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A convenient synthesis of novel 2,3,4-trisubstituted 1,5-benzothiazepines bearing a sulfonyl pharmacophore

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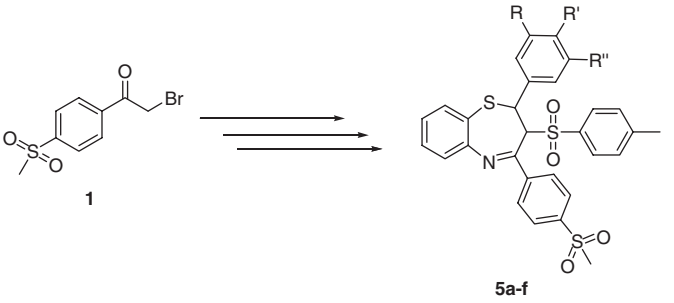
2-(Substituted phenyl)-3-[(methyl phenyl) sulfonyl] [(methyl sulfonyl) phenyl]-2,3-dihydro-1,5-benzothiazepines (**5a**–**f**) have been obtained in moderate yields by condensing 2-aminothiophenol with the chalcones 1-[(4′-methyl sulfonyl)phenyl]-2-[(4-methyl phenyl)sulfonyl]-prop-2-en-1-ones (**4a**–**f**) in toluene using trifluoroacetic acid as the catalyst. The benzothiazepines have also been synthesized by carrying out neat cyclocondensations of the chalcones supported on silica and 2-aminothiophenol at 80 °C. The precursors, chalcones (**4a**–**f**), were freshly prepared from α-(4′-methyl sulfonyl phenyl)-4-methyl sulfonyl acetophenone (**3**).



Keywords: 2-aminothiophenol; cyclocondensation; 1, 5-benzothiazepine; sulfonyl; convenient

1. Introduction

1,5-Benzothiazepines are a very important class of organic compounds because of their wide pharmacological properties (*1*). These heterocycles are found to act as cardiovascular modulators, vasodilators (*2*, *3*), antiarrythmic (*4*), protease inhibitors (*5*), elastase (*6*), angiotensin converting enzyme (ACE)-inhibitors (*7*) and antagonistic of G-protein coupled receptors such as cholecystokinin receptors (*8*) and as interleukin-1b converting enzyme inhibitors and the angiotensin II receptor (ACE) inhibitors (*9*). Some of the 1,5-benzothiazepine derivatives are

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also used clinically for central nervous system disorders which includes thiazesim (*10*) and quetiapine fumarate (*11*). Considering the significance of these seven-membered fused heterocycles, various 2,4-disubstituted 2,3-dihydro-1,5-benzothiazepines have been reported in the literature.

Incorporation of sulfonyl pharmacophores in the molecular frameworks have resulted in COX-2 inhibition activity (*12*). Celecoxib and rofecoxib are the well-established anti-inflammatory drugs having sulfonyl pharamacophore (*13*, *14*).

A literature survey reveals that there are various routes to obtain 1,5 benzothiazepines using 2-aminothiophenols as one of the precursors. It has been found that most of the common synthetic routes involve the cyclocondensation of 2-aminothiophenols with α, β-unsaturated ketones (*9*).

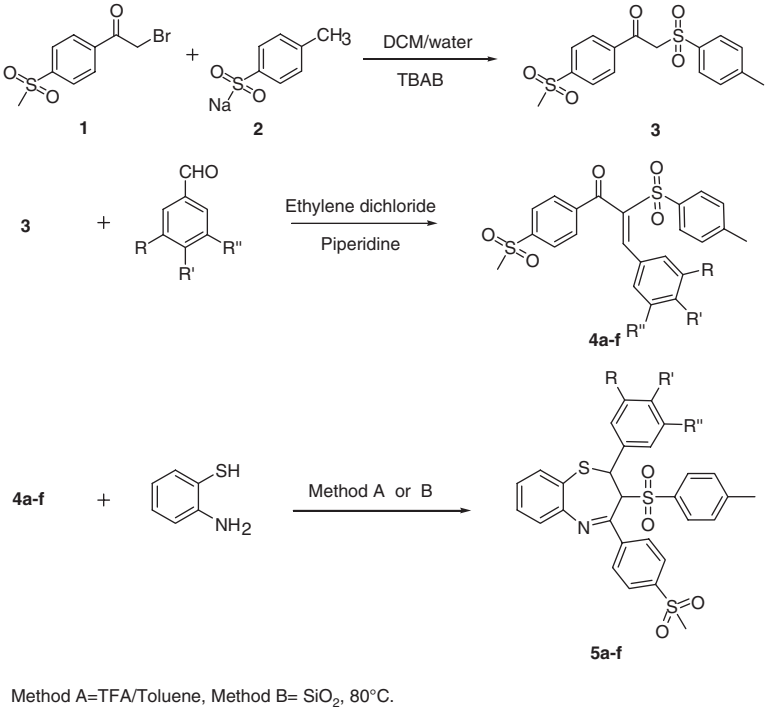
Several attempts have been made to optimize the reaction conditions of the cyclocondensation to obtain high yields and to reduce condensation time. Cyclocondensations have been carried out in inert solvents such as ethanol using bi-catalysts, organic bases and acids (*15*), and it was noticed that the reaction time required for the completion of the condensation was longer and the product isolation was also tedious.

Therefore, more attention has been directed to the development of convenient and rapid routes for the synthesis of 2,4-disubstituted 1,5-benzothiazepines, for obtaining new leads.

Considering the dire need of providing rapid and excellent synthetic routes for benzothiazepines and as well as generating new benzothiazepines, we here in report the continuation of our earlier interest (*16*), the synthesis of new 2,3,4-trisubstituted 1,5-benzothiazepines.

2. Results and discussion

With the aim to obtain 2,3,4-trisubstituted 1,5-benzothiazepines bearing sulfonyl pharmacophores, the following attempts have been made and the developed reaction path is presented in Scheme 1.



Scheme 1. Synthesis of 2,3,4-trisubstituted 1,5-benzothiazepines.

α-(4′-Methyl sulfonyl phenyl)-4-methyl sulfonyl acetophenone (**3**) was subjected to Claisen–Schmidt condensation with aryl aldehydes in the presence of piperidine in ethylene dichloride (EDC) to give the intermediates 1-[(4′-methyl sulfonyl)phenyl]-2-[(4-methyl phenyl)sulfonyl]-prop-2-en-1-ones (Table 1, **4a–f**). This condensation was carried out using KOH/NaOH or organic bases by following the normal Claisen–Schmidt condensation protocol. It was noticed that the condensation was not complete at room temperature and even at elevated temperature. It was then carried out in EDC in the presence of piperidine under reflux using a Dean and Stark system for removal of water, these conditions gave excellent yields of 1,3-propen-1-ones (**4a–f**) within 3 h.

The starting α-(4′-methyl sulfonyl phenyl)-4-methyl sulfonyl acetophenone (**3**) was obtained by the condensation of α-bromo-4-methyl sulfonyl acetophenones (**1**) and 4-methyl sodium benzene sulfinate (**2**).

When the chalcones (**4a–f**) were allowed to interact with 2-aminothiophenol in refluxing alcohol using piperidine and acetic acid as a bi-catalyst system, the expected products were not generated even with longer heating. Several variations have also been made to optimize the cyclocondensation of 2-aminothiophenol and the chalcones by varying medium and bases. It was noticed that cyclocondensation when run in refluxing toluene using catalytical amounts of trifluoroacetic acid as catalyst gave better yields of the desired 2-(substituted phenyl)-3-[(methyl phenyl) sulfonyl] [(methyl sulfonyl) phenyl]-2,3-dihydro-1,5-benzothiazepines (**5a–f**). It was also observed that the neat cyclocondensations of the chalcones supported on silica gel with 2-aminothiophenol occur rapidly at 80 °C and gave better yields of the desired trisubstituted 1,5-benzothiazepines (Table 2, **5a–f**).

Here, there is a possibility of getting more than two diastereomers. It was confirmed by high-performance liquid chromatography (HPLC) and TLC that the cyclocondensed product has a single isomeric form. The configurations of the chiral centers were not confirmed.

All the products and intermediates are well characterized by IR, mass and ^{1}H NMR spectral techniques. The purity of the products was also determined by HPLC.

Table 1. Characterization data of 1-[(4′-methyl sulfonyl)phenyl]-2-[(4-methyl phenyl)sulfonyl]-prop-2-en-1-ones (**4a–f**).

Product	R	R′	R″	Yields (%)	HPLC purity (%)	Melting point (°C)
4a	H	F	H	55	98	208–210
4b	OCH_3	OCH_3	OCH_3	52	92	195–196
4c	H	OCH_3	OCH_3	53	93	185–187
4d	H	OH	H	50	88	177–179
4e	H	OCH_3	H	60	96	204–205
4f	H	Cl	H	54	91	Liquid

Table 2. Characterization data of 2-(substituted phenyl)-3-[(methyl phenyl) sulfonyl] [(methyl sulfonyl) phenyl]-2, 3-dihydro-1,5-benzothiazepines (**5a–f**).

				Yields (%)			
Product	R	R′	R″	Method A	Method B	HPLC purity (%)	Melting point (°C)
5a	H	F	H	60	76	88	263–265
5b	OCH_3	OCH_3	OCH_3	54	64	86	213–214
5c	H	OCH_3	OCH_3	56	69	87	235–237
5d	H	OH	H	59	72	83	205–207
5e	H	OCH_3	H	61	78	88	242–243
5f	H	Cl	H	51	59	84	218–219

3. Experimental

3.1. *General*

Melting points were determined by the open capillary method and are uncorrected. IR spectra were scanned on a Paragon 1000 FT-IR spectrophotometer, and ^{1}H and ^{13}C NMR spectra were recorded on a Brucker 400 MHz. Mass spectra were obtained using API 3000 LCMSMS using NH_4 as an adduct. Elemental analyses were performed on Perkin Elmer elemental auto analyzer and Thermo Finnigan CHNS auto analyzer. The purity of products and the progress of the reaction were monitored by Water's HPLC systems.

3.1.1. *Synthesis of α-(4′-methyl sulfonyl phenyl)-4-methyl sulfonyl acetophenone (**3**)*

To the stirred solution of α-bromo-4-methyl sulfonyl acetophenone (**1**) (0.18 mol) in dichloromethane (DCM) (250 ml) was added sodium-*p*-tolyl sulphinate (**2**) (0.198 mol) and water (150 ml). To this biphasic solution, tetrabutylammonium bromide (1 g) was added and the reaction mixture was heated with stirring at 40–45 °C. The progress of the reaction was monitored by HPLC. After 3 h of reaction, the reaction mass was cooled. An organic layer was separated and washed with water (2 × 150 ml) and then dried over anhydrous sodium sulphate. The organic layer was distilled off under vacuum. Then to the crude residue, ethanol (300 ml) was added and the mass was heated to reflux. It was then cooled slowly to 10–15 °C and the obtained solid was filtered, washed with ethanol and dried under vacuum to give the pure product (**3**):

IR (KBr, cm^{-1}): 3104, 2932, 1679, 1396 and 1180; ^{1}H NMR (DMSO-d_6, 400 MHz) δ ppm: 2.40 (s, 3H), 3.30 (s, 3H) 5.36 (s, 2H, CH_2) 7.41 (d, 2H, $J = 8$ Hz, Ar-H), 7.75 (d, 2H, $J = 8$ Hz, Ar-H) 8.03 (d, 2H, $J = 8$ Hz, Ar-H) and 8.16 (d, 2H, $J = 8$ Hz, Ar-H). MS: m/z (% intensity): 370 (93, M+NH_4), 371 (18, M+1+NH_4).

3.1.2. *Synthesis of 1-[(4′-methyl sulfonyl)phenyl]-2-[(4-methyl phenyl)sulfonyl]-prop-2-en-1-ones (**4a–f**)*

To the solution of α-(4′-methyl sulfonyl phenyl)-4-methyl sulfonyl acetophenone (**3**) (0.0142 mol) in EDC (100 ml), substituted benzaldehyde (0.015 mol) and piperidine (0.5 ml) were added and the reaction mass was then heated to reflux. Water formed in the reaction was removed simultaneously by a Dean–Stark trap and the progress of the reaction was monitored by HPLC. After 3 h of reaction, it was cooled to room temperature and poured into ice-cold water (150 ml). The organic layer was separated and washed with water (2 × 50 ml). Then it was dried over anhydrous sodium sulphate. The solvent was then distilled off under vacuum from the organic layer. The residue was stirred with ethanol (100 ml) and the alcoholic mass was refluxed to get a clear solution. It was then cooled to 20–25 °C and stirred for 1 h and the separated solid product was filtered and washed with cold ethanol. The crude product was then dried under vacuum. Physical characterizations of a series of compounds are incorporated in Table 1.

3.1.3. *Spectral characterization of 2-[4′(methyl phenyl) sulfonyl]-1-[4-(methyl sulfonyl) phenyl]-3-[4″-fluorophenyl]-2-prop-en-1-one (**4a**)*

IR (KBr, cm^{-1}): 3004, 2922, 1673, 1601, 1509, 1398, 1220 and 1146. ^{1}H NMR (DMSO-d_6, 400 MHz) δ ppm: 2.91 (s, 3H, Ar-CH_3), 3.27 (s, 3H, SO_2CH_3), 7.81 (d, 2H, Ar-H, $J = 8$ Hz), 8.00 (dd, 4H, Ar-H), 7.72 (d, 2H, Ar-H, $J = 8$ Hz), 8.23 (s, 1H, Vinylic-H). MS: m/z (% intensity): 476 (93, M+NH_4), 477 (25, M + 1 + NH_4); ^{13}C NMR: 21.12, 49.94, 116.39, 127.64, 127.80, 128.21, 130.08, 130.2, 132.7, 132.77, 132.86, 136.28, 138.09, 141.36, 145.09, 162.34, 164.84, 191.35.

3.1.4. *Synthesis of 2-(substituted phenyl)-3-[(methyl phenyl) sulfonyl] [(methyl sulfonyl) phenyl]-2, 3-dihydro-1,5-benzothiazepines (**5a–f**)*

3.1.4.1. Method A. To the stirred solution of chalcones (**4a–f**) (6.5 mmol) in toluene (60 ml), 2-aminothiophenol (7 mmol) and few drops of triflouro acetic acid were added. The reaction mixture was refluxed and the reaction water formed was simultaneously removed by a Dean–Stark trap. The progress of the reaction was monitored by HPLC. After 4 h of reflux, toluene was removed under vacuum. To the residue, cold water was added, and the content was then stirred at room temperature for 20–30 min. The separated solid was filtered and washed with water. The crude product was crystallized from ethanol. The characterization data of the 1,5-benzothiazepines (**5a–f**) are presented in Table 2.

3.1.4.2. Method B. Silica gel (10 g) was added to the solution of **4a–f** (6.5 mmol) in diethyl ether (60 ml). The heterogeneous mass was stirred for 30 min at room temperature. Then the ether was removed by using a rotary evaporator. 2-Aminothiophenol (10.5 mmol) was added to the above residue and the mixture was warmed at 80 °C under nitrogen atmosphere. The progress of the reaction was monitored by HPLC for the absence of chalcones (**4a–f**). After 2 h of heating, ethyl acetate (100 ml) was added to the reaction mixture and stirred for 30 min. The silica gel was separated by filtration. The solvent was removed from the filtrate under reduced pressure and the products were purified by successive crystallization from ethanol.

3.1.5. *Spectral characterization of 2-(4′-fluorophenyl) 3-[(methyl phenyl) sulfonyl] 4-[(methyl sulfonyl) phenyl]-2,3-dihydro 1,5-benzothiazepine (**5a**)*

IR (KBr, cm^{-1}): 3353, 3019, 2919, 1646, 1396, 1255 and 1145. ^{1}H NMR (DMSO-d_6, 400 MHz) δ ppm: 2.50 (s, 3H, Ar-CH), 3.27 (s, 3H, SO_2CH), 3.44–3.71 (two undiagonistic doublets, 2H, 2 methine protons), 6.82–8.13 (m, overlap, 16H, Ar-H); ^{13}C NMR: 23.1, 32.5, 45.2, 64.7, 123.8, 127.6, 128.2, 127.9, 161.5, 129.1, 126.4, 140.5, 145.3, 132.2, 129.5, 139.2, 142.7, 130.1, 132.0, 140.5, 135.1, 158.6, 165.7. MS: m/z (% intensity): 584 [97, $(M + NH_4)^+$], 585 [31, $(MH + NH_4)^+$] Anal. for $C_{29}H_{24}FNO_4S_3$ Calcd. C, 61.57; H, 4.28; N, 2.48; S, 17.50. Found: C, 61.73; H, 4.66; N, 2.54; S, 17.13.

3.1.6. *4-(4-(Methyl sulfonyl) phenyl)-3-tosyl-2-(3,4,5-trimethoxyphenyl)-2,3-dihydrobenzo[b] [1,4]thiazepine (**5b**)*

^{1}H NMR (DMSO-d_6, 400 MHz): 2.25 (s, 3H, Ar-CH), 3.16 (s, 3H, SO_2CH), 3.78 (s, 6H, 2 OCH_3), 3.86 (s, 3H, OCH_3) 3.92–3.98 (dd, 2H, 2 methine protons), 6.18–8.10 (m, overlap, 14H, Ar-H); ^{13}C NMR: 23.5, 33.3, 47.1, 64.4, 59.7 (2 OCH_3), 60.5, 124.2, 128.5, 130.2, 128.3, 139.7, 159.2, 110.4, 140.4, 132.2, 129.5, 139.2, 142.7, 130.1, 134.1, 144.6, 137.8, 159.6, 167.3; Anal. for $C_{32}H_{31}NO_7S_3$ Calcd. C, 60.26; H, 4.90; N, 2.20; S, 15.08. Found: C, 60.48; H, 4.97; N, 2.24; S, 15.17.

3.1.7. *2-(3,4-Dimethoxyphenyl)-4-(4-(methyl sulfonyl) phenyl)-3-tosyl-2,3-dihydrobenzo[b] [1,4]thiazepine (**5c**)*

^{1}H NMR (DMSO-d_6, 400 MHz): 2.28 (s, 3H, Ar-CH), 3.10 (s, 3H, SO_2CH), 3.73 (s, 3H, OCH_3), 3.79 (S, 3H, OCH_3), 3.78–3.81 (dd, 2H, 2 methine protons), 6.08–7.91 (m, overlap, 15H, Ar-H); ^{13}C NMR: 24.6, 35.3, 48.9, 68.4, 55.2 (2 OCH_3), 55.8, 125.0, 129.9, 132.1, 128.3, 150.8, 153.6, 120.3, 130.4, 117.7, 138.2, 134.1, 128.3, 149.2, 152.7, 135.1, 132.9, 140.2, 133.0, 154.8, 168.6.

Anal. for $C_{31}H_{29}NO_6S_3$ Calcd. C, 61.26; H, 4.81; N, 2.30; S, 15.83. Found: C, 61.15; H, 4.92; N, 2.21; S, 15.97.

3.1.8. *4-(4-(4-(Methyl sulfonyl) phenyl)-3-tosyl-2,3-dihydrobenzo[b][1,4]thiazepin-2-yl) phenol (**5d**)*

^{1}H NMR (DMSO-d_6, 400 MHz): 2.15 (s, 3H, Ar-CH), 2.79 (s, 3H, SO_2CH), 3.51–3.86 (dd, 2H, 2 methine protons), 6.12–8.09 (m, overlap, 16H, Ar-H), 10.36 (s, 1H, OH, exchangeable with D_2O); ^{13}C NMR: 24.1, 35.5, 47.8, 61.9, 122.8, 137.6, 130.2, 128.1, 160.4, 118.91, 130.4, 135.7, 135.1, 128.2, 141.6, 143.8, 131.3, 132.5, 143.2, 131.1, 159.6, 169.3. Anal. for $C_{29}H_{25}NO_5S_3$ Calcd. C, 61.79; H, 4.47; N, 2.48; S, 17.06. Found: C, 61.89; H, 4.50; N, 2.54; S, 17.19.

3.1.9. *2-(4-Methoxyphenyl)-4-(4-(methyl sulfonyl) phenyl)-3-tosyl-2,3-dihydrobenzo[b][1,4] thiazepine (**5e**)*

^{1}H NMR (DMSO-d_6, 400 MHz): 2.32 (s, 3H, Ar-CH), 3.92 (s, 3H, SO_2CH), 3.96 (s, 3H, CH_3), 3.98–4.12 (dd, 2H, 2 methine protons), 6.21–8.15 (m, overlap, 16H, Ar-H); ^{13}C NMR: 22.4, 30.2, 41.2, 63.8, 57.1, 121.3, 125.6, 126.7, 127.9, 160.3.5, 117.1, 132.5, 155.5, 131.2, 127.3, 136.7, 140.9, 131.1, 131.3, 139.5, 133.4, 157.1, 164.5. Anal. for $C_{30}H_{27}NO_5S_3$ Calcd. C, 62.37; H, 4.71; N, 2.42; S, 16.65. Found: C, 62.53; H, 4.68; N, 2.35; S, 16.49.

3.1.10. *2-(4-Chlorophenyl)-4-(4-(methyl sulfonyl) phenyl)-3-tosyl-2,3-dihydrobenzo[b] [1,4] thiazepine (**5f**)*

^{1}H NMR (DMSO-d_6, 400 MHz): 2.48 (s, 3H, Ar-CH), 3.12 (s, 3H, SO_2CH), 3.40–3.79 (dd, 2H, methine protons), 6.78–8.28 (m, overlap, 16H, Ar-H); ^{13}C NMR: 24.4, 30.2, 45.2, 63.2, 1202, 128.5, 124.3, 128.9, 132.5, 129.0, 130.9, 140.1, 132.6, 129.8, 139.6, 142.3, 130.5, 132.6, 140.1, 135.6, 158.2, 164.9. Anal. for $C_{29}H_{24}ClNO_4S_3$ Calcd. C, 59.83; H, 4.16; N, 2.41; S, 16.52. Found C, 59.68; H, 4.13; N, 2.47; S, 16.61.

4. Conclusions

We have synthesized 2,3,4-trisubstituted 1,5-benzothiazepines bearing a sulfonyl groups in good yields using the modified classical synthetic method.

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