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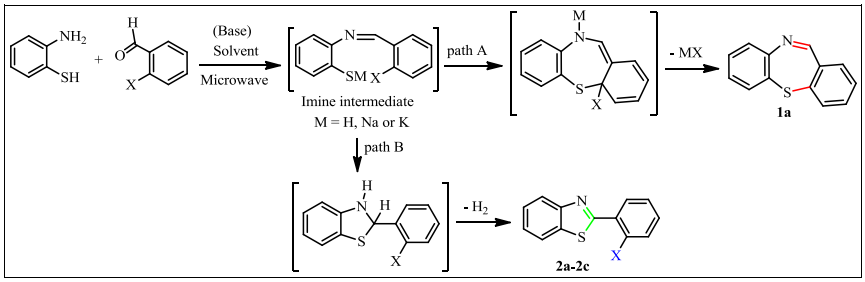

A highly efficient synthesis for possessing 7-membered rings with two heteroatoms is described, using efficient microwave-assisted one-pot method to synthesize (substituted) dibenzo[*b*,*f*][1,4]thiazepines [1] and dibenzo[*b*,*f*][1,4]oxazepines [2] in high yields (up to 99%) by cyclocondensations of *o*-aminothiophenol or *o*-aminophenol with *o*-halobenzaldehydes, *o*-fluoroacetophenone, and *o*-fluorobenzophenone. In the absence of base, *o*-aminothiophenol reacted with *o*-halobenzaldehydes to afford benzothiazoles.

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INTRODUCTION

Many important physiological materials comprise thiazepines [1], oxazepines [2], benzothiazoles, benzimidazoles [3], and the related structures. Dibenzo[*b*,*f*][1,4]thiazepine and dibenzo[*b*,*f*][1,4]oxazepine, the analogs of thiazepine and oxazepine having an additional fused aromatic ring, have also received intensive attention. These compounds possessing 7-membered rings with two heteroatoms have been prepared through various synthetic routes. For example, dibenzo[*b*,*f*][1,4]thiazepine has been prepared from 9*H*-thioxanthen-9-ol with *o*-mesitylenesulfonylhydroxylamine [4] . 1,4-Dibenzothiazepine has been synthesized by reaction of lithiated 2-aminodiphenyl sulfide with DMF [5]. Cyclization of *o*-nitrobenzene halides with *o*-thiosalicylic acid esters, followed by reduction and dehydration, also afford dibenzothiazepine products [6]. We describe herein a novel and efficient synthesis of dibenzo[*b*,*f*][1,4]thiazepines and of the related heteroaromatic derivatives in one-pot procedure.

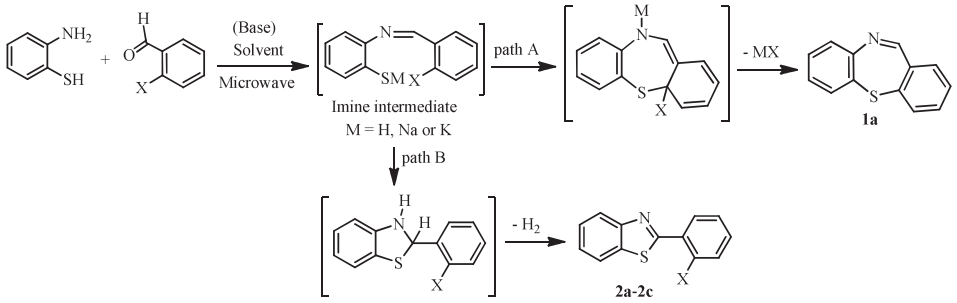
RESULTS AND DISCUSSION

In an attempt to find the optimized condition for the microwave-assisted synthesis of 1,4-benzothiazepine, the cyclocondensations of *o*-aminothiophenol with *o*-halobenzaldehyde were investigated in details with varied reaction factors including time, temperature, solvent, and base (Scheme 1 and Table 1). The microwave-assisted cyclocondensations of *o*-aminothiophenol with *o*-fluorobenzaldehyde were successfully conducted in the solvent of DMF, DMSO, or NMP using *t*-BuOK as the base. The reaction mixture was heated at 100°C under microwave irradiation for 3–7 min to afford 53–82% yield of dibenzo[*b*,*f*][1,4]thiazepine (**1a**) (entries 1–3, pt?>Table 1). The yield of **1a** was greatly increased at elevated reaction temperature. Thus, the cyclocondensation was achieved by microwave irradiation at 120–140°C for 1–3 min in DMF in the presence of *t*-BuOK to afford **1a** in 99% yield (entries 5 and 6, Table 1). In this case, use of a mild base $NaHCO_3$ was inferior, requiring a prolonged reaction time (14 min) to give a moderate yield (57%) of the desired product **1a** (entry 7, Table 1).

The cyclocondensations of *o*-aminothiophenol with *o*-chlorobenzaldehyde, *o*-bromobenzaldehyde, and *o*-iodobenzaldehyde were similarly carried out (entries 8–10, Table 1). Of the four *o*-halobenzaldehydes studied, the relative reactivity of **1a** formation appeared to decrease in the order of F > Cl > Br > I. This is a typical example of element effect. The reaction was considered to proceed with an imine intermediate, followed by intramolecular nucleophilic attack of sulfide to halide (path A). The order of the reaction (F > Cl > Br > I) suggested that an S_NAr mechanism was operating, in which the rate determining step was favored by the nucleophilic substitution at the less hindered and more electronegative floride atom.

To our surprise, the microwave-assisted reactions of *o*-aminothiophenol with *o*-halobenzaldehydes produced good yields (up to 97%) of 2-(*o*-halophenyl)benzothiazoles in the absence of base (entries 11–13, Table 1). Because of the

Scheme 1



high nucleophilicity of thiophenol, attack of imine might be favored to form a benzothiazoline intermediate (path B), which was readily converted to benzothiazoline **2a–c** by autoxidation.

Various methods for the synthesis of dibenzo[*b*,*f*][1,4]oxazepines have been reported in the literature [7–9]. The microwave-assisted cyclocondensation of *o*-aminophenol with *o*-fluorobenzaldehyde always gave dibenzo[*b*,*f*][1,4]oxazepine (**3a**) whether in the presence or absence of base (Scheme 2 and entries 1–3 in Table 2). Phenoxide is a weaker nucleophile than thiophenoxide, so that the formation of **3a** required a prolonged time (20 min) at 140°C in comparison with the reaction of *o*-aminothiophenol (entries 6 and 7, Table 1). The relative reactivity of *o*-halobenzaldehydes in **3a** formation (entries 3–6, Table 2) followed the similar trend (F > Cl > Br > I). Unlike *o*-aminothiophenol, no side product of 2-(*o*-halophenyl) benzoles was observed in the microwave-assisted condensation of *o*-aminothiophenol with *o*-halobenzaldehydes.

In sharp contrast, the microwave-assisted reactions of *o*-phenylenediamine with 2-fluorobenzaldehyde and 2-chlorobenzaldehyde in DMF delivered only 2-arylbenzimidazoles in 93% and 89% yields, respectively (Scheme 2 and entries 8 and 9 in Table 2). No dibenzo[*b*,*f*][1,4]diazepine was formed whether in the presence or absence of base. This microwave-assisted method thus provided an alternative synthesis of 2-arylbenzimidazoles from *o*-phenylenediamine and appropriate aldehydes using air as oxidant without any catalyst [10].

We next explored the effects of substituents on the nucleophile and aldehyde components. The 2-halobenzaldehydes bearing nitro, trifluoromethyl, or methoxy substituents reacted with *o*-aminothiophenol and *o*-aminophenol under microwave irradiation to give the corresponding cyclocondensation products in 51–85% yields (Table 3). The benzaldehydes bearing electron-withdrawing groups (NO_2 or CF_3) inclined to give higher yields of cyclocondensation products than the benzaldehydes bearing electron-donating substituent (OCH_3). The electron donating substituent might retard the efficiency of the incoming *S*- and *O*-nucleophiles. Attempts to carry out the similar cyclocondensation of 6-bromo-3,4-dimethoxybenzaldehyde failed even by microwave irradiation at 200°C for 80 min.

Using substituted nucleophiles in the cyclocondensation reactions with substituted *o*-fluorobenzaldehydes would provide a straightforward method to generate libraries of dibenzo[*b*,*f*][1,4]thiazepines and dibenzo[*b*,*f*][1,4]oxazepines. To demonstrate this application, 2-amino-4-methylphenol and

Table 1

Reactions of *o*-halobenzaldehydes with *o*-aminothiophenol under microwave irradiation.

Entry	X	Base	Solvent	Temperature (°C)	Time (min)	Product (yield, %)
1	F	*t*-BuOK	DMF	100	7	**1a** (82)
2	F	*t*-BuOK	DMSO	100	4	**1a** (65)
3	F	*t*-BuOK	NMP	100	3	**1a** (53)
4	F	*t*-BuOK	DMF	110	3	**1a** (85)
5	F	*t*-BuOK	DMF	120	3	**1a** (99)
6	F	*t*-BuOK	DMF	140	1	**1a** (99)
7	F	$NaHCO_3$	DMF	140	14	**1a** (57)
8	Cl	*t*-BuOK	DMF	120	4	**1a** (99)
9	Br	*t*-BuOK	DMF	120	5	**1a** (99)
10	I	*t*-BuOK	DMF	140	10	**1a** (93)
11	F	–	DMF	140	16	**2a** (97)
12	Cl	–	DMF	140	16	**2b** (92)
13	Br	–	DMF	140	16	**2c** (90)

2-amino-4-chlorophenol were used to react with (substituted) *o*-fluorobenzaldehydes under microwave irradiation at 140°C to afford good yields (60–86%) of the desired cyclocondensation products **5a–h** (Table 4).

Scheme 2

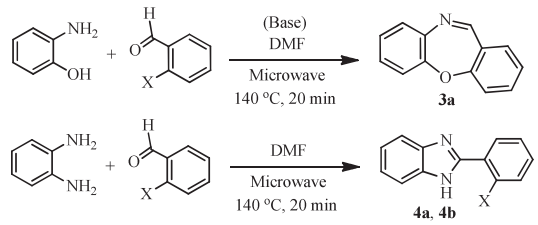


Table 2

Reactions of *o*-aminophenol and *o*-phenylenediamine with *o*-halobenzaldehydes in DMF at 140°C for 20 min under microwave irradiation.

Entry	X	Nucleophile	Base	Product (yield, %)
1	F	*o*-Aminophenol	*t*-BuOK	**3a** (55)
2	F	*o*-Aminophenol	$NaHCO_3$	**3a** (82)
3	F	*o*-Aminophenol	–	**3a** (74)
4	Cl	*o*-Aminophenol	–	**3a** (39)
5	Br	*o*-Aminophenol	–	**3a** (30)
6	I	*o*-Aminophenol	–	**3a** (14)
7	F	*o*-Phenylenediamine[a]	–	**4a** (72)
8	F	*o*-Phenylenediamine	–	**4a** (93)
9	Cl	*o*-Phenylenediamine	–	**4b** (89)

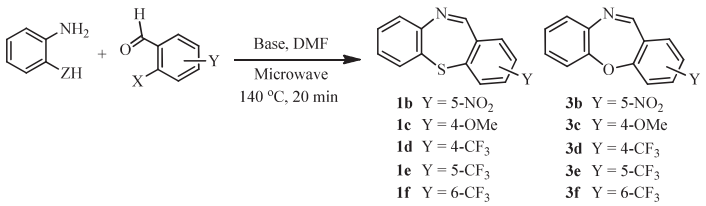
[a]NMP was used as solvent.

In addition to (substituted) *o*-fluorobenzaldehydes, the microwave-assisted cyclocondensation reactions of *o*-fluorophenones were also achieved (Table 5). Using *t*-BuOK as the base, *o*-aminothiophenol was reacted with *o*-fluorobenzophenone under microwave irradiation at 180°C for 20–30 min in NMP to give 67% yield of 11-phenyldibenzo[*b*,*f*][1,4]thiazepine. The yield was increased to 87% when the reaction was conducted at higher temperature (200°C). The reaction of *o*-aminophenol with *o*-fluorobenzophenone in the presence of *t*-BuOK occurred in a similar manner to afford a 49% yield of 11-phenyldibenzo[*b*,*f*][1,4]oxazepine (entry 3, Table 5). The microwave-assisted reaction of *o*-aminophenol with *o*-fluoroacetophenone in NMP occurred at 180°C to give the corresponding 11-methyldibenzo[*b*,*f*][1,4]oxazepine in 62% yield (entry 4, Table 5). In general, the cyclocondensation reactions of phenones required higher reaction temperature and longer times than the reactions of benzaldehydes. The yields of the cyclocondensations appeared to decrease with bulkier substrates.

In conclusion, we have successfully demonstrated a novel and efficient microwave-assisted one-pot method to synthesize (substituted) dibenzo[*b*,*f*][1,4]thiazepines and dibenzo[*b*,*f*][1,4]oxazepines in high yields (up to 99%) by cyclocondensations of *o*-aminothiophenol or *o*-aminophenol with *o*-halobenzaldehydes, *o*-fluoroacetophenone, and *o*-fluorobenzophenone. In the absence of base, *o*-aminothiophenol and *o*-phenylenediamine reacted with *o*-halobenzaldehydes to afford benzothiazoles and benzimidazoles.

Table 3

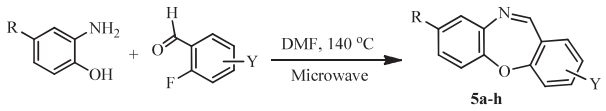
Reactions of substituted *o*-halobenzaldehydes with *o*-aminothiophenol and *o*-aminophenol in DMF at 140°C under microwave irradiation.



Entry	X	Y	Z	Base	Time (min)	Product (yield, %)
1	Cl	5-NO_2	S	*t*-BuOK	10	74
2	F	4-OMe	S	$NaHCO_3$	30	52
3	F	4-CF_3	S	$NaHCO_3$	15	67
4	F	5-CF_3	S	$NaHCO_3$	15	79
5	F	6-CF_3	S	$NaHCO_3$	10	85
6	F	6-CF_3	S	*t*-BuOK	10	67
7	Cl	5-NO_2	O	$NaHCO_3$	18	73
8	F	4-OMe	O	$NaHCO_3$	20	51
9	F	4-CF_3	O	$NaHCO_3$	30	60
10	F	5-CF_3	O	$NaHCO_3$	30	73
11	F	6-CF_3	O	$NaHCO_3$	30	72

Table 4

Reactions of *p*-methyl-*o*-aminophenol and *p*-chloro-*o*-aminophenol with substituted *o*-fluorobenzaldehydes in DMF at 140°C under microwave irradiation.



Entry	R	Y	Base	Time (min)	Product (yield, %)
1	Me	H	–	20	**5a** (76)
2	Me	H	$NaHCO_3$	20	**5a** (86)
3	Me	4-OMe	$NaHCO_3$	20	**5b** (84)
4	Me	5-CF_3	$NaHCO_3$	20	**5c** (63)
5	Me	6-CF_3	$NaHCO_3$	20	**5d** (78)
6	Cl	H	$NaHCO_3$	14	**5e** (71)
7	Cl	4-OMe	$NaHCO_3$	20	**5f** (66)
8	Cl	5-CF_3	$NaHCO_3$	30	**5g** (60)
9	Cl	6-CF_3	$NaHCO_3$	25	**5h** (83)

EXPERIMENTAL

^{1}H NMR spectra were measured in DMSO-d_6 solution on a Varian Inova 600 (California, USA) spectrometer. Reactions were monitored by analytical thin-layer chromatography using silica gel 60 F-254 (0.2 mm layer thickness). Flash chromatography was carried out by utilizing silica gel 60 (70–230 mesh ASTM).

General procedure for the reaction of *o*-halobenzaldehydes with nucleophiles. In a reaction vessel (12 mL), a nucleophile (0.11 mmol) and an *o*-halobenzaldehyde (0.1 mmol) in an appropriate solvent (1 mL) were placed. A base *t*-BuOK or $NaHCO_3$ (2.0 equiv versus nucleophile) could be added in appropriate cases. The reaction vessel was then placed into the cavity of a focused monomode microwave reactor (CEM Discover) and irradiated for the period listed in Tables 1–5. The reaction temperature was maintained by modulating the power level of the reactor. The desired products were purified by silica gel chromatography eluting with a mixture of hexane and ethyl acetate.

***Dibenzo[b,f][1,4]thiazepine.* (1a)**. Yield: 0.021 g (99%); yellow solid, mp 130–132°C; IR (ν, cm^{-1}, KBr) 2923, 1616, 1577, 1496; ^{1}H NMR (600 MHz, DMSO-d_6) δ8.95 (s, 1H), 7.58–7.56 (m, 2H), 7.34–7.29 (m, 3H), 7.27–7.22 (m, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ162.6, 148.2, 138.2, 136.8, 132.6, 131.9, 131.3, 129.9, 129.6, 128.8, 128.0, 127.3, 126.5; MS m/e 211 (M^+), 179, 167, 91, 69; HRMS m/e Calcd for 211.2868, found 211.0461. *Anal*. Calcd for $C_{13}H_9NS$; C, 73.90; H, 4.29; N, 6.63. Found: C, 74.42; H, 4.44; N, 6.65.

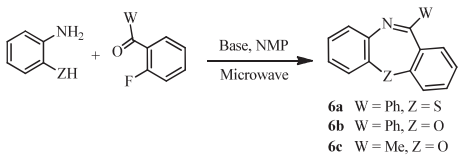
***2-Nitrodibenzo[b,f][1,4]thiazepine.* (1b)**. Yield: 0.019 g (74%); yellow solid, mp 199–201°C; IR (ν, cm^{-1}, KBr) 2921, 1617, 1456, 1317, 1112. ^{1}H NMR (600 MHz, DMSO-d_6) δ9.05 (s, 1H, NCH), 8.51 (d, J = 2.4 Hz, 1H), 8.29 (dd, J = 9.0, 2.4 Hz, 1H),, 7.74 (d, J = 9.0 Hz, 1H), 7.49–7.44 (m, 2H), 7.32–7.28 (m, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ161.1, 147.9, 147.6, 146.2, 137.3, 133.0, 132.7, 130.3, 127.9, 126.7, 126.5, 126.2, 124.9; MS m/e 256 (M^+), 210, 166, 69; HRMS m/e Calcd for 256.2824, found 256.0301. *Anal*. Calcd for $C_{13}H_8N_2O_2S$; C, 60.92; H, 3.14; N, 10.93. Found: C, 60.75; H, 3.01; N, 10.81.

***3-Methoxydibenzo[b,f][1,4]thiazepine.* (1c)**. Yield: 0.013 g (52%); yellow liquid; IR (ν, cm^{-1}, KBr) 2924, 1655, 1596, 1253, 1025. ^{1}H NMR (600 MHz, DMSO-d_6) δ8.82 (s, 1H, NCH), 7.54 (d, J = 8.4 Hz, 1H), 7.42 (dd, J = 8.4, 1.2 Hz, 1H), 7.39 (td, J = 8.4, 1.2 Hz, 1H), 7.25–7.22 (m, 2H), 7.04–7.02 (m, 2H), 3.80 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ162.0, 161.9, 148.5, 139.6, 132.6, 131.8, 129.7, 129.6, 127.6, 127.1, 126.6, 116.0, 114.6, 55.8; MS m/e 241 (M^+), 149, 135, 121, 107; HRMS m/e Calcd for 241.3126, found 241.0565. *Anal*. Calcd for $C_{14}H_{11}NOS$; C, 69.68; H, 4.59; N, 5.80. Found: C, 69.82; H, 4.68; N, 5.83.

***3-(Trifluoromethyl)dibenzo[b,f][1,4]thiazepine.* (1d)**. Yield: 0.019 g (67%); white solid, mp 79–81°C; IR (ν, cm^{-1}, KBr) 2936, 1587, 1480, 1227, 1025. ^{1}H NMR (600 MHz, DMSO-d_6) δ9.06 (s, 1H, NCH), 7.88–7.84 (m, 2H), 7.83 (br, 1H), 7.48 (dd, J = 7.8, 1.2 Hz, 1H), 7.44 (td, J = 7.8, 1.2 Hz, 1H), 7.31 (dd, J = 7.8, 1.2 Hz, 1H), 7.28 (td, J = 7.8, 1.2 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ161.7, 148.0, 140.0, 139.6, 132.9, 130.9, 130.1, 127.9 (2C), 127.7, 127.2, 126.6, 125.8 (2C); MS m/e 279 (M^+), 149, 135, 69, 57; HRMS m/e Calcd for 279.2854, found 279.0336. *Anal*. Calcd for $C_{14}H_8NSF_3$; C, 60.21; H, 2.89; N, 5.02; Found: C, 60.52; H, 2.99; N, 5.13.

Table 5

Reactions of *o*-aminothiophenol and *o*-aminophenol with phenones in NMP under microwave irradiation.



Entry	Nucleophile	Base	W	Z	Temperature (°C)	Time (min)	Product (yield, %)
1	*o*-Aminothiophenol	*t*-BuOK	Ph	S	180	20	67
2	*o*-Aminothiophenol	*t*-BuOK	Ph	S	200	30	87
3	*o*-Aminophenol	*t*-BuOK	Ph	O	200	60	49
4	*o*-Aminophenol	$NaHCO_3$	Me	O	180	30	62

***2-(Trifluoromethyl)dibenzo[b,f][1,4]thiazepine.* (1e)**. Yield: 0.022 g (79%); yellow liquid; IR (ν, cm^{-1}, KBr) 2926, 1587, 1482, 1327, 1120. ^1H NMR (600 MHz, DMSO-d_6) δ9.02 (s, 1H, NCH), 8.07 (d, J = 1.8 Hz, 1H), 7.86 (dd, J = 8.4, 1.8 Hz, 1H), 7.70 (d, J = 8.4 Hz, 1H), 7.48–7.42 (m, 2H), 7.31–7.26 (m, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ161.6, 148.0, 143.3, 137.2, 132.9, 132.3, 130.1, 128.3 (2C), 127.7, 127.0, 126.9 (2C), 126.6; MS m/e 279 (M^+), 210, 135, 69, 57; HRMS m/e Calcd for 279.2854, found 279.0338. *Anal.* Calcd for $C_{14}H_8NSF_3$; C, 60.21; H, 2.89; N, 5.02; Found: C, 60.45; H, 3.01; N, 5.07.

***1-(Trifluoromethyl)dibenzo[b,f][1,4]thiazepine.* (1f)**. Yield: 0.024 g (85%); white solid, mp 144–146°C; IR (ν, cm^{-1}, KBr) 2923, 1606, 1460, 1327, 1120. ^1H NMR (600 MHz, DMSO-d_6) δ9.13 (s, 1H, NCH), 7.84 (d, J = 7.8 Hz, 2H), 7.69 (t, J = 7.8 Hz, 1H), 7.49 (dd, J = 7.8, 1.2 Hz, 1H), 7.43 (td, J = 7.8, 1.2 Hz, 1H), 7.29 (dd, J = 7.8, 1.2 Hz, 1H), 7.24 (td, J = 7.8, 1.2 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ159.0, 147.9, 142.8, 136.0, 132.8, 132.5, 131.9, 130.1, 127.6 (2C), 127.1, 126.7, 126.6, 125.1; MS m/e 279 (M^+), 210, 135, 69, 57; HRMS m/e Calcd for 279.2854, found 279.0338. *Anal*. Calcd for $C_{14}H_8NSF_3$; C, 60.21; H, 2.89; N, 5.02; Found: C, 60.57; H, 2.96; N, 5.09.

***2-(2-Fluorophenyl)benzo[d]*thiazole. (2a)**. Yield: 0.022 g (97%); white solid, mp 95–98°C; IR (ν, cm^{-1}, KBr) 2924, 1630, 1582, 1453; ^1H NMR (600 MHz, DMSO-d_6) δ 8.39–8.36 (m, 1H), 8.20–8.19 (m, 1H), 8.13–8.12 (m, 1H), 7.67–7.63 (m, 1H), 7.60–7.58 (m, 1H), 7.52–7.48 (m, 2H), 7.46–7.43 (m, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ160.7, 159.0, 152.0, 133.2, 133.1, 129.3, 126.7, 125.7, 125.4, 123.0, 122.2, 116.8, 116.6; MS m/e 229 (M^+), 108, 69; HRMS m/e Calcd for 229.2773, found 229.0358. *Anal*. Calcd for $C_{13}H_8NSF$; C, 68.10; H, 3.52; N, 6.10. Found: C, 68.01; H, 3.38; N, 5.96.

***2-(2-Chlorophenyl)benzo[d]*thiazole. (2b)**. Yield: 0.023 g (92%); white solid, mp 90–92°C; IR (ν, cm^{-1}, KBr) 2925, 1631, 1580, 1454; ^1H NMR (600 MHz, DMSO-d_6) δ 8.20 (d, J = 1.2 Hz, 1H), 8.18 (d, J = 1.2 Hz, 1H), 8.12 (d, J = 8.4 Hz, 1H), 7.71–7.69 (m, 1H), 7.61–7.51 (m, 4H); ^{13}C NMR (150 MHz, DMSO-d_6) δ163.5, 152.1, 135.5, 132.3, 131.8, 131.6, 131.5, 131.0, 128.0, 126.9, 126.0, 123.3, 122.3; MS m/e 245 (M^+), 210, 108; HRMS m/e Calcd for 245.7259, found 245.0067. *Anal*. Calcd for $C_{13}H_8NSCl$; C, 63.54; H, 3.28; N, 5.70. Found: C, 63.18; H, 3.07; N, 5.38.

***2-(2-Bromophenyl)benzo[d]*thiazole. (2c)**. Yield: 0.026 g (90%); pale yellow solid, mp 63–65°C; IR (ν, cm^{-1}, KBr) 2924, 1629, 1580, 1454; ^1H NMR (600 MHz, DMSO-d_6) δ 8.18 (d, J = 7.8 Hz, 1H), 8.11 (d, J = 7.8 Hz, 1H), 8.00 (dd, J = 7.8, 1.2 Hz, 1H), 7.85 (d, J = 8.4 Hz, 1H), 7.60–7.56 (m, 2H), 7.53–7.48 (m, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ165.1, 152.4, 135.6, 134.2, 133.8, 132.3, 132.2, 128.3, 126.8, 126.0, 123.3, 122.3, 121.3; MS m/e 289 (M^+), 210, 108; HRMS m/e Calcd for 290.1769, found 288.9564. *Anal*. Calcd for $C_{13}H_8NSBr$; C, 53.81; H, 2.78; N, 4.82. Found: C, 53.64; H, 2.49; N, 4.98.

***Dibenzo[b,f][1,4]*oxazepine [8]. (3a)**. Yield: 0.014 g (74%); yellow solid, mp 70–72°C, (lit. 67–70°C); ^1H NMR (600 MHz, DMSO-d_6) δ8.63 (s, 1H), 7.62–7.60 (m, 1H), 7.51–7.47 (m, 3H), 7.45–7.44 (m, 1H), 7.41–7.38 (m, 1H), 7.28–7.26 (m, 1H), , 7.25–7.22 (m, 1H) ; ^{13}C NMR (150 MHz, DMSO-d_6) δ160.9, 159.6, 152.1, 140.3, 133.8, 130.5, 128.9, 128.6, 126.9, 125.9, 125.5, 121.3, 120.4; MS m/e 195 (M^+), 167, 139, 89; HRMS m/e Calcd for 195.2258, found 195.0677.

***2-Nitrodibenzo[b,f][1,4]*oxazepine. (3b)**. Yield: 0.018 g (73%); white solid, mp 160–162°C; ^1H NMR (600 MHz, DMSO-d_6) δ8.72 (s, 1H, NCH), 8.54 (d, J = 3.0 Hz, 1H), 8.42 (dd, J = 9.0, 3.0 Hz, 1H), 7.51(d, J = 9.0 Hz, 1H), 7.38–7.35 (m, 2H), 7.31–7.29 (m, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ164.1, 159.3, 151.1, 144.7, 139.7, 129.6, 129.0, 128.9, 127.3, 126.7, 126.5, 122.1, 121.6; MS m/e 240 (M^+), 194, 166, 139; HRMS m/e Calcd for 240.2178, found 240.0544. *Anal*. Calcd for $C_{13}H_9N_2O_3$; C, 65.00; H, 3.25; N, 11.66. Found: C, 64.88; H, 3.29; N, 11.73.

***3-Methoxydibenzo[b,f][1,4]*oxazepine. (3c)**. Yield: 0.012 g (51%); yellow liquid, IR (ν, cm^{-1}, KBr) 2923, 1603, 1499, 1208, 1029; ^1H NMR (600 MHz, DMSO-d_6) δ8.48 (s, 1H, NCH), 7.49 (d, J = 8.4 Hz, 1H), 7.29–7.27 (m, 2H), 7.24–7.19 (m, 2H), 6.88 (dd, J = 8.4, 2.4 Hz, 1H), 6.85 (d, J = 2.4 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ163.9, 161.1, 160.4, 151.8, 140.5, 131.9, 128.7, 128.6, 125.9, 121.4, 119.9, 111.5, 105.8, 55.9; MS m/e 225 (M^+), 149, 135, 107; HRMS m/e Calcd for 225.2456, found 225.0787. *Anal*. Calcd for $C_{14}H_{11}NO_2$; C, 74.65; H, 4.92; N, 6.22. Found: C, 74.52; H, 5.33; N, 6.12.

***3-(Trifluoromethyl)dibenzo[b,f][1,4]*oxazepine. (3d)**. Yield: 0.016 g (60%); yellow solid, mp 48–50°C; IR (ν, cm^{-1}, KBr) 2925, 1621, 1423, 1325, 1127; ^1H NMR (600 MHz, DMSO-d_6) δ8.74 (s, 1H, NCH), 7.83 (d, J = 7.8 Hz, 1H), 7.73–7.72 (m, 2H), 7.38–7.32 (m, 3H), 7.30–7.27 (m, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ159.9, 159.6, 151.5, 139.9, 131.7, 130.2, 129.5, 128.8, 126.4, 122.4 (2C), 121.5, 117.8 (2C); MS m/e 263 (M^+), 149, 69, 57; HRMS m/e Calcd for 263. 2181, found 263.0550. Calcd for $C_{14}H_8NOF_3$; C, 63.88; H, 3.06; N, 5.32. Found: C, 63.92; H, 3.26; N, 5.25.

***2-(Trifluoromethyl)dibenzo[b,f][1,4]*oxazepine. (3e)**. Yield: 0.019 g (73%); yellow solid, mp 80–82°C; IR (ν, cm^{-1}, KBr) 2919, 1617, 1473, 1335, 1116. ^1H NMR (600 MHz, DMSO-d_6) δ8.71 (s, 1H, NCH), 8.06 (d, J = 2.4 Hz, 1H), 7.96 (dd, J = 8.4, 2.4 Hz,, 1H), 7.49 (d, J = 8.4 Hz, 1H), 7.37–7.34 (m, 2H), 7.30–7.28 (m, 2H); MS m/e 263 (M^+), 244, 235, 166, 139, 69, 57; ^{13}C NMR (150 MHz, DMSO-d_6) δ162.3, 159.7, 151.4, 139.9, 130.7 (2C), 129.4, 128.9, 128.1 (2C), 127.3, 126.4, 121.7, 121.5; HRMS m/e Calcd for 263.2181, found 263.0552. *Anal*. Calcd for $C_{14}H_8NOF_3$; C, 63.88; H, 3.06; N, 5.32. Found: C, 63.99; H, 3.28; N, 4.93.

***1-(Trifluoromethyl)dibenzo[b,f][1,4]*oxazepin. (3f)**. Yield: 0.018 g (72%); white solid, mp 96–101°C; IR (ν, cm^{-1}, KBr) 2923, 1455, 1314, 1116. ^1H NMR (600 MHz, DMSO-d_6) δ8.85 (s, 1H, NCH), 7.81 (t, J = 7.8 Hz, 1H), 7.73 (d, J = 7.8 Hz, 1H), 7.69 (d, J = 7.8 Hz, 1H), 7.39 (dd, J = 7.8, 1.2 Hz, 1H), 7.37–7.29 (m, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ161.9, 156.1, 151.4, 139.9, 134.1, 129.1, 127.7, 126.5, 125.6, 123.4, 123.3 (2C), 121.0 (2C); MS m/e 263 (M^+), 147, 69, 57; HRMS m/e Calcd for 263.2181, found 263.0552. *Anal*. Calcd for $C_{14}H_8NOF_3$; C, 63.88; H, 3.06; N, 5.32. Found: C, 63.95; H, 3.35; N, 5.21.

***2-(2-Fluorophenyl)-1H-*benzo[d]imidazole. (4a)**. Yield: 0.020 g (93%); white solid, mp 232–235°C; IR (ν, cm^{-1}, KBr) 2919, 1622, 1584, 1220; ^1H NMR (600 MHz, DMSO-d_6) δ12.61 (s, 1H, NCH), 8.23 (td, J = 7.8, 1.8 Hz, 1H), 7.69 (d, J = 7.8 Hz, 1H), 759–7.55 (m, 2H), 7.46–7.38 (m, 2H), 7.26–7.20 (m, 2H) ; ^{13}C NMR (150 MHz, DMSO-d_6) δ160.3, 158.7, 146.5, 143.0, 135.1, 131.9, 130.3, 125.2, 122.9, 122.0, 119.0, 116.5, 112.0; MS m/e 212 (M^+), 193, 91, 75; HRMS m/e Calcd for 212.2259, found 212.0748. *Anal*. Calcd for $C_{13}H_9N_2F$; C, 73.57; H, 4.27; N, 13.20. Found: C, 73.78; H, 4.62; N, 13.03.

***2-(2-Chlorophenyl)-1H-*benzo[d]imidazole. (4b)**. Yield: 0.020 g (89%); white solid, mp 246–248°C; IR (ν, cm^{-1}, KBr) 2923, 1622, 1590, 1230, 1055; ^1H NMR (600 MHz, DMSO-d_6) δ12.72 (s, 1H, NCH), 7.90 (dd, J = 7.8, 1.8 Hz, 1H), 7.73

(d, J = 7.8 Hz, 1H), 7.65 (dd, J = 7.8, 1.8 Hz, 1H), 7.58–7.50 (m, 3H), 7.26–7.22 (m, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ149.1, 143.2, 134.6, 132.1, 131.6, 131.2, 130.3, 130.0, 127.4, 122.7, 121.7, 119.1, 111.7; MS m/e 228.5 (M^+), 193, 114, 75; HRMS m/e Calcd for 228.5505, found 228.0448. *Anal*. Calcd for $C_{13}H_9N_2Cl$; C, 68.26; H, 3.96; N, 12.26. Found: C, 68.58; H, 4.09; N, 12.11.

***8-Methyldibenzo[b,f][1,4]oxazepine.* (5a)**. Yield: 0.018 g (86%); pale yellow liquid; IR (v, cm^{-1}, KBr) 2923, 1604, 1478; ^{1}H NMR (600 MHz, DMSO-d_6) δ8.61 (s, 1H, NCH), 7.57–7.55 (m, 2H), 7.32–7.29 (m, 1H), 7.23 (d, J = 7.8 Hz, 1H), 7.13 (s, 1H), 7.09 (br, 2H) , 2.26 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ160.9, 159.7, 149.9, 139.9, 135.2, 133.7, 130.5, 129.3, 128.8, 126.9, 125.4, 120.9, 120.3, 20.1; MS m/e 209 (M^+), 180, 58; HRMS m/e Calcd for 209.2466, found 209.0848. *Anal*. Calcd for $C_{14}H_{11}NO$; C, 80.36; H, 5.30; N, 6.69. Found: C, 80.19; H, 5.08; N, 6.38.

***8-Methyl-3-methoxydibenzo[b,f][1,4]oxazepine.* (5b)**. Yield: 0.020 g (84%); yellow liquid; IR (v, cm^{-1}, KBr) 2924, 1602, 1483, 1124; ^{1}H NMR (600 MHz, DMSO-d_6) δ8.45 (s, 1H, NCH), 7.47 (d, J = 8.4 Hz, 1H), 7.09–7.07 (m, 3H), 7.59 (s, 1H), 6.86 (dd, J = 8.4, 2.4 Hz, 1H), 6.81 (d, J = 2.4 Hz, 1H), 3.81 (s, 3H), 2.62 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ163.8, 161.2, 160.3, 149.6, 140.1, 135.1, 131.9, 128.9, 128.8, 121.0, 119.9, 111.3, 105.7, 55.8, 20.1; MS m/e 239 (M^+), 210, 149, 135, 57; HRMS m/e Calcd for 239.2724 found 239.0945. *Anal*. Calcd for $C_{15}H_{13}NO_2$; C, 75.29; H, 5.48; N, 5.85. Found: C, 75.13; H, 5.38; N, 5.66.

***8-Methyl-2-(trifluoromethyl)dibenzo[b,f][1,4]oxazepine.* (5c)**. Yield: 0.018 g (63%); white solid, mp 68–70°C; IR (v, cm^{-1}, KBr) 2922, 1612, 1456, 1373, 1123. ^{1}H NMR (600 MHz, DMSO-d_6) δ8.66 (s, 1H, NCH), 8.01 (d, J = 1.8 Hz, 1H), 7.92 (dd, J = 9.0, 1.8 Hz, 1H), 7.44 (d, J = 9.0 Hz, 1H), 7.15–7.13 (m; 3H), 2.27 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ162.6, 159.9, 149.5, 139.6, 136.1, 130.9, 130.0, 129.2, 128.3, 127.6, 126.5, 126.3, 121.9, 121.3, 20.3; MS m/e 277 (M^+), 258, 248, 69, 57; HRMS m/e Calcd for 277.2457, found 277.0722. *Anal*. Calcd for $C_{15}H_{10}NOF_3$; C, 64.98; H, 3.63; N, 5.05. Found: C, 65.12; H, 3.90; N, 4.89.

***8-Methyl-1-(trifluoromethyl)dibenzo[b,f][1,4]oxazepine.* (5d)**. Yield: 0.022 g (78%); white solid, mp 75–77°C; IR (v, cm^{-1}, KBr) 2923, 1603, 1455, 1315, 1118. ^{1}H NMR (600 MHz, DMSO-d_6) δ8.82 (s, 1H, NCH), 7.79 (t, J = 7.8 Hz, 1H), 7.71 (d, J = 7.8 Hz, 1H), 7.66 (d, J = 7.8 Hz, 1H), 7.21–7.19 (m, 2H), 7.14 (dd, J = 7.8, 1.8 Hz, 1H) , 2.28 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ162.0, 156.0, 149.7, 139.5, 135.9, 134.0, 129.5 (2C),, 127.8, 125.6, 123.5, 123.2 (2C), 120.6, 20.2; ; MS m/e 277 (M^+), 248, 149, 57; HRMS m/e Calcd for 277.2457, found 277.0721. *Anal*. Calcd for $C_{15}H_{10}NOF_3$; C, 64.98; H, 3.63; N, 5.05. Found: C, 65.11; H, 3.77; N, 5.16.

***8-Chlorodibenzo[b,f][1,4]oxazepine.* (5e)**. Yield: 0.016 g (71%); yellow solid, mp 74–76°C; IR (v, cm^{-1}, KBr) 2922, 1605, 1468; ^{1}H NMR (600 MHz, DMSO-d_6) δ8.68 (s, 1H, NCH), 7.62–7.59 (m, 2H), 7.37–7.33 (m, 3H), 7.28–7.26 (m, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ162.5, 159.4, 150.9, 141.4, 134.2, 130.8, 129.6, 128.5, 127.9, 126.7, 125.8, 123.0, 120.5; MS m/e 229 (M^+), 201, 166, 139; HRMS m/e Calcd for 229.6646, found 229.0301. *Anal*. Calcd for $C_{13}H_8NOCl$; C, 67.98; H, 3.51; N, 6.10. Found: C, 68.15; H, 4.01; N, 5.72.

***8-Chloro-3-methoxydibenzo[b,f][1,4]oxazepine.* (5f)**. Yield: 0.017 g (66%); pale yellow solid, mp 100–102°C; IR (v, cm^{-1}, KBr) 2925, 1608, 1468, 1291, 1130. ^{1}H NMR (600 MHz, DMSO-d_6) δ8.41 (s, 1H, NCH), 7.43 (d, J = 8.4 Hz, 1H), 7.29 (dd, J = 8.4, 2.4 Hz, 1H), 7.24 (d, J = 2.4 Hz, 1H), 7.19 (d, J = 8.4 Hz, 1H), 6.84 (dd, J = 8.4, 1.8 Hz, 1H), 6.80 (d, J = 1.8 Hz, 1H), 3.75 (s, 3H, OCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ165.9, 163.8, 162.2, 151.9, 141.9, 133.9, 131.4, 130.0, 128.7, 124.5, 120.5, 113.1, 107.2, 57.1; MS m/e 259 (M^+), 244, 196, 63. HRMS m/e Calcd for 259.6916, found 259.0393; *Anal*. Calcd for $C_{14}H_{10}NO_2Cl$; C, 64.75; H, 3.88; N, 5.39. Found: C, 64.96; H, 4.03; N, 5.11.

***8-Chloro-2-(trifluoromethyl)dibenzo[b,f][1,4]oxazepine.* (5g)**. Yield: 0.018 g (60%); yellow solid, mp 79–81°C; IR (v, cm^{-1}, KBr) 2922, 1672, 1496, 1324, 1109. ^{1}H NMR (600 MHz, DMSO-d_6) δ8.75 (s, 1H, NCH), 8.09 (d, J = 1.8 Hz, 1H), 7.99 (dd, J = 8.4, 1.8 Hz, 1H), 7.50 (d, J = 8.4 Hz, 1H), 7.42–7.40 (m, 2H), 7.34–7.32 (m, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ162.1, 161.3, 150.3, 141.0, 131.1 (2C), 130.2, 128.9, 128.4 (2C), 128.1, 127.2, 123.2, 121.9; MS m/e 297 (M^+), 239, 191, 69, 57; HRMS m/e Calcd for 297.6629, found 297.0163. *Anal*. Calcd for $C_{14}H_7NOClF_3$; C, 56.49; H, 2.37; N, 4.70. Found: C, 56.62; H, 2.57; N, 4.49.

***8-Chloro-1-(trifluoromethyl)dibenzo[b,f][1,4]oxazepin.* (5h)**. Yield: 0.025 g (83%); white solid, mp 90–92°C; IR (v, cm^{-1}, KBr) 2923, 1624, 1455, 1311, 1107. ^{1}H NMR (600 MHz, DMSO-d_6) δ8.88 (s, 1H, NCH), 7.83 (t, J = 7.8 Hz, 1H), 7.75 (d, J = 7.8, 1H), 7.71 (d, J = 7.8 Hz, 1H), 7.47 (d, J = 2.4 Hz, 1H), 7.43–7.38 (m, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ161.8, 157.7, 150.8, 140.9, 134.5, 130.3, 128.8, 127.0 125.7, 123.7, 123.6, 123.2, 122.8, 122.2; MS m/e 297 (M^+), 262, 242, 234, 63; HRMS m/e Calcd for 297.6629, found 297.0165. *Anal*. Calcd for $C_{14}H_7NOClF_3$; C, 56.49; H, 2.37; N, 4.70. Found: C, 56.71; H, 2.59; N, 4.71.

***11-Phenyldibenzo[b,f][1,4]thiazepine.* (6a)**. Yield: 0.025 g (87%); Yellow solid, mp 118–120°C; IR (v, cm^{-1}, KBr) 2923, 1610, 1578, 1443; ^{1}H NMR (600 MHz, DMSO-d_6) δ7.73–7.71 (m, 2H), 7.61 (dd, J = 7.8, 1.2, 1H), 7.56–7.53 (m, 2H), 7.52–7.49 (m, 3H), 7.44–7.38 (m, 2H), 7.33–7.32 (m, 1H), 7.21 (dd, J = 7.8, 1.2, 1H), 7.16 (td, J = 7.8, 1.2, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ167.8, 148.3, 140.1, 139.7, 136.5, 132.3, 132.0, 131.6, 131.0, 130.3, 129.6, 129.2 (2C), 128.5, 128.4 (2C), 127.9, 126.0, 125.2; MS m/e 287 (M^+), 254, 167, 91, 77; HRMS m/e Calcd for 287.3824, found 287.0762. *Anal*. Calcd for $C_{19}H_{13}NS$; C, 79.41; H, 4.56; N, 4.87; Found: C, 79.50; H, 5.05; N, 4.47.

***11-Phenyldibenzo[b,f][1,4]oxazepine.* (6b)**. Yield: 0.013 g (49%); yellow liquid; IR (v, cm^{-1}, KBr) 2924, 1594, 1447; ^{1}H NMR (600 MHz, DMSO-d_6) δ7.78–7.77 (m, 2H), 7.65–7.63 (m, 1H), 7.57 (t, J = 7.2 Hz, 1H), 7.52 (t, J = 7.2 Hz, 2H), 7.43–7.40 (m, 2H), 7.32–7.30 (m, 1H), 7.29–7.26 (m, 3H), 7.19 (dd, J = 7.8, 1.2 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ166.3, 161.3, 151.9, 140.3, 139.2, 133.7, 130.9, 130.8, 129.3 (2C), 128.4 (2C), 127.9, 127.6, 126.4, 125.9, 125.1, 121.0, 120.8; MS m/e 271 (M^+), 241, 139, 77; HRMS m/e Calcd for 271.3174, found 271.0988; *Anal*. Calcd for $C_{19}H_{13}NO$; C, 84.11; H, 4.82; N, 5.16. Found: C, 84.42; H, 4.95; N, 5.01.

***11-Methyldibenzo[b,f][1,4]oxazepine.* (6c)**. Yield: 0.013 g (62%); White solid, mp 94–96°C; IR (v, cm^{-1}, KBr) 2919, 1597, 1444, 1366; ^{1}H NMR (600 MHz, DMSO-d_6) δ7.66 (dd, J = 7.8, 1.2 Hz, 1H), 7.54 (td, J = 7.8, 1.2 Hz, 1H), 7.31–7.29 (m, 2H), 7.24–7.18 (m, 4H), 2.59 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ167.4, 160.1, 152.0, 140.4, 133.3, 129.0, 128.4, 127.4, 127.3, 125.8, 125.6, 120.7, 120.6, 27.4; MS m/e 209 (M^+), 194, 180, 139; HRMS m/e Calcd for 209.2466, found 209.0833. *Anal*. Calcd for $C_{14}H_{11}NO$; C, 80.36; H, 5.29; N, 6.69. Found: C, 80.62; H, 5.54; N, 6.43.

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