RSC Advances

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Cite this: *RSC Advances*, 2013, **3**, 1862

Expeditious synthetic approach and photophysical properties of fluorescent benzimidazo[1,2-*d*]dibenzo[*b*,*f*][1,4]diazepine derivatives†

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Received 16th October 2012,
Accepted 22nd November 2012

DOI: 10.1039/c2ra22527a

www.rsc.org/advances

A short and efficient synthetic route to novel benzimidazo[1,2-*d*]dibenzo[*b*,*f*][1,4]diazepines has been developed using a copper catalyzed intramolecular Ullmann type C–N bond forming reaction as a key step. Copper iodide and 1,10-phenanthroline furnished the desired compounds in good yield. The products are intensely fluorescent with appreciably long lifetimes. Looking at their prospective use as markers for biomacromolecules and in biochemical analysis, we have explored the photophysical properties of these compounds. The spectrophotometric and spectrofluorometric studies reveal that while the absorbance maxima of the compounds are in the UV region, the emission maxima fall in the visible (blue-green) region.

Introduction

Over the past few years, interest has been growing in the synthesis of various benzimidazole fused medium ring heterocycles due to the pharmacological, medicinal and biological activities associated with hybrid structures involving benzimidazole[1–4] and medium rings.[5,6] Among them, benzimidazo benzodiazepines play an important role in pharmaceuticals.[7–11] For example tetrahydroimidazo[4,5,1-*jk*][l,4]benzodiazepi-2(1*H*)-thione (TIBO),[10,11] the first member of a series of potent selective, non-competitive inhibitors of HIV-l reverse transcriptase and Tivirapine (8-chloro TIBO), a preclinical lead belong to the class of benzimidazobenzodiazepines while UK-129 485 is an imidazobenzodiazepine.[7–9] A search in the literature revealed that there are only few reports on the synthesis of benzimidazoles fused with benzazepine and benzodiazepine.[12] These include ring-closing metathesis, metal induced C–C bond formation, microwave irradiation or other methods. However the synthesis of dibenzofused benzimidazobenzodiazepine ring has not been reported so far. For quite sometime, we have been engaged in the synthesis of several benzannulated and dibenzannulated medium ring heterocycles by means of the most effective alternative, Buchwald–Hartwig intramolecular C–N/C–O bond forming cyclization reaction in the presence of Pd based catalyst and phosphine ligands.[13–21] A blemish in this amination reaction is that these ligands are often air-sensitive, toxic, and expensive. Consequently, the copper-based protocols of Ullmann type amination attracted our attention in view of its low cost and low toxicity. We therefore became interested in taking up a project on the synthesis of this new class of compounds, benzimidazole fused dibenzodiazepines exploiting copper chemistry. We herein report our results on Cu catalyzed intramolecular cycloamination reaction,[22–26] leading to the formation of benzimidazodibenzodiazepines.

The synthesized compounds are fluorescent with appreciably long lifetimes. So they are promising agents to be tagged with biomacromolecules like DNA, RNA *etc.* to serve as markers for biochemical analysis. Fluorescence has been a major topic for photofunctional materials, and has found extensive applications in a variety of fields such as organic light emitting diodes (OLED), photovoltaic cells, laser chemistry, fluorescent probes and related areas.[27] Organic electroluminescent devices employing organic fluorophore emitters have been the focus of considerable interest because of their possible applications as displays for mobile phones, personal computers, and televisions.[28–33] The strong fluorescence of some of our synthesized compounds leads to the optimism that they may also be used as promising emitters for the fabrication of electroluminescent devices covering a wide range of color. Considering the prospects in this area, we have studied the photophysical properties of the synthesized compounds in some detail.

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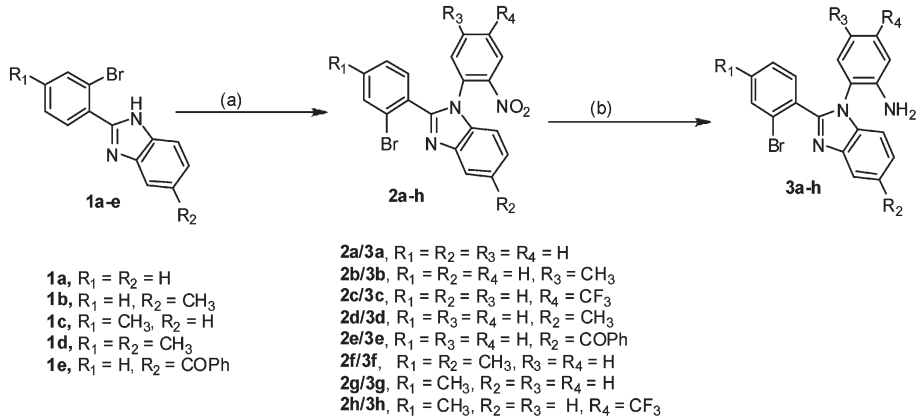
† Electronic supplementary information (ESI) available: Copies of ^{1}H NMR and ^{13}C NMR spectra for all the synthesized compounds and COSY, NOSY spectra of **4e**. See DOI: 10.1039/c2ra22527a



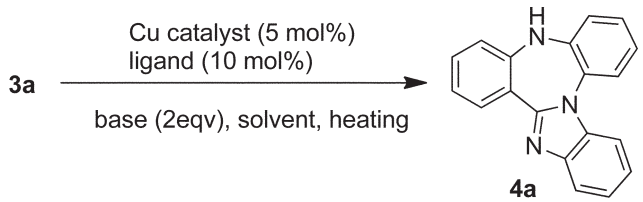
Scheme 1 Synthesis of benzimidazole fused aromatic amines. *Reagents and conditions*: (a) acetone, KOH, *o*-fluoronitrobenzenes, reflux, 5 h. (b) Fe, AcOH, 80 °C, 1 h.

Results and discussion

The starting materials **1a–e** were synthesized[34] by heating a mixture of commercially available *o*-phenylenediamines and *o*-bromobenzoic acids with polyphosphoric acid (PPA) in neat conditions. These products were then refluxed in dry acetone for 4–5 h in presence of *o*-fluoronitrobenzenes and KOH to give the intermediates **2a–h** (Scheme 1) in good yield. However, **2d** and **2f** were isolated as regioisomeric mixtures. When we used **1e**, the reaction was somewhat more complex and the separation was difficult. So we subjected the mixture directly to the next step. All the *N*-arylated benzimidazoles were reduced in presence of iron and acetic acid to afford the amines **3a–h** in good to excellent yield (Scheme 1). The spectral data of **3a–h** are in full agreement with the assigned structures. For example, the ^{1}H NMR of **3a** consisted of one exchangeable sharp singlet for amine ($-NH_2$) protons (δ = 3.67) along with appropriate chemical shifts for the twelve aromatic protons of the three aromatic moieties.

The amine precursor **3a** was chosen as a representative substrate for the optimization studies of intramolecular cycloamination reaction using copper source, ligands, solvents and bases (Table 1). In order to optimize this coupling protocol, the influence of each parameter on the outcome of the reaction was thoroughly investigated. As shown in Table 1, various copper salts including CuI, CuCl, $Cu(OAc)_2\cdot H_2O$, and $CuSO_4\cdot 5H_2O$ were studied as alternative catalyst precursors. Although all these copper compounds are catalytically active, none of them is as effective as CuI (Entry 6, Table 1). The best result was obtained with 5 mol% catalyst loading. Ligands

Table 1 Optimization of copper catalysts, ligands, solvents and bases on the cyclization of amine precursor **3a** to benzimidazodibenzdiazepine **4a**



Entry	Catalyst (5 mol%)	Ligand (10 mol%)	Base (2 equiv.)	Solvent (8 mL)	Time (h)	Yield[a] (%)
1	CuI	—	K_2CO_3	DMF	17 h	2
2	CuI	—	KO-*t*Bu	DMF	17 h	5
3	CuI	L_1[b]	K_2CO_3	DMF	17 h	30
4	CuI	L_1	KO-*t*Bu	DMF	18 h	45
5	CuI	L_1	K_2CO_3	Toluene	18 h	52
6	CuI	L_1	KO-*t*Bu	Toluene	17 h	72
7	CuI	L_2[c]	KO-*t*Bu	Toluene	17 h	52
8	CuI	L_3[d]	KO-*t*Bu	Toluene	17 h	47
9	CuI	L_1	KO-*t*Bu	DME	16 h	35
10	CuI	L_1	KO-*t*Bu	THF	17 h	25
11	CuI	L_1	KO-*t*Bu	1,4-Dioxane	18 h	42
12	$CuSO_4\cdot 5H_2O$	L_1	KO-*t*Bu	Toluene	18 h	12
13	$Cu(OAc)_2\cdot H_2O$	L_1	KO-*t*Bu	Toluene	18 h	18
14	CuCl	L_1	KO-*t*Bu	Toluene	18 h	22

[a] Isolated Yield. [b] L_1: 1,10 phenanthroline monohydrate. [c] L_2: (±)-*trans*-1,2-cyclohexane diamine. [d] L_3: *N*,*N*′-dimethylethylene diamine.

including 1,10-phenanthroline monohydrate (L_1), (±)-*trans*-1,2-cyclohexane diamine (L_2) and *N*,*N*′-dimethylethylenediamine (L_3) were screened, with L_2 and L_3 proving less efficient than L_1. Bases were found to have dramatic influence on the cyclization reaction and KO-*t*Bu (2 equiv.) was the most effective one. A study of the solvent effect (THF, DMF, DME, 1,4-dioxane and toluene) suggested that toluene was the solvent of choice. The optimal temperature for the coupling proved to be 110–120 °C (higher temperatures gave the same results) and the reaction was complete within 17 h, as revealed by the consumption of the aryl bromide by TLC. The optimized conditions for the aryl amination reaction of **3a** employed CuI (5 mol%) as a catalyst, 1,10-phenanthroline monohydrate (10 mol%) as a ligand, KO-*t*Bu (2 equiv.) as a base, and toluene as solvent. To the best of our knowledge, this is the first copper catalyzed intramolecular aryl amination reaction using benzimidazole fused aromatic primary amines.

With **3d** and **3f** the products (**4d** and **4f**, Fig. 1) were isolated as difficult to separate regioisomeric mixtures (**4d** and **4d***;**4f** and **4f***, Fig. 1). Interestingly, **3e** furnished a single isomer **4e** (Fig. 1). The structure of **4e** could be predicted using COSY and NOESY spectral analysis. The singlet at δ 8.13 can only belong to the proton lying between the imidazole ring and the benzoyl group. As it showed NOESY correlation with the proton signal at δ 7.76 (doublet), assignable to H-9 of the neighbouring benzene ring, only the isomer **4e** (Fig. 1) appeared likely.

We have made spectrophotometric and fluorometric studies of the synthesized compounds **4a–h** in dichloromethane medium. The normalized absorption and fluorescence spectra are depicted in Fig. 2 and 3 respectively to reveal the spectral shifts for the different molecular systems. For the absorption measurements, concentrations of all the compounds in the experimental solution were $\sim 10^{-6}$ mol dm^{-3}. As is obvious from the figures the spectral behavior of the compounds do not differ very much from one another except **4e** for which both the absorption and the fluorescence spectra show remarkable bathochromic shifts.

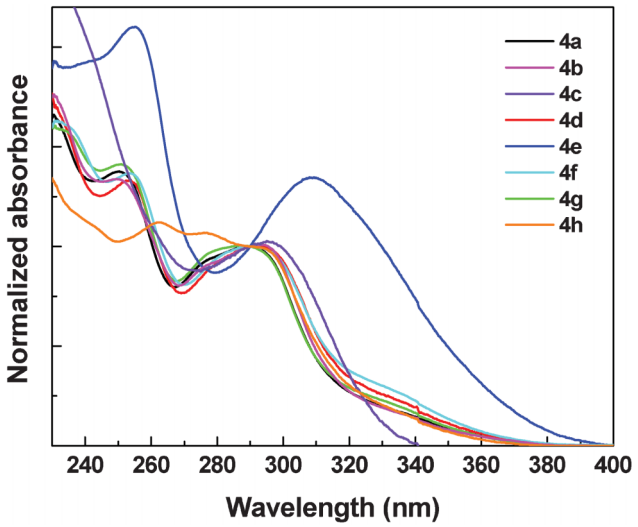


Fig. 2 Normalized absorption spectra of **4a–h** in dichloromethane (normalized at 290 nm).

The fluorescence maxima are reported in Table 2. A remarkable bathochromic shift in the emission spectrum of **4e** compared to the others is worth mentioning. This may be ascribed to an extension of conjugation of the π electrons from the benzimidazole ring to the benzoyl (–COPh) group. The fluorescence quantum yields (Φ_f) of the products, measured using quinine sulphate in 1.0 N sulfuric acid solution as a standard ($\Phi_f \approx 0.54$),[35] were found to vary widely in the range 0.02–0.22 (Table 2). A critical look at selected pairs of compounds differing in one methyl substitution (**4a-4b**, **4a-**

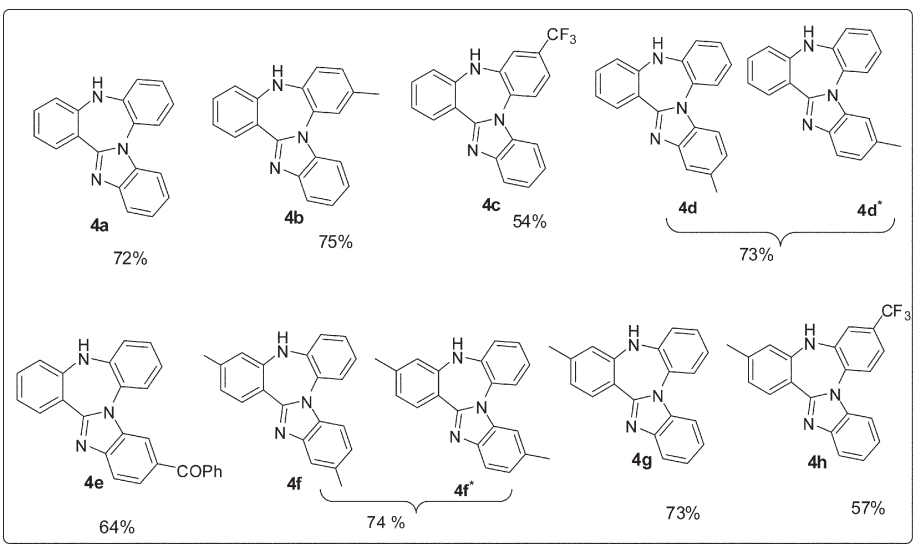


Fig. 1 List of products formed by intramolecular aryl amination of aryl bromides with CuI. *Reaction conditions*: CuI (5 mol%), 1,10 phenanthroline·H_2O (10 mol%), KO-*t*Bu (2 equiv.), toluene, 110 °C, 17–19 h.

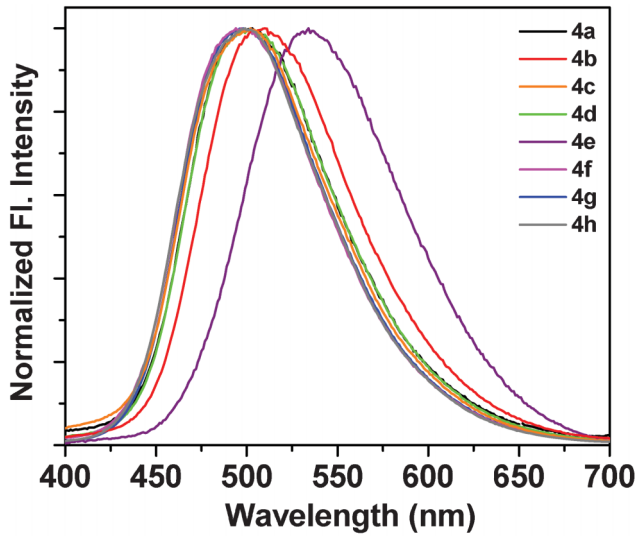


Fig. 3 Normalized fluorescence spectra of **4a–h** in dichloromethane. λ_{exc} = 358 nm.

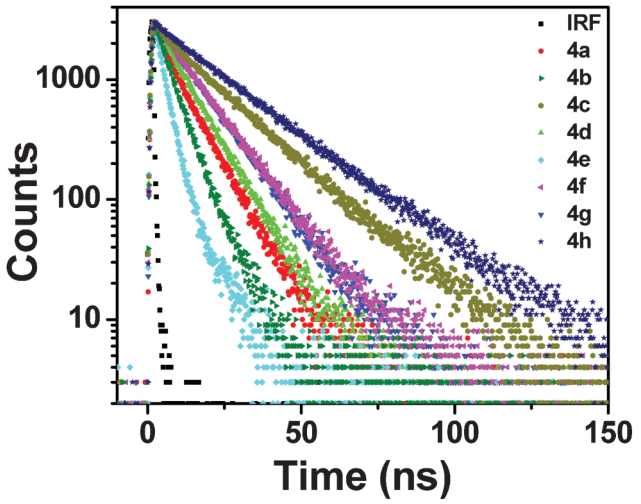


Fig. 4 Fluorescence decays of the synthesized compounds in dichloromethane. The samples are indicated in the legends. The sharp profile in black represents the instrumental response function (IRF).

4g, **4a-4d**, **4g-4f**, **4c-4h**) reveals that introduction of the methyl group leads to an increase in the fluorescence quantum yield; although the increment in the Φ_f value depends on the particular point of attachment of the group. Similarly, a comparison with **4a-4c** and **4g-4h** reveals that introduction of a $-CF_3$ group induces a remarkable enhancement in the fluorescence quantum yield, although we cannot offer any specific reason for this increase at this moment. The high fluorescence quantum yields of some of the compounds, particularly **4h**, render them useful as fluorescence standards as well as markers of the biological samples like DNA.

The fluorescence lifetimes of the compounds were determined from time-resolved intensity decays by the method of time-correlated single-photon counting (TCSPC). All the samples were excited at 370 nm. The monitoring wavelength was 500 nm for all the samples except **4e** for which it was 535 nm. The fluorescence decays of all the compounds were single exponentials (Fig. 4). The lifetimes (τ) of the excited species were extracted through deconvolution and the values are presented in Table 3. Interestingly, all these compounds exhibit relatively long fluorescence lifetimes. The radiative (k_r) and non-radiative (k_{nr}) decay constants for all the compounds were determined from the fluorescence quantum yields (Φ_f) and lifetimes (τ) using the following relations. The values are displayed in Table 3.

$$k_r = \frac{\phi_f}{\tau_f} \quad (1)$$

$$k_r + k_{nr} = \frac{1}{\tau_f} \quad (2)$$

Both high fluorescence quantum yield and long lifetime should render some of these novel compounds efficient fluorescent markers for biosystems to be studied *in vivo* using single molecule fluorescence techniques. The positive fluorometric behavior may also be exploited towards developing electroluminescent display devices.

Table 2 Steady state photophysical parameters of compounds **4a–h**

Compound	λ_{exc} [a] (nm)	λ_{em} [b] (nm)	Φ_f [c]
4a	291	499	0.045
4b	293	510	0.058
4c	292	502	0.122
4d	293	510	0.080
4e	309	533	0.025
4f	293	497	0.138
4g	288	498	0.133
4h	292	499	0.219

[a] Excitation wavelength. [b] Emission wavelength. [c] Fluorescence quantum Yield.

Table 3 Dynamic photophysical parameters of compounds **4a–h**

Compound	Φ_f	τ_f (ns)[a]	k_r (s^{-1}) (Φ_f/τ_f)[b]	k_{nr} (s^{-1})[c]
4a	0.045	8.60	5.23×10^6	11.11×10^7
4b	0.058	5.59	10.38×10^6	16.85×10^7
4c	0.122	18.56	6.57×10^6	4.73×10^7
4d	0.080	9.50	8.42×10^6	9.68×10^7
4e	0.025	3.14	7.96×10^6	31.05×10^7
4f	0.138	12.30	11.22×10^6	7.01×10^7
4g	0.133	11.98	11.10×10^6	7.24×10^7
4h	0.219	22.56	9.71×10^6	3.46×10^7

[a] Fluorescence lifetime. [b] Radiative decay constant. [c] Non-radiative decay constant.

Conclusions

In summary, we have developed a simple and efficient three-step synthetic route to benzimidazole fused dibenzodiazepines using a copper catalyzed intramolecular Ullmann type amination reaction as the key step. The presence of –NH group in the diazepine unit offers more opportunities for further functionalization. The photophysical studies reveal that some of these compounds are novel fluorophores having high fluorescence quantum yields and long lifetime. Apart from the pharmaceutical prospect of the synthesized compounds, the fluorometric properties are expected to make them promising for their use as biomarkers in cells.

Experimental section

General

Some reagents were obtained from commercial sources and used without purification. The solvents used were of technical grade, and freshly distilled prior to use. All melting points were obtained on a laboratory devices melting point bath and are uncorrected. ^{1}H (300 MHz, 600 MHz) and ^{13}C (75 MHz, 150 MHz) NMR spectra were recorded using $CDCl_3$ as solvent and tetramethyl silane (TMS) as internal standard on Bruker DPX 300 MHz and Bruker DRX 600 MHz NMR instruments at ambient temperature. Chemical shifts are stated in parts per million in δ scales. Infrared spectra were recorded on a JASCO-FTIR Model-410, using KBr pellets. Mass spectra were measured in EIMS, ESIMS(+) and HRMS (ESI^+) mode. EIMS were done on a SHIMADZU GCMS (model: GCMS-QP5050A) mass spectrometer. ESIMS and HRMS (ESI^+) were done on a Waters Micromass Q-TOF micro™ Mass Spectrometer. TLC was performed on pre-coated plates (0.25 nm, silica gel 60 F_{254}). A SHIMADZU (model UV-1700) UV-vis Spectrophotometer was used for recording UV-vis spectra keeping concentrations of the compounds at $\sim 10^{-6}$ mol dm^{-3}. The corrected fluorescence spectra were recorded with SPEX Fluorolog II spectrofluorometer at right angle configuration. Fluorescence lifetimes were determined from the time resolved fluorescence decays by the method of time-correlated single photon counting (TCSPC) using Horiba Jobin Yvon Fluorocube spectrofluorometer with excitation source NanoLED-03 at 370 nm and TBX-04 detector. The instrument response time was ~ 1 ns.

General procedure for the synthesis of 2: 2-(2-Bromophenyl)-1-(2-nitrophenyl)benzimidazole (2a). To the solution of benzimidazole **1a** (0.20 g, 0.740 mmol) in acetone (7 mL), KOH (0.082 g, 2 equiv.) was added and the reaction mixture was stirred for 30 min. at room temperature. To this, *o*-fluoronitrobenzene (0.08 mL, 0.735 mmol) was added and the mixture was refluxed for 4 h. Acetone was evaporated under vacuum and the resulting reaction mixture was diluted with ethylacetate and washed with water and brine. The combined organic layer was dried over sodium sulphate and evaporated under vacuum to get the crude mixture. The crude material was purified by column chromatography over silica gel (100–200 mesh) eluting with 12% ethylacetate in Pet. ether to get a pure yellow solid **2a** (0.221 g, 76%) ; mp 155–157 °C, IR (KBr, ν_{max}) 3062, 1602, 1530, 1442, 1381, 1345, 1320, 1260, 1192, 1123, 1025, 849, 761, 748, 700, 620 cm^{-1}; EtOAc : Pet.ether (3 : 7); R_f 0.47. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14 (d, J = 7.8 Hz, 1H), 7.22–7.33 (m, 3H), 7.35–7.40 (m, 1H), 7.42–7.46 (m, 1H), 7.52–7.56 (m, 1H), 7.59–7.61 (m, 1H), 7.65–7.75 (m, 2H), 7.94 (d, J = 8.1 Hz, 1H), 8.00 (dd, J = 8.1, 1.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 109.6, 120.6, 123.3, 123.4, 124.1, 125.7, 127.4, 129.4, 130.0, 131.0, 131.2, 131.5, 132.5, 132.7, 134.0, 135.6, 142.9, 145.8, 151.1. ESI-MS m/z : 394, 396 ($M+H^+$ for ^{79}Br, ^{81}Br), 416, 418 ($M+Na^+$ for ^{79}Br, ^{81}Br). Anal. Calcd $C_{19}H_{12}BrN_3O_2$; C, 57.89; H, 3.07; N, 10.66; found C, 58.09; H, 3.02; N, 10.81.

2-(2-Bromophenyl)-1-(5-methyl-2-nitrophenyl)benzimidazole (2b). Yellow solid, yield (0.244 g, 72%), mp 157–159 °C; IR (KBr, ν_{max}) 3051, 1599, 1522, 1447, 1344, 1319, 1257, 1126, 1023, 826, 747 cm^{-1}; EtOAc : Pet. ether (3 : 7); R_f 0.50. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.45 (s, 3H), 7.13 (d, J = 7.5 Hz, 1H), 7.24–7.38 (m, 5H), 7.43 (d, J = 10.5 Hz, 2H), 7.52 (d, J = 7.2 Hz, 1H), 7.92 (d, J = 8.1 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.3, 109.7, 120.4, 123.2, 124.0, 125.7, 127.3, 129.3, 130.5, 130.9, 131.0, 131.4, 131.5, 132.4, 132.5, 132.6, 135.5, 142.8, 145.8, 151.1. EI-MS m/z : 407, 409 (for ^{79}Br, ^{81}Br). Anal. Calcd $C_{20}H_{14}BrN_3O_2$; C, 58.84; H, 3.46; N, 10.29; found C, 59.09; H, 3.49; N, 10.14.

2-(2-Bromophenyl)-1-(2-nitro-4-trifluoromethylphenyl)benzimidazole (2c). Pale yellow solid, yield (0.288 g, 85%), mp 147–149 °C; IR (KBr, ν_{max}) 3068, 1618, 1543, 1445, 1381, 1321, 1256, 1180, 1142, 1088, 1031, 741, 636 cm^{-1}; EtOAc : Pet. ether (3 : 7); R_f 0.53. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (d, J = 7.8 Hz, 1H), 7.27–7.36 (m, 2H), 7.37–7.40 (m, 1H), 7.43–7.48 (m, 2H), 7.55 (dd, J = 1.2, 7.6 Hz, 1H), 7.84 (d, J = 8.1 Hz, 1H), 7.94–8.00 (m, 2H), 8.26 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 109.4, 120.9, 123.3, 123.8, 124.6, 127.8, 130.5, 130.6, 130.7, 131.90, 132.2, 132.4, 132.7, 133.0, 135.2, 143.1, 145.6, 150.8. ESI-MS m/z : 462, 464 ($M+H^+$ for ^{79}Br, ^{81}Br), 484, 486 ($M+Na^+$ for ^{79}Br, ^{81}Br). Anal. Calcd $C_{20}H_{11}BrF_3N_3O_2$; C, 51.97; H, 2.40; N, 9.09; found: C, 52.24; H, 2.36; N, 9.24.

2-(2-Bromophenyl)-1-(2-nitrophenyl)-5-methylbenzimidazole (2d). Yellow solid, yield (0.260 g, 73%), mp 165–167 °C; IR (KBr, ν_{max}) 2918, 1599, 1530, 1491, 1441, 1383, 1343, 1024, 950, 757, 537 cm^{-1}; EtOAc : Pet. ether (3 : 7); R_f 0.49. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.53 (s, 3H), 7.02 (d, J = 8.4 Hz, 1H), 7.15 (d, J = 8.1 Hz, 1H), 7.22–7.31 (m, 2H), 7.43 (d, J = 7.2 Hz, 1H), 7.53 (d, J = 7.8 Hz, 1H), 7.58 (d, J = 8.1 Hz, 1H), 7.63 (d, J = 6.9 Hz, 1H), 7.70 (d, J = 8.1 Hz, 2H), 8.00 (d, J = 8.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.4, 109.1, 120.2, 123.4, 125.5, 125.6, 127.3, 129.4, 129.8, 131.0, 131.3, 132.4, 132.6, 133.04, 133.6, 134.0, 134.2, 143.1, 145.7, 151.0. ESI-MS m/z 408, 410 ($M+H^+$ for ^{79}Br, ^{81}Br), 430, 432 ($M+Na^+$ for ^{79}Br, ^{81}Br). Anal. calcd. $C_{20}H_{14}BrN_3O_2$; C, 58.84; H, 3.46; N, 10.29; found C, 59.09; H, 3.51; N, 10.42.

2-(2-Bromo-4-methylphenyl)-1-(2-nitrophenyl)-5-methylbenzimidazole (2f). Yellow solid, yield (0.151 g, 72%), mp 94–96 °C; IR (KBr, ν_{max}) 3032, 1605, 1530, 1489, 1463, 1382, 1346, 1206, 1147, 1037, 819, 788, 729 cm^{-1}; EtOAc : Pet. ether (3 : 7); R_f 0.46. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.30 (s, 3H), 2.52, 2.45 (2 × s, total 3H), 6.9–7.01 (m, 1H), 7.07 (d, J = 7.2 Hz, 1H), 7.12–7.20 (m, 1H), 7.26–7.34 (m, 2H), 7.53–7.61 (m, 1H), 7.63–7.66 (m, 1H), 7.67–7.80 (m, 2H), 7.99 (ddd, J = 1.2, 3.3, 8.1 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 21.0, 21.5, 109.1, 120.0, 124.8, 125.6, 128.2, 129.7, 131.1, 132.2, 133.1, 133.6, 133.9, 134.1, 135.7, 141.0, 141.9, 143.2, 145.7, 150.77, 151.0. ESI-MS *m*/*z* : 422, 424 ($M+H^+$ for ^{79}Br, ^{81}Br), 444, 446 ($M+Na^+$ for ^{79}Br, ^{81}Br). Anal. calcd $C_{21}H_{16}BrN_3O_2$; C, 59.73; H, 3.82; N, 9.95; found; C, 60.01; H, 3.77; N, 10.09.

2-(2-Bromo-4-methylphenyl)-1-(2-nitrophenyl)benzimidazole (2g). Yellow solid, yield (0.311 g, 73%), mp 164–166 °C; IR (KBr, ν_{max}) 3043, 1605, 1528, 1449, 1379, 1346, 1256, 1037, 825, 753 cm^{-1}; EtOAc : Pet. ether (3 : 7); R_f 0.50. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.31 (s, 3H), 7.07 (d, *J* = 3.9 Hz, 1H), 7.12 (d, *J* = 3.9 Hz, 1H), 7.29–7.32 (m, 2H), 7.35 (s, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 7.8 Hz, 1H), 7.65 (d, *J* = 3.9 Hz, 1H), 7.72 (t, *J* = 7.5 Hz, 1H), 7.93 (d, *J* = 3.9 Hz, 1H), 8.00 (d, *J* = 4.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.0, 109.6, 120.5, 123.1, 123.3, 124.0, 125.7, 127.9, 128.3, 129.6, 129.9, 131.3, 132.2, 133.2, 134.0, 135.6, 142.1, 143.0, 145.8, 151.3. ESI-MS *m*/*z* : 408, 410 ($M+H^+$ for ^{79}Br, ^{81}Br), 430, 432 ($M+Na^+$ for ^{79}Br, ^{81}Br). Anal. Calcd $C_{20}H_{14}BrN_3O_2$; C, 58.84; H, 3.46; N, 10.29; found C, 59.14; H, 3.38; N, 10.42.

2-(2-Bromo-4-methylphenyl)-1-(2-nitro-4-trifluoromethylphenyl)benzimidazole (2h). Yellow solid, yield (0.313 g, 84%), mp 128–130 °C; IR (KBr, ν_{max}) 3062, 2318, 1616, 1544, 1450, 1382, 1321, 1256, 1181, 1141, 1095, 974, 908, 822, 743; EtOAc : Pet. ether (3 : 7); R_f 0.48. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.35 (s, 3H), 7.13 (d, *J* = 7.8 Hz, 2H), 7.31–7.44 (m, 4H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.93–7.99 (m, 2H), 8.26 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.0, 109.3, 120.8, 122.9, 123.3, 123.7, 124.4, 127.3, 128.6, 130.6, 132.2, 132.3, 132.8, 133.4, 135.1, 142.6, 143.1, 145.5, 151.0. ESI-MS *m*/*z* 476, 478 ($M+H^+$ for ^{79}Br, ^{81}Br), 498, 500 ($M+Na^+$ for ^{79}Br, ^{81}Br). Anal. Calcd. $C_{21}H_{13}BrF_3N_3O_2$; C, 52.96; H, 2.75; N, 8.82; found C, 53.18; H, 2.61; N, 8.96.

General procedure for the synthesis of 3: 1-(2-Aminophenyl)-2-(2-bromophenyl) benzimidazole (3a). To the solution of compound **2a** (0.20 g, 0.508 mmol) in AcOH (5 mL), Fe powder (0.142 g, 2.54 mmol) was added and the reaction mixture was heated at 90 °C for one hour. Then the reaction mixture was cooled and poured onto ice water. The white precipitate was filtered and the resulting solution was extracted with ethylacetate. The organic layer was washed with saturated bicarbonate, water and brine. The combined organic layer was dried over sodium sulphate, filtered and concentrated under reduced pressure to get the crude product that was further purified by column chromatography over silica gel (100–200 mesh) eluting with 14% ethylacetate in pet. ether furnishing **3a** (0.169 g, 92%), yellowish brown solid, mp 164–166 °C; IR (KBr, ν_{max}) 3439, 3301, 3180, 1637, 1609, 1502, 1455, 1381, 1317, 1265, 1191, 1152, 1033, 976, 910, 831, 752, 622 cm^{-1}; EtOAc : Pet. ether (3 : 7); R_f 0.37. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.67 (s, 2H), 6.66 (t, *J* = 7.2 Hz, 1H), 6.78 (d, *J* = 7.8 Hz, 1H), 7.0 (d, *J* = 7.5 Hz, 1H), 7.14–7.38 (m, 7H), 7.57 (d, *J* = 6.6 Hz, 1H), 7.92 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 111.0, 116.4, 118.4, 120.3, 120.96, 123.0, 123.6, 123.7, 126.8, 129.1, 130.0, 130.9, 131.9, 132.0, 132.8, 134.9, 142.9, 152.0. ESI-MS *m*/*z*: 364, 366 ($M+H^+$ for ^{79}Br, ^{81}Br), 386, 388 ($M+Na^+$ for ^{79}Br, ^{81}Br). Anal. Calcd $C_{19}H_{14}BrN_3$; C, 62.65; H, 3.87; N, 11.54; found C, 62.89; H, 3.82; N, 11.66.

1-(2-Amino-5-methylphenyl)-2-(2-bromophenyl)benzimidazole (3b). Pale brown solid, yield (0.166 g, 90%), mp 105–107 °C; IR (KBr, ν_{max}) 3312, 3190, 3044, 2919, 2851, 2313, 1630, 1512, 1454, 1375, 1316, 1258, 1153, 1023, 816, 751, 547 cm^{-1}; EtOAc : Pet. ether (3 : 7); R_f 0.36. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.14 (s, 3H), 3.52 (s, 2H), 6.70 (d, *J* = 8.4 Hz, 1H), 6.81 (s, 1H), 6.98 (dd, *J* = 1.2, 7.8 Hz, 1H), 7.19 (d, *J* = 7.2 Hz, 1H), 7.23–7.27 (m, 2H), 7.28–7.35 (m, 1H), 7.37–7.43 (m, 2H), 7.60 (dd, *J* = 1.8, 7.8 Hz, 1H), 7.93 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.1, 111.0, 116.5, 120.3, 120.9, 122.9, 123.5, 123.7, 126.7, 128.0, 129.2, 130.7, 130.9, 131.9, 132.0, 132.8, 135.0, 140.4, 142.8, 152.0. EI-MS *m*/*z* 377, 379 (for ^{79}Br, ^{81}Br). Anal. Calcd. $C_{20}H_{16}BrN_3$; C, 63.50; H, 4.26; N, 11.11; found C, 63.70; H, 4.30; N, 11.24.

1-(2-Amino-4-trifluoromethylphenyl)-2-(2-bromophenyl)benzimidazole (3c). Yellow solid; yield (0.196g, 84%), mp 169–171 °C; IR (KBr, ν_{max}) 3462, 3310, 3158, 1644, 1518, 1445, 1383, 1322, 1258, 1163, 1125, 976, 872, 752 cm^{-1}; EtOAc : Pet. ether (3 : 7); R_f 0.38. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.94 (s, 2H), 6.90 (d, *J* = 7.5 Hz, 1H), 7.04–7.10 (m, 2H), 7.18 (d, *J* = 6.6 Hz, 1H), 7.26–7.28 (m, 2H), 7.34–7.40 (m, 3H), 7.60 (d, *J* = 6.3 Hz, 1H), 7.94 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 110.9, 113.1, 114.8, 120.6, 123.4, 123.5, 123.6, 124.0, 127.0, 129.7, 131.3, 131.5, 132.0, 133.0, 134.4, 142.9, 143.1, 151.7. ESI-MS *m*/*z* 432, 434 ($M+H^+$ for ^{79}Br, ^{81}Br), 454, 456 ($M+Na^+$ for ^{79}Br, ^{81}Br). Anal. Calcd $C_{20}H_{13}BrF_3N_3$; C, 55.57; H, 3.03; N, 9.72 ; found C, 55.77; H, 2.99; N, 9.60.

1-(2-Aminophenyl)-2-(2-bromophenyl)-5-methylbenzimidazole (3d). Brown solid, yield (0.159 g, 86%), mp 99–101 °C; IR (KBr, ν_{max}) 3460, 3378, 3194, 3037, 2920, 2855, 1623, 1505, 1455, 1378, 1318, 1264, 1200, 1150, 1030, 977, 800, 756 cm^{-1}; EtOAc : Pet. ether (3 : 7); R_f 0.36. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.47, 2.53 (2 × s, 3H), 3.7 (brs, 2H), 6.64–6.69 (m, 1H), 6.77–6.80 (m, 1H), 6.97–7.0 (m, 1H), 7.08 (d, *J* = 8.4 Hz, 1H), 7.15 (d, *J* = 7.5 Hz, 2H), 7.20–7.28 (m, 2H), 7.38–7.41 (m, 1H), 7.58 (dd, *J* = 2.1, 7.5 Hz, 1H), 7.72 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.4, 110.57, 116.3, 118.2, 119.8, 120.8, 123.6, 125.0, 126.7, 129.0, 130.0, 130.8, 131.7, 131.9, 132.7, 132.7, 132.8, 142.8, 142.9, 151.8. ESI-MS *m*/*z* : 378, 380 ($M+H^+$ for ^{79}Br, ^{81}Br), 400, 402 ($M+Na^+$ for ^{79}Br, ^{81}Br). Anal. Calcd $C_{20}H_{16}BrN_3$; C, 63.50; H, 4.26; N, 11.11; found C, 63.72; H, 4.31; N, 10.97.

1-(2-Aminophenyl)-2-(2-bromophenyl)-6-benzoylbenzimidazole (3e). Pale brown solid, yield (0.142 g, 76%), mp 114–116°c; IR (KBr, ν_{max}) 3453, 3356, 3058, 1633, 1505, 1439, 1381, 1320, 1271, 1109, 1026, 9771, 907, 835, 727, 427 cm^{-1}; EtOAc : Pet. ether (3 : 7); R_f 0.30. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.68 (s, 2H), 6.68 (t, *J* = 7.5 Hz, 1H), 6.79 (d, *J* = 8.1 Hz, 1H), 7.01 (d, *J* = 7.5 Hz, 1H), 7.17 (t, *J* = 7.8 Hz, 1H), 7.28–7.31 (m, 2H), 7.42–7.50 (m, 3H), 7.55–7.62 (m, 2H), 7.81 (t like, *J* = 7.8 Hz, 4H), 7.97 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 113.6, 116.7, 118.6, 119.7, 120.3, 123.5, 125.8, 126.9, 128.2, 129.0, 130.0, 130.4, 131.3, 131.4, 131.9, 132.2, 133.0, 133.2, 134.8, 138.1, 142.8, 146.0, 154.9, 196.5. ESI-MS *m*/*z* 468, 470 ($M+H^+$ for ^{79}Br, ^{81}Br), 490, 492 ($M+Na^+$ for ^{79}Br, ^{81}Br). Anal. Calcd $C_{26}H_{18}BrN_3O$; C, 66.68; H, 3.87; N, 8.97; found C, 66.90; H, 3.91; N, 8.82.

1-(2-Aminophenyl)-2-(2-bromo-4-methylphenyl)-5-methylbenzimidazole (3f). Brown solid, yield (0.180 g, 87%), mp 97–99 °C; IR (KBr, ν_{max}) 3461, 3316, 3193, 3032, 2919, 2857, 1617,

1503, 1460, 1380, 1315, 1264, 1203, 1151, 1036, 976, 815, 745, 605, 430 cm^{-1}; EtOAc : Pet. ether (3 : 7); R_f 0.38. ^1H NMR (300 MHz, $CDCl_3$) δ 2.31 (s, 3H), 2.46 (s, 3H), 2.53 (s, 3H), 3.66 (s, 2H), 6.65–6.71 (m, 1H), 6.78–6.81 (m, 1H), 6.96–7.07 (m, 3H), 7.12–7.20 (m, 2H), 7.25–7.27 (t, J = 7.5 Hz, 1H), 7.40 (s, 1H), 7.71–7.81 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.0, 21.5, 110.5, 116.3, 118.4, 120.0, 121.2, 123.4, 124.5, 125.0, 127.6, 129.0, 129.2, 129.8, 130.0, 131.7, 133.3, 141.3, 142.9, 143.2, 152.0. ESI-MS m/z : 392, 394 ($M+H^+$ for ^{79}Br, ^{81}Br), 414, 416 ($M+Na^+$ for ^{79}Br, ^{81}Br). Anal. Calcd $C_{21}H_{18}BrN_3$; C, 64.30; H, 4.62; N, 10.71; found C, 64.12; H, 4.67; N, 10.85.

1-(2-Aminophenyl)-2-(2-bromo-4-methylphenyl)benzimidazole (3g). Yellow solid; yield (0.247 g, 89%), mp 197–199 °C; IR (KBr, ν_{max}) 3461, 3300, 3176, 2921, 1636, 1604, 1502, 1455, 1380, 1317, 1262, 1150, 1036, 974, 821, 748, 533 cm^{-1}; EtOAc : Pet. ether (3 : 7); R_f 0.35. ^1H NMR (600 MHz, $CDCl_3$) δ 2.31 (s, 3H), 3.66 (s, 2H), 6.68 (t, J = 7.2 Hz, 1H), 6.80 (d, J = 8.4 Hz, 1H), 7.00 (d, J = 7.8 Hz, 1H), 7.05 (d, J = 7.2 Hz, 1H), 7.13 (t, J = 8.4 Hz, 2H), 7.27 (d, J = 7.8 Hz, 1H), 7.31 (t like, J = 7.8 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.41 (s, 1H), 7.93 (d, J = 7.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.0, 111.0, 116.4, 118.4, 120.2, 121.0, 122.9, 123.3, 123.5, 127.7, 128.7, 129.2, 129.9, 131.7, 133.3, 134.9, 141.4, 142.8, 142.9, 152.1. EI-MS m/z : 377, 379 (^{79}Br, ^{81}Br). Anal. Calcd $C_{20}H_{16}BrN_3$ C, 63.50; H, 4.26; N, 11.11; found C, 63.77; H, 4.22; N, 11.26.

1-(2-Amino-4-trifluoromethylphenyl)-2-(2-bromo-4-methylphenyl)benzimidazole (3h). Pale brown solid, yield (0.213 g, 83%), mp 144–146 °C; IR (KBr, ν_{max}) 2666, 2315, 1633, 1516, 1447, 1383, 1325, 1258, 1167, 1127, 824, 748, 536 cm^{-1}; EtOAc : Pet. ether (3 : 7); R_f 0.37. ^1H NMR (300 MHz, $CDCl_3$) δ 2.34 (s, 3H), 3.90 (s, 2H), 6.91 (d, J = 6.9 Hz, 1H), 7.04–7.10 (m, 4H), 7.17 (d, J = 7.5 Hz, 1H), 7.30–7.37 (m, 2H), 7.40 (d, J = 8.1 Hz, 1H), 7.94 (d, J = 7.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.0, 110.9, 113.1, 113.1, 114.8, 120.5, 123.2, 123.3, 123.6, 123.8, 128.0, 128.3, 130.0, 131.7, 133.5, 134.4, 141.9, 142.8, 143.2, 151.8. EI-MS m/z 445, 447 (for ^{79}Br, ^{81}Br). Anal. Calcd $C_{21}H_{15}BrF_3N_3$; C, 56.52; H, 3.39; N, 9.42; found C, 56.67; H, 3.44; N, 9.32.

General procedure for the synthesis of cyclized product 4

To the stirred solution of **3a** (0.150 g, 0.413 mmol) in dry toluene (8 mL), KO-*t*Bu (0.092 g, 2 equiv.), 1,10 phenanthroline (10 mol%), and CuI (5 mol%) were added. Then the reaction mixture was refluxed for 17 h under nitrogen atmosphere. After completion of the reaction (monitored by TLC), toluene was evaporated under vacuum, and the crude reaction mixture was extracted with ethyl acetate (3 × 25 mL). The organic layer was washed with water (3 × 25 mL) followed by brine (2 × 15 mL). The total organic layer was dried over sodium sulphate, filtered, and the solvent was evaporated under reduced pressure. The crude mass was purified by column chromatography over silica gel (100–200 mesh) eluting with 12% EtAOc in Pet. ether to get the desired compound **4a** (0.084 g, 72% yield).

5*H*-Benzimidazo[1,2-*d*]dibenzo[*b*,*f*][1,4]diazepine (4a). Pale yellow solid, yield (0.084 g, 72%), mp 198–200 °C; IR (KBr, ν_{max}) 3276, 1607, 1502, 1458, 1385, 1258, 746 cm^{-1}; EtOAc : Pet. ether (3 : 7); R_f 0.48. ^1H NMR (600 MHz, $CDCl_3$) δ 5.49 (s, 1H, NH), 6.90 (d, J = 7.8 Hz, 1H), 7.08 (d, J = 7.8 Hz, 1H), 7.14 (t, J = 7.2 Hz, 1H), 7.21–7.25 (m, 1H), 7.26–7.36 (m, 3H), 7.66 (dd, J = 14.4, 7.8, 2H), 7.89 (d, J = 7.8, 1H), 8.19 (d, J = 7.2, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 111.5, 119.5, 120.1, 121.6, 121.9, 123.1, 123.2, 123.5, 124.0, 127.7, 129.0, 130.9, 131.3, 134.8, 143.3, 144.0, 149.2, 152.3. ESI-MS m/z 284 $(M+H)^+$; HRMS (ESI^+): calcd for $C_{19}H_{12}N_3Na$ $[M+Na]^+$ 306.1007, found 306.1031.

8-Methyl-5*H*-benzimidazo[1,2-*d*]dibenzo[*b*,*f*][1,4]diazepine (4b). Pale yellow solid, yield (0.148 g, 75%), mp 214–216 °C, IR (KBr, ν_{max}): 3270, 1602, 1516, 1461, 1373, 1309, 1267, 815, 742 cm^{-1}; EtOAc : Pet. ether (3 : 7); R_f 0.49. ^1H NMR (300 MHz, $CDCl_3$) δ 2.37 (s, 3H), 5.35 (s, 1H, NH), 6.88 (d, J = 7.8, 1H), 6.97 (d, J = 8.1, 1H), 7.04 (d, J = 8.7, 1H), 7.13 (t, J = 7.5 Hz, 1H), 7.28–7.36 (m, 3H), 7.48 (s, 1H), 7.65 (dd like, J = 2.4, 6.9 Hz, 1H), 7.87 (dd like, J = 2.4, 6.9, Hz, 1H), 8.16 (dd like, J = 1.2, 7.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.6, 111.6, 119.4, 120.0, 121.6, 121.7, 123.0, 123.2, 123.4, 124.3, 128.2, 128.8, 130.9, 131.3, 133.9, 134.8, 140.7, 144.0, 149.5, 152.4. ESI-MS m/z 298 $(M+H)^+$, 320 $(M+Na)^+$. HRMS (ESI^+) calcd for $C_{20}H_{15}N_3Na$ $[M+Na]^+$ 320.1164, found 320.1196.

7-Trifluoromethyl-5*H*-benzimidazo[1,2-*d*]dibenzo[*b*,*f*][1,4]-diazepine (4c). White solid, yield (0.088 g, 54%), mp 224–226 °C, IR (neat, ν_{max}) 2921, 1597, 1507, 1445, 1383, 1323, 1211, 1164, 1123, 1072, 746 cm^{-1}; EtOAc : Pet. ether (3 : 7); R_f 0.47. ^1H NMR (600 MHz, $CDCl_3$) δ 5.54 (s, 1H, NH), 6.95 (d, J = 7.8 Hz, 1H), 7.19 (t, J = 15 Hz, 1H), 7.34 (t, J = 14.4, 2H), 7.36–7.39 (m, 2H), 7.48 (d, J = 8.4 Hz, 1H), 7.62 (d, J = 7.8 Hz, 1H), 7.80 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 7.8 Hz, 1H), 8.20 (d, J = 7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 111.3, 118.9, 119.7, 120.4, 121.0, 123.7, 123.8, 124.2, 124.3, 124.4, 131.2, 131.8, 132.0, 143.0, 143.4, 148.2, 151.9. ESI-MS m/z 352 $(M+H)^+$, 374 $(M+Na)^+$. HRMS (ESI^+): calcd for $C_{20}H_{12}F_3N_3Na$ $[M+Na]^+$, 374.0881 found 374.0869.

12-Methyl-5*H*-benzimidazo[1,2-*d*]dibenzo[*b*,*f*][1,4]diazepine (4d). Yellow solid, yield (0.115 g, 73%), mp 204–206 °C; IR (KBr, ν_{max}): 3028, 1594, 1505, 1461, 1382, 1247, 761 cm^{-1}. EtOAc : Pet. ether (3 : 7); R_f 0.50. ^1H NMR (300 MHz, $CDCl_3$) δ 2.50 (s, 3H), 5.43 (s, major, 1H, NH), 6.89 (d, J = 6 Hz, 1H), 7.11–7.31(m, 8H), 7.44–7.74 (m, 3H), 8.15 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 22.0, 112.1, 116.3, 116.5, 120.5, 123.1, 123.9, 124.0, 124.1, 124.2, 127.0, 129.8, 129.9, 130.9, 134.3, 144.5, 150.7, 172.6. ESI-MS m/z 298 $(M+H)^+$, 320 $(M+Na)^+$; HRMS (ESI^+): calcd for $C_{20}H_{15}N_3Na$ $[M+Na]^+$, 320.1164. found 320.1199.

11-Benzoyl-5*H*-benzimidazo[1,2-*d*]dibenzo[*b*,*f*][1,4]diazepine (4e). Pale yellow solid, yield (0.132 g, 64%), mp 191–193 °C; IR (KBr, ν_{max}) 2919, 1649, 1605, 1503, 1465, 1280, 903, 759 cm^{-1}; EtOAc : Pet. ether (3 : 7); R_f 0.45. ^1H NMR (300 MHz, $CDCl_3$) δ 5.5 (s, 1H, NH), 6.94 (d, J = 8.1 Hz, 1H), 7.11 (dd, J = 7.5, 1.5 Hz, 1H), 7.19 (d, J = 8.7 Hz, 1H), 7.24–7.30 (m, 2H), 7.35–7.41 (m, 1H), 7.50 (m, 2H), 7.58 (d, J = 7.5 Hz, 1H), 7.65–7.68 (m, 1H), 7.76–7.84 (m, 3H), 7.90 (d, J = 8.4 Hz, 1H), 8.19 (d, J = 1.2 Hz, 1H), 8.21 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 114.2, 119.4, 119.7, 121.2, 122.1, 123.7, 124.2, 124.5, 126.2, 128.2, 128.3, 128.6, 130.0, 131.2, 132.0, 132.1, 132.7, 134.8, 138.2, 143.4, 147.2, 149.6, 155.3, 196.5. ESI-MS m/z 388 $(M+H)^+$, 410

$(M+Na)^+$. HRMS (ESI^+): calcd for $C_{26}H_{17}N_3ONa$ $[M+Na]^+$, 410.1269. found 410.1305.

3,12-Dimethyl-5*H*-benzimidazo[1,2-*d*]dibenzo[*b*,*f*][1,4]diazepine (4f). Pale yellow solid, yield (0.088 g, 74%), mp 183–185 °C; IR (KBr, ν_{max}) 3201, 3024, 2921, 1611, 1507, 1456, 1375, 1323, 1249, 809, 758 cm^{-1}; EtOAc : Pet. ether (3 : 7); R_f 0.48. ^1H NMR (300 MHz, $CDCl_3$) δ 2.34 (s, 3H), 2.49, 2.50 (2 × s, 3H), 5.33 (s, 1H, NH), 6.72 (s, 1H), 6.96 (d, J = 7.8 Hz, 1H), 7.07 (d, J = 7.5 Hz, 2H), 7.12–7.26 (m, 2H), 7.43–7.74 (m, 3H), 8.04 (d, J = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.2, 21.5, 21.9, 111.0, 111.4, 119.4, 119.7, 120.0, 121.7, 123.9, 124.0, 124.44, 124.5, 124.7, 127.5, 129.2, 129.3, 130.7, 141.8, 143.1, 148.9, 148.9. ESI-MS m/z 312 $(M+H)^+$, 334 $(M+Na)^+$. HRMS (ESI^+): calcd for $C_{21}H_{17}N_3Na$ $[M+Na]^+$, 334.1320; found 334.1339.

3-Methyl-5*H*-benzimidazo[1,2-*d*]dibenzo[*b*,*f*][1,4]diazepine (4g). Pale yellow solid, yield (0.158 g, 73%), mp 267–269 °C; IR (KBr, ν_{max}): 3269, 1606, 1506, 1451, 1320, 1263, 813, 755 cm^{-1}; EtOAc : Pet. ether (3 : 7); R_f 0.49. ^1H NMR (300 MHz, $CDCl_3$) δ 2.33 (s, 3H), 5.36 (s, 1H, NH), 6.72 (s, 1H), 6.96 (d, J = 8.1 Hz, 1H) , 7.07 (dd, J = 1.2, 7.2 Hz, 1H), 7.16–7.25 (m, 2H), 7.27–7.35 (m, 2H), 7.65 (t, J = 8.7 Hz, 2H), 7.85 (d, J = 7.5 Hz, 1H), 8.06 (d, J = 8.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.2, 111.5, 118.7, 119.9, 120.1, 121.8, 123.0, 123.2, 123.9, 124.0, 124.5, 127.6, 129.0, 130.8, 134.8, 142.0, 143.3, 144.0, 149.1, 152.5. ESI-MS m/z 298 $(M+H)^+$, 320 $(M+Na)^+$. HRMS (ESI^+): calcd for $C_{20}H_{15}N_3Na$ $[M+Na]^+$, 320.1164; found 320.1195.

3-Methyl-7-trifluoromethyl-5*H*-benzimidazo[1,2-*d*]dibenzo[*b*,*f*][1,4]diazepine (4h). Yellow solid, yield (0.163 g, 57%), mp 241–243 °C; IR (KBr, ν_{max}) 3228, 1611, 1508, 1451, 1378, 1329, 1227, 1171, 1127, 980, 886, 815, 744 cm^{-1}; EtOAc : Pet. ether (3 : 7); R_f 0.48. ^1H NMR (300 MHz, $CDCl_3$) δ 2.36 (s, 3H), 5.48 (s, 1H, NH), 6.76 (s, 1H), 7.0 (d, J = 7.8 Hz, 1H), 7.28–7.38 (m, 3H), 7.45 (d, J = 8.1 Hz, 1H), 7.60 (d, J = 8.1 Hz, 1H), 7.79 (d, J = 8.1 Hz, 1H), 7.87 (d, J = 8.4 Hz, 1H), 8.07 (d, J = 8.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.2, 111.3, 118.6, 118.8, 118.9, 120.3, 120.8, 120.9, 123.5, 123.7, 124.3, 125.0, 129.4, 131.0, 132.2, 134.6, 142.5, 143.5, 144.2, 148.1, 152.1. EI-MS m/z 365; HRMS (ESI^+): calcd for $C_{21}H_{15}F_3N_3$ $[M+H]^+$, 366.1218; found 366.1239.

Acknowledgements

Financial support from the Department of Science and Technology (DST), New Delhi, Government of India is gratefully acknowledged. S. M. thanks the Council of Scientific and Industrial Research (CSIR) for providing a senior research fellowship (SRF). We acknowledge Dr G. S. Kumar for providing us the UV-vis spectrophotometer and Dr B. Achari for his valuable suggestions.

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