and 1131 (SO_2). ^{1}HNMR ($CDCl_3$): 1.35 (s, 19H, 2 tBu), 0.4.27 (s, 2H, NH). LRMS (CI): 209 $[M+H]^+$, 151.

N,N'-Dicyclohexylsulfamide (1e)

Compound **1e** was obtained as a white solid in 66% yield. R_f = 0.38 [SiO_2, CH_2Cl_2/MeOH (95:5)]; Mp: 154–155°C. IR (KBr, $\bar{\upsilon}$ cm^{-1}): 3283 (NH), 1337 and 1138 (SO_2). ^{1}HNMR ($CDCl_3$): 4.35 (d, J = 7.6 Hz, *2H*, NH); 3.16 (m, *2H*, CH); 1.12–2.01 (m, 20H, 2(CH_2)5). ^{13}C NMR ($CDCl_3$): 52.63 (*α*-C), 34.01 (β-C), 25.27 (δ = C), 24.78 (*γ*-C). LRMS (CI): 261 $[M+H]^+$, 179, 83.

N,N'-Di(3-bromopropyl)sulfamide (1f)[12]

Compound **4c** was obtained as a white solid in 73% yield. R_f = 0.58 (SiO_2, CH_2Cl_2:MeOH = 95:5); Mp: 72–74°C; IR (KBr, $\bar{\upsilon}$ cm^{-1}): 3286 (NH), 1133 and 1351 (SO_2); ^1H NMR (300 MHz, $CDCl_3$, ppm): 2.13 (t, 4H, β-CH_2), 3.26 (q, 4H, *α*-CH_2), 3.51 (t, 4H, *γ*-CH_2), 4.39 (t, *2H*, NH); LRMS (CI): 339 $[M+H]^+$, 257, 231, 138.

General procedure for the double acylation under conventional heating

A solution of acylating agent (oxalyl chloride, malonyl chloride, or orthophtaloyl chloride) (1 equiv, 1 mmol) in dry benzene (10 mL) was added dropwise to a mixture of *N,N*-bis sulfonamide (**1a-1f**) (1 equiv, 1 mmol) and TEA (2.2 equiv) in the same solvent 20 mL in a round-bottomed flask and the reaction mixture was left to stir under reflux for 3 to 4 h (monitored by TLC). Upon completion of the reaction, the reaction mixture was cooled to room temperature and followed by solvent removal under reduced pressure. The residue was taken up in CH_2Cl_2, washed with $NaHCO_3$ (5%, 2 × 10 mL), brine (2 × 10 mL), dried over anhydrous Mg_2SO_4, and the solvent was evaporated to give a crude product. Flash chromatography on silica gel using ethyl acetate CH_2Cl_2 as the eluent afforded the corresponding pure cyclic sulfamides (1,2,5-thiadiazolidine; 1,2,6-Thiadiazine, or benzothiadiazepine).

General procedure for the double acylation using ZSM-5-SO_3H under microwave-assisted solvent-free

N,N-bis sulfonamide (1 mmol) and ZSM-5-SO_3H (0.01 g) were ground altogether into fine powder, and acylating agent (oxalyl chloride, malonyl chloride, or phthaloyl chloride) (1 mmol) was added under vigorous stirring at low temperature in an ice bath and then was stirred at room temperature. The system was heated in a microwave oven at 300 W for a few minutes (monitored by TLC). Upon completion of the reaction, CH_2Cl_2 (20 mL) was added and the catalyst was filtered and washed with additional solvent (10 mL). The filtrate was washed with $NaHCO_3$ (5%, 10 mL) water (10 mL) and dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography over silica gel using ethyl acetate n-hexane (1:3) as the eluent. The products were obtained in high yields (>90%).

2,5-Dibenzyl-1,2,5-thiadiazolidine-3,4-dione 1,1-dioxide (2a)

This compound was prepared using oxalyl chloride (1 equiv, 1 mmol) and TEA (2.2 equiv). Compound **2a** was obtained as a white solid in 82% yield by conventional heating and 91% by MWI. R_f = 0.45 (SiO_2, CH_2Cl_2); Mp: 115–116°C; IR (KBr, $\bar{\upsilon}$ cm^{-1}): 1761 and 1772 (C=O), 1187 and 1356 (S=O); ^1H NMR (300 MHz, $CDCl_3$, ppm): 4.90 (s, 4H, CH_2), 7.35–7.44 (m, 10H, 2Ph).; LRMS (CI): 331 [M+H], 91(100%).

2,5-Dipropyl-1,2,5-thiadiazolidin-3,4-dione 1,1-dioxide (2b)

This compound was prepared using oxalyl chloride (1 equiv, 1 mmol) and TEA (2.2 equiv). Compound **2b** was obtained as yellow oil in 63% yield by conventional heating and 94% by MWI. R_f = 0.42 (SiO_2, CH_2Cl_2); IR (KBr, $\bar{\upsilon}$ cm^{-1}): 1765 (C=O), 1191 and 1336 (S=O); ^1H NMR (300 MHz, $CDCl_3$, ppm): 1.01 (t, 6H, $2CH_3$), 1.86 (m, 4H, $2CH_2$), 3.77 (t, 4H, $2CH_2$-N).; LRMS (CI): 235 [M+H], 193, 151.

2,5-Dibutyl-1,2,5-thiadiazolidine-3,4-dione 1,1-dioxide (2c)

This compound was prepared using oxalyl chloride (1 equiv, 1 mmol) and TEA (2.2 equiv). Compound **2c** was obtained as a white solid in 80% yield by conventional heating and 89% by MWI. R_f = 0.46 (SiO_2, CH_2Cl_2); Mp: 36–38°C; IR (KBr, $\bar{\upsilon}$ cm^{-1}): 1773 (C=O), 1185 and 1344 (S=O); ^1H NMR (300 MHz, $CDCl_3$, ppm): 0.97 (t, 6H, $2CH_3$), 1.42 (m, 4H, $2CH_2$), 1.81 (m, 4H, $2CH_2$), 3.80 (t, 4H, $2CH_2$).; LRMS (CI): 263 [M+H] (100%), 207.

2,5-Ditertbutyl-1,2,5-thiadiazolidin-3,4-dione 1,1-dioxide (2d)

This compound was prepared using oxalyl chloride (1 equiv, 1 mmol) and TEA (2.2 equiv). Compound **2d** was obtained as a white solid in 76% yield by conventional heating and 97% by MWI. R_f = 0.44 (SiO_2, CH_2Cl_2); Mp: 132–134°C; IR (KBr, $\bar{\upsilon}$ cm^{-1}): 1751 and 1647 (C=O), 1161 and 1350 (S=O); ^1H NMR (300 MHz, $CDCl_3$, ppm): 1.71 (s, 18H, 2*t*Bu).; LRMS (CI): 263 [M+H], 207(100%).

2,5-Dicyclohexyl-1,2,5-thiadiazolidin-3,4-dione 1,1-dioxide (2e)

This compound was prepared using oxalyl chloride (1 equiv, 1 mmol) and TEA (2.2 equiv). Compound **2e** was obtained as a white solid in 75% yield by conventional heating and 85% by MWI. R_f = 0.58 (SiO_2, CH_2Cl_2); Mp: 140–142°C; IR (KBr, $\bar{\upsilon}$ cm^{-1}): 1755 (C=O), 1186 and 1346 (S=O); ^1H NMR (300 MHz, $CDCl_3$, ppm): 1.25–2.06 (m, 20H, 2($5CH_2$)), 4.12 (m, *2H*, 2CH).; LRMS (CI): 331 [M+H], 91(100%).

2,5-Di(3-bromopropyl)-1,2,5-thiadiazolidine-3,4-dione 1,1-dioxide (2f)

This compound was prepared using oxalyl chloride (1 equiv, 1 mmol) and TEA (2.2 equiv). Compound **2f** was obtained as a white solid in 75% yield by conventional heating and 90% by MWI. R_f = 0.44 (SiO_2, CH_2Cl_2); Mp: 95–97°C; IR (KBr, $\bar{\upsilon}$ cm^{-1}): 1770 (C=O), 1166 and 1348 (S=O); ^1H NMR (300 MHz, $CDCl_3$, ppm): 2.38 (m, 4H, $2CH_2$), 3.47 (t, 4H, $2CH_2$-Br), 4.01 (t, 4H, $2CH_2$-N).; LRMS (CI): 233, 83.

2,6-Dipropyl-1,2,6-thiadiazine-3,5-dione 1,1-dioxide (3a)

This compound was prepared using malonyl chloride (1 equiv, 1 mmol) and TEA (2.2 equiv). Compound **3a** was obtained as yellow oil in 76% yield by conventional heating and 91% by MWI. R_f = 0.34 (SiO_2, CH_2Cl_2); IR (KBr, ν cm^{-1}): 1707 and 1731 (C=O), 1152 and 1372 (S=O); ^1H NMR (300 MHz, $CDCl_3$, ppm): 0.95 (t, 6H, $2CH_3$); 1.72 (m, 4H, $2CH_2$); 3.82 (t, 4H, $2CH_2$-N); 3.93 (s, *2H*, CH_2carb); LRMS (CI): 249 [M+H], 207.

2,6-Di(3-bromopropyl)-1,2,6-thiadiazine-3,5-dione 1,1-dioxide (3b)

This compound was prepared using malonyl chloride (1 equiv, 1 mmol) and TEA (2.2 equiv). Compound **3b** was obtained as yellow oil in 81% yield by conventional heating

and 92% by MWI. R_f = 0.37 (SiO_2, CH_2Cl_2); IR (KBr, $\bar{\upsilon}$ cm^{-1}): 1708 and 1731 (C=O), 1152 and 1372 (S=O); ^1H NMR (300 MHz, $CDCl_3$, ppm): 2.26 (m, 4H, $2CH_2$); 3.41 (t, 4H, $2CH_2$-Br); 3.96 (s, *2H*, CH_2 carb); 4.02 (t, 4H, $2CH_2$-N); LRMS (CI): 407 [M+H], 327 and 325.

2,4-Dibenzylbenzo[d][1,2,7]thiadiazepine-1,5(2H)-dione-3,3-dioxide (4a)

This compound was prepared using phthaloyl chloride (1 equiv, 1 mmol) and TEA (2.2 equiv) Compound **4a** was obtained as a white solid in 84% yield by conventional heating and 93% by MWI. R_f = 0.53 (SiO_2, CH_2Cl_2); Mp: 170–172°C; IR (KBr, $\bar{\upsilon}$ cm^{-1}): 1732 and 1772 (C=O), 1138 and 1314 (S=O); ^1H NMR (300 MHz, $CDCl_3$, ppm): 4.77–4.86 (*dd*, 4H, CH_2Ph), 7.34 (s *broad*, 10H, 2Ph), 7.67–7.70 (*dd*, *2H*, H-Ar), 7.86–7.89 (*dd*, *2H*, H-Ar).; LRMS (CI): 407 [M+H], 227, 161. Elemental analysis: Calcd. for C_2*2H*$_{18}O_4N_2S$: C=65.01; H=4.46; N=6.89; O=15.74; S=7.89; Found: C=65.02; H=4.43; N=6.89; O=15.76; S=7.90.

2,4-Dipropylbenzo[d][1,2,7]thiadiazepine-1,5(2H)-dione-3,3-dioxide (4b)

This compound was prepared using phthaloyl chloride (1 equiv, 1 mmol) and TEA (2.2 equiv). Compound **4b** was obtained as a white solid in 77% yield by conventional heating and 93% by MWI. Mp: 77–78°C, R_f = 0.46 (SiO_2, CH_2Cl_2); IR (KBr, $\bar{\upsilon}$ cm^{-1}): 1772 and 1595 (C=O); 1139 and 1332 (SO_2); ^1H NMR (300 MHz, $CDCl_3$, ppm): 0.99 (t, 6H, CH_3), 1.80 (s, 4H, CH_2), 3.92–4.06 (*dd*, *2H*, CH_aH_b), 7.66–7.69 (*dd*, *2H*, H-Ar); 7.85 (*dd*, *2H*, H-Ar); LRMS (CI): 311 [M+H], 269. Elemental analysis: Calcd. for $C_{14}H_{18}O_4N_2S$: C=54.18; H=5.85; N=9.03; O=20.62; S=10.33; Found: C=54.20; H=5.81; N=9.04; O=20.64; S=10.31.

2,4-Di(3-bromopropyl)benzo[d][1,2,7]thiadiazepine-1,5(2H)-dione-3,3-dioxide (4c)

This compound was prepared using phthaloyl chloride (1 equiv, 1 mmol) and TEA (2.2 equiv). Compound **4c** was obtained as a white solid in 82% yield by conventional heating and 91% by MWI. R_f = 0.37, (SiO_2, CH_2Cl_2); Mp: 75–77°C; IR (KBr, $\bar{\upsilon}$ cm^{-1}): 1667 (C=O); 1174 and 1399 (SO_2); ^1H NMR (300 MHz, $CDCl_3$, ppm): 2.23 (m, 4H, $2CH_2$), 3.46 (t, *2H*, CH_2), 3.63 t, *2H*, CH_2), (4.12–4.14 (t, 4H, CH_2), 7.70–7.72 (*dd*, *2H*, H-Ar), 7.88–7.91 (*dd*, *2H*, H-Ar); LRMS (CI): 469 and 451 [M+H], 249 and 251, 149.

Elemental analysis: Calcd. for $C_{14}H_{16}Br_2O_4N_2S$: C=35.92; H=3.44; Br=34.14; N=5.98; O=13.67; S=6.85; Found: C=35.90; H=3.42; Br=34.16; N=5.96; O=13.65; S=6.83.

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