CHAPTER 3

Developing a Sustainable Metal and Catalyst Free Chemoselective Synthesis of Benzimidazole and Benzothiazole under Controlled Reaction Conditions via Solid-State Oxidative Cyclization

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3.1 Introduction

Nitrogen and sulphur containing heterocycles such as benzimidazole, benzothiazole and there derivatives occupy an important place in both medicinal and industrial chemistry for human welfare (Kanwal et al. 2019, Prajapati et al. 2014). These compounds play an important role in the metabolism of all living cells. Benzimidazole and benzothiazole derivatives exhibit numerous significant in biological activities such as antiallergic (Nakano et al. 2000), anticancer (Azam et al. 2015), antimicrobial (Pawar et al. 2004), antiulcer (Patil et al. 2008), antifungal (Shi et al. 2019), antihistaminic (Mavrova et al. 2007), antiviral (Budow et al. 2009), anti-inflammatory (Lazer et al. 1987), antihypertensive (Kubo et al. 1993), antidiabetic (Vinodkumar et al. 2008), anti HIV (Roth et al. 1997), antiprotozoal (Navarrete-Vázquez et al. 2001), anti-hepatitis B virus (Li et al. 2006), anti-tumor (Denny et al. 1990), anti-oxidant (Kus et al. 2004) and antitrichinellosis activity (Mavrova et al. 2010) (**Figure 3.1**). Moreover, these derivatives have remarkable applications in material science, polymer and dye synthesis (Berrada et al. 2002) and also found pervasive application in fluorescence (Shao et al. 2009), chemosensing (Singh et al. 2007), crystal engineering (Li et al. 2007) and corrosion science (Roque et al. 2008).

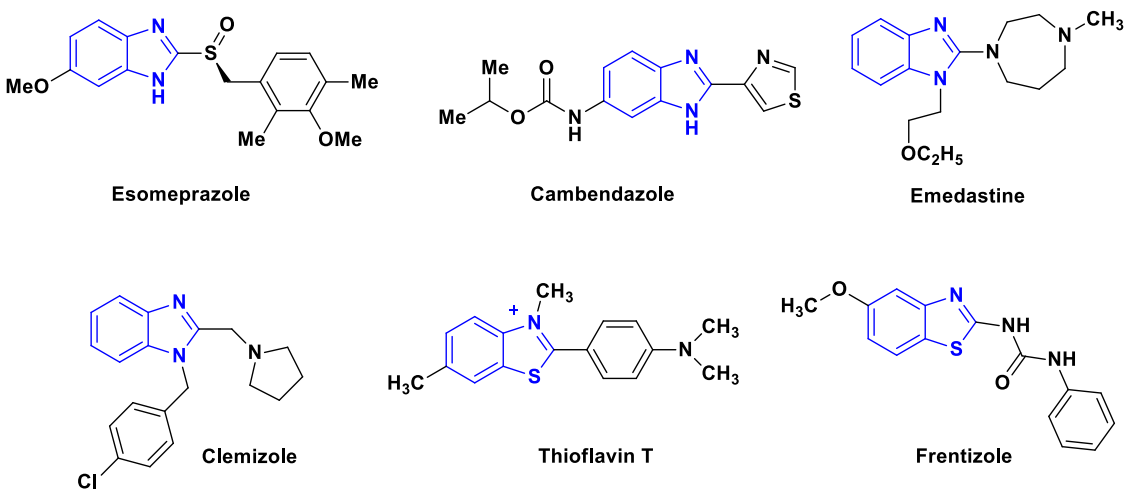


Figure 3.1 Some pharmacologically active benzimidazole and benzothiazole compounds

Several distinctive synthetic methods have been reported for achieving benzimidazoles and benzothiazoles due to their wide range of applications in organic chemistry as intermediates and ligands for the asymmetric catalysis. Traditionally, these fused heterocycles have been synthesized by the condensation of aldehydes with *o*-phenylenediamine/ 2-aminothiophenol in the presence of different catalysts and oxidants like K-10 (Landge et al. 2008), I_2 (Aniket et al. 2015), glycerol (Radatz et al. 2011), PEG-400 (Mekala et al. 2015), lactic acid (Yu et al. 2016), glyoxylic acid (Pawar et al. 2008), thiamine hydrochloride (Lei et al. 2012), $FeCl_3$ (Liu et al. 2012), $FePO_4$ (Behbahani et al. 2012), SnP_2O_7 (Merroun et al. 2019), $NH_4Fe(SO_4)_2$ (Khazaei et al. 2016), $NiCl_2$ (Bera et al. 2019), P_2O_5/SiO_2 (Shaterian et al. 2011), Indion 190 Resin (Reddy et al. 2011), $NiFe_2O_4@SiO_2@$amino glucose (Fekri et al. 2018), nano In_2O_3 (Santra et al. 2012), Ir/TiO_2 (Fukutake et al. 2018), Zn-Proline (Ravi et al. 2007), ZnO (Sharma et al. 2015), Cu/Al_2O_3

(Pogula et al. 2017), $LnCl_3$ (Zhang et al. 2012), $SnCl_4$ (Mirjalili et al. 2019), $Er(OTf)_3$ (Cano et al. 2016), $MnO_2/ZrCl_4$ (Wang et al. 2014), UiO-66-$NHSO_3H$ (Homaee et al. 2019), laccase (Maphupha et al. 2018), SDS micelles (Bahrami et al. 2010), ZrO_2-b-cyclodextrin (Girish et al. 2015), Cu(I) glycosyltriazole (Mishra et al. 2019), TAP-Cu (Xu et al. 2017), silica@ytterbium (Samanta et al. 2018), chitosan@Fe_3O_4 (Maleki et al. 2014) and natural wool@Fe_2O_4 nanoparticles (Shaabani et al. 2017). Bose *et. al.*, have reported synthesis of 1,2-disubstituted benzimidazoles via an intramolecular C(sp3)–H imination with PhI– mCPBA (Bose et al. 2019) and Chopra *et. al.*, have reported visible light promoted synthesis of 2-substituted benzimidazole (Chopra et al. 2019). Recently the formation of 2-substituted, 1,2-disubstituted benzimidazoles from *o*-phenylenediamine and alcohol using manganese catalyst in strong basic medium have been reported by Srimani and coworkers (Das et al. 2018). Most of these existing methods require metal catalysts, bases, solvents, stoichiometric amount of oxidants, higher reaction temperature and longer reaction time etc. However green sustainable method for selective synthesis of 1,2-disubstituted benzimidazoles and 2-substituted benzimidazoles/ benzothiazoles is highly desirable.

UHP is a white crystalline solid, soluble in water, stable at room temperature and easy to handle. UHP is an important oxidizing reagent widely used in various organic transformations such as synthesis of amides by the hydrolysis of cyano group, epoxidation of double bond, thiols to disulfides, secondary alcohols to ketones, sulfides to sulfoxides

and sulfones, pyridine to pyridine-N-oxide. Dakin and Baeyer–Villiger oxidation reaction was also carried out in the presence of UHP as well as chemoselective ipso- hydroxylation of arylboronic acids (Laha et al. 2001, Varma et al. 1999, Marcantoni et al. 1995, Gupta et al. 2016).

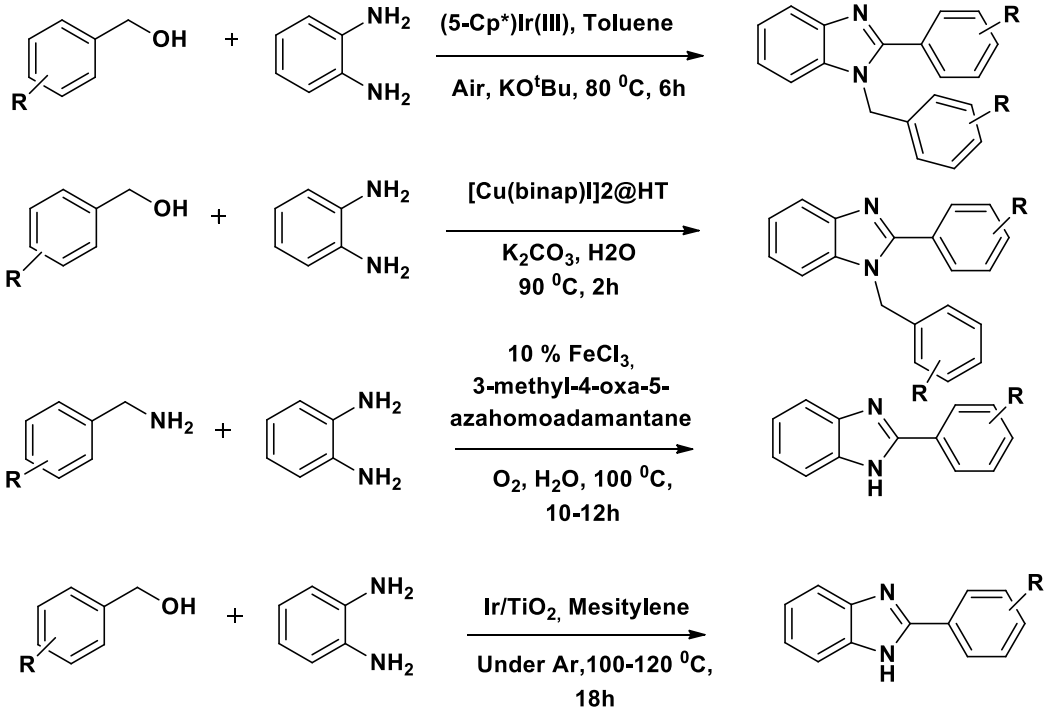
Green chemistry has become an important tool in the field of synthetic organic chemistry. In organic synthesis transition metal catalysts and volatile organic solvents are replaced by green catalysts and solvents like water, ionic liquids, bio-based green solvents (poly ethylene glycol and glycerol), supercritical carbon dioxide or reaction in solvent free condition (Singh et al. 2016, Datta et al. 2012, Mohira et al. 2019). Reactions in neat condition (i.e in solid state) are ideal because solvent free condition reduces environmental pollution and cost of the solvents. Alternative energy source for the chemical reactions is another concern of green chemistry, utilization of non-classical energy sources such as mechanochemical ball milling technique, ultrasound, microwave irradiation and UV light radiation in order to save energy and time. In grinding method reaction starts with the transfer of the very small amount of mechanical energy which is generated by grinding the reactants in a mortar and pestle in solvent free condition and leads to the formation of the product. Since it has several advantages in terms of environmental impact, effectiveness, requires no special apparatus, cost of solvents & energy sources and easiness of the reaction protocol (Hematinezhad et al. 2019, Zangade et al. 2019, Abdelrazek et al. 2019).

Methyl arenes are naturally available cheap and abundant starting materials used in the development of organic transformations. Fundamental challenges in the oxidation of

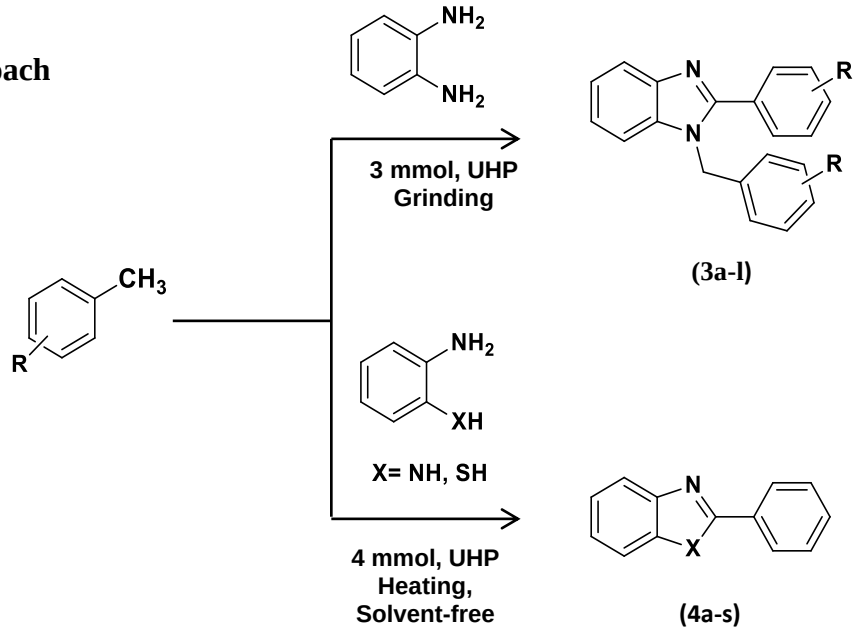
methyl arenes which involves C-H bond activation. Chemoselective oxidation of toluene under controlled reaction conditions is still challenging because different oxidized products are formed like benzyl alcohol, benzaldehyde and benzoic acid but under harsh reaction conditions it gave over oxidized product benzoic acid. These are very important starting material in synthetic organic chemistry and industrial point of view (Mahyari et al. 2014, Gaster et al. 2017, Shaabani et al. 2008).

In continuation of our efforts towards development of simple, eco-friendly reaction protocols for organic transformations (Verma et al. 2019, Chauhan et al. 2018), here we report a practical and sustainable protocol for the chemoselective synthesis of 1,2–disubstituted benzimidazoles, 2-substituted benzimidazoles/ benzothiazoles by urea hydrogen peroxide complex (UHP) initiated oxidative coupling of methyl arenes with *o*-phenylenediamine/ 2-aminothiophenol in one pot by varying reaction parameters. To the best of our knowledge synthesis of these fused heterocycles directly from methyl arenes and 1,2-diaminebenzene/ 2-aminothiphenol in the presence of UHP by oxidative coupling has not been reported. A comparison of the previous and present methodologies is illustrated in **Scheme 3.1**.

Previous approaches



Present approach



Scheme 3.1 An illustration of the previous and present reports for the synthesis of 1,2-disubstituted benzimidazole and 2- substituted benzimidazole/ benzothiazoles derivatives.

3.2 Results and discussion

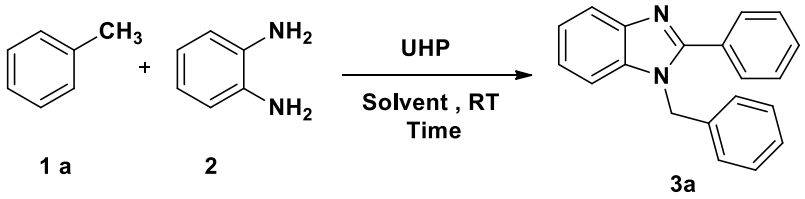
3.2.1 Optimization of Reaction Conditions

To optimize the reaction conditions for the synthesis of 1,2-disubstituted benzimidazoles and 2-substituted benzimidazoles a model reaction was carried out using toluene **1a** (2.0 mmol) and *o*-phenylenediamine **2** (1.0 mmol) in the presence of UHP (2.0 mmol). Various reaction parameters were optimized like solvent, amount of UHP, reaction temperature on the model reaction.

At the outset, the optimization experiments were carried out with the model reaction at room temperature by stirring in different polar and non-polar solvents and the progress of the reaction was monitored by TLC. Non-polar solvents (xylene, toluene) gave negligible amount of product even after 2h stirring at room temperature (**Table 3.1, entry 1 and 2**). However polar aprotic solvents like tetrahydrofuran, chloroform, acetonitrile and 1,4-dioxane gave the product (**3a**) but the yield was very low (15-20%) (**Table 3.1, entries 3-6**). However polar protic solvents like water, methanol and ethanol also gave desired product in better yield (30-40%) (**Table 3.1, entries 7-9**). In order to improve the yield of the product an attempt was made under grinding in solvent-free condition to our surprise it gave 70% yield of product in shorter reaction time 25 min (**Table 3.1, entry 10**). Furthermore, UHP loading was also investigated with 0, 3, 6, 8 mmol, without UHP no product was obtained, with 3 equiv. of UHP it gave 92 % yield (**Table 3.1, entries 11-15**) while further increasing the amount of the UHP did not increase the % yield of the product in all cases it gave exclusively 1,2-disubstituted benzimidazoles. In case of grinding at

room temperature the molar ratio of the reactants were also varied by taking 1 mmol of toluene and 1 or 2 mmoles of *o*-phenylenediamine with UHP gave only 1,2-disubstituted benzimidazole.

Table 3.1 Optimization of reaction conditions for the synthesis of 1,2-disubstituted benzimidazole[a]



S. No	Solvent[b]	UHP (mmol)	Reaction Condition at rt	Time (min)	Yield [%] [c]
1	Benzene	2	Stirring	120	10
2	Toluene	2	Stirring	120	10
3	THF	2	Stirring	120	15
4	$CHCl_3$	2	Stirring	120	20
5	CH_3CN	2	Stirring	120	15
6	1, 4 dioxin	2	Stirring	120	20
7	Water	2	Stirring	60	40
8	Methanol	2	Stirring	60	30
9	Ethanol	2	Stirring	60	40
10	Solvent-free	2	Grinding	25	70

11	Solvent-free	-	Grinding	25	NR
12	Solvent-free	3	Grinding	25	92
13	Solvent-free	6	Grinding	25	92
14	Solvent-free	8	Grinding	25	92
15	Solvent-free	3	Grinding	40	92

[a]**Reaction conditions:** Toluene **1a** (2.0 mmol), *o*-phenylenediamine **2** (1.0 mmol) and UHP at room temperature. [b] 2 mL solvent, [c] % isolated yield .

So the optimal conditions for chemoselective synthesis of 1,2-disubstituted benzimidazole are toluene (2.0 mmol), *o*-phenylenediamine (1.0 mmol) and UHP (3.0 mmol) under grinding at room temperature in solvent-free condition. The product (**3a**) was characterized by spectral data (IR, ^{1}H, ^{13}C NMR) and confirmed by comparing with the reported.

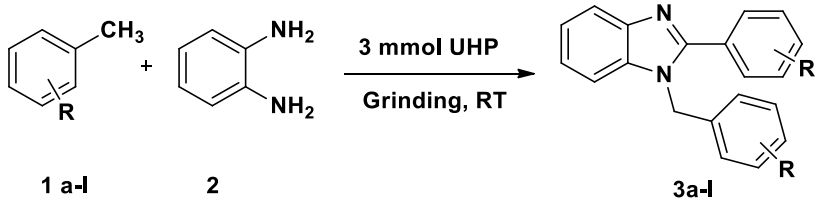
3.2.2 Substrates Scope for 1,2-disubstituted benzimidazoles

After finding the optimized reaction conditions (**Table 3.1, entry 12**), a variety of methyl arenes containing electron donating groups like 4- methoxy, 4-N,N- dimethyl, 3,4-dimethoxy, 2- hydroxyl as well as electron withdrawing groups such as 2-chloro, 3-chloro, 4-bromo and 4-flouro with *o*-phenylenediamine were used to explore the generality and substrate scope of this protocol. Toluene (**1a**), 1-methoxy-4-methylbenzene (**1b**), N,N,4-trimethylaniline (**1c**), 1,2-dimethoxy-4-methylbenzene (**1d**), *o*-cresol (**1e**), 1-chloro-3-methylbenzene (**1f**), 1-chloro-2-methylbenzene (**1g**), 1-bromo-4-methylbenzene (**1h**),

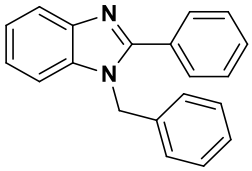
1-fluoro-4-methylbenzene (**1i**), 2-methylnaphthalene (**1j**), 2-methylfuran (**1k**), 2-methylpyridine (**1l**) with *o*-phenylenediamine (**2**) gave compound **(3**) viz. 1-benzyl-2-phenyl-1H-benzo[d]imidazole (**3a**), 1-(4-methoxybenzyl)-2-(4-methoxyphenyl)-1H-benzo[d]imidazole (**3b**), 4-(1-(4-(dimethylamino)benzyl)-1H-benzo[d]imidazol-2-yl)-N,N-dimethylaniline (**3c**), 1-(3,4-dimethoxybenzyl)-2-(3,4-dimethoxyphenyl)-1H-benzo[d]imidazole (**3d**), 2-(1-(2-hydroxybenzyl)-1H-benzo[d]imidazol-2-yl)phenol **(3e),** 1-(3-chlorobenzyl)-2-(3-chlorophenyl)-1H-benzo[d]imidazole **(3f),** 1-(2-chlorobenzyl)-2-(2-chlorophenyl)-1H-benzo[d]imidazole **(3g),** 1-(4-bromobenzyl)-2-(4-bromophenyl)-1H-benzo[d]imidazole **(3h)**, 1-(4-fluorobenzyl)-2-(4-fluorophenyl)-1H-benzo[d]imidazole **(3i)**, 2-(naphthalen-2-yl)-1-(naphthalen-2-ylmethyl)-1H-benzo[d]imidazole **(3j)**, 2-(furan-2-yl)-1-(furan-2-ylmethyl)-1H-benzo[d]imidazole (**3k**) and 2-(pyridin-2-yl)-1-(pyridin-2-ylmethyl)-1H-benzo[d]imidazole **(3l)** in good to excellent yield (86-94%) in shorter reaction time (20-30 min). The chemical structures of the synthesized compounds were established from their spectral data. The structure of the products along with their reaction time and yields are summarized in (**Table 3.2**).

To our delight the present method is compatible with a wide range of functional groups and the nature of the functional group does not affect the yield of the reaction. When *o*-aminothiophenol was treated with toluene under the same optimized condition no product, i.e. 1,2- benzothiazole was obtained while starting material was remained as such.

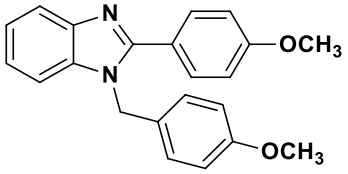
Table 3.2 Synthesis of 1,2-disubstituted benzoimidazoles (3a-l)



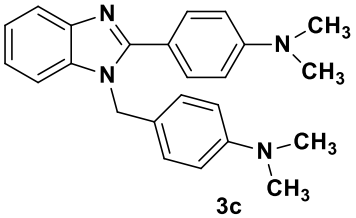
1 a-l 2 3a-l



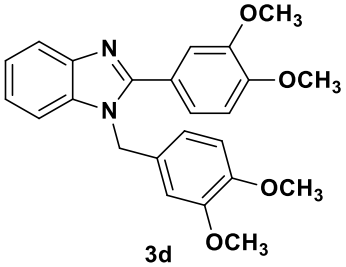
3a
(92%, 25 min)



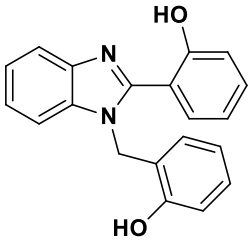
3b
(90%, 20 min)



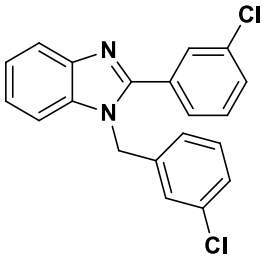
3c
(93%, 20 min)



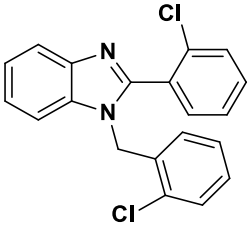
3d
(94%, 25 min)



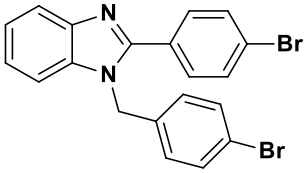
3e
(89%, 20 min)



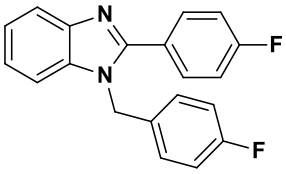
3f
(87%, 20 min)



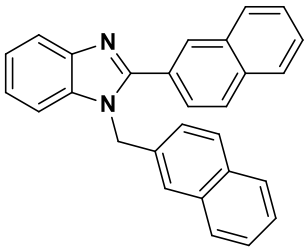
3g
(88%, 22 min)



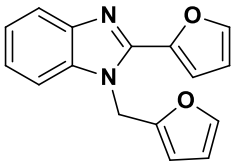
3h
(86%, 20 min)



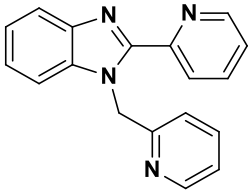
3i
(88%, 20 min)



3j
(91%, 25 min)



3k
(89%, 30 min)



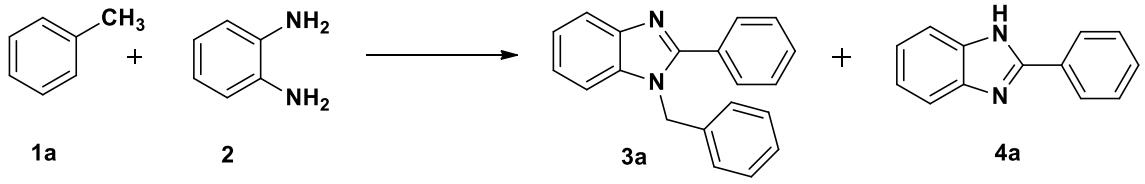
3l
(88%, 30 min)

[a]**Reaction conditions**: Toluene derivatives 1a-l (2 mmol) , *o*-phenylenediamine 2 (1.0 mmol) and of UHP (3 mmol) were grinded in solvent free condition at room temperature . [b] % yield

In order to obtain 2-substituted benzimidazole the model reaction was grinded with higher amounts of UHP and also for longer time up to 60 min but exclusively 1,2-disubsituted benzimidazole was obtained. UHP shows very interesting results by varying reaction temperature and amount of the oxidant in solvent-free condition. Model reaction mixture was stirred with 3 mmol of UHP at room temperature but no product was obtained while starting material was remained as such (**Table 3.3, entry 1**). As temperature of the reaction increases, yield of 3a decreases while yield of 4a increases. The reaction temperature was increased up to 100 ^{0}C with 3 mmol of UHP it gave a mixture of 3a and 4a (**Table 3.3, entries 2-6**). The reaction was also carried out with different loading of UHP (4-6 mmol) at 80 ^{0}C, with 4 mmol of the UHP, exclusively 2-substituted benzimidazole 4a was obtained in 92% yield (**Table 3.3, entry 7**). Further increase in UHP amount by 6 mmol there is no improvement in % yield of 4a (**Table 3.3, entry 8**) and at higher temperature 100 ^{0}C with 4 mmol of UHP no significant improvement in the % yield of 4a

was obtained (**Table 3.3, entry 9**). The product (**4a**) was characterized by spectral data (IR, ^{1}H, ^{13}C NMR) and confirmed by comparing with the reported.

Table 3.3 Effect of temperature and amount of the oxidant on the model reaction



S. No	Oxidant (UHP)	Temperature (^{o}C)	Product (3a)[b]	Product (4a)[c]
1	3 mmol	RT	NR	NR
2	3 mmol	50	60	30
3	3 mmol	60	45	43
4	3 mmol	70	32	58
5	3 mmol	80	15	72
6	3 mmol	100	12	76
7	4 mmol	80	-	92
8	6 mmol	80	-	92
9	4 mmol	100	-	92

[a]**Reaction conditions:** Toluene **1**(1.0 mmol), *o*-phenylenediamine **2** (1.0 mmol) and UHP were treated at different temperature without solvent. [b] % yield of 3a. [c] % yield of 4a.

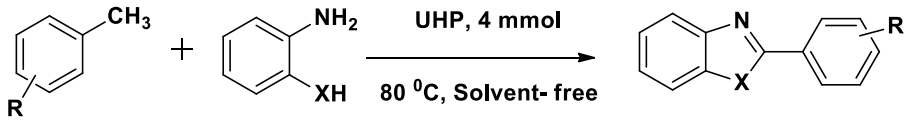
So the optimized conditions for chemoselective synthesis of 2-phenylbenzimidazole is toluene (1 mmol), *o*-phenylenediamine (1.0 mmol) and UHP (4.0 mmol) at 80 ^{0}C in solvent-free condition (**Table 3.2, entry 7)**.

3.2.3 Substrates Scope for 2-substituted benzimidazole/ benzothiazoles

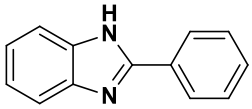
Having been encouraged by the observation, we extended the synthesis of 2-substituted benzimidazoles/ benzothiazoles by using different methyl arene derivatives with 1,2-diaminobenzene/ 2-aminothiophenol. All methyl arenes carrying either electron donating (methoxy, methyl, N,N dimethyl) or electron-withdrawing (nitro, chloro, fluoro, bromo) gave chemoselective 2-substituted benzimidazoles like 2-phenyl-1H-benzo[d]imidazole (**4a**), 2-(1H-benzo[d]imidazol-2-yl)-3-bromophenol (**4b**), 2-(4-nitrophenyl)-1H-benzo[d]imidazole (**4c**), 2-(4-chlorophenyl)-1H-benzo[d]imidazole (**4d**), 2-(4-bromophenyl)-1H-benzo[d]imidazole (**4e**), 2-(4-fluorophenyl)-1H-benzo[d]imidazole (**4f**), 2-(naphthalen-2-yl)-1H-benzo[d]imidazole **(4g)** and 2-(pyridin-2-yl)-1H-benzo[d]imidazole (**4h**). Under the same optimized condition 2-substituted benzothiazoles also achieved in excellent yield. Methyl arenes derivatives and 2-aminothiophenol gave benzothiazole derivatives viz 2-phenylbenzo[d]thaizole (**4i**), 2-(4-methoxyphenyl)benzo[d]thaizole (**4j**), 4-(benzo[d]thiazol-2-yl)-N,N-dimethylaniline (**4k**), 2-(3,4 dimethoxyphenyl)benzo[d]thaizole (**4l**), 2-(4-nitrophenyl)benzo[d]thaizole (**4m**), 2-(4-bromophenyl)benzo[d]thaizole (**4n**), 2-(4-chlorophenyl)benzo[d]thaizole **(4o)**, 2-(4-fluorophenyl)benzo[d]thaizole (**4p**), 2-(naphthalen-2-yl)benzo[d]thaizole (**4q**), 2-(furan-2-

yl)benzo[d]thaizole (**4r**) and 2-(pyridin-2-yl)benzo[d]thaizole (**4s**) in good to excellent yield (**Table 3.4**). 2-Aminothiophenol gave excellent yield in shorter reaction time than *o*-phenylenediamine because sulfur is more nucleophile than nitrogen atom.

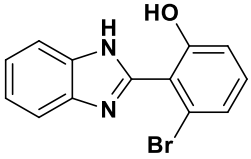
Table 3.4 Synthesis of 2- substituted benzoheterocycles (4a-s)



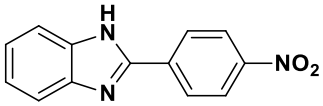
1a-k 2 4a-4s



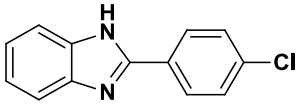
4a
(92%, 20 min)



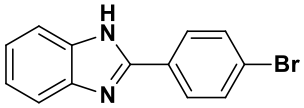
4b
(85%, 30 min)



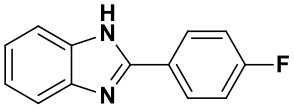
4c
(87%, 25 min)



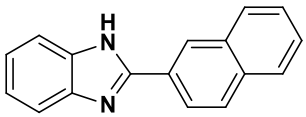
4d
(87%, 26 min)



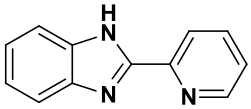
4e
(87%, 25 min)



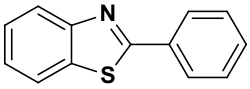
4f
(92%, 22 min)



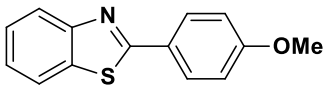
4g
(89%, 25 min)



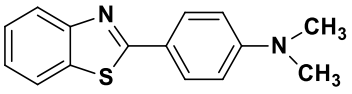
4h
(88%, 25 min)



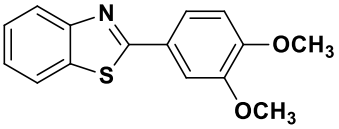
4i
(93%, 15 min)



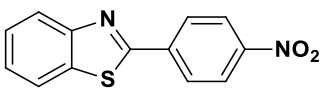
4j
(89%, 10 min)



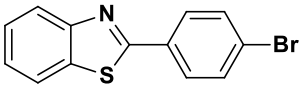
4k
(86%, 10 min)



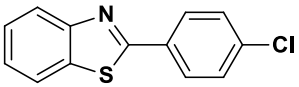
4l
(85%, 10 min)



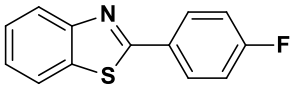
4m
(86%, 10 min)



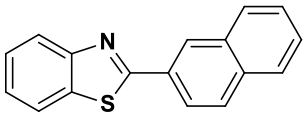
4n
(88%, 10 min)



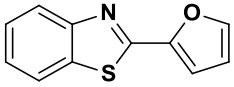
4o
(85%, 10 min)



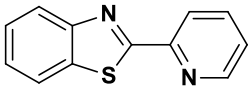
4p
(85%, 15 min)



4q
(90%, 15 min)



4r
(88%, 15 min)

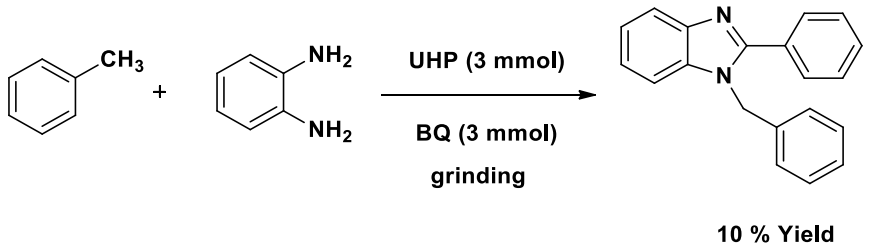


4s
(92%, 15 min)

[a]**Reaction conditions** toluene derivatives **1a-o** (1 mmol) *o*-phenylenediamine or *o*-aminothiophenol **2** (1 mmol) and UHP (4 mmol) were fused at 80 ^{0}C. [b] % yield of the reaction

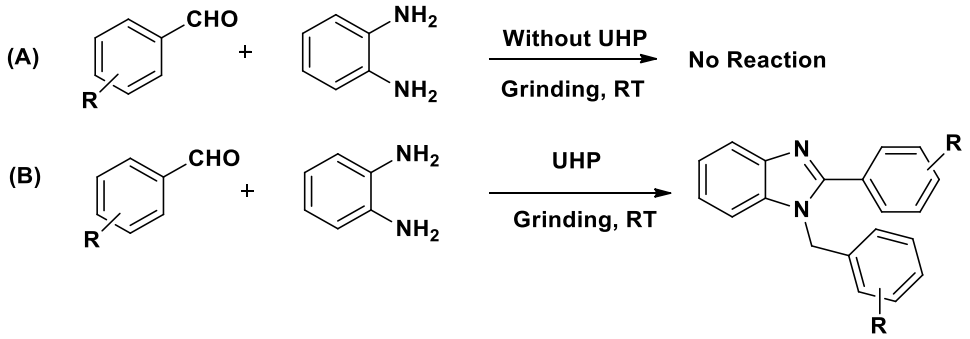
3.3 Controlled Experiments and Mechanistic studies

In order to establish the reaction mechanism, some controlled experiments were performed, when the model reaction was carried in the presence of UHP (3 mmol) under grinding condition with radical scavenger 1,4-benzoquinone (Zhao et al. 2018) (3 mmol), only 10% of the desired product (**3a**) (**Scheme 3.2**) was obtained. This observation shows that the reaction proceeds through radical pathway. When toluene (1.0 mmol), alone was treated with UHP (3.0 mmol) under grinding at room temperature it gave selectively benzaldehyde.



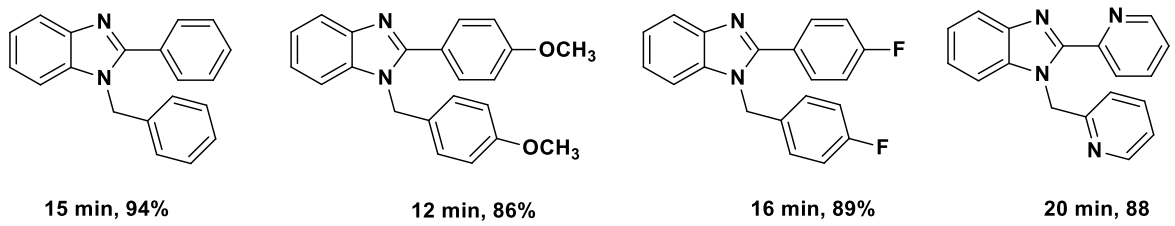
Scheme 3.2 Control experiment using benzoquinone as radical trapping agents

In order to investigate the role of UHP in condensation reaction a controlled experiment was performed by the reaction of benzaldehyde with *o*-phenylenediamine under grinding in the absence of UHP at room temperature. This reaction did not provide the desired product even after 2 hrs **(Scheme 3.3, A)**. When the same reaction was carried out in the presence of UHP it gave the product (**3a**) in **94%** yield **(Scheme 3.3, B)**. In fact, not only benzaldehyde, but also many other substituted benzaldehydes underwent condensation with *o*-phenylenediamine (**2**) and provided products in good yields (**Table 3.5**). These results show that UHP taking part not only in the oxidation of methyl arenes to aldehyde but also in the cyclization step.



Scheme 3.3 Controlled experiment with and without UHP

Table 3.5 Conversion of aldehyde derivatives into corresponding 1,2-disubstituted benzimidazoles.



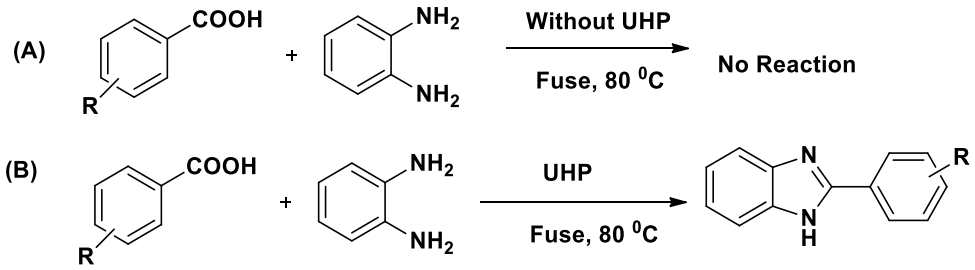
[a]**Reaction condition** benzaldehyde derivatives (1.0 mmol), *o*-phenylenediamine (1.0 mmol) and UHP (3 mmol) were grinded at room temperature. .[b] % yield of the product.

3.3.1 Plausible Reaction Mechanism

A proposed mechanism for the synthesis of 1,2-disubstituted benzimidazole is shown in **Figure 3.2**. In the initial step, decomposition of UHP gives hydrogen peroxide and urea. Hydrogen peroxide gives radical path for the oxidation of methyl arenes via hydroxyl radical ($HO^{\bullet}$). After oxidation, aldehyde (**A**) undergoes condensation reaction with *o*-phenylenediamine and forms diamine (**B**). Intra molecular cyclization followed by 1, 3 hydride shift (**C**) affords final product (**3**). Reaction mechanism for 2-substituted benzimidazole, in initial step aldehyde derivatives react with OH radical give acid derivatives (**D**) which undergoes condensation reaction with *o*-phenylenediamine to form amine (**E**) and intra molecular cyclization affords product (**4**). The formation of reaction intermediate aldehyde derivative (**A)** and benzoic acid derivative (**D**) were confirmed ^{1}H NMR and ^{13}C NMR.

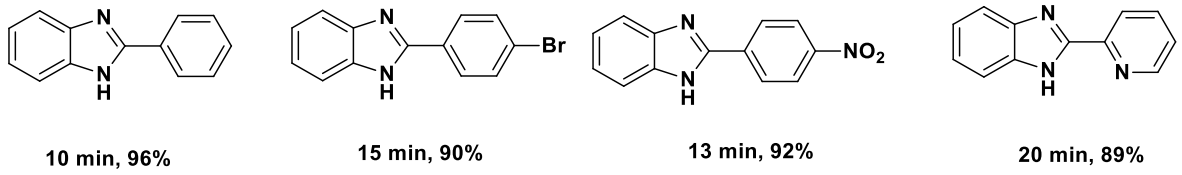
When toluene (1.0 mmol) alone was treated with UHP (3.0 mmol) at 80 ^{0}C it gave completely benzoic acid. To understand the path of the reaction and the role of UHP in the

synthesis of 2-substituted benzimidazole, controlled experiments were performed by the reaction of benzoic acid with *o*-phenylenediamine at 80 ^{0}C in the absence of UHP at room temperature. This reaction did not provide the desired product even after 2 hrs (**Scheme 3.4, A**). When the same reaction was carried out in the presence of UHP it gave the product (**4a**) in **96 %** yield (**Scheme 3.6, B**). In fact, not only benzoic acid, but also many other substituted benzoic acid underwent condensation with *o*-phenylenediamine (**2**) and provided products in good yields (**Table 3.6**). These results show that UHP taking part not only in the oxidation of methyl arenes to benzoic acid but also in the cyclization step.



Scheme 3.4 Controlled experiment with and without UHP

Table 3.6 Conversion of benzoic acid derivatives into corresponding 2-substituted benzimidazoles



10 min, 96% | 15 min, 90% | 13 min, 92% | 20 min, 89%

Reaction conditions: Benzoic acid derivatives (1.0 mmol), *o*-phenylenediamine (1.0 mmol) and UHP were fused at 80^{0}C, [b] % yield of the product.

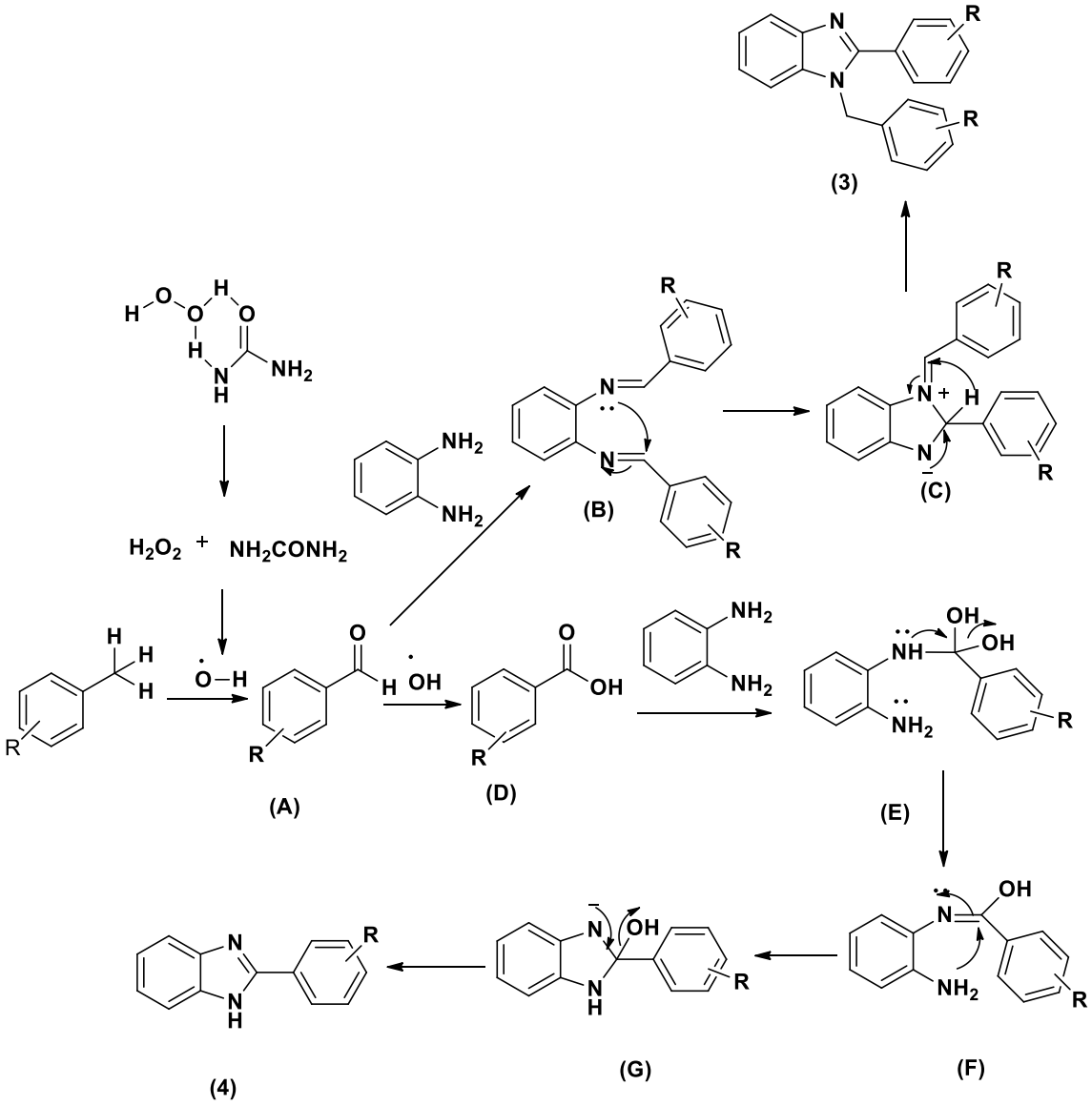


Figure 3.2 Proposed mechanism for the formation of 1,2-disubstituted benzimidazoles and 2-substituted benzimidazoles

3.4 Gram-scale synthesis of 1,2-disubstituted benzimidazoles and 2-substituted benzimidazoles

To establish the potential synthetic application of this methodology the synthesis of 1-benzyl-2-phenyl-1H-benzo[d]imidazole (**3a**) was carried out on gram scale with toluene (**1a**) (2.13 mL, 20 mmol) and *o*-phenylenediamine (**2**) (1 g, 10 mmol) using of UHP (3 mmol) under optimized reaction conditions it gave desired products (**3a**) in 90% yield (5.2 g). 2-Phenyl-1H-benzo[d]imidazole (**4a**) was also synthesized on gram scale toluene (**1a**) (2.13 mL, 20 mmol), *o*- phenylenediamine (**2**) (2 g, 20 mmol) and 4 mmol of UHP at 80 ^{0}C without solvent, gave 88 % (4.98 g) yield of (**4a**).

3. 5 Experimental Section

3.5.1 General Procedure for the Synthesis of 1,2-Disubstituted Benzimidazole (3a-3l)

A mixture of appropriate methyl arene derivatives (2.0 mmol), *o*-phenylenediamine (1.0 mmol) and UHP (3.0 mmol) were taken in mortar and pestle and ground continuously for appropriate time. The progress of the reaction was monitored by TLC. After completion of the reaction, mixture was diluted with ethyl acetate and washed with water. The organic layer was dried over anhydrous sodium sulfate (Na_2SO_4), evaporated under reduced pressure and purified by column chromatography over silica gel (60-120 mesh) with ethyl acetate/hexane solvent system to obtain pure desired products.

3.5.2 General Procedure for the Synthesis of 2-substituted benzimidazoles and benzothiazoles (4a-4s)

o-Phenylenediamine (1.0 mmol), methyl arenes (1.0 mmol) and UHP (4 mmol) were heated at 80 ^{0}C in solvent-free condition. The progress of the reaction was monitored by TLC. After completion of the reaction, mixture was diluted with ethyl acetate and washed with water. The organic layer was dried over anhydrous sodium sulfate (Na_2SO_4), evaporated under reduced pressure and purified by column chromatography over silica gel (60-120 mesh) with ethyl acetate/hexane solvent system to obtain pure desired products.

The ^{1}H NMR and ^{13}C NMR of the 1,2-disubstituted benzimidazoles and 2-substituted benzimidazoles/ benzothiazoles were compared with literature reports.

3.6 Analytical data

3.6.1 Analytical data of 1,2-disubstituted benzimidazoles and 2-disubstituted benzimidazoles/ benzothiazoles

1-benzyl-2-phenyl-1H-benzo[d]imidazole (3a) Yield 92%; White powder; m.p. 132-133 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.81-7.79 (d, 2H), 7.63-7.61(d, 2H), 7.40- 7.37 (t, 3H), 7.27-7.22 (m, 4H), 7.18-7.13 (m, 2H) , 7.04-7.02 (d, 2H), 5.39 (s, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 154.22, 143.20, 136.40, 136.06, 130.11, 129.88, 129.26, 129.04, 128.72, 127.76, 125.97, 123.01, 122.65, 120.00, 110.38, 48.28.

1-(4-methoxybenzyl)-2-(4-methoxyphenyl)-1H-benzo[d]imidazole (3b) Yield 90%; White powder; m.p. 128-130 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.78- 7.77 (d, 1H),

7.58- 7.56 (d, 2H), 7.22-7.21 (d, 1H), 7.15- 7.14 (d, 2H) 6.97-6.96 (d, 2H) 6.91-6.89 (d, 2H), 6.79-6.78 (d, 2H), 5.32 (s, 2H) 3.78 (s, 3H) 3.72 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 160.86, 159.00, 153.99, 142.93, 135.89, 130.69, 128.35, 127.20, 122.71, 122.50, 122.40, 119.65, 114.41, 114.17, 110.34, 55.35, 55.27, 47.87.

4-(1-(4-(dimethylamino)benzyl)-1H-benzo[d]imidazol-2-yl)-N,N-dimethylaniline (3c) Yield 93%; Yellow powder; m.p. 255 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.84-7.83 (d, 1H), 7.66-7.64 (d, 2H), 7.29-7.26 (t, 1H), 7.22-7.19 (t, 2H), 7.05-7.03 (d, 2H), 6.76-6.75 (d, 2H), 6.71-6.69 (d, 2H), 5.39 (s, 2H), 3.03 (s, 6H), 2.95 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 151.21, 149.97, 143.20, 130.30, 126.92, 124.30, 122.15, 119.21, 112.79, 111.80, 110.37, 48.05, 40.52, 40.18.

1-(3,4-dimethoxybenzyl)-2-(3,4-dimethoxyphenyl)-1H-benzo[d]imidazole (3d) Yield 94%; White powder; m.p. 174-175 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.86-7.85 (d, 2H), 7.38-7.28 (m, 6H), 6.93-6.91 (d, 1H), 6.81-6.80 (d, 1H), 6.66 (s, 1H), 5.40 (s, 2H), 3.92 (s, 3H), 3.85 (s, 3H), 3.78 (s, 3H), 3.77(s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 154.12, 150.50, 149.53, 149.11, 148.58, 136.32, 129.11, 122.91, 122.66, 121.86, 119.78, 118.12, 112.36, 111.54, 110.99, 110.26, 109.04, 55.98, 55.96, 55.92, 55.86, 48.17.

2-(1-(2-hydroxybenzyl)-1H-benzo[d]imidazol-2-yl)phenol (3e) Yield 89%; White powder; m.p. 210-212 °C; **^{1}H NMR** (500 MHz, DMSO) δ (ppm): 9.48 (s, 1H), 7.69-7.67 (d, 1H), 7.55-7.54 (d, 1H), 7.37-7.35 (d, 1H), 7.23-7.18 (m, 2H), 7.05-7.02 (t, 3H) 6.99-6.97 (d, 1H), 6.89-6.87 (d, 1H), 6.74- 6.71 (t, 1H), 6.61-6.58 (t, 1H), 6.55-6.53 (d, 1H), 5.49 (s, 2H); **^{13}C NMR** (125 MHz, DMSO) δ (ppm):157.71, 153.80, 151.25, 139.72,

134.74, 130.52, 127.94, 126.88, 125.54, 121.65, 118.74, 117.72, 117.15, 114.57, 112.50, 109.60, 44.30.

1-(2-chlorobenzyl)-2-(2-chlorophenyl)-1H-benzo[d]imidazole (3f) Yield 87%; White powder; m.p. 159-160 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.43-841 (d, 2H), 7.90-788 (d, 1H), 7.51(m, 2H), 7.43 (m,2H), 7.34 (m, 2H), 7.32 (m, 2H), 7.27 (s, 2H), 6.65 (s, 1H), 5.37 (s, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 151.50, 149.00, 143.04, 132.09, 129.88, 129.56, 128.95, 127.73, 127.09, 123.09, 123.35, 122.69, 120.33, 110.50, 45.68.

1-(3-chlorobenzyl)-2-(3-chlorophenyl)-1H-benzo[d]imidazole (3g) Yield 88%; White powder; m.p. 202-204 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.93-7.91 (d, 1H), 7.73-7.71 (m, 2H), 7.49 -7.47 (t, 3H), 7.36-7.33 (m, 4H), 7.27–7.24 (m, 2H), 7.14-7.12 (d, 2H), 5.48 (s, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ (ppm): 154.08, 142.98, 136.40, 136.04, 130.03, 129.96, 129.31, 129.08, 128.78, 127.81, 126.00, 123.09, 122.74, 120.00, 110.56, 77.31, 77.06, 76.81, 48.51.

1-(4-bromobenzyl)-2-(4-bromophenyl)-1H-benzo[d]imidazole (3h) Yield 86%; White powder; m.p. 160-162 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.87 (d, 1H), 7.60 (d, 2H), 7.52 (d, 2H), 7.46 (d, 2H), 7.33 (t, 1H), 7.26 (d, 1H), 7.19 (d, 1H), 6.96 (d, 2H), 5.37 (s, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 152.91, 143.13, 135.89, 132.33, 130.52, 128.84, 127.48, 123.06, 121.90, 120.22, 110.27, 47.84.

1-Benzyl-5-fluoro-2-phenyl-1 H-benzo[d]imidazole (3i) Yield 88%; White powder; m.p. 110-112 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.10-8.07 (m, 2H), 7.65-7.63 (d, 3H), 7.27-7.26 (t, 3H), 7.26-715 (m, 4H), 5.40 (s, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm):

164.73, 162.77, 161.32, 153.08, 143.09, 135.90, 131.25, 127.66, 126.20, 123.23, 120.10, 116, 110.30, 47.72.

2-(naphthalen-2-yl)-1-(naphthalen-2-ylmethyl)-1H-benzo[d]imidazole (3j) Yield 91%; White powder; m.p. 124-125 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.92 (d, 2H), 7.72 (d, 4H), 7.49 (s, 4H), 7.34 (s, 4H), 7.25 (d, 3H), 7.13 (d, 3H), 5.48 (s, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 154.14, 143.04, 136.34, 135.98, 129.90, 129.25, 129.02, 128.72, 127.75, 125.94, 123.03, 122.68, 119.94, 110.50, 48.34.

2-(furan-2-yl)-1-(furan-2-ylmethyl)-1H-benzo[d]imidazole (3k) Yield 89%; White powder; m.p. 88-89 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.79-7.77 (d, 1H), 7.64 (s, 1H), 7.50-7.48 (t, 2H), 7.32-7.28 (m, 2H), 7.22- 7.21 (d, 1H), 6.60 (s, 1H), 6.27-6.23 (d, 2H), 5.63 (s, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 149.54, 145.34, 143.90, 142.91, 142.60, 135.43, 123.19, 122.87, 119.75, 112.86, 112.01, 110.47, 109.94, 108.31, 41.62.

2-(pyridin-4-yl)-1-(pyridin-4-ylmethyl)-1H-benzo[d]imidazole (3l) Yield 88%; Yellow powder; m.p. 293-294 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.93-7.91 (d, 1H), 7.73-7.71 (d, 2H), 7.50-7.46 (m, 3H), 7.36-7.33 (t, 2H), 7.27-7.25(t, 2H), 7.14-7.12 (t, 2H), 5.48 (s, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 143.00, 138.34, 134.82, 133.99, 130.53, 130.36, 129.87, 127.46, 126.30, 126.03, 125.62, 122.85, 122.36, 110.50, 45.58.

2-phenyl-1H-benzo[d]imidazole (4a) Yield 92%; Yellow powder; m.p. 293-294 °C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ (ppm): 12.92 (s, 1H), 8.19 -8.18 (d, 2H), 7.67 (s, 1H), 7.57-7.54 (t, 3H), 7.50-7.47 (t, 1H), 7.21 (s, 2H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ (ppm): 150.75, 143.32, 134.51, 129.37, 128.47, 125.95, 122.07, 121.22, 118.36, 110.83.

2-(1H-benzo[d]imidazol-2-yl)-3-bromophenol (4b) Yield 85%; Yellow powder; m.p. 252-254 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 13.04 (s, 1H), 8.56 (s, 1H), 7.50 (d, 2H), 7.44 (d, 1H), 7.38-7.37 (s, 1H), 7.26 (s, 1H), 6.96-6.94 (d, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 162.32, 160.30, 141.99, 136.03, 134.25, 128.25, 120.51, 119.54, 110.48,

2-(4-nitrophenyl)-1H-benzo[d]imidazole (4c) Yield 87%; Yellow powder; m.p. >300 °C; **^{1}H NMR** (500 MHz, DMSO) δ (ppm): 13.28 (s, 1H), 8.41 (s, 4H), 7.66 (d, 2H), 7.26 (d, 2H); **^{13}C NMR** (125 MHz, DMSO) δ (ppm): 149.46, 148.27, 144.28, 136.49, 135.53, 127.85, 124.76, 124.08, 122.79, 119.91, 112.28.

2-(4-chlorophenyl)-1H-benzo[d]imidazole (4d) Yield 87%; Yellow powder; m.p. > 300 °C; **^{1}H NMR** (500 MHz, DMSO) δ (ppm): 12.99 (s, 1H, NH), 8.20-8.18 (d, 2H), 7.64-7.54 (m, 4H), 7.22-7.12 (d, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 149.62, 143.21, 134.03, 133.96, 128.54, 127.61, 122.25, 121.33, 118.43, 110.90.

2-(4-bromophenyl)-1H-benzo[d]imidazole (4e) Yield 87%; Yellow powder; m.p. >300 °C; **^{1}H NMR** (500 MHz, DMSO) δ (ppm): 8.43-8.39 (t, 4H), 7.66 (s, 2H), 7.28-7.26 (d, 2H); **^{13}C NMR** (125 MHz, DMSO) δ (ppm): 143.30, 132.67, 129.32, 128.68, 125.03, 118.61.

2-(4-fluorophenyl)-1H-benzo[d]imidazole (4f) Yield 92%; Yellow powder; m.p. 256-258 °C; **^{1}H NMR** (500 MHz, $CDCl_3$ & DMSO) δ (ppm): 8.46 (s, 1H), 8.13-8.12(d, 4H), 7.81-7.76 (t, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$ & DMSO) δ (ppm): 150.17, 143.38, 134.64, 131.21, 128.79, 127.73, 123.20, 122.34, 121.39, 118.47, 110.79.

2-(naphthalen-2-yl)-1H-benzo[d]imidazole (4g) Yield 89%; Yellow powder; m.p. 260-262 °C; **^{1}H NMR** (500 MHz, DMSO) δ (ppm): 8.81 (s, 1H), 8.39 (s, 1H), 8.26 (d, 1H), 8.00 (t, 2H), 7.63-7.54 (m, 2H), 7.19 (d, 1H), 6.99 (t, 1H), 6.75 (d, 1H), 6.59 (t, 1H), 5.25 (s, 1H); **^{13}C NMR** (125 MHz, DMSO) δ (ppm): 155.69, 143.62, 134.71, 133.93, 133.84, 132.32, 130.24, 128.16, 127.86, 127.38, 127.24, 127.00, 126.29, 123.42, 116.48, 115.79, 114.30.

2-(pyridin-4-yl)-1H-benzo[d]imidazole (4h) Yield 88%; White powder; m.p. 260-262 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 11.33 (s, NH, 1H), 8.66-8.65 (d, 1H), 8.51-8.47 (d, 1H), 7.91-7.89 (m, 2H), 7.46-7.45 (d, 1H), 7.39-7.38 (d, 1H), 7.31-7.30 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 150.81, 149.05, 148.43, 144.44, 137.42, 124.62, 123.95, 122.70, 121.81, 120.15, 111.27.

2-phenylbenzo[d]thaizole (4i) Yield 93%; Yellow powder; m.p. 115-116 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.05-8.02 (m, 2H), 7.87-85 (d, 1H), 7.45-7.42 (m, 4H), 7.35-7.32 (t, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 168.08, 154.18, 154.18, 135.06, 133.68, 130.98, 129.03, 127.58, 123.26, 125.20, 123.22, 121.63.

2-(4-methoxyphenyl)benzo[d]thaizole (4j) Yield 89%; Yellow powder; m.p. 134-125 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.06-8.00 (m, 3H), 7.88 (d, 1H), 7.47 (t, 1H), 7.35 (t, 1H), 7.00 (d, 2H), 3.89 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 167.87, 161.94, 154.23, 134.86, 129.12, 126.46, 126.19, 124.78, 122.82, 121.50, 114.38, 55.46.

4-(benzo[d]thiazol-2-yl)-N,N-dimethylaniline (4k) Yield 86%; Yellow powder; m.p. 170-171 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.97 (t, 3H), 7.84 (d, 1H), 7.43 (t, 1H),

7.30 (t, 1H), 6.75 (d, 2H), 3.05 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 167.87, 161.94, 154.23, 134.86, 129.12, 126.46, 126.19, 124.78, 122.82, 121.50, 114.38, 55.46.

2-(3,4-dimethoxyphenyl)benzo[d]thaizole (4l) Yield 85%; Yellow powder; m.p. 132-134 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.97 (d, 1H), 7.81 (d, 1H), 7.65 (d, 1H), 7.60 - 7.47 (m, 1H), 7.47-7.36 (m, 1H), 7.34-7.25 (m, 1H), 6.88 (d, 1H), 3.96 (s, 3H), 3.89 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 167.91, 126.70, 126.25, 124.90, 122.85, 121.52, 121.16, 111.03, 109.80, 56.11.

2-(4-nitrophenyl)benzo[d]thaizole (4m) Yield 86%; Yellow powder; m.p. 230-231 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.29 (s, 2H), 8.22 (s, 2H), 8.08 (d, 1H), 7.90 (d, 1H), 7.54-7.44 (m, 1H), 7.44-7.34 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 164.85, 154.12, 139.19, 135.54, 128.25, 126.92, 126.23, 124.32, 123.94, 121.84.

2-(4-bromophenyl)benzo[d]thaizole (4n) Yield 88%; Yellow powder; m.p. 132-134 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.01 (d, 1H), 7.90 (d, 2H), 7.85 (d, 1H), 7.60-7.53 (m, 2H), 7.45 (s, 1H), 7.35 (d, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 166.70, 154.07, 135.04, 132.55, 132.23, 128.91, 126.50, 125.43, 123.32, 121.66.

2-(4-chlorophenyl)benzo[d]thaizole (4o) Yield 85%; Yellow powder; m.p. 110-112 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.01 (d, 1H), 7.97 (d, 2H), 7.84 (d, 1H), 7.47-7.37 (m, 3H), 7.34 (t, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 166.60, 154.08, 137.03, 135.06, 132.13, 129.26, 128.71, 126.47, 125.40, 123.30, 121.64.

2-(4-fluorophenyl)benzo[d]thaizole (4p) Yield 85%; Yellow powder; m.p. 101-103°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.02 (d, 3H), 7.84 (d, 1H), 7.44 (t, 1H), 7.33

(t, 1H), 7.13 (t, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 166.73, 165.45, 154.09, 135.04, 129.51, 126.41, 125.24, 123.18, 121.61, 116.24, 116.07.

2-(naphthalen-2-yl)benzo[d]thaizole (4q) Yield 90%; Yellow powder; m.p. 123-125 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.52 (s, 1H), 8.17-8.15 (m, 1H), 8.07-8.05 (d, 1H), 7.93-7.82 (m, 4H), 7.51-7.45 (m, 3H), 7.37-7.34 (t, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 168.14, 154.20, 135.16, 134.62, 133.22, 131.00, 128.84, 127.89, 127.61, 127.48, 126.91, 126.41, 125.22, 123.26, 121.66.

2-(furan-2-yl)benzo[d]thaizole (4r) Yield 88%; Yellow powder; m.p. 104-105 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.99 (d, 1H), 7.83 (d, 1H), 7.60-7.49 (m, 1H), 7.45-7.38 (m, 1H), 7.34 (s, 1H), 7.13 (d, 1H), 6.54 (d, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 157.57, 153.79, 148.79, 144.70, 134.30, 126.48, 125.20, 123.15, 121.57, 112.53, 111.42.

2-(pyridin-2-yl)benzo[d]thaizole (4s) Yield 92%; Yellow powder; m.p. 133-135 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.71 (d, 1H), 8.40 (d, 1H), 8.12 (d, 1H), 7.99 (d, 1H), 7.87 (t, 1H), 7.53 (d, 1H), 7.42 (d, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 169.37, 154.27, 151.40, 149.65, 137.00, 136.11, 126.26, 125.63, 125.25, 123.56, 122.00, 120.75.

3.6.2 Spectral data of product (1-benzyl-2-phenyl-1H-benzo[d]imidazole (3a)

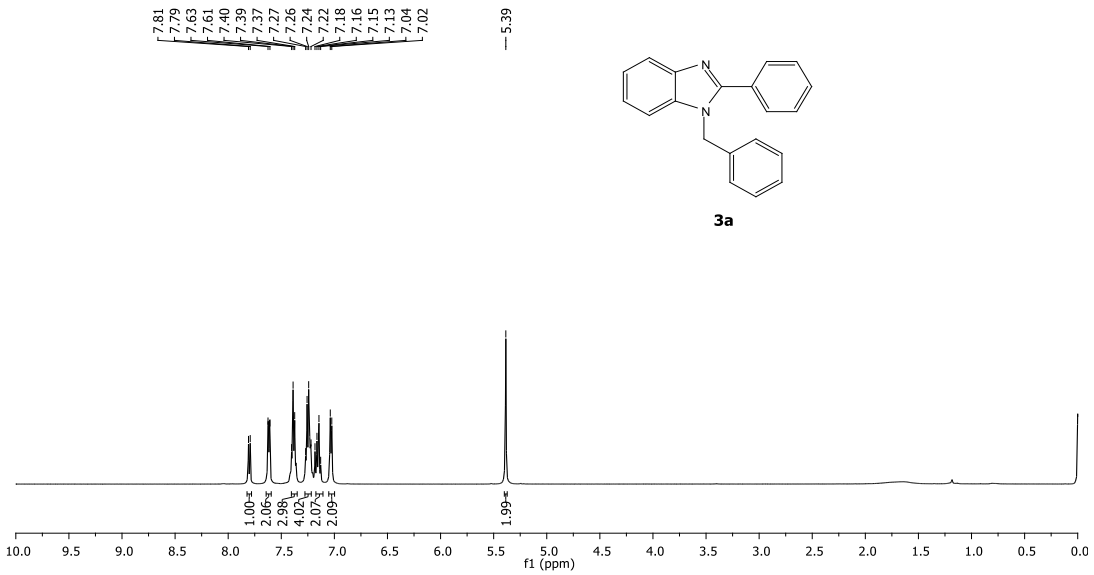


Figure 3.3 ^{1}H NMR of 1-benzyl-2-phenyl-1H-benzo[d]imidazole (3a)

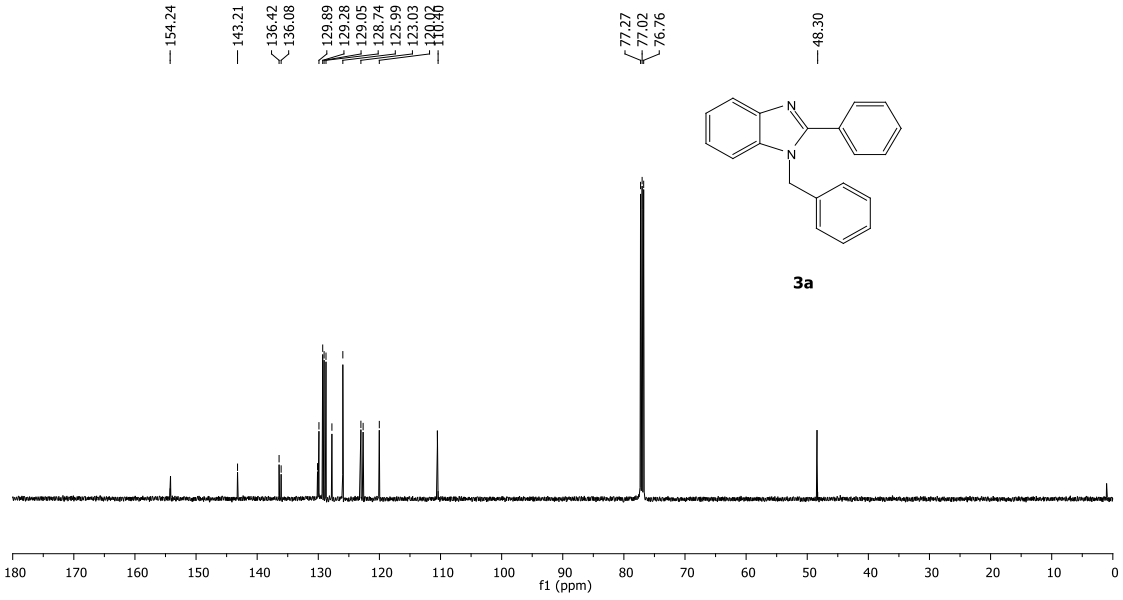


Figure 3.4 ^{13}C NMR of 1-benzyl-2-phenyl-1H-benzo[d]imidazole (3a)

3.6.3 Spectral data of product 2-phenyl-1H-benzo[d]imidazole (4a)

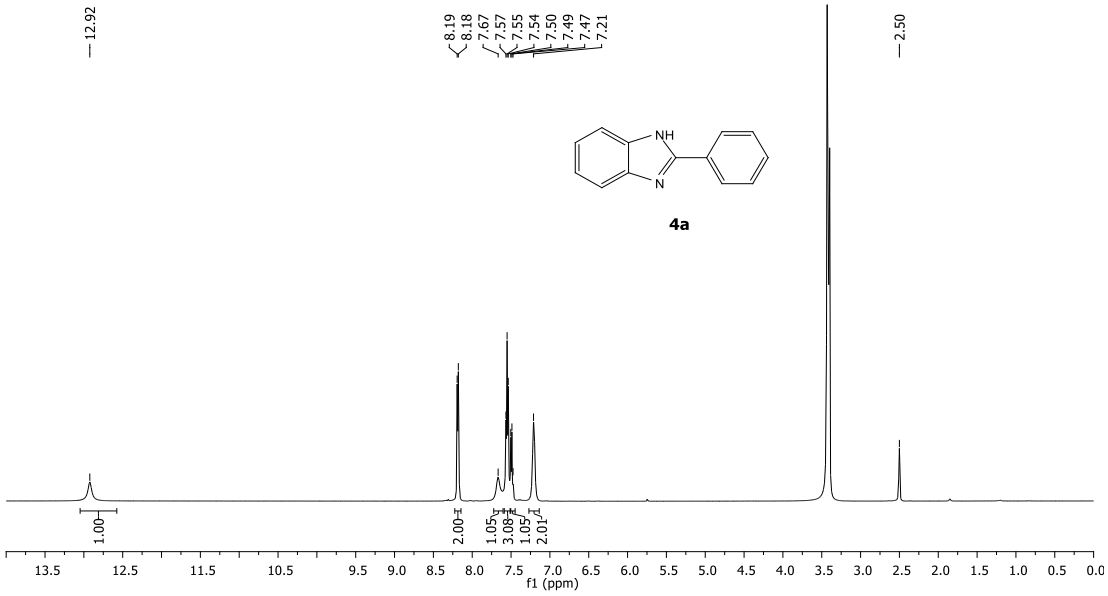


Figure 3.5 ^{1}H of 2-phenyl-1H-benzo[d]imidazole

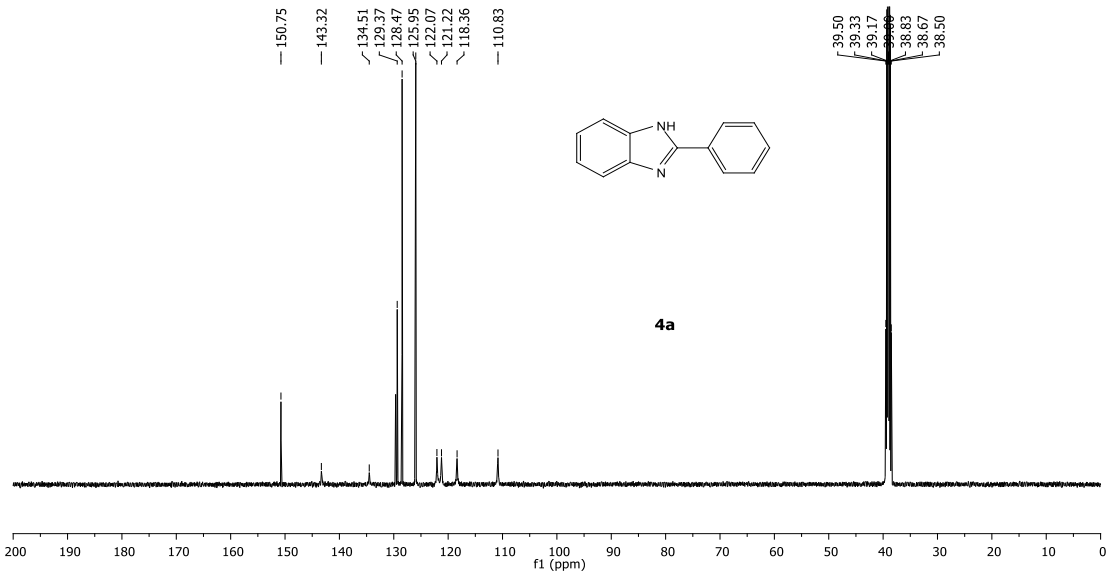


Figure 3.6 ^{13}C NMR of 2-phenyl-1H-benzo[d]imidazole

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