Organocatalytic Green Approach Towards the Fabrication of Fused Benzo *N*,*N*-containing Heterocycles Facilitated by Ultrasonic Irradiation

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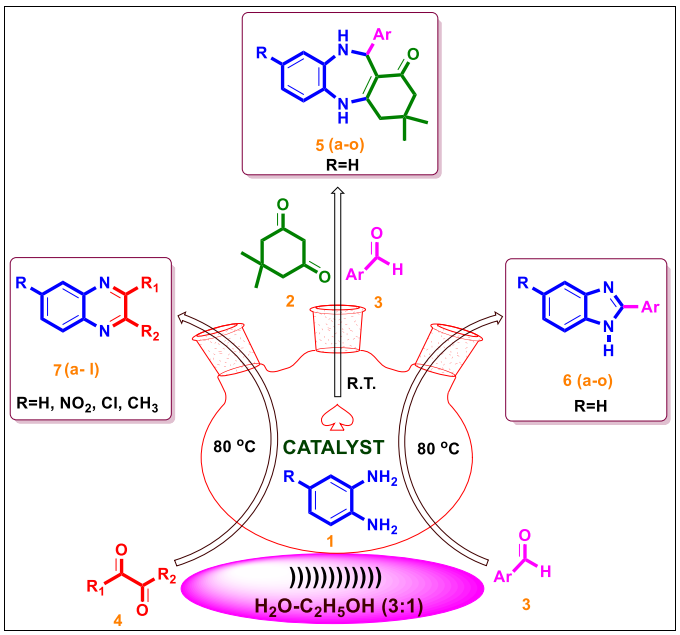

The development of a metal-free protocol for transformations in organic synthesis offers a significant potential environmental benefit. This article reports the exploration of meglumine, a nontoxic and biodegradable amino sugar, as an organocatalyst for the synthesis of biologically active 1*H*-dibenzo[*b*,*e*][1,4]diazepin-1-ones, highly regioselective benzimidazole derivatives and derivatives of quinoxalines. Operational simplicity, mild reaction conditions, shorter reaction times, and use of green solvents are the highlights of this protocol. The advantage of ultrasonic irradiation has been significantly explored for the synthesis of the aforesaid compounds. Furthermore, the multifaceted use of *o*-phenylenediamine has also been accentuated in the study.

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INTRODUCTION

Heterocyclic compounds constitute the basic building blocks of many natural and synthetic biologically significant molecules. *N*-Containing heterocycles are often regarded as "privileged" structures owing to their importance in the development and synthesis of new drugs. This is evident from the fact that most of the top-selling drugs, like Nexium, sofosbuvir, and Abilify, contain *N*-heterocycles in their skeleton. Benzodiazepines, benzimidazoles, and quinoxalines containing moieties represent a significant class of *N*-heterocycles owing to their varied applications. They are known to exhibit remarkable pharmacological activity such as anti-microbial [1–3], anti-inflammatory [4–6], antidepressants [7–9], analgesic [10–12], and anticancer activities [13–15]. Biologically active 1,4-benzodiazepines have demonstrated considerable utility in the central nervous system drug design [16], HIV-1 reverse transcriptase inhibitor. Benzimidazoles, apart from containing a significant moiety in the nucleotides, have also been found to exhibit promising pharmaceutical property by displaying a broad spectrum of biological activity ranging from anti-ulcer to anti-protozoal activity [17]. It also finds importance as ligands in various material applications [18,19]. Quinoxaline derivatives find its applications not only in the pharmaceuticals but also as an important component in dyes [20] and photochemical materials.

The synthesis of these heterocycles has been achieved by employing a wide range of catalysts, which include

salts [21–24], acids [25–28], ionic liquids [27,29], and nano-catalysts [30–33]. The great demand for syntheses involving environmental benign protocol has prompted the replacement of expensive and hazardous catalysts with inexpensive and nontoxic ones.

Meglumine or *N*-methyl-D-glucamine is a water-soluble amino sugar, which can be considered as an environmentally friendly catalyst owing to its low toxicity and biodegradable nature [34,35]. However, its use as a catalyst has not been explored to its fullest potential. The versatility of meglumine as a catalyst lies in the fact that it can activate the electrophilic as well as the nucleophilic components of a reaction owing to the presence of an amino, and primary and secondary alcohol groups in its structure.

The use of ultrasound as an alternate energy source in organic syntheses has been widely reported. Its use has not only reduced the reaction time drastically but also improved the yield of the products. This observation has been attributed to the cavitation phenomenon, which develops high temperature and pressure in the microenvironment, thereby creating turbulence and facilitating mass transfer [36].

As a part of our ongoing effort to develop an efficient and environmental benign protocol for various organic transformations, we report herein the manifold use of 1,2-phenylenediamine as one of the common starting components for the efficient synthesis of benzodiazepine, benzimidazole, and quinoxaline derivatives catalyzed by meglumine.

RESULTS AND DISCUSSION

A three-component reaction comprising 1,2-phenylenediamine, dimedone, and aryl aldehydes was carried out in ethanol–water (1:3) medium at room temperature. The reaction was facilitated by ultrasound in the presence of meglumine as a catalyst (Scheme 1).

In order to optimize the catalyst loading, a model reaction comprising 1,2-phenylenediamine, dimedone, and tolualdehyde was subjected to ultrasonication in ethanol by varying the amount of the catalyst. It was found that 5 mol% of the catalyst was sufficient for the best yield of **5b** at room temperature (<25°C) (Fig. 1).

Further, the effect of various solvent on the efficacy of the reaction, using the optimized amount of the catalyst, was studied. It was observed that polar protic solvents enhanced the reaction, with ethanol being the most favorable. It may also be noted that there was no significant change in the product yield when ethanol or the combination of ethanol–water was used. Hence, ethanol–water in the ratio of 1:3 was selected as the appropriate reaction medium (Fig. 2).

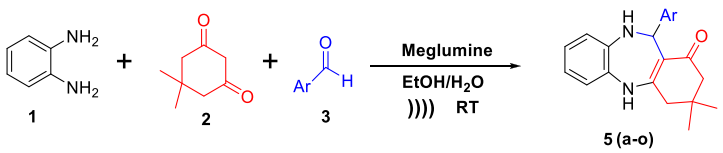
The reaction was also studied under both ultrasound irradiations and at room temperature stirring. It was found that the time taken for completion of the model reaction was 20 min under ultrasound irradiation, whereas in case of room temperature stirring condition, satisfactory yield of the product could not be obtained even after 5 h of the reaction. To broaden the scope of the reaction, aromatic aldehydes bearing both the electron-withdrawing and electron-donating groups were screened to provide the corresponding benzodiazepinones in good to excellent yield (Table 1).

The plausible mechanism for the formation of **5a** is given in Scheme 2A and B, whereby the dual nature of meglumine is highlighted. In Scheme 2A, the mechanism proceeds via the electrophilic activation of dimedone, whereas in Scheme 2B, it proceeds via the nucleophilic activation of dimedone [34]. Both pathways are suggested to go through an α,β-unsaturated ketone intermediate, formed by the condensation of aldehyde with dimedone. This intermediate then undergoes Michael addition with the diamine followed by cyclization to give the desired product.

The reaction was further extended to a two-component condensation between 1,2-phenylenediamine and aryl aldehydes to give highly regioselective benzimidazoles (Scheme 3) and 1,2-phenylenediamines with diketones to give quinoxaline derivatives (Scheme 4).

Similarly, catalyst loading (refer to Fig. 1) and solvent optimization (refer to Fig. 2) were also studied, taking 1,2-phenylenediamine and *p*-tolualdehyde for the synthesis of **6b** and 1,2-phenylenediamine and benzil for the synthesis of **7a** as model reactions. However, in these cases, 8 mol% of the catalyst supplemented with a higher temperature (50°C) was found to be a requisite condition for the formation of the products with optimal yield. As for solvent, a mixture of ethanol–water mixture in the

Scheme 1. Synthesis of 1*H*-dibenzo[*b*,*e*][1,4]diazepin-1-ones. [Color figure can be viewed at wileyonlinelibrary.com]



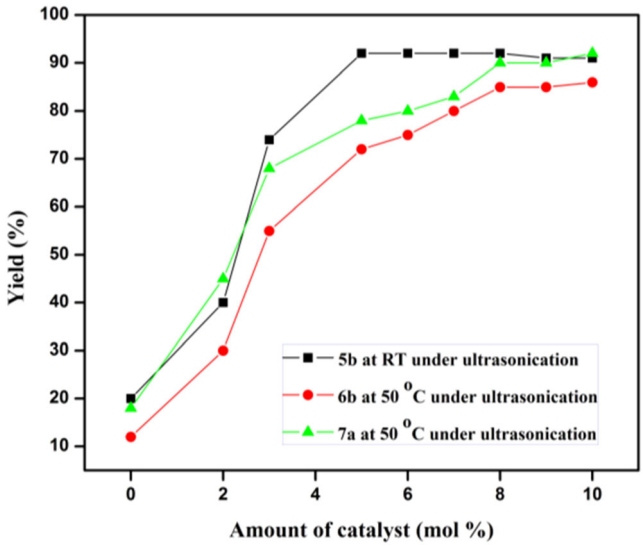


Figure 1. Catalyst optimization. [Color figure can be viewed at wileyonlinelibrary.com]

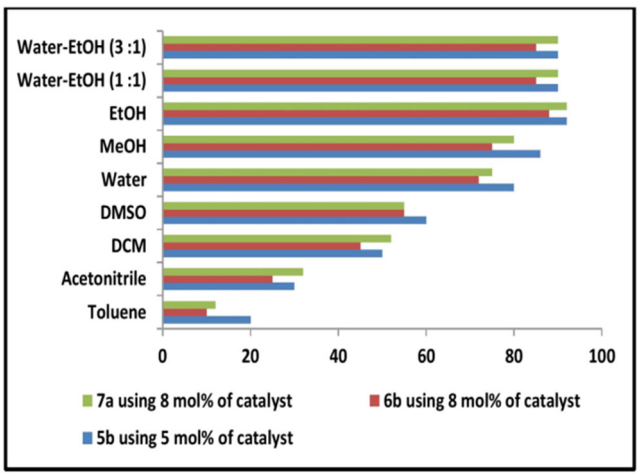


Figure 2. Optimization of solvent. [Color figure can be viewed at wileyonlinelibrary.com]

ratio of 1:3 was chosen as the favorable medium. In this case also, aromatic aldehydes containing both electron-withdrawing and electron-donating substituents were studied, and the results are given in Table 2. In case of quinoxaline derivatives, differently substituted 1,2-phenylenediamine was made to react with various 1,2-diketones under similar conditions to give the desired products (Table 3).

CONCLUSIONS

In summary, we have demonstrated the catalytic ability of meglumine in aqueous ethanol for the synthesis of some *N*,*N*-containing heterocycles. The advantage of the protocol includes easily available starting material, operational simplicity, simple workup procedure, and satisfactory yield of the product in addition to the application of a less toxic, cost-effective, and versatile organocatalyst. Moreover, the appendage of ultrasonic irradiation has drastically reduced the reaction time. This promising environmentally benign methodology can be further explored for application to numerous organic transformations.

EXPERIMENTAL SECTION

Reactants and solvents were procured from commercial sources (Alfa Aesar, Merck, Kenilworth, NJ) and used without further purification. The progress of the reaction was monitored by thin-layer chromatography (TLC) using pre-coated aluminum sheets (silica gel 60 F 254, 0.2 mm thickness) and was developed with iodine vapors

Table 1

Synthesis of 1*H*-dibenzo[*b*,*e*][1,4]diazepin-1-one derivatives catalyzed by meglumine.

Entry	Ar	Product	Ultrasonication		RT stirring (5 h)
			Time (min)	Yield[a] (%)	Yield[a] (%)
1	C_6H_5	**5a**	20	92	65
2	4-$CH_3C_6H_4$	**5b**	20	92	68
3	4-$OCH_3C_6H_4$	**5c**	20	88	65
4	4-ClC_6H_4	**5d**	25	90	60
5	4-BrC_6H_4	**5e**	25	92	68
6	4-$NO_2C_6H_4$	**5f**	30	85	58
7	4-OHC_6H_4	**5g**	25	88	60
8	4-N $(CH_3)_2C_6H_4$	**5h**	30	88	64
9	2-ClC_6H_4	**5i**	25	82	62
10	2-$NO_2C_6H_4$	**5j**	30	85	55
11	1-Naphthyl	**5k**	25	88	55
12	Furfuryl	**5l**	30	88	64
13	$C_6H_5CH{=}CH$	**5m**	30	82	60
14	4-(OH),3-$(OCH_3)C_6H_3$	**5n**	25	90	65
15	3,4-$(OCH_3)_2C_6H_3$	**5o**	20	90	60

RT, room temperature.
[a]Isolated yield.

or under UV light. Melting points were determined in open capillaries in Optics Technology melting point apparatus and are uncorrected. Fourier transformation infrared (FTIR) spectra were recorded with a PerkinElmer Spectrum BX FTIR apparatus (λ_{max} in cm^{-1}) on KBr discs. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance II-400 spectrometer (Bruker Corp., Billerica, MA) at 400 and 100 MHz, respectively, in DMSO-d_6. Mass spectra were recorded on a Waters (ZQ 4000) mass spectrometer. The reactions were carried out in an ultrasonic bath of make Takashi Model U4.5H/H, Japan.

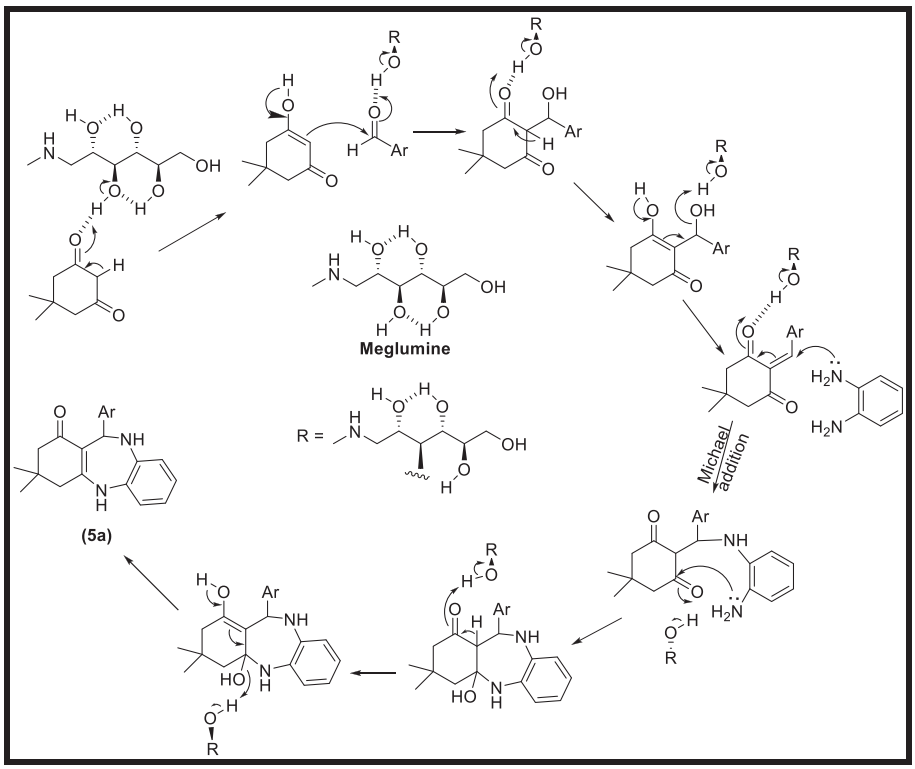
General method for the synthesis of compound 5(a–o). To 10 mL of water–ethanol (3:1) solution, 1.0 mmol of 1,2-phenylenediamine, 1.0 mmol of dimedone, 1.0 mmol of the corresponding aldehyde, and 5 mol% of meglumine were added and ultrasonicated for the time indicated in Table 1. Upon completion of the reaction (monitored by TLC at regular intervals), the precipitated product was filtered, washed, and dried. In some cases, the precipitate was further purified by recrystallization from hot ethanol.

Spectral data of selected products. ***3,3-Dimethyl-11-phenyl-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one (5a).*** Light yellow solid, m.p. 248–250°C. IR (KBr): *v* 3295, 3233, 2955, 1578, 1426, 1388, 1279 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 8.51 (s, 1H, NH), 6.87–6.84 (m, 4H, Ar–H), 6.75–6.74 (m, 1H, ArH), 6.66 (d, 1H, *J* = 7.2 Hz, Ar–H), 6.34–6.25 (m, 3H, Ar–H), 5.92 (d, 1H, *J* = 6.4 Hz, NH), 5.45 (d, 1H, *J* = 6.4 Hz, CH), 2.33 (bs, 2H, CH_2), 1.95 (d, 1H, *J* = 16.0 Hz, CH_2), 1.83 (d, 1H, *J* = 16.0 Hz, CH_2), 0.83 (s, 3H, CH_3), 0.78 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 192.0, 154.7, 144.0, 138.4, 130.9, 127.6, 127.2, 125.7, 122.5, 120.4, 119.9, 119.4, 110.0, 55.8, 49.4, 44.0, 31.7, 28.5, 27.3 ppm. ESI–MS: *m*/*z* 318 $[M]^+$. Anal. Calcd for $C_{21}H_{22}N_2O$: C 79.21, H 6.96, N 8.80%; found C 79.21, H 6.96, N 8.79%.

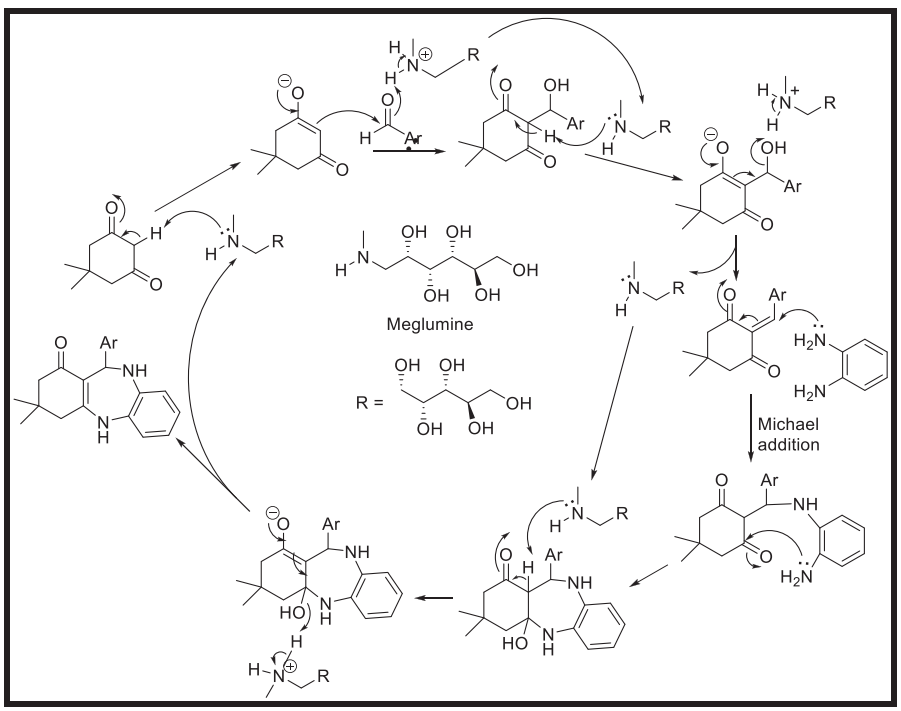
3,3-Dimethyl-11-(p-tolyl)-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one (5b). Yellow solid, m.p. 232–234°C. IR (KBr): *v* 3306, 3248, 3147, 2966, 1599, 1542, 1472, 1378, 1276 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 8.72 (s, 1H, NH), 6.96–6.94 (m, 2H, Ar–H), 6.90–6.87 (m, 3H, Ar–H), 6.60–6.49 (m, 3H, Ar–H), 6.11 (d, 1H, *J* = 4.8 Hz, NH), 5.64 (d, 1H, *J* = 6.0 Hz, CH), 2.56 (bs, 2H, CH_2), 2.18 (d, 1H, *J* = 16.0 Hz, CH_2), 2.12 (s, 3H, CH_3), 2.06 (d, 1H, *J* = 16.0 Hz, CH_2), 1.07 (s, 3H, CH_3), 1.01 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 192.0, 154.6, 141.6, 138.5, 134.6, 131.0, 128.2, 127.1, 122.5, 120.4, 119.8, 119.3, 110.3, 55.5, 49.4, 44.0, 31.7, 28.5, 27.3, 20.4 ppm. ESI–MS: *m*/*z* 332 $[M]^+$. Anal. Calcd for $C_{22}H_{24}N_2O$: C 79.48, H 7.28, N 8.43%; found C 79.28, H 7.30, N 8.39%.

11-(4-Methoxyphenyl)-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one (5c). Yellow solid, m.p. 212–214°C. IR (KBr): *v* 3445, 3316, 2959, 1547, 1473, 1380, 1332, 1249 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 8.74 (s, 1H, NH), 7.00 (d, 1H, *J* = 8.4 Hz, Ar–H), 6.92–6.90 (m, 1H, Ar–H), 6.66 (d, 2H, *J* = 8.4 Hz, Ar–H), 6.62–6.51 (m, 3H, Ar–H), 6.11 (d, 1H, *J* = 6.0 Hz, NH), 5.64 (d, 1H, *J* = 5.2 Hz, CH), 3.61 (s, 3H, OCH_3), 2.62–2.53 (m, 2H, CH_2), 2.20 (d, 1H, *J* = 16.2 Hz, CH_2), 2.07 (d, 1H, *J* = 15.6 Hz, CH_2), 1.08 (s, 3H, CH_3), 1.03 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 191.9, 157.2, 154.5, 138.6, 136.6, 131.0, 128.2, 122.5, 120.4, 119.8, 119.3, 112.9, 110.4, 55.1, 54.7, 49.4, 48.5, 44.0, 31.7, 28.5, 27.3 ppm. ESI–MS: *m*/*z* 348 $[M]^+$. Anal. Calcd

Scheme 2. (A) Proposed mechanistic pathway via the electrophilic activation of dimedone. (B) Proposed mechanistic pathway via the nucleophilic activation of dimedone.

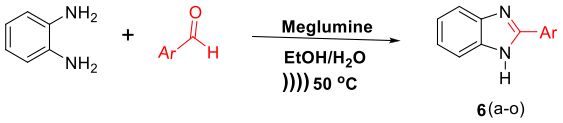


A

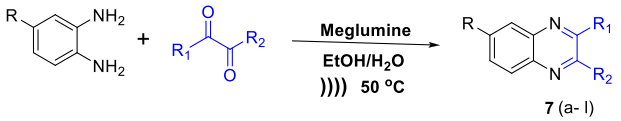


B

Scheme 3. Synthesis of 2-substituted benzimidazoles. [Color figure can be viewed at wileyonlinelibrary.com]



Scheme 4. Synthesis of quinoxaline derivatives. [Color figure can be viewed at wileyonlinelibrary.com]



for $C_{22}H_{24}N_2O_2$: C 75.83, H 6.94, N 8.04%; found C 75.80, H 6.95, N 8.03%.

11-(4-Chlorophenyl)-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one (5d). Yellow solid, m.p. 234–236°C. IR (KBr): *v* 3289, 3231, 2960, 1571, 1508, 1464, 1379, 1280 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 8.60 (s, 1H, NH), 7.04 (d, 2H, *J* = 8.4 Hz, Ar–H), 6.76 (d, 2H, *J* = 8.0 Hz, Ar–H), 6.67 (d, 1H, *J* = 7.2 Hz, Ar–H), 6.39–6.32 (m, 2H, Ar–H), 6.25 (d, 1H, *J* = 7.2 Hz, Ar–H), 5.93 (d, 1H, *J* = 6.0 Hz, NH), 5.39 (d, 1H, *J* = 5.6 Hz, CH), 2.32 (bs, 2H, CH_2), 1.93 (d, 1H, *J* = 16.0 Hz, CH_2), 1.83 (d, 1H, *J* = 16.0 Hz, CH_2), 0.82 (s, 3H, CH_3), 0.76 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 192.6, 154.3, 138.6, 136.2, 132.4, 130.8, 128.1, 128.0, 126.9, 125.7, 121.9, 120.5, 120.3, 119.1, 110.3, 54.1, 49.4, 43.0, 40.0, 31.7, 28.3, 27.1 ppm. ESI–MS: *m/z* 352 $[M]^+$. Anal. Calcd for $C_{21}H_{21}ClN_2O$: C 71.48, H 6.00, N 7.94%; found C 71.42, H 6.01, N 7.92%.

11-(4-Bromophenyl)-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one (5e). Dirty white solid, m.p. 238–240°C. IR (KBr): *v* 3370, 3293, 3056, 2931, 1537, 1423, 1382, 1281 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 8.84 (s, 1H, NH), 7.28 (d, 2H, *J* = 8.4 Hz, Ar–H), 7.00 (d, 2H, *J* = 7.6 Hz, Ar–H), 6.92 (d, 1H, *J* = 7.2 Hz, Ar–H), 6.63–6.56 (m, 2H, Ar–H), 6.50 (d, 1H, *J* = 7.2 Hz, Ar–H), 6.17 (d, 1H, *J* = 6.0 Hz, NH), 5.63 (d, 1H, *J* = 6.0 Hz, CH), 2.56 (bs, 2H, CH_2), 2.18 (d, 1H, *J* = 17.2 Hz, CH_2), 2.07 (d, 1H, *J* = 16.0 Hz, CH_2), 1.06 (s, 3H, CH_3), 1.00 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 192.0, 154.0, 144.1, 138.2, 131.0, 130.5, 129.4, 122.7, 120.5, 120.0, 119.7, 118.9, 109.5, 55.4, 49.3, 43.9, 31.7, 28.3, 27.5 ppm. ESI–MS: *m/z* 396 $[M]^+$, 398 $[M + 2]^+$. Anal. Calcd for $C_{21}H_{21}BrN_2O$: C 63.48, H 5.33, N 7.05%; found C 63.47, H 5.33, N 7.05%.

3,3-Dimethyl-11-(4-nitrophenyl)-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one (5f). Orange solid, m.p. 274–276°C. IR (KBr): *v* 3356, 3278, 2954, 1578, 1505, 1425, 1381, 1343, 1279 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 8.83 (s, 1H, NH), 7.89 (d, 2H, *J* = 8.4 Hz, Ar–H), 7.20 (d, 2H, *J* = 8.8 Hz, Ar–H), 6.86–6.84 (m, 1H, Ar–H), 6.51–6.49 (m, 2H, Ar–H), 6.42–6.39 (m, 1H, Ar–H), 6.25 (d, 1H, *J* = 6.0 Hz, NH), 5.66 (d, 1H, *J* = 5.6 Hz, CH), 2.38 (bs, 2H, CH_2), 2.09 (d, 1H, *J* = 16.0 Hz, CH_2), 1.98 (d, 1H, *J* = 16.0 Hz, CH_2), 0.96 (s, 3H, CH_3), 0.91 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 192.7, 155.5, 153.2, 146.1, 138.2, 131.4, 128.8, 123.5, 121.0, 120.7, 120.5, 109.3, 56.3, 49.7, 44.4, 32.2, 28.7, 28.0 ppm. ESI–MS: *m/z* 363

Table 2

Synthesis of 2-substituted benzimidazole derivatives catalyzed by meglumine.

Entry	Ar	Product	Ultrasonication (50°C)		Reflux (5 h)
			Time (min)	Yield[a] (%)	Yield[a] (%)
1	C_6H_5	**6a**	30	90	68
2	4-$CH_3C_6H_4$	**6b**	30	85	65
3	4-$OCH_3C_6H_4$	**6c**	30	88	60
4	4-BrC_6H_4	**6d**	25	90	65
5	4-ClC_6H_4	**6e**	25	88	66
6	2-ClC_6H_4	**6f**	30	80	60
7	3-ClC_6H_4	**6g**	30	80	58
8	3-$OCH_3C_6H_4$	**6h**	35	85	62
9	2-$NO_2C_6H_4$	**6i**	35	82	60
10	4-$NO_2C_6H_4$	**6j**	25	88	60
11	2-OHC_6H_4	**6k**	35	85	55
12	3,4-$(OCH_3)_2C_6H_3$	**6l**	30	90	58
13	1-Naphthyl	**6m**	30	88	50
14	$C_6H_5CH{=}CH$	**6n**	35	85	60
15	Furfuryl	**6o**	35	85	62

[a]Isolated yield.

Table 3

Synthesis of quinoxaline derivatives catalyzed by meglumine.

Entry	R	R_1	R_2	Product	Ultrasonication (50°C)		Reflux (5 h)
					Time (min)	Yield[a] (%)	Yield[a] (%)
1	H	C_6H_5	C_6H_5	**7a**	30	90	76
2	H	C_6H_5	H	**7b**	30	88	65
3	H	CH_3	CH_3	**7c**	35	80	65
4	NO_2	C_6H_5	C_6H_5	**7d**	25	90	60
5	NO_2	H	H	**7e**	30	88	68
6	NO_2	H	C_6H_5	**7f**	25	90	74
7	NO_2	CH_3	CH_3	**7g**	30	85	62
8	Cl	C_6H_5	C_6H_5	**7h**	35	86	65
9	Cl	H	C_6H_5	**7i**	35	86	60
10	CH_3	H	C_6H_5	**7j**	30	90	60
11	CH_3	C_6H_5	C_6H_5	**7k**	30	90	66

[a]Isolated yield.

$[M]^+$. Anal. Calcd for $C_{21}H_{21}N_3O_3$: C 69.41, H 5.82, N 11.56%; found C 69.35, H 5.84, N 11.54%.

11-(4-Hydroxyphenyl)-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one (5g). Dirty white solid, m.p. 222–224°C. IR (KBr): *v* 3467, 3293, 2958, 1602, 1584, 1383, 1263 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 9.03 (s, 1H, OH), 8.69 (s, 1H, NH), 6.89–6.84 (m, 3H, Ar–H), 6.60–6.44 (m, 5H, Ar–H), 6.03 (d, 1H, *J* = 6.0 Hz, NH), 5.58 (d, 1H, *J* = 5.6 Hz, CH), 2.55 (bs, 2H, CH_2), 2.17 (d, 1H, *J* = 16.0 Hz, CH_2), 2.05 (d, 1H, *J* = 16.0 Hz, CH_2), 1.06 (s, 3H, CH_3), 1.01 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 191.9, 155.1, 154.5, 138.7, 135.0, 131.0, 128.2, 122.4, 120.5, 119.8, 119.3, 114.3, 110.6, 55.2, 49.4, 44.0, 31.7, 28.5, 27.3 ppm. ESI–MS: *m*/*z* 334 $[M]^+$. Anal. Calcd for $C_{21}H_{22}N_2O_2$: C 75.42, H 6.63, N 8.38%; found C 75.35, H 6.64, N 8.36%.

11-(4-(Dimethylamino)phenyl)-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one (5h). Yellow solid, m.p. 224–226°C. IR (KBr): *v* 3435, 3307, 2961, 1602, 1567, 1380, 1335, 1279 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 8.41 (s, 1H, NH), 6.53–6.33 (m, 2H, Ar–H), 6.34–6.24 (m, 4H, Ar–H), 6.19 (d, 2H, *J* = 8.4 Hz, Ar–H), 5.80 (d, 1H, *J* = 5.2 Hz, NH), 5.32 (d, 1H, *J* = 5.6 Hz, CH), 2.34–2.28 (m, 2H, CH_2), 2.23 (s, 6H, CH_3), 1.93 (d, 1H, *J* = 15.6 Hz, CH_2), 1.79 (d, 1H, *J* = 16.0 Hz, CH_2), 0.81 (s, 3H, CH_3), 0.76 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 191.8, 154.3, 138.8, 132.4, 130.9, 127.8, 122.4, 120.4, 119.7, 119.2, 111.7, 110.8, 55.0, 49.4, 44.0, 40.0, 31.7, 28.6, 27.2 ppm. ESI–MS: *m*/*z* 361 $[M]^+$. Anal. Calcd for $C_{23}H_{27}N_3O$: C 76.42, H 7.53, N 11.62%; found C 76.32, H 7.54, N 11.59%.

11-(2-Chlorophenyl)-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one (5i). White solid, m.p. 230–232°C. IR (KBr): *v* 3282, 3230, 2964, 1583, 1506, 1470, 1381, 1279 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 8.95 (s, 1H, NH), 7.32 (d, 1H, *J* = 8.4 Hz, Ar–H), 7.06–6.92 (m, 3H, Ar–H), 6.75 (d, 1H, *J* = 7.2 Hz, Ar–H), 6.64–6.55 (m, 2H, Ar–H), 6.45 (d, 1H, *J* = 7.6 Hz, Ar–H), 5.98 (d, 1H, *J* = 6.4 Hz, NH), 5.58 (d, 1H, *J* = 6.0 Hz, CH), 2.63 (bs, 2H, CH_2), 2.18 (d, 1H, *J* = 16.0 Hz, CH_2), 2.05 (d, 1H, *J* = 15.6 Hz, CH_2), 1.08 (s, 3H, CH_3), 1.02 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6): δ 191.9, 155.5, 140.7, 137.4, 133.2, 131.6, 129.1, 128.0, 127.4, 126.1, 122.9, 120.7, 120.4, 119.9, 108.9, 54.4, 49.3, 44.0, 31.8, 28.2, 27.4 ppm. ESI–MS: *m*/*z* 352 $[M]^+$. Anal. Calcd for $C_{21}H_{21}ClN_2O$: C 71.48, H 6.00, N 7.94%; found C 71.33, H 6.03, N 7.90%.

3,3-Dimethyl-11-(2-nitrophenyl)-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one (5j). Yellow solid, m.p. 232–234°C. IR (KBr): *v* 3432, 2961, 1606, 1535, 1469, 1384, 1329, 1292 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 9.14 (s, 1H, NH), 7.86 (d, 1H, *J* = 7.2 Hz, Ar–H), 7.35–7.28 (m, 2H, Ar–H), 7.10 (d, 1H, *J* = 8.0 Hz, Ar–H), 6.82 (d, 1H, *J* = 6.8 Hz, Ar–H), 6.74–6.70 (m, 1H, Ar–H), 6.66–6.62 (m, 1H, Ar–H), 6.51 (d, 1H, *J* = 7.2 Hz, Ar–H), 6.04 (d, 1H, *J* = 5.6 Hz, NH), 5.44 (d, 1H, *J* = 5.2 Hz, CH), 2.68–2.59 (m, 2H, CH_2), 2.14 (d, 1H, *J* = 15.6 Hz, CH_2), 1.99 (d, 1H, *J* = 16.0 Hz, CH_2), 1.06 (s, 3H, CH_3), 0.95 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 194.2, 156.8, 151.0, 140.8, 138.5, 134.3, 133.3, 129.6, 129.4, 126.2, 125.2, 123.1, 122.6, 122.2, 110.7, 54.8, 51.4, 45.9, 33.7, 29.9, 29.2 ppm. ESI–MS: *m*/*z* 363 $[M]^+$. Anal. Calcd for $C_{21}H_{21}N_3O_3$: C 69.41, H 5.82, N 11.56%; found C 69.38, H 5.83, N 11.55%.

3,3-Dimethyl-11-(naphthalen-1-yl)-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one (5k). White solid, m.p. 214–216°C. IR (KBr): *v* 3342, 3137, 2890, 1671, 1586, 1519, 1444, 1296 cm^{-1}.^1H NMR (400 MHz, DMSO-d_6): δ 8.94 (s, 1H, NH), 8.51 (d, 1H, *J* = 8.4 Hz, Ar–H), 7.84 (d, 1H, *J* = 8.0 Hz, Ar–H), 7.63–7.48 (m, 3H, Ar–H), 7.10 (t, 1H, *J* = 8.0 Hz, Ar–H), 6.97 (d, 1H, *J* = 7.2 Hz,

Ar–H), 6.85 (d, 1H, *J* = 6.4 Hz, Ar–H), 6.55–6.48 (m, 2H, Ar–H), 6.39 (t, 1H, *J* = 7.2 Hz, Ar–H), 6.06 (d, 1H, *J* = 6.0 Hz, NH), 5.89 (d, 1H, *J* = 6.0 Hz, 6H), 2.67 (bs, 2H), 2.20 (d, 1H, *J* = 15.6 Hz), 2.04 (d, 1H, *J* = 16.0 Hz), 1.10 (s, 3H), 1,04 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 192.1, 155.3, 139.4, 137.7, 133.4, 131.7, 128.4, 126.9, 125.9, 124.5, 123.9, 122.9, 122.5, 120.2, 119.9, 119.8, 110.6, 52.7, 49.5, 44.1, 31.9, 28.3, 27.4 ppm. ESI–MS: *m*/*z* 368 $[M]^+$. Anal. Calcd for $C_{25}H_{24}N_2O$: C 81.49, H 6.57, N 7.60%; found C 81.34, H 6.59, N 7.58%.

3,3-Dimethyl-11-styryl-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one (5m). Light brown solid, m. p. 250–252°C. IR (KBr): *v* 3390, 3313, 2919, 1677, 1638, 1611, 1608, 1377 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.74 (s, 1H, NH), 7.12–7.07 (m, 3H, Ar–H), 6.99 (d, 1H, *J* = 7.6 Hz, Ar–H), 6.77–6.71 (m, 2H, Ar–H), 6.66–6.62 (m, 1H, Ar–H), 6.17 (d, 1H, *J* = 15.6 Hz, CH), 6.01 (d, 1H, *J* = 6.4 Hz, NH), 5.98–5.96 (m, 1H, CH), 5.23 (d, 1H, *J* = 5.6 Hz, CH), 2.48 (m, 2H, CH_2), 2.17 (d, 1H, *J* = 16.0 Hz, CH_2), 2.07 (d, 1H, *J* = 15.6 Hz, CH_2), 1.03 (s, 3H, CH_3), 0.99 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 192.2, 154.4, 138.9, 137.2, 132.9, 130.8, 129.0, 128.7, 127.5, 126.2, 123.2, 120.7, 120.6, 119.9, 110.5, 53.7, 49.9, 44.4, 32.2, 28.8, 27.7 ppm. ESI–MS: *m*/*z* 344 $[M]^+$. Anal. Calcd for $C_{24}H_{26}N_2O$: C 80.41, H 7.31, N 7.81%; found C 80.26, H 7.33, N 7.79%.

11-(4-Hydroxy-3-methoxyphenyl)-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one (5n). Yellow solid, m.p. 208–210°C. IR (KBr): *v* 3435, 3307, 2961, 1602, 1517, 1464, 1380, 1335, 1279 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.68 (s, 1H, NH), 8.57 (s, 1H, OH), 6.87 (d, 1H, *J* = 7.2 Hz, Ar–H), 6.74 (s, 1H, Ar–H), 6.58–6.52 (m, 2H, Ar–H), 6.43–6.34 (m, 2H, Ar–H), 6.04 (d, 1H, *J* = 5.2 Hz, NH), 5.58 (d, 1H, *J* = 4.8 Hz, CH), 3.57 (s, 3H,OCH_3), 2.59–2.54 (m, 2H, CH_2), 2.18 (d, 1H, *J* = 16.0 Hz, CH_2), 2.05 (d, 1H, *J* = 15.6 Hz, CH_2), 1.05 (s, 3H, CH_3), 1.02 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 192.3, 155.0, 147.3, 144.8, 139.3, 136.1, 131.6, 122.9, 121.0, 120.2, 119.7, 114.8, 112.2, 111.0, 55.9, 55.6, 49.9, 44.4, 32.1, 29.1, 27.5 ppm. ESI–MS: *m*/*z* 364 $[M]^+$. Anal. Calcd for $C_{22}H_{24}N_2O_3$: C 72.51, H 6.64, N 7.69%; found C 72.44, H 6.65, N 7.67%.

11-(3,4-Dimethoxyphenyl)-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one (5o). Yellow solid, m.p. 238–240°C. IR (KBr): *v* 3415, 3309, 2932, 1638, 1584, 1428, 1281 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.81 (s, 1H, NH), 7.16–7.15 (m, 2H, Ar–H), 7.07–7.05 (m, 2H, Ar–H), 6.92–6.90 (m, 1H, Ar–H), 6.60–6.59 (m, 1H, Ar–H), 6.50–6.48 (m, 1H, Ar–H), 6.19 (d, 1H, *J* = 5.6 Hz, NH), 5.66 (d, 1H, *J* = 5.2 Hz, CH), 3.35 (s, 6H, OCH_3), 2.57 (s, 2H, CH_2), 2.18 (d, 1H, *J* = 15.2 Hz, CH_2), 2.07 (d, 1H, *J* = 15.6 Hz, CH_2), 1.06 (s, 3H, CH_3), 1.01 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 192.0, 154.8, 143.7,138.2, 131.0, 129.0, 127.6, 122.7, 120.5, 120.0, 119.7, 109.5, 55.4, 49.3, 43.9, 31.7, 28.3, 27.5 ppm. ESI–MS: *m*/*z* 378 $[M]^+$. Anal. Calcd for $C_{23}H_{26}N_2O_3$: C 72.99, H 6.92, N 7.40%; found C 72.40, H 7.02, N 7.28%.

General method for the synthesis of compound 6(a–o) and 7(a–l). To 10 mL of ethanol–water (1:3) mixture, 1.0 mmol of 1,2-phenylenediamine, 1.0 mmol of the corresponding aldehyde (in case of **6**)/1,2 diketone (in case of **7**), and 8 mol% of meglumine were ultrasonicated at 50°C for the given time. On completion of reaction, monitored by TLC, the solution was cooled, and the precipitated product was filtered, washed, and collected. In some cases, the precipitate was further recrystallized from hot ethanol.

Spectral data of selected products. ***2-Phenyl-1H-benzo[d]imidazole (6a).*** Light brown solid, m.p. 286–288°C. IR (KBr): *v* 3411, 1590, 1541, 1410, 1276 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.0 (s, 1H, NH), 8.30 (d, 2H, *J* = 8.0 Hz, Ar–H), 7.70–7.62 (m, 5H, Ar–H), 7.34–7.32 (m, 2H, Ar–H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$/DMSO-d_6): δ 146.5, 133.9, 124.8, 124.3, 123.3, 121.3, 116.8, 109.6 ppm. ESI–MS: *m*/*z* 194$[M]^+$. Anal. Calcd for $C_{13}H_{10}N_2$: C 80.39, H 5.19, N 14.42%; found C 80.25, H 5.21, N 14.38%.

2-(p-Tolyl)-1H-benzo[d]imidazole (6b). Light yellow solid, m.p. 270–272°C. IR (KBr): *v* 3444, 1621, 1500, 1430, 1274 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.84 (s, 1H, NH), 8.07 (d, 2H, *J* = 7.6 Hz, Ar–H), 7.65 (d, 1H, *J* = 7.2 Hz. Ar–H), 7.51 (d, 1H, *J* = 7.2 Hz, Ar–H), 7.36 (d, 2H, *J* = 8.0 Hz, Ar–H), 7.22–7.16 (m, 2H, Ar–H), 2.38 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 151.3, 143.7, 139.5, 134.9, 129.4, 127.4, 126.3, 122.2, 121.5, 118.6, 111.1, 20.9 ppm. ESI–MS: *m*/*z* 208 $[M]^+$. Anal. Calcd for $C_{14}H_{12}N_2$: C 80.74, H 5.81, N 13.45%; found C 80.48, H 5.85, N 13.37%.

2-(4-Methoxyphenyl)-1H-benzo[d]imidazole (6c). Light yellow solid, m.p. 210–212°C. IR (KBr): *v* 3433, 1612, 1502, 1437, 1252 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.74 (s, 1H, NH), 8.10 (d, 2H, *J* = 8.8 Hz, Ar–H), 7.60 (d, 1H, *J* = 7.2 Hz, Ar–H), 7.48 (d, 1H, *J* = 6.8 Hz, Ar–H), 7.19–7.14 (m, 2H, Ar–H), 7.10 (d, 2H, *J* = 9.2 Hz, Ar–H), 3.83 (s, 3H, OCH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.5, 151.2, 127.9, 122.5, 114.3, 55.2 ppm. ESI–MS: *m*/*z* 224 $[M]^+$. Anal. Calcd for $C_{14}H_{12}N_2O$: C 74.98, H 5.39, N 12.49%; found C 74.71, H 5.44, N 12.40%.

2-(4-Bromophenyl)-1H-benzo[d]imidazole (6d). Light brown solid, m.p. 258–260°C. IR (KBr): *v* 3433, 1622, 1539, 1427, 1273 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.01 (s, 1H, NH), 8.11 (d, 2H, *J* = 8.8 Hz, Ar–H), 7.76 (d, 2H, *J* = 8.8 Hz, Ar–H), 7.63–7.54 (m, 2H, Ar–H), 7.21–7.20 (m, 2H, Ar–H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 155.6, 136.6, 134.2, 133.1,

128.6, 127.2 ppm. ESI–MS: *m/z* 272[M]$^+$, 274 [M + 2]$^+$. Anal. Calcd for $C_{13}H_9BrN_2$: C 57.17, H 3.32, N 10.26%; found C 57.05, H 3.38, N 10.20%.

2-(4-Chlorophenyl)-1H-benzo[d]imidazole (6e). Dirty white, m.p. 278–280°C. IR (KBr): *v* 3436, 1611, 1526, 1446, 1349, 1278 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.98 (s, 1H, NH), 8.17 (d, 2H, *J* = 8.4 Hz, Ar–H), 7.63–7.54 (m, 4H, Ar–H), 7.21–7.20 (m, 2H, Ar–H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 150.3, 134.9, 128.5, 128.4, 127.6, 122.0 ppm. ESI–MS: *m/z* 228 [M]$^+$. Anal. Calcd for $C_{13}H_9ClN_2$: C 68.28, H 3.97, N 12.25%; found C 68.28, H 3.97, N 12.25%.

2-(2-Chlorophenyl)-1H-benzo[d]imidazole (6f). Dirty white solid, m.p. 224–226°C. IR (KBr): *v* 3446, 1590, 1539, 1405, 1274 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.70 (s, 1H, NH), 7.89–7.87 (m, 1H, Ar–H), 7.69–7.62 (m, 2H, Ar–H), 7.55–7.48 (m, 3H, Ar–H), 7.25–7.18 (m, 2H, Ar–H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 149.0, 143.1, 134.6, 132.0, 131.5, 131.1, 130.3, 129.9, 127.3, 122.7, 121.6, 119.0, 111.6 ppm. ESI–MS: *m/z* 228[M]$^+$. Anal. Calcd for $C_{13}H_9ClN_2$: C 68.28, H 3.97, N 12.25%; found C 68.15, H 4.00, N 12.20%.

2-(3-Chlorophenyl)-1H-benzo[d]imidazole (6g). Light brown solid, m.p. 218–220°C. IR (KBr): *v* 3365, 1672, 1571, 1442, 1285 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.83 (s, 1H, NH), 8.01 (s, 1H, Ar–H), 7.92 (d, 1H, *J* = 7.2 Hz, Ar–H), 7.46–7.33 (m, 4H, Ar–H), 7.09–6.92 (m, 2H, Ar–H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 149.6, 133.7, 132.1, 130.9, 129.5, 125.9, 124.9, 122.9, 121.9, 119.0, 111.4 ppm. ESI–MS: *m/z* 328[M]$^+$. Anal. Calcd for $C_{13}H_9ClN_2$: C 68.28, H 3.97, N 12.25%; found C 68.24, H 3.98, N 12.23%.

2-(3-Methoxyphenyl)-1H-benzo[d]imidazole (6h). Light yellow solid, m.p. 196–198°C. IR (KBr): *v* 3436, 1611, 1574, 1446, 1278 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.88 (s, 1H, NH), 7.75–7.73 (m, 2H, Ar–H), 7.65–7.64 (d, 1H, *J* = 6.8 Hz, Ar–H), 7.52–7.50 (d, 1H, *J* = 6.4 Hz, Ar–H), 7.44 (t, 1H, *J* = 8.8 Hz, Ar–H), 7.26–7.18 (m, 2H), 7.05–7.03 (m, 1H), 3.84 (s, 3H, OCH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 159.5, 151.0, 143.6, 134.8, 131.3, 130.0, 122.5, 121.6, 118.6, 115.8, 111.3, 55.2 ppm. ESI–MS: *m/z* 224 [M]$^+$. Anal. Calcd for $C_{14}H_{12}N_2O$: C 74.98, H 5.39, N 12.49%; found C 74.93, H 5.40, N 12.47%.

2-(2-Nitrophenyl)-1H-benzo[d]imidazole (6i). Light orange solid, m.p. 216–218°C. IR (KBr): *v* 3436, 1672, 1578, 1450, 1284 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.0 (s, 1H, NH), 8.03 (d, 1H, *J* = 8.0 Hz, Ar–H), 7.98 (d, 1H, *J* = 6.8 Hz, Ar–H), 7.86 (t, 1H, *J* = 7.2 Hz, Ar–H), 7.77–7.73 (m, 1H, Ar–H), 7.66 (d, 1H, *J* = 7.2 Hz, Ar–H), 7.57 (d, 1H, *J* = 7.2 Hz, Ar–H), 7.27–7.24 (m, 2H, Ar–H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 148.9, 147.2, 132.5, 130.8, 124.2, 124.1, 123.0, 121.8, 119.2, 111.6 ppm. ESI–MS: *m/z* 239[M]$^+$. Anal. Calcd for $C_{13}H_9N_3O_2$: C 65.27, H 3.79, N 17.56%; found C 65.21, H 3.82, N 17.71%.

2-(3,4-Dimethoxyphenyl)-1H-benzo[d]imidazole (6l). Yellow solid, m.p. 226–228°C. IR (KBr): *v* 3445, 1658, 1572, 1430, 1278 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.8 (s, 1H, NH), 7.63 (d, 1H, *J* = 7.2 Hz, Ar–H), 7.45–7.39 (m, 2H, Ar–H), 7.28–7.22 (m, 4H, Ar–H), 3.88 (s, 6H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 156.3, 152.0, 143.3, 136.4, 130.0, 126.2, 124.4, 116.6, 116.2, 111.4, 55.6 ppm. ESI–MS: *m/z* 254[M]$^+$. Anal. Calcd for $C_{15}H_{14}N_2O_2$: C 70.85, H 5.55, N 11.02%; found C 69.25, H 5.89, N 10.49%.

2-(Naphthalen-1-yl)-1H-benzo[d]imidazole (6m). Yellow solid, m.p. 256–258°C. IR (KBr): *v* 3384, 1602, 1540, 1429, 1273 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.95 (s, 1H, NH), 9.11 (d, 1H, *J* = 8.8 Hz, Ar–H), 8.09 (d, 1H, *J* = 8.0 Hz, Ar–H), 8.04–8.00 (m, 2H, Ar–H), 7.78 (d, 1H, *J* = 7.2 Hz, Ar–H), 7.70–7.64 (m, 2H, Ar–H), 7.63–7.57 (m, 2H, Ar–H), 7.29–7.22 (m, 2H, Ar–H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 151.3, 143.8, 134.4, 133.5, 130.4, 130.1, 128.3, 127.8, 127.0, 126.3, 125.2, 122.6, 121.5, 119.0, 111.3 ppm. ESI–MS: *m/z* 244[M]$^+$. Anal. Calcd for $C_{17}H_{12}N_2$: C 83.58, H 4.95, N 11.47%; found C 83.37, H 4.97, N 11.66%.

2-Styryl-1H-benzo[d]imidazole (6n). Light brown solid, m.p. 214–216°C. IR (KBr): *v* 3424, 1634, 1581, 1432, 1270 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.90 (s, 1H, NH), 7.59 (d, 2H, *J* = 7.2 Hz, Ar–H), 7.60–7.23 (m, 7H, Ar–H), 6.43 (d, 1H, *J* = 16.0 Hz, CH), 6.35 (d, 1H, *J* = 16.0 Hz, CH) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 150.9, 143.2, 135.9, 129.1, 128.8, 126.5, 123.2, 122.7, 119.4, 111.9 ppm. ESI–MS: *m/z* 220[M]$^+$. Anal. Calcd for $C_{15}H_{12}N_2$: C 81.79, H 5.49, N 12.72%; found C 80.54, H 5.69, N 12.36%.

2-(Furan-2-yl)-1H-benzo[d]imidazole (6o). Light brown solid, m.p. 284–286°C. IR (KBr): *v* 3426, 1656, 1578, 1430, 1281 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.94 (s, 1H, NH), 7.93–7.87 (m, 1H, Ar–H), 7.60–7.57 (m, 2H, Ar–H), 7.23–7.15 (m, 3H, Ar–H), 6.73–6.70 (m, 1H, Ar–H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 149.2, 144.3, 143.2, 134.5, 122.9, 121.0, 118.7, 113.2, 111.3 ppm. ESI–MS: *m/z* 184[M]$^+$. Anal. Calcd for $C_{11}H_8N_2O$: C 71.73, H 4.38, N 15.21%; found C 70.03, H 4.78, N 14.45%.

2,3-Diphenylquinoxaline (7a). White solid, m.p. 120–122°C. IR (KBr): *v* 3072, 1615, 1578, 1345, 764 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.17–8.15 (m, 2H, Ar–H), 7.90–7.87 (m, 2H, Ar–H), 7.49–7.47 (m, 4H, Ar–H), 7.41–7.34 (m, 6H, Ar–H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.9, 140.3, 138.6, 130.3, 129.6, 128.7, 127.9 ppm. ESI–MS: *m/z* 282[M]$^+$. Anal. Calcd for $C_{20}H_{14}N_2$: C 85.08, H 5.00, N 9.92%; found C 84.92, H 5.04, N 9.87%.

2-Phenylquinoxaline (7b). Dirty white solid, m.p. 90–92°C. IR (KBr): *v* 3050, 2924, 1616, 1524, 1348, 764 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 9.57 (s, 1H, CH), 8.33–8.31 (m, 2H, Ar–H), 8.13–8.09 (m, 2H, Ar–H), 7.88–7.70 (m, 2H, Ar–H), 7.61–7.55 (m, 3H, Ar–H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 150.8, 143.6, 141.3, 140.9, 135.9, 130.5, 130.3, 129.8, 129.1, 129.0, 128.7, 127.3 ppm. ESI–MS: *m/z* 206 $[M]^+$. Anal. Calcd for $C_{14}H_{10}N_2$: C 81.53, H 4.89, N 13.58%; found C 81.53, H 4.89, N 13.58%.

6-Nitro-2,3-diphenylquinoxaline (7d). Dirty white solid, m.p. 186–188°C. IR (KBr): *v* 3072, 1615, 1578, 1345, 764 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 8.92 (d, 1H, *J* = 2.4 Hz, Ar–H), 8.55 (dd, 1H, *J* = 2.8 Hz, *J* = 9.0 Hz, Ar–H), 8.36 (d, 1H, *J* = 9.2 Hz, Ar–H), 7.52–7.50 (m, 4H, Ar–H), 7.45–7.36 (m, 6H, Ar–H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 155.9, 155.3, 147.5, 142.9, 139.1, 137.9, 137.8, 130.7, 129.7, 129.6, 129.5, 129.3, 128.1, 124.7, 123.5 ppm. ESI–MS: *m/z* 327. Anal. Calcd for $C_{20}H_{13}N_3O_2$: C 73.38, H 4.00, N 12.84%; found C 73.31, H 4.02, N 12.81%.

6-Nitroquinoxaline (7e). Light brown solid, m.p. 150–152°C. IR (KBr): *v* 3052, 1556, 1485, 1349, 765 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 9.15 (s, 2H, Ar–H), 8.88 (d, 1H, *J* = 2.8 Hz, Ar–H), 8.47 (dd, 1H, *J* = 2.4 Hz, 9.2 Hz, Ar–H), 8.32 (d, 1H, *J* = 8.8 Hz, Ar–H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 149.2, 148.5, 147.9, 145.0, 141.3, 131.6, 125.6, 123.8 ppm. ESI–MS: *m/z* 175 $[M]^+$. Anal. Calcd for $C_8H_5N_3O_2$: C 54.86, H 2.88, N 23.99%; found C 54.70, H 2.97, N 23.77%.

6-Nitro-2-phenylquinoxaline (7f). Light brown solid, m. p. 146–148°C. IR (KBr): *v* 3052, 1598, 1554, 1477, 1342, 792 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 9.78 (s, 1H, CH), 8.89 (s, 1H, Ar–H), 8.55 (d, 1H, *J* = 7.6 Hz, Ar–H), 8.45–8.40 (m, 2H, Ar–H), 8.32 (d, 1H, *J* = 7.6 Hz, Ar–H), 7.70–7.60 (m, 3H, Ar–H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 150.3, 146.2, 135.7, 131.4, 131.0, 130.8, 129.2, 128.0, 127.8, 124.9, 123.9, 123.4, 123.0 ppm. ESI–MS: *m/z* 251 $[M]^+$. Anal. Calcd for $C_{14}H_9N_3O_2$: C 66.93, H 3.61, N 16.73%; found C 66.85, H 3.63, N 16.68%.

2,3-Dimethyl-6-nitroquinoxaline (7g). Light brown solid, m.p. 136–138°C. IR (KBr): *v* 3042, 2923, 1618, 1529, 1450, 1345, 740 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 8.45 (d, 1H, *J* = 2.4 Hz, Ar–H), 8.14 (dd, 1H, *J* = 2.8 Hz, 9.2 Hz, Ar–H), 7.83 (d, 1H, *J* = 9.2 Hz, Ar–H), 3.08 (s, 6H, CH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 157.8, 157.7, 147.3, 142.7, 139.2, 130.3, 124.4, 122.7, 26.4, 25.7 ppm. ESI–MS: *m/z* 203 $[M]^+$. Anal. Calcd for $C_{10}H_9N_3O_2$: C 59.11, H 4.46, N 20.68% found C 58.97, H 4.52, N 20.55%.

6-Chloro-2,3-diphenylquinoxaline (7h). Dirty white solid, m.p. 118–120°C. IR (KBr): *v* 3034, 1601, 1578, 1374, 749 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 8.20 (d, 1H, *J* = 1.6 Hz, Ar–H), 8.36 (d, 1H, *J* = 9.2 Hz, Ar–H), 7.87 (dd, 1H, *J* = 2.4 Hz, 8.8 Hz, Ar–H), 7.46–7.44 (m, 4H, Ar–H), 7.39–7.33 (m, 6H, Ar–H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 153.9, 139.0, 138.3, 138.2, 134.5, 130.8, 130.5, 129.6, 128.9, 128.0, 127.4 ppm. ESI–MS: *m/z* 316 $[M]^+$. Anal. Calcd for $C_{20}H_{13}ClN_2$: C 75.83, H 4.14, N 8.84%; found C 75.67, H 4.17, N 8.81%.

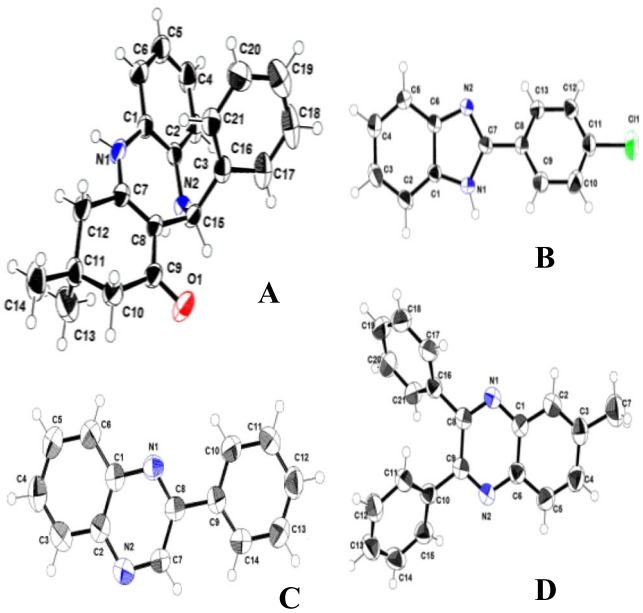


Figure 3. ORTEP image of (A) **5a** (CCDC no. 1847612), (B) **6e** (CCDC no. 1847719), (C) **7b** (CCDC no. 1847611), and (D) **7k** (CCDC no. 1847575). [Color figure can be viewed at wileyonlinelibrary.com]

6-Chloro-2-phenylquinoxaline (7i). Dirty white solid, m. p. 110–112°C. IR (KBr): *v* 3045, 1605, 1581, 1386, 763 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 9.46 (s, 1H, Ar–H), 8.14 (d, 1H, *J* = 2.4 Hz, Ar–H), 8.06 (d, 1H, *J* = 8.8 Hz, Ar–H), 7.77 (dd, 1H, *J* = 2.8 Hz, 9.2 Hz, Ar–H), 7.46–7.34 (m, 5H, Ar–H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 150.7, 142.9, 139.0, 138.6, 135.0, 131.0, 130.7, 129.4, 127.1, 127.6, 126.9 ppm. ESI–MS: *m/z* 240 $[M]^+$. Anal. Calcd for $C_{14}H_9ClN_2$: C 69.86, H 3.77, N 11.64%; found C 69.02, H 4.00, N 11.34%.

6-Methyl-2-phenylquinoxaline (7j). Light brown solid, m.p. 136–138°C. IR (KBr): *v* 3060, 2939, 1621, 1384, 1345, 825 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 9.51 (s, 1H, Ar–H), 8.30–8.28 (m, 2H, Ar–H), 8.02–7.97 (m, 1H, Ar–H), 7.91–7.88 (m, 1H, Ar–H), 7.71–7.65 (m, 1H, Ar–H), 7.60–7.53 (m, 3H, Ar–H), 2.55 (s. 3H, CH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 150.0, 143.4, 141.0, 140.0, 139.7, 136.0, 132.6, 130.1, 129.0, 128.7, 127.5, 127.3, 127.2, 21.2 ppm. ESI–MS: *m/z* 220 $[M]^+$. Anal. Calcd for $C_{15}H_{12}N_2$: C 81.79, H 5.49, N 12.72%; found C 81.58, H 5.51, N 12.92%.

6-Methyl-2,3-diphenylquinoxaline (7k). Brown solid, m. p. 120–122°C. IR (KBr): *v* 3054, 2917, 1615, 1542, 1384, 831. ^1H NMR (400 MHz, DMSO-d_6): δ 8.02 (d, 1H, *J* = 8.8 Hz, Ar–H), 7.91 (s, 1H, Ar–H), 7.69 (dd, 1H, *J* = 1.6 Hz, 8.8 Hz, Ar–H), 7.44–7.42 (m, 4H, Ar–H), 7.36–7.30 (m, 6H, Ar–H), 2.56 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.7, 152.0, 140.5, 140.4, 138.8, 132.4, 129.6, 128.6, 128.5, 127.9, 127.4, 21.3 ppm. ESI–MS: *m/z* 296 $[M]^+$. Anal. Calcd for $C_{21}H_{16}N_2$: C 85.11, H 5.44, N 9.45%; found C 85.10, H 5.44, N 9.45%.

X-ray crystallography. The X-ray crystallography data of **5a**, **6e**, **7b**, and **7k** were collected at 293 K with an Agilent Xcalibur (Eos-Gemini) diffractometer equipped with a graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). The data were collected and refined in CrysAlis PRO software, and data reduction was performed using the CrysAlis PRO. The structures were solved by direct method and refined by olex2. An ORTEP view of **5a**, **6e**, **7b**, and **7k** is illustrated in Figure 3.

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