Efficient and Eco-friendly Syntheses of 1,5-Benzothiazepines and 1,5-Benzodiazepines Catalyzed by [*Hmim*][NO_3] under Mild Conditions

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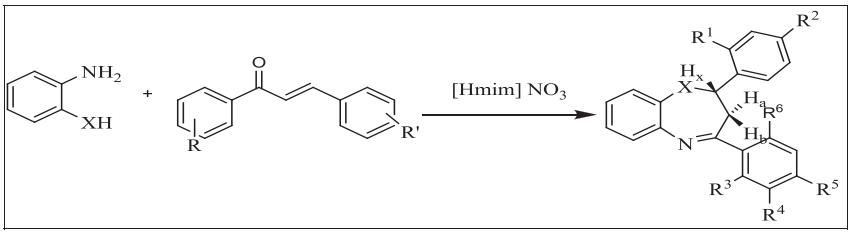

This article presents a synthetic method and reaction mechanism of the 1,5-benzothiazepines and 1, 5-benzodiazepines derivatives. In this research, 36 thiazepines and diazepines (mostly new) with a new method have been prepared and their structures have been characterized by spectroscopic methods. Crystal structures of a new thiazepine and diazepine (seven-membered rings) have also been determined and compared with thiazine (six-membered ring). In this method, *N*-methylimidazolium nitrate [*Hmim*][NO_3] has been used as a catalyst that acts as an environmental friendly system.

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INTRODUCTION

In the last decades, synthesis of N-S or N-N containing heterocyclic compounds, especially benzothiazepines and benzodiazepines, has retained the interest of researchers because of their structural properties and broad spectrum of biological activities [1,2]. For example, 1,5-benzothiazepines derivatives exhibit many pharmacological activities, such as anticonvulsant [3], antidepressant [4], central nervous system depressant [5], antipsychotic [6], neuroleptic [7], antimicrobial [8], cytotoxic agents [9], anticancer drug [10], calcium antagonists [11], antiarrhythmic [12], antibacterial [13], and antihypertensive [14].

Many members of the benzodiazepine derivatives are also widely used as antianxiety, analgesic, sedative, antidepressant, and hypnotic agents [15]. Some of these compounds have also find applications in industries, such as in photography and dyes for acrylic fibers [16]. In addition, these compounds are key intermediates in the synthesis of various fused ring compounds such as triazolobenzodiazepines [17].

Because of their wide range of biological, industrial, and synthetic applications, the development of a milder and more efficient method for their synthesis continues to challenge synthetic organic chemists.

A general way to construct 1,5-benzothiazepines and 1, 5-benzodiazepines is the reaction of *o*-aminothiophenol and *o*-phenylenediamine with α,β-unsaturated carbonyl (1,3-diarylprop-2-enones) compounds, respectively. Various Lewis or Brönsted acids such as HCl/MeOH,[2] $Ga(OTf)_3$ [18], $HClO_4$–SiO_2 [19], $Sc(OTf)_3$ [20], sodium dodecylsulfate [21], $SbCl_3$–Al_2O_3 [22], [BPy][HSO_4], [23] EtOH/HCl [24], dehydroacetic acid [25], nano-Al_2O_3, [26] aluminum oxide [27], and HBF_4–SiO_2 [28] as well as the Lewis base, Et_3N [10,29], have been used for their synthesis. These existing methods, however, suffer from several drawbacks such as harsh reaction conditions, use of toxic solvents and metal-based catalysts, low yield, relatively long reaction times, high catalyst loading, low selectivity, occurrence of several side reactions, and the requirement of special apparatus. Consequently, a more convenient and greener methods for the preparation of these heterocycles need to be developed.

Ionic liquids (I.L.s), particularly imidazolium salts I.L.s, have been receiving a great deal of attention as new reaction media and catalysts for many reactions in the past several years [30–32]. For example, 1,3-di-*n*-butylimidazolium bromide ([*bbim*][Br]) has been used for the synthesis of 1,5-benzodiazepines via the condensation of *o*-phenylenediamines with two mmol ketones [33].

Herein, we would like to report synthesis and formation mechanism of 1,5-benzothiazepines and 1,5-benzodiazepines derivatives using a novel catalyst *N*-methylimidazolium nitrate, as a nonvolatile, air stable, easy to prepare and handle, and environmentally friendly catalyst as well as the reaction medium. Also the crystal structures of seven-membered rings of thiazepine and diazepine that is compared with crystal structure of a six-membered ring of thiazine.

RESULTS AND DISCUSSION

In this work, 36 of 1,5-benzothiazepine and 1,5-benzodiazepine derivatives were prepared in one-pot cyclocondensation reaction of *o*-aminothiophenol or *o*-phenylenediamine with α,β-unsaturated carbonyl compounds through a [4 + 3] annulation reaction in the presence of *N*-methylimidazolium nitrate [*Hmim*][NO_3] as a Brönsted acidic I.L. under thermal condition (Scheme 1). This useful I.L.is not only cheap but also easily dissolves in the starting materials and is readily recyclable. The reusability of a catalyst is important from environmental and economic points of view. The reusability of this I.L. was therefore examined using sequential reactions. The results indicated that the catalyst could be recovered and reused successfully for several times without remarkable decrease in its activity. Different temperatures (70, 80, and 90°C) have been used for these reactions, and the best yield was obtained when the reaction is carried out at 80°C (oil bath) for 0.5–2 h. Different amounts of *N*-methylimidazolium nitrate (0.5, 0.7, 1.0, 1.2, and 1.5 mmol) have also been used with respect to 1.0 mmol of chalcones and *o*-phenylenediamine to ascertain capabilities. For 1,5-benzothiazepines, we observed that in the presence of an excess 0.2 mmol 2-aminobenzothiazol, maximum yields of the products were obtained with 1 mmol I.L. However, for 1,5-benzodiazepines, the best ratio of the starting materials to I.L.s observed were 1:1:1. The times for the completion of the reactions and some important ^{1}H and ^{13}C NMR data are given in Tables 1 and 2.The best yield of the corresponding thiazepine, from the reaction between *o*-aminothiophenol and chalcone in [*Hmim*][NO_3], was also obtained under the same conditions. The catalytic activities of different Brønsted acid I.L.s such as [*Hmim*][BF_4], [*Hmim*][HSO_4], and [*Hmim*][NO_3] were investigated in the reaction of 4-chloro-2-hydroxychalcone with *o*-aminothiophenol under thermal conditions. [*Hmim*][NO_3] was observed to be the more effective catalyst in term of the yield of the corresponding product, 4-(4-chlorophenyl)-2-(2-hydroxyphenyl)-2,3-dihydro-1,5-benzothiazepines (95%), whereas in the presence of other I.L.s ([*Hmim*][BF_4] and [*Hmim*][HSO_4]), the yield of the desired product obtained was lower (63–86%) (Table 1). In the absence of I.L, the yield of product was very low, 30–40%. The generality of this reaction for the synthesize of the corresponding 1,5-benzothiazepines derivatives in high to excellent yields is demonstrated with a wide range of substituted and structurally diverse chalcones carrying either electron-withdrawing or electron-donating groups (Table 1).

To further generalize this method, the reaction between *o*-phenylenediamine and chalcones in [*Hmim*][NO_3] was also examined, and the results indicated that benzodiazepines were synthesized in high yields (Table 1).

To show the efficiency and applicability of this method, the result of the reaction of chalcone with *o*-aminothiophenol by our method has been compared with some of the previously reported methods [23]. These studies show that this catalytic system is superior to the ones previously reported in terms of the amount of catalyst, cost, and availability of the precursors for the preparation of catalyst.

The mechanism of the reaction is most likely to be involve in the intermolecular hydrogen bonding promoted by [*Hmim*][NO_3] I.L.s that activates chalcone towards the nucleophilic attack by amino group of the *o*-phenelenediamine or sulfur in 2-aminothiophenol to afford the intermediate (**A**). 1,3-Hydrogen shift occurs to give an isomeric enamine (**B**) that cyclizes to give the seven-membered ring product (Scheme 2).

The structures of all new compounds have been elucidated by their mass, IR, ^{1}H, and ^{13}CNMR spectra and also elemental analysis. In their IR spectra, a characteristic C═N band was observed around 1600 cm^{-1}, referring to the presence of a C═N double bond in the seven-membered ring heterocycle.

A weak but distinct molecular ion was detected in the EI 70 eV mass spectra of the tetracyclic 1,5-benzothiazepines **1–30**. In the course of their fragmentation, these benzothiazine molecules are split into two major fragment ions, for example, for the compound **6** (Scheme 3).

The fragmentation of compound **6** could proceed via two pathways: In path *a*, the molecule losses benzopyrane, and in path b, *p*-cholorostyrene is lost. It is important to note that the observation of these fragments in the mass spectra of compound is a good indication for the proposed structure and fragmentation. Similar fragmentations have been observed for 2-hydroxy diazepines (**30–36**) where the base peak for these compounds corresponds to 2-hydroxyphenylbenzimidazole *m/z* = 210 because of loss of some part of the molecule with the phenylethylene moiety.

Thiazepines in ^{1}H NMR spectrum showed a triplet at 2.76–3.13 ppm for the H_a and two dd around 3.13–3.46 and 4.97–5.44 ppm for the H_b and H_x because of an abx

Scheme 1. Synthesis of 1,5-benzothiazepines and 1,5-benzodiazepines.

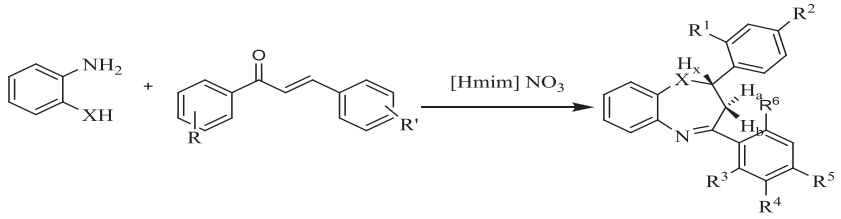
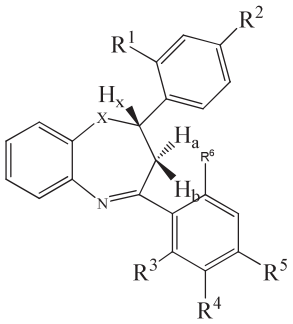


Table 1

Some ^{1}H NMR data and yields of 1,5-benzothiazepines and 1,5-benzodiazepines.



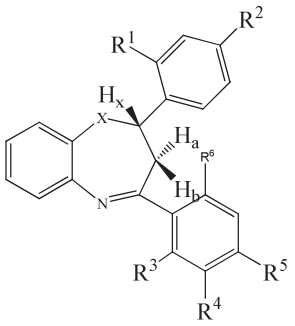
Compound no.	X	R^1	R^2	R^3	R^4	R^5	R^6	H_a	H_b	H_x	Yield[a]
1	S	H	Cl	OH	H	H	H	3.08	3.42	5.06	95
2	S	H	Cl	H	H	H	H	3.03	3.30	4.96	97
3	S	H	Cl	H	H	Me	H	3.01	3.28	4.94	98
4	S	H	Cl	H	H	OMe	H	3.01	3.26	4.93	80
5	S	H	F	H	H	Me	H	3.01	3.28	4.97	95
6	S	H	Cl	H	H	Cl	H	3.02	3.24	4.94	95
7	S	H	NMe_2	H	H	Cl	H	3.05	3.31	5.01	80
8	S	H	OMe	H	H	Cl	H	3.05	3.22	4.97	95
9	S	H	Br	OH	H	H	H	3.05	3.35	4.98	98
10	S	H	Me	OH	H	H	H	3.11	3.43	5.06	95
11	S	H	F	OH	H	H	H	3.08	3.44	5.09	95
12	S	H	H	OH	H	H	H	3.10	3.42	5.07	95
13	S	H	OMe	OH	H	H	H	3.09	3.42	5.08	95
14	S	H	SMe	OH	H	H	H	3.07	3.39	5.03	95
15	S	H	MNe_2	OH	H	H	H	2.95	3.40	5.06	80
16	S	H	OMe	H	H	OMe	H	3.09	3.41	4.99	98
17	S	H	Me	H	H	Cl	H	3.13	3.35	4.99	95
18	S	H	OMe	H	H	H	H	3.05	3.30	4.98	90
19	S	H	Br	H	H	H	H	3.12	3.46	4.98	97
20	S	H	SMe	H	H	H	H	3.06	3.29	4.97	98
21	S	H	H	H	H	Cl	H	3.07	3.20	4.97	97
22	S	H	Br	H	H	Br	H	3.07	3.33	4.95	98
23	S	H	Br	OH	H	OMe	OMe	3.12	3.33	4.97	85
24	S	H	Cl	OH	H	OMe	OMe	2.88	3.63	5.19	90
25	S	H	NO_2	H	H	OMe	H	3.04	3.29	5.00	90
26	S	OMe	OMe	H	H	Cl	H	2.87	3.24	5.44	85
27	S	Cl	Cl	H	H	NH_2	H	2.76	3.13	5.27	95
28	S	H	$=(CH)_4$	H	H	OMe	H	3.18	3.35	5.13	82
29	S	H	OMe	OMe	H	H	H	3.09	3.32	5.00	85
30	NH	H	Cl	OH	H	H	H	3.11	3.33	5.26	92
31	NN	H	Br	OH	H	H	H	3.06	3.28	5.21	90
32	NH	H	Me	OH	H	H	H	3.05	3.34	5.15	90
33	NH	H	SMe	OH	H	H	H	3.05	3.31	5.18	80
34	NH	H	F	OH	H	H	H	3.05	3.29	5.28	80
35	NH	H	OMe	OH	H	H	H	3.04	3.32	5.16	80
36	NH	H	Br	OMe	H	OMe	H	3.19	4.05	5.54	75

[a]Isolated yields.

system, respectively. This pattern for the diazepines, however, is different wherein the H_a resonated a quartet at 3.04–3.19 ppm because of an additional compelling with N-H and two dd at 3.28–4.05 and 5.15–5.54 ppm for the H_b and H_x, respectively (Table 1). For thiazepines and diazepines containing a phenolic hydrogen, a broad signal appears at 14.35–16.57 ppm, whereas an additional band at 3.79–5.09 ppm appears for the N-H band in diazepines (Table 2).While preparing the thiazepine with methyl group on phenyl rings, two new (**37** and **38**) compounds

Table 2

Some ^1H and ^{13}C NMR data and reaction times of 1,5-benzothiazepines and 1,5-benzodiazepines.

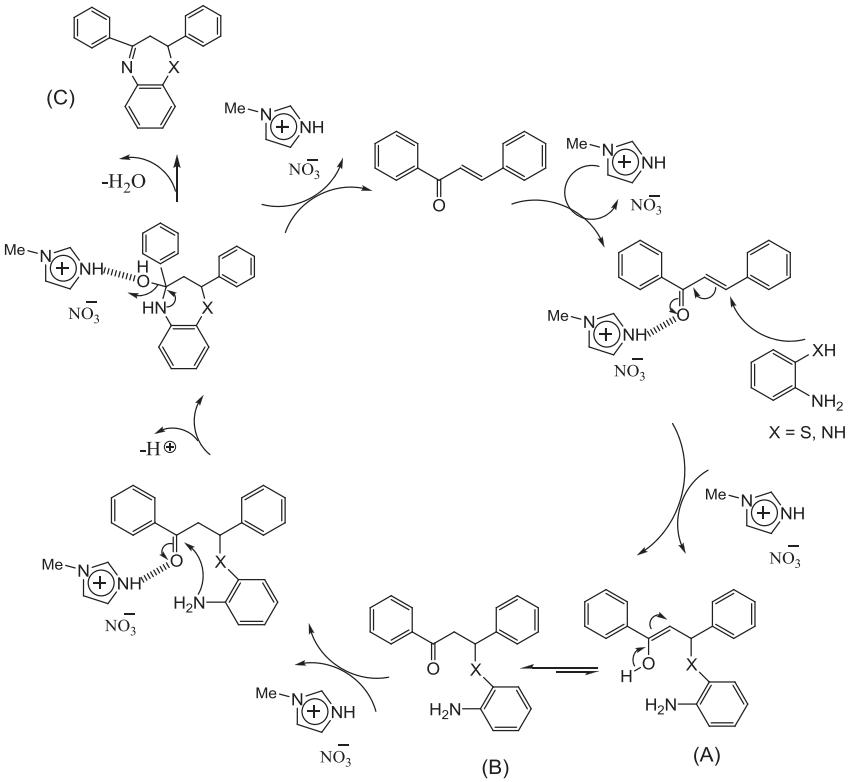


Compound no.	X	CH	CH_2	C=N	NH	OH	Reaction times (min)	References	mp (°C)
1	S	59.65	37.14	173.30	—	14.35	30	[26,29]	170–172
2	S	59.74	37.48	168.74	—	—	45	[19,21,26,28]	126–128
3	S	59.71	37.38	168.58	—	—	45	—	132–134
4	S	59.64	37.23	167.86	—	—	75	[29]	137–139
5	S	59.71	37.66	168.61	—	—	30	—	131–133
6	S	59.72	37.33	167.52	—	—	75	—	124–126
7	S	59.24	36.69	167.52	—	—	45	—	155–157
8	S						90	[29,43]	132–134
9	S	59.27	36.62	172.83	—	14.50	30	—	174–176
10	S				—	14.37	120	[18,26,29,44]	156–158
11	S	59.31	37.02	172.93	—	14.50	60	[2,26,29,45]	161–163
12	S				—	14.51	60	[18,26]	145–147
13	S				—	14.38	120	[2,18]	160–162
14	S	59.65	36.78	162.79	—	14.48	60	—	162–164
15	S	60.11	37.11	173.22	—	14.51	135	—	191–193
16	S				—	—	60	[29,43]	111–113
17	S	60.39	37.53	167.78	—	—	120	—	134–136
18	S				—	—	80	[19,26,29,28,43]	127–129
19	S				—	—	75	[29,46]	119–121
20	S				—	—	45	[22]	136–138
21	S				—	—	45	[21,22,29,28,43]	131–133
22	S	59.80	37.29	167.58	—	—	45	—	134–136
23	S	60.63	36.76	172.51	—	14.94	30	—	184–186
24	S	58.59	41.46	172.21	—	16.57	120	—	175–177
25	S				—	—	100	[18]	191–193
26	S	53.69	36.05	168.12	—	—	60	—	152–154
27	S	54.98	33.89	167.37	—	—	40	—	208–210
28	S	55.57	37.24	168.24	—	—	40	—	128–130
29	S	55.79	31.24	162.00			40	—	122–124
30	NH	69.43	39.39	171.67	—	15.09	30	—	168–170
31	NH	69.67	36.17	171.24	3.82	15.13	45	—	178–180
32	NH	69.53	36.73	171.10	3.84	15.40	60	—	109–111
33	NH	69.65	36.41	171.13	3.80	15.20	60	—	142–144
34	NH	69.71	36.35	171.22	3.79	15.20	90	—	125–127
35	NH	55.70	37.04	171.40	—[a]	15.30	90	[18]	136–138
36	NH	52.44	38.43	172.00	4.05	—	90	—	220–222

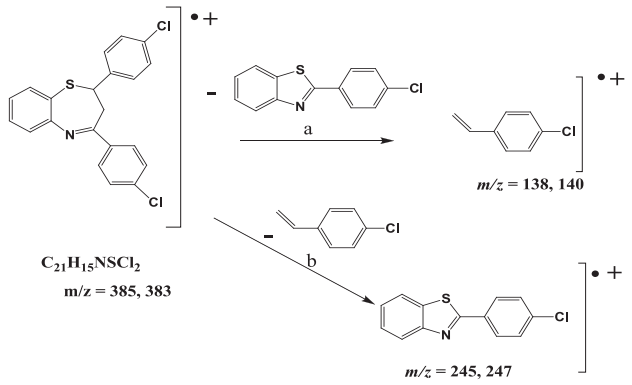
[a]N-H band was not absorbed around 3.8–4.2 ppm.

(which are intermediates for thiazepines) were prepared. The ^1H NMR data of these compounds showed that the position of triplet (H_x) in thiazepines at 2.76–3.13 ppm have been moved to 4.73 and 4.68 ppm, respectively, whereas the position of the dd became closer to each other at a higher field of 3.56 and 3.64 ppm for the compound **37** and 3.50 and 3.54 ppm for compound **38**. The two hydrogens on thiazepine ring (H_a and H_b) are rigid because of

Scheme 2. Proposed mechanism for the preparation of thiazepines and diazepines.



Scheme 3. Fragmentation of compound **6**.



shielding and deshielding ring effects of phenyl and so their chemical shifts are completely different (AMX system). However, for compound **37** because of the free rotation of the single bond, there is not much difference between the two hydrogens (ABX system), and the phenyl ring has no effect on the H_x hydrogen. Most indicatively, in the ^{13}C NMR spectrum of the quaternary carbonyl, the resonances of the imine carbon nuclei are found between 162.00–173.30 ppm. The methin and methylene carbon nuclei resulting from the Michael addition of the thiazepines and diazepines appear at 52.44–60.63 and 36.17–41.46 ppm, respectively. The ^{13}C NMR spectra of compounds **37** and **38** showed signals at 197.28 and 197.26 ppm for the carbonyl carbons, respectively. The IR spectra of these compounds showed a characteristic NH_2 band at 3452 and 3354 cm^{-1} referring to vibration of primary amine and a sharp band at 1677 cm^{-1} for the carbonyl group stretching.

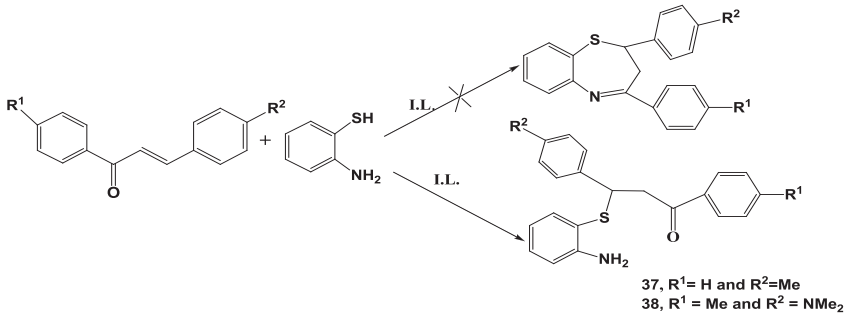
All spectroscopic data confirm that ring closure did not occur because of the long hyperconjugation between methyl and carbonyl groups. Instead, aminoketones **37** and **38** were produced during the reactions (Scheme 4).

For comparison, the ^1H NMR spectra of compound **37** from 3.5–4.75 ppm and compound **18** are given in Figure 1.

The crystal structure of some 1,5-benzodiazepines [34] and 1,5-benzothiazepines [18,35] have also been studied. For the 1,5-benzodiazepines, it has been reported that the ring exhibits a puckered boat-like conformation. Continuing our search for supramolecular synthons of importance in the crystal engineering of substituted aromatic compounds, our group has focused considerable interest on the crystalline properties of some benzodiazepines and benzothiazepines particularly in their packing by intermolecular hydrogen bonding. X-ray structural analysis of thiazepine (compound **28**), diazepine (compound **33**), and thiazine **39** have been obtained (Figs 2–4).

A summary of the crystallographic data and details of the structure refinements of **28**, **33**, and **39** are listed in Table 3. To obtain better crystallization of compound **28**, it was passed through a basified silica column.

Scheme 4. Route for the preparation of aminoketone **37** and **38**.



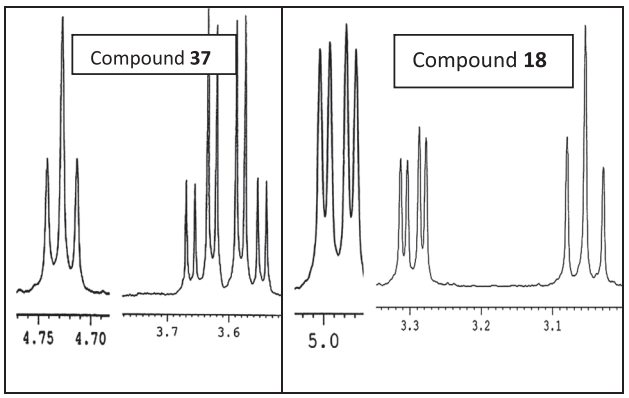


Figure 1. Comparison of ^{1}H NMR of spin–spin coupling between CH and CH_2 of the compounds **18** and **37**.

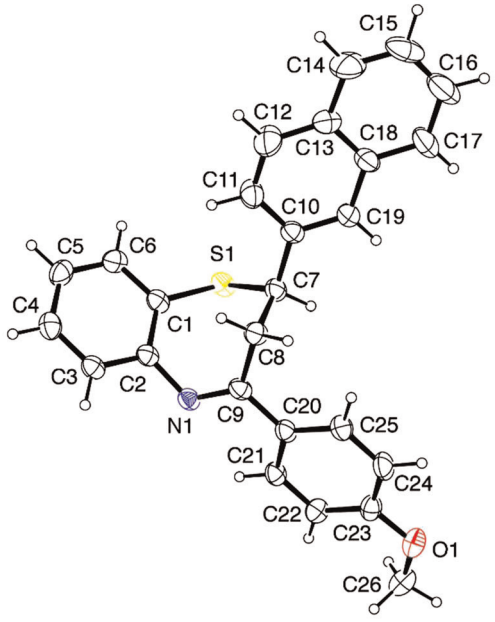


Figure 2. ORTEP drawing of **28** with the atom numbering scheme. The displacement ellipsoids are drawn at the 50% probability level. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Surprisingly, while doing this, the seven-membered ring was transformed to a six-membered ring. Spectroscopic

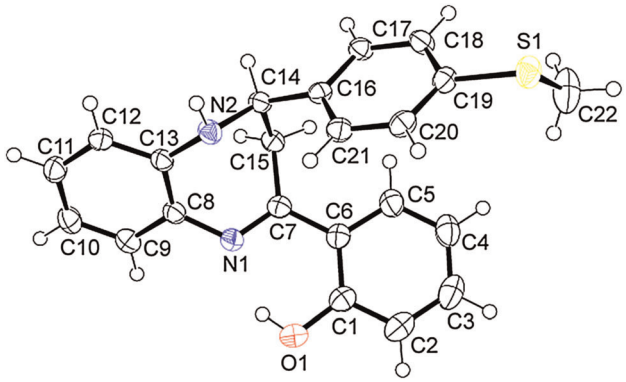


Figure 3. ORTEP drawing of **33** with the atom numbering scheme. The displacement ellipsoids are drawn at the 50% probability level. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

data and X-ray analysis confirmed this conversion. The ^{1}H NMR spectrum showed that all signals belonging to CH_2 and CH have shifted downfield because of this ring contraction (Scheme 5 and Fig.5). The molecular structure of compound **39** is shown in Figure4. As shown in Figures 2 and 3, in crystalline phase, a seven-membered ring is formed in thiazepine (S_1-C_1-C_2-N_1-C_9-C_8-C_7) and diazepine (N_2-C_{13}-C_8-N_1-C_7-C_{15}-C_{14}), but in thiazine, a six-membered ring (S_1-C_{12}-C_{19}-N_1-C_{18}-C_{13}) is formed that is more stable.

CONCLUSION

In conclusion, a green, efficient, new, and simple one-pot synthesis of 1,5-benzothiazepines and1,5-benzodiazepines from chalcone in the presence of [*Hmim*][NO_3], which act as an environmentally friendly catalytic system, has been established. In all cases, the rates of reactions were enhanced, and products were obtained in high to excellent yield. These transformations according to the methods described here are fast and performed in high to excellent yields that will be highly useful especially in the total syntheses of natural products.

EXPERIMENTAL

Melting points were obtained by a Stuart Scientific SMP2 apparatus (Bibby Scientific Limited, Stone, Staffordshire, UK)

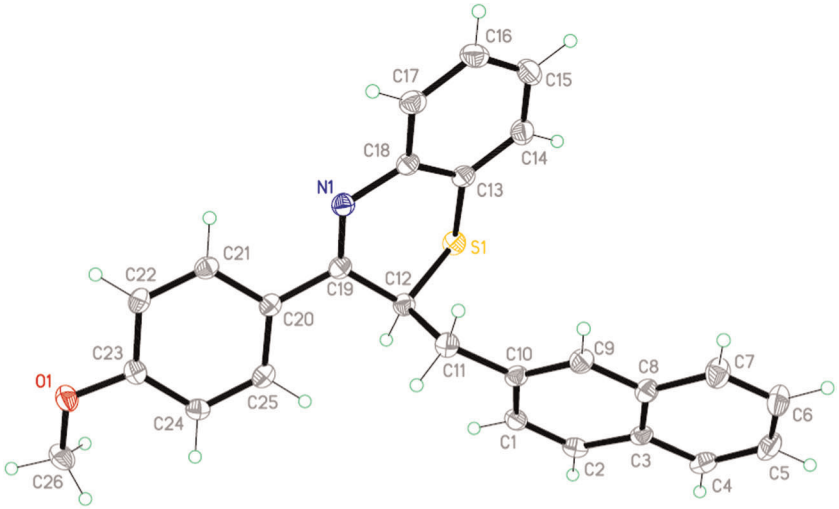


Figure 4. ORTEP drawing of **39** with the atom numbering scheme. The displacement ellipsoids are drawn at the 50% probability level. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table 3

Crystallography data for compounds **28**, **33**, and **39**.

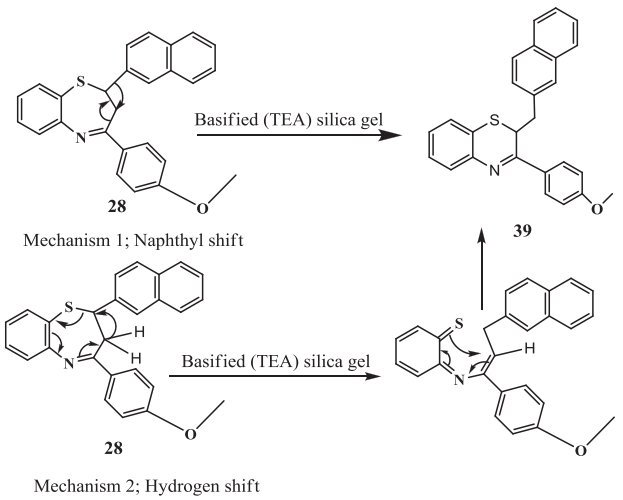
	28	**33**	**39**
Empirical formula	$C_{26}H_{20}NOS$	$C_{22}H_{20}N_2OS$	$C_{26}H_{21}NOS$
Formula weight	394.51	360.47	395.50
Crystal color, habit	Pale, yellow, columnar	Yellow, platelet	Yellow, block
Crystal dimensions	0.30 × 0.08 × 0.06 mm	0.30 × 0.20 × 0.10 mm	0.30 × 0.20 × 0.10 mm
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Lattice parameters	a = 18.821(2) Å b = 5.1632(6) Å c = 20.450(3) Å β = 94.463(4)° V = 1981.2(4) Å^3	a = 7.4650(5) Å b = 18.5752(14) Å c = 13.3869(9) Å β = 107.162(2)° V = 1773.6(2) Å^3	a = 8.9621(7) Å b = 12.2332(9) Å c = 18.2916(14) Å β = 90.00° V = 2005.4(3) Å^3
Space group	$P2_1/n$ (#14)	$P2_1/a$ (#14)	$P2ac2ab$
Z value	4	4	4
D_{calc}	1.323 g/cm^3	1.350 g/cm^3	1.310 g/cm^3
F_{000}	828.00	760.00	832.00
Radiation	MoKα (λ = 0.71075 Å	MoKα (λ = 0.71075 Å)	MoKα (λ = 0.71073 Å)
Detector aperture	280 mm × 256 mm	280 mm × 256 mm	280 mm × 256 mm
ω oscillation range (χ = 45.0, ϕ = 0.0)	130.0–190.0°	130.0–190.0°	130.0–190.0°
Exposure rate	300.0 sec/°	170.0 sec/°	170.0 sec/°
ω oscillation range (χ = 45.0, ϕ = 180.0)	0.0–160.0°	0.0–160.0°	0.0–160.0°
Structure solution	Direct methods	Direct methods	Direct methods
Refinement	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2

and are uncorrected. Yields refer to isolated products and all products were characterized by their physical and spectral data. IR spectra were recorded on FT-IR Nicolet 400 D (SpectraLab Scientific Inc., Ontario, Canada). ^{1}H and ^{13}C NMR (400 and 100 MHz) spectra were recorded on a Bruker-Avance AQS 500 spectrometer (The Wagner Lab, Boston) in $CDCl_3$. Mass spectra were obtained on platform II spectrometer from Micro mass; EI mode at 70 eV. Elemental analysis was done on LECO, CHNS-932 (General Facility-Science, Kuwait). All chalcones were characterized by comparison of their spectroscopic data (IR, 1H NMR) and melting points with those of reported in the literature [38–44].

Synthesis of 1-methylimidazolium nitrate, [*Hmim*][NO3]. A dilute nitric acid solution [5.059 g of nitric acid (65 wt%) in 20 mL H_2O] was added to a solution of 1.05 equiv of *N*-methylimidazol (4.089 g, 49.79 mmol) at 0°C. The reaction mixture was allowed to warm to room temperature. Water was removed by sweeping compressed air above the solution at 80°C. The mixture was cold to room temperature, and white solid was separated. The resulting solid material was washed with diethyl ether and dried in vacuum at 40°C. IL was decolorized by refluxing the aqueous solution in the presence of charcoal for 24 h. The mixture was filtered, and H_2O content of filtrate was removed in vacuum for 12 h.

General procedure for the one-pot synthesis of 1,5-benzothiazepines and 1,5-benzodiazepines. A mixture of chalcone (1.0 mmol), *o*-aminothiophenol (1.2 mmol, 150 mg) or *o*-phenylenediamine (1.0 mmol, 108 mg), and [*Hmim*][NO_3] as a catalyst

Scheme 5. Proposed mechanism for the conversion of seven-membered ring to six-membered ring.



medium (1 mmol) was stirred vigorously at 80°C for the appropriate times according to Table 2 under nitrogen atmosphere. The progress of the reaction was followed by TLC (eluent: ethyl acetate/ petroleum ether, 1:10). After completion of the reaction, ethyl acetate (10 mL) and H_2O (10 mL) were added and stirred. The solution was transferred to the funnel and the organic layer was separated. The organic solvent was dried and evaporated. The crude product was purified by crystallization in ethanol to afford the pure products.

2-(4-Chlorophenyl)-4-(2-hydroxyphenyl)-2,3-dihydro-1,5-benzothiazepine (1). Yellowish needles; mp 170–172°C (Lit. [26] 168–170°C); IR (KBr) ν: 3423, 3056, 1598, 1488, 1253, 827, 748, 502 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.08 (t, 1H, J = 13.0 Hz, CH_2), 3.42 (dd, 1H, J_1 = 13.2 Hz, J_2 = 4.7 Hz, CH_2), 5.06 (dd, 1H, J_1 = 12.3 Hz, J_2 = 4.7 Hz, CH), 6.95 (t, 1H, J = 8.03 Hz), 7.26 (d, 1H, J = 8.3 Hz), 7.26–7.45 (m, 6H), 7.46 (t, 1H, J = 6.8 Hz), 7.59 (t, 1H, J = 6.8 Hz), 7.66 (d, 1H, J = 7.4 Hz), 7.67 (d, 1H, J = 7.7 Hz), 14.35 (s, 1H, OH); ^{13}C NMR (125 MHz, $CDCl_3$): 37.14 (CH_2), 59.65 (CH), 118.57, 119.10, 119.18, 124.45, 126.15, 126.97, 127.89, 128.74, 129.46, 130.59, 134.20, 134.24, 135.61, 142.48, 149.16, 163.17 (Ar C), 173.30 (C═N); MS (EI, 70 eV) *m/z* (%): 367.00 (32.05) $[M+2]^+$, 365.00 (75.45) $[M^+]$, 348.02 (7.05), 272.06 (5.97), 254.10 (3.59), 240.10 (7.39), 227.13 (100.00), 199.16 (36.14), 198.16 (23.64), 138.12 (21.14), 109.15 (31.36), 91.14 (18.41), 77.16 (11.31), 65.19 (13.69), 51.19 (17.27).

2-(4-Chlorophenyl)-4-phenyl-2,3-dihydro-1,5-benzothiazepine (2). White crystals; mp 126–128°C (Lit. [28] 128°C); IR (KBr) ν: 3056, 2854, 1612, 1489, 1406, 1319, 1240, 1089, 832, 758, 690 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.03 (t, 1H, J = 12.8 Hz, CH_2), 3.30 (dd, 1H, J_1 = 12.8 Hz, J_2 = 4.8 Hz, CH_2), 4.96 (dd, 1H, J_1 = 12.8 Hz, J_2 = 4.8 Hz, CH), 7.16 (t, 1H, J = 7.4 Hz), 7.24–7.33 (m, 5H), 7.47–7.54 (m, 3H), 7.60 (d, 1H, J = 7.6 Hz), 8.58 (d, 2H, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 37.48 (CH_2), 59.74 (CH), 122.44, 125.42, 125.46, 127.43, 127.49, 128.84, 128.94, 129.98, 131.22, 133.48, 135.06, 137.60, 142.59, 152.47 (Ar C), 168.74 (C═N); MS (EI, 70 eV) *m/z* (%): 351.02 (2.97) $[M+2]^+$, 349.02 (7.97) $[M^+]$, 272.04 (2.46), 211.18 (100.00), 138.09 (15.07), 109.11 (18.56), 108.08 (86.90), 103.12 (18.56), 77.17 (12.77), 69.09 (25.76), 51.14 (19.43).

2-(4-Chlorophenyl)-4-(4-methylphenyl)-2,3-dihydro-1,5-benzothiazepine (3). White crystals; mp 132–134°C; IR (KBr) ν: 3046, 1600, 1452, 1318, 1245, 1087, 810, 768 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.45 (s, 3H, CH_3), 3.01 (t, 1H, J = 12.6 Hz, CH_2), 3.28 (dd, 1H, J_1 = 13.0 Hz, J_2 = 4.8 Hz, CH_2), 4.94 (dd, 1H, J_1 = 12.4 Hz, J_2 = 4.8 Hz, CH), 7.14 (t, 1H, J = 7.2 Hz), 7.23–7.32 (m, 7H), 7.48 (t, 1H, J = 7.8 Hz), 7.59 (d, 1H, J = 6.8 Hz), 7.95 (d, 2H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): 21.54 (CH_3), 37.38 (CH_2), 59.71 (CH), 122.45, 125.25, 125.43, 127.44, 127.50, 128.50, 128.92, 129.57, 129.95, 133.43, 134.84, 135.03, 141.69, 142.67, 152.59 (Ar C), 168.58 (C═N); MS (EI, 70 eV) *m/z* (%): 365.03 (3.87) $[M+2]^+$, 363.02 (9.79) $[M^+]$, 238.14 (2.08), 225.18 (100.00), 210.12 (3.47), 138.04 (11.75), 109.08 (8.49), 108.07 (24.63), 91.16 (8.96), 77.17 (9.70), 69.08 (45.90), 65.12 (33.96), 63.10 (27.61); *Anal.* Calcd for $C_{22}H_{18}ClNS$: C, 72.61; H, 4.99; N, 3.85; S, 8.81. Found: C, 73.04; H, 5.18; N, 3.81; S, 8.72.

4-(4-Chlorophenyl)-2-(4-methoxyphenyl)-2,3-dihydro-1,5-benzothiazepine (4). White crystals; mp 137–139°C; IR (KBr) ν: 3053, 2836, 1596, 1512, 1323, 1257, 1175, 1029, 826, 743 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.01 (t, 1H, J = 12.6 Hz, CH_2), 3.26 (dd, 1H, J_1 = 13.0 Hz, J_2 = 4.6 Hz, CH_2), 3.90 (s, 3H, CH_3), 4.93 (dd, 1H, J_1 = 12.4 Hz, J_2 = 4.8 Hz, CH), 7.00 (d, 2H, J = 8.8 Hz), 7.13 (t, 1H, J = 7.4 Hz), 7.23–7.30 (m, 5H), 7.47 (t, 1H, J = 7.4 Hz), 7.58 (d, 1H, J = 7.6 Hz), 8.01 (d, 2H, J = 8.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): 37.23 (CH_2), 55.49 (CH_3), 59.64 (CH), 114.14, 122.43, 125.05, 125.41, 127.50, 128.91, 129.17, 129.24, 129.91, 130.22, 133.45, 134.99, 142.65, 152.73, 162.21 (Ar C), 167.86 (C═N); MS (EI, 70 eV) *m/z* (%): 380.89 (34.29) $[M+2]^+$, 378.90 (73.88) $[M^+]$, 347.90 (4.77), 344.90 (7.65), 271.91

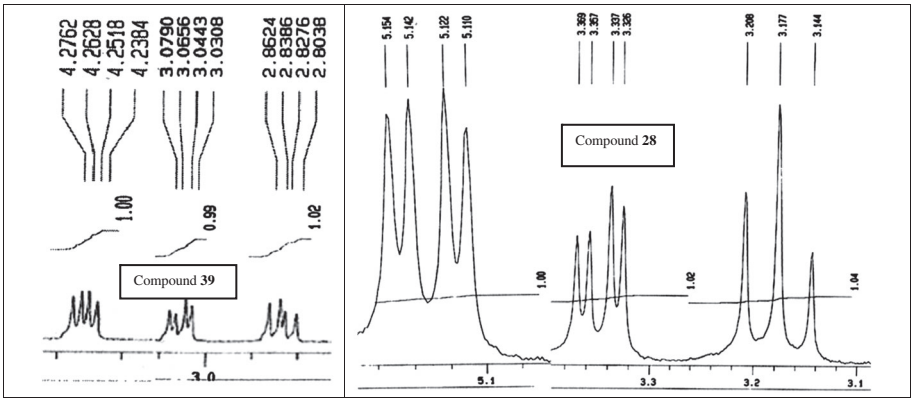


Figure 5. Comparison of ^{1}H NMR of spin–spin coupling between CH and CH_2 of the compounds **28** and **39**.

(10.92), 253.96 (37.14), 240.98 (100.00), 225.96 (85.71), 197.97 (84.08), 196.95 (73.88), 137.95 (61.22), 108.95 (33.88), 102.99 (67.76), 77.02 (65.71); *Anal.* Calcd for $C_{22}H_{18}NSOCl$: C, 69.55; H, 4.78; N, 3.96; S, 8.44. Found: C, 68.98; H, 4.77; N, 3.67; S, 8.15.

2-(4-Fluorophenyl)-4-(4-methylphenyl)-2,3-dihydro-1,5-benzothiazepine (5). White crystals; mp 131–133°C; IR (KBr) ν: 3026, 2891, 1602, 1505, 1451, 1321, 1321, 1220, 1155, 819, 744 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$): δ 2.45 (s, 3H, CH_3), 3.01 (t, 1H, J = 12.8 Hz, CH_2), 3.28 (dd, 1H, J_1 = 13.0 Hz, J_2 = 4.6 Hz, CH_2), 4.97 (dd, 1H, J_1 = 12.2 Hz, J_2 = 4.6 Hz, CH), 7.00 (t, 2H, J = 8.4 Hz), 7.15 (t, 1H, J = 7.2 Hz), 7.30 (d, 5H, J = 7.6 Hz), 7.48 (t, 1H, J = 8.0 Hz), 7.60 (d, 1H, J = 7.6 Hz), 7.95 (d, 2H, J = 7.6 Hz) cm^{-1}; ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.50 (CH_3), 37.68 (CH_2), 59.71 (CH), 122.57, 125.19, 125.40, 127.42, 127.69, 127.77, 129.53, 129.85, 134.88, 135.00, 140.12, 141.63, 152.57, 163.38 (Ar C), 168.61 (C═N); MS (EI, 70 eV) *m/z* (%): 374.05 (4.17) [M^+], 256.09 (2.66), 238.10 (2.91), 225.10 (100.00), 210.06 (3.05), 197.04 (2.29), 122.08 (6.08), 91.12 (15.77), *Anal.* Calcd for $C_{22}H_{18}FNS$: C, 76.05; H, 5.22; N, 4.02; S, 9.23; Found: C, 75.85; H, 5.38; N, 3.87; S, 9.01.

2-(4-Chlorophenyl)-4-(4-chlorophenyl)-2,3-dihydro-1,5-benzothiazepine (6). White crystals; mp 124–126°C; IR (KBr) ν: 3052, 2883, 1607, 1562, 1486, 1398, 1319, 1088, 1010, 806, 757 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.02 (t, 1H, J = 12.8 Hz, CH_2), 3.24 (dd, 1H, J_1 = 13.2 Hz, J_2 = 4.8 Hz, CH_2), 4.94 (dd, 1H, J_1 = 12.2 Hz, J_2 = 5.0 Hz, CH), 7.17 (t, 1H, J = 7.6 Hz), 7.23–7.31 (m, 6H), 7.46–7.51 (m, 2H), 7.60 (d, 1H, J = 7.6 Hz), 7.99 (d, 1H, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): 37.33 (CH_2), 59.72 (CH), 122.37, 125.43, 125.60, 127.46, 128.75, 128.97, 129.04, 129.33, 130.05, 133.59, 135.09, 135.99, 137.43, 142.31, 152.21 (Ar C), 167.52 (C═N); MS (EI, 70 eV) *m/z* (%): 384.88 (2.19) [$M+2$]$^+$, 382.88 (3.03) [M^+], 271.94 (3.89), 248.93 (5.52), 246.94 (84.68), 244.94 (100.00), 209.99 (19.5), 137.98 (27.94), 108.97 (17.57), 107.96 (85.37), 68.98 (47.68); *Anal.* Calcd for $C_{21}H_{15}Cl_2NS$: C, 65.63; H, 3.93; N, 3.64; S, 8.34. Found: C, 65.24; H, 3.52; N, 3.61; S, 7.89.

4-(4-Chlorophenyl)-2-(4-(N,N-dimethylamino)phenyl)-2,3-dihydro-1,5-benzothiazepine (7). White crystals; mp 155–157°C; IR (KBr) ν: 3056, 2868, 1621, 1475, 1416, 1322, 1237, 1078, 841, 755 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.05 (t, 1H, J = 12.6 Hz, CH_2), 3.31 (dd, 1H, J_1 = 13.0 Hz, J_2 = 4.6 Hz, CH_2), 3.91 (s, 6H, CH_3), 5.01 (dd, 1H, J_1 = 12.6 Hz, J_2 = 4.2 Hz, CH), 7.02 (d, 2H, J = 8.4 Hz), 7.16 (t, 1H, J = 7.4 Hz), 7.32 (d, 1H, J = 8.0 Hz), 7.47–7.52 (m, 3H), 7.58 (d, 1H, J = 8.0 Hz), 8.02 (d, 2H, J = 8.8 Hz), 8.19 (d, 2H, J = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): 36.69 (CH_2), 55.51 (CH_3), 59.24 (CH), 76.72, 114.20, 121.66, 124.18, 125.27, 125.52, 127.04, 129.13, 129.91, 130.32, 134.98, 147.30, 150.89, 152.74, 162.32 (Ar C), 167.52 (C═N).

4-(4-Chlorophenyl)-2-(4-methoxyphenyl)-2,3-dihydro-1,5-benzothiazepine (8). White crystals; mp 132–134°C (Lit. [28] 133–135°C); IR (KBr) ν: 3000, 2895, 1605, 1509, 1451, 1243, 1088, 1007, 826, 755 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.05 (t, 1H, J = 12.6 Hz, CH_2), 3.22 (dd, 1H, J_1 = 13.2 Hz, J_2 = 4.8 Hz, CH_2), 3.81 (s, 3H, CH_3), 4.97 (dd, 1H, J_1 = 12.6 Hz, J_2 = 4.6 Hz, CH), 6.84 (d, 2H, J = 8.8 Hz), 7.16 (t, 1H, J = 8.0 Hz), 7.23 (d, 2H, J = 8.8 Hz), 7.29 (d, 1H, J = 7.27 Hz), 7.46 (d, 2H, J = 8.4 Hz), 7.48 (t, 2H, J = 8.0 Hz), 7.61 (d, 1H, J = 8.0 Hz), 7.99 (d, 2H, J = 8.0 Hz).

2-(4-Bromophenyl)-4-(2-hydroxyphenyl)-2,3-dihydro-1,5-benzothiazepine (9). Yellowish needles; mp 174–176°C; IR (KBr) ν: 3439, 3055, 2901, 1598, 1564, 1483,1448, 1253, 1009, 809, 748, 499 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.05 (t, 1H, J = 12.6 Hz, CH_2), 3.35 (dd, 1H, J_1 = 19.2 Hz, J_2 = 10.6 Hz, CH_2), 4.98 (dd, 1H, J_1 = 24.4 Hz, J_2 = 9.6 Hz, CH), 6.93 (t, 1H, J = 7.2 Hz), 7.09 (d, 1H, J = 7.2 Hz), 7.22 (d, 2H, J = 8.4 Hz), 7.33 (d, 1H, J = 8.4 Hz), 7.46 (d, 4H, J = 6.4 Hz), 7.57 (d, 1H, J = 6.8 Hz), 7.63 (d, 1H, J = 7.2 Hz), 14.5 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): 36.62 (CH_2), 59.27 (CH), 118.65, 118.75, 121.82, 123.95, 125.73, 126.51, 127.79, 128.28, 130.18, 132.00, 133.77, 135.18, 142.69, 162.77 (Ar C), 172.83 (C═N); MS (EI, 70 eV) *m/z* (%): 410.96 (4.27) [$M+2$]$^+$, 408.97 (4.11) [M^+], 240.02 (4.16), 227.00 (100.00), 198.96 (40.41), 197.95 (30.85), 181.85 (7.35), 108.89 (16.90), 102.89 (20.84), 90.89 (16.65), 76.89 (50.38), 64.91 (32.43); *Anal.* Calcd for $C_{21}H_{16}NSOBr$: C, 61.47; H, 3.93; N, 3.41; S, 7.81. Found: C, 60.95; H, 4.37; N, 3.96; S, 7.48.

4-(2-Hydroxyphenyl)-2-(4-methylphenyl)-2,3-dihydro-1,5-benzothiazepine (10). Light yellow crystals; mp 156–158°C (Lit [28] 155–157°C); IR (KBr) ν: 3434, 3049, 2980, 1596, 1448, 1256, 1207, 810, 745, 498 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.37 (s, 3H, CH_3), 3.11 (t, 1H, J = 12.8 Hz, CH_2), 3.43 (d, 1H, J = 12.8 Hz, CH_2), 5.06 (d, 1H, J = 12 Hz, CH), 6.94 (t, 1H, J = 8.0 Hz), 7.4 (s, 1H),7.15 (d, 2H, J = 8.0 Hz), 7.22 (d, 3H, J = 8.0 Hz), 7.35 (d, 1H, J = 8.0 Hz), 7.42 (t, 1H, J = 8.0 Hz), 7.52 (t, 1H, J = 8.0 Hz), 7.36 (q, 2H, J = 8.0 Hz), 14.35 (S, 1H, OH); MS (EI, 70 eV) *m/z* (%): 345.09 (2.97) [M^+], 240.06 (2.97), 227.03 (100.00), 199.05 (31.91), 198.05 (19.68), 118.04 (12.41), 108.97 (10.37).

2-(4-Fluorophenyl)-4-(2-hydroxyphenyl)-2,3-dihydro-1,5-benzothiazepine (11). Light yellow crystals; mp 161–163°C; IR (KBr) ν: 3431, 3054, 1598, 1505,1448, 1214, 1155, 823, 746 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.08 (t, 1H, J = 12.4 Hz, CH_2), 3.44 (d, 1H, J = 12 Hz, CH_2), 5.09 (d, 1H, J = 10.8 Hz, CH), 6.94 (t, 1H, J = 7.2 Hz), 7.04 (t, 2H, J = 8.0 Hz), 7.18 (t, 1H, J = 8.0 Hz), 7.30–7.38 (m, 3H), 7.45 (dd, 2H, J_1 = 32 Hz, J_2 = 7.2 Hz), 7.60 (d, 2H, J = 11.2 Hz), 7.75 (d, 1H, J = 12.8 Hz), 14.5 (s, 1H, OH); ^{13}C NMR (125 MHz, $CDCl_3$): 37.02 (CH_2), 59.31 (CH), 115.65, 115.82, 118.62, 118.75, 125.73, 126.47, 127.77, 127.84, 128.35, 130.09, 133.72, 135.17, 139.53, 148.87, 161.35, 162.82, 163.32 (Ar C), 172.93 (C═N); MS (EI, 100 eV) *m/z* (%): 348.96 (56.54) [M^+], 331.94 (6.45), 255.99 (10.43), 239.98 (13.09), 227.00 (100.00), 199.00 (84.29), 197.99 (76.44), 122.00 (47.64), 108.98 (43.98); *Anal.* Calcd for $C_{21}H_{16}NSOF$: C, 72.18; H, 4.62; N, 4.51; S, 9.18. Found: C, 71.72; H, 5.19; N, 4.21; S, 8.71.

4-(2-Hydroxyphenyl)-2-phenyl-2,3-dihydro-1,5-benzothiazepine (12). Light yellow crystals; mp 145–147°C (Lit. [18] 146–147°C); IR (KBr) ν: 3325, 2836, 1592, 1467, 1350, 1294, 889, 749 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.10 (t, 1H, J = 12.9 Hz, CH_2), 3.42 (dd, 1H, J_1 = 13.3 Hz, J_2 = 4.4 Hz, CH_2), 5.07 (dd, 1H, J_1 = 12.4 Hz, J_2 = 4.4 Hz, CH), 6.92 (t, 1H, J = 7.6 Hz), 7.08 (d, 1H, J = 8.3 Hz), 7.25 (t, 1H, J = 7.5 Hz), 7.29–7.34 (m, 5H), 7.43 (t, 1H, J = 7.7 Hz), 7.51 (t, 1H, J = 7.6 Hz), 7.60 (d, 1H, J = 8.0 Hz), 7.67 (d, 1H, J = 7.7 Hz), 14.51 (s, 1H, OH); MS (EI, 70 eV) *m/z* (%): 331.04 (79.08) [M^+], 314.05 (8.79), 254.10 (3.79), 238.11 (4.58), 227.10 (100.00), 199.11 (90.38), 198.11 (61.09), 173.09 (30.13), 167.14 (33.89), 109.11 (61.51), 91.15 (25.21), 77.14 (32.64), 65.14 (49.37), 51.12 (35.98).

4-(2-Hydroxyphenyl)-2-(4-methoxyphenyl)-2,3-dihydro-1,5-benzothiazepine (13). Light yellow crystals; mp 160–162°C (Lit. [18] 160–161°C); IR (KBr) ν: 3008, 2958, 1597, 1555, 1511, 1251, 1030, 827, 757 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.09 (t, 1H, J = 12.8 Hz, CH_2), 3.42 (d, 1H, J = 11.2 Hz, CH_2), 3.82 (s, 1H, CH_3), 5.08 (d, 1H, J = *10.*8 Hz, CH), 6.87 (d, 2H, J = 8.0 Hz), 6.93 (t, 1H, J = 7.2 Hz), 7.14 (d, 1H, J = 8.0 Hz), 7.25 (t, 2H, J = 8.0 Hz), 7.35 (t, 2H, J = 8.0 Hz), 7.44 (t, 1H, J = 8.0 Hz),

7.52 (t, 1H, J = 8.0 Hz), 7.60 (d, 1H, J = 8.0 Hz), 7.67 (d, 1H, J = 8.0 Hz); 14.38 (s, 1H, OH); MS (EI, 70 eV) *m/z* (%): 361.01 (3.22) [M^+], 240.09 (2.07), 227.06 (100.00), 199.09 (52.27), 198.09 (38.07), 134.13 (84.85), 109.04 (9.85).

4-(2-Hydroxyphenyl)-2-(4-thiomethylphenyl)-2,3-dihydro-1,5-benzothiazepine (14). White solid; mp 162–164°C; IR (KBr) ν: 3421, 1607, 1454, 1320, 1257, 1091, 812, 758, 687 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.49 (s, 3H, SMe), 3.07 (t, 1H, J = 12.9 Hz, CH_2), 3.39 (dd, 1H, J_1 = 13.3 Hz, J_2 = 4.7 Hz, CH_2), 5.03 (dd, 1H, J_1 = 12.4 Hz, J_2 = 4.6 Hz, CH), 6.92 (t, 1H, J = 7.2 Hz), 7.08 (d, 1H, J = 8.1 Hz), 7.23 (q, 5H, J = 8.4 Hz), 7.32 (d, 1H, J = 7.0 Hz), 7.42 (t, 1H, J = 8.4 Hz), 7.50 (d, 1H, J = 7.7 Hz), 7.58 (d, 1H, J = 8.0 Hz), 7.64 (d, 1H, J = 7.7 Hz), 14.48 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): 15.28 (CH_3), 36.78 (CH_2), 59.65 (CH), 118.70, 124.30, 125.69, 126.45, 126.54, 126.83, 127.44, 128.40, 128.81, 130.03, 133.70, 135.23, 138.47, 140.49, 148.80, 162.79 (Ar C), 173.03 (C═N); MS (EI, 100 eV) *m/z* (%): 377.05 (2.18) [M^+], 227.10 (26.16), 199.09 (12.96), 198.08 (10.19), 150.10 (100.00), 109.08 (4.46); *Anal*. Calcd for $C_{22}H_{19}NOS_2$: C, 69.99; H, 5.07; N, 3.71; S, 16.99. Found: C, 69.67; H, 5.45; N, 3.45; S, 16.47.

4-(2-Hydroxyphenyl)-2-(4-(N,N-dimethylamino)phenyl)-2,3-dihydro-1,5-benzothiazepine (15). Light yellow crystals; mp 191–193°C; IR (KBr) ν: 3429, 2883, 1596, 1520, 1442, 1338, 1259, 1162, 812, 751 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.95 (t, 1H, J = 12.9 Hz CH_2), 3.05 (s, 6H, CH_3), 3.40 (d, 1H, J = 13.2 Hz, CH_2), 5.06 (d, 1H, J = 12 Hz, CH), 6.92 (t, 1H, J = 8.0 Hz), 7.09 (d, 1H, J = 8.4 Hz), 7.24 (t, 2H, J = 8.0 Hz), 7.34 (d, 2H, J = 8.0 Hz), 7.43 (t, 2H, J = 8.0 Hz), 7.52 (t, 2 H, J = 8.0 Hz), 7.59 (d, 1H, J = 8.0 Hz), 7.65 (d, 1H, J = 8.0 Hz), 14.51 (s, 1H, OH); ^{13}C NMR (125 MHz, $CDCl_3$): 37.11 (CH_2), 40.52 (Me), 53.40 (Me), 60.11 (CH), 112.50, 118.47, 118.51, 118.63, 124.98, 125.57, 126.23, 126.82, 128.50, 129.64, 131.70, 133.49, 135.24, 148.74, 150.36, 162.84 (Ar C), 173.22 (C═N); MS (EI, 70 eV) *m/z* (%): 374.01 (2.46) [M^+], 227.04 (37.18), 198.07 (29.06), 147.12 (100.00), 109.04 (15.81).

2-(4-Methoxyphenyl)-4-(4-methoxyphenyl)-2,3-dihydro-1,5-benzothiazepine (16). White crystals; mp 111–113°C (Lit. [35] 107–108°C); IR (KBr) ν: 2995, 2831, 1595, 1509, 1452, 1321, 1253, 1175, 1030, 828, 744 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.09 (t, 1H, J = 12.4 Hz, CH_2), 3.41 (d, 1H, J = 10.0 Hz, CH_2), 3.81 (s, 3H, OCH_3), 3.94 (s, 3H, OCH_3), 4.99 (d, 1H, J = 9.2 Hz, CH), 6.85 (d, 2H, J = 8.0 Hz), 7.06 (d, 2H, J = 8.0 Hz), 7.21 (d, 2H, J = 8.0 Hz) 7.54 (t, 1H, J = 6.8 Hz), 7.65 (d, 2H, J = 8.0 Hz), 7.89 (d, 1H, J = 8.8 Hz), 8.21 (s, 2H).

4-(4-Chlorophenyl)-2-(4-methylphenyl)-2,3-dihydro-1,5-benzothiazepine (17). White crystals; mp 134–136°C; IR (KBr) ν: 3047, 1604, 1450, 1318, 1255, 1088, 812, 761 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.36 (s, 3H, CH_3), 3.13 (t, 1H, J = 12.0 Hz, CH_2), 3.35 (d, 1H, J = 9.6 Hz, CH_2), 4.99 (d, 1H, J = 10.0 Hz, CH), 7.16 (q, 3H, J = 7.6 Hz), 7.26 (d, 2H, J = 9.6 Hz), 7.53 (t, 4H, J = 8.0 Hz), 7.66 (d, 1H, J = 8.0 Hz), 8.10 (d, 2H, J = 8.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): 21.12 (CH_3), 37.53 (CH_2), 60.39 (CH), 123.02, 125.36, 125.43, 125.94, 128.79, 128.97, 129.47, 129.75, 135.12, 136.24, 137.28, 137.74, 141.03, 152.26 (Ar C), 167.78 (C═N); MS (EI, 70 eV) *m/z* (%): 364.92 (2.23) [M + 2]$^+$, 362.92 (5.26) [M^+], 258.94 (2.86), 244.93 (98.37), 209.98 (22.69), 149.00 (34.31), 118.03 (100.00), 108.99 (39.01), 107.95 (89.19).

2-(4-Methoxylphenyl)-4-phenyl-2,3-dihydro-1,5-benzothiazepine (18). Pale yellow crystals; mp 127–129°C (Lit. [28] 127–128°C); IR (KBr) ν: 2891, 1607, 1509, 1452, 1245, 1175, 1031, 823, 760, 690 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.05 (t, 1H, J = 12.7 Hz, CH_2), 3.30 (dd, 1H, J_1 = 12.9 Hz, J_2 = 4.7 Hz, CH_2), 3.80 (s, 3H, OMe), 4.98 (dd, 1H, J_1 = 12.5 Hz, J_2 = 4.7 Hz, CH), 6.84 (d, 2H, J = 11.15 Hz), 7.15 (t, 1H, J = 7.5 Hz), 7.23 (d, 2H, J = 8.6 Hz), 7.31 (d, 1H, J = 7.9 Hz), 7.46–7.53 (m, 4H), 7.61 (d, 1H, J = 7.6 Hz), 8.06 (d, 2H, J = 7.15 Hz).

2-(4-Bromophenyl)-4-phenyl-2,3-dihydro-1,5-benzothiazepine (19). Pale yellow crystals; mp 119–121°C (Lit. [28] 131°C); IR (KBr) ν: 3053, 2902, 1609, 1452, 1318, 1073, 1009, 826, 752, 689 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.12 (t, 1H, J = 12.8 Hz, CH_2), 3.46 (d, 1H, J = 13.2 Hz, CH_2), 4.98 (d, 1H, J = 12.0 Hz, CH), 7.17 (d, 2H, J = 8.0 Hz), 7.30 (d, 1H, J = 8.0 Hz), 7.46 (d, 2H, J = 8.0 Hz), 7.58 (t, 3H, J = 6.4 Hz), 6.65 (t, 2H, J = 6.8 Hz), 8.19 (d, 2H, J = 8.0 Hz).

4-Phenyl-2-(4-thiomethylphenyl)-2,3-dihydro-1,5-benzothiazepine (20). White crystals; mp 136–138°C (Lit. [28] 136–138°C); IR (KBr) ν: 3053, 2897, 1606, 1490, 1453, 1320, 812, 757, 687 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.48 (s, 3H, SMe), 3.06 (t, 1H, J = 12.8 Hz, CH_2), 3.29 (dd, 1H, J_1 = 13.0 Hz, J_2 = 4.8 Hz, CH_2), 4.97 (dd, 1H, J_1 = 12.4 Hz, J_2 = 4.6 Hz, CH), 7.15 (t, 1H, J = 7.6 Hz), 7.21 (q, 4H, J = 8.7 Hz), 7.32 (d, 1H, J = 7.8 Hz), 7.46–7.53 (m, 4H), 7.61 (d, 1H, J = 7.6 Hz), 8.06 (d, 2H, J = 8.1 Hz).

4-(4-Chlorophenyl)-2-phenyl-2,3-dihydro-1,5-benzothiazepine (21). White crystals; mp 131–133°C (Lit. [22] 132°C); IR (KBr) ν: 2880, 1611, 1564, 1450, 1304, 1045, 818, 753, 695 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.07 (t, 1H, J = 12.8 Hz, CH_2), 3.20 (dd, 1H, J_1 = 13.1 Hz, J_2 = 4.8 Hz, CH_2), 4.97 (dd, 1H, J_1 = 12.4 Hz, J_2 = 4.8 Hz, CH), 7.16 (td, 1H, J_1 = 15.1 Hz, J_2 = 1.2 Hz), 7.28–7.34 (m, 6H), 7.46–7.50 (m, 3H), 7.62 (dd, 1H, J_1 = 7.65 Hz, J_2 = 1.1 Hz), 7.99 (d, 2H, J = 8.6 Hz).

2-(4-Bromophenyl)-4-(4-bromophenyl)-2,3-dihydro-1,5-benzothiazepine (22). Pale yellow crystals; mp 134–136°C; IR (KBr) ν: 3049, 2901, 1607, 1485, 1314, 1070, 1006, 811, 754 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.07 (t, 1H, J = 12.4 Hz, CH_2), 3.33 (d, 1H, J = 10.4 Hz, CH_2), 4.95 (d, 1H, J = 11.2 Hz, CH), 7.17 (d, 2H, J = 8.0 Hz), 7.25 (t, 1H, 6.4 Hz), 7.46 (d, 1H, J = 8.0 Hz), 7.53 (s, 2H), 7.64 (d, 1H, J = 8.0 Hz), 7.68 (d, 2H, J = 8.0 Hz), 7.99 (d, 2H, J = 8.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): 37.22 (CH_2), 59.80 (CH), 121.69, 122.39, 125.43, 125.59, 125.93, 127.79, 128.94, 130.03, 131.94, 132.01, 135.07, 136.50, 142.79, 152.24 (Ar C), 167.58 (C═N); MS (EI, 70 eV) *m/z* (%): 474.86 (2.02) [M + 4]$^+$, 472.86 (3.68) [M + 2]$^+$, 470.84 (2.03) [M^+], 315.90 (3.21), 288.90 (100.00), 210.03 (54.86), 183.97 (23.57), 108.99 (14.00), 107.98 (72.00).

2-(4-Bromophenyl)-4-(2-hydroxy-3,4-dimethoxyphenyl)-2,3-dihydro-1,5-benzothiazepine (23). Yellow crystals; mp 184–186°C; IR (KBr) ν: 3049, 2926, 1607, 1453, 1281, 1215,1123, 1079, 1009, 822, 783 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.02 (t, 1H, J = 12.8 Hz, CH_2), 3.33 (dd, 1H, J_1 = 13.3 Hz, J_2 = 4.7 Hz, CH_2), 3.94 (s, 3H, OMe), 3.96 (s, 3H, OMe), 4.97 (dd, 1H, J_1 = 12.1 Hz, J_2 = 4.7 Hz, CH), 6.51 (d, 1H, J = 9.0 Hz), 7.19 (dd, 2H, J_1 = 8.4 Hz), 7.21 (d, 1H, J = 7.6 Hz), 7.30 (dd, 2H, J_1 = 8.4 Hz, J_2 = 4.3 Hz), 7.45 (d, 2H, J = 8.4 Hz), 7.50 (t, 1H, J = 7.4 Hz), 7.61 (d, 1H, J = 7.6 Hz), 14.94 (b, 1H, OH); ^{13}C NMR (125 MHz, $CDCl_3$): 36.76 (CH_2), 56.11 (OMe), 59.18 (OMe), 60.63 (CH), 102.74, 113.44, 121.83, 124.13, 124.26, 125.74, 126.41, 127.84, 130.22, 131.99, 135.13, 137.28, 142.56, 148.55, 156.76, 157.55 (Ar C), 172.51 (C═N); MS (EI, 70 eV) *m/z* (%): 468.99 (43.62) [M + 2]$^+$, 470.99 (46.31) [M^+], 453.97 (4.87), 438.00 (12.42), 390.03 (2.32), 314.04 (9.14),288.07 (24.66), 269.08 (48.32), 244.11 (21.81), 201.11 (33.22), 173.13 (100.00), 109.14 (26.68), 103.17 (31.71), 77.17 (27.01), 65.17 (24.50); *Anal*. Calcd for

$C_{23}H_{20}BrNO_3S$: C, 58.73; H, 4.29; N, 2.98; S, 6.82; Found: C, 58.69; H, 4.23; N, 3.03; S, 6.66.

2-(4-Chlorophenyl)-4-(2-hydroxy-4,6-dimethoxyphenyl)-2,3-dihydro-1,5-benzodiazepine (24). Yellow crystals; mp 175–177°C; IR (KBr) ν: 3051, 2936, 1610, 1524, 1443, 1033, 1012, 831, 762 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 2.88 (t, 1H, J = 12.4 Hz, CH_2), 3.63 (dd, 1H, J_1 = 12.3 Hz, J_2 = 4.3 Hz, CH_2), 3.85 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 5.19 (dd, 1H, J_1 = 12.5 Hz, J_2 = 4.3 Hz, CH), 5.97 (s, 1H), 6.23 (s, 1H), 7.20–7.29 (m, 6H), 7.48 (t, 1H, J = 7.5 Hz), 7.62 (d, 1H, J = 7.5 Hz), 16.57 (b, 1H, OH); ^{13}C NMR (125 MHz, $CDCl_3$): 41.46 (CH_2), 55.53 (OMe), 55.67 (OMe), 58.59 (CH), 90.78, 94.78, 103.64, 125.56, 125.67, 126.23, 127.37, 128.95, 130.03, 133.34, 135.19, 143.32, 147.06, 161.70, 164.59, 168.09 (Ar C), 172.21 (C═N); MS (EI, 70 eV) *m/z* (%): 426.04 (2.06) [M^+], 271.15 (2.16), 244.97 (3.80), 226.18 (3.26), 185.91 (4.09), 154.05 (15.29), 137.98 (100.00), 103.02 (81.57), 77.01 (43.92), 51.09 (45.10); *Anal*. Calcd for $C_{23}H_{20}ClNO_3S$: C, 64.86; H, 4.73; N, 3.29; S, 7.53; Found: C, 64.55; H, 4.90; N, 3.01; S, 7.4.

4-(4-Methoxyphenyl)-2-(4-nitrophenyl)-2,3-dihydro-1,5-benzothiazepine (25). White solid; mp 191–193°C (Lit. [18] 193°C); IR (KBr) ν: 1596, 1514, 1453, 1345, 1259, 1174, 1029, 830, 740 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 3.04 (t, 1H, J = 12.8 Hz, CH_2), 3.29 (dd, 1H, J_1 = 13.0 Hz, J_2 = 4.8 Hz, CH_2), 3.90 (s, 3H, OMe), 5.00 (dd, 1H, J_1 = 12.5 Hz, J_2 = 4.8 Hz, CH), 7.01 (d, 2H, J = 8.8 Hz), 7.15 (t, 1H, J = 7.45 Hz), 7.31 (d, 1H, J = 7.8 Hz), 7.47 (d, 2H, J = 8.6 Hz), 7.50 (d, 1H, J = 7.6 Hz), 7.57 (d, 1H, J = 7.55 Hz), 8.02 (d, 2H, J = 8.6 Hz), 8.18 (d, 2H, J = 8.8 Hz).

4-(4-Chlorophenyl)-2-(2,4-dimethoxyphenyl)-2,3-dihydro-1,5-benzothiazepine (26). White crystals; mp 152–154°C (Lit. [22] 153–155°C); IR (KBr) ν: 3326, 1593, 1467, 1308, 1245, 1077, 802, 749 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 2.87 (t, 1H, J = 12.8 Hz, CH_2), 3.24 (dd, 1H, J_1 = 12.8 Hz, J_2 = 4.4 Hz, CH_2), 3.80 (s, 3H, OMe), 3.87 (s, 3H, OMe), 5.44 (dd, 1H, J_1 = 12.71 Hz, J_2 = 4.4 Hz, CH), 7.13 (t, 1H, J = 7.5 Hz), 7.27 (m, 3H), 7.43 (t, 2H, J = 8.5 Hz), 7.46 (d, 2H, J = 8.5 Hz), 7.66 (d, 1H, J = 7.6 Hz), 8.08 (d, 2H, J = 8.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): 36.05 (CH_2), 53.69 (CH), 55.44 (OCH_3), 55.54 (OCH_3), 98.48, 104.37, 123.59, 124.57, 125.19, 125.31, 127.61, 128.88, 129.42, 135.19, 136.34, 137.9, 152.47, 156.24, 160.35 (Ar C), 168.12 (C═N).

4-(4-Aminophenyl)-2-(2,4-dichlorophenyl)-2,3-dihydro-1,5-enzothiazepine (27). White solid; mp 205–210°C; IR (KBr) ν: 3037, 1614, 1445, 1308, 1245, 1078, 802, 751 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ 2.76 (dd, 1H, J_1 = 13.2 Hz, J_2 = 5.1 Hz, CH_2), 3.13 (dd, 1H, J_1 = 13.2 Hz, J_2 = 5.1 Hz, CH_2), 5.27 (dd, 1H, J_1 = 13.9 Hz, J_2 = 5.1 Hz, CH), 5.85 (s, 2H, NH_2), 6.63 (d, 2H, J = 8.5 Hz), 7.08 (t, 1H, J = 7.1 Hz), 7.17 (d, 1H, J = 7.8 Hz) 7.41–7.53 (m, 4H), 7.66 (s, 1H), 7.83 (d, 2H, J = 8.5 Hz); ^{13}C NMR (125 MHz, DMSO-d_6): 33.89 (CH_2), 54.98 (CH), 113.27, 121.17, 123.77, 124.34, 125.01, 127.87, 128.60, 128.82, 129.09, 130.12, 131.72, 132.63, 134.72, 139.78, 152.14, 153.07(Ar C), 167.37 (C═N).

4-(4-Methoxyphenyl)-2-(nphthalen-2-yl)-2,3-dihydro-1,5-benzodiazepine (28). Light yellow crystals; mp 128–130°C; IR (KBr) ν: 1596, 1569, 1513, 849, 832, 815, 772, 745 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.18 (t, 1H, J = 12.4 Hz, CH_2), 3.35 (dd, 1H, J_1 = 12.8 Hz, J_2 = 4.8 Hz, CH_2), 5.13 (dd, 1H, J_1 = 12.8 Hz, J_2 = 4.8 Hz, CH), 7.0 (d, 2H, J = 8.8 Hz), 7.14 (t, 1H, J = 7.2 Hz), 7.25 (s, 1H), 7.31 (d, 1H, J = 8.0 Hz), 7.45–7.49 (m, 5H), 7.62 (d, 1H, J = 8.0 Hz),7.68 (s,1H), 7.77–782 (m, 4H), 8.05 (d, 3H, J = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): 37.29 (CH_2), 55.57 (CH), 60.66 (OCH_3), 114.19, 124.29, 125.14, 125.36, 127.78, 128.04, 128.94, 129.29, 129.88, 141.51, 152.77, 162.04 (Ar C), 168.24 (C═N); HRMS (EI, 70 eV) *m/z* (%): 395.0 (15) [M^+], 254.0 (100), 239.0 (8.25), 223 (16.8).

2-(3,4-Methoxyphenyl)-4-(phenyl)-2,3-dihydro-1,5-benzodiazepine (29). White crystals; mp 122–124°C; IR (KBr) ν: 1604, 1514, 1449, 1265, 762, 589 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.09 (t, 1H, J = 12.0 Hz, CH_2), 3.32 (dd, 1H, J_1 = 18.0 Hz, J_2 = 5.2 Hz, CH_2), 4.98 (s, 3H, OCH_3), 4.99 (s, 3H, OCH_3), 5.00 (dd, 1H, J_1 = 16.8 Hz, J_2 = 4.8 Hz, CH), 6.79–6.85 (m, 2H), 6.88 (d, 1H, J = 1.6 Hz), 7.16 (tt, 1H, J_1 = 16.4 Hz, J_2 = 1.2 Hz), 7.34 (dd, 1H, J_1 = 9.2 Hz, J_2 = 1.2 Hz),), 7.46 (dd, 1H, J_1 = 9.2 Hz, J_2 = 1.6 Hz), 7.47–7.54 (m, 4H), 8.34 (dd, 2H, J_1 = 9.6 Hz, J_2 = 1.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): 31.24 (CH_2), 55.79 (CH), 56.03 (OCH_3), 56.20 (OCH_3), 108.94, 110.39, 111.04, 126.91, 127.84, 128.06, 128.52, 128.75, 130.06, 133.13 (Ar C), 162.00 (C═N); MS (EI, 70 eV) *m/z* (%): 359.0 (0.15) [M^+], 195.22 (2.30), 164.09 (100).

2-(4-Chlorophenyl)-4-(2-hydroxyphenyl)-2,3-dihydro-1,5-benzodiazepine (30). Light yellow crystals; mp 168–170°C; IR (KBr) ν: 3353, 2889, 1593, 1470, 1257, 1089, 886, 787, 755 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 3.11 (dd, 1H, J_1 = 13.9 Hz, J_2 = 7.8 Hz, CH_2), 3.33 (dd, 1H, J_1 = 13.9 Hz, J_2 = 3.8 Hz, CH_2), 3.49 (s, 1H, NH), 5.26 (dd, 1H, J_1 = 7.8 Hz, J_2 = 3.8 Hz, CH), 6.76 (t, 1H, J = 7.3 Hz), 6.90 (d, 1H, J = 7.8 Hz), 7.09 (t, 1H, J = 8.0 Hz), 7.15–7.22 (m, 3H), 7.34 (q, 6H, J = 8.2 Hz), 15.09 (b, 1H, OH); ^{13}C NMR (125 MHz, $CDCl_3$): 36.39 (CH_2), 69.43 (CH), 118.24, 118.58, 118.66, 121.01, 122.04, 127.37, 137.91, 128.26, 128.48, 129.18, 134.07, 134.22, 138.96, 142.07, 162.49 (Ar C), 171.67 (C═N); MS (EI, 70 eV) *m/z* (%): 349.97 (19.64) [$M+2$]$^+$, 347.97 (59.52) [M^+], 332.95 (88.69), 330.97 (7.25), 256.99 (6.88), 255.00 (21.73), 237.05 (16.22), 210.04 (100.00), 182.05 (31.40), 181.04 (32.74), 137.97 (13.39), 119.01 (75.60), 111.02 (12.95), 103.00 (15.03), 102.00 (20.98), 91.01 (46.43), 77.02 (37.05), 65.05 (53.57); *Anal*. Calcd for $C_{22}H_{21}ClN_2O$: C, 72.42; H, 5.80; N, 7.68; Found: C, 71.92; H, 5.56; N, 7.76.

2-(4-Bromophenyl)-4-(2-hydroxyphenyl)-2,3-dihydro-1,5-benzodiazepine (31). Light yellow crystals; mp 178–180°C; IR (KBr) ν: 3353, 2887, 1592, 1470, 1257, 1070, 1004, 882, 753 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 3.06 (dd, 1H, J_1 = 13.8 Hz, J_2 = 8.0 Hz, CH_2), 3.28 (dd, 1H, J_1 = 13.8 Hz, J_2 = 3.9 Hz, CH_2), 3.82 (s, 1H, NH), 5.21 (dd, 1H, J_1 = 8.0 Hz, J_2 = 3.9 Hz, CH), 6.75 (t, 1H, J = 7.4 Hz), 6.86 (d, 1H, J = 7.8 Hz), 7.06 (dd, 2H, J = 6.0 Hz), 7.15 (td, 1H, J_1 = 7.5 Hz, J_2 = 1.1 Hz), 7.19 (d, 1H, J = 7.5 Hz), 7.27–7.34 (m, 4H), 7.47 (d, 2H, J = 8.3 Hz), 15.13 (b, 1H, OH); ^{13}C NMR (125 MHz, $CDCl_3$): 36.17 (CH_2), 69.67 (CH), 118.25, 118.45, 118.81, 120.90, 121.95, 122.13, 127.74, 128.16, 128.18, 132.08, 133.31, 135.03, 138.83, 142.94, 162.52 (Ar C), 171.24 (C═N); MS (EI, 70 eV) *m/z* (%): 394.02 (17.66) [$M+2$]$^+$, 392.01 (20.56) [M^+], 377.00 (33.01), 375.01 (3.17), 299.01 (7.49), 237.12 (9.84), 210.11 (100.00), 182.07 (36.41), 181.09 (30.41), 119.07 (59.14), 102.02 (30.32), 91.04 (91.04), 77.04 (48.15), 65.07 (55.89); *Anal*. Calcd for $C_{21}H_{17}N_2SBr$: C, 64.13; H, 4.36; N, 7.12; Found: C, 63.76; H, 4.66; N, 7.05.

4-(2-Hydroxyphenyl)-2-(4-methylphenyl)-2,3-dihydro-1,5-benzodiazepine (32). Yellow crystals; mp 109–111°C; IR (KBr) ν: 3344, 3016, 2830, 1596, 1479, 1298, 1255, 755 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 2.40 (s, 3H, CH_3), 3.05 (dd, 1H, J_1 = 14.0 Hz, J_2 = 9.2 Hz, CH_2), 3.34 (dd, 1H, J_1 = 14.0 Hz, J_2 = 3.2 Hz, CH_2), 3.84 (s, 1H, NH), 5.15 (dd, 1H, J_1 = 9.0 Hz, J_2 = 3.0 Hz, CH), 6.78 (t, 1H, J = 7.6 Hz), 6.84 (d, 1H, J = 8.0 Hz),

7.01–7.06 (m, 2H), 7.14 (t, 1H, J = 7.4 Hz), 7.18 (d, 2H, J = 7.6 Hz), 7.31–7.36 (m, 5H), 15.4 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): 21.19 (CH_3), 36.73 (CH_2), 69.53 (CH), 118.07, 118.37, 119.15, 120.74, 121.34, 125.82, 127.47, 128.12, 128.43, 129.66, 132.88, 135.03, 138.11, 139.15, 141.49, 162.70 (Ar C), 171.10 (C═N); MS (EI, 70 eV) *m/z* (%): 327.98 (99.18) [M^+], 312.98 (100.00), 310.95 (55.10), 236.94 (73.47), 234.95 (80.82), 209.96 (97.14), 181.92 (80.82), 180.92 (81.63), 118.90 (91.02), 117.90 (80.41), 101.87 (54.29), 90.88 (88.16), 76.89 (84.49), 64.90 (84.90), 50.93 (71.43); *Anal*. Calcd for $C_{22}H_{20}N_2O$: C, 80.46; H, 6.14; N, 8.53; Found: C, 80.00; H, 6.48; N, 8.57.

4-(2-Hydroxyphenyl)-2-(4-thiomethylphenyl)-2,3-dihydro-1,5-benzodiazepine (33). Yellow crystals; mp 142–144°C; IR (KBr) ν: 3325, 2836, 1592, 1467, 1350, 1225, 889, 749 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.49 (s, 3H, CH_3), 3.05 (dd, 1H, J_1 = 14.0 Hz, J_2 = 8.8 Hz, CH_2), 3.31 (dd, 1H, J_1 = 14.0 Hz, J_2 = 3.6 Hz, CH_2), 3.80 (s, 1H, NH), 5.18 (dd, 1H, J = 8.8 Hz, J_2 = 3.6 Hz, CH), 6.77 (t, 1H, J = 7.6 Hz), 6.85 (d, 1H, J = 8.0 Hz), 7.00–7.07 (m, 3H), 7.14 (t, 1H, J = 7.6 Hz), 7.26 (d, 2H, J = 8.0 Hz), 7.33 (dd, 2H, J_1 = 16.8, J_2 = 8.0 Hz) 15.2 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): 15.90 (CH_3), 36.41 (CH_2), 69.65 (CH), 118.34, 119.10, 120.81, 121.60, 122.19, 126.44, 127.00, 127.46, 128.12, 128.32, 132.92, 135.32, 138.67, 138.97, 141.08, 162.60 (Ar C), 171.13 (C═N); MS (EI, 70 eV) *m/z* (%): 359.97 (56.60) [M^+], 344.95 (85.53), 342.95 (9.08), 266.99 (16.98), 237.03 (11.16), 210.03 (100.00), 182.02 (30.35), 182.02 (30.35), 149.98 (40.88), 119.01 (53.46), 101.98 (13.84), 91.00 (44.65), 77.01 (28.62), 65.03 (39.62); *Anal*. Calcd for $C_{22}H_{20}N_2SO$: C, 73.30; H, 5.59; N, 7.77; S, 8.90; Found: C, 73.35; H, 5.42; N, 7.85; S, 8.53.

2-(4-Fluorophenyl)-4-(2-hydroxyphenyl)-2,3-dihydro-1,5-benzodiazepine (34). Yellow crystals; mp 125–127°C; IR (KBr) ν: 3354, 3064, 2891, 1603, 1444, 1217, 1157, 831, 753 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.05 (dd, 1H, J_1 = 14.0 Hz, J_2 = 8.0 Hz, CH_2), 3.29 (dd, 1H, J_1 = 14.0 Hz, J_2 = 3.6 Hz, CH_2), 3.79 (s, 1H, NH), 5.26 (dd, 1H, unresolved, CH), 6.74 (t, 1H, J = 7.6 Hz), 6.86 (d, 1H, J = 8.0 Hz), 6.99–7.08 (m, 4H), 7.14 (t, 1H, J = 7.4 Hz), 7.19 (d, 1H, J = 8.4 Hz), 7.32 (t, 1H, J = 7.0 Hz), 7.41 (dd, 2H, J_1 = 8.0, J_2 = 5.6 Hz), 15.2 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): 36.35 (CH_2), 69.71 (CH), 115.66, 115.88, 118.07, 118.33, 119.07, 120.83, 121.81, 127.46, 127.62, 127.69, 128.11, 128.24, 132.94, 135.60, 138.85, 140.02, 161.27, 162.53, 163.72 (Ar C); 171.22 (C═N); MS (EI, 70 eV) *m/z* (%): 331.94 (86.67) [M^+], 316.94 (96.11), 314.94 (11.81), 238.97 (37.78), 236.98 (23.33), 209.99 (100.00), 195.96 (38.89), 181.98 (41.67), 180.96 (43.33), 121.94 (27.22), 118.96 (96.67), 101.93 (18.06), 100.93 (22.36), 90.94 (61.11), 76.96 (42.22), 64.98 (67.22), 51.03 (24.44); *Anal*. Calcd for $C_{21}H_{17}N_2OF$: C, 75.89; H, 5.16; N, 8.43; Found: C, 75.67; H, 5.32; N, 8.49.

4-(2-Hydroxyphenyl)-2-(4-methoxyphenyl)-2,3-dihydro-1,5-benzodiazepine (35). Yellow crystals; mp 136–138°C (Lit. [18] 138–139°C); IR (KBr) ν: 3351, 3007, 2834, 1608, 1475, 1296, 1242, 1024, 886, 754 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.04 (dd, 1H, J_1 = 13.6 Hz, J_2 = 9.2 Hz, CH_2), 3.32 (d, 1H, J = 13.6 Hz, CH_2), 3.81 (s, 3H, OCH_3), 3.83 (s, 1H, NH), 5.16 (d, 1H, J = 5.6 Hz, CH_2), 6.77 (t, 1H, J = 7.2 Hz), 6.83 (d, 1H, J = 8.0 Hz), 6.89 (d, 2H, J = 8.8 Hz), 7.03 (q, 2H, J = 8.0 Hz), 7.33 (q, 6H, J = 8.0 Hz), 15.3 (s, 1H, OH).

2-(4-Bromophenyl)-4-(3,5-dimethoxyphenyl)-2,3-dihydro-1,5-benzodiazepine (36). Yellow crystals; mp 220–222°C; IR (KBr) ν: cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.22 (s, 3H, OCH_3), 2.33(s, 3H, OCH_3), 3.19(t, 1H, J = 11.0, CH_2), 4.24 (t, 1H, J = 4.64 Hz, CH_2), 5.09 (s, 1H, NH), 5.55 (d, 1H, J = 12.0 Hz, CH), 6.73 (d, 2H, J = 8.5 Hz), 6.92 (d, 2H, J = 8.3 Hz), 6.98 (t, 1H, J = 8.3 Hz), 7.14 (d, 1H, J = 8.5 Hz), 7.24 (t, 2H, J = 8.5 Hz), 7.40 (d, 2H, J = 8.5 Hz), 7.65 (d, 2H, J = 8.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): 38.43 (CH_2), 47.37 (OCH_3), 49.94 (OCH_3), 52.44 (CH), 126.35, 126.62, 127.08, 128.14, 128.35, 128.49, 128.97, 129.08, 129.57 (Ar C), 172.00 (C═N), 205.57, 206.56 (CBr); MS (EI, 70 eV) *m/z* (%): 458 (0.25) [M^+], 288 (100), 254 (40), 253 (92).

3-(2-Aminophenylthio)-1-phenyl-3-p-tolylpropan-1-one (37). White crystals; mp 134–139°C; IR (KBr) ν: 3452, 3354, 1678, 1603 1477, 854, 760, 744, 688 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.31 (s, 3H, Me), 3.56 (dd, 1H, J_1 = 17.40 and J_2 = 7.15 Hz, CH_2), 3.64 (dd, 1H, J_1 = 17.4 and J_2 = 7.15 Hz CH_2), 4.46 (s, 2H, NH_2), 4.73 ((t, 1H, J = 7.15 Hz, CH), 6.55 (tt, 1H, J_1 = 7.5 Hz, J_2 = 1.15), 6.70 (d, 1H, J = 7.85 Hz), 7.06 (d, 2H, J = 8.1 Hz), 7.09 (d, 2H, J = 7.6 Hz), 7.15 (d, 2H, J = 8.0 Hz), 7.44 (t, 2H, J = 8.0 Hz), 7.55 (t, 1H, J = 7.4 Hz), 7.89 (d, 2H, J = 7.2 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): 21.10 (CH_3), 44.30 (CH_2), 46.98 (CH), 114.85, 118.05, 127.49, 128.09, 128.60, 129.11, 130.58, 133.18, 136.85, 136.95, 137.65, 138.59, 149.47, 197.28. (Ar C); MS (EI, 70 eV) *m/z* (%): 347.17 (5.18) [M^+], 222.12 (7.99), 221.09 (1.05), 207.04 (2.33), 124.93 (3.60), 104.86 (100.00).

3-(2-Aminophenythio)-3-(4-dimethylamino)phenyl-1-p-tolyl-propan-1-one (38). White crystals; mp 134–136°C; IR (KBr) ν: 3455, 3356, 1672, 1603 818, 790, 741 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.39 (s, 3H, Me), 2.90 (s, 6H, NMe_2), 3.50(dd, 1H, J_1 = 17.4 and J_2 = 7.2 Hz, CH_2), 3.58 (dd, 1H, J_1 = 17.4 J_2 = 7.2 Hz, CH_2), 4.44 (s, 2H, NH_2), 4.68 (t, 1H, J = 6.8 Hz, CH), 6.58 (t, 1H, J = 14.8 Hz), 6.60 (d, 1H, J = 8.8 Hz), 6.69 (d, 2H, J = 6.8 Hz), 7.07–7.15 (m, 3H), 7.21 (d, 2H, J = 8.0 Hz), 7.26 (s, 1H), 7.77 (d, 2H, J = 7.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): 40.66 (Me), 44.31 (NMe_2), 47.17 (NMe_2), 112.48, 114.86, 116.56, 118.07, 128.32, 128.40, 129.32, 130.47, 134.48, 137.78, 143.98, 149.53, 149.85, 197.26 (Ar C). HRMS (EI, 70 eV) *m/z* (%): 390 (0.23) [M^+], 254 (100).

3-(4-Methoxyphenyl)-2-(naphthalen-2-ylmethyl)-2-H-benzo[b][1,4]thiazine (39). Yellow needle crystals; mp 157–158°C (from 5% ethyl acetate/*n*-hexane); IR (KBr) ν: 1601, 1592, 1542, 1249, 838, 821, 726 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.83 (dd, 1H, J_1 = 23.44 Hz, J_2 = 9.52 Hz, CH_2), 3.05 (dd, 1H, J_1 = 19.28 Hz, J_2 = 5.36 Hz, CH_2), 3.84 (s, 3H, OCH_3), 4.25 (dd, 1H, J_1 = 15.12 Hz, J_2 = 5.36 Hz, CH), 6.92 (d, 1H, J = 9.0 Hz), 7.19 (t, 1H, J = 7.36 Hz), 7.25–7.32 (m, 3H) 7.39–7.46 (m, 4H),7.54 (s,1H), 7.58 (d, J = 7.8 Hz), 7.75–7.80 (m, 4H), 7.94 (d, 2H,J = 9.0 Hz).^{13}C NMR (100 MHz, $CDCl_3$): 35.79 (CH_2), 37.21 (CH), 55.42 (OCH_3), 114.04, 119.84, 125.61, 126.06, 126.53, 126.61, 127.61, 127.65, 127.68, 127.99, 128.29, 129.24, 129.73, 132.37, 133.36, 134.87, 143.07, 158.32 (Ar C), 161.80 (C═N); HRMS (EI, 70 eV) *m/z* (%): 395.0 (15) [M^+], 254.0 (100), 239.0 (8.25), 223 (16.8).

X-ray crystallography for 28, 33, and 39. Pale yellow, columnar crystal of **28**, yellow platelet crystal of **33**, and block yellow crystal of **39** were mounted with a cryoloop and flash-cooled by cold nitrogen stream. All measurements were made at 100(2) K on a Rigaku R-AXIS RAPID imaging plate area detector (Chemical and Biophysical Instrumentation Centre (CBIC), Yale, New Haven, CT) with graphite monochromated Mo-Kα radiation. Absorption corrections were applied by the numerical method [47]. Crystal data, together with other relevant information on structure determination, are listed in Table 3. The structure was solved by the direct method using SIR2004 [48] and refined on F^2 with all independent reflections by full-matrix least-square method using SHELXL97 program [49]. The nonhydrogen atoms were

refined anisotropically. Hydrogen atoms were positioned geometrically in a riding model approximation and constrained to refine with the parent atoms with $U_{iso}(H) = 1.2$ or $1.5\,U_{eq}(C)$.

APPENDIX A. ELECTRONIC SUPPLEMENTARY MATERIAL

CCDC 843305, 830818, and 830658 contain the supplementary crystallographic data for **28**, **33**, and **39**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, fax: (+44) 1223-336-033, or e-mail: deposit@ccdc.cam.ac.uk.

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