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*J. Org. Chem.*, **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.7b00165 • Publication Date (Web): 05 Apr 2017



## Just Accepted



ACS Publications

The Journal of Organic Chemistry is published by the American Chemical Society.
1155 Sixteenth Street N.W., Washington, DC 20036

# Benzimidazoles from Aryl Alkyl Ketones and 2-Amino Anilines by an Iodine Catalyzed Oxidative C(CO)−C(alkyl) Bond Cleavage

Owk Ravi,[a] Altab Shaikh,[a] Atul Upare,[a] Kiran Kumar Singarapu[b] and

Surendar Reddy Bathula*[a]

[a]Division of Natural Products Chemistry, CSIR-Indian Institute of Chemical Technology, Hyderabad 500607, India

[b]Centre for Nuclear Magnetic Resonance, CSIR-Indian Institute of Chemical Technology, Hyderabad, 500 007, India.

E-mail: bsreddy@iict.res.in

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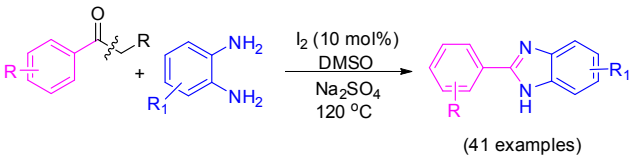
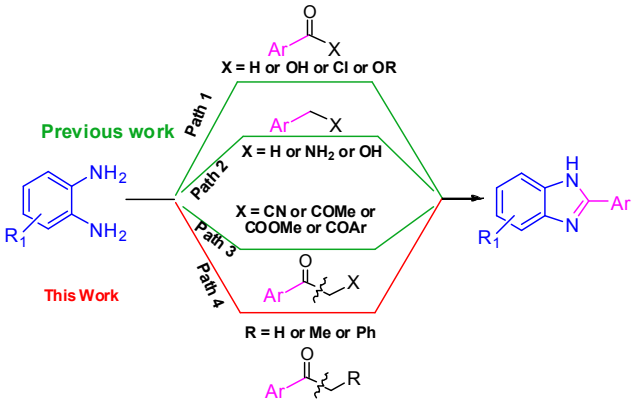



**ABSTRACT**: A novel molecular iodine catalyzed cyclization reactions of 2-amino anilines with aryl alkyl ketones under oxidant and metal free conditions are described. The reaction likely involves, sequential C-N bond formation followed by C(CO)-C(alkyl) bond cleavage. Various 2-substituted benzimidazoles are obtained in moderate to good yields in single step from readily available acetophenones, propiophenones and phenylacetophenones.

KEYWORDS: Benzimidazoles, C-C bond cleavage, Iodine catalysis, Acetophenones.

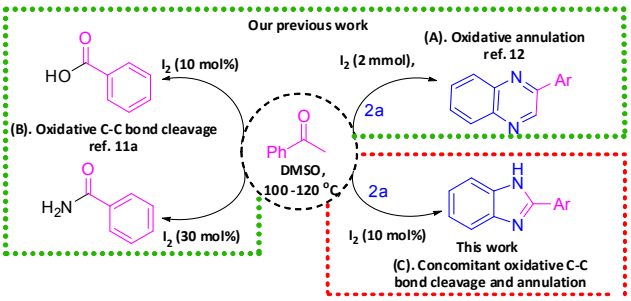
Benzimidazoles represent an important and abundant class of dinitrogen containing fused heterocycles. Compounds that contain the benzimidazoles motif are acclaimed for their widespread applications as enzyme inhibitors, drugs, dyes and polymers.[1] Moreover, huge market of commercially available benzimidazole based drugs (esomeprazole, lansoprazole, rabeprazole, telmisartan, bendazol and bendamustine) signifies the need to develop new, economical and more environment friendly synthetic methods.




**Scheme 1**. Different Pathways for the Synthesis of Benzimidazoles by Using 1,2-Diaminoarenes

Generally, these bicyclic compounds are prepared through the condensation of 1,2-diaminoarenes with carboxylic acids[2] , carboxylic acid derivatives[3] and aldehydes[4] (Scheme 1, path 1) under oxidative conditions. Benzylalcohol[5] or amine[6] or methylarene[7] (Scheme 1, path 2) are also employed as substrates in the place of above carbonyls. Most of the above reactions require harsh conditions, use of expensive, air-sensitive and toxic reagents. Further β-diketones[8], β-keto nitriles[9] and keto esters[10] (Scheme 1, path 3) have also been used for the synthesis of benzimidazoles. On the other hand, readily available aryl alkyl ketones are underutilized. This

could be due to the involvement of challenging C(CO)-C(alkyl) bond cleavage reaction. In continuation of our previous work on the oxidative C-C bond cleavage,[11] herein we report the synthesis of the title compounds from more simpler and readily available aryl alkyl ketones.

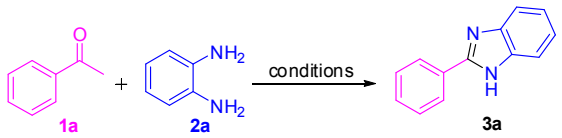



**Scheme 2**. Design of Present Approach Based on our Previous Findings

Earlier, we have reported the synthesis of pyrazines and quinoxalines by utilizing stoichiometric quantity of molecular iodine (2 equiv.) through the (CO)-C bond oxidative cyclization (Scheme 2A) from aryl methyl ketones, wherein α-ketoaldehydes were generated in situ.[12] Interestingly, our subsequent research revealed that the use of catalytic amount of iodine on similar substrates lead to the oxidative C-C bond cleavage (Scheme 2B) for benzoic acids and benzamides.[11a] This work led us to explore the synthesis of benzimidazoles via iodine catalysed concomitant oxidative C-C bond cleavage and annulation (Scheme 2C) of aryl alkyl ketones and o-phenylenediamines.

To initiate our study, the test reaction between acetophenone (**1a**, 1 mmol) and 2-amino aniline (**2a**, 1 mmol) was carried out in the presence of iodine (0.1 mmol) in DMSO at 100 $^{o}$C. As expected, the above combination of reagents gave desired product (**3a**), but in low yields (20%) (entry 1 in Table 1). This can be attributed to possible chemical equilibrium during imine formation and can be resolved by adding desiccants to the reaction mixture.

**Table 1:** Optimization of the Reaction Conditions




1a 2a 3a

| s. no. | catalyst (mol %) | solvent | drying agent | temp (°C) | time (h) | yield[b] (%) |
|---|---|---|---|---|---|---|
| 1 | $I_2$ (10) | DMSO | --- | 100 | 24 | 20 |
| 2 | $I_2$ (10) | DMSO | $Na_2SO_4$ | 100 | 24 | 40 |
| 3 | $I_2$ (20) | DMSO | $Na_2SO_4$ | 100 | 24 | 41 |
| 4 | $I_2$ (30) | DMSO | $Na_2SO_4$ | 100 | 24 | 42 |
| 5 | $I_2$ (10) | DMSO | $Na_2SO_4$ | 110 | 12 | 63 |
| **6** | **$I_2$ (10)** | **DMSO** | **$Na_2SO_4$** | **120** | **12** | **70** |
| 7 | $I_2$ (10) | DMSO | $Na_2SO_4$ | 130 | 12 | 71 |
| 8 | $I_2$ (10) | DMF | $Na_2SO_4$ | 120 | 24 | trace |
| 9 | $I_2$ (10) | dioxane | $Na_2SO_4$ | 120 | 24 | n.r. |
| 10 | $I_2$ (10) | $CH_3CN$ | $Na_2SO_4$ | 120 | 24 | n.r. |

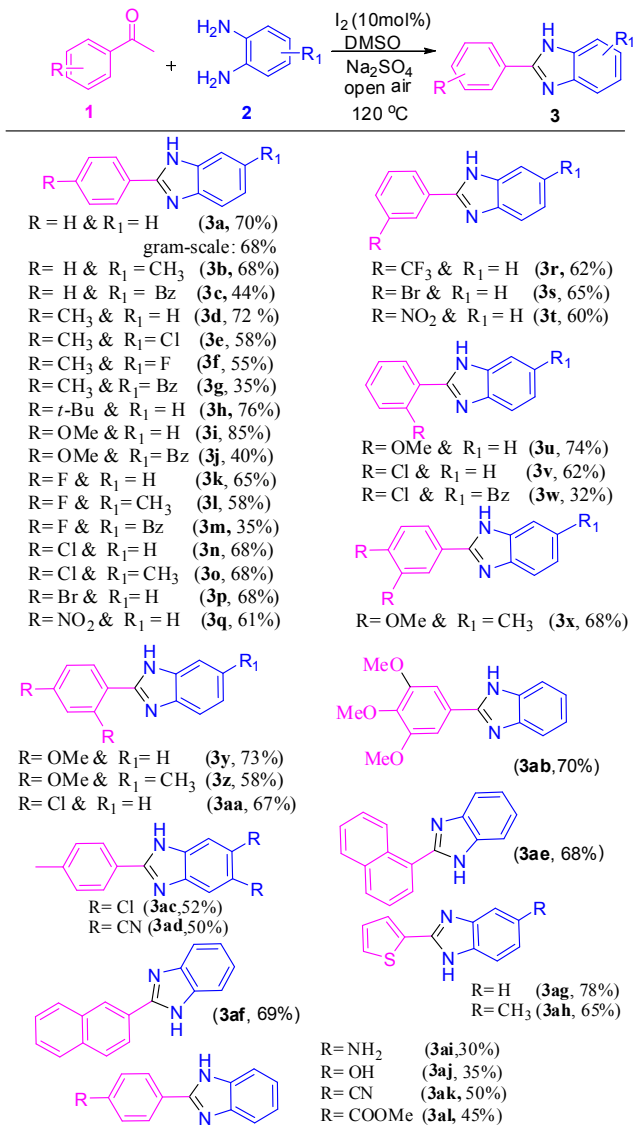
[a] Reaction conditions: 1 mmol of **1a** and 1 mmol of **2a** in the presence of catalyst and dehydrating agent in solvent (6 mL) at 120 °C for 12 h in air. [b] Isolated yields.

We have tried magnesium sulfate, molecular sieves and sodium sulfate to disrupt the equilibrium and it was observed that addition of 5 mmol of $Na_2SO_4$, improved the yield of **3a** to 40% (entry 2). Besides increase in the catalyst loading did not show any significant improvement on the yield of **3a** at 100 °C (entries 3 & 4). However, increase in temperature to 110 and 120 °C with 0.1 mmol of iodine furnished **3a** in 63% and 70% yield in 12 h time respectively (entries 5 & 6). Furthermore, additional increase of temperature did not improve the yield of the products (entry 7). On the other hand change of solvents to dioxane, $CH_3CN$ or DMF was also not advantageous (entries 8-10) to improve the yield. With the optimized conditions (entry 6 in Table 1) in hand, we next evaluated the generality of the method (Table 2). We first studied the reaction of different substituted acetophenones. Various functional groups as in alkyl products **3d** (72%), **3h** (76%), alkoxyl products **3i** (85%), **3u** (74%), **3y** (73%), **3ab** (70%), halogen products **3k** (65%), **3n** (68%), **3p** (68%), **3s** (65%), **3v** (62%), **3aa** (67%), trifluoromethyl product **3r** (62%) and

nitro products **3q** (61%), and **3t** (60%) were tolerated under the optimized conditions. It is noteworthy that aryl methyl ketones bearing electron-donating groups were found to give better results than those with electron-withdrawing groups (Table 2). To our delight, some of the fused acetophenones (α/β-acetyl naphthalenes) and heteroaromatic ketone (2-acetylthiophene) also resulted the corresponding products **3ae-3ah** with 65-78% yield. Unprotected functional groups like amine (**3ai**), hydroxyl(**3aj**), nitrile (**3ak**), ester (**3al**), acid (**3am**) containing acetophenones were also tolerated under standard condition to give desired products in low to moderate yields (25-50%).

Expanding the scope of the reaction, different o-phenylenediamines were employed in this reaction. Methyl substituted benzene-1,2-diamine reacts with both electron- rich and poor aryl/heteroaryl methyl ketones afforded the products in good yields (Table 2, **3b**, **3l**, **3o**, **3x**, **3z** & **3ah**, 58-68%). Furthermore o-phenylenediamine bearing electron-withdrawing groups like 4-flouro & 4-chloro o-phenylenediamine produced products **3f** (55%) and **3e** (58%) in good yields. Additionally 4, 5 dichloro-substituted o-phenylenediamine furnished the product **3ac** in 52% yield. Surprisingly, benzoyl substituted o-phenylenediamine gave very low yield with electron-rich acetophenones **3c** (44%), **3g** (35%), **3j** (40%), **3m** (35%), **3w** (32%), and no product formed with electron deficient substrates. Interestingly, diaminomaleonitrile offered corresponding imidazole **3ad** in 50% yield.

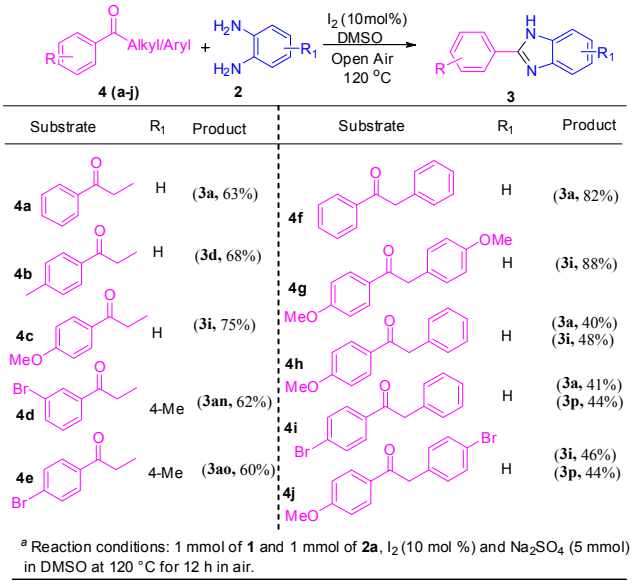
**Table 2**. Synthesis of Various Benzimidazoles from Aromatic Ketones and o-Phenylenediamines[a]




[a] Reaction conditions: 1 mmol of **1** and 1 mmol of **2**, $I_2$ (10 mol %) and $Na_2SO_4$ (5 mmol) in DMSO at 120 °C for 12 h in air.

Aforementioned results prompted us to test the fate of the more challenging aryl higher alkyl/benzyl ketones (**4a-4j**) in place of preceding methyl ketones under the standard conditions

**Table 3**. Synthesis of Benzimidazoles from Aryl Alkyl/Benzyl Ketones and o-Phenylenediamines[a]



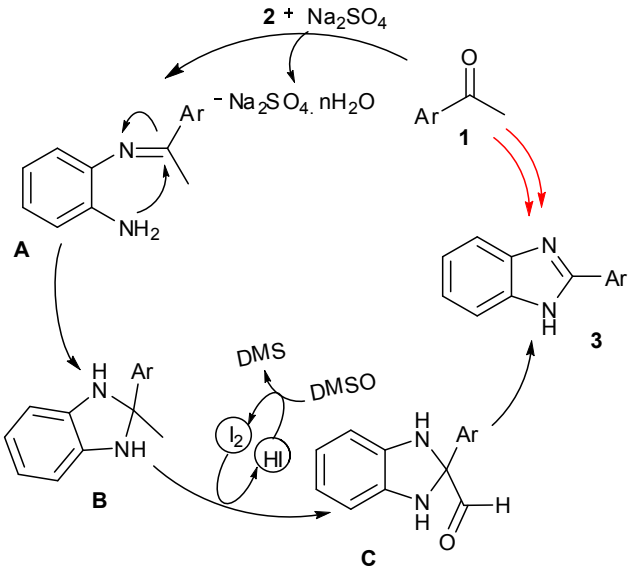

| Substrate | $R_1$ | Product | Substrate | $R_1$ | Product |
|---|---|---|---|---|---|
| 4a | H | (3a, 63%) | 4f | H | (3a, 82%) |
| 4b | H | (3d, 68%) | 4g | H | (3i, 88%) |
| 4c | H | (3i, 75%) | 4h | H | (3a, 40%) (3i, 48%) |
| 4d | 4-Me | (3an, 62%) | 4i | H | (3a, 41%) (3p, 44%) |
| 4e | 4-Me | (3ao, 60%) | 4j | H | (3i, 46%) (3p, 44%) |

[a] Reaction conditions: 1 mmol of **1** and 1 mmol of **2a**, $I_2$ (10 mol %) and $Na_2SO_4$ (5 mmol) in DMSO at 120 °C for 12 h in air.

(Table 3). To our delight, propiophenone and its derivatives reacted well to produce corresponding benzimidazoles (**3a**, **3d**, **3i**, **3an**, **3ao**) in good yields (60 to 75%). In the case of aryl benzyl ketones, interestingly both ends of the substrate were converted to the corresponding benzimidazoles. In particular, both ends of symmetrically substituted aryl benzyl ketones **4f** and **4g** were converted to single benzimidazole **3a** and **3i** respectively in 82% & 88% yield (Note: the product was more than one mmol from one mmol of starting material). Whereas aryl benzyl ketones with distinct substitutions (**4h-j**) produced two different benzimidazoles. An $^1$H NMR study during the course of the reaction also indicated the formation of second benzimidazole adduct from benzylic terminal (as shown in Figure S1). Moreover, no other by-product from this benzyl terminal was observed. Moving forward, we have tested the scalability of the method by

conducting the reaction in gram scale. Under the standard conditions 1g of **1a** has produced 1.09g of **3a** with 68% yield.

Before proposing the mechanism, some control experiments (Scheme S1) were conducted to rule out the formation of phenacyl iodide or phenylglyoxal as intermediates. We then propose a possible mechanism as shown in scheme 3. The reaction starts with the Schiff base (**A**) formation followed by cyclization to obtain dihydro benzimidazole (**B**). Intermediate "**B**" undergoes iodinate on followed by oxidation[13] to produce its oxo derivative "**C**", which was detected in the




**Scheme 3**. Proposed Mechanism

$^1$H NMR spectrum of a crude product (Figure S2). Subsequently, aromatization of "**C**" with the loss of formaldehyde produces 2-aryl benzimidazole product **3**.

## CONCLUSION

In summary, we have demonstrated a facile synthetic method to convert aryl alkyl ketones to benzimidazoles for the first time via C (sp2)–C bond cleavage. The reaction is executed by a catalytic amount of iodine under metal free conditions. Some control experiments and NMR studies were carried out to support the mechanism. This method constitutes a simple and inexpensive route to obtain 2-aryl substituted benzimidazoles which are of great importance in medicinal chemistry.

**EXPERIMENTAL SECTION**:

Reactions were monitored by thin-layer chromatography carried out on silica plates using UV-light, and Ninhydrin for visualization. Column chromatography was performed on silica gel (60–120 mesh) using hexane and ethyl acetate as eluents. Evaporation of solvents was done under reduced pressure at temperature less than 40 °C. IR spectra were recorded as neat compound. $^{1}H$ and $^{13}C$ NMR spectra were recorded in $CDCl_3$ and DMSO-$d_6$ solvents on a 300 MHz and 500 MHz spectrometer. Chemical shifts $\delta$ and coupling constants $J$ are given in ppm (parts per million) and Hz (hertz) respectively. Chemical shifts are reported relative to residual solvent as an internal standard for $^{1}H$ and $^{13}C$ ($CDCl_3$: $\delta$ 7.26 ppm for $^{1}H$, and 77.0 ppm for $^{13}C$, DMSO-$d_6$: $\delta$ 2.50 ppm for $^{1}H$, and 39.5 ppm for $^{13}C$). HRMS data were recorded by electrospray ionization with a Q-TOF mass analyzer. Melting points were measured on micro melting point apparatus. Commercially available substituted acetophenones, iodine and DMSO were used without further purification.

General procedure for the synthesis of Benzimadazoles from acetophenones(A) : mixture of acetophenone (1 equiv), benzene-1, 2-diamine (1 equiv), iodine (10 mol %) and sodium sulphate (5 equiv) in DMSO (10 mL) was stirred at 120 °C under open air for the appropriate time (Table 1). After completion of the reaction, as indicated by TLC, the mixture was diluted

with water and filtered. The filtrate was extracted with EtOAc (4×15 mL) and extract was washed with brine, drying over $Na_2SO_4$ and evaporation, the crude product was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc) to afford the product.Characterization data for new compounds is given below.

*2-phenyl-1H-benzo[d]imidazole (**3a**)*:[6a] According to general procedure, **1a** (120 mg, 1 mmol) gave **3a** (135 mg, 70%) as a white solid. Rf = 0.3 (EtOAc/hexanes, 3:7); m.p. 290 - 292 ºC; $^1$H NMR (300 MHz, DMSO - d) δ: 12.9 (bs, 1H), 8.18 (d, *J* = 7.04 Hz, 2H), 7.62 - 7.51 (m, 5H), 7.22 - 7.19 (m, 2H) ppm; $^{13}$C NMR (75 MHz, DMSO - d) δ: 151.1, 130.0, 129.8, 128.9, 126.4, 122.1, 115.1, 115.0 ppm; IR (KBr) ν: 2940, 1219.8, 1378.0, 1167.0, 772.5 cm$^{-1}$; MS (EI) m/z 195 $[M+1]^+$.

*5-methyl-2-phenyl-1H-benzo[d]imidazole (**3b**)*:[6a] According to general procedure, **1a** (120 mg, 1 mmol) gave **3b** (140 mg, 68%) as a white solid. $R_f$ = 0.3 (EtOAc/hexanes, 3:7); m.p. 240 - 242 ºC; $^1$H NMR (300 MHz, DMSO - d) δ: 8.15 (d, *J* = 7.01 Hz, 2H), 7.56 - 7.44 (m, 4H), 7.37 (s, 1H), 7.02 (d, *J* = 8.15 Hz, 1H), 2.42 (s, 3H) ppm; $^{13}$C NMR (75 MHz, DMSO - d) δ: 150.9, 138.9, 138.7, 131.3, 130.2, 129.7, 128.9, 126.3, 123.6, 114.6, 114.4, 21.3 ppm; IR (KBr) ν: 2922.0, 1412.1, 1219.6, 1057.0, 772.6 cm$^{-1}$; MS (EI) m/z 209 $[M+1]^+$.

*phenyl(2-phenyl-1H-benzo[d]imidazol-5-yl)methanone (**3c**)*:[6a] According to general procedure, **1a** (120 mg, 1 mmol) gave **3c** (131 mg, 44%) as a white solid. Rf = 0.3 (EtOAc/hexanes, 3:7); m.p. 222 - 224 ºC; $^1$H NMR (300 MHz, DMSO - d) δ: 13.3 (bs, 1H), 8.21 (d, *J* = 6.56 Hz, 2H), 7.96 (bs, 1H), 7.78 - 7.60 (m, 5H), 7.60 - 7.55 (m, 5H); $^{13}$C NMR (75 MHz, DMSO - d) δ: 195.5, 138.0, 132.0, 131.0, 130.4, 129.4, 129.3, 129.0, 128.3, 126.7; IR (KBr) ν: 3012.5, 1641.0, 1317.7, 1216.2, 772.8 cm$^{-1}$; MS (EI) m/z 299 $[M+1]^+$.

*2-(p-tolyl)-1H-benzo[d]imidazole (**3d**)*:[6a] According to general procedure, **1b** (134 mg, 1 mmol) gave **3d** (149 mg, 72%) as a white solid. Rf = 0.3 (EtOAc/hexanes, 3:7); m.p. 274 - 276 ºC; $^{1}$H NMR (300 MHz, DMSO - d) δ: 12.82 (bs, 1H), 8.05 (d, *J* = 8.10 Hz, 2H), 7.63 (d, *J* = 6.90 Hz, 1H), 7.50 (d, *J* = 6.90 Hz, 1H), 7.34 (d, *J* = 7.97 Hz, 2H), 7.20 - 7.11(m, 2H), 2.37 (s, 3H) ppm; $^{13}$C NMR (75 MHz, DMSO - d) δ: 151.3, 139.5, 129.4, 127.4, 126.3, 122.0, 121.86, 121.80, 20.9 ppm; IR (KBr) ν: 2944.2, 1219.7, 892.2, 772.5 cm$^{-1}$; MS (EI) m/z 209 [M +1] $^{+}$.

*6-chloro-2-p-tolyl-1H-benzo[d]imidazole (**3e**)*:[4a] According to general procedure, **1b** (134 mg, 1 mmol) gave **3e** (140 mg, 58%) as a off white solid. Rf = 0.3 (EtOAc/hexanes, 3:7); m.p. 230 – 232 ºC; $^{1}$H NMR (300 MHz, DMSO - d) δ: 13.03 (s, 1H), 8.05 (d, *J* = 8.1 Hz, 3H), 7.58 (s, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.21 (dd, *J* = 8.5, 1.7 Hz, 1H), 2.38 (s, 3H) ppm; $^{13}$C NMR (75 MHz, DMSO - d) δ: 152.9, 140.1, 129.6, 126.9, 126.5, 126.3, 122.2, 21.2 ppm; MS (EI) m/z 243 [M+1] $^{+}$.

*6-fluoro-2-p-tolyl-1H-benzo[d]imidazole (**3f**)*:[14a] According to general procedure, **1b** (134 mg, 1 mmol) gave **3f** (124 mg, 55%) as a white solid. Rf = 0.3 (EtOAc/hexanes, 3:7)); m.p. 232 - 234ºC; $^{1}$H NMR (300 MHz, DMSO - d) δ: δ 12.95 (s, 1H), 8.05 (d, *J* = 8.0 Hz, 2H), 7.56 (s, 1H), 7.36 (d, *J* = 7.9 Hz, 3H), 7.11 – 6.96 (m, 1H), 2.37 (s, 3H) ppm; $^{13}$C NMR (75 MHz, DMSO - d) δ: 126 MHz, $CDCl_3$) δ 159.5, 157.6, 152.8, 139.8, 129.5, 129.5, 127.1, 126.3, 110.0, 20.1 ppm; MS (EI) m/z 227 [M+1] $^{+}$.

*Phenyl(2-(p-tolyl)-1H-benzo[d]imidazol-5-yl)methanone(**3g**)*:[14b] According to general procedure, **1b** (134 mg, 1 mmol) gave **3g** (107 mg, 35%) as a white solid. Rf = 0.3 (EtOAc/hexanes, 3:7); m.p. 233 - 235 ºC; $^{1}$H NMR (300 MHz, DMSO - d) δ: 13.21 (bs, 1H), 8.09 (d, *J* = 8.08 Hz, 2H), 7.94 (bs, 1H), 7.77 - 7.55 (m, 7H), 7.39 (d, *J* = 7.39 Hz, 2H), 2.39 (s, 3H) ppm; $^{13}$C NMR (75 MHz, DMSO - d) δ: 195.5, 140.3, 138.1, 131.9, 130.8, 129.5, 129.3, 128.3, 126.7, 126.6, 124.0,

20.9 ppm; IR (KBr) ν: 3101.2, 1646.1, 1443.8, 1317.8, 1218.8, 826.9, 771.8 $cm^{-1}$; MS (EI) m/z 313 $[M+1]^+$.

*2-(4-(tert-butyl)phenyl)-1H-benzo[d]imidazole (**3h**):*[14c] According to general procedure, **1c** (176 mg, 1 mmol) gave **3h** (190 mg, 76%) as a white solid. Rf = 0.3 (EtOAc/hexanes, 3:7); m.p. 256 - 258 ºC; $^1$H NMR (300 MHz, DMSO - d) δ: 12.83 (bs, 1H), 8.11 (d, *J* = 8.38 Hz, 2H), 7.64 (d, *J* = 7.60 Hz, 1H), 7.56 (d, *J* = 8.39 Hz, 2H), 7.51 (d, *J* = 6.98 Hz, 1H), 7.22 - 7.14 (m, 2H), 1.33(s, 9H) ppm; $^{13}$C NMR (75 MHz, DMSO - d) δ: 152.4, 151.2, 143.8, 134.9, 127.4, 126.1, 125.6, 122.2, 121.04, 118.6, 111.1, 34.5, 30.9 ppm; IR (KBr) ν: 2962.8, 1430.3, 1362.9, 1211.2, 966.0, 770.7 $cm^{-1}$; MS (EI) m/z 251 $[M+1]^+$.

*2-(4-methoxyphenyl)-1H-benzo[d]imidazole (**3i**):*[6a] According to general procedure, **1d** (150 mg, 1 mmol) gave **3i** (189 mg, 85%) as a white solid. $R_f$ = 0.3 (EtOAc/hexanes, 7:3); m.p. 224 - 226 ºC; $^1$H NMR (300 MHz, DMSO - d) δ: 12.70 (bs, 1H), 8.10 (d, *J* = 8.86 Hz, 2H), 7.62 - 7.47 (m, 2H), 7.18 - 7.09 (m, 4H), 3.83 (s, 3H) ppm; $^{13}$C NMR (75 MHz, DMSO - d) δ: 160.5, 151.3, 143.8, 143.7, 134.9, 127.9, 121.4, 118.4, 114.3, 110.9, 55.3 ppm; IR (KBr) ν: 2944.2, 2392.0, 1612.6, 1513.2, 1388.6, 1252.4, 1177.6, 1031.6, 838.5, 772.4 $cm^{-1}$; MS (EI) m/z 225 $[M+1]^+$.

*(2-(4-methoxyphenyl)-1H-benzo[d]imidazol-5-yl)(Phenyl)methanone (**3j**):*[14d] According to general procedure, **1d** (150 mg, 1 mmol) gave **3j** (130 mg, 40%) as a white solid. $R_f$ = 0.2 (EtOAc/hexanes, 3:7); m.p. 190 - 192 ºC; $^1$H NMR (300 MHz, DMSO - d) δ: 13.14 (d, *J* = 17.8 Hz, 1H), 8.14 (d, *J* = 8.84 Hz ,2H), 7.86-7.54 (m, 8H), 7.13 (d, *J* = 8.70 Hz, 2H), 3.84 (s, 3H) ppm; $^{13}$C NMR (75 MHz, DMSO - d) δ: 195.4, 161.0, 154.5, 153.6, 147.4, 143.2, 138.2, 134.5, 131.9, 130.6, 129.3, 128.3, 124.2, 123.7, 121.9, 121.2, 118.1, 114.4, 113.8, 111.1, 55.3 ppm; IR (KBr) ν: 3126.2, 1613.2, 1495.6, 1292.1, 1255.2, 1178.5, 1029.2, 834.5, 771.8 $cm^{-1}$; MS (EI) m/z 329 $[M+1]^+$.

*2-(4-fluorophenyl)-1H-benzo[d]imidazole (**3k**)*:[6a] According to general procedure, **1e** (138 mg, 1 mmol) gave **3k** (137 mg, 65%) as off white solid. $R_f$ = 0.3 (EtOAc/hexanes, 3:7); m.p. 245 - 247 ºC; $^1$H NMR (300 MHz, DMSO - d) δ: 12.90 (bs, 1H), 8.24-8.19 (m, 2H), 7.59 (bs, 2H), 7.43-7.37 (m, 2H), 7.21-7.19 (m, 2H) ppm; $^{13}$C NMR (75 MHz,$CDCl_3$ + DMSO - d) δ: 164.7, 161.4, 150.5, 139.0, 128.4, 128.3, 126.3, 126.2, 121.8, 115.4, 115.1, 114.6 ppm; IR (KBr) ν: 2998.0, 1612.6, 1496.0, 1436.2, 1218.8, 772.1 cm$^{-1}$; MS (EI) m/z 213 $[M+1]^+$.

*2-(4-fluorophenyl)-5-methyl-1H-benzo[d]imidazole (**3l**)*:[4e] According to general procedure, **1e** (138 mg, 1 mmol) gave **3l** (130 mg, 58%) as a white solid. $R_f$ = 0.4 (EtOAc/hexanes, 3:7); m.p. 180 - 182 ºC; $^1$H NMR (300 MHz, DMSO - d) δ: 8.21 - 8.16 (m, 2H), 7.47 (d, *J* = 8.17 Hz, 1H), 7.41 - 7.35 (m, 3H), 7.02 (d, *J* = 8.22 Hz, 1H), 2.42 (s, 3H) ppm; $^{13}$C NMR (75 MHz, DMSO - d) δ: 164.6, 161.3, 150.1, 139.0, 138.0, 131.4, 128.7, 128.5, 126.96, 126.94, 123.6, 116.1, 115.8, 115.1, 114.4, 21.3 ppm; IR (KBr) ν: 2924.5, 1435.6, 1220.5, 922.0, 772.5 cm$^{-1}$; MS (EI) m/z 227 $[M+1]^+$.

*(2-(4-fluorophenyl)-1H-benzo[d]imidazol-5-yl)(phenyl)methanone (**3m**)*: According to general procedure, **1e** (138 mg, 1 mmol) gave **3m** (110 mg, 35%) as a white solid. $R_f$ = 0.3 (EtOAc/hexanes, 3:7); m.p. 238 - 240 ºC; $^1$H NMR (300 MHz, DMSO - d) δ: 13.3 (bs, 1H), 8.27-8.22 (m, 2H), 8.00 - 7.65 (m, 6H), 7.60 - 7.57 (m, 2H), 7.44 (t, *J* = 8.98 Hz, 2H) ppm; $^{13}$C NMR (75 MHz, DMSO - d) δ: 195.5, 165.0, 161.7, 138.0, 129.3, 129.0, 126.1, 116.2, 115.9 ppm; IR (KBr) ν: 3126.3, 1618.2, 1489.3, 1319.9, 1225.5, 772.3 cm$^{-1}$. HRMS (ESI) calcd for $C_{20}H_{13}FN_2O$ $[M + Na]^+$ 339.0904, found 339.0909.

*2-(4-chlorophenyl)-1H-benzo[d]imidazole (**3n**)*:[6a] According to general procedure, **1f** (154 mg, 1 mmol) gave **3n** (154 mg, 68%) as a white solid. $R_f$ = 0.3 (EtOAc/hexanes, 3:7); m.p. 268 - 270 ºC; $^1$H NMR (300 MHz, DMSO - d) δ: 13.00 (bs, 1H), 8.18 (d, *J* = 8.60 Hz, 2H), 7.62 (d, *J* =

8.62 Hz, 4H), 7.23 - 7.20 (m, 2H) ppm; $^{13}$C NMR (75 MHz, DMSO - d) δ: 150.1, 143.7, 135.0, 134.4, 129.0, 128.0, 121.8, 118.9, 111.3 ppm; IR (KBr) ν: 3119.0, 1442.1, 1403.3, 1216.2, 1051.9, 968.5, 743.7 cm$^{-1}$; MS (EI) m/z 229 [M+1] $^{+}$.

*2-(4-chlorophenyl)-5-methyl-1H-benzo[d]imidazole (**3o**):*[14a] According to general procedure, **1f** (154 mg, 1 mmol) gave **3o** (163 mg, 68%) as a white solid. $R_f$ = 0.4 (EtOAc/hexanes, 3:7); m.p. 224 – 226 ºC; $^{1}$H NMR (300 MHz, DMSO - d) δ: 12.83 (d, *J* = 11.0 Hz, 1H), 8.15 (d, *J* = 8.43 Hz, 2H), 7.61 (d, *J* = 8.56 Hz, 2H), 7.52 - 7.31 (m, 2H), 7.03 (t, *J* = 8.54 Hz, 1H), 2.42 (s, 3H) ppm; $^{13}$C NMR (75 MHz, DMSO - d) δ: 149.8, 134.2, 131.6, 131.4, 129.1, 128.9, 127.9, 127.0, 123.7, 118.7, 118.6, 111.2 ,111.1, 21.3 ppm; IR (KBr) ν: 2997.3, 1445.3, 1311.6, 1219.6, 1053.0, 770.3, 731.9 cm$^{-1}$; MS (EI) m/z 243 [M+1] $^{+}$.

*2-(4-bromophenyl)-1H-benzo[d]imidazole (**3p**):*[14a] According to general procedure, **1g** (197 mg, 1 mmol) gave **3p** (183 mg, 68%) as a off white solid. $R_f$ = 0.3 (EtOAc/hexanes, 3:7); m.p. 255 - 257 ºC; $^{1}$H NMR (300 MHz, DMSO - d) δ: 8.12 (d, *J* = 8.53 Hz, 2H), 7.76 (d, *J* = 8.48 Hz, 2H), 7.67 (d, *J* = 7.20 Hz, 1H), 7.53 (d, *J* = 6.83 Hz, 1H), 7.24 - 7.17 (m, 2H) ppm; $^{13}$C NMR (75 MHz, DMSO - d) δ: 150.1, 143.7, 134.9, 131.9, 129.3, 128.3, 123.3, 122.7, 121.8, 111.4 ppm; IR (KBr) ν: 2939.0, 1436.0, 1216.2, 772.5 cm$^{-1}$; MS (EI) m/z 273 [M+2] $^{+}$.

*2-(4-nitrophenyl)-1H-benzo[d]imidazole (**3q**):*[14a] According to general procedure, **1h** (165 mg, 1 mmol) gave **3q** (145 mg, 61%) as a light yellow solid. $R_f$ = 0.3 (EtOAc/hexanes, 3:7); m.p. 262 - 264 ºC; $^{1}$H NMR (300 MHz, DMSO - d) δ: 8.45 - 8.35 (m, 4H), 7.61 - 7.64 (m, 2H),7.27 - 7.24 (m, 2H) ppm; $^{13}$C NMR (75 MHz, DMSO - d) δ: 149.0, 147.7, 139.6, 136.1, 130.0, 127.3, 124.2, 122.8, 122.6, 115.6 ppm; IR (KBr) ν: 2943.2, 1523.9, 1389.2, 1349.2, 772.3 cm$^{-1}$; MS (EI) m/z 240 [M+1] $^{+}$.

*2-(3-(trifluoromethyl)phenyl)-1H-benzo[d]imidazole (**3r**)*:[6a] According to general procedure, **1i** (188 mg, 1 mmol) gave **3r** (162 mg, 62%) as a white solid. $R_f$ = 0.3 (EtOAc/hexanes, 3:7); m.p. 209 - 211 ºC; $^1$H NMR (300 MHz, DMSO - d) δ: 13.17 (bs, 1H), 8.53 - 8.47 (m, 2H), 7.87 - 7.77 (m, 2H), 7.70 (d, *J* = 6.88 Hz, 1H), 7.57 (d, *J* = 7.05 Hz, 1H), 7.24 - 7.23 (m, 2H) ppm; $^{13}$C NMR (75 MHz, DMSO - d) δ: 149.6, 143.6, 135.0, 131.1, 130.4, 130.1, 130.0, 129.6, 126.1, 125.8, 122.8, 122.7, 122.2, 121.9, 119.1, 111.5 ppm; IR (KBr) ν: 2963.2, 1405.8, 1328.4, 1165.7, 1128.7, 1074.7, 772.0 cm$^{-1}$; MS (EI) m/z 263 [M+1] $^+$.

*2-(3-bromophenyl)-1H-benzo[d]imidazole (**3s**)*:[14a] According to general procedure, **1j** (197 mg, 1 mmol) gave **3s** (175 mg, 65%) as a white solid. $R_f$ = 0.3 (EtOAc/hexanes, 3:7); m.p. 222 - 224 ºC; $^1$H NMR (300 MHz, DMSO - d) δ: 13.30 (bs, 1H), 8.36 (s, 1H), 8.18 (d, *J* = 7.84 Hz, 1H), 7.70 - 7.67 (m, 2H), 7.55 - 7.49 (m, 2H), 7.27 - 7.18 (m, 2H) ppm; $^{13}$C NMR (75 MHz, DMSO - d) δ: 149.5, 143.6, 134.9, 131.1, 128.8, 125.3, 122.2, 121.9, 119.0, 111.4 ppm; IR (KBr) ν: 2915.0, 1219.8, 1159.0, 772.4 cm$^{-1}$; MS (EI) m/z 273 [M+2] $^+$.

*2-(3-nitrophenyl)-1H-benzo[d]imidazole (**3t**)*:[6a] According to general procedure, **1k** (165 mg, 1 mmol) gave **3t** (143 mg, 60%) as a light yellow solid. $R_f$ = 0.3 (EtOAc/hexanes, 3:7); m.p. 205 - 207 ºC; $^1$H NMR (300 MHz, DMSO - d) δ: 13.30 (bs, 1H), 9.01 (t, *J* = 1.76 Hz, 1H), 8.61 (d, *J* = 7.90 Hz, 1H), 8.33 (dd, *J* = 8.16,1.90 Hz, 1H), 7.85 (t, *J* = 8.08 Hz, 1H), 7.72 (d, *J* = 7.41 Hz, 1H), 7.58 (d, *J* = 7.27 Hz, 1H), 7.32 - 7.21 (m, 2H) ppm; $^{13}$C NMR (75 MHz, DMSO - d) δ: 149.0, 148.3, 143.5, 135.0, 132.4, 131.7, 130.6, 124.1, 123.2, 122.1, 120.7, 119.2, 111.6 ppm; IR (KBr) ν: 2954.0, 1523.9, 1389.0, 1349.2, 772.3 cm$^{-1}$; MS (EI) m/z 240 [M+1] $^+$.

*2-(2-methoxyphenyl)-1H-benzo[d]imidazole (**3u**)*:[15a] According to general procedure, **1l** (150 mg, 1 mmol) gave **3u** (165 mg, 74%) as a white solid. $R_f$ = 0.3 (EtOAc/hexanes, 3:7); m.p. 178 - 180 ºC; $^1$H NMR (300 MHz, DMSO - d) δ: 12.13 (bs, 1H), 8.35 - 8.33 (m, 1H), 7.64 - 7.61 (m,

2H), 7.49 - 7.44 (m, 1H), 7.24 - 7.09 (m, 4H), 4.02 (s, 3H) ppm; $^{13}$C NMR (75 MHz, DMSO - d) δ: 156.7, 148.9, 131.1, 129.7, 121.7, 120.8, 118.1, 112.0, 55.7 ppm; IR (KBr) ν: 2924.0, 1439.9, 1342.0, 1243.7, 886.0, 772.1 cm$^{-1}$; MS (EI) m/z 225 [M+1] $^{+}$.

*2-(2-chlorophenyl)-1H-benzo[d]imidazole(**3v**):*[15a] According to general procedure, **1m** (154 mg, 1 mmol) gave **3v** (141 mg, 62%) as a white solid. $R_f$ = 0.4 (EtOAc/hexanes, 3:7); m.p. 231 - 233 ºC; $^{1}$H NMR (300 MHz, DMSO - d) δ: 12.71 (bs, 1H), 7.92 - 7.88 (m, 1H), 7.67 - 7.51 (m, 5H), 7.24 - 7.23 (m, 2H) ppm; $^{13}$C NMR (75 MHz, DMSO - d) δ: 149.0, 132.0, 131.1, 130.3, 129.9, 127.3, 122.0, 119.0, 111.8, 111.7, 111.5 ppm; IR (KBr) ν: 2984.6, 1442.1, 1403.3, 1216.2, 1051.9, 968.5, 743.7 cm$^{-1}$. MS (EI) m/z 229 [M+1] $^{+}$.

*2-(2-chlorophenyl)-1H-benzo[d]imidazol-5-yl)(phenyl)methanone (**3w**):* According to general procedure, **1m** (180 mg, 1 mmol) gave **3w** (106 mg, 32%) as a white solid. $R_f$ = 0.3 (EtOAc/hexanes, 3:7); m.p. 146 - 148 ºC; $^{1}$H NMR (300 MHz, DMSO - d) δ: 13.12 (bs, 1H), 8.00 (bs, 1H), 7.94 (d, *J* = 6.72 Hz, 1H), 7.78 - 7.66 (m, 6H), 7.61 - 7.51 (m, 4H) ppm; $^{13}$C NMR (75 MHz, DMSO - d) δ: 195.6, 138.0, 132.1, 132.0, 131.6, 130.4, 129.4, 128.3, 127.5 ppm; IR (KBr) ν: 3052.2, 1649.3, 1630.0, 1618.0, 1443.5, 1319.9, 1219.3, 1109.9, 1051.6, 851.1, 761.0 cm$^{-1}$. HRMS (ESI) calcd for $C_{20}H_{13}ClN_2O$ $[M + Na]^+$ 355.0609, found 355.0611.

*2-(3,4-dimethoxyphenyl)-5-methyl-1H-benzo[d]imidazole(**3x**):*[15b] According to general procedure, **1n** (180 mg, 1 mmol) gave **3x** (182 mg, 68%) as a white solid. $R_f$ = 0.2 (EtOAc/hexanes, 3:7); m.p. 203 - 205 ºC; $^{1}$H NMR (300 MHz, DMSO - d) δ: 12.60 (d, *J* = 10.37 Hz ,1H), 7.74 - 7.69 (m, 2H), 7.50 - 7.27 (m, 2H), 7.11 (d, *J* = 8.32 Hz, 1H), 3.87 (s, 3H), 3.82 (s, 3H), 2.42 - 2.40 (s, 3H) ppm; $^{13}$C NMR (75 MHz, DMSO - d) δ: 151.0, 150.1, 148.8, 123.3, 123.0, 122.9, 119.1, 118.0, 111.7, 111.0, 109.6, 55.5, 21.3 ppm; IR (KBr) ν: 2941.0, 1503.8, 1264.2, 1225.9, 1024.6, 768.4 cm$^{-1}$; MS (EI) m/z 269 [M+1] $^{+}$.

*2-(2,4-dimethoxyphenyl)-1H-benzo[d]imidazole (**3y**)*:[15d] According to general procedure, **1o** (180 mg, 1 mmol) gave **3y** (185 mg, 73%) as a off white solid. $R_f$ = 0.3 (EtOAc/hexanes, 3:7)); m.p. 278 - 280 ºC; $^1$H NMR (300 MHz, DMSO - d) δ: 11.96 (bs, 1H), 8.25 (d, *J* = 8.66 Hz, 1H), 7.59 - 7.57 (m, 1H), 7.15 - 7.14 (m, 2H), 6.75 (d, *J* = 2.32 Hz, 1H), 6.71 (dd, *J* = 8.70, 2.39 Hz, 1H) 3.85 (s, 3H) ppm; $^{13}$C NMR (75 MHz, DMSO - d) δ: 161.9, 158.0, 149.1, 130.8, 121.3, 115.1, 114.9, 114.8, 114.6, 114.4, 111.0, 106.2, 98.5, 55.8, 55.4 ppm; IR (KBr) ν: 2939.0, 1613.5, 1582.5, 1210.3, 769.05, 749.1 cm$^{-1}$; MS (EI) m/z 255 [M+1] $^+$.

*2-(2,4-dimethoxyphenyl)-5-methyl-1H-benzo[d]imidazole(**3z**)*:[15c] According to general procedure, **1o** (180 mg, 1 mmol) gave **3z** (155 mg, 58%) as a white solid. $R_f$ = 0.2 (EtOAc/hexanes, 3:7); m.p. 203 - 205 ºC; 1H NMR (300 MHz, DMSO - d) δ: 11.97 (d, *J* = 10.66 Hz ,1H), 7.85 (s, 1H), 7.53 - 7.39 (m, 2H), 7.16 (d, *J* = 9.22 Hz, 1H), 7.03 (dd, *J* = 9.12, 3.18 Hz, 2H), 3.96 (s, 3H), 3.79 (s, 3H), 2.42 (s, 3H) ppm; $^{13}$C NMR (75 MHz, DMSO - d) δ: 153.1, 150.9, 148.3, 123.3, 118.6, 116.8, 113.4, 113.3, 56.0, 55.4, 21.3 ppm; IR (KBr) ν: 2941.0, 1503.8, 1264.1, 1225.9, 1024.6, 768.4 cm$^{-1}$. MS (EI) m/z 269 [M+1] $^+$.

*2-(2,4-dichlorophenyl)-1H-benzo[d]imidazole (**3aa**)*:[15c] According to general procedure, **1p** (187 mg, 1 mmol) gave **3aa** (185 mg, 67%) as a white solid. $R_f$ = 0.3 (EtOAc/hexanes, 3:7); m.p. 218 - 220 ºC; $^1$H NMR (300 MHz, DMSO - d) δ: 7.90 (d, J = 8.49 Hz, 1H), 7.60 - 7.58 (m, 2H), 7.46 - 7.45 (m, 1H), 7.31 (dd, *J* = 8.36, 1.90 Hz, 1H), 7.19 - 7.16 (m, 1H) ppm; $^{13}$C NMR (75 MHz, DMSO - d) δ: 148.2, 143.0, 135.1, 133.3, 132.7, 129.9, 128.8, 127.8, 123.0, 122.1, 119.2, 111.9 ppm; IR (KBr) ν: 2913.2, 1422.8, 1216.2, 1100.0, 995.0, 772.1 cm$^{-1}$; MS (EI) m/z 263 [M+1] $^+$.

*2-(3, 4, 5-trimethoxyphenyl)-1H-benzo[d]imidazole (**3ab**)*:[15d] According to general procedure , **1q** (210 mg, 1 mmol) gave **3ab** (198 mg, 70%) as a white solid. $R_f$ = 0.2 (EtOAc/hexanes, 3:7); m.p. 259 - 261 ºC; $^1$H NMR (300 MHz, DMSO - d) δ: 12.84 (bs, 1H), 7.59 (bs, 2H), 7.52 (bs,

2H), 7.21 - 7.18 (m, 2H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$+DMSO - d) δ: 152.9, 151.4, 138.8, 125.2, 121.7, 144.6, 114.4, 114.2, 103.6, 60.2, 55.7 ppm; IR (KBr) ν: 2912.6, 1590.0, 1429.9, 1220.5, 1128.6, 772.2cm$^{-1}$. MS (EI) m/z 285 $[M+1]^+$.

*5, 6-dichloro-2-p-tolyl-1H-benzo[d]imidazole (**3ac**):*[16a] According to general procedure, **1b** (134 mg, 1 mmol) gave **3ac** (144 mg, 52%) as a yellow solid. $R_f$ = 0.3 (EtOAc/hexanes, 3:7); m.p. 223 - 225 ºC; $^1$H NMR (300 MHz, DMSO - d) δ: δ 13.16 (s, 1H), 8.05 (d, *J* = 8.1 Hz, 2H), 7.91 (s, 1H), 7.73 (s, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 2.38 (s, 3H) ppm; $^{13}$C NMR (75 MHz, DMSO - d) δ: 153.9, 143.5, 140.4, 134.5, 129.6, 126.7, 124.5, 124.0, 119.7, 112.5, 21.0 ppm; MS (EI) m/z 277 $[M+1]^+$.

*2-p-tolyl-1H-imidazole-4,5-dicarbonitrile (**3ad**):*[16b] According to general procedure, **1b** (134 mg, 1 mmol) gave **3ad** (104 mg, 50%) as a yellow solid. $R_f$ = 0.3 (EtOAc/hexanes, 3:7); m.p. 143 – 145 ºC; $^1$H NMR (300 MHz, $CDCl_3$ + DMSO - d) δ 7.83 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 2.35 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$ + DMSO - d) δ: 150.9, 140.5, 129.3, 126.0, 124.6, 115.6, 110.8, 20.9 ppm; MS (EI) m/z 208 $[M+1]^+$.

*2-(naphthalen-1-yl)-1H-benzo[d]imidazole (**3ae**):*[15c] According to general procedure, **1r** (170 mg, 1 mmol) gave **3ae** (165 mg, 68%) as a white solid. $R_f$ = 0.3 (EtOAc/hexanes, 3:7); m.p. 217 - 219 ºC; $^1$H NMR (300 MHz, DMSO - d) δ: 12.93 (bs, 1H), 9.11 (d, *J* = 7.72 Hz, 1H), 8.11 - 8.00 (m, 3H), 7.78 (d, *J* = 6.85 Hz, 1H), 7.71 - 7.56 (m, 4H), 7.28 - 7.23 (m, 2H) ppm; $^{13}$C NMR (75 MHz, DMSO - d) δ: 151.3, 143.8, 134.4, 133.5, 130.4, 130.1, 127.8, 127.5, 127.0, 126.3, 125.2, 122.6, 121.5, 119.0, 111.3 ppm; IR (KBr) ν: 2917.2, 1389.2, 1221.3, 772.8 cm$^{-1}$; MS (EI) m/z 225 $[M+1]^+$.

*2-(naphthalen-2-yl)-1H-benzo[d]imidazole (**3af**):*[14a] According to general procedure, **1s** (170 mg, 1 mmol) gave **3af** (168 mg, 69%) as a white solid. $R_f$ = 0.3 (EtOAc/hexanes, 3:7); m.p. 201 -

203 ºC; $^{1}$H NMR (300 MHz, DMSO - d) δ: 8.68 (bs, 1H), 8.29 (dd, *J* = 8.60, 1.59 Hz, 1H), 7.88 (d, *J* = 8.71 Hz, 1H), 7.84 - 7.79 (m, 2H), 7.64 - 7.61 (m, 2H), 7.49 - 7.43 (m, 2H), 7.21 - 7.18 (m, 2H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$+DMSO - d) δ: 151.5, 139.3, 139.2, 133.3, 132.6, 127.9, 127.2, 126.4, 126.1, 125.9, 123.6, 121.9, 114.6 ppm; IR (KBr) ν: 2927.5, 1385.2, 1221.5, 772.8 $cm^{-1}$; MS (EI) m/z 225 $[M+1]^{+}$.

*2-(thiophen-2-yl)-1H-benzo[d]imidazole (**3ag**)*:[6a] According to general procedure, **1t** (126 mg, 1 mmol) gave **3ag** (156 mg, 78%) as a brown solid. $R_f$ = 0.3 (EtOAc/hexanes, 3:7); m.p. 342 - 344 ºC; $^{1}$H NMR (300 MHz, DMSO - d) δ: 12.94 (bs, 1H), 7.82 (dd, *J* = 3.56, 0.84 Hz, 1H), 7.72 (dd, *J* = 4.98, 0.84 Hz, 1H), 7.58 - 7.51 (m, 2H), 7.24 - 7.18 (m, 3H) ppm; $^{13}$C NMR (75 MHz, DMSO - d) δ: 147.0, 133.7, 128.7, 128.2, 126.6, 122.2, 122.1, 118.6, 118.5, 111.1, 111.0 ppm; IR (KBr) ν: 2912.0, 1405.1, 1220.9, 741.6, 700.8 $cm^{-1}$; MS (EI) m/z 201 $[M+1]^{+}$.

*5-methyl-2-(thiophen-2-yl)-1H-benzo[d]imidazole (**3ah**)*:[16c] According to general procedure, **1t** (126 mg, 1 mmol) gave **3ah** (139 mg, 65%) as a white solid. $R_f$ = 0.3 (EtOAc/hexanes, 3:7); m.p. 225 - 227 ºC; $^{1}$H NMR (300 MHz, DMSO - d) δ: 12.79 (bs, 1H), 7.79 (d, *J* = 2.96 Hz, 1H), 7.69 (d, *J* = 4.90 Hz, 1H), 7.42 (d, *J* = 8.22 Hz, 1H), 7.32 (s, 1H), 7.22 - 7.20 (m, 2H), 7.00 (d, *J* = 8.05 Hz, 1H), 2.41 (s, 3H) ppm; $^{13}$C NMR (75 MHz, DMSO - d) δ: 146.6, 133.8, 131.6, 131.3, 128.3, 128.1, 126.3, 123.5, 21.2 ppm; IR (KBr) ν: 2937.1, 1420.2, 1218.4, 941.5, 767.8, 710.3 $cm^{-1}$; MS (EI) m/z 215 $[M+1]^{+}$.

*4-(1H-benzo[d]imidazol-2-yl)aniline (**3ai**)*:[16d] According to general procedure, **1u** (135 mg, 1 mmol) gave **3ai** (62 mg, 30%) as a pale yellow solid. $R_f$ = 0.2 ( EtOAc/hexane, 8:2); m.p. 245 - 248 ºC; $^{1}$H NMR (300 MHz, $CDCl_3$+DMSO) δ: 12.28 (bs, 1H), 7.93 (d, *J* = 70.0 Hz, 2H), 7.43 (s, 2H), 7.06 (s, 2H), 6.64 (s, 2H), 5.24 (s, 2H) $^{13}$C NMR (101 MHz, DMSO) δ 152.5, 150.6, 127.7, 121.2, 117.2, 113.5 ppm; MS (EI) m/z 210 $[M+1]^{+}$.

*4-(1H-benzo[d]imidazol-2-yl)phenol(**3aj**)*:[4b] According to general procedure, **1v** (136 mg, 1 mmol) gave **3aj** (73.5 mg, 35%) as a pale yellow solid. $R_f$ = 0.3 (EtOAc/hexane, 8:2); m.p. 243 - 245 ºC; $^1$H NMR (300 MHz, $CDCl_3$+DMSO) δ 12.63 (s, 1H), 9.94 (s, 1H), 8.00 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 32.7 Hz, 2H), 7.07 (d, *J* = 47.9 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$+DMSO) δ 159.0, 151.7, 127.9, 121.3, 121.0, 115.5 ppm; MS (EI) m/z 211 $[M+1]^+$.

*4-(1H-benzo[d]imidazol-2-yl)benzonitrile (**3ak**)*:[3c] According to general procedure, **1w** (145 mg, 1 mmol) gave **3ak** (110 mg, 50%) as a pale yellow solid. $R_f$ = 0.4 (EtOAc/hexane, 4:6); m.p. 247 - 249 ºC; 1H NMR (300 MHz, DMSO) δ 13.20 (s, 1H), 8.34 (d, *J* = 8.5 Hz, 1H), 8.03 (d, *J* = 8.5 Hz, 1H), 7.72 (d, *J* = 7.4 Hz, 1H), 7.58 (d, *J* = 7.2 Hz, 1H), 7.38 – 7.16 (m, 1H). 13C NMR (75 MHz, CDCl3+DMSO) δ 149.2, 134.1, 132.4, 126.8, 122.5, 118.2, 111.9 ppm; MS (EI) m/z 220 $[M+1]^+$.

*methyl 4-(1H-benzo[d]imidazol-2-yl)benzoate (**3al**)*:[17a] According to general procedure, **1x** (178 mg, 1 mmol) gave **3al** (113 mg, 45%) as a pale yellow solid. $R_f$ = 0.4 (EtOAc/hexane, 3:7); m.p. 201 - 203 ºC; $^1$H NMR (500 MHz, DMSO) δ 13.13 (s, 1H), 8.32 (d, *J* = 8.4 Hz, 2H), 8.11 (t, *J* = 12.7 Hz, 2H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.37 – 7.10 (m, 2H), 3.90 (s, 3H). $^{13}$C NMR (101 MHz, DMSO) δ 165.8, 149.9, 143.8, 135.1, 134.3, 130.3, 129.8, 126.6, 123.1, 122.0, 119.2, 111.6, 52.3 ppm; MS (EI) m/z 253 $[M+1]^+$.

*4-(1H-benzo[d]imidazol-2-yl)benzoic acid (**3am**)*:[17b]According to general procedure, **1y** (164 mg, 1 mmol) gave **3am** (60 mg, 25%) as a pale yellow solid. $R_f$ = 0.2 (EtOAc/hexane, 8:2); m.p.

297 - 299 ºC; $^{1}$H NMR (500 MHz, DMSO) δ 13.10 (s, 2H), 8.20 (d, *J* = 94.3 Hz, 4H), 7.63 (s, 2H), 7.24 (s, 2H). $^{13}$C NMR (101 MHz, DMSO) δ 166.8, 150.1, 133.9, 129.9, 126.4, 122.5 ppm; MS (EI) m/z 239 [M+1] $^{+}$.

*2-(3-bromophenyl)-5-methyl-1H-benzo[d]imidazole (**3an**):*[16c] According to general procedure, **4d** (212 mg, 1 mmol) gave **3ai** (177 mg, 62%) as a white solid. $R_f$ = 0.4 (EtOAc/hexane, 3:7); m.p. 201 - 203 ºC; $^{1}$H NMR (300 MHz, DMSO - d) δ: 13.1(bs, 1H), 8.98 (s, 1H), 8.58 (d, *J* = 7.88 Hz, 1H), 8.30 (dd, *J* = 8.22, 1.56 Hz, 1H), 7.83 (t, *J* = 8.04 Hz, 1H), 7.52 - 7.42 (m, 2H), 7.07 (d, *J* = 7.98 Hz, 1H), 2.44 (s, 3H) ppm; $^{13}$C NMR (75 MHz, DMSO - d) δ: 148.6, 148.3, 132.2, 132.1, 132.0, 131.8, 130.5, 124.1, 123.9, 120.6, 21.3 ppm; IR (KBr) ν: 2969.2, 1522.9, 1418.0, 1347.2 ,772.2 cm$^{-1}$; MS (EI) m/z 287 [M+2] $^{+}$.

*2-(4-bromophenyl)-5-methyl-1H-benzo[d]imidazole (**3ao**):*[16c] According to general procedure, **4e** (212 mg, 1 mmol) gave **3j** (172 mg, 60%) as a white solid. $R_f$ = 0.4 (EtOAc/hexane, 3:7); m.p. 215 - 217 ºC; $^{1}$H NMR (300 MHz, DMSO - d) δ: 12.84 (d, *J* = 11.71 Hz, 1H), 8.08 (d, *J* = 8.53 Hz, 2H), 7.74 (d, *J* = 8.61 Hz, 2H), 7.54 - 7.31 (m, 2H), 7.03 (t, *J* = 8.77 Hz, 1H), 2.43 (s, 3H) ppm; $^{13}$C NMR (75 MHz, DMSO - d) δ: 149.6, 141.8, 135.2, 131.8, 128.1, 122.9, 118.5, 111.0, 110.9, 21.3 ppm; IR (KBr) ν: 2969.2, 1522.9, 1418.0, 1347.2 ,772.2 cm$^{-1}$; MS (EI) m/z 287 [M+2] $^{+}$.

*2-(4-Methoxy-phenyl)-pyrazine:*[12]

Column chromatography (flash silica gel, Hexane/EtOAc): $R_f$ = 0.40 (EtOAc/hexane, 3:7); yield 85 %; Colorless solid; $^{1}$H NMR (400 MHz, $CDCl_3$) δ = 9.30 (bs, 1H), 8.19 (d, *J* = 8.95 Hz, 2H), 8.14 - 8.09 (m, 2H), 7.79 - 7.70 (m, 2H), 7.04 (d, *J* = 8.86 Hz, 2H), 3.91 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) δ = 161.6, 151.6, 143.2, 142.5, 141.4, 130.3, 129.5, 129.4, 129.2, 129.1, 114.7, 55.6 ppm.

**ACKNOWLEDGEMENTS**

This work was supported by CSIR-ORIGIN (CSC0108), New Delhi. We are thankful to NMR, Mass divisions of CSIR-IICT, for providing the analytical facilities. O.R, A.U and A.S thank CSIR and UGC for the Ph.D. fellowships.

**Supporting Information Available**. $^{1}H$ & $^{13}C$ NMR spectra of all compounds. This material is available free of charge *via* the Internet at http://pubs.acs.org

**References and Notes**:

1. (a) Yadav, G.; Ganguly, S. *Eur. J. Med. Chem*. **2015**, *97*, 419-443. (b) Bansal, Y.; Silakari, O. *Bioorg. Med. Chem*. **2012**, *20*, 6208-6236. (c) Carvalho, L. C.; Fernandes, E.; Marques, M. M. B. *Chem. Eur. J*. **2011**, *17*, 12544-12555. (d) Min, J.; Won, J.; Kang, Y. S.; Nagase, S. *J. Photochem. Photobiol. A: Chem*. **2011**, *219*, 148–153. (e) O'Hagan, D. *J. Fluorine Chem*. **2010**, *131*, 1071-1081. (f) Wang, T.; Zhao, Z.; Wei, B.; Zhang, L.; Ji, L. *J. Mol. Struct*. **2010**, *970*, 128-133.

2. (a) Wen, X.; El Bakali, J.; Deprez-Poulain, R.; Deprez, B. *Tetrahedron Lett*. **2012**, *53*, 2440-2443. (b) Hein, D.; Alheim, R. J.; Leavitt, J. *J. Am. Chem. Soc*. **1957**, *79*, 427-429. (c) Phillips, M. *A. J. Chem. Soc*. **1928**, 2393-2399. (d) Rambabu, D.; Murthi, P. R. K.; Dulla, B.; Basaveswara Rao, M.; Pal, M. *Synth. Commun*. **2013**, *43*, 3083-3092.

3. (a) Tandon, V. K.; Kumar, M. *Tetrahedron Lett*. **2004**, *45*, 4185-4187. (b) Bommegowda, Y. K.; Lingaraju, G. S.; Thamas, S.; Kumar, K. S. V.; Kumara, C. S. P.; Rangappa, K. S.; Sadashiva, M. P. *Tetrahedron Lett*. **2013**, *54*, 2693-2695. (c) Pinder, J. L.; Davis, R. E.; Charrier, J.-D. *Tetrahedron Lett*. **2014**, *55*, 4853-4855. (d) Dubois, N.; Glynn, D.; McInally, T.; Rhodes, B.; Woodward, S.; Irvine, D. J.; Dodds, C. *Tetrahedron*. **2013**, *69*, 9890-9897.

4. (a) Kawashita, Y.; Nakamichi, N.; Kawabata, H.; Hayashi, M. *Org. Lett*. **2003**, *5*, 3713-3715. (b) Bahrami, K.; Khodaei, M. M.; Nejati, A. *Green Chem*. **2010**, *12*, 1237-1241. (c) Gadekar, L. S.; Arbad, B. R.; Lande, M. K. *Chin.Chem. Lett*. **2010**, *21*, 1053-1056. (d) Mukhopadhyay, C.; Tapaswi, P. K. *Catal. Commun*. **2008**, *9*, 2392-2394. (e) Bahrami, K.; Khodaei, M. M.; Naali, F. *J. Org. Chem*. **2008**, *73*, 6835-6837. (f) Zhang, C.; Zhang, L.; Jiao, N. *Green Chem*. **2012**, *14*, 3273-3276. (g) Tumelty, D.; Cao, K.; Holmes, C. P. *Org. Lett*. **2001**, *3*, 83-86. (h) Wu, Z.; Rea, P.; Wickham, G. *Tetrahedron Lett*. **2000**, *41*, 9871-9874.

5. (a) Xu, C.; Xiao, Z. Q.; Li, H. M.; Han, X.; Wang, Z. Q.; Fu, W. J.; Ji, B. M.; Hao, X. Q.; Song, M. P. Euro. *J. Org. Chem*. **2015**, *2015*, 7427-7432. (b) Shiraishi, Y.; Sugano, Y.; Tanaka, S.; Hirai, T. *Angew. Chem. Int. Ed*. **2010**, *49*, 1656-1660. (c) Shi, X.; Guo, J.; Liu, J.; Ye, M.; Xu, Q. *Chem. Euro. J*. **2015**, *21*, 9988-9993. (d) Sun, Z.; Bottari, G.; Barta, K. *Green Chem*. **2015**, *17*, 5172-5181. (e) Blacker, A. J.; Farah, M. M.; Hall, M. I.; Marsden, S. P.; Saidi, O.; Williams, J. M. *Org. Lett*. **2009**, *11*, 2039-2042.

6. (a) Naresh, G.; Kant, R.; Narender, T. *J. Org. Chem*. **2014**, *79*, 3821-3829. (b) Nguyen, T. B.; Ermolenko, L.; Al-Mourabit, A. *Green Chem*. **2013**, *15*, 2713-2717. (c) Nguyen, T. B.; Ermolenko, L.; Dean, W. A.; Al-Mourabit, A. *Org. Lett*. **2012**, *14*, 5948-5951.

7. Nguyen, T. B.; Ermolenko, L.; Al-Mourabit, A. *J. Am. Chem. Soc*. **2012**, *135*, 118-121.

8. (a) Wang, Z. X.; Qin, H. L. *J. heterocycl.chem*. **2005**, *42*, 1001-1005. (b) Mayo, M. S.; Yu, X.; Zhou, X.; Feng, X.; Yamamoto, Y.; Bao, M. *Org.Lett*. **2014**, *16*, 764-767.

9. (a) Kano, S.; Yuasa, Y.; Ono, T.; Shibuya, S. *Heterocycles*. **1979**, 10. (b) Kamila, S.; Koh, B.; Biehl, E. R. *J. heterocycl.chem*. **2006**, *43*, 1609-1612.

10. (a) Khalid, B.; Mohamed, S. *Tetrahedron Lett*. **1995**, *36*, 3683-3686. (b) Li, Z.; Dong, J.; Chen, X.; Li, Q.; Zhou, Y.; Yin, S.-F. *J. Org. Chem*. **2015**, *80*, 9392-9400.

11. (a) Sathyanarayana, P.; Upare, A.; Ravi, O.; Muktapuram, P. R.; Bathula, S. R. *RSC Adv*. **2016**, *6*, 22749-22753. (b) Sathyanarayana, P.; Ravi, O.; Muktapuram, P. R.; Bathula, S. R. *Org. Biomol. Chem*. **2015**, *13*, 9681-9685.

12. Viswanadham, K. D. R.; Reddy, M. P.; Sathyanarayana, P.; Ravi, O.; Kant, R.; Bathula, S. R. *Chem. Comm*. **2014**, *50*, 13517-13520.

13. Mohammed , S.; Vishwakarma, R. A.; Bharate, S. B. *J. Org. Chem*. **2015**, *80*, 6915-6921.

14. (a) Mahesh, D.; Sadhu, P.; Punniyamurthy, T. *J. org. chem* .**2015**, *80*, 1644-1650. (b) Sharghi, H.; Beyzavi, M. H.; Doroodmand, M. M. *Eur. J. org. chem*. **2008**, *2008*, 4126-4138. (c) Düfert, M. A.; Billingsley, K. L.; Buchwald, S. L. *J. Am. Chem. Soc*. **2013**, *135*, 12877 - 2885. (d) Maiti, D. K.; Halder, S.; Pandit, P.; Chatterjee, N.; De Joarder, D.; Pramanik, N.; Saima, Y.; Patra, A.; Maiti, P. K. *J. org. chem*. **2009**, *74*, 8086-8097.

15. (a) Brasche, G.; Buchwald, S. L. *Angew. Chem. Int. Ed*. **2008**, *120*, 1958-1960. (b) Navarrete-Vázquez, G.; Moreno-Diaz, H.; Estrada-Soto, S.; Torres-Piedra, M.; León-Rivera, I.; Tlahuext, H.; Muñoz-Muñiz, O. Torres-Gómez, H. *Synth. Commun*. **2007**, *37*, 2815-2825. (c) Das, B.; Holla, H.; Srinivas, Y.*Tetrahedron Lett*. **2007**, *48*, 61-64. (d) Yu, J.; Xia, Y.; Lu, M. *Synth. Commun*. **2014**, *44*, 3019-3026.

16. (a) Khan, A. T.; Parvin, T.; Choudhury, L. H. *Synth. Commun*. **2009**, *39*, 2339-2346. (b) Park, S. Jung, J.; Cho, E. J. *Eur. J. org. chem*. **2014**, *2014*, 4148-4154. (c) Lin, S.; Yang, L. *Tetrahedron Lett*. **2005**, *46*, 4315-4319. (d) raju, D.; Mukherjee, N.; Ahmmed, S.; Ranu, B. C. *Chem. Comm*. **2012**, *48*, 7982–7984.

17. (a) Lee, Y. S.; Cho, Y. H.; Lee, S.; Bin, J. K.; Yang, J.; Chae, G.; Cheon,C. H. *Tetrahedron*. **2015,** *71***,** 532-538. (b) Digwal, C. S.; Yadav, U.; Sakla, A. P.; Ramya, P. V. S.: Aaghaz, S.; Kamal, A. A. *Tetrahedron Lett.* **2016,** *57*, 4012–4016.