HETEROCYCLES, Vol. 89, No. 12, 2014, pp. 2777- 2785. © 2014 The Japan Institute of Heterocyclic Chemistry
Received, 17th October, 2014, Accepted, 3rd December, 2014, Published online, 12th December, 2014
DOI: 10.3987/COM-14-13110

ONE-POT SYNTHESIS OF NEW BENZOIMIDAZOLINE DERIVATIVES PROMOTED BY POTASSIUM CARBONATE

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Abstract – An efficient method for synthesis of new benzoimidazoline derivatives has been accomplished via a one-pot reaction of aromatic aldehyde, *o*-phenylenediamine / 4-Cl-*o*-phenylenediamine and acetic anhydride promoted by K_2CO_3. In this method, although aryl substituted aldehydes with electron-releasing substituents did not work in the reaction, a series of aryl substituted aldehydes carrying electron-withdrawing substituents gave the corresponding benzoimidazoline derivatives with good yields of 62 % - 93 %.

Benzimidazoles possess various bioactivities, such as anti-HIV-I,[1] antibacterial,[2] antiproliferation,[3] glucokinase activator[4] and so on. Meanwhile, as excellent moleculars for transfering intramolecular proton, benzimidazoles are widely used in molecular / ion recognition,[5] photoelectric material[6] and metal organic catalysts,[7] etc. There is currently considerable interest given to benzimidazole derivatives due to their broad-spectrum activities, such molecules have important significance in the application of optoelectronic devices.

During the past decades, numerous imidazole derivatives have been synthesized.[8-10] However, to the best of our knowledge, there are less reports on one pot synthesis of *N*,*N*-bisubstituted benzoimidazoline derivatives. Herein, we report a new simple protocol for an environment-friendly and convenient synthesis of new benzoimidazoline derivatives in good yields through a one-pot three component condensation reaction of aromatic aldehyde with *o*-phenylenediamine / 4-Cl-*o*-phenylenediamine and acetic anhydride.

Initially, we studied the tandem condensation of 2-chlorobenzaldehyde, *o*-phenylenediamine and acetic anhydride in one pot under refluxing in the presence of K_2CO_3, the first derivative of benzoimidazoline

(1,1'-(2-(4-chlorophenyl)-1*H*-benzo[*d*]imidazole-1,3(2*H*)-diyl)diethanone, compound **1a** was obtained from the reaction with good yield. Then we were surprised to find that this compound emits a beautiful blue light under UV irradiation when dissolved in ethyl acetate. This greatly aroused the interest of our study, then we expand its range of substrates to the reaction, some good results were achieved.

To optimize the conditions, 2-chlorobenzaldehyde, *o*-diaminobenzene and acetic anhydride were selected as the model substrates to give compound **1a**. Several promoters were screened, and K_2CO_3 was relatively efficient with 72% yield of **1a** (Table 1, Entry 1). In the reaction, acetic anhydride is not only a substrate but also a solvent, so the amount of acetic anhydride was screened too. As can be seen from Table 1, when the amount of acetic anhydride was 8 mL, the yield of the reaction was the best. Then the amount of the promoter was evaluated and 80% mol K_2CO_3 showed the best effect (Table 1, Entry 13). Finally we found the reaction was the most efficient when conducted with 80% mol K_2CO_3 in the presence of 8 mL acetic anhydride.

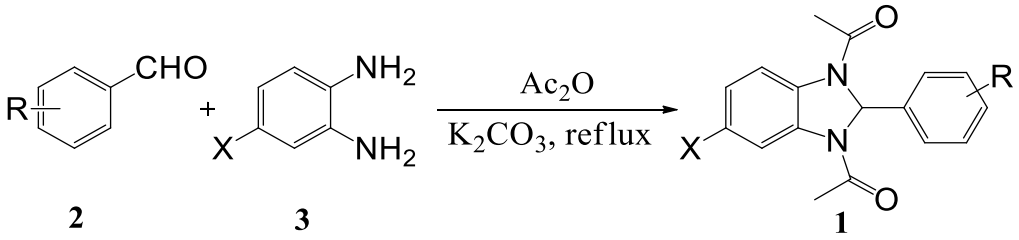
Table 1. Optimization of reaction conditions[a]

Entry	Promoter	Amount of the promoter (% mol)	Amount of acetic anhydride (ml)	Yield (%)
1	K_2CO_3	100	6	72
2	Na_2CO_3	100	6	53
3	$KHCO_3$	100	6	35
4	$NaHCO_3$	100	6	31
5	KOAc	100	6	60
6	NaOAc	100	6	56
7	K_2CO_3	100	4	23
8	K_2CO_3	100	8	73
9	K_2CO_3	100	10	75
10	K_2CO_3	100	12	57
11	K_2CO_3	40	8	45
12	K_2CO_3	60	8	58
13	K_2CO_3	80	8	86
14	K_2CO_3	120	8	61

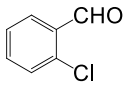
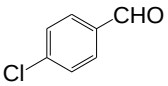
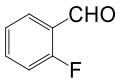
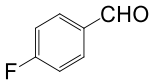
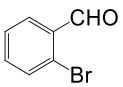
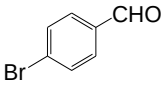
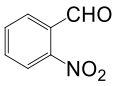
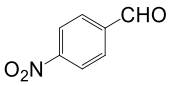
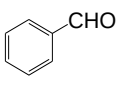
[a] Reaction condition: 2-chlorobenzaldehyde 0.7 g (5 mmol), *o*-diaminobenzene 0.54 g (5 mmol).

With the optimized condition in hand, the scope and limitations of this reaction were examined. We extended the procedure to various aryl substituted aldehydes carrying either electron-releasing or electron-withdrawing substituents in the ortho and para positions. Furthermore, 4-Cl-*o*-phenylenediamine was examed. Overall the results showed that aryl substituted aldehydes with electron-withdrawing substituents such as 2-chloro, 4-chloro, 2-bromo, 4-bromo and even 4-nitro substituent worked well (Table 2, Entry 1-16), benzaldehyde gave 1q or 1r with a relatively low yield (Table 2, Entry 17, 18), whereas aryl substituted aldehydes carrying electron-releasing substituents such as 2-methyl, 4-methyl, 2-amino or 4-(dimethylamino) did not work. Compared with *o*-phenylenediamine, 4-Cl-*o*-phenylenediamine is known to be less active in the synthesis of 1,1'-(2-1*H*-benzo [*d*]imidazole-1, 3(2*H*)-diyl)diethanones.

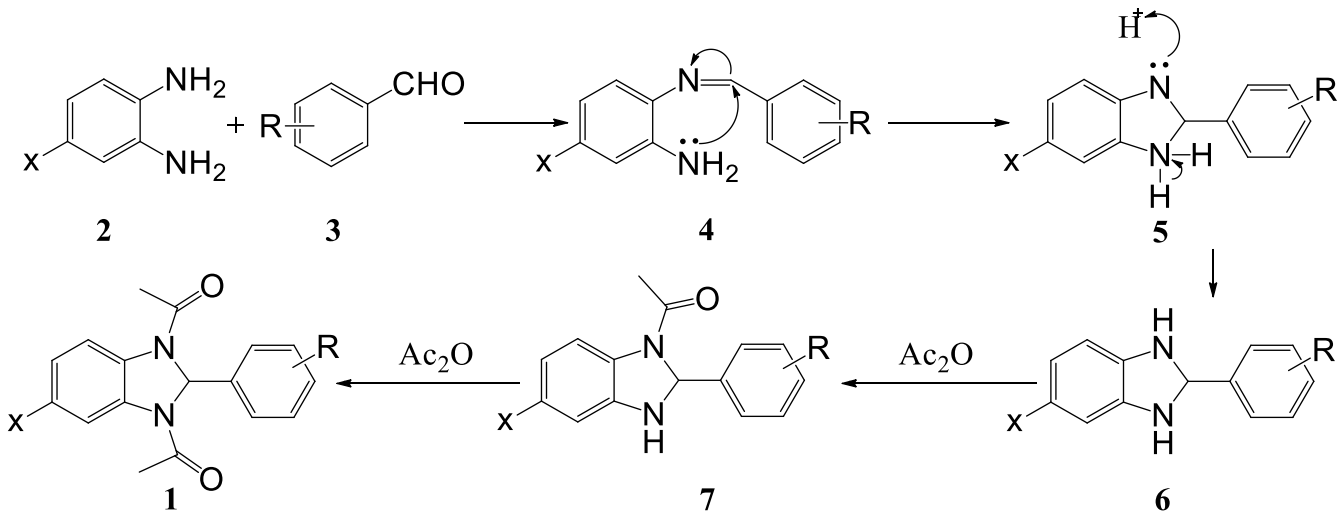
Table 2. Synthesis of 1,1'-(2-phenyl-1*H*-benzo[*d*]imidazole-1,3(2*H*)-diyl)diethanone derivatives (**1**)



2 **3** **1**

Entry	Substrate **2**	Substrate **3**	Product	Yield/%
1		**3a** (X=H)	**1a**	86
2		**3b** (X=Cl)	**1b**	78
3		**3a**	**1c**	93
4		**3b**	**1d**	76
5		**3a**	**1e**	81
6		**3b**	**1f**	80
7		**3a**	**1g**	85
8		**3b**	**1h**	73
9		**3a**	**1i**	79
10		**3b**	**1j**	67
11		**3a**	**1k**	82
12		**3b**	**1l**	77
13		**3a**	**1m**	68
14		**3b**	**1n**	62
15		**3a**	**1o**	70
16		**3b**	**1p**	66
17		**3a**	**1q**	58
18		**3b**	**1r**	51

The possible mechanism is proposed for the formation of 1,1'-(2-phenyl-1*H*-benzo[*d*]imidazole-1,3(2*H*)-diyl)diethanones (**1**) in Scheme 1. The reaction occurs via the initial formation of Schiff base **4** from the condensation of aryl substituted aldehyde (**3**) and *o*-phenylenediamine / 4-Cl-*o*-phenylenediamine (**2**), in which the electron rich nitrogen from amino approaches to the electron deficient carbon center. Intramolecular cyclization is facilitated to form the intermediate **5**. Subsequent transfer of hydrogen happens in **5** to give intermediate **6**. Finally, **1** is formed by acylation of **6** in two steps.



Scheme 1. Proposed reaction mechanism

In summary, a variety of 1,1'-(2-phenyl-1*H*-benzo[*d*]imidazole-1,3(2*H*)-diyl)diethanone derivatives were synthesized by condensation and acylation in a one-pot process. Aryl substituted aldehydes carrying electron-withdrawing substituents worked well to afford the new products. Further studies on the application of these products to the synthesis of fluorescent compounds are in progress.

EXPERIMENTAL

All reactions were monitored by thin-layer chromatography (TLC). The melting points were obtained on a Laboratory Devices X-4 melting apparatus and are uncorrected. The ^{1}HNMR spectra were determined in $CDCl_3$ using TMS as an internal reference with a BRUKER AVANCE AV-300 NMR spectrometer operating at 300 MHz. The ^{13}C NMR spectra were run in the same instrument at 75 MHz. high-resolution MS spectra (EI, 70 eV) were measured by a Finnigan-MAT4510 spectrometer. A crystal of compound **1a** with dimensions of 0.25 × 0.75 × 0.19 mm^3 was used on an Enraf Noius & Enraf Noius CAD4/PC, operating at 293±2 K. The structure was solved by direct methods with SHELXS-97 program and refined by full-matrix least-squares on F2 with SHELXL-97 program.

Starting Materials. All the chemicals used in this study were commercially available and were used without further purification.

General Procedure for the Preparation of 1,1'-(2-1*H*-benzo[*d*]imidazole-1,3(2*H*)-diyl) diethanones. Aromatic aldehyde (5 mmol), potassium carbonate (4 mmol), acetic anhydride (8 mL), *o*-diaminobenzene / 4-chloro-*o*-diaminobenzene (5 mmol) were added to a 50 mL round bottomed three neck bottle, The mixture was heated with stirring to reflux slowly for 2-5 h until the starting material disappeared (monitored by TLC with EtOAc/petroleum ether = 1 / 3), then it was cooled to room temperature, The crude product was washed by 20 mL water and then separated by column chromatography.

The crystal data of compound 1a.

The molecular structure of compound **1a** was confirmed by single-crystal X-ray diffraction, the crystal structure is showed in Figure 1. Selected bond lengths and bond angles are given in Table 3. X-Ray diffraction analysis of the crystal structure showed that **1a** crystallizes in monoclinic, space group *C*2/*c* with a = 25.341(5), b = 7.5290(15), c = 19.011(4) Å, β = 125.46(3)°, V = 2954.39(6314) Å^3 and Z = 8. In the crystal structure, the C(14)–O(1) and C(16)–O(2) in 1.216(3) and 1.218(3) Å are double bonds. The five-membered ring formed by atoms C(1), C(6), N(1), C(7), and N(2) is not coplanar and exhibits a torsional structure. The torsional angles are 4.8º (C(1)–C(6)–N(1)–C(7)), –10.2º (C(6)–N(1)–C(7)–N(2)), 12.3º (N(1)–C(7)–N(2)–C(1)), –10.1º (C(7)–N(2)–C(1)–C(6)) and 3.3º (N(2)–C(1)–C(6)–N(1)), respectively. The dihedral angle between the two phenyl rings is 85.0º. The structure of the molecule is stabilized by intramolecular C–H···O and C–H···Cl interactions.

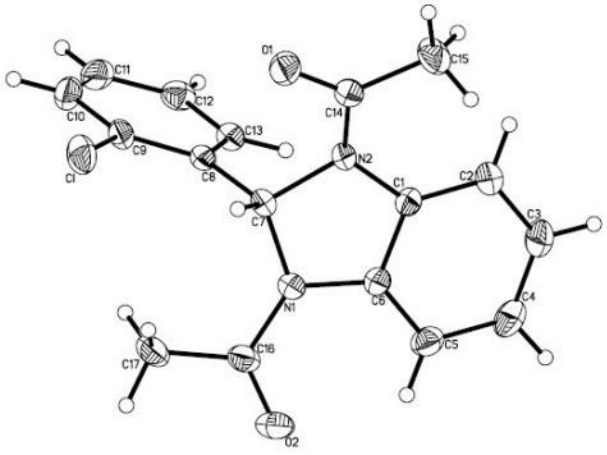


Figure 1. X-Ray single-crystal structure of compound **1a**

Table 3. Selected bond lengths (Å) and bond angles (°)

Bond	Dist.	Bond	Dist.
Cl–C(9)	1.743(2)	C(1)–C(2).	1.379(3)
O(1)–C(14)	1.216(3)	N(2)–C(14)	1.369(3)
N(1)–C(16)	1.375(3)	O(2)–C(16)	1.218(3)
C(2)－C(3)	1.385(3)	C(16)－ C(17)	1.496(3)
Angle	(°)	Angle	(°)
C(16)–N(1)–C(6)	124.47(18)	N(2)–C(7)–N(1)	101.98(15)
C(6)–N(1)–C(7)	109.41(16)	C(11)–C(10)–C(9)	119.5(2)
C(2)–C(1)–C(6)	120.3(2)	C(11)–C(12)–C(13)	119.6(2)
C(2)–C(1)–N(2)	131.3(2)	C(12)–C(13)–C(8)	121.5(2)
C(6)–C(1)–N(2)	108.38(17)	O(1)–C(14)–N(2)	119.6(2)
C(14)–N(2)–C(1)	130.52(17)	O(2)–C(16)–N(1)	120.8(2)
C(14)–N(2)–C(7)	117.68(17)	O(2)–C(16)–C(17)	122.0(2)

Spectroscopic data of 1,1'-(2-1*H*-benzo[*d*]imidazole-1,3(2*H*)-diyl)diethanones.

1,1'-(2-(2-Chlorophenyl)-1*H*-benzo[*d*]imidazole-1,3(2*H*)-diyl)diethanone (1a): Pale yellow solid. mp 177-179 °C. ^{1}H NMR δ: 2.17 (s, 3H, CH_3), 2.28 (s, 1H, CH), 2.42 (s, 3H, CH_3), 7.14-7.49 (m, 8H, Ph-H). ^{13}C NMR δ 23.67, 28.84, 73.07, 121.92, 123.65, 127.21, 127.75, 127.95, 128.63, 129.61, 129.86, 131.08, 131.85, 133.56, 138.62, 166.91 (2C). Anal. Calcd for $C_{17}H_{15}N_2O_2Cl$: C, 64.87; H, 4.80; N, 8.90. Found (%): C, 64.85; H, 4.78; N, 8.91. ESI-MS: $[M+H]^+$ peak at *m/z* 315.0944.

1,1'-(5-Chloro-2-(2-chlorophenyl)-1*H*-benzo[*d*]imidazole-1,3(2*H*)-diyl)diethanone (1b): Yellow solid. mp 196-197 °C. ^{1}H NMR δ: 2.18 (s, 3H, CH_3), 2.29 (s, 1H, CH), 2.45 (s, 3H, CH_3), 7.15-7.55 (m, 7H, Ph-H). ^{13}C NMR δ 23.66, 28.85, 73.05, 121.95, 123.55, 127.23, 127.78, 127.91, 128.64, 129.69, 131.57, 131.90, 133.35, 133.56, 138.62, 166.91 (2C). Anal. Calcd for $C_{17}H_{14}N_2O_2Cl_2$: C, 58.47; H, 4.04; N, 8.02. Found (%): C, 58.51; H, 4.06; N, 8.01. ESI-MS: $[M+H]^+$ peak at *m/z* 349.0437.

1,1'-(2-(4-Chlorophenyl)-1*H*-benzo[*d*]imidazole-1,3(2*H*)-diyl)diethanone (1c): Pale yellow solid. mp 168-169 °C. ^{1}H NMR δ: 2.17 (s, 3H, CH_3), 2.28 (s, 1H, CH), 2.39 (s, 3H, CH_3), 7.14-7.48 (m, 8H, Ph-H). ^{13}C NMR δ 23.69, 28.86, 74.07, 121.94, 123.60, 127.26, 127.76, 127.95, 128.62, 129.61 (2C), 131.05, 131.88, 133.54, 138.64, 166.90 (2C). Anal. Calcd for $C_{17}H_{15}N_2O_2Cl$: C, 64.87; H, 4.80; N, 8.90. Found (%): C, 64.86; H, 4.79; N, 8.90. ESI-MS: $[M+H]^+$ peak at *m/z* 315.0947.

1,1'-(5-Chloro-2-(4-chlorophenyl)-1*H*-benzo[*d*]imidazole-1,3(2*H*)-diyl)diethanone (1d): Yellow solid. mp 191-192 °C. ^{1}H NMR δ: 2.19 (s, 3H, CH_3), 2.28 (s, 1H, CH), 2.47 (s, 3H, CH_3), 7.15-7.56 (m, 7H, Ph-H). ^{13}C NMR δ 23.70, 28.83, 73.05, 121.96, 123.63, 127.29, 127.80, 127.96, 128.66, 129.65, 131.10 (2C), 133.57, 133.89, 138.69, 166.92 (2C). Anal. Calcd for $C_{17}H_{14}N_2O_2Cl_2$: C, 58.47; H, 4.04; N, 8.02. Found (%): C, 58.50; H, 4.10; N, 8.05. ESI-MS: $[M+H]^+$ peak at *m/z* 349.0428.

1,1'-(2-(2-Fluorophenyl)-1*H*-benzo[*d*]imidazole-1,3(2*H*)-diyl)diethanone (1e): White solid. mp 153-154 °C. ^{1}H NMR δ: 2.15 (s, 3H, CH_3), 2.24 (s, 1H, CH), 2.41 (s, 3H, CH_3), 7.11-7.43 (m, 8H, Ph-H). ^{13}C NMR δ 23.56, 28.67, 73.12, 121.87, 123.63, 127.16, 127.73, 127.98, 128.59, 129.63, 129.82, 131.10,

131.86, 132.51, 145.57, 166.86 (2C). Anal. Calcd for $C_{17}H_{15}FN_2O_2$: C, 68.45; H, 5.07; N, 9.39. Found (%): C, 68.41; H, 4.80; N, 8.87. ESI-MS: $[M+H]^+$ peak at *m/z* 299.1125.

1,1'-(5-Chloro-2-(2-fluorophenyl)-1*H*-benzo[*d*]imidazole-1,3(2*H*)-diyl)diethanone (1f): Pale yellow solid. mp 175-176 °C. ^{1}H NMR δ: 2.15 (s, 3H, CH_3), 2.31 (s, 1H, CH), 2.46 (s, 3H, CH_3), 7.16-7.52 (m, 7H, Ph-H). ^{13}C NMR δ 23.64, 28.83, 72.98, 121.92, 123.67, 127.37, 127.91, 127.98, 128.66, 129.75, 131.53, 131.96, 133.49, 133.68, 146.89, 166.95 (2C). Anal. Calcd for $C_{17}H_{14}N_2O_2FCl$: C, 61.36; H, 4.24; N, 8.42. Found (%): C, 61.32; H, 4.26; N, 8.38. ESI-MS: $[M+H]^+$ peak at *m/z* 333.0736.

1,1'-(2-(4-Fluorophenyl)-1*H*-benzo[*d*]imidazole-1,3(2*H*)-diyl)diethanone (1g): White solid. mp 142-143 °C. ^{1}H NMR δ: 2.10 (s, 3H, CH_3), 2.29 (s, 1H, CH), 2.37 (s, 3H, CH_3), 7.14-7.49 (m, 8H, Ph-H). ^{13}C NMR δ 23.65, 28.84, 74.15, 121.92, 123.69, 127.23, 127.74, 127.97, 128.66, 129.53 (2C), 131.09, 131.83, 132.54, 136.47, 166.76 (2C). Anal. Calcd for $C_{17}H_{15}FN_2O_2$: C, 68.45; H, 5.07; N, 9.39. Found (%): C, 68.40; H, 4.81; N, 8.85. ESI-MS: $[M+H]^+$ peak at *m/z* 299.1125.

1,1'-(5-Chloro-2-(4-fluorophenyl)-1*H*-benzo[*d*]imidazole-1,3(2*H*)-diyl)diethanone (1h): Pale yellow solid. mp 169-170 °C. ^{1}H NMR δ: 2.16 (s, 3H, CH_3), 2.30 (s, 1H, CH), 2.43 (s, 3H, CH_3), 7.15-7.50 (m, 7H, Ph-H). ^{13}C NMR δ 23.71, 28.85, 73.09, 121.99, 123.65, 127.27, 127.85, 127.98, 128.73, 129.64, 130.95 (2C), 133.51, 133.86, 138.48, 166.95 (2C). Anal. Calcd for $C_{17}H_{14}N_2O_2FCl$: C, 61.36; H, 4.24; N, 8.42. Found (%): C, 61.30; H, 4.26; N, 8.39. ESI-MS: $[M+H]^+$ peak at *m/z* 333.0742.

1,1'-(2-(2-Bromophenyl)-1*H*-benzo[*d*]imidazole-1,3(2*H*)-diyl)diethanone (1i): Brown yellow solid. mp 189-190 °C. ^{1}H NMR δ: 2.19 (s, 3H, CH_3), 2.30 (s, 1H, CH), 2.47 (s, 3H, CH_3), 7.15-7.53 (m, 8H, Ph-H). ^{13}C NMR δ 23.75, 28.89, 73.15, 121.96, 122.29, 123.63, 127.12, 127.68, 127.87, 129.17, 129.56, 131.13, 131.25, 133.37, 135.43, 166.89 (2C). Anal. Calcd for $C_{17}H_{15}N_2O_2Br$: C, 56.84; H, 4.21; N, 7.80. Found (%): C, 56.82; H, 4.22; N, 7.81. ESI-MS: $[M+H]^+$ peak at *m/z* 359.0323.

1,1'-(5-Chloro-2-(2-bromophenyl)-1*H*-benzo[*d*]imidazole-1,3(2*H*)-diyl)diethanone (1j): Brown yellow solid. mp 202-203 °C. ^{1}H NMR δ: 2.17 (s, 3H, CH_3), 2.33 (s, 1H, CH), 2.49 (s, 3H, CH_3), 7.11-7.53 (m, 7H, Ph-H). ^{13}C NMR δ 23.71, 28.88, 73.12, 121.97, 122.25, 123.67, 127.15, 127.73, 127.84, 129.19, 129.54, 131.15, 131.29, 133.24, 135.35, 166.81 (2C). Anal. Calcd for $C_{17}H_{14}N_2O_2ClBr$: C, 51.87; H, 3.58; N, 7.12. Found (%): C, 51.89; H, 3.60; N, 7.09. ESI-MS: $[M+H]^+$ peak at *m/z* 392.9930.

1,1'-(2-(4-Bromophenyl)-1*H*-benzo[*d*]imidazole-1,3(2*H*)-diyl)diethanone (1k): Brown yellow solid. mp 181-182 °C. ^{1}H NMR δ: 2.16 (s, 3H, CH_3), 2.28 (s, 1H, CH), 2.41 (s, 3H, CH_3), 7.12-7.43 (m, 8H, Ph-H). ^{13}C NMR δ 23.67, 28.86, 74.07, 121.94, 122.15, 123.65, 127.18, 127.54, 128.60, 129.57 (2C), 131.09, 131.68, 133.53, 135.62, 166.47 (2C). Anal. Calcd for $C_{17}H_{15}N_2O_2Br$: C, 56.84; H, 4.21; N, 7.80. Found (%): C, 56.85; H, 4.20; N, 7.79. ESI-MS: $[M+H]^+$ peak at *m/z* 359.0320.

1,1'-(5-Chloro-2-(4-bromophenyl)-1*H*-benzo[*d*]imidazole-1,3(2*H*)-diyl)diethanone (1l): Brown yellow solid. mp 190-191 °C. ^{1}H NMR δ: 2.20 (s, 3H, CH_3), 2.25 (s, 1H, CH), 2.49 (s, 3H, CH_3),

7.19-7.50(m, 7H, Ph-H). ^{13}C NMR δ 23.65, 28.83, 73.75, 121.52, 123.18, 127.13, 127.72, 127.95, 128.53, 129.82, 130.23 (2C), 133.25, 133.36, 136.63, 166.91 (2C). Anal. Calcd for $C_{17}H_{14}N_2O_2ClBr$: C, 51.87; H, 3.58; N, 7.12. Found (%): C, 51.90; H, 3.59; N, 7.11. ESI-MS: $[M+H]^+$ peak at *m/z* 392.9932.

1,1'-(2-(2-Nitrophenyl)-1*H*-benzo[*d*]imidazole-1,3(2*H*)-diyl)diethanone (1m): Yellow solid. mp 152-153 °C. ^{1}H NMR δ: 2.12 (s, 3H, CH_3), 2.43 (s, 3H, CH_3), 4.63 (s, 1H, CH), 7.19 (s, 2H), 7.30 (s, 1H), 7.47 (s, 1H), 7.55 (s, 1H), 7.65 (s, 1H), 8.15 (s, 1H), 8.26 (s, 1H). ^{13}C NMR δ 23.79, 28.85, 73.23, 121.99, 122.27, 123.65, 127.14, 127.63, 127.86, 129.16, 129.58, 131.24, 131.33, 143.36, 146.95, 166.96 (2C). Anal. Calcd for $C_{17}H_{15}N_3O_4$: C, 62.76; H, 4.65; N, 12.92. Found (%): C, 62.69; H, 4.71; N, 12.94. ESI-MS: $[M+H]^+$ peak at *m/z* 326.1057.

1,1'-(5-Chloro-2-(2-nitrophenyl)-1*H*-benzo[*d*]imidazole-1,3(2*H*)-diyl)diethanone (1n): Yellow solid. mp 164-166 °C. ^{1}H NMR δ: 2.14 (s, 3H, CH_3), 2.47 (s, 3H, CH_3), 4.60 (s, 1H, CH), 7.16 (s, 1H), 7.28 (s, 1H), 7.33 (s, 1H), 7.59 (s, 1H), 7.68 (s, 1H), 8.16 (s, 1H), 8.25 (s, 1H). ^{13}C NMR δ 23.76, 28.85, 73.18, 121.95, 122.29, 123.73, 127.17, 127.78, 127.86, 129.16, 129.53, 131.12, 131.27, 133.30, 135.37, 166.85 (2C). Anal. Calcd for $C_{17}H_{14}N_3O_4Cl$: C, 51.87; H, 3.58; N, 7.12. Found (%): C, 51.85; H, 3.53; N, 7.10. ESI-MS: $[M+H]^+$ peak at *m/z* 360.0685.

1,1'-(2-(4-Nitrophenyl)-1*H*-benzo[*d*]imidazole-1,3(2*H*)-diyl)diethanone (1o): Yellow solid. mp 141-142 °C. ^{1}H NMR δ: 2.09 (s, 3H, CH_3), 2.41 (s, 3H, CH_3), 4.60 (s, 1H, CH), 7.17 (s, 2H), 7.31 (s, 1H), 7.63 (s, 2H), 8.18 (s, 2H), 8.28 (s, 1H). ^{13}C NMR δ 23.07, 27.98, 74.79, 121.58, 122.26, 123.72, 123.95, 126.50, 127.31, 127.53 (2C), 131.25, 131.57, 145.35, 149.60, 166.74 (2C). Anal. Calcd for $C_{17}H_{15}N_3O_4$: C, 62.76; H, 4.65; N, 12.92. Found (%): C, 62.70; H, 4.69; N, 12.91. ESI-MS: $[M+H]^+$ peak at *m/z* 326.1071.

1,1'-(5-Chloro-2-(4-nitrophenyl)-1*H*-benzo[*d*]imidazole-1,3(2*H*)-diyl)diethanone (1p): Yellow solid. mp 147-148 °C. ^{1}H NMR δ: 2.11 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 4.63 (s, 1H, CH), 7.26 (s, 1H), 7.51 (s, 1H), 7.53 (s, 1H), 8.19 (s, 2H), 8.27 (s, 1H). ^{13}C NMR δ 23.14, 27.95, 74.73, 121.89, 122.35, 123.96, 126.57, 127.37, 127.78 (2C), 131.16, 131.69, 135.81, 145.52, 149.77, 166.81 (2C). Anal. Calcd for $C_{17}H_{14}N_3O_4Cl$: C, 56.75; H, 3.92; N, 11.68. Found (%): C, 56.71; H, 3.97; N, 11.65. ESI-MS: $[M+H]^+$ peak at *m/z* 360.0661.

1,1'-(2-Phenyl-1*H*-benzo[*d*]imidazole-1,3(2*H*)-diyl)diethanone (1q): Pale yellow oil. ^{1}H NMR δ 2.16 (s, 3H), 2.32 (s, 1H, CH), 2.49 (s, 3H), 7.15-7.49 (m, 9H). ^{13}C NMR δ 23.09 (2C), 79.69, 124.28 (2C), 125.53 (2C), 126.12, 126.30 (2C), 128.67 (2C), 135.37 (2C), 142.55, 166.76 (2C). Anal. Calcd for $C_{17}H_{16}N_2O_2$: C, 72.84; H, 5.75; N, 9.99. Found (%): C, 72.88; H, 5.76; N, 9.95. ESI-MS: $[M+H]^+$ peak at *m/z* 281.1239.

1,1'-(5-Chloro-2-phenyl-1*H*-benzo[*d*]imidazole-1,3(2*H*)-diyl)diethanone (1r): Pale yellow oil. ^{1}H NMR δ 2.15 (s, 3H), 2.35 (s, 1H, CH), 2.52 (s, 3H), 7.16-7.47(m, 8H). ^{13}C NMR δ 23.10 (2C), 79.47,

115.24, 116.83, 124.26, 125.91 (2C), 126.20, 126.33(2C), 127.72, 135.36, 137.58, 143.56, 166.83 (2C). Anal. Calcd for $C_{17}H_{15}N_2O_2Cl$: C, 64.87; H, 4.80; N, 8.90. Found (%): C, 64.63; H, 4.77; N, 8.91. ESI-MS: $[M+H]^+$ peak at *m/z* 315.0826.

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