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Metal Catalyst Free One-Pot Synthesis of 2-Arylbenzimidazoles From α-Aroylketene Dithioacetals (AKDTAs)

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An efficient green synthetic approach has been developed towards the synthesis of 2-aryl substituted benzimidazoles from α-aroylketene dithioacetals (AKDTAs) **1** and *o*-phenylenediamine (OPD) **2**. The reaction has been achieved in water with a catalytic amount of acetic acid. 2-Arylbenzimidazoles have been synthesized in remarkable yields under both thermal and microwave conditions. The metal catalyst free condition makes this transformation very green, practical and attractive.

Introduction

A great number of biologically active molecules contain the benzimidazole scaffold and especially 2-substituted benzimidazole has been found to be biologically more potent. Their application is further extended as poli(ADP-ribose) phosphorilase inhibitors[1] Histamine H4 receptor binders,[2] antiparasitic,[3] cardiovascular,[4] anticancer, [5] antimicrobial,[6] and antihypertensive[6] agents. In addition, benzimidazoles have been found to have antiulcer activity and ionodilator applications (Fig 1).[7] The AKDTAs **1** are three carbon synthons, and they are highly functionalized α,β-unsaturated ketones containing both electron withdrawing carbonyl group and electron donating alkylthio substituents well known as polarised or push-pull or donor-acceptor double bond. The alkylthio group is a very good leaving group and it can be easily replaced by nucleophiles. In several reactions, the AKDTAs **1** behave as α,β-unsaturated carbonyl compounds wherein, depending upon the nucleophile / reaction conditions either 1,2- or 1,4- addition takes place. In acidic media nucleophiles, prefer 1,2- addition and it has been extensively used for the synthesis of wide variety of heterocyclic compounds.[8]

Several methods have been reported for the synthesis of 2-substituted benzimidazole.[9-11] Generally, the conventional method involves the reaction of aryl aldehyde / carboxylic acid or their derivatives with 1,2-diamines to afford benzimidazole at elevated temperature in the presence of strong acids like polyphosphoric acid,[12] and mineral acid,[13-15] Several other catalysts like indium triflate,[16] iodine,[17] cetylpyridinium bromide[18] PEG-400 [19] (bromodimethyl)sulfonium bromide,[20] ammonium acetate,[21] cobalt(II) chloride hexahydrate,[22] ceric ammonium nitrate [23] and enzymatic catalyst Lipozyme[24] have been used instead of mineral acids for this cyclocondensation. Recently, substituted benzimidazole has been reported by reacting **2** with aryl aldehydes using 4-OMe-TEMPO as the catalyst under aerobic condition.[25] In addition, C-N bond formation *via* a cross coupling reaction, direct C-H activation, using transition metal catalyst have also been reported to construct the benzimidazole skeleton.[26]

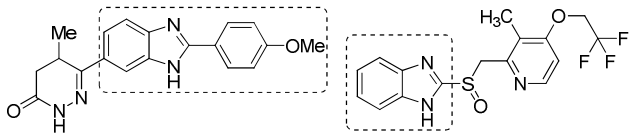

Fig 1 Structures of representative benzimidazole core motif

The distinctive methods of assembling these valuable heterocycles are highly dependent on using **2** as the precursor. The literature for the other methods to the synthesis of 2-arylbenzimidazoles have been seriously reviewed (Scheme 1).[27-32]

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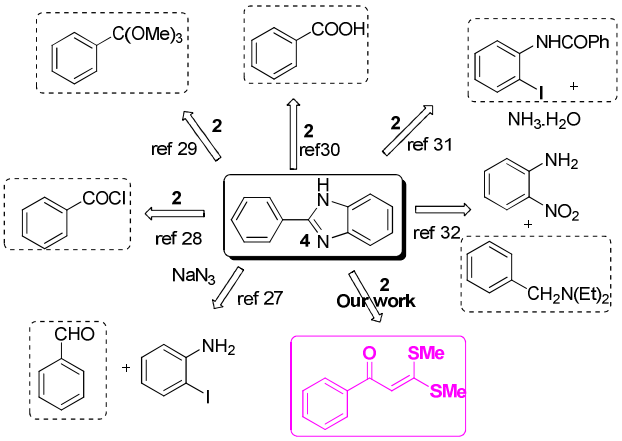
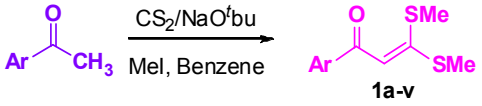


Scheme 1 Strategies for the synthesis of 2-arylbenzimidazoles

Water mediated organic synthesis has become one of the most attractive protocol in view of the environment aspects. We now report a conceptually novel, simple and effective metal catalyst free direct cyclocondensation of readily available AKDTAs **1**

with **2** in the presence of acetic acid as a catalyst in water to afford **4** in excellent yields. The development of lab route for the synthesis of benzimidazole **4** under metal catalyst free and eco-friendly condition is worth to consider for it's practical approach on a larger scale operations. *Rao et al* reported trisubstituted pyrrole[33] and 3-aroyl coumarin[34] by reacting AKDTA with TosMIC and salicylaldehydes respectively. In continuation of exploring the synthetic pontential of AKDTAs **1**, we were interested to construct seven membered benzodiazepine derivatives which are pharmacologically and biologically valuable.[35-37]

Table 1 Synthesis of AKDTA **1a-v**[34]

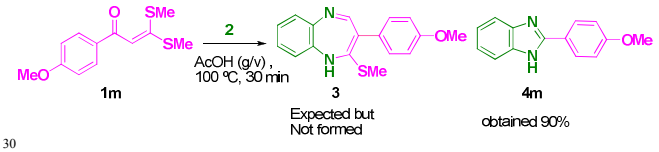


1a-v

Entry	Ar		Yield[a] (%)
1	C_6H_5	**1a**	88
2	2-naphthyl	**1b**	92
3	1-naphthyl	**1c**	85
4	4-Cl C_6H_4	**1d**	92
5	4-CH_3 C_6H_4	**1e**	82
6	Ferrocenyl	**1f**	85
7	Pyrenyl	**1g**	80
8	3- NO_2 C_6H_4	**1h**	80
9	3-OCH_3 C_6H_4	**1i**	85
10	2-F C_6H_4	**1j**	84
11	3-CF_3 C_6H_4	**1k**	85
12	4-Br C_6H_4	**1l**	80
13	4-OCH_3 C_6H_4	**1m**	80
14	2,4-Cl_2 C_6H_3	**1n**	82
15	3,4-F_2 C_6H_3	**1o**	83
16	3,4-Cl_2 C_6H_3	**1p**	79
17	3-Br C_6H_4	**1q**	84
18	2-CF_3 C_6H_4	**1r**	84
19	2-F,5-CF_3 C_6H_3	**1s**	70
20	4-I C_6H_4	**1t**	77
21	2-F,4-CF_3 C_6H_3	**1u**	72
22	3-CF_3,4-Cl C_6H_3	**1v**	77

[a]isolated yield after recrystallizations

Following the literature[34], a variety of AKDTAs **1** has been synthesized (Table 1). Further, heated the mixture of AKDTA **1m** and **2** in the presence of glacial acetic acid (g/v) at 100 ºC for 30 min (Scheme 2). The reaction went smoothly and the crude product was purified by recrystallization with ethanol.



Scheme 2 Cyclocondensation between **1m** & **2** in AcOH

The isolated product was well characterized by ^1H and ^{13}C NMR spectra. Anticipating the compound to be **3,** the ^1H NMR spectrum displayed a singlet at δ 12.86 for the aromatic NH-proton and one singlet at δ 3.82 for OMe group, a pair of doublets at δ 7.09, 8.09 ppm with mutual coupling a constant J = 8.8 Hz for the two CH proton of phenyl group of **1m**. Two multiplets were appeared at δ 7.14-7.15 & 7.46-7.59 for the CH aromatic protons of **2**. But no peak was noticed for the -SMe group and the olefinic proton at δ 2.48 ppm and δ 6.86 ppm. Thus the NMR data is not matching with compound **3** but it is perfectly matching with **4m** and mass spectrum [m/z 225 (M+1)] also confims the formation of benzimidazole. Extensive literature studies revealed that this is the first report to the synthesis of 2-arylbenzimidazole **4** from AKDTA **1**. Some of the earlier reports for the synthesis of 2-arylbenzimidazole involve the use of expensive metal catalysts, more reaction time & steps and expensive reagents. The advantages of the present method is, metal calyst free and less reaction time with excellent yields. The starting materials AKDTA **1**, all of them are solids & stable, high melting points and can be easily preparable with simple reaction techniques. Hence, we report the synthesis of 2-arylbenzimidazole by conceptually novel method of cyclocondesation between AKDTAs **1** and **2** is worth to consider. The cyclocondensation was optimized with **4**, which was observed through several reactions between AKDTA **1** and **2** (Table 2).

Table 2 Optimization of the reaction condition towards the synthesis of **4** from **1**& **2**.

Entry	Solvent	Catalyst (mol %)	Tem. (˚C)	time (h)	*Yield* (%)
1	None	None	100	3	Nr[a]
2	None	AcOH (100)	rt	72	60[b]
3	None	AcOH(100)	100	0.25	75
4	None	AcOH (40)	100	0.5	87
5	None	AcOH (30)	100	0.5	65[b]
6	None	Formic acid (50)	80	3	-[c]
7	EtOH	None	90	3	Nr[a]
8	EtOH	AcOH (40)	90	3	60[b]
9	MeCN	AcOH (40)	80	2	75[b]
10	MeCN	$Yb(OTf)_2$ (50)	80	5	65[b]
11	DMF	$Yb(OTf)_2$ (50)	100	5	75[b]
12	EtOH	*p*-TsOH (40, MW)	100	0.5	83
13	EtOH	*p*-TsOH (40, MW)	100	0.02	85[e]
14	H_2O	*p*-TsOH (MW)	100	0.02	50
15	H_2O	H_2SO_4 (1M)	100	0.5	-[c]
16	H_2O	HCl (1M)	100	0.5	50[b]
17	H_2O	AcOH (100)	100	1	87
18	H_2O	AcOH (40)	rt	120	20[b]
19	**H_2O**	**AcOH (40)**	**100**	**2**	**95[d]**

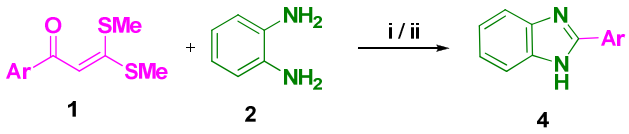
[a] reaction failed to occur [b] unreacted **1** & **2** recovered
[c]Complex reaction mixture [d]Isolated yield.

Once **4m** had been synthesized, several cyclocondensation were tried by variation of reaction conditions (Table 2). The reaction time increased gradually when we reduced the amount of AcOH. Absence of acetic acid did not give the product **4m** (Table 2, entry 1). We examined the mild Lewis acid Ytterbium (III) trifluoromethanesulfonate ($Yb(OTf)_3$) with two different solvents to afford **4m** in 65 & 75% yields (Table 2, entry 10 & 11). With catalytic amount of *p*-TsOH in ethanol, the reaction proceeded smoothly in both thermal (30 mins) and MW (2 mins) condition with good yield (Table 2, entry 12-13). The drawback of this condition is, in water / *p*-TsOH media under microwave condition only 50% of product was observed (Table 2, entry 14). In HCl, the yield was very low and under H_2SO_4, formic acid media did not give the desired product (Table 2, entry 15 -16 & 6). The reaction was performed in ethanol, acetonitrile and water as

solvents in the presence of AcOH (40 mol %) at 100 °C. Among the above solvents, mixture of water-AcOH (40 mol %) gave **4m** in maximum yield (95%, Table 2, entry 19). The optimal reaction conditions were as a result of 2-(4-methoxyphenyl)-1*H*-benzo[d]imidazole **4m** with **2** in the presence of water-AcOH (40 mol %) at 100 °C for 2 h. Overall, the synthesis of 2-arylbenzimidazoles from AKDTA **1** and **2** proceeds only in the presence of acid medium.

In the next step, variation of the aryl groups was studied and synthesized several 2-arylbenzimidazole derivatives **4a-v** using the optimal reaction condition (Table 3). Halogens substituted aryls, polyaryls such as 1 & 2-naphthyl, pyrene and ferrocene substituted benzimidazoles were consecutively investigated and the yields were excellent. Some of the final products **4a, 4c, 4f-4g, 4j, 4l** and **4t** were obtained as pure crystalline product after the simple work-up with saturated sodium bicarbonate solution. Later, we carried out the reaction between **1** and **2** under the microwave irradiation at 100ºC for 5 min to furnish **4a-v** in good to excellent yields (78-90 %, Table 3). There is not much differences in yield of the product, when compared with thermal conditions. Thus the shorter reaction time and good to excellent yields encouraged us to repeat all the reactions under microwave irradiation (Table 3).

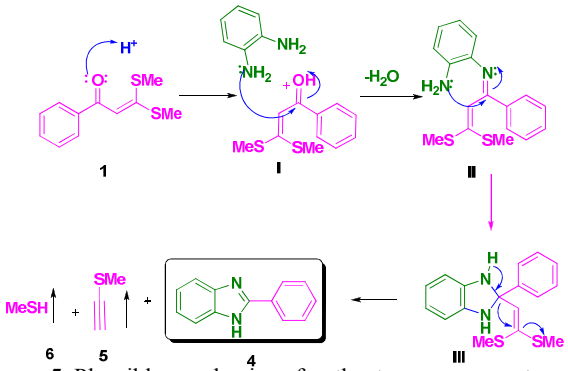
Table 3: Synthesis of **4a-v** from **1** & **2** in H_2O-AcOH (40 mol %) medium for both thermal and MW conditions.[a]



Entry	Ar		Yield Thermal (%)	Yield MW[c] (%)
1	C_6H_5	**4a**	95[b]	90
2	2-naphthyl	**4b**	92	88
3	1-naphthyl	**4c**	93[b]	87
4	4-Cl C_6H_4	**4d**	88	82
5	4-CH_3 C_6H_4	**4e**	87	82
6	Ferrocenyl	**4f**	88[b]	83
7	Pyrenyl	**4g**	90	87
8	3- NO_2 C_6H_4	**4h**	89	82
9	3-OCH_3 C_6H_4	**4i**	88	83
10	2-F C_6H_4	**4j**	82	79
11	3-CF_3 C_6H_4	**4k**	84	80
12	4-Br C_6H_4	**4l**	90[b]	85
13	4-OCH_3 C_6H_4	**4m**	90	88
14	2,4-Cl_2 C_6H_3	**4n**	85	81
15	3,4-F_2 C_6H_3	**4o**	84	78
16	3,4-Cl_2 C_6H_3	**4p**	83	80
17	3-Br C_6H_4	**4q**	89	84
18	2-CF_3 C_6H_4	**4r**	83	79
19	2-F,5-CF_3 C_6H_3	**4s**	80	78
20	4-I C_6H_4	**4t**	90[b]	86
21	2-F,4-CF_3 C_6H_3	**4u**	87	82
22	3-CF_3, 4-Cl C_6H_3	**4v**	87	83

[a] All reactions carried out with (1mmol), **2** (1mmol), AcOH (40 mol %), water at 100 ºC (i) thermal 2 h. (ii) MW, 5 min . [b]yields after recrystallization, [c]isolated yield.

There are number of mechanism envisioned for the formation of 2-arylbenzimidazole **4** from *o*-phenylenediamine **2** with aldehyde or acid or acid chloride etc. Based on the results, we propose a plausible mechanism for the one-pot synthesis of **4** by the cyclocondensation of AKDTA **1** and **2** (Scheme 3). When the mixture of AKDTA **1** and **2** with catalytic glacial acetic acid heated at 100 °C, initially **1** get protonated followed by instantaneous nucleophilic addition of amine group of **2** at C-1 position to give imine (II). This imine formation makes the C-1 position more electron deficient and attract the further nucleophilic addition by another amine group of **2** to afford five membered heterocycle 2-(2,2-bis(methylthio)vinyl)-2-phenyl-2,3-dihydro-1*H*-benzo[d]imidazole (III). In order to achieve the aromaticity, elimination of ethynyl(methyl)sulfane **5** by cleavage of C-C bond of ketene group and MeSH **6** has occurred to afford **4** in excellent yields. Elimination of **5** & **6** is the driving force for the formation of **4**.



Scheme 5 Plausible mechanism for the two component cyclo condensation

Conclusions

In summary, we have demonstrated the synthesis of substituted aryl benzimidazoles from AKDTAs **1a-v** and readily available **2** under mild and greener medium in excellent yields for both thermal and MW conditions. It is noteworthy that this methodology is very simple, less time, metal catalyst free, involving eco-friendly solvent and milder reaction conditions. The economical and environmental advantages of their protocol adds practical value for the industrial applications.

Experimental Section

General methods

The melting points reported in the work are uncorrected. Unless stated otherwise, solvents and chemicals were obtained from commercial sources and used without further purification. The ^1H and ^{13}CNMR spectra of the new compounds were measured at 300,400MHz in DMSO-d_6 and $CDCl_3$.Chemical shifts are reported as δ values (ppm) relative to tetramethylsilane (δ 0.0) as

internal standard. Mass spectra were obtained using electrospray ionization (ESI) mass spectrometer and recorded in positive and negative mode. Infrared spectra were recorded on an FT-IR spectrometer with the major peaks listed. HRMS (ESI-TOF) analysis were recorded on mass spectrometer. Petroleum ether employed in column chromatographic purification refers to the fraction which boils at 40-60 ºC. Microwave reactions have been carried out in a Biotage Microwave Synthesizer

General procedure for the preparation of 3,3-bis(methylthio)-1-arylprop-2-en-1-one (1a-v):

To a stirred suspension of freshly prepared sodium *tert*-butoxide (6.0g, 0.0625mol) in dry benzene (5ml) at 0ºC a solution of arylethanone (3g, 0.0250mol) and carbon disulfide (2.87g, 0.0375mol) in dry benzene (5ml) was added through a pressure equalizer funnel and the mixture was vigorously stirred at 0ºC for 90min. Appearance of a reddish solid in the reaction medium indicated the formation of disodium 3-oxo-3-(3-phenyl)-1-propene-1,1-dithiolate. A solution of methyl iodide (4.26g, 0.030mol) in dry benzene (5ml) was carefully added to this suspension, drop-wise during 10 min at 0°C and the reaction mixture was allowed to stir at 0°C for 90min. After completion of the reaction (TLC; hexanes: EtOAc = 7:3), the mixture was transferred into a 100ml beaker containing 50g of crushed ice and the contents of the beaker were stirred well. A light yellow coloured solid formed was filtered and washed with water (10ml × 3). The crude solid was re-crystallized from EtOH to furnish 3.10g of 1,1-di(methylsulfanyl)-3-(aryl)-1-propen-3-one in 80-92% yield as light yellow colored crystals.

3,3-bis(methylthio)-1-phenylprop-2-en-1-one[34] (1a).
Pale yellow solid; yield 88%, mp. 94-96 °C; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ_H: 2.48 (s, 3H), 2.64 (s, 3H), 6.86 (s, 1H), 7.49 (d, J = 7.6Hz, 2H), 7.56 (d, J = 7.6Hz, 1H), 7.94 (d, J = 6.8Hz, 1H), 7.94 (m, 2H). ^{13}C NMR (75 MHz, CDCl$_3$) δ_C: 14.9, 17.2, 109.3, 127.6, 128.3, 131.6, 139.2, 166.3, 185.5. LC-MS calcd. m/z 224, found 225[(M+1)]$^+$.

3,3-bis(methylthio)-1-(naphthalen-2-yl)prop-2-en-1-one[34](1b).
Yellow solid; yield 92%, mp. 96-98 °C; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ_H: 2.49 (s, 3H), 2.71 (s, 3H), 7.05 (s, 1H), 7.57-7.64 (m, 2H), 7.95 - 8.02 (m, 3H), 8.10 (d, J = 7.2Hz, 1H), 8.62 (s, 1H). ^{13}C NMR (75 MHz, CDCl$_3$) δ_C: 15.1, 17.4, 109.6, 124.3, 126.5, 127.6, 127.7, 128.4, 129.3, 132.6, 134.9, 136.6, 166.3, 185.5. LC-MS calcd. m/z 274, found 275[(M+1)]$^+$.

3,3-bis(methylthio)-1-(naphthalen-1-yl)prop-2-en-1-one[34] (1c).
Yellow solid; yield 85%, mp. 79-82 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ_H: 2.46 (s, 3H), 2.57 (s, 3H), 6.56 (s, 1H), 7.45–7.54 (m, 2H), 7.70 (d, J = 8Hz, 1H), 7.92 (d, J = 12Hz, 1H). ^{13}C NMR (75 MHz, CDCl$_3$) δ_C: 14.8, 17.1, 113.5, 124.5, 125.8, 126.0, 126.8, 128.1, 130.1, 130.7, 133.6, 138.9, 165.9, 189.3. LC-MS calcd. m/z 274, found 275[(M+1)]$^+$.

1-(4-chlorophenyl)-3,3-bis(methylthio)prop-2-en-1-one[34] (1d).
Yellow solid; yield 92%, mp. 104-106 °C; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ_H: 2.47 (s, 3H), 2.65 (s, 3H), 6.84 (s, 1H), 7.54 (d, J = 8.4 Hz, 2H), 7.97 (d, J = 8.4 Hz, 2H).^{13}C NMR (75 MHz, CDCl$_3$) δ_C: 14.9, 17.3, 108.9, 128.6, 129.0, 137.7, 183.8. * LC-MS calcd. m/z 258, found 259[(M+1)]$^+$. [*Two carbon signals have merged together].

3,3-bis(methylthio)-1-*p*-tolylprop-2-en-1-one[34] (1e).
Yellow solid; yield 82%, mp. 98-100 °C; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ_H: 2.49 (s, 3H), 2.63 (s, 3H), 2.78 (s, 1H), 6.84 (s, 1H), 7.23(d, J = 8.8 Hz, 2H), 7.64 (d, J = 8.8 Hz, 2H).^{13}C NMR (75 MHz, CDCl$_3$) δ_C: 15.0, 17.3, 55.4, 21.5, 109.6, 127.8, 129.1, 136.7, 142.3, 165.5, 185.4. LC-MS calcd. m/z 238, found 239[(M+1)]$^+$.

3,3-bis(methylthio)-1-ferrocenyl-2-propen-1-one[34] (1f).
Yellow solid; yield: 85%, mp. 112-114 ºC; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ_H: 2.42 (s, 3H), 2.60 (s, 3H), 4.16 (s, 4H), 4.50 (s, 1H), 4.83 (s, 2H), 6.41 (s, 1H). ^{13}C NMR (75 MHz, CDCl$_3$) δ_C: 14.9, 17.4, 69.0, 69.8, 71.6, 81.6, 111.3, 160.9, 189.3. LC-MS calcd. m/z, found [(M+1)]$^+$.

3,3-bis(methylthio)-1-pyrenyl-2-propen-1-one[33] (1g).
Yellow solid; yield: 80% yield, mp. 150-152 °C; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ_H: 2.56 (s, 3H), 2.61 (s, 3H), 6.82 (s, 1H), 7.35 (s, 1H), 8.13 (t, J = 8 Hz, 1H), 8.22 - 8.29 (m, 3H), 8.33 - 8.38 (m, 4H), 8.63(d, J = 9.2Hz, 1H) ^{13}C NMR (100 MHz, CDCl$_3$) δ_C: 15.0, 17.3, 114.2, 124.2, 124.8, 124.9, 125.5, 126.2, 127.1, 128.3, 128.5, 128.7, 128.8, 130.6, 132.7, 135.7, 189.6 *. LC-MS calcd. m/z 348, found 349[(M+1)]$^+$. [*Two carbon signals have merged together].

3,3-bis(methylthio)-1-(3-nitrophenyl)prop-2-en-1-one[38] (1h).
Yellow solid; yield: 80%, M.pt. 110-112 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ_H: 2.57 (s, 3H), 2.62 (s, 3H), 6.74 (s, 1H), 7.64 (t, J = 8Hz, 1H), 8.26 (d, J = 8Hz, 1H), 8.35 (d, J = 8Hz, 1H), 8.71 (s, 1H). ^{13}C NMR (75 MHz, CDCl$_3$) δ_C: 14.5, 16.8, 107.3, 121.7, 125.3, 128.9, 132.9, 140.1, 147.6, 169.6, 181.9. LC-MS calcd. m/z 269, found 270[(M+1)]$^+$.

1-(3-methoxyphenyl)-3,3-bis(methylthio)prop-2-en-1-one[38] (1i).
Yellow solid; yield 84%, mp. 88-90 ºC; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ_H: 2.49 (s, 3H), 2.65 (s, 3H), 3.80 (s, 3H), 6.83 (s, 1H), 7.13 (d, J = 8 Hz, 1H), 7.41 (t, J = 8 Hz, 2H), 7.54 (d, J = 8Hz, 1H). ^{13}C NMR (75 MHz, CDCl$_3$) δ_C: 14.9, 17.3, 55.3, 109.4, 112.4, 117.9, 119.9, 129.3, 140.7, 159.7, 166.5, 185.2. LC-MS calcd. m/z 254, found 255[(M+1)]$^+$.

1-(2-fluorophenyl)-3,3-bis(methylthio)prop-2-en-1-one[38] (1j).
Yellow solid; yield: 84%, mp. 70-72 °C. ^{1}H NMR (400 MHz, DMSO-d$_6$) δ_H: 2.50 (s, 3H), 2.58 (s, 3H), 6.66 (s, 1H), 7.28 - 7.33 (m, 2H), 7.55-7.61 (m, 1H), 7.75 (t, J = 8Hz, 1H).^{13}C NMR (75 MHz, CDCl$_3$) δ_C: 15.1, 17.3, 113.2, 113.3, 116.0, 116.3, 124.4, 127.5, 127.7, 131.2, 132.9, 133.1, 158.8, 162.1, 167.0, 182.3. LC-MS calcd. m/z 242, found 243[(M+1)]$^+$.

3,3-bis(methylthio)-1-(3-(trifluoromethyl)phenyl)prop-2-en-1-one[38] (1k).
Yellow solid; yield: 85%, mp. 88-90 °C; ^{1}H NMR (400 MHz,

DMSO-d$_6$) δ_H: 2.49 (s, 3H), 2.68 (s, 3H), 6.90 (s, 1H), 7.74 (t, J = 8 Hz, 1H), 7.92 (d, J = 8 Hz, 1H), 8.18 (s, 1H), 8.28 (d, J = 7.6 Hz, 1H). ^{13}C NMR (75 MHz, CDCl$_3$) δ_C: 15.0, 17.3, 108.4, 124.4, 128.0, 128.9, 130.7, 131.1, 139.9, 168.8, 183.7. LC-MS calcd. m/z 292, found 293[(M+1)]$^+$.

1-(4-bromophenyl)-3,3-bis(methylthio)prop-2-en-1-one[39] (1l).
Yellow solid; yield: 80%, mp. 100-104 °C; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ_H: 2.50 (s, 3H), 2.66 (s, 3H), 6.84 (s, 1H), 7.69 (d, J = 8.8 Hz, 1H), 7.91 (d, J = 8.4 Hz, 1H).^{13}C NMR (75 MHz, CDCl$_3$) δ_C: 14.4, 16.8, 108.3, 125.8, 129.0, 131.1, 137.5, 167.1, 183.2 *. LC-MS calcd. m/z 303, found 304[(M+1)]$^+$. [*Two carbon signals have merged together].

1-(4-methoxyphenyl)-3,3-bis(methylthio)prop-2-en-1-one[39] (1m).
Yellow solid; yield: 80%, mp. 100-102 °C; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ_H: 2.45 (s, 3H), 2.63 (s, 3H), 3.82 (s, 1H), 6.84 (s, 1H), 7.00 (d, J = 8.8 Hz, 2H), 7.94 (d, J = 8.8 Hz, 2H).^{13}C NMR (75 MHz, CDCl$_3$) δ_C: 15.1, 17.3, 55.4, 109.8, 113.7, 129.4, 132.2, 162.6, 164.6, 184.6 *. LC-MS calcd. m/z 254, found 255[(M+1)]$^+$. [* Two carbon signals have merged together].

1-(2,4-dichlorophenyl)-3,3-bis(methylthio)prop-2-en-1-one[40] (1n).
Yellow solid; yield: 82%, mp. 108-110 °C; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ_H: 2.49 (s, 3H), 2.54 (s, 3H), 6.44 (s, 1H), 7.50 (d, J = 9.2 Hz, 1H), 7.58 (d, J = 8 Hz, 1H), 7.68 (s, 1H).^{13}C NMR (75 MHz, CDCl$_3$) δ_C: 15.0, 17.2, 112.5, 127.2, 129.9, 130.8, 131.7, 136.2, 138.8, 167.7, 184.9. LC-MS calcd. m/z 293, found 294[(M+1)]$^+$.

1-(3,4-difluorophenyl)-3,3-bis(methylthio)prop-2-en-1-one (1o).
Yellow solid; yield: 83%, mp. 137 °C; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ_H: 2.49 (s, 3H), 2.68 (s, 3H), 6.81 (s, 1H), 7.43- 7.48 (m, 1H), 7.65 (d, J = 6.8 Hz, 1H). ^{13}C NMR (75 MHz, CDCl$_3$) δ_C: 15.0, 17.3, 106.7, 108.1, 110.3, 110.7, 142.5, 161.1, 161.3, 164.4, 164.6, 169.5, 182.3. LC-MS calcd. m/z 260 found 261[(M+1)]$^+$. HRMS (ESI-TOF) calcd for $C_{11}H_{10}F_2OS_2Na$ [M + Na]$^+$ 283.0039 found 283.0034.

1-(3,4-dichlorophenyl)-3,3-bis(methylthio)prop-2-en-1-one (1p).
Yellow solid; yield: 79%, mp. 118-120 °C; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ_H: 2.48 (s, 3H), 2.67 (s, 3H), 6.83 (s, 1H), 7. 73 (d, J = 8.4 Hz, 1H), 7.93 (d J = 8.4 Hz, 1H), 8.14 (s, 1H).^{13}C NMR (75 MHz, CDCl$_3$) δ_C: 15.1, 17.4, 108.1, 126.7, 129.6, 130.4, 132.8, 135.9, 138.9, 168.9, 182.6. LC-MS calcd. m/z 293, found 294[(M+1)]$^+$. HRMS (ESI-TOF) calcd for $C_{11}H_{10}Cl_2OS_2Na$ [M + Na]$^+$ 314.9448 found 314.9440.

1-(3-bromophenyl)-3,3-bis(methylthio)prop-2-en-1-one (1q).
Yellow solid; yield: 84%, mp. 78-80 °C; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ_H: 2.48 (s, 3H), 2.67 (s, 3H), 6.83 (s, 1H), 7.46 (t, J = 8 Hz, 1H), 7.75 (d, J = 8 Hz, 1H), 7.96 (d, J = 7.6 Hz, 1H), 8.07 (s, 1H). ^{13}C NMR (75 MHz, CDCl$_3$) δ_C: 15.1, 17.5, 108.7, 122.7, 126.3, 130.1, 130.8, 134.5, 141.3, 168.3, 183.9. LC-MS calcd. m/z 303, found 304[(M+1)]$^+$. HRMS (ESI-TOF) calcd for $C_{11}H_{11}BrOS_2Na$ [M + Na]$^+$ 324.9332 found 324.9326.

3,3-bis(methylthio)-1-(2-(trifluoromethyl)phenyl)prop-2-en-1-one (1r)
Pale yellow solid; yield: 84%, mp. 108-110 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ_H: 2.46 (s, 3H), 2.54 (s, 3H), 6.26 (s, 1H), 7.27-7.61 (m, 3H), 7.69 (d, J = 8Hz, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ_C: 16.9, 19.1, 78.6, 79.0, 79.4, 114.1, 128.2, 128.3, 129.1, 130.1, 131.3, 133.7, 143.4, 169.8, 189.5. LC-MS calcd. m/z 292, found 293[(M+1)]$^+$. HRMS (ESI-TOF) calcd for $C_{12}H_{11}F_3OS_2Na$ [M + Na]$^+$ 315.0101 found 315.0093

1-(2-fluoro-5-(trifluoromethyl)phenyl)-3,3-bis(methylthio)prop-2-en-1-one (1s).
Yellow solid; yield: 70%, mp. 88-90 °C; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ_H: 2.51 (s, 3H), 2.58 (s, 3H), 6.66 (s, 1H), 7.57 (t, J = 9.2 Hz, 1H), 7.95 - 8.02 (m, 1H). ^{13}C NMR (75 MHz, CDCl$_3$) δ_C: 15.3, 17.4, 112.4, 117.1, 119.4, 124.8, 126.3, 127.5, 128.2, 129.2, 129.9, 160.8, 163.3, 169.6, 180.4. LC-MS calcd. m/z 310, found 311[(M+1)]$^+$. HRMS (ESI-TOF) calcd for $C_{12}H_{10}F_4OS_2Na$ [M + Na]$^+$ 333.0007 found 333.0003

1-(4-iodophenyl)-3,3-bis(methylthio)prop-2-en-1-one (1t).
Yellow solid; yield: 77%, mp. 88-90 °C; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ_H: 2.49 (s, 3H), 2.64 (s, 3H), 6.82 (s, 1H), 7.73 (d, J = 8 Hz, 1H), 7.86 (d, J = 8 Hz, 1H). ^{13}C NMR (75 MHz, CDCl$_3$) δ_C: 15.1, 17.4, 99.1, 108.7, 128.0, 129.3, 137.7, 138.7, 167.7, 184.68* LC-MS calcd. m/z 350, found 351[(M+1)]$^+$. HRMS (ESI-TOF) calcd for $C_{11}H_{11}IOS_2Na$ [M + Na]$^+$ 372.9194 found 372.9190. [*Two carbon signals have merged together].

1-(2-fluoro-4-(trifluoromethyl)phenyl)-3,3-bis(methylthio)prop-2-en-1-one (1u).
Yellow solid; yield: 72%, mp. 84-86 °C; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ_H: 2.51 (s, 3H), 2.57 (s, 3H), 6.63 (s, 1H), 7.67 (d, J = 8 Hz, 1H), 7.79 (d, J = 10.4 Hz, 1H), 7.92 (t, J = 8 Hz, 1H). ^{13}C NMR (75 MHz, CDCl$_3$) δ_C: 15.2, 17.4, 112.4, 113.8, 113.9, 114.0, 121.3, 121.4, 121.5, 124.3, 130.7, 132.2, 134.3, 134.7, 158.6, 161.2, 169.6, 180.7. LC-MS calcd. m/z 310, found 311[(M+1)]$^+$. HRMS (ESI-TOF) calcd for $C_{12}H_{10}F_4OS_2Na$ [M + Na]$^+$ 333.0007 found 333.0001.

1-(4-chloro-3-(trifluoromethyl)phenyl)-3,3-bis(methylthio)prop-2-en-1-one (1v).
Yellow solid; yield: 77%, mp. 126-128 °C; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ_H: 2.49 (s, 3H), 2.68 (s, 3H), 6.88 (s, 1H), 7.85 (d, J = 8 Hz, 1H), 8.25 (s, 1H), 8.29 (d, J = 8 Hz, 1H). ^{13}C NMR (75 MHz, CDCl$_3$) δ_C: 15.2, 17.5, 107.9, 121.2, 123.9, 126.8, 126.9, 128.5, 128.8, 131.7, 135.0, 135.6, 137.9, 169.8, 182.7. LC-MS calcd. m/z 326, found 327[(M+1)]$^+$. HRMS (ESI-TOF) calcd for $C_{12}H_{10}ClF_3OS_2Na$ [M + Na]$^+$ 348.9711 found 348.9708.

2. General method for the synthesis of (*E*)-aryl 1*H*-benzo[d]-benzimidazole (4a-v).

Method I (Conventional heating method). To the mixture of AKDTA **1** (1mmol), *o*-phenylenediamine **2** (1mmol), acetic acid (40 mol %) in water (6ml) was added and heated at 100 ºC for 2h.

The reaction mixture was treated with sodium bicarbonate and extracted with ethyl acetate. The combined ethylacetate extracts were washed with water, dried and concentrated under rotary vacuum evaporation. The crude residue was recrystallized to obtain pure solid product **4a-v** (80-95% yields).

Method II (Microwave irradiation method). A 10 ml glass vial sealed by septum, containing a mixture of AKDTA **1** (1mmol) *o*-phenylenediamine **2** (1mmol), and acetic acid (40 mol %) in water (6ml) was placed in microwave synthesizer. The vial was then subjected to microwave irradiation programmed at 120W, 100 ºC with 1bar pressure. After completion of the reaction (5min), the vial was cooled to room temperature and extracted with ethyl acetate and the crude was purifed by recrystallization in ethanol to yield pure **4a-v** (78-90%).

2-phenyl-1*H*-benzo[*d*]imidazole[41] (4a)

Off white crystalline solid; yield: 95% (thermal), 90% (MW), mp. 296 ºC. UV λ_{max} (MeOH) = 241 nm (log ε = 2.39), 202 nm (log ε = 2.61), ^{1}H NMR (400MHz, DMSO-d$_6$) δ_H: 7.15-7.22 (m, 2H), 7.46-7.75 (m, 4H), 7.65 (d, *J* = 7.6Hz, 1H,), 8.16 (d, *J* = 6.8Hz, 2H), 12.86 (s, 1H).^{13}C NMR (75MHz, DMSO-d$_6$) δ_C: 111.3, 118.9, 121.7, 122.5, 126.4, 128.9, 129.8, 130.2, 135.0, 143.8, 151.2. LC-MS calcd. m/z: 194, found 195 [(M+1)]$^+$.

2-(naphthalene-2-yl)1*H*-benzo[*d*]imidazole[42] (4b)

Off white solid; yield: 92% (thermal), 90% (MW), mp. 214-215 ºC. UV λ_{max} (MeOH) = 316 nm (log ε = 2.75), 281 nm (log ε = 2.65), 241 nm (log ε = 2.88). ^{1}H NMR (400MHz, DMSO-d$_6$) δ_H: 7.19-7.23 (m, 2H), 7.54-7.69 (m, 4H), 7.97-8.08 (m, 3H), 8.30 (d, *J* = 8.4Hz, 1H), 8.72 (s, 1H), 13.03 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d$_6$) δ_C: 129.0, 131.1, 131.6, 131.8, 132.7, 133.3, 133.3, 137.9, 138.6, 156.7. * LC-MS calcd.m/z: 244 found 245[(M+1)]$^+$. [*Two carbon signals have merged together].

2-(naphthalene-1-yl)1*H*-benzo[*d*]imidazole[41] (4c)

Off white solid; yield: 93% (thermal), 87% (MW), mp 270-272 ºC; UV λ_{max} (MeOH) = 306nm (log ε = 2.58), 226 nm (log ε = 2.88), ^{1}H NMR (400MHz, DMSO-d$_6$) δ_H: 7.22 - 7.26 (m, 2H), 7.58-7.68 (m, 5H), 7.80-8.04 (m, 2H), 8.08 (d, *J* = 8.4Hz, 1H), 9.10 (d, *J* = 7.6Hz, 1H), 12.92 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d$_6$) δ_C: 122.4, 125.5, 126.6, 126.8, 127.3, 128.3, 128.7, 130.4, 131.1, 134.0, 151.8. LC-MS calcd.m/z: 244, found 245 [(M+1)]$^+$.

2-(4-chlorophenyl)1*H*-benzo[*d*]imidazole[41] (4d)

Off white solid; yield: 88% (thermal), 82% (MW), mp. 290-292 ºC; UV (MeOH) λ_{max} = 307 nm (log ε = 2.77), 245 nm (log ε = 2.45). ^{1}H NMR (400MHz, DMSO-d$_6$) δ_H: 7.20 (s, 2H), 7.52 (d, *J* = 6.8Hz, 1H), 7.61(d, *J* = 8.8Hz, 2H), 7.66 (s, 1H), 8.17 (d, *J* = 8.4Hz, 2H), 12.94 (s, 1H). ^{13}C NMR (75MHz, DMSO-d$_6$) δ_C: 122.5, 128.3, 129.1, 129.3, 135.3, 150.7*. LC-MS calcd.m/z: 228, found 229 [(M+1)]$^+$ [*Two carbon signals have merged together].

2-*p*-tolyl-1*H*-benzo[*d*]imidazole[41] (4e)

Off white solid; yield: 87% (thermal), 82% (MW), mp. 275-277 ºC; UV λ_{max} (MeOH) = 304nm (log ε = 2.77), 243 nm (log ε = 2.53). ^{1}H NMR (400MHz, DMSO-d$_6$) δ_H: 7.13 - 7.20 (m, 2H), 7.34 (d, *J* = 8Hz, 2H), 7.49 (d, *J* = 6.4Hz, 1H), 7.62 (d, *J* = 7.6Hz, 1H), 8.05 (d, *J* = 8Hz, 2H), 12.76 (s, 1H). ^{13}C NMR (75MHz, DMSO-d$_6$) δ_C: 22.0, 112.8, 127.4, 128.4, 130.3, 140.4, 152.5*. LC-MS calcd.m/z: 208, found 209 [(M+1)]$^+$. [*Two carbon signals have merged together].

2-(ferrocenyl-2-yl)1*H*-benzo[*d*]imidazole[43] (4f)

Off white solid; yield: 88% (thermal), 83% (MW), mp. 300 ºC; UV λ_{max} (MeOH) = 304 nm (log ε = 2.70), 206 nm (log ε = 2.93). ^{1}H NMR (400MHz, DMSO-d$_6$) δ_H: 4.08 (s, 4H), 4.45 (s, 2H),5.02 (s, 2H), 7.08-7.15 (m, 2H), 7.42 (d, *J* = .8Hz, 1H), 7.52 (d, *J* = 7.6Hz, 1H), 12.30 (s, 1H) ^{13}C NMR (100MHz, DMSO-d$_6$) δ_C: 60.7, 69.8, 70.2, 74.8, 110.9, 118.4, 121.8, 153.4. LC-MS calcd.m/z: 303, found 304 [(M+1)]$^+$.

2-(pyren-2-yl)1*H*-benzo[*d*]imidazole (4g)

Off white solid; yield: 90% (thermal), 87% (MW), mp. 300 ºC; UV λ_{max} (MeOH) = 351 nm (log ε = 3.51), 278 nm (log ε = 2.69), 241 nm (log ε = 2.87). IR (KBr): 3423, 3043, 1743, 1649, 1421, 1278, 1018, 842, 746 cm^{-1}. ^{1}H NMR (400MHz, DMSO-d$_6$) δ_H: 7.26-7.28 (m, 2H), 7.71-7.74 (m, 2H). 8.20 (t, *J* = 7.6Hz, 1H), 8.27-8.37 (m, 3H), 8.45 (d, *J* = 8Hz, 1H), 8.56 (d, *J* = 8Hz, 1H), 9.51(d, *J* = 9.2Hz, 1H), 13.13 (s, 1H).^{13}C NMR (100MHz, DMSO-d$_6$) δ_C: 122.6, 124.2, 124.8, 125.1, 125. 3, 126.0, 126.1, 126.4, 127.1, 127.8, 128.9, 129.1, 130.8, 131.4, 132.0. LC-MS calcd.m/z: 318, found 319 [(M+1)]$^+$. HRMS (ESI-TOF) calcd for $C_{23}H_{16}N_2Na$ [M + Na]$^+$ 343.1211 found 343.1208.

2-(3-nitrophenyl)1*H*-benzo[*d*]imidazole[44] (4h).

Off white solid; yield: 89% (thermal), 82% (MW), mp. 208-210 ºC; UV λ_{max} (MeOH) = 306 nm (log ε = 2.64), 245 nm (log ε = 2.52),.^{1}H NMR (400MHz, DMSO-d$_6$) δ_H: 7.20-7.28 (m, 2H), 7.57 (d, *J* = 7.6Hz, 1H), 7.71 (d, *J* = 8Hz, 1H), 7.85 (t, *J* = 8Hz, 1H), 8.32 (d, *J* = 8.4Hz, 1H), 8.60 (d, *J* = 8Hz, 1H), 9.00 (s, 1H), 13.25 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d$_6$) δ_C: 111.8, 119.5, 121.3, 122.3, 123.4, 124.1, 130.4, 132.2, 132.7, 135.4, 143.9, 148.6, 149.4. LC-MS calcd.m/z: 239, found 240 [(M+1)]$^+$.

2-(3-methoxyphenyl)1*H*-benzo[*d*]imidazole[45] (4i)

Off white solid; yield: 88% (thermal), 83% (MW), mp. 210-212 ºC; UV λ_{max} (MeOH) = 306 nm (log ε = 2.74), 210 nm (log ε = 2.91). ^{1}H NMR (400MHz, DMSO-d$_6$) δ_H: 3.85 (s, 3H), 7.03-7.06 (m, 1H), 7.19 (s, 2H), 7.44 (t, *J* = 8.4Hz, 1H), 7.53 (s, 1H), 7.64 (s, 1H), 7.73-7.75 (m, 2H), 12.84 (s, 1H).^{13}C NMR (100MHz, DMSO-d$_6$) δ_C: 55.8, 111.9, 116.3, 119.2, 122.6 130.6, 131.9, 151.6, 160.1*. LC-MS calcd.m/z: 224, found 225 [(M+1)]$^+$. [*Two carbon signals have merged together].

2-(2-fluorophenyl)1*H*-benzo[*d*]imidazole (4j)

Off white solid; yield: 82% (thermal), 79% (MW), mp. 205-206 ºC; UV λ_{max} (MeOH) = 303 nm (log ε = 2.87), 206 nm (log ε = 3.02). IR (KBr): 3425, 2854, 1739, 1423, 1018, 748 cm^{-1}. ^{1}H NMR (400MHz, DMSO-d$_6$) δ_H: 7.12-7.25 (m, 2H), 7.36-7.45 (m, 2H), 7.52-7.58 (m, 2H), 7.68 (d, *J* = 7.2Hz, 1H), 8.23 (t, *J* = 8Hz, 1H), 12.53 (s, 1H). ^{13}C NMR (75MHz, DMSO-d$_6$) δ_C: 115.9, 116.3, 117.3, 117.5, 125.1, 125.1, 130.1, 130.1, 131.5, 131.6, 131.6, 146.9, 158.6, 161.9. LC-MS calcd.m/z: 212, found 213

$[(M+1)]^+$ HRMS (ESI-TOF) calcd for $C_{13}H_9FN_2Na$ $[M + Na]^+$ 235.0647 found 235.0641.

2-(3-(trifluoromethyl)phenyl)1*H*-benzo[*d*]imidazole[46] (4k)

Off white solid; yield: 84% (thermal), 80% (MW), mp. 206-208 ºC; UV λ_{max} (MeOH) = 306 nm (log ε = 2.77), 206 nm (log ε = 2.90). ^{1}H NMR (400MHz, DMSO-d_6) δ_H: 7.19-7.26 (m, 2H), 7.56 (d, *J* = 7.6Hz, 1H), 7.69 (d, *J* = 7.2Hz, 1H) 7.77-7.85 (m, 2H), 8.46 (d, *J* = 7.6Hz, 1H), 8.51 (s, 1H), 13.12 (s, 1H).^{13}C NMR (75MHz, DMSO-d_6) δ_C: 111.4, 119.3, 122.2, 123.1, 123.6 126.0, 129.4, 130.0, 130.7, 131.1, 131.4, 135.2, 150.3. LC-MS calcd.m/z: 262, found 263 $[(M+1)]^+$.

2-(4-bromophenyl)1*H*-benzo[*d*]imidazole[44] (4l)

Off white solid; yield: 90% (thermal), 85% (MW), mp. 296-298 ºC; UV λ_{max} (MeOH) 308 nm (log ε = 2.72), 246 nm (log ε = 2.46),.^{1}H NMR (400MHz, DMSO-d_6) δ_H: 7.16-7.24 (m, 2H), 7.52 (d, *J* = 7.2Hz, 1H), 7.65 (d, *J* = 7.6Hz, 1H), 7.75 (d, *J* = 8.4Hz 2H), 8.10 (d, *J* = 8.4Hz, 2H), 12.94 (s, 1H).^{13}C NMR (75 MHz, DMSO-d_6) δ_C: 122.6, 123.8, 128.6, 129.7, 132.0, 150.8. * LC-MS calcd.m/z: 212, found 213 $[(M+1)]^+$.[*Two carbon signals have merged together].

2-(4-methoxyphenyl)1*H*-benzo[*d*]imidazole[44] (4m)

Off white solid; yield: 90% (thermal), 88% (MW), mp. 225-226 ºC; UV λ_{max} (MeOH) = 307nm (log ε = 2.82), 248 nm (log ε = 2.52), ^{1}H NMR (400MHz, DMSO-d_6) δ_H: 3.82 (s, 3H), 7.09 (d, *J* = 8.8Hz, 2H), 7.14-7.15 (m, 2H), 7.46-7.59 (m, 2H), 8.09 (d, *J* = 8.8Hz, 2H), 12.68 (s, 1H).^{13}C NMR (75MHz, DMSO-d_6) δ_C: 14.6, 122.1, 123.2, 128.4, 151.9, 161.0 *. LC-MS calcd.m/z: 224, found 225 $[(M+1)]^+$.[*Two carbon signals have merged together].

2-(2,4-dichlorophenyl)1*H*-benzo[*d*]imidazole[47] (4n)

Off white solid; yield: 85% (thermal), 81% (MW), mp. 216-218 ºC; UV λ_{max} (MeOH) = 296 nm (log ε = 2.56), 207 nm (log ε = 2.95). ^{1}H NMR (400MHz, DMSO-d_6) δ_H: 7.23-7.24 (m, 2H), 7.59-7.62 (m, 3H), 7.82 (s, 1H), 7.93 (d, *J* = 8.4Hz, 1H), 12.72 (s, 1H).^{13}C NMR (75MHz, DMSO-d_6) δ_C: 127.4, 132.2, 133.5, 134.3, 137.6, 137.8, 140.5, 153.2. * LC-MS calcd.m/z: 262, found 263$[(M+1)]^+$.[*Two carbon signals have merged together].

2-(3,4-difluorophenyl)1*H*-benzo[*d*]imidazole (4o)

Off white solid; yield: 84% (thermal), 78% (MW), mp. 230 ºC; UV λ_{max} (MeOH) = 306 nm (log ε = 2.69), 242 nm (log ε = 2.39). IR (KBr): 3445, 3300, 1620, 1400, 1200, 1080, 760 cm^{-1}. ^{1}H NMR (400MHz, DMSO-d_6) δ_H: 7.19-7.28(m, 2H), 7.36-7.40 (m ,1H), 7.55 (d, *J* = 8Hz, 1H), 7.68 (d, *J* = 7.6Hz, 1H), 7.84 (d, *J* = 7.4Hz, 2H), 13.05 (s, 1H).^{13}C NMR (75MHz, DMSO-d_6) δ_C: 104.9, 105.2, 105.6, 109.6, 109.9, 111.9, 119.6, 122.5, 123.5, 133.8, 133.9, 134.1, 135.3 143.9, 149.3, 161.4, 161.6, 164.7, 164.88. LC-MS calcd.m/z: 230, found 231 $[(M+1)]^+$.HRMS (ESI-TOF) calcd for $C_{13}H_8F_2N_2Na$ $[M + Na]^+$ 253.0553 found 253.0548.

2-(3,4-dichlorophenyl)1*H*-benzo[*d*]imidazole (4p)

Off white crystalline solid; yield: 83% (thermal), 80% (MW), mp. 235 ºC; UV λ_{max} (MeOH) = 294 nm (log ε = 2.60), 205 nm (log ε = 2.90). IR (KBr): 3439, 3380, 1590, 1590, 1312, 1020, 800 cm^{-1}. ^{1}H NMR (400MHz, DMSO-d_6) δ_H: 7.23 (t, *J* = 8.4Hz, 2H), 7.54 (d, *J* = 7.2Hz, 1H), 7.67 (d, *J* = 7.6Hz, 1H), 7.83 (d, *J* = 8.4Hz, 1H), 8.14 (d, *J* = 8.8Hz, 1H), 8.38 (s, 1H), 13.05 (s, 1H). ^{13}C NMR (75MHz, DMSO-d_6) δ_C: 115.8, 122.7, 127.8, 129.2, 130.2, 132.9, 133.5, 135.5, 139.3, 148.5 *. LC-MS calcd.m/z: 263, found 264 $[(M+1)]^+$. HRMS (ESI-TOF) calcd for $C_{13}H_8Cl_2N_2Na$ $[M + Na]^+$ 284.9962 found 284.9955. [*Two carbon signals have merged together].

2-(3-bromophenyl)1*H*-benzo[*d*]imidazole[44] (4q)

Off white solid; yield: 89% (thermal), 84% (MW), mp. 262-264 ºC; UV λ_{max} (MeOH) = 306 nm (log ε = 2.79), 207 nm (log ε = 2.95). ^{1}H NMR (400MHz, DMSO-d_6) δ_H: 7.19-7.27 (m, 2H), 7.50 - 7.56 (m, 2H), 7.67 - 7.70 (m, 2H), 8.18 (d, *J* = 8Hz, 1H), 8.37 (s, 1H), 13.00 (s, 1H). ^{13}C NMR (75MHz, DMSO-d_6) δ_C: 155.0, 137.4, 137.2, 135.4, 130.2, 127.5.* LC-MS calcd.m/z: 273, found 274 $[(M+1)]^+$. [*Two carbon signals have merged together].

2-(2-(trifluoromethyl)phenyl)1*H*-benzo[*d*]imidazole[48] (4r)

White crystalline solid; yield: 83% (thermal), 79% (MW), mp. 274-276 ºC; UV λ_{max} (MeOH) = 282 nm (log ε = 2.47), 206 nm (log ε = 2.92). ^{1}H NMR (400MHz, DMSO-d_6) δ_H: 7.18 - 7.26 (m, 2H), 7.52 (d, *J* = 8Hz, 1H), 7.67 (d, *J* = 7.6Hz, 1H), 7.74-7.85 (m, 3H), 7.93 (d, *J* = 7.6Hz, 1H), 12.72 (s, 1H). ^{13}C NMR (75MHz, DMSO-d*6*) δ_C: 127.1, 131.1, 133.5, 134.5, 136.5, 137.1, 154.4.* LC-MS calcd. m/z: 262, found 263 $[(M+1)]^+$. [*Two carbon signals have merged together].

2-(2-fluoro-5-(trifluoromethyl)phenyl)1*H*-benzo[*d*]imidazole (4s)

Off white crystalline solid; yield: 80% (thermal), 78% (MW), mp. 215ºC; UV λ_{max} (MeOH) = 307 nm (log ε = 2.73), 206 nm (log ε = 2.89). IR (KBr): 3441, 3053, 2924, 1789, 1404, 1332, 1159, 752 cm $^{-1}$. ^{1}H NMR (400MHz, DMSO-d_6) δ_H: 7.24 - 7.30 (m, 2H), 7.61 (d, *J* = 7.6Hz), 7.75 (dd, *J* = 8.4Hz, *J* = 7.2Hz, 2H), 7.94 (d, *J* = 10.8Hz, 1H), 8.46 (t, *J* = 8Hz, 1H), 12.77 (s, 1H). ^{13}C NMR (75MHz, DMSO-d_6) δ_C: 105.2, 109.6, 109.9, 111.9, 119.6, 122.5, 123.5, 133.9, 134.1, 135.3, 143.9, 149.3, 161.6, 164.7. LC-MS calcd.m/z: 280, found 281 $[(M+1)]^+$. HRMS (ESI-TOF) calcd for $C_{14}H_8F_4N_2Na$ $[M + Na]^+$ 303.0521 found 303.0516.

2-(4-iodophenyl)1*H*-benzo[*d*]imidazole[49] (4t)

Off white crystalline solid; yield: 90% (thermal), 86% (MW), mp. 290-292 ºC; UV λ_{max} (MeOH) = 310 nm (log ε = 2.82), 252 nm (log ε = 2.53).^{1}H NMR (400MHz, DMSO-d_6) δ_H: 7.16-7.19 (m, 1H), 7.56-7.58 (m, 1H), 7.92 (dd, *J* = 8Hz, 8.4Hz, 2H).^{13}C NMR (75MHz, DMSO-d_6) δ_C: 96.2, 122.4, 128.6, 130.2, 137.9, 150.9*. LC-MS calcd.m/z: 320, found 321$[(M+1)]^+$.[*Two carbon signals have merged together].

2-(2-fluoro-4-(trifluoromethyl)phenyl)1*H*-benzo[*d*]imidazole (4u).

Off white solid; yield: 87% (thermal), 82% (MW), mp. 230 ºC; UV λ_{max} (MeOH) = 308 nm (log ε = 2.75), 206 nm (log ε = 2.85). IR (KBr): 3441, 3086, 1770, 1444, 1332, 1130, 740^{-1}. ^{1}H NMR (400MHz, DMSO-d_6) δ_H: 7.24-7.30 (m, 2H), 7.61 (d, *J* = 7.6Hz, 1H), 7.75 (dd, *J* = 8.4Hz, *J* = 7.2Hz, 2H), 7.94 (d, *J* = 10.8Hz,

1H), 8.46 (t, *J* = 8Hz, 1H), 12.77 (s, 1H). ^{13}C NMR (75MHz, DMSO-d_6) δ_C: 112.4, 113.8, 114.1, 119.4, 121.7, 122.4, 123.5, 131.4, 135.4, 143.2, 157.7, 161.1. LC-MS calcd.m/z: 280, found 281 [(M+1)].$^+$ HRMS (ESI-TOF) calcd for $C_{14}H_8F_4N_2Na$ [M + Na]$^+$ 303.0521 found 303.0516.

2-(4-chloro-3-(trifluoromethyl)phenyl)1*H*-benzo[*d*]imidazole (4v)

Off white solid; yield: 87% (thermal), 83% (MW), mp. 200 ºC; UV λ_{max} (MeOH) = 309 nm (log ε = 2.78), 246 nm (log ε = 2.50). IR (KBr): 3444, 3053, 1618, 1438, 1317, 1180, 743 cm $^{-1}$. ^{1}H NMR (400MHz, DMSO-d_6) δ_H: 7.20 - 7.28 (m, 2H), 7.56 (d, *J* = 7.6Hz, 1H), 7.69 (d, *J* = 8Hz, 1H), 7.92 (d, *J* = 8.4Hz, 1H), 8.44 (d, *J* = 8.4Hz, 1H), 8.61(s, 1H).13.18 (s, 1H). ^{13}C NMR (75MHz, DMSO-d_6) δ_C: 129.3, 130.6, 133.1, 133.5, 134.4, 135.7, 136.6, 137.6, 154.2. * LC-MS calcd.m/z: 296, found 297 [(M+1)] $^+$. HRMS (ESI-TOF) calcd for $C_{14}H_8ClF_3N_2Na$ [M + Na]$^+$ 319.0226 found 319.0220. [*Two carbon signals have merged together].

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