Water mediated expeditious and highly selective synthesis of 2-aryl-1-arylmethyl-1*H*-benzimidazoles by Dowex 50W: fluorescence properties of some representative compounds

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Abstract

Dowex 50W in aqueous medium proved to be a very efficient and reusable catalyst for the highly selective synthesis of 2-aryl-1-arylmethyl-1*H*-benzimidazoles in excellent yields from a wide variety of substituted *ortho*-phenylenediamines and aromatic aldehydes. A new technique for work-up has been developed that eliminates column chromatography for purification. The products can serve in further functionalization to produce molecular diversity including ionic liquids. Detailed DFT (Density Functional Theory) calculations have been done to establish the mechanism and justify the formation of the selective regioisomer from unsymmetrical *ortho*-phenylenediamine. The X-ray crystal data of one such product has been reported that clearly reveals the formation of one particular regioisomer. The fluorescence spectroscopic properties of some representative compounds have been studied in three solvents, dichloromethane, acetonitrile, methanol and their quantum yields calculated. The presented methodology has the advantages of one-pot operation and minimal environmental impact.

Keywords: Green synthesis, 2-aryl-1-arylmethyl-1*H*-benzimidazoles, Dowex 50W, aqueous medium, aromatic aldehydes, DFT calculation, fluorescence, quantum yield

Introduction

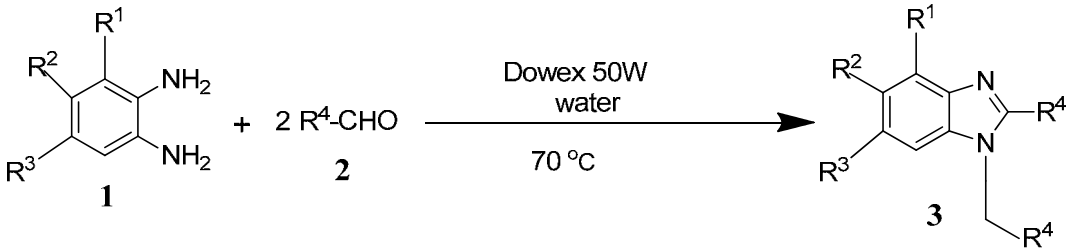
Excessive pressure from governmental and non-governmental organizations force organic chemists to explore alternative solvents to carry out chemical reactions simultaneously protecting our environment. In this context, water as a green reaction medium is highly appreciated. As a solvent, water possesses the following distinct advantages of being safe, nonflammable, readily available in large quantities, operationally very simple and devoid of any carcinogenic effects.

Therefore, water mediated organic reactions for the preparation of biologically active molecules constitutes a major challenge for chemists involved in organic synthesis.

1*H*-2-Substituted benzimidazole nuclei have diverse applications in medicinal chemistry.[1] Due to their affinity towards enzymes and protein receptors, they have been appropriately classified as "privileged sub-structures" for drug design.[2a] They should also serve as good starting materials of a variety of ionic liquids.[2b] Thus, synthesis of such nuclei is always a great challenge to the organic chemist.

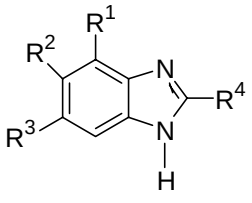
Results and Discussion

In continuation of our efforts in exploring the synthetic applicability of Dowex 50W (a sulfonic acid cation exchange resin) in aqueous medium towards the synthesis of a wide range of heterocycles,[3] we carried out a study of reaction of 4-chlorobenzaldehyde (2 mmol) and *ortho*-phenylene diamine (1 mmol) with Dowex 50W (acid form) (Scheme1, R^1=R^2=R^3=H, R^4=4-Cl-C_6H_4). Different solvent mixtures with different mole ratios of the catalyst were employed and the results are depicted in Table 1. The best result was obtained with 10 mol% of Dowex 50W in purely aqueous medium at 70 ºC (entry 3, Table 1). In all the cases, the 2-(4-chlorophenyl)-1-(4-chlorophenylmethyl)-1*H*-benzimidazole **3k** was the sole product isolated and the 2-(4-chlorophenyl)-1*H*-benzimidazole **4k** (R^1=R^2=R^3=H, R^4=4-Cl-C_6H_4) (Figure 1) was never obtained (not even a mixed ratio of the two). It should be also realized that, without Dowex 50W, the desired reaction did not take place at all (entry 1, Table 1).



(for various R^1,R^2, R^3 and R^4, please refer to Table 3)

Scheme 1. Synthesis of 2-aryl-1-arylmethyl-1*H*-benzimidazoles with Dowex 50W (10 mol %) in aqueous medium.



4 (not obtained)

Figure 1

Table 1. Optimisation of the reaction condition for the synthesis of 2-(4-chlorophenyl)-1-(4-chlorophenylmethyl)-1*H*-benzimidazole **3k** with Dowex 50W in aqueous medium at 70 ºC

Entry	solvent mixtures (volume : volume in mL)	Dowex 50W (mol %)	heating period (hours)	yield (%) (w.r.t. starting aldehyde)
1	water (5)	0	20	0
2	water (5)	5	10	30
3	water (5)	10	8	88
4	water (5)	20	9	86
5	water (5)	40	8	87
6	water : MeOH (2.5 +2.5)	10	8	35
7	water : EtOH (2.5 +2.5)	10	9	40
8	water : THF (2.5 +2.5)	10	8	30
9	water (10)	10	9	86

The structure of **3k** (R^1=R^2=R^3=H, R^4=4-Cl-C_6H_4) was confirmed by ^{1}H NMR, ^{13}C NMR and IR spectral analyses. The starting aldehyde : *ortho*-phenylenediamine mole ratio employed was (2:1) for the formation of **3k**. Thus, the initial mole ratios are very vital for this synthesis. With a equimolar mole ratio of the starting materials, **4k** was obtained as the sole product. [3c] In the spectra of **3k**, the –NCH_2 protons being benzylic at the same time, appears at δ 5.40 in ^{1}H NMR and at δ 47.80 in ^{13}C NMR and were well established in ^{13}C- DEPT.-135 experiment. Table 2 below depicts the catalysts that were studied.

Table 2. Choice of catalyst for 2-(4-chlorophenyl)-1-(4-chlorophenylmethyl)-1*H*-benzimidazole **3k** formation

Entry	Catalyst (mol%)	Solvent (5 mL)(temperature ºC)	Yield (isolated)[ref]
1	Amberlyst-15 (10)	water (70)	40
2	Silica-H_2SO_4 (30)	water (35)	50[4]
3	Dowex 50 (10)	water (70)	88
4	L-proline (10)	chloroform (35)	70[5]
5	PSSA (10)	water (80)	36
6	Silica-$HClO_4$ (10)	water (80)	45

Since Dowex 50W in water gave the optimum result (Table 1, entry 3 and Table 2, entry 3), our subsequent idea was to react a number of aromatic, heterocyclic and aliphatic aldehydes with a variety of substituted or un-substituted *ortho*-phenylenediamines under the same reaction

conditions (Scheme 1). The results are all depicted in Table 3. Although other catalysts have been employed for the synthesis of this system, [4-7] but using Dowex 50W, shows the reaction to be very clean and selective without the formation of N-unsubstituted benzimidazoles.

Table 3. Dowex 50W catalysed reactions of aldehydes with *ortho* –phenylenediamines in water at 70 ºC

Entry	starting *ortho*-phenylenediamine **1**			Product **3**	starting aldehyde **2** $R^4 = R^5$-C_6H_4 (aryl) R^5	heating period (hours)	yield (%) (isolated)	References
	R^1	R^2	R^3					
1	H	H	H	**a**	H	8	83	4
2	H	H	H	**b**	4-OMe	11	79	4
3	H	H	H	**c**	3-Br	9	76	5
4	H	H	H	**d**	4-OH	9	84	6
5	H	H	H	**e**	2-OMe	8	86	4
6	H	H	H	**f**	3-OMe-4-OH	12	78	7
7	H	H	H	**g**	3-OH	10	85	8
8	H	H	H	**h**	2-Cl	8	90	9
9	H	H	H	**i**	4-NMe_2	9	91	5, 10
10	H	H	H	**j**	4-Br	10	87	9
11	H	H	H	**k**	4-Cl	8	88	5
12	H	H	H	**l**	2-NO_2	15	77	9
13	H	H	H	**m**	4-NO_2	14	78	5
14	H	H	H	**n**	R^5-C_6H_4 =2-furyl	4	92	5
15	H	H	H	**o**	4-CN	12	83	–
16	Me	H	H	**p**	4-Br	15	86	–
17	H	Me	Me	**q**	R^5-C_6H_4 =2-furyl	4	92	–
18	Me	H	H	**r**	2-Cl	8	93	–
19	H	Cl	Cl	**s**	R^5-C_6H_4 =2-furyl	4	80	–
20	H	H	H	**t**	3.4-(2×OMe)	10	4	–
21	H	H	H	**u**	2.5-(2×OMe)	10	77	–
22	Me	H	H	**v**	R^5-C_6H_4 =2-furyl	04	92	–
23	Me	H	H	**w**	3-OH	10	87	–
24	Me	H	H	**x**	2.5-(2×OMe)	16	75	–

Table 3. Continued

Entry	starting *ortho*-phenylenediamine **1**			Product **3**	starting aldehyde **2**	heating period (hours)	yield (%) (isolated)	References
	R^1	R^2	R^3		$R^4 = R^5$-C_6H_4 (aryl) R^5			
25	H	Cl	Cl	**y**	4-OMe	08	83	–
26	H	Me	Me	**z**	4-OMe	08	84	–
27	H	Me	Me	**a'**	3-NO_2	12	82	–
28	H	Me	Me	**b'**	3,4-(2×OMe)	09	88	–
29	H	Me	Me	**c'**	2.5-(2×OMe)	09	79	–
30	H	Me	Me	**d'**	3-Br	07	83	–
31	H	Me	Me	**e'**	4-Br	08	74	–
32	H	Me	Me	**f'**	2-Cl	07	77	–
33	H	Cl	Cl	**g'**	4-Br	09	75	–
34	H	Cl	Cl	**h'**	2.5-(2×OMe)	09	81	–
35	H	Cl	Cl	**i'**	4-Cl	05	77	–
36	H	Cl	Cl	**j'**	2-Cl	06	82	–
37	H	Cl	Cl	**k'**	3-Br	08	73	–
38	Me	H	H	**l'**	3-Br	09	85	–
39	H	Cl	Cl	**m'**	3,4-(2×OMe)	09	79	–
40	Me	H	H	**n'**	3,4-(2×OMe)	10	80	–
41	H	H	H	**o'**	R^4=ethyl	10	trace	11
42	H	H	H	**p'**	R^4=n-propyl	11	trace	11

On careful analysis of Table 3 we can say that our methodology is quite a general one being applicable to reactions with substitutions in the diamine (with H, Me, Cl) and wide variations in the aldehyde parts. Almost all the products are obtained in excellent yields except those from aliphatic aldehydes where the yield being too low, the final compound could not be isolated in pure form. This is perhaps due to aldolisation of the aliphatic aldehyde in addition to the absence of the conjugation of the aromatic ring in the product. The reaction could be easily scaled up to 50 mmol (done for entry 11, Table 3), with the same yield of the product.

A methodology has been developed that does not envisage the need for column chromatography for purification of the product. Water (5 mL) is used for the reaction. Ethanol (5 mL) is added to it; the total liquid filtered to remove Dowex 50W, and this 10 mL aqueous ethanol is kept overnight in the refrigerator to obtain almost pure crystals of 1*H*-arylmethyl-2-aryl-benzimidazoles. The crystals were filtered, dried and recrystallized from aqueous ethanol to obtain the final compounds. The Dowex 50W was washed with acetone to remove any adhering organic compound, air dried and finally, vacuum dried to be used again. In this fashion, Dowex 50W could be recycled at least 6 times without substantial activity loss.

The probable mechanism of the formation of **3** is depicted below (Figure 2) (for entry 18, Table 3). The initial formation of dibenzylidene-*ortho*-phenylenediamine takes place followed by its ring closure. Finally, aromatization takes place via deprotonation and reprotonation processes.

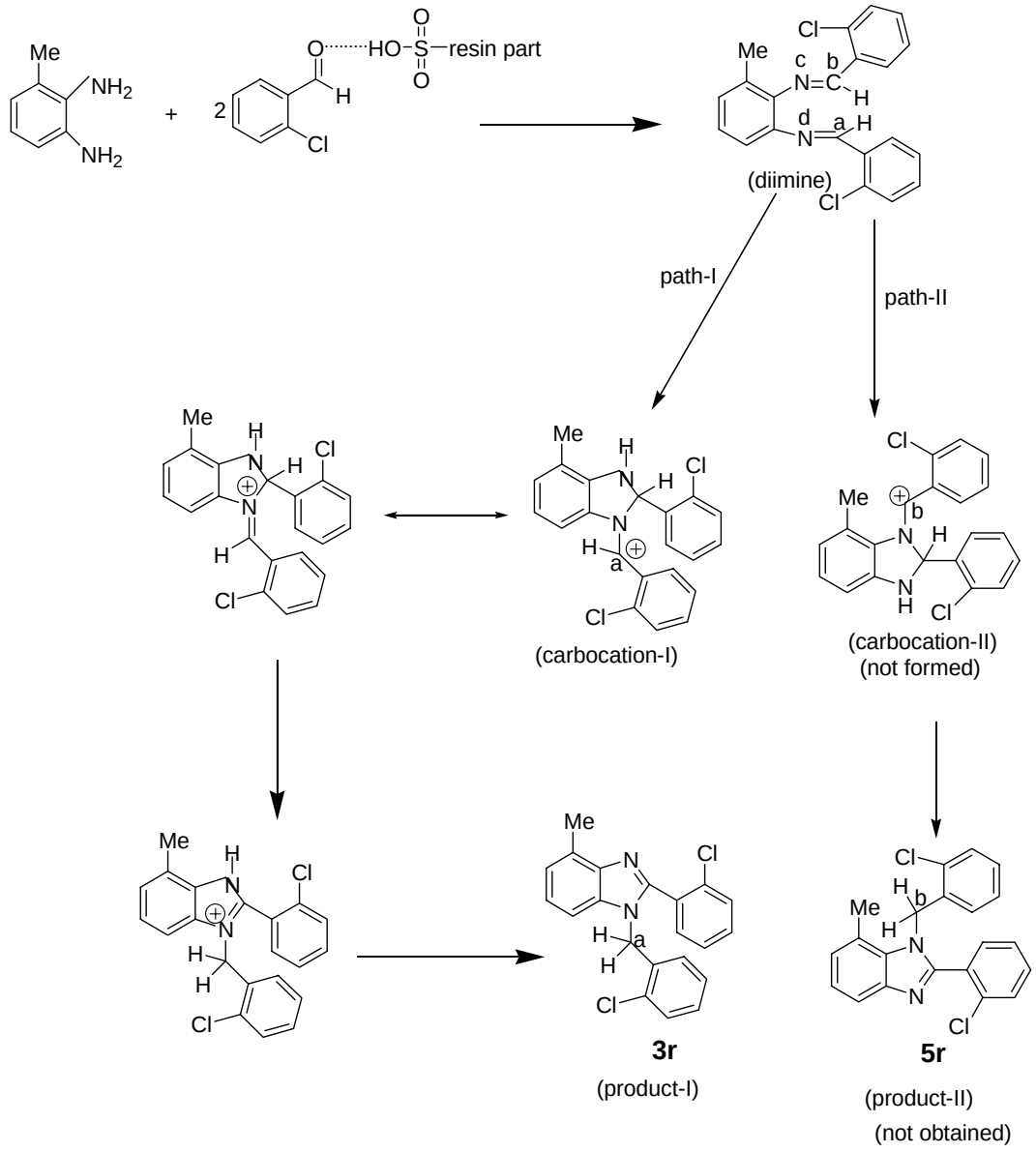


Figure 2. Mechanism of the formation of 2-(2-chlorophenyl)-1-(2-chlorophenylmethyl)-1*H*-benzimidazole.

For entry 18, Table 3, with *ortho*-chlorobenzaldehyde and 2, 3-diaminotoluene, formation of either or both regioisomers **3r** and **5r** (Figure 2) are possible. Very little work has been actually done with unsymmetrical *ortho*-phenylenediamines. No work has been done earlier on the mechanistic studies with unsymmetrical *ortho*-phenylenediamines. At the first sight, steric

interactions between the CH_3 and the $–NCH_2$ groups probably eliminate its formation (single isomer in TLC). The formation of **3r** has been confirmed after assignments of all protons and carbons by the 2D-NMR data (500 MHz) (^1H-^1H homonuclear and ^1H-^{13}C heteronuclear). Absence of any long range interactions between the CH_3 and the $–NCH_2$ protons in 2D-NMR data eliminate the formation of **5r**. Finally, the formation of **3r** has been confirmed by an X-ray crystallography (CCDC 695543) of its single crystal. The ortep plot of the single crystal of **3r** is shown here in Figure 3.

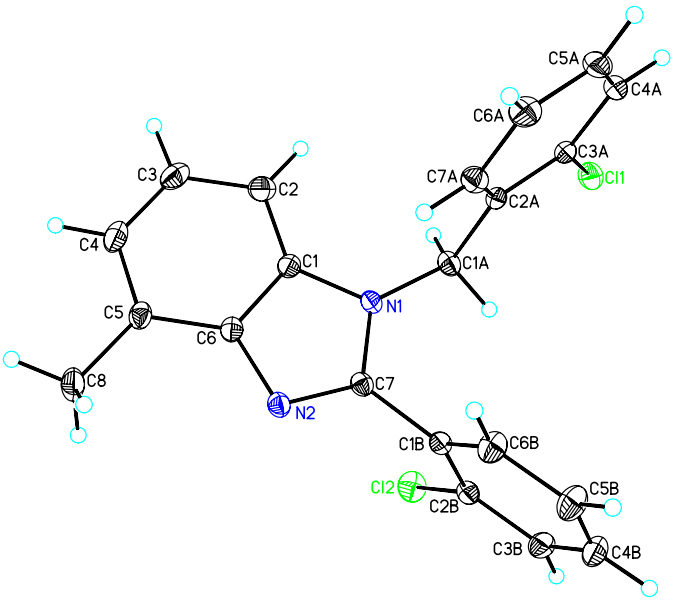


Figure 3. Ortep plot of the single crystal of **3r** showing the crystallographic numbering.

The unit cell of **3r** showing all the weak interactions are shown here in Figure 4.

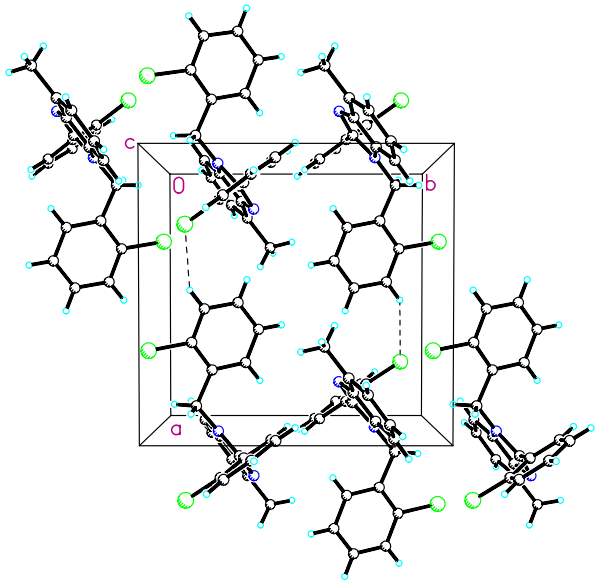


Figure 4. Unit cell of **3r** showing all the weak interactions.

Quantum chemical calculation

The same result of obtaining **3r** (and not **5r**) as the particular regioisomer from the reaction of 2, 3-diaminotoluene and 2-chlorobenzaldehyde has also been obtained by quantum chemical calculations. Structural calculation for one of the products **3r** and some of the intermediates for the production **3r** has been done at the DFT level with B3LYP functional and 6-31g basis set using Gaussian 03 software. [12] Natural bond orbital (NBO) analysis [13, 14] for the optimized structure of the intermediate diimine has been done to see the orbital occupancy of individual atomic orbital and the natural charge at each atom. It is found that during the course of reaction, in the first step, two amino groups simultaneously involve to form diimine. As per the calculated results the two double bonds site of the diimine is found to be structurally in the trans configuration. The Mullikan population analysis shows that the positive charge at the non-methyl side imine-carbon center (marked a in the diimine, Figure 2) (0.032593) is more positive other imine-carbon atom (marked b in the diimine, Figure 2) (0.007458). The natural population analysis from NBO for the lowest energy structure of the Schiff base shows that the imine-carbon atom (0.08840) at the non-methyl side (marked a in the carbocation I, Figure 2) has more positive natural charge than the other imine-carbon atom (marked b in the carbocation II, Figure 2) (0.04413), i.e. that non-methyl-imine-carbon favours relatively more positive character than the other carbon atom. On the other hand, the electron occupancy on the π-oribital (1.89237) is more at the non-methyl side double bond (1.89175). This may indicate that cation formation in the next step may favour through path I than path II. In the second step of the reaction there are two possibilities for the cyclization to form cation. Calculation at the same level shows that the stability of the carbocation at the non-methyl substituted (marked a) is more than the other side (marked b) (ΔE=3554 cm^{-1}). Such a large stability for carbocation also suggests the formation of cation through path I than through path II. In the next step between the two possible products obtained by two possible paths, the product **3r** is more stable than the counter part **5r** by 1493cm^{-1}. So, the between the two possible paths, in each step calculation shows that path I is more favourable than path II. Hence, the product obtained should be **3r** and not the other regioisomer **5r**. All these results are summarized below in the following Figure 5.

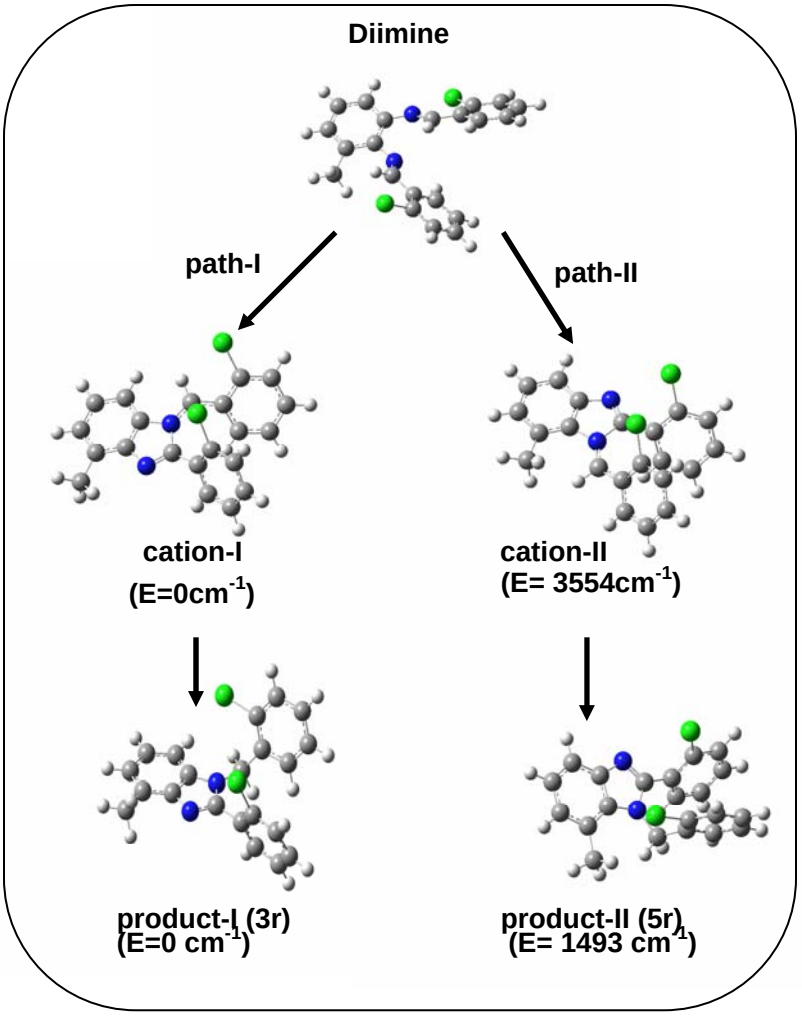


Figure 5. Schematic representation of the two possible pathways (I and II) leading to the formation of two possible products **3r** and **5r**.

Spectral properties

A. Absorption spectra

The absorption spectra (Hitachi UV-Vis, Model U-3501) of some of the synthesized 2-aryl-1-arylmethyl-1*H*-benzimidazoles (entries 1-14, Table 4) were taken in non-polar dichloromethane, polar aprotic acetonitrile and polar protic methanol solvents at room temperature and the concentration of the solute were maintained within the range 10^{-5}-10^{-6} M. All absorption band maxima are presented in Table 3 and spectra for **3p**, **3r**, **3w**, **3n'** are shown in Figure 6 in acetonitrile. In all cases, the synthesized 2-aryl-1-arylmethyl-1*H*-benzimidazole systems have two types of chromophore- one the substituted imidazole ring system and another the substituted benzene ring. The spectral pattern and the band maxima clearly indicate that the observed absorption band corresponds to the imidazole ring. The benzene aromatic ring absorption is found to ~270nm. Therefore, the observed absorption band maxima corresponds to the HOMO-

LUMO transition at the imidazole ring, i.e. S_0 state to S_1 state transition. High absorbance values indicate that these transitions arise from $\pi \rightarrow \pi^*$ transition of the imidazole ring. It is found that the absorption band maxima are slightly solvent dependent indicating less polar character of these molecules in the ground state. In protic solvent the band shows a blue shift due to intermolecular hydrogen bond between solvent methanol and the solute with several possible hydrogen bond making centers.

B. Emission spectra

Usually imidazole compounds are highly fluorescent after excitation to the locally excited state and some of the imidazole derivatives show interesting photo-induced properties such as isomerisation reaction in the excited state. Therefore, we have tried to measure emission and excitation spectra of these molecules in all the three solvents after excitation of the absorption band maxima. As shown in Figure 7, the excitation of each molecule at their corresponding absorption band of each substituted imidazole shows single emission band (Perkin Elmer: Model LS-50B fluorimeter) in the wavelength range ~360nm to ~420nm which was assigned to emission from their locally excited state. The emission band maxima and the corresponding fluorescence quantum yields are shown in Table 4. In general, in the emission spectra, the emission bands are found to be similar in dichloromethane and acetonitrile solvents. This indicates that stabilization of the ground and excited state is not modified with polarity of the solvents. On the other hand, in methanol, the emission band shifts to the blue due to intramolecular hydrogen bond interaction between solvent and solute. As the absorption band shifts to the blue, the emission band also shifts to the blue and this blue shifted emission is nothing but the local emission from the hydrogen bonded clusters. We have measured fluorescence quantum yield of these compounds by secondary method using ß-naphthol as reference (ϕ_{ref} =0.23 in methyl cyclohexane). As shown in Table 4, the fluorescence quantum yield of these studied systems is very high in polar aprotic solvent and very poor in hydrogen bonding solvent methanol. Weak intermolecular hydrogen bonding interaction usually triggered non-radiative channels and hence fluorescence quantum yield is very low in methanol solvent.[15]

Another interesting feature is that halo-substituted molecules have less fluorescence quantum yield than that of methoxy substituted compounds. This could be due to quenching of fluorescence with halogen atoms as the substitution. High quantum yield of these molecules and sensitivity of the emission band on polarity and hydrogen bonding ability could be useful to be a good fluorescence sensor.

Table 4. Spectroscopic properties of some of compounds obtained from steady state absorption and emission spectral data at room temperature in the condensed phase

Entry	Products	Solvents	λ_{abs} (nm)	λ_{em} (nm)	Quantum Yield (ϕ_f)
1	**3p**	CH_2Cl_2	293	382	6.9×10^{-2}
		CH_3CN	291	361	6.7×10^{-1}
		CH_3OH	275	-	-
2	**3r**	CH_2Cl_2	277	405	0.98×10^{-2}
		CH_3CN	267	406	4.5×10^{-1}
		CH_3OH	272	-	-
3	**3w**	CH_2Cl_2	294	390	8.5×10^{-2}
		CH_3CN	283	368	6.1×10^{-1}
		CH_3OH	282	363	1.3×10^{-2}
4	**3n′**	CH_2Cl_2	286	422	1.6×10^{-2}
		CH_3CN	275	373	3.3×10^{-1}
		CH_3OH	271	377	2.6×10^{-2}
5	**3f′**	CH_2Cl_2	284	375	0.2×10^{-2}
		CH_3CN	290	373	4.5×10^{-1}
		CH_3OH	284	-	-
6	**3c′**	CH_2Cl_2	295	376	4.4×10^{-2}
		CH_3CN	296	375	4.7×10^{-1}
		CH_3OH	272	373	0.4×10^{-3}
7	**3d′**	CH_2Cl_2	296	373	1.9×10^{-2}
		CH_3CN	301	373	5.7×10^{-1}
		CH_3OH	288	373	0.7×10^{-2}
8	**3a′**	CH_2Cl_2	258	375	0.1×10^{-2}
		CH_3CN	269	-	-
		CH_3OH	271	-	-
9	**3j′**	CH_2Cl_2	301	364	0.8×10^{-1}
		CH_3CN	295	358	6.0×10^{-2}
		CH_3OH	270	-	-
10	**3y**	CH_2Cl_2	302	377	1.9×10^{-2}
		CH_3CN	315	344,358	2.9×10^{-1}
		CH_3OH	272	343,360	1.8×10^{-2}
11	**3g′**	CH_2Cl_2	310	370	0.2×10^{-2}
		CH_3CN	274	360	3.6×10^{-1}
		CH_3OH	275	343, 358	0.2×10^{-2}
12	**3i′**	CH_2Cl_2	311	363	0.5×10^{-2}
		CH_3CN	303	360	9.5×10^{-1}
		CH_3OH	305	343, 365	7.4×10^{-2}

Table 4. Continued

Entry	**Products**	Solvents	λabs (nm)	λem (nm)	Quantum Yield (ϕf)
13	**3u**	CH_2Cl_2	303	375	6.1×10^{-2}
		CH_3CN	285	373	8.8×10^{-1}
		CH_3OH	271	378	2.7×10^{-2}
14	**3o**	CH_2Cl_2	276	385	1.5×10^{-1}
		CH_3CN	298	390	6.4×10^{-1}
		CH_3OH	300	390	6.5×10^{-2}

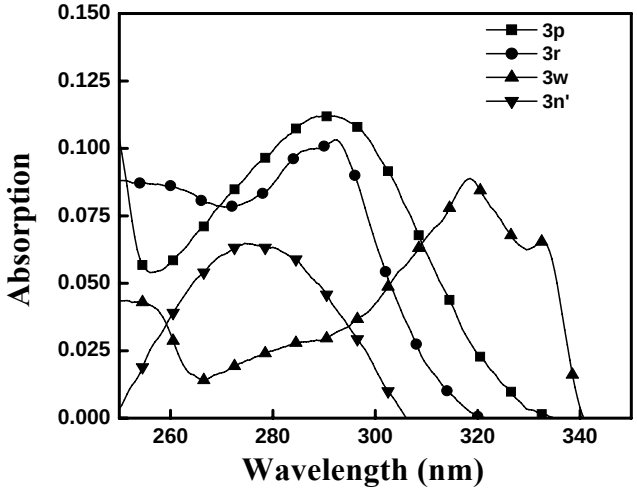


Figure 6. Absorption spectra of compounds **3p**, **3r**, **3w** and **3n'** in acetonitrile solvent at room temperature.

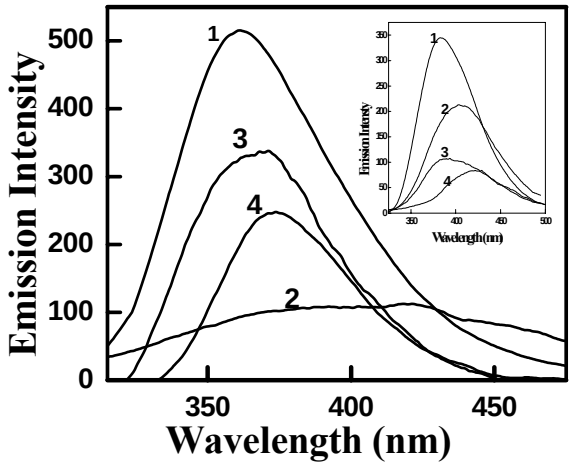


Figure 7. Emission spectra of compounds **3p (1)**, **3r (2)**, **3w (3)** and **3n'(4)** in acetonitrile solvent at room temperature when excited at the band maxima of the absorption band.
Inset: Emission spectra of **3p(1)**, **3r(2)**, **3w(3)** and **3n′(4)** in dichloromethane solvent.

Conclusions

In conclusion, we have developed a new and highly efficient green methodology for the synthesis of a wide variety of 2-aryl-1-arylmethyl-1*H*-benzimidazoles using Dowex 50 W in water. All these products can serve in further functionalization to produce molecular diversity. The main advantages of our process compared with the earlier published methods [4,5] include: (i) use of water as the solvent and therefore protecting our environment (ii) absolutely new technique for purification of the products by easy crystallization and simple filtration without requiring column chromatography (iii) formation of a single regioisomeric product for unsymmetrical *ortho*-phenylenediamines (iv) elimination of the formation of benzimidazoles **4** (v) use of Dowex 50W as a heterogeneous and reusable catalyst (vi) wide applicability to a variety of substrates particularly starting with 4,5-dimethyl and 4,5-dichloro-orthophenylenediamine whose references are very rare in the literature. We therefore hope that this methodology would be beneficial to both academia and industry. A detailed DFT calculation study has been done to establish both the mechanism and also the formation of one particular regioisomer from an unsymmetrical *ortho*-phenylenediamine. Fluorescence studies of some selected products have been done in three solvents, non-polar, polar aprotic, polar protic and their quantum yields calculated.

Experimental Section

General. Ethanol was distilled before use. All the chemicals were purchased from Aldrich Chemical Company and Spectrochem, Pvt. Ltd. (Mumbai, India). Silica Gel G with binder from Spectrochem, Pvt. Ltd. Mumbai, India was used for thin layer chromatography. Dowex 50W was purchased from Loba Chemie, India and was used in the acid form. ^{1}H and ^{13}C NMR spectra were obtained on Bruker 300 MHz instrument at 300 and 75 MHz respectively. The 2D NMR spectra were recorded on a Bruker 500MHz Ultra Shield NMR instrument. $CDCl_3$ was purchased from Aldrich Chemical Company and UV-grade CH_2Cl_2, CH_3CN and MeOH from Spectrochem, India. Melting points were determined on an electrical melting point apparatus with an open capillary and are uncorrected. IR spectra were recorded on a Perkin Elmer Spectrophotometer RX / FT- IR system. Mass spectra of the compounds were recorded on a Waters LC-MS-MS (quattro micro mass) instrument.

General procedure for the synthesis of 2-aryl-1-arylmethyl-1*H*-benzimidazoles

To a suspension of Dowex 50W (acid form) (10 mol %) in water (5 mL) were added successively *ortho*-phenylenediamines **1** (1mmol) and aldehydes **2** (2 mmol). The heterogeneous reaction mixture was then heated at 70 °C with stirring for the time specified in Table 3. After the reaction was complete (indicated by the absence of starting materials in TLC), the reaction mixture was cooled, 5 mL ethanol added to it and the total liquid was filtered to remove Dowex

50W. This 10 mL aqueous ethanol was kept in the refrigerator (4 °C) overnight to obtain almost pure crystals of 2-aryl-1-arylmethyl-1*H*-benzimidazoles which were recrystallized again from aqueous ethanol to obtain the pure crystals that were characterized by spectral studies. The IR, ^{1}H NMR, ^{13}C NMR and mass spectral data of all the previously unknown compounds (twenty six in number) are given below:

2-(4-Cyanophenyl)-1(4'-cyanophenylmethyl)-1*H*-benzimidazole (entry15, Table 3). m.p.: 216-218 ºC (aqueous EtOH); UV [λ_{max} (MeOH)]= 300.0 nm (log ε = 4.47);
IR (KBr): 3424, 2368, 2227, 1608, 1458, 1409, 848 and 759 cm^{-1};^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.91 (d, *J*=7.5 Hz, 1H, imidazolyl C_4-H), 7.76 (s, 4H, C_2-, C_3-, C_5- and C_6-H), 7.67 (d, *J*=8.4 Hz, 2H, $C_{3'}$- and $C_{5'}$-H), 7.39 (dt, *J*=9.0, 1.2 Hz, 1H, imidazolyl C_5-H / C_6-H), 7.32 (dt, *J*=9.0, 1.2 Hz, 1H, imidazolyl C_6-H / C_5-H), 7.22 (m, 3H, $C_{2'}$-, $C_{6'}$-, C_7-H), 5.52 (s, 2H, -NCH_2);^{13}C NMR (75MHz, $CDCl_3$) δ: 151.7 (C_2), 143.1 (C_{3a}), 141.0 (C_{7a}), 135.9 (C_1), 134.1 ($C_{1'}$), 133.1 (C_2, C_6), 132.6 (C_3, C_5), 129.6 ($C_{3'}$, $C_{5'}$), 126.5 ($C_{2'}$, $C_{6'}$), 124.3 (imidazolyl C_5), 123.6 (imidazolyl C_6), 120.7 (imidazolyl C_4), 118.0 (CN), 118.0 (CN), 113.8 (C_4), 112.4 ($C_{4'}$), 110.2 (C_7), 48.10 (CH_2).Anal. calcd. for $C_{22}H_{14}N_4$; C: 79.02 , H: 4.22 , N: 16.76 . Found: C: 78.86, H: 4.34, N: 16.55 %.

2-(4-Bromophenyl)-1(4'-bromophenylmethyl)-4-methyl-1*H*-benzimidazole (entry 16, Table 3). M.p.: 154 ºC (aqueous EtOH); UV [λ_{max} (CH_2Cl_2)] = 293 nm (log ε = 4.31);
IR (KBr): 3434, 2919, 2373, 1601, 1448, 1397, 1340, 1072, 1008, 829 and 751 cm^{-1};
^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.58 (d, *J*=8.3 Hz, 2H, C_3-, C_5-H), 7.50 (d, *J*=8.3 Hz, 2H, C_2-, C_6-H), 7.44 (d, *J*=8.2 Hz, 2H, $C_{3'}$-, $C_{5'}$-H), 7.17-7.11 (m, 2H, imidazolyl C_5-, C_6-H), 7.01 (d, *J*=7.7 Hz, 1H, C_7-H), 6.93 (d, *J*=8.1 Hz, 2H, $C_{2'}$-, $C_{6'}$-H), 5.32 (s, 2H, NCH_2), 2.73 (s, 3H, -CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 152.2 (C_2), 142.5 (C_{3a}), 135.5 (C_{7a}), 135.4 (C_1), 132.3 (C_3, C_5), 132.1 ($C_{3'}$, $C_{5'}$), 130.8 (C_2, C_6), 130.4 ($C_{1'}$), 129.1 (C_4), 127.6 ($C_{2'}$, $C_{6'}$), 124.5 ($C_{4'}$), 123.4 (C_5, C_6), 121.8 (imidazolyl C_4), 107.8 (C_7), 47.8 (NCH_2), 16.8 (CH_3); MS: m/z (%): 169.0 (48), 171.0 (46), 283.1 (11), 454.9 (M-2) (51), 456.9 (M^+) (100), 458.9 (M+2) (46), 460.0 (M+3) (11).Anal. calcd. for $C_{21}H_{16}Br_2N_2$; C: 55.29 , H: 3.54 , N: 6.14 . Found: C: 55.17, H: 3.62, N: 6.07 %.

5,6-Dimethyl-2-(2-furanyl)-1(2'-furylmethyl)- 1*H*-benzimidazole (entry 17, Table 3). m.p.:118-120 ºC (aqueous EtOH); UV [λ_{max} (CH_2Cl_2)]= 317.4 nm (log ε = 4.41);
IR (KBr): 3882, 2379, 1702, 1445, 1382, 1344, 1010 and 749 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.64 (s, 1H, furyl C_5-H), 7.56 (s, 1H, imidazolyl C_4-H), 7.36 (s, 1H, furyl $C_{5'}$-H), 7.26 (s, 1H, imidazolyl C_7-H), 7.18 (d, *J*=2.6 Hz, 1H, furyl C_3-H), 6.61(s, 1H, furyl C_4-H), 6.30 (s, 1H, furyl $C_{4'}$-H), 6.22 (s, 1H, furyl $C_{3'}$-H), 5.61(s, 2H, -NCH_2), 2.42 (s, 3H, C_6-CH_3), 2.39 (s, 3H, C_5-CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 149.9 (C_2), 145.7 (furyl C_2), 143.7 (furyl C_5), 143.2 ($C_{2'}$), 142.5 (furyl $C_{5'}$), 141.6 (C_{3a}), 134.1 (C_{7a}), 132.6 (C_6), 131.9 (imidazolyl C_5), 119.8 (imidazolyl C_4), 112.3 (furyl C_3), 112.0 (furyl C_4), 110.5 ($C_{4'}$), 110.1 (C_7), 108.1 ($C_{3'}$), 41.7 (-NCH_2), 20.7 (C_6-CH_3), 20.3 (C_5-CH_3).
MS: m/z (%): 293.1 (M+1) (100), 294.1 (M+2) (22), 315.1(9). Anal. calcd. for $C_{18}H_{16}N_2O_2$; C: 73.96, H: 5.52, N: 9.58 . Found: C: 73.89, H: 5.67, N: 9.64 %.

2-(2-Chlorophenyl)-1(2'-chlorophenylmethyl)-4-methyl-1*H*-benzimidazole (entry 18, Table 3). M.p.: 152-154 ºC (aqueous EtOH) ; UV [λ_{max} (CH_2Cl_2)]= 277 nm (log ε = 3.63); IR (KBr): 3436, 3055, 2922, 2373, 1604, 1441, 1382, 1046 and 755 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.52-7.39 (m, 3H, C_3-H, $C_{3'}$-H and C_6-H), 7.33 (d, *J*=7.9 Hz, 1H, C_4-H), 7.27 (d, *J*=7.7 Hz, 1H, $C_{4'}$-H), 7.20-7.12 (m, 3H, C_5-H, $C_{5'}$-H and $C_{6'}$-H), 7.05 (t, *J*=7.5 Hz, 2H, imidazolyl C_5-H and C_6-H), 6.63 (d, *J*=7.5 Hz, 1H, C_7-H), 5.33 (s, 2H, -NCH_2), 2.75 (s, 3H, -CH_3); ^{13}C NMR (75MHz, $CDCl_3$) δ: 150.6 (C_2), 142.3 (C_{3a} and C_{7a}), 134.5 (C_1), 134.4 (C_2 and $C_{2'}$), 133.4 ($C_{1'}$), 132.3 (C_4), 131.3 (C_6), 130.3 (imidazolyl C_4), 129.8 ($C_{4'}$), 129.5 ($C_{6'}$), 128.9 (C_3), 127.8 ($C_{3'}$), 127.0 (C_5), 126.9 ($C_{5'}$), 123.3 (imidazolyl C_6), 123.1 (imidazolyl C_5), 107.9 (C_7), 45.7 (-NCH_2), 16.8 (-CH_3); MS: m/z (%): 125.1 (22), 127.1 (7), 367.0 (M^+, 100), 369.0 (M+2) (67), 389.0 (19), 391.0 (12). Anal. calcd. for $C_{21}H_{16}Cl_2N_2$; C: 68.68 , H: 4.39 , N: 7.63 . Found: C: 68.47,H: 4.51, N: 7.59 %.

5,6-Dichloro-2-(2-furyl)-1(2'-furylmethyl)- 1*H*-benzimidazole (entry 19, Table 3). m.p:136-138 ºC (aqueous EtOH); UV [λ_{max} (CH_2Cl_2)]= 322.0 nm (log ε = 3.44);
IR (KBr): 3435, 2372, 1448, 1343, 1219, 1013 and 770 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.86 (s, 1H, imidazolyl C_4-H), 7.70 (s, 1H, furyl C_5-H), 7.62 (s, 1H, C_7-H), 7.38 (s, 1H, furyl $C_{5'}$-H), 7.28 (d, *J*=3.3 Hz, 1H, furyl C_3-H), 6.66 (d, *J*=1.6 Hz, 1H, furyl C_4-H), 6.34 (s, 1H, furyl $C_{4'}$-H), 6.31 (s,1H, furyl $C_{3'}$-H), 5.63 (s, 2H, -NCH_2); ^{13}C NMR (125MHz, $CDCl_3$) δ: 148.8 (C_2), 145.7 (furyl C_2), 144.8 ($C_{2'}$), 144.5 (furyl C_5), 143.0 ($C_{5'}$), 142.4 (C_{3a}), 134.8 (C_{7a}), 127.2 (C_6), 127.1 (imidazolyl C_5), 120.8 (imidazolyl C_4), 113.9 (furyl C_3), 112.3 (furyl C_4), 111.5 (C_7), 110.6 ($C_{4'}$), 108.8 ($C_{3'}$), 42.0 (-NCH_2).
MS: m/z (%): 333.0 (6), 339.0 (M^+, 33), 355.0 (100), 356.9 (73), 359.0 (14). Anal. calcd. for $C_{16}H_{10}Cl_2N_2O_2$; C: 57.68 , H: 3.03 , N: 8.41 . Found: C: 57.59, H: 3.11, N: 8.52 %.

2-(3, 4-Dimethoxyphenyl)-1(3',4'-dimethoxyphenylmethyl)-1*H*-benzimidazole (entry 20, Table 3). M.p:170-172 ºC (aqueous EtOH); UV [λ_{max} (CH_2Cl_2)] = 307.0 nm (log ε = 4.02); IR (KBr): 2918, 2376, 1507, 1451, 1248, 1135 and 1021 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.86 (d, J=7.8 Hz, 1H, C_4-H), 7.33-7.28 (m, 2H, C_2-H and C_6-H), 7.24-7.22 (m, 3H, imidazolyl C_5-H, C_6-H and C_7-H), 6.91 (d, *J*=8.1Hz, 1H, C_5-H), 6.79 (d, *J*=8.4 Hz, 1H, $C_{5'}$-H), 6.65-6.61 (m, 2H, $C_{2'}$-H and $C_{6'}$-H), 5.38 (s, 2H, -NCH_2), 3.90 (s, 3H, C_4-OMe), 3.83 (s, 3H, $C_{4'}$-OMe), 3.77 (s, 3H, C_3-OMe), 3.76 (s, 3H, $C_{3'}$-OMe); ^{13}C NMR (75MHz, $CDCl_3$) δ: 153.9 (C_4), 150.3 (C_3), 149.3 ($C_{4'}$), 148.9 ($C_{3'}$), 148.4 (imidazolyl C_2), 142.7 (C_{3a}), 136.1 (C_{7a}), 128.9 (C_1), 122.7 and 122.5 (C_5 and C_6), 122.3 ($C_{1'}$), 121.7 (imidazolyl C_4), 119.5 ($C_{6'}$), 118.0 (C_6), 112.2 ($C_{5'}$), 111.4 (C_5), 110.9 (C_2), 110.10 ($C_{2'}$), 108.9 (C_7), 55.8 (2 × -OCH_3), 55.7 (-O CH_3), 55.6 (-O CH_3), 47.9 (-NCH_2); MS: m/z (%): 151.2 (100), 152.2 (10), 405.1 (M+1) (44), 406.2 (M+2) (11), 427.2 (5). Anal. calcd. for $C_{24}H_{24}N_2O_4$; C: 71.27 , H: 5.98 , N: 6.93 . Found: C: 71.14, H: 6.05, N: 6.72 %.

2-(2,5-Dimethoxyphenyl)-1(2',5'-dimethoxyphenylmethyl)-1*H*-benzimidazole (entry 21, Table 3). M.p.:94-96 ºC (aqueous EtOH) ; UV [λ_{max} (CH_2Cl_2)]= 303 nm (log ε = 3.49); IR (KBr): 3453, 2944, 2372, 1592, 1491, 1282, 1220, 1040 and 741 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.87 (d, *J*=7.5 Hz, 1H, imidazolyl C_4-H), 7.27 (d, *J*=6.9 Hz, 1H, imidazolyl C_7-H), 7.23-7.17 (m, 2H, imidazolyl C_5-H and imidazolyl C_6-H), 7.11 (d, *J*=3.0 Hz, 1H, C_6-H), 6.98

(dd, *J*=9.0 Hz and 2.7 Hz, 1H, C_4-H), 6.88 (d, *J*=9.0 Hz, 1H, C_3-H), 6.72 (d, *J*=8.7 Hz, 1H, $C_{3'}$-H), 6.67 (dd, *J*=6.0 Hz and 2.7 Hz, 1H, $C_{4'}$-H), 6.28 (d, *J*=2.7 Hz, 1H, $C_{6'}$-H), 5.23 (s, 2H, -NCH_2), 3.72 (s, 3H, -OCH_3), 3.69 (s, 3H, -OCH_3), 3.56 (s, 3H, -OCH_3), 3.52 (s, 3H, -OCH_3); ^{13}C NMR (75MHz, $CDCl_3$) δ: 153.4 (C_2), 153.3 (C_5), 151.7 ($C_{2'}$), 151.5 ($C_{5'}$), 150.6 (imidazolyl C_2), 142.2 (C_{3a}), 135.0 (C_{7a}), 125.3 (C_1), 122.6 (imidazolyl C_4), 122.1 (imidazolyl C_6), 119.5 ($C_{1'}$), 119.2 (imidazolyl C_5), 117.4 (C_4), 116.8 (C_6), 114.3 (C_3), 112.6 ($C_{3'}$), 112.2 ($C_{4'}$), 110.9 ($C_{6'}$), 110.7 (C_7), 55.6 (2 × -OCH_3), 55.5 (-OCH_3), 55.3 (-OCH_3), 43.3 (-NCH_2); MS: m/z (%): 151.2 (20), 405.1 (M+1) (100), 406.1 (M+2) (30), 427.1 (12). Anal. calcd. for $C_{24}H_{24}N_2O_4$; C: 71.27 , H: 5.98 , N: 6.93 . Found: C: 71.39, H: 5.84, N: 6.81 %.

2-(2-Furyl)-1(2'-furylmethyl)-4-methyl-1*H*-benzimidazole (entry 22, Table 3). M.p.:64-66 ºC (aqueous EtOH); UV [λ_{max} (CH_2Cl_2)]= 304.0 nm (log ε = 4.00);
IR (KBr): 3394, 2366, 1601, 1507, 1437, 1376, 1336, 1152, 1015 and 746 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.65 (dd, *J*=3.5 Hz and 0.7 Hz , 1H, furyl C_5-H), 7.33-7.31 (m, 2H, C_6-H and furyl $C_{5'}$-H), 7.23-7.18 (m, 2H, C_5-H and furyl C_3-H), 7.10 (d, *J*=7.5 Hz, 1H, C_7-H), 6.60 (dd, *J*=3.6 Hz and 1.8 Hz, 1H, furyl $C_{4'}$-H), 6.29-6.27 (m, 1H, furyl $C_{3'}$-H), 6.21 (dd, *J*=3.3 Hz and 0.6 Hz, 1H, furyl $C_{4'}$-H), 5.60 (s, 2H, -NCH_2), 2.71 (s, 3H, -CH_3);
^{13}C NMR (75MHz, $CDCl_3$) δ: 149.6 (C_2), 145.0 (furyl C_2), 144.0 (furyl C_5), 143.2 ($C_{2'}$), 142.6 (furyl $C_{5'}$), 142.0 (C_{3a}), 135.1 (C_{7a}), 130.0 (imidazolyl C_4), 123.3 (imidazolyl C_6), 123.2 (imidazolyl C_5), 113.0 (furyl C_3), 112.0 (furyl C_4), 110.5 ($C_{4'}$), 108.3 (C_7), 107.4 ($C_{3'}$), 41.7 (-NCH_2), 16.7 (-CH_3); MS: m/z (%): 279.1 (M+1) (100), 260.1 (M+2) (19), 301.1 (16).Anal. calcd. for $C_{17}H_{14}N_2O_2$; C: 73.37 , H: 5.07 , N: 10.07 . Found: C: 73.24, H: 5.12, N: 10.19 %.

2-(3-Hydroxyphenyl)-1(3'-hydroxyphenylmethyl)-4-methyl-1*H*-benzimidazole (entry 23, Table 3). M.p.:> 300 ºC (aqueous EtOH); UV [λ_{max} (CH_2Cl_2)]= 294 nm (log ε = 2.11); IR (KBr): 3423, 2926, 2371, 1638, 1587, 1484, 1165, 1005, 675 and 576 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.72 (s, 1H, C_3-OH), 9.35 (s, 1H, $C_{3'}$-OH), 7.27 (t, *J*=7.8 Hz, 1H, C_5-H), 7.16-7.12 (m, 3H, C_2-H, C_6-H and imidazolyl C_6-H), 7.09-6.99 (m, 3H, $C_{5'}$-H, $C_{6'}$-H and imidazolyl C_5-H), 6.87 (qd, *J*=9.0 Hz, 1.5 Hz and 0.87 Hz, 1H, C_4-H), 6.58 (dd, *J*=7.7 Hz and 1.6 Hz, 1H, $C_{4'}$-H), 6.40 (d, *J*=7.6 Hz, 1H, C_7-H), 6.33 (d, *J*=1.6Hz, 1H, $C_{2'}$-H), 5.41 (s, 2H, -NCH_2), 2.55 (s, 3H, -CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 157.9 (C_3), 157.8 ($C_{3'}$), 153.0 (imidazolyl C_2), 142.1 (C_{3a}), 138.8 (C_1), 135.7 (C_{7a}), 131.6 ($C_{1'}$), 130.3 (C_5), 130.2 ($C_{5'}$), 129.2 (imidazolyl C_4), 123.1 (imidazolyl C_6), 123.0 (imidazolyl C_5), 120.0 (C_6), 117.3 (C_4), 117.1 ($C_{6'}$), 116.4 (C_2), 114.8 ($C_{4'}$), 113.1 ($C_{2'}$), 109.0 (C_7), 47.8 (-NCH_2), 16.8 (-CH_3); MS: m/z (%): 107.1 (23), 225.1 (100), 226.1 (15), 331.1 (M+1) (22). Anal. calcd. for $C_{21}H_{18}N_2O_2$; C: 76.35 , H: 5.49 , N: 8.48 . Found: C: 76.23, H: 5.60, N: 8.25 %.

2-(2,5-Dimethoxyphenyl)-1(2',5'-dimethoxyphenylmethyl)-4-methyl-1*H*-benzimidazole (entry 24, Table 3). M.p.:168-170 ºC (aqueous EtOH); UV [λ_{max} (CH_2Cl_2)]= 288.5 nm (log ε = 4.40); IR (KBr): 3433, 2928, 2375, 1516, 1427, 1255, 1141, 1024 and 758 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.22-7.20 (2H, m, imidazolyl C_5- and C_6-H), 7.14-7.06 (m, 3H, C_4-H, $C_{4'}$-H and C_7-H), 6.90 (d, *J*=8.7 Hz, 1H, C_3-H), 6.77 (d, *J*=7.8 Hz, 1H, $C_{3'}$-H), 6.63 (s, 1H, C_6-H), 6.60 (s, 1H, $C_{6'}$-H), 5.34 (s, 2H, -NCH_2), 3.90 (s, 3H, C_2-OCH_3), 3.83 (s, 3H, $C_{2'}$-OCH_3), 3.75 (s, 3H, C_5-

OCH_3), 3.74 (s, 3H, $C_{5'}$-OCH_3), 2.73 (s, 3H, C_4-CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 153.4 (C_2), 150.4 (C_5), 149.5 ($C_{2'}$), 149.0 ($C_{5'}$), 148.5 (imidazolyl C_2), 142.4 (C_{3a}), 135.8 (C_{7a}), 129.9 (C_1), 129.3 (imidazolyl C_4), 123.0 ($C_{1'}$), 122.9 (imidazolyl C_6), 122.8 (imidazolyl C_5), 122.1 (C_4), 118.2 (C_6), 112.6 (C_3), 111.5 ($C_{4'}$), 111.1 (C_7), 109.2 ($C_{3'}$), 107.7 ($C_{6'}$), 56.0 (C_2-OCH_3), 55.9 (C_5-OCH_3 and $C_{2'}$-O CH_3), 55.8 ($C_{5'}$-OCH_3), 48.1 (-NCH_2), 16.8 (-CH_3); MS: m/z (%): 150.9 (28), 419.0 (M+, 100), 420.0 (M+1) (54), 421.0 (M+2) (9).Anal. calcd. for $C_{25}H_{26}N_2O_4$; C: 71.76 , H: 6.26 , N: 6.69. Found: C: 71.59, H: 6.37, N: 6.75 %.

5,6-Dichloro-2-(4-methoxyphenyl)-1(4'-methoxyphenylmethyl)-1*H*-benzimidazole (entry 25, Table 3). M.p.:168-169 ºC (aqueous EtOH); UV [λ_{max} (CH_2Cl_2)]= 302 nm (log ε = 4.00); IR (KBr): 3435, 2378, 1610, 1514, 1458, 1299, 1251, 1175 and 773 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.90 (s, 1H, imidazolyl C_4-H), 7.62 (dd, *J*=8.4 Hz and 1.5 Hz, 2H, C_2-H and C_6-H), 7.27 (dd, *J*=6.3 Hz and 0.6 Hz, 2H, $C_{2'}$-H and $C_{6'}$-H), 7.01-6.70 (m, 3H, C_3-H, C_5-H and C_7-H), 6.88 (dd, *J*=8.7 and 1.4 Hz, 2H, $C_{3'}$-H and $C_{5'}$-H), 5.34 (s, 2H, -NCH_2), 3.86 (s, 3H, -OCH_3), 3.81 (s, 3H, -OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 161.3 (C_4), 159.4 ($C_{4'}$), 156.1 (imidazolyl C_2), 142.6 (C_{3a}), 135.4 (C_{7a}), 130.7 (C_2 and C_6), 127.5 [imidazolyl (C_5 and C_6)], 127.1 ($C_{2'}$ and $C_{6'}$), 126.6 (C_1), 121.6 ($C_{1'}$), 120.9 (imidazolyl C_4), 114.7 (C_3 and C_5), 114.4 ($C_{3'}$ and $C_{5'}$), 111.71 (C_7), 55.4 (-OCH_3), 55.3 (-OCH_3), 48.2 (-NCH_2); MS: m/z (%): 120.8 (100), 121.8 (7), 412.9 (M+, 60), 414.8 (M+2) (41), 415.8 (M+3) (10).Anal. calcd. for $C_{22}H_{18}Cl_2N_2O_2$; C: 63.87 , H: 4.51 , N: 6.87. Found: C: 63.94, H: 4.39, N: 6.78 %.

5,6-Dimethyl-2-(4-methoxyphenyl)-1(4'-methoxyphenylmethyl)-1*H*-benzimidazole (entry 26, Table 3). M.p.:146-148 ºC (aqueous EtOH); UV [λ_{max} (CH_2Cl_2)]= 303.0 nm (log ε = 4.18); IR (KBr): 3423, 2928, 2374, 1610, 1457, 1247, 1175, 1027 and 831 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.60 (dd, *J*=6.9 and 1.9 Hz, 2H, C_2-H and C_6-H), 7.04 (s, 1H, imidazolyl C_4-H), 7.01 (s, 1H, C_7-H), 6.97-6.92 (m, 4H, C_3-H, C_5-H, $C_{2'}$-H and $C_{6'}$-H), 6.85 (d, *J*=8.6 Hz, 2H, $C_{3'}$-H and $C_{5'}$-H), 5.32 (s, 2H, -NCH_2), 3.83 (s, 3H, -OCH_3), 3.78 (s, 3H, -OCH_3), 2.38 (s, 3H, -CH_3), 2.32 (s, 3H, -CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 160.7 (C_4), 159.0 ($C_{4'}$), 153.3 (imidazolyl C_2), 141.7 (C_{3a}), 134,6 (C_{7a}), 131.8 (imidazolyl C_6), 131.3 (imidazolyl C_5), 130.6 (C_2 and C_6), 128.8 (C_1), 127.1 ($C_{2'}$ and $C_{6'}$), 122.7 ($C_{1'}$), 119.7 (imidazolyl C_4), 114.4 (C_3 and C_5), 114.1 ($C_{3'}$ and $C_{5'}$), 110.5 (C_7), 55.3 (2×-OCH_3), 47.7 (-NCH_2), 20.5 (-CH_3), 20.2 (-CH_3); MS: m/z (%): 373.0 (M^+, 100), 373.9 (M+1) (59), 375.0 (M+2) (10).Anal. calcd. for $C_{24}H_{24}N_2O_2$; C: 77.40 , H: 6.50 , N: 7.52. Found: C: 77.33, H: 6.62, N: 7.81 %.

5,6-Dimethyl-2-(3-nitrophenyl)-1(3'-nitrophenylmethyl)-1*H*-benzimidazole (entry 27, Table 3). M.p.:188-190 ºC (aqueous EtOH); UV [λ_{max} (CH_2Cl_2)] = 258 nm (log ε = 4.16); IR (KBr): 3435, 2374, 1527, 1346, 1086 and 730 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.44 (t, *J*=1.7 Hz, 1H, C_2-H), 8.29 (dd, *J*=8.2 and 1.3 Hz, 1H, C_4-H), 8.18 (dd, *J*=8.0 and 1.0 Hz, 1H, $C_{4'}$-H), 8.01-8.00 (m, 2H, $C_{2'}$-H and C_6-H), 7.66-7.61 (m, 2H, C_5-H and imidazolyl C_4-H), 7.53 (t, *J*=8.0 Hz, 1H, $C_{5'}$-H), 7.35 (d, *J*=7.7 Hz, 1H, $C_{6'}$-H), 7.00 (s, 1H, C_7-H), 5.52 (s, 2H, -NCH_2), 2.40 (s, 3H, -CH_3), 2.35 (s, 3H, -CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 150.3 (imidazolyl C_2), 148.8 (C_3), 148.3 ($C_{3'}$), 141.7 (C_{3a}), 138.2 (C_{7a}), 134.8 (C_6), 134.5 (C_1), 133.8 ($C_{1'}$), 132.8 (imidazolyl C_5 and C_6), 131.7 ($C_{6'}$), 130.5 (C_5), 130.1 (C_4), 124.4 ($C_{5'}$), 123.7 (imidazolyl C_4), 123.2 ($C_{2'}$), 121.1

($C_{4'}$), 120.6 ($C_{2'}$), 110.1 (C_7), 47.7 (-NCH_2), 20.7 (-CH_3), 20.3 (-CH_3); MS: m/z (%): 187.0 (7), 268.0 (100), 269.0 (21), 373.0 (18), 374.0 (5), 403.0 (M^+, 99), 404.0 (M+1) (25), 419.1 (19), 420.1 (6), 508.1 (8).Anal. calcd. for $C_{22}H_{18}N_4O_4$; C: 65.67 , H: 4.51 , N: 13.92. Found: C: 65.51, H: 4.62, N: 13.84 %.

2-(3,4-Dimethoxyphenyl)-1(3',4'-dimethoxyphenylmethyl)-5,6-dimethyl-1*H*-benzimidazole (entry 28, Table 3). M.p.:130 ºC (aqueous EtOH) ; UV [λ_{max} (CH_2Cl_2)] = 281.0 nm (log ε = 4.20); IR (KBr): 3426, 2923, 2373, 1508, 1460, 1252, 1133, 1019 and 805 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.61 (s, 1H, imidazolyl C_4-H), 7.25 (s, 1H, C_2-H), 7.21 (dd, *J*=8.4 Hz and 2.1 Hz, 1H, C_6-H), 7.01 (s, 1H, C_7-H), 6.90 (d, *J*=8.4 Hz, 1H, C_5-H), 6.81 (d, *J*=8.4 Hz, 1H, $C_{5'}$-H), 6.67-6.62 (m, 2H, $C_{2'}$-H and $C_{6'}$-H), 5.35 (s, 2H, -NCH_2), 3.91 (s, 3H, -OCH_3), 3.86 (s, 3H, -OCH_3), 3.78 (s, 3H, -OCH_3), 3.76 (s, 3H, -OCH_3), 2.39 (s, 3H, -CH_3), 2.34 (s, 3H, -CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 153.3 (C_4), 150.3 (C_3), 149.5 ($C_{4'}$), 149.0 ($C_{3'}$), 148.5 (imidazolyl C_2), 141.6 (C_{3a}), 134.9 (C_{7a}), 132.1 (imidazolyl C_6), 131.5 (imidazolyl C_5), 129.4 (C_1), 122.8 ($C_{1'}$), 121.7 (imidazolyl C_4), 119.8 (C_6), 118.1 ($C_{6'}$), 112.3 (C_5), 111.6 ($C_{5'}$), 111.0 (C_2), 110.3 ($C_{2'}$), 109.1 (C_7), 55.9 (2× -OCH_3), 55.8 (2×-OCH_3), 48.0 (-NCH_2), 20.5 (-CH_3), 20.3 (-CH_3); Anal. calcd. for $C_{26}H_{28}N_2O_4$; C: 72.21 , H: 6.53 , N: 6.48. Found: C: 72.13, H: 6.69, N: 6.35 %.

2-(2,5-Dimethoxyphenyl)-1(2',5'-dimethoxyphenylmethyl)-5,6-dimethyl-1*H*-benzimidazole (entry 29, Table 3). M.p.:168-170 ºC (aqueous EtOH) ; UV [λ_{max} (CH_2Cl_2)]= 295 nm (log ε = 4.15); IR (KBr): 2934, 2377, 1605, 1496, 1269, 1222, 1040 and 753 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.58 (s, 1H, imidazolyl C_4-H), 7.07 (d, *J*=3.0 Hz, 1H, C_6-H), 7.02 (s, 1H, C_7-H), 6.97 (dd, *J*=9.0 Hz and 3.0 Hz, 1H, C_4-H), 6.87 (d, *J*=9.0 Hz, 1H, C_3-H), 6.75 (d, *J*=8.8 Hz, 1H, $C_{3'}$-H), 6.69 (dd, *J*=8.9 Hz and 2.9 Hz, 1H, $C_{4'}$-H), 6.25 (d, *J*=2.7 Hz, 1H, $C_{6'}$-H), 5.17 (s, 2H, -NCH_2), 3.75 (s, 3H, -OCH_3), 3.73 (s, 3H, -OMe), 3.55 (s, 3H, -OMe), 3.54 (s, 3H, -OMe), 2.37 (s, 3H, -CH_3), 2.32 (s, 3H, -CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 153.5 (C_2), 153.4 (C_5), 151.8 ($C_{2'}$), 151.2 ($C_{5'}$), 150.7 (imidazolyl C_2), 141.8 (C_{3a}), 134.0 (C_{7a}), 131.6 (imidazolyl C_6), 130.7 (imidazolyl C_5), 126.1 (C_1), 120.6 ($C_{1'}$), 119.8 (imidazolyl C_4), 117.1 (C_4), 116.9 (C_6), 114.2 (C_3), 112.4 ($C_{3'}$), 112.4 ($C_{4'}$), 110.8 ($C_{6'}$), 110.7 (C_7), 55.8 (-OCH_3), 55.7 (-OCH_3), 55.6 (-OCH_3), 55.5 (-OCH_3), 43.2 (-NCH_2), 20.5 (-CH_3), 20.2 (-CH_3).Anal. calcd. for $C_{26}H_{28}N_2O_4$; C: 72.21 , H: 6.53 , N: 6.48. Found: C: 72.37, H: 6.61, N: 6.32 %.

2-(3-Bromophenyl)-1(3'-bromophenylmethyl)-5,6-dimethyl-1*H*-benzimidazole (entry 30, Table 3). M.p.:134-136 ºC (aqueous EtOH); UV [λ_{max} (CH_2Cl_2)]= 296 nm (log ε = 4.16); IR (KBr): 3423, 3065, 2918, 2375, 1572, 1462, 1381, 1320, 1071 and 779 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.83 (t, *J*=1.8 Hz, 1H, C_2-H), 7.66 (s, 1H, imidazolyl C_4-H), 7.52 (qd, *J*=7.8, 1.2, 0.9 and 0.9 Hz, 1H, C_6-H), 7.47 (td, *J*=8.1, 1.5 and 0.9 Hz, 1H, C_4-H), 7.37 (brd, *J*=7.8 and 0.9 Hz, 1H, $C_{6'}$-H), 7.26-7.20 (m, 2H, $C_{2'}$-H and C_5-H), 7.13 (t, *J*=7.8 Hz, 1H, $C_{5'}$-H), 6.95 (s, 1H, C_7-H), 6.91 (d, *J*=7.8 Hz, 1H, $C_{4'}$-H), 5.28 (s, 2H, -NCH_2), 2.35 (s, 3H, -CH_3), 2.29 (s, 3H, -CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 151.3 (imidazolyl C_2), 141.1 (C_{3a}), 138.7 (C_{7a}), 134.4 (C_1), 133.2 (imidazolyl C_6), ,132.9 (C_4), 132.4 (imidazolyl C_5), 132.3 (C_2), 131.7 ($C_{1'}$), 131.2 (C_5), 130.8 ($C_{4'}$), 130.3 ($C_{2'}$), 129.1 ($C_{5'}$), 127.4 (C_6), 124.5 ($C_{6'}$), 123.3 (C_3), 123.0 ($C_{3'}$), 120.1

(imidazolyl C_4), 110.5 (C_7), 47.7 (-NCH_2), 20.7 (-CH_3), 20.4 (-CH_3).Anal. calcd. for $C_{22}H_{18}Br_2N_2$; C: 56.20, H: 3.86, N: 5.96. Found: C: 56.11, H: 3.94, N: 6.06 %.

2-(4-Bromophenyl)-1(4'-bromophenylmethyl)-5,6-dimethyl-1*H*-benzimidazole (entry 31, Table 3). M.p.:184-186 ºC (aqueous EtOH); UV [λ_{max} (CH_2Cl_2)]= 284.5 nm (log ε = 3.87); IR (KBr): 3450, 2930, 2374, 1577, 1475, 1406, 1069, 1008, 828 and 720 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.53 (s, 1H, imidazolyl C_4-H), 7.57 (td, *J*=6.6 and 2.0 Hz, 2H, C_2-H and C_6-H), 7.51-7.44 (m, 4H, C_3-H, C_5-H, $C_{2'}$-H and $C_{6'}$-H), 6.97-6.94 (m, 3H, imidazolyl C_7-H, $C_{3'}$-H and $C_{5'}$-H), 5.32 (s, 2H, -NCH_2), 2.39 (s, 3H, -CH_3), 2.34 (s, 3H, -CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 152.1 (imidazolyl C_2), 141.7 (C_{3a}), 135.5 (C_{7a}), 134.6 (C_1), 132.8 (imidazolyl C_5 and C_6), 132.3 (C_3 and C_5), 132.0 ($C_{3'}$ and $C_{5'}$), 130.5 (C_2 and C_6), 129.1 (C_4), 127.5 ($C_{2'}$ and $C_{6'}$), 124.3 ($C_{1'}$), 121.8 ($C_{4'}$), 120.2 (imidazolyl C_4), 110.3 (C_7), 47.7 (-NCH_2), 20.6 (-CH_3), 20.3 (-CH_3). Anal. calcd. for $C_{22}H_{18}Br_2N_2$; C: 56.20, H: 3.86, N: 5.96. Found: C: 56.04, H: 3.98, N: 5.83 %.

2-(2-Chlorophenyl)-1(2'-chlorophenylmethyl)-5,6-dimethyl-1*H*-benzimidazole (entry 32, Table 3). M.p.:176-178 ºC (aqueous EtOH); UV [λ_{max} (CH_2Cl_2)]= 283.5 nm (log ε = 3.97); IR (KBr): 3434, 2920, 2446, 1705, 1443, 1397, 1241, 1040 and 760 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.65 (s, 1H, imidazolyl C_4-H), 7.48 (d, *J*=7.9 Hz, 1H, C_6-H), 7.43-7.36 (m, 2H, C_3-H and C_5-H), 7.33-7.25 (m, 2H, $C_{3'}$-H and $C_{5'}$-H), 7.15 (dt, *J*=7.8 and 0.5 Hz, 1H, C_4-H), 7.04 (t, *J*=7.6 Hz, 1H, $C_{4'}$-H), 6.97 (s, 1H, C_7-H), 6.61 (d, *J*=7.6 Hz, 1H, $C_{6'}$-H), 5.30 (s, 2H, -NCH_2), 2.39 (s, 3H, -CH_3), 2.32 (s, 3H, -CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 150.58 (imidazolyl C_2), 141.61 (C_{3a}), 134.36 (C_1), 133.52 (C_{7a}), 133.32 (C_2), 132.54 ($C_{2'}$), 132.18 (imidazolyl C_6), 132.06 (C_4), 131.58 (imidazolyl C_5), 131.14 (C_6), 129.82 ($C_{1'}$), 129.77 ($C_{4'}$), 129.43 ($C_{6'}$), 128.76 (C_3), 127.54 ($C_{3'}$), 127.02 (C_5), 126.79 ($C_{5'}$), 120.26 (imidazolyl C_4), 110.46 (C_7), 45.49 (-NCH_2), 20.49 (-CH_3), 20.18 (-CH_3).

Anal. calcd. for $C_{22}H_{18}Cl_2N_2$; C: 69.30 , H: 4.76 , N: 7.35. Found: C: 69.17, H: 4.88, N: 7.29 %.

2-(4-Bromophenyl)-1(4'-bromophenylmethyl)-5,6-dichloro-1*H*-benzimidazole (entry 33, Table 3). M.p.:177-178 ºC (aqueous EtOH); UV [λ_{max} (CH_2Cl_2)]= 310 nm (log ε = 4.04); IR (KBr): 3434, 2378, 1444, 1401 and 772 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.93 (s, 1H, imidazolyl C_4-H), 7.61 (td, *J*=8.4 and 1.8 Hz, 2H, C_2-H and C_6-H), 7.50 (m, 3H, C_3-H, C_5-H and C_7-H), 7.27 (td, *J*=5.7 and 1.2 Hz, 2H, $C_{3'}$-H and $C_{5'}$-H), 6.92 (d, *J*=8.4 Hz, 2H, $C_{2'}$-H and $C_{6'}$-H), 5.33 (s, 2H, -NCH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 154.8 (imidazolyl C_2), 142.4 (C_{3a}), 135.2 (C_1), 134.2 (C_{7a}), 132.6 (C_3 and C_5), 132.3 (C_2 and C_6), 130.6 ($C_{3'}$ and $C_{5'}$), 128.0 (imidazolyl C_6), 127.6 (imidazolyl C_5), 127.4 ($C_{2'}$ and $C_{6'}$), 127.3 (C_4), 125.3 ($C_{1'}$), 122.3 ($C_{4'}$), 121.4 (imidazolyl C_4), 111.6 (C_7), 48.1 (-NCH_2).

Anal. calcd. for $C_{20}H_{12}Br_2Cl_2N_2$; C: 47.01, H: 2.37, N: 5.48. Found: C: 46.84 , H: 2.49, N: 5.68 %.

5,6-Dichloro-2-(2,5-dimethoxyphenyl)-1(2',5'-dimethoxyphenylmethyl)-1*H*-benzimidazole (entry 34, Table 3). M.p.:150-154 ºC (aqueous EtOH); UV [λ_{max} (CH_2Cl_2)]= 302.0 nm (log ε = 4.10); IR (KBr): 3426, 2951, 2371, 1592, 1478, 1433, 1276, 1217, 1044, 1021 and 803 cm^{-1};^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.88 (s, 1H, imidazolyl C_4-H), 7.40 (s, 1H, C_7-H), 7.04 (d, *J*=2.1 Hz,

1H, C_6-H), 7.01 (d, *J*=3.0 Hz, 1H, $C_{6'}$-H), 6.93 (td, *J*=9.6 and 1.8 Hz, 1H, C_4-H), 6.77 (d, *J*=9.0 Hz, 1H, C_3-H), 6.72 (dd, *J*=9.5 and 2.7 Hz, 1H, $C_{4'}$-H), 6.20 (d, *J*=2.4 Hz, 1H, $C_{3'}$-H), 5.17 (s, 2H, -NCH_2), 3.75 [s, 6H, 2× (-OCH_3)], 3.63 (s, 3H, -OCH_3), 3.59 (s, 3H, -OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 154.0 (C_2), 153.7 (C_5), 153.5 ($C_{2'}$), 151.6 ($C_{5'}$), 150.8 (imidazolyl C_2), 142.5 (C_{3a}), 134.7 (C_{7a}), 126.4 (imidazolyl C_6), 126.0 (imidazolyl C_5), 124.7 (C_1), 120.9 (imidazolyl C_4), 119.6 ($C_{1'}$), 117.8 (C_4), 116.8 (C_6), 114.6 (C_3), 113.1 ($C_{3'}$), 112.5 ($C_{4'}$), 112.2 ($C_{6'}$), 111.1 (C_7), 55.9 (-OCH_3), 55.8 (-OCH_3), 55.6 (-OCH_3), 55.5 (-OCH_3), 43.7 (-NCH_2). Anal. calcd. for $C_{24}H_{22}Cl_2N_2O_4$; C: 60.88, H: 4.68, N: 5.91. Found: C: 60.74, H: 4.89, N: 5.78 %.

2-(4-Chlorophenyl)-1(4'-chlorophenylmethyl)-5,6-dichloro-1*H*-benzimidazole (entry 35, Table 3). M.p.:178-180 ºC (aqueous EtOH); UV [λ_{max} (CH_2Cl_2)] = 310.5 nm (log ε = 3.91); IR (KBr): 2930, 2371, 1686, 1591, 1429, 1406, 1305, 1092, 1012, 829 and 761 cm^{-1};^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.94 (s, 1H, imidazolyl C_4-H), 7.57 (dd, *J*=6.6 and 1.8 Hz, 2H, C_2-H and C_6-H), 7.43 (dd, *J*=7.8 and 1.8 Hz, 2H, C_3-H and C_5-H), 7.34 (dd, *J*=9.0 and 1.8 Hz, 2H, $C_{3'}$-H and $C_{5'}$-H), 7.28 (s, 1H, C_7-H), 6.98 (d, *J*=8.4 Hz, 2H, $C_{2'}$-H and $C_{6'}$-H), 5.35 (s, 2H, -NCH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 154.7 (imidazolyl C_2), 142.2 (C_4), 137.0 (C_{3a}), 135.0 (C_1), 134.3 ($C_{4'}$), 133.6 (C_{7a}), 130.4 (C_2 and C_6), 129.6 (C_3 and C_5), 129.3 ($C_{2'}$ and $C_{6'}$), 127.6 (imidazolyl C_6), 127.3 (imidazolyl C_5), 127.3 ($C_{1'}$), 127.1 ($C_{3'}$ and $C_{5'}$), 121.3 (imidazolyl C_4), 111.6 (C_7), 48.0 (-NCH_2). Anal. calcd. for $C_{20}H_{12}Cl_4N_2$; C: 56.90, H: 2.86, N: 6.63. Found: C: 56.77, H: 2.98, N: 6.78 %.

2-(2-Chlorophenyl)-1(2'-chlorophenylmethyl)-5,6-dichloro-1*H*-benzimidazole (entry 36, Table 3). M.p.:146-148 ºC (aqueous EtOH); UV [λ_{max} (CH_2Cl_2)]= 301 nm (log ε = 3.79); IR (KBr): 3754, 3069, 2924, 1449, 1384, 1302, 1044 and 755 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.93 (s, 1H, imidazolyl C_4-H), 7.65-7.41 (m, 3H, C_3-H, C_4-H and C_6-H), 7.39-7.27 (m, 3H, C_7-H, $C_{3'}$-H and $C_{4'}$-H), 7.20 (dt, *J*=7.5 and 1.5 Hz, 1H, C_5-H), 7.09 (dt, *J*=7.2 and 1.1 Hz, 1H, $C_{5'}$-H), 6.63 (d, *J*=7.6 Hz, 1H, $C_{6'}$-H), 5.31 (s, 2H, -NCH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 153.4 (imidazolyl C_2), 142.2 (C_{3a}), 134.1 (C_1), 134.0 (C_{7a}), 132.5 (C_2), 132.3 ($C_{2'}$), 131.8 (C_4), 131.7 (C_6), 131.3 (C_3), 130.5 ($C_{4'}$), 129.9 ($C_{3'}$), 129.8 ($C_{6'}$), 129.4 (C_5), 128.8 ($C_{1'}$), 127.4 (imidazolyl C_6), 127.0 ($C_{5'}$), 126.9 (imidazolyl C_5), 121.4 (imidazolyl C_4), 111.8 (C_7), 46.04 (-NCH_2). Anal. calcd. for $C_{20}H_{12}Cl_4N_2$; C: 56.90, H: 2.86, N: 6.63. Found: C: 57.07, H: 2.74, N: 6.53 %.

2-(3-Bromophenyl)-1(3'-bromophenylmethyl)-5,6-dichloro-1*H*-benzimidazole (entry 37, Table 3). M.p.:155-158 ºC (aqueous EtOH); UV [λ_{max} (CH_2Cl_2)] = 308.5 nm (log ε = 4.01); IR (KBr): 3424, 2375, 1570, 1482, 1300, 1075 and 785 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.93 (d, *J*=0.9 Hz, 1H, C_2-H), 7.83 (d, *J*=1.5 Hz, 1H, $C_{2'}$-H), 7.63 (dd, *J*=8.0 and 0.9 Hz, 1H, C_6-H), 7.48 (dt, *J*=9.0 and 0.9 Hz, 2H, C_4-H and C_5-H), 7.34 (d, *J*=7.8 Hz, 2H, $C_{4'}$-H and imidazolyl C_4-H), 7.26-7.20 (m, 2H, C_7-H and $C_{5'}$-H), 6.93 (d, *J*=7.8 Hz, 1H, $C_{6'}$-H), 5.35 (s, 2H, -NCH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 154.2 (imidazolyl C_2), 142.1 (C_{3a}), 137.4 (C_1), 135.0 (C_{7a}), 133.6 (C_4), 132.3 (C_2), 131.6 (C_5), 130.9 ($C_{4'}$), 130.8 ($C_{2'}$), 130.4 (imidazolyl C_5 and C_6), 128.9 ($C_{5'}$), 127.7 ($C_{1'}$), 127.3 (C_6), 124.3 ($C_{6'}$), 123.5 (C_3), 123.1 ($C_{3'}$), 121.4 (imidazolyl C_4), 111.6 (C_7), 48.0 (-NCH_2).Anal. calcd. for $C_{20}H_{12}$ $Br_2Cl_2N_2$; C: 47.01, H: 2.37, N: 5.48. Found: C: 47.14, H: 2.45, N: 5.34 %.

2-(3-Bromophenyl)-1(3'-bromophenylmethyl)-4-methyl-1*H*-benzimidazole (entry 38, Table 3). Oil : UV [λ_{max} (CH_2Cl_2)]= 293.0 nm (log ε = 4.12); IR (KBr): 2945, 2837, 2314, 1714, 1599, 1492, 1454, 1275, 1226, 1041 and 743 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.80 (t, *J*=1.5 Hz, 1H, C_2-H), 7.58 (qd, *J*=9.0 and 1.2 Hz, 1H, C_6-H), 7.47 (td, *J*=7.8 and 1.2 Hz, 1H, C_4-H), 7.41 (m, 1H, C_5-H), 7.32 (td, *J*=5.7 and 1.8 Hz, 1H, $C_{6'}$-H), 7.25 (t, *J*=2.4 Hz, 1H, $C_{2'}$-H), 7.20-7.11 (m, 3H, imidazolyl C_5-H, C_6-H and $C_{5'}$-H), 7.03 (dd, *J*=9.0 and 0.9 Hz, 1H, C_7-H), 6.92 (dd, *J*=7.5 and 0.3 Hz, 1H, $C_{4'}$-H), 5.32 (s, 2H, -NCH_2), 2.74 (s, 3H, -CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 151.5 (imidazolyl C_2), 143.5 (C_{3a}), 142.0 (C_{7a}), 138.4 (C_1), 132.9 (C_4), 132.3 (C_2), 131.0 (imidazolyl C_4), 130.6 (C_5), 130.1 ($C_{4'}$), 130.1 ($C_{5'}$), 129.5 ($C_{2'}$), 127.5 ($C_{1'}$), 125.0 (C_6), 124.5 ($C_{6'}$), 123.5 (imidazolyl C_6), 123.4 (imidazolyl C_5), 123.1 (C_3), 122.8 ($C_{3'}$), 107.7 (C_7), 47.7 (-NCH_2), 16.7 (-CH_3). Anal. calcd. for $C_{21}H_{16}Br_2N_2$; C: 55.29, H: 3.53, N: 6.14. Found: C: 55.17, H: 3.68, N: 6.05 %.

5,6-Dichloro-2-(3,4-dimethoxyphenyl)-1(3',4'-dimethoxyphenylmethyl)-1*H*-benzimidazole (entry 39, Table 3). M.p.:199-201 ºC (aqueous EtOH); UV [λ_{max} (CH_2Cl_2)] = 313.5 nm (log ε = 4.11); IR(KBr): 3433, 2924, 2376, 1507, 1451, 1255, 1135, 1023 and 820 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.91 (s, 1H, imidazolyl C_4-H), 7.33 (s, 1H, C_7-H), 7.27-7.20 (m, 2H, C_2-H and C_6-H), 6.92 (d, *J*=8.2 Hz, 1H, C_5-H), 6.83 (d, *J*=8.1 Hz, 1H, $C_{5'}$-H), 6.61 (m, 2H, $C_{2'}$-H and $C_{6'}$-H), 5.36 (s, 2H, -NCH_2), 3.92 (s, 3H, -OMe), 3.87 (s, 3H, -OCH_3), 3.79 (s, 3H, -OCH_3), 3.78 (s, 3H, -OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 156.1 (C_4), 150.9 (C_3), 149.7 ($C_{4'}$), 149.3 ($C_{3'}$), 148.9 (imidazolyl C_2), 142.4 (C_{3a}), 135.6 (C_{7a}), 128.1 (C_1), 126.8 (imidazolyl C_6), 126.7 (imidazolyl C_5), 121.9 (imidazolyl C_4), 121.6 ($C_{1'}$), 120.8 (C_6), 118.0 ($C_{6'}$), 112.2 (C_5), 111.7 ($C_{5'}$), 111.6 (C_2), 111.1 ($C_{2'}$), 108.9 (C_7), 56.0 (2×-OCH_3), 55.9 (2×-OCH_3), 48.4 (-NCH_2).Anal. calcd. for $C_{24}H_{22}Cl_2N_2O_4$; C: 60.88, H: 4.68, N: 5.91. Found: C: 60.94, H: 4.39, N: 5.84 %.

2-(3,4-Dimethoxyphenyl)-1(3',4'-dimethoxyphenylmethyl)-4-methyl-1*H*-benzimidazole (entry 40, Table 3). M.p.:102-104 ºC (aqueous EtOH); UV [λ_{max} (CH_2Cl_2)]= 286 nm (log ε = 4.15); IR(KBr): 3434, 2934, 2373, 1607, 1497, 1268, 1222, 1040 and 753 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.12-7.06 (m, 4H, C_2-H, imidazolyl C_5-H, imidazolyl C_6-H and C_7-H), 6.98 (dd, *J*=9.0 and 3.0 Hz, 1H, C_6-H), 6.89 (d, *J*=9.0 Hz, 1H, C_5-H), 6.74 (d, *J*=8.7 Hz, 1H, $C_{5'}$-H), 6.69 (dd, *J*=8.7 and 3.0 Hz, 1H, $C_{6'}$-H), 6.28 (d, *J*=2.7 Hz, 1H, $C_{2'}$-H), 5.20 (s, 2H, -NCH_2), 3.75 (s, 3H, -OCH_3), 3.74 (s, 3H, -OCH_3), 3.59 (s, 3H, -OCH_3), 3.56 (s, 3H, -OCH_3), 2.73 (s, 3H, -CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 153.6 (C_4), 153.5 (C_3), 151.9 ($C_{4'}$), 151.2 ($C_{3'}$), 150.8 (imidazolyl C_2), 142.5 (C_{3a}), 135.1 (C_{7a}), 129.7 (C_1), 125.9 (imidazolyl C_4), 122.5 (imidazolyl C_6), 122.4 (imidazolyl C_5), 120.6 ($C_{1'}$), 117.3 (C_6), 117.2 ($C_{6'}$), 114.5 (C_5), 112.6 ($C_{5'}$), 112.3 (C_2), 110.9 ($C_{2'}$), 108.2 (C_7), 55.9 (-OCH_3), 55.8 (-OCH_3), 55.7 (-OCH_3), 55.6 (-OCH_3), 43.3 (-NCH_2), 16.85 (-CH_3). Anal. calcd. for $C_{25}H_{26}N_2O_4$; C: 71.75, H: 6.26, N: 6.66. Found: C: 71.62, H: 6.41, N: 6.52 %.

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