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Note

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Selective Synthesis of 2-substituted and 1,2-disubstituted Benzimidazoles Directly from Aromatic Diamines and Alcohols Catalyzed by Molecularly Defined Non-Phosphine Manganese (I) Complex.

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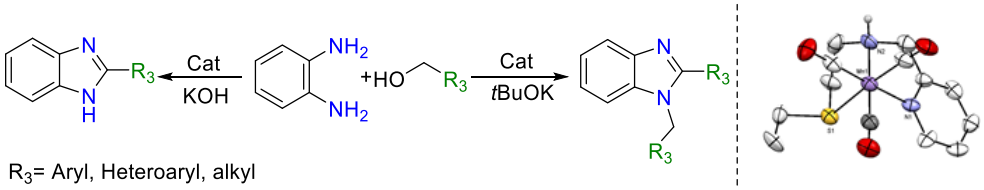
Supporting Information



ABSTRACT: Herein, we present a selective synthesis of 2-substituted and 1,2-disubstituted benzimidazoles by acceptorless dehydrogenative coupling of aromatic diamine with primary alcohols. The reaction is catalyzed by phosphine free tridentate NNS ligand derived manganese (I) complex.

Over the past few years, benzimidazoles and their derivatives have attracted significant attention due to their important biological as well as pharmacological properties.[1] Several pharmaceutically important compounds having benzimidazole core are known for their antiallergic,[2] antihistaminic,[3] anti-ulcerative,[4] antihypertensive[5] and antipyretic properties.[6] Furthermore, benzimidazole derivatives are also effective against HIV[7] and human cytomegalovirus (HCMV).[8] The classical approach to synthesize benzimidazoles is the condensation of *o*-phenylenediamine with carboxylic acids or carboxylic acid-derivatives under strong acidic conditions.[9] Another widely used strategy involves the condensation 1,2-phenelynediamine with aldehyde/alcohol in the presence of different oxidizing agents.[10] Several other different catalytic approaches to synthesize benzimidazoles are also reported.[11-14] However many of these method suffers either from the use of stoichiometric amount of oxidizing agents or expensive catalysts. Another major problem is the selectivity during the synthesis of 2-substituted and 1,2-disubstituted benzimidazoles. In recent times, acceptorless dehydrogenation strategies for synthesis of different heterocycles directly from alcohols[15] are becoming more and more important, as alcohols can be readily obtained from renewable lignocellulose.[16] Thus, the synthesis of benzimidazoles[17] directly from primary alcohol and *o*-phenylenediamine has recently attracted much attention and most of these methodologies use precious noble metals and/or acceptors.[18] One of the earliest example of such type of reaction was developed by Watanbe and coworkers.[18a] The reaction is catalyzed by ruthenium complex at elevated temperature (215 °C). Recently, Kempe and coworkers developed an elegant method to synthesize 2-substituted benzimidazoles under relatively milder condition.[18b] The reaction is catalyzed by iridium pincer complex and does not involve any acceptor. Selective synthesis of 1,2-disubstituted imidazole from diamine and alcohol catalysed by Ir(III) complexes was also accomplished recently.[18c]

The replacement of costly noble-metal catalyst by inexpensive environmentally benign earth-abundant metals is an important goal in homogenous catalysis. In the recent years, considerable efforts were made towards the development of several different de(hydrogenative) reaction methodologies using base metal complexes.[19] Although manganese is less expensive abundant and nontoxic metal, the catalytic de(hydrogenative) reactions with manganese is still in the nascent stage. The (de)hydrogenative reactions catalyzed by Mn-pincer complexes became a very important topic in the area of catalysis after the seminal works published independently by the group of Milstein, Beller, Kempe and Kirchner in 2016.[20] Subsequent to these reports a significant number of intriguing transformations catalyzed by Mn-complexes have been developed.[21]

Very recently, the formation of 2-substituted benzimidazoles catalyzed by cobalt pincer[22] complex has been reported by Milstein and co-workers. However, selective synthesis of both 2-substituted and 1,2-disubstituted benzimidazoles from 1,2-diamino benzene and alcohol using earth-abundant, nontoxic metal catalyst is highly desirable. To the best of our knowledge the synthesis of benzimidazoles directly from 1,2-diaminobenzene and alcohol catalyzed by manganese has not been reported. Herein, we describe a general and selective method to synthesize both 2-substituted and 1,2-disubstituted benzimidazoles from 1,2-diamino benzene and alcohol using non-phosphine-manganese complex. At the outset, we prepared new NNS-Manganese (I) complex (**1**) by refluxing 2-(ethylthio)-N

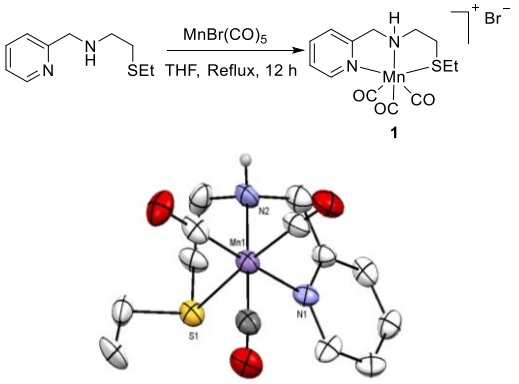
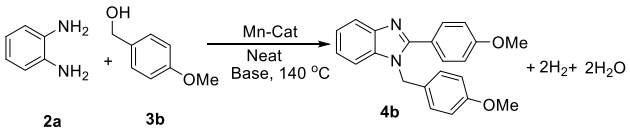


Figure 1. Synthesis of tridentate NNS ligand based manganese (I) complex and molecular structure of **1** with thermal ellipsoid 30% probability level. (all the hydrogens except N_2 and the counter ion are not shown for the clarity)

-(pyridin-2-ylmethyl)ethanamine with $MnBr(CO)_5$ in THF. Single crystal suitable for X-ray diffraction was made by layering THF solution of the complex **1** with toluene. The crystal structure of **1** is more like octahedral geometry around Mn-center, which is formed by tridentate ligand and three carbonyl groups. The crystal structure reveals that both the N atoms and the S atom are *cis* to each other and the three carbonyls are *cis* to each other (Figure 1).

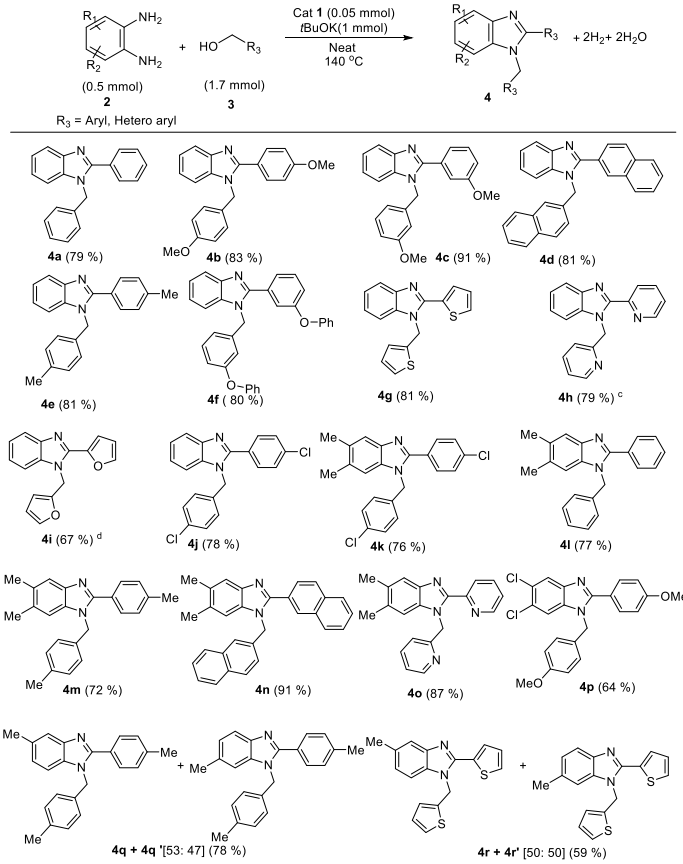
Table 1. Optimization of the reaction conditions for the synthesis of 1,2-disubstituted benzimidazole[a, b]



Entry	Cat	Base (mmol)	Time (h)	Amine : Alcohol (mmol)	% Yield [b]
1	1	tBuOK (1.2)	20	0.5 : 1.5	63
2	1	tBuOK(1.2)	20	0.5 : 1.7	71
3	1	tBuOK(1.2)	24	0.5 : 2.0	71
4	1	tBuOK (1.4)	20	0.5 : 1.7	56
5	1	tBuOK(2.0)	24	0.5 : 1.7	56
6	1	tBuOK (1.0)	20	0.5 : 1.7	83
7	1	tBuOK (0.75)	20	0.5 : 1.7	42
8[c]	1	tBuOK (1.0)	20	0.5 : 1.7	55
9[d]	1	tBuOK (1.0)	24	0.5 : 1.7	-
10	-----	tBuOK (1.0)	20	0.5 : 1.7	-
11	1	-----	20	0.5 : 1.7	-
12	1	KOH (1.0)	20	0.5 : 1.7	61
13	1	K_2CO_3 (1.0)	20	0.5 : 1.7	-
14	$MnBr(CO)_5$	tBuOK (1.0)	20	0.5 : 1.7	-

[a]Reaction conditions: **2a** (0.5 mmol), 3**b** (1.5-2.0 mmol), *t*BuOK (0.75-2.0 mmol), Cat **1** (0.05 mmol), under argon. [b]NMR yield using CH_3CN as internal standard. [c]0.025 mmol cat used. [d]80 °C

Table 2. Scope of the reaction to synthesize 1,2-disubstituted benzimidazole [a, b]

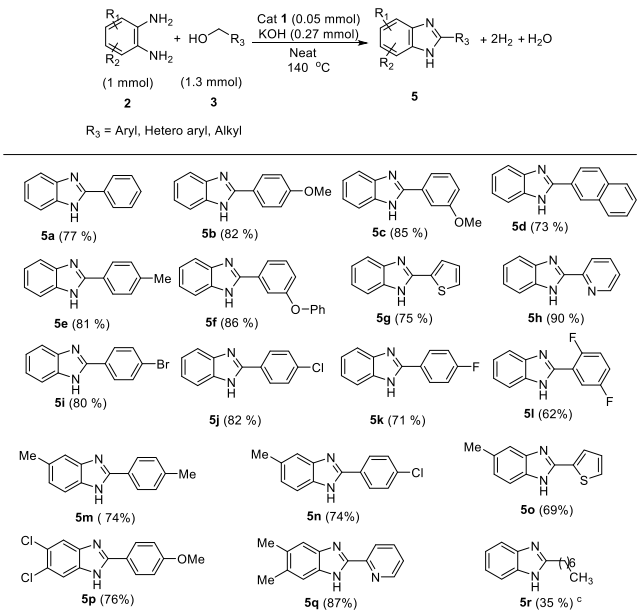


[a]Reaction conditions: Diamine **2** (0.5 mmol), alcohol **3** (1.7 mmol), *t*BuOK (1 mmol), Cat **1** (0.05 mmol), 20 h, under argon, [b]Isolated yield, [c]44 h, [d]26 h

The catalytic applicability of complex **1** towards the synthesis of 1,2-disubstituted benzimidazole, directly from 1,2-phenylenediamines and alcohols has been investigated. To find out the optimum conditions, the reaction between 1,2-phenylenediamine and 4-methoxybenzylalcohol was studied under neat condition. It was found that the particular ratio of base and substrate and specific ratio of amine and alcohol is important for good yield of the desired products. Potassium tert-butoxide was found to be more effective base than KOH or K_2CO_3 (Table 1 entries 6, 12 and 13). $MnBr(CO)_5$ gave only trace amount of the desired product under the similar reaction conditions. The control experiments were also performed and it was observed that in the absence of catalyst, no desired product was obtained and similarly without the presence of base, complex **1** failed to give any desired product (Table 1 entries 10, 11).

Here, a wide range of 1-benzyl-2-aryl-1H-benzo[d]imidazole derivatives were also synthesized from 1,2-diaminobeznene and primary alcohol (Table 2). Differently substituted benzylic alcohols as well as 2-naphthalenemethanol reacted well with o-phenylenediamine to give good yield of the desired products. Moderate to good yield of the desired 1,2-disubstituted benzimidazoles were achieved when heterocyclic alcohols such as 2-pyridinemethanol, furfural or 2-thiophenemethanol have been employed as substrates. A small amount of bis N-alkylated

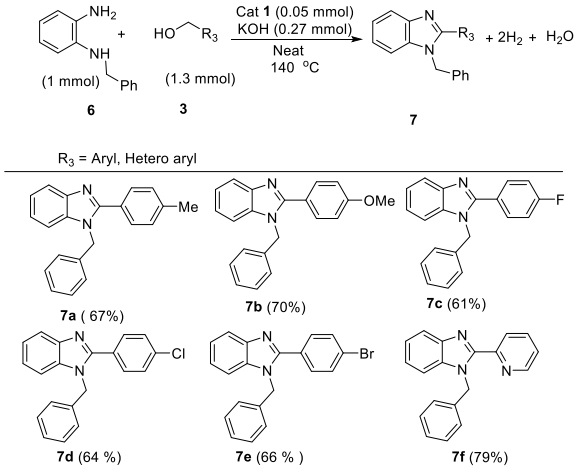
Table 3. Synthesis of 2-substituted benzimidazole [a, b]



[a]Reaction conditions: Diamine (1.0 mmol), alcohol (1.3 mmol), KOH (0.27 mmol), Cat **1** (0.05 mmol), 20 h, under air. [b]Isolated yield, [c]72 h

product of the o- phenylenediamine was also observed in some cases, which might be due to the hydrogenation of bis-imines formed *in-situ* during the reaction. Furthermore, 4,5-Dimethyl-1,2-phenylenediamine, 4,5-Dichloro-o-phenylenediamine and 3,4-diaminotoluene reacted smoothly under the optimized reaction condition. 3,4-diaminotoluene gave mixture of two isomeric 1-benzyl-2-aryl-1H-benzo[d]imidazole derivatives. It is important to note that synthesis of 2-aryl-1H-benzo[d]imidazole derivatives could also be achieved just by tuning the reaction conditions (Table 3).

Table 4. Synthesis of 1-benzyl-2-aryl-1H-benzo[d]imidazoles[a, b]

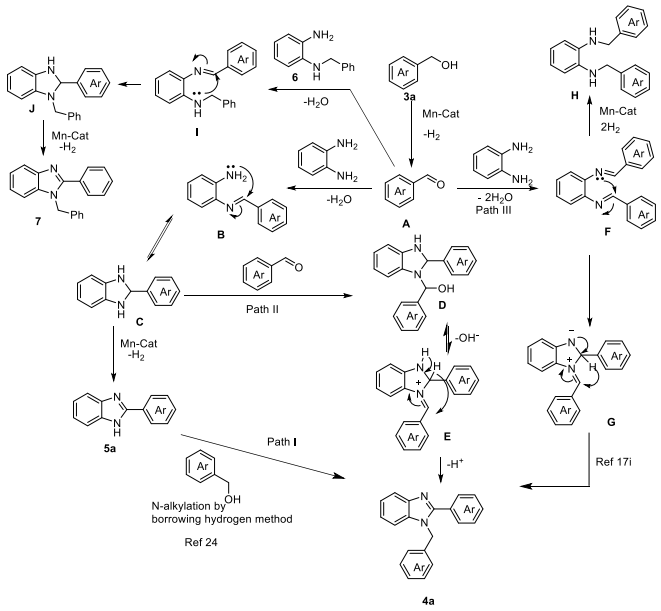


[a]Reaction conditions: N-Benzyl-1,2-diaminobenzene (1.0 mmol), alcohol (1.3 mmol), KOH (0.27 mmol), Cat **1** (0.05 mmol), 20 h, under air. [b]Isolated yield.

Excellent yield of the desired products were obtained with the benzyl alcohols having both electron donating and electron withdrawing group in the aromatic ring. For example, 4-methylbenzyl alcohol and 4-methoxybenzyl alcohol gave 81% and 82% yield of the desired benzimidazole respectively, which is even higher than the yield reported by Ru[18a] or cobalt catalyst.[22] However, the reaction is slower with aliphatic alcohols. Thus, when 1-octanol was used as substrate, 35% of the 2-ethyl-1H-benzo[d]imidazole was obtained after 72 hours. To our delight, complex **1** also able to catalyse the dehydrogenative coupling of N-Benzyl-1,2-diaminobenzene (**6**) with different benzyl alcohols to afford 1-benzyl-2-aryl-1H-benzo[d]imidazole derivatives (**7**) in good yield (Table 4).

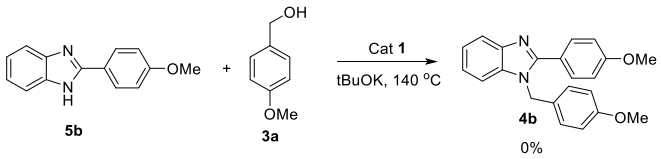
In addition, three possible mechanistic pathways are proposed which are depicted in the (Scheme 1). At first, the aldehyde was formed by the assistance of Mn-complex **1**. The diamine can react with the aldehyde **A** to form monoamine **B** which can further undergo nucleophilic addition to the imine carbon to form benzimidazoline intermediate **C**. This intermediate benzimidazoline **C** either undergoes oxidation leading to the formation of 2-substituted benzimidazole **5a** or reacts further with the aldehyde **A** to generate intermediate **D** which will finally transform to 1,2-disubstituted imidazole **4a** (Path II). There is also a possibility of N-alkylation of 2-substituted benzimidazole[23] by primary alcohol through borrowing hydrogen strategy, which will eventually transform **5a**, to **4a** (Path I). Furthermore, diamine also can lead to the formation of bis-imine **F** which undergoes rearrangement to afford 1,2-disubstituted benzimidazole (Path III).[17i]

Scheme 1. Plausible mechanistic pathway



Although the exact pathway is not fully clear at this point, yet we tried to shed light on the mechanism by controlling experiment. First of all, when 2-(4-methoxyphenyl)-1H-benzo[d]imidazole **5b** was treated with 4-methoxybenzyl alcohol **3a** in presence of Cat **1** and *t*BuOK, no N-alkylated product, 1-(4-methoxybenzyl)-2-(4-methoxyphenyl)-1H-benzo[d]imidazole **4b** was observed (Scheme 2). Thus, it is clear that the reaction is not following Path I. MS analysis of the crude reaction mixture of o-phenylenediamine and 4-methoxybenzyl alcohol after 2 h, showed peak which corresponds either to bisimine (**F**, Ar=

Scheme 2. Study of N-alkylation of 2-substituted benzimidazole By Cat 1



p-C_6H_4OMe) or 1,2 disubstituted benzimidazole **4b** (as the molecular weight of both the compound are same) while the ion peak corresponds to intermediate (**D**, Ar = p-C_6H_4OMe) was not observed. We have also isolated small amount bis-amine **H** during the synthesis of 1-benzyl-2-aryl-1H-benzo[d]imidazole derivatives which finally validate the involvement of bis-imine intermediate **F** and formation of 1,2 disubstituted imidazole derivatives via Path III.

In Summary, we have synthesized a new tridentate NNS-ligand based manganese (I) complex, which catalyzes the dehydrogenative coupling of diamine and primary alcohol to synthesize a wide range of benzimidazole derivatives. The main advantage of this methodology is 3-fold: selectively 2-substituted and 1,2 di-substituted benzimidazoles are synthesized using a single catalyst just by tuning the reaction conditions, the reactions are catalyzed by earth abundant metal and catalytic reactions are performed under phosphine free condition.

EXPERIMENTAL SECTION

General Considerations: Unless otherwise mentioned, all the chemicals were purchased from common commercial sources and used as received. All solvents were dried by using standard procedure. The preparation of catalyst was carried out under argon atmosphere with freshly distilled dry THF. All catalytic reactions were carried out with air and/or under argon atmosphere using dried glassware and standard syringe/septa techniques. DRX-400 Varian spectrometer and Bruker Avance III 600 and 400 spectrometers were used to record ^{1}H and ^{13}C NMR spectra using $CDCl_3$ and DMSO-d6 as solvent and TMS as an internal standard. Chemical shifts (δ) are reported in ppm and spin-spin coupling constant (J) are expressed in Hz, and other data are reported as follows: s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, and br s = broad singlet. X-ray crystallographic data were collected using Agilent Super Nova (Single source at offset, Eos) diffractometer. FTIR were collected on PerkinElmer IR spectrometer. Q-Tof ESI-MS instrument (model HAB 273) was used for recording mass spectra. SRL silica gel (100-200 mesh) were used for column chromatography.

Synthesis and characterization of NNS-Mn-complex 1: Ligand[24] [($PyCH_2$)HN(CH_2CH_2SEt)] (0.302g, 1.54 mmol) was taken in 4 mL dry THF and was added dropwise to the orange-yellow suspension of [$MnBr(CO)_5$] (0.423g, 1.54 mmol) in 8 mL degassed dry THF. Then, the suspension was refluxed for overnight under argon atmosphere. After cooling it down to the room temperature, the solvent was evaporated to obtain the residue, which was further washed with hexane and dried under vacuum to get yellow solid of Mn-complex **1** (yield 0.610g, 95%). The single crystal was grown by slow diffusion of toluene in the THF solution of the complex. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.69 (s, 1H), 8.26 (br s, 1H), 7.87 (br s, 1H), 7.71 (br s, 1H), 7.40 (br s, 1H), 4.81(br s, 1H), 4.58 (br s, 1H), 3.39-3.35 (m, 2H), 2.98-2.87 (m, 2H), 2.05 (br s, 2H), 1.45 (s, 3H); [25] ^{13}C NMR (150 MHz, $CDCl_3$) δ 218.92, 216.57, 161.90, 152.64, 139.58, 125.25, 122.70, 60.41, 54.57, 33.07, 31.85, 13,42. IR (cm^{-1}): 3059, 2920, 2875, 2030, 1946, 1920, 1609, 1462, 1286, 1196, 1083, 949, 910, 821, 769, 689, 637. HRMS (ESI) calcd for $C_{13}H_{16}MnN_2O_3S$ $[M]^+$: 335.0262; found, 335.0263.

General experimental procedure for the synthesis of 1,2-disubstituted benzimidazoles: A mixture of *o*-phenylenediamine (0.5 mmol), primary alcohol (1.7 mmol), KO^{t}Bu (1.0 mmol) and complex **1** (0.05 mmol) was stirred at 140 ˚C for the specified time under solvent free condition in an open system under argon. Then the reaction mixture was cooled to room temperature and was diluted with chloroform. Then it was filtered through celite and the filtrate was concentrated under vacuum. The residue obtained was further purified by column chromatography on silica gel using 10%-30 % ethyl acetate in hexane as an eluent.

General experimental procedure for the synthesis of 2-substituted benzimidazoles: A mixture of 1,2-diaminobenzene (1.0 mmol), primary alcohol (1.3 mmol), KOH (0.27 mmol) and catalyst **1** (0.05 mmol) was stirred under neat condition at 140 ˚C for 20 h in open air. After cooling, MeOH was added to dilute the mixture and filtered through celite. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography using 10% -30 % ethyl acetate in hexane as an eluent to get pure compound.

General experimental procedure for the synthesis of 1-benzyl-2-aryl-1H-benzo[d]imidazoles: A mixture of N-Benzyl-1,2-diaminobenzene (1.0 mmol), primary alcohol (1.3 mmol), KOH (0.27 mmol) and catalyst **1** (0.05 mmol) was stirred under neat condition at 140 ˚C for 20 h in open air. After cooling, $CHCl_3$ was added to dilute the mixture and then it was filtered through celite. The filtrate was concentrated under vacuum and the residue was purified by silica gel column chromatography using 10% -30 % ethyl acetate in hexane as an eluent to get pure compound.

1-Benzyl-2-phenyl-1H-benzo[d]imidazole (4a).[17a] White solid, (0.113mg, 79% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (d, J = 8.04 Hz, 1H), 7.62-7.60 (m, 2H), 7.40- 7.36 (m, 3H), 7.27-7.21 (m, 4H), 7.18-7.13 (m, 2H), 7.03 (d, J = 7.02 Hz, 2H), 5.39 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.3, 143.3, 136.5, 136.2, 130.2, 130.0, 129.4, 129.2, 128.9, 127.9, 126.1, 123.2, 122.8, 120.1, 110.7, 48.5.

1-(4-methoxybenzyl)-2-(4-methoxyphenyl)-1H-benzo[d]imidazole (4b).[17a] White solid, (0.129mg, 83% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, J = 7.98 Hz, 1H), 7.55 (d, J = 8.7 Hz, 2H), 7.22-7.18 (m, 1H), 7.15-7.12 (m, 2H), 6.94 (d, J = 8.52 Hz, 2H), 6.88 (d, J = 8.7 Hz, 2H), 6.76 (d, J = 8.7 Hz, 2H), 5.29 (s, 2H), 3.75 (s, 3H), 3.69 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.0, 159.2, 154.2, 143.2, 136.2, 130.8, 128.6, 127.3, 122.8, 122.6, 122.5, 119.8, 114.5, 114.3, 110.5, 55.5, 55.4, 48.0.

1-(3-methoxybenzyl)-2-(3-methoxyphenyl)-1H-benzo[d]imidazole (4c).[18c] White solid, (0.156mg, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 5.32Hz, 1H), 7.29-7.23 (m, 2H), 7.19-7.16 (m, 5H), 6.95-6.96 (m, 1H), 6.75 (dd, J = 7.2 Hz, 1.14 Hz, 1H), 6.62 (d, J = 5.12 Hz, 1H), 6.58 (s,1H), 5.36 (s, 2H), 3.66 (s, 3H), 3.65 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$); δ 160.3, 159.8, 154.1, 143.1, 138.3, 136.3, 131.3,

130.3, 130.0, 123.2, 122.8, 121.5, 120.1, 118.3, 116.7, 114.1, 113.0, 112.0, 110.6, 55.4, 55.3, 48.4.

2-(naphthalen-2-yl)-1-(naphthalen-2-ylmethyl)-1H-benzo[d]imidazole (4d).[17a] White solid, (0.155mg, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.88-7.75 (m, 6H), 7.67-7.63 (m, 2H), 7.49-7.39 (m, 5H), 7.30-7.16 (m, 4H), 5.59 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 143.4, 136.5, 134.1, 133.8, 133.5, 133.02, 132.9, 129.4, 129.2, 128.7, 128.7, 128.0, 127.9, 127.4, 126.8, 126.8, 126.4, 126.2, 124.9, 124.0, 123.4, 123.0, 120.2, 110.7, 48.9.

1-(4-methylbenzyl)-2-(p-tolyl)-1H-benzo[d]imidazole (4e).[17a] White solid, (0.126mg, 81% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, J = 8.04 Hz, 1H), 7.51 (d, J = 8.16 Hz, 2H), 7.23-7.21 (m, 1H), 7.19 -7.17 (m, 2H), 7.16- 7.11 (m, 2H), 7.06 (d, J = 7.92 Hz, 2H), 6.92 (d, J = 8.04 Hz, 2H), 5.33 (s, 2H), 2.33 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.5, 143.3, 140.1, 137.5, 136.2, 133.6, 129.8, 129.6, 129.3, 127.3, 126.0, 122.9, 122.7, 119.9, 110.6, 48.3, 21.6, 21.2.

1-(3-phenoxybenzyl)-2-(3-phenoxybenzyl)-1H-benzo[d]imidazole (4f).[26] Brown liquid, (0.186mg, 80% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, J = 7.98 Hz, 1H), 7.34 -7.29 (m, 2H), 7.24-7.21 (m, 6H), 7.19-7.16 (m, 1H), 7.14-7.12 (m, 2H), 7.05-7.0 (m, 3H), 6.92 (dd, J = 8.58 Hz, 1.02 Hz, 2H), 6.86 (dd, J =8.46 Hz, 1.02 Hz, 2H), 6.80 (d, J = 6.72 Hz, 1H), 6.64 (d, J = 6.84 Hz, 2H); 5.31 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$); δ 158.1, 157.9, 156.6, 153.5, 143.1, 138.3, 136.0, 131.7, 130.5, 130.3, 130.0, 129.9, 129.8, 123.9, 123.9, 123.8, 123.4, 122.9, 120.6, 120.2, 120.2, 119.4, 119.3, 119.2, 117.9, 116.3,110.6, 48.2.

2-(thiophen-2-yl)-1-(thiophen-2-ylmethyl)-1H-benzo[d]imidazole (4g).[17a] White solid, (0.121mg, 81% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, J = 7.08 Hz, 1H), 7.45 (dd, J = 5.37 Hz, 1.02 Hz, 1H), 7.40 (dd, J = 3.75 Hz, 1.02 Hz, 1H), 7.31-7.29 (m, 1H), 7.25-7.19 (m, 2H), 7.17 (dd, J = 5.1 Hz, 1.14 Hz, 1H), 7.08-7.06 (m, 1H), 6.88-6.87 (m, 1H), 6.80-6.79 (m, 1H), 5.63 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$); δ 147.7, 143.1, 138.9, 136.0, 132.0, 129.1, 128.1, 128.1, 127.4, 125.6, 125.5, 123.4, 123.1, 120.1, 110.0, 44.2.

2-(pyridin-2-yl)-1-(pyridin-2-ylmethyl)-1H-benzo[d]imidazole (4h).[17a] White solid, (0.113mg, 79% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.50 (t, J=5.02 Hz, 2H), 8.39 (d, J = 8.0 Hz, 1H), 7.80-7.74 (m, 2 H), 7.42-7.38 (dt, J = 7.74, 1.68 Hz, 1H), 7.29 (d, J = 7.92 Hz, 1H), 7.25-7.16 (m, 3H), 7.07-7.04 (m, 1H), 6.82 (d, J = 7.92 Hz, 1H), 6.22 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 150.5, 150.0, 149.3, 148.8, 142.8, 137.0, 137.0, 136.9, 124.7, 124.0, 123.8, 123.1, 122.4, 121.1, 120.2, 110.9, 51.2.

2-(furan-2-yl)-1-(furan-2-ylmethyl)-1H-benzo[d]imidazole (4i).[17a] White solid, (0.089mg, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72-7.69 (m,1H), 7.57 (d, J =0.96 Hz, 1H), 7.44-7.40 (m,1H), 7.25-7.18 (m, 3H),7.14 (d, J = 3.44 Hz, 1H), 6.54-6.53 (m, 1H), 6.21-6.16 (m, 2H), 5.57 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$); δ 149.7, 145.5, 144.1, 144.0, 143.1,142.8, 135.6, 123.4, 123.1, 119.9, 113.1, 112.2, 110.7, 110.1, 108.5, 41.8.

1-(4-chlorobenzyl)-2-(4-chlorobenzyl)-1H-benzo[d]imidazole (4*j*).[17a] White solid, (0.137mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J =7.92 Hz, 1H), 7.51 (d, J = 8.52 Hz, 2H), 7.37 (d, J = 8.52 Hz, 2H), 7.30 - 7.22 (m, 3H), 7.20-7.12 (m, 2H), 6.95 (d, J = 8.44 Hz, 2H), 5.33 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 143.2, 136.5, 136.1, 134.8, 134.0, 130.6, 129.5, 129.3, 128.5, 127.4, 123.6, 123.2, 120.3, 110.4, 47.9.

1-(4-chlorobenzyl)-2-(4-chlorophenyl)-5,6-dimethyl-1H-benzo[d]imidazole (4k).[27] White solid, (0.145mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.56 (d, J = 8.48 Hz, 2H), 7.41 (d, J = 8.48 Hz, 2H), 7.31 (d, J = 8.40 Hz, 2H), 7.01 (d, J = 8.24 Hz, 2H), 6.95 (s, 1H), 5.34 (s, 2H), 2.39 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 141.9, 136.2, 135.1, 134.7, 133.9, 132.9, 132.2, 130.5, 129.5, 129.2, 128.8, 127.3, 120.3, 110.5, 47.8, 20.7, 20.5.

1-benzyl-5,6-dimethyl-2-phenyl-1H-benzo[d]imidazole (4l).[28] White solid, (0.121mg, 77% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67-7.65 (m, 2H), 7.63 (s, 1H), 7.45-7.40 (m, 3H), 7.35-7.28 (m, 3H), 7.10 (d, J = 7.08 Hz, 2H), 6.97 (s, 1H), 5.41 (s, 2H), 2.39 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.5, 141.9, 136.8, 134.8, 132.4, 131.7, 130.4, 129.8, 129.3, 129.2, 128.8, 127.8, 126.0, 120.1, 110.7, 48.4, 20.7, 20.5.

5,6-Dimethyl-1-(4-methylbenzyl)-2-(4-methylphenyl)-1H-benzimidazole (4m).[27] White solid, (0.122mg, 72% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.55 (d, J = 8.04 Hz, 2H), 7.22 (d, J = 7.92 Hz, 2H), 7.13 (d, J = 7.86 Hz, 2H), 6.99 (d, J = 7.92 Hz, 2H), 6.96 (s, 1H), 5.36 (s, 2H), 2.39 (s, 3H), 2.38 (s, 3H), 2.34 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.6, 141.8, 139.8, 137.4, 134.8, 133.9, 132.1, 131.5, 129.8, 129.5, 129.2, 127.5, 125.9, 120.0, 110.7, 48.2, 21.5, 21.2, 20.7, 20.5.

5,6-dimethyl-2-(naphthalen-2-yl)-1-(naphthalen-2-ylmethyl)-1H-benzo[d]imidazole (4n).[28] White solid, (0.187mg, 91% yield). ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.18 (s, 1H), 7.90-7.82 (m, 5H), 7.74-7.70 (m, 3H), 7.57 (s, 1H), 7.53-7.46 (m, 4H), 7.33 (d, J = 8.46 Hz, 1H), 7.05 (s, 1H), 5.63(s, 2H), 2.42 (s, 3H), 2.33(s, 3H); ^{13}C NMR (150MHz, $CDCl_3$) δ 153.6, 142.1, 135.1, 134.4, 133.7, 133.6, 133.0, 132.9, 132.6, 131.9, 129.2, 129.1, 128.7, 128.6, 128.1, 127.9, 127.9, 127.7, 127.2, 126.7, 126.7, 126.3, 126.3, 124.7, 124.0, 120.2, 110.7, 48.8, 20.8, 20.5.

5,6-dimethyl-2-(pyridin-2-yl)-1-(pyridin-2-ylmethyl)-1H-benzo[d]imidazole (4o).[29] Orange solid, (0.137mg, 87% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.59 (d, J = 4.56 Hz, 1H), 8.53 (d, J = 4.56 Hz, 1H), 8.44 (d, J = 8.04 Hz, 1H), 7.81 (dt, J =7.83 Hz, 1.56 Hz, 1H), 7.62 (s, 1H), 7.47 (dt, J = 7.71 Hz, 1.68 Hz, 1H), 7.27-7.25 (m, 1H), 7.15-7.13 (m, 1H), 7.11 (s, 1H), 6.83 (d, J = 7.92 Hz, 1H), 6.25 (s, 2H), 2.38 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.8, 150.6, 149.2, 149.2, 148.7, 141.4, 137.0, 136.9, 135.5, 133.3, 132.1, 124.4, 123.7, 122.3, 120.9, 120.1, 110.8, 51.2, 20.8, 20.5.

5,6-dichloro-1-(4-methoxybenzyl)-2-(4-methoxyphenyl)-1H-benzo[d]imidazole (4p).[17d] White solid, (0.122mg, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.62 (d, J = 8.64 Hz, 2H), 7.28 (s, 1H), 6.99 (t, J = 8.24 Hz, 4H), 6.88 (d, J =8.52Hz, 2H), 5.34 (s, 2H), 3.86 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 159.5, 156.2, 142.7, 135.5, 130.8, 127.6, 127.2, 126.7, 126.7, 121.7, 121.0, 114.8, 114.5, 111.9, 55.6, 55.5, 48.2.

5-methyl-1-(4-methylbenzyl)-2-(p-tolyl)-1H-benzo[d]imidazole & 6-methyl-1-(4-methylbenzyl)-2-(p-tolyl)-1H-benzo[d]imidazole (4q & 4q′).[17f] White solid, (0.127mg, 78% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (d, J = 8.16 Hz, 1H), 7.63 (s, 1H), 7.58-7.55 (m, 4H), 7.25-7.22 (m, 4H), 7.15-7.11 (m, 5H), 7.07-7.02 (m, 2H), 7.00-6.98 (m, 5H), 5.36 (s, 4H), 2.48 (s, 3H), 2.42 (s, 3H), 2.39 (s, 3H), 2.39 (s,

3H), 2.34 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.3, 154.0, 143.5, 141.3, 140.0, 139.9, 137.5, 137.4, 136.5, 134.3, 133.7, 133.7, 133.0, 132.3, 129.8, 129.8, 129.5, 129.5, 129.2, 129.2, 127.4, 126.0, 125.9, 124.4, 124.3, 119.7, 119.4, 110.4, 110.1, 48.3, 48.1, 22.0, 21.7, 21.5, 21.5, 21.2, 21.2.

5-methyl-2-(thiophen-2-yl)-1-(thiophen-2-ylmethyl)-1H-benzo[d]imidazole & 6-methyl-2-(thiophen-2-yl)-1-(thiophen-2-ylmethyl)-1H-benzo[d]imidazole (4r & 4r′).[17f] Yellow solid, (0.091mg, 59% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (d, J = 8.22, 1H), 7.61 (s, 1H), 7.51-7.49 (m, 2H), 7.45-7.42 (m, 2H), 7.26-7.23 (m, 3H), 7.15-7.09 (m, 5H), 6.96-6.93 (m, 2H), 6.86-6.85 (m 2H), 5.67 (s, 2H), 5.66 (s, 2H), 2.48 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.6, 147.2, 143.4, 141.2, 139.1, 139.1, 136.2, 134.1, 133.6, 132.9, 132.1, 132.1, 128.9, 128.8, 128.0, 128.0, 127.8, 127.4, 127.3, 125.5, 125,5, 125.4, 124.9, 124.8, 119.8, 119.5, 109.8, 109.5, 44.2, 44.1, 22.1, 21.7.

1-benzyl-2-(p-tolyl)-1H-benzo[d]imidazole (7a).[17b] White solid, (0.201mg, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.0 Hz, 1H), 7.49 (d, J = 8.08Hz, 2H), 7.25-7.19 (m, 4H), 7.16 (d, J = 8.0 Hz, 2H), 7.13-7.09 (m, 2H), 7.01 (d, J = 6.84 Hz, 2H), 5.35 (s, 2H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 143.3, 140.1, 136.6, 136.2, 129.5, 129.2, 129.1, 127.8, 127.2, 126.1, 123.0, 122.7, 120.0, 110.5, 48.5, 21.5**.**

1-benzyl-2-(4-methoxyphenyl)-1H-benzo[d]imidazole (7b).[17b] White solid, (0.219mg, 70% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, J = 8.04 Hz, 1H), 7.63 (d, J = 8.82 Hz, 2H), 7.34- 7.28 (m, 4H), 7.23-7.18 (m, 2H), 7.11(d, J = 7.38 Hz, 2H), 6.96 (d, J = 8.76 Hz, 2H), 5.43 (s, 2H), 3.83 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.0, 154.2, 143.2, 136.6, 136.2, 130.7, 129.1, 127.8, 126.0, 122.8, 122.6, 122.4, 119.8, 114.3, 110.5, 55.4, 48.4.

1-benzyl-2-(4-fluorophenyl)-1H-benzo[d]imidazole (7c).[17b] White solid, (0.184mg, 61% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, J = 8.04 Hz, 1H), 7.68-7.65(m, 2H), 7.35-7.31(m, 4H), 7.26-7.22 (m, 2H), 7.14 (t, J = 8.58 Hz, 2H), 7.09 (d, J = 7.2, 2H), 5.43 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.8 (d, J=249 Hz), 153.3, 143.1, 136.3, 136.2, 131.4, 131.3, 129.3, 128.0, 126.3 (d, J=3 Hz), 126.0, 123.1 (d, J=55.5 Hz), 120.1, 116.1 (d, J=21 Hz), 110.6, 48.4.

1-benzyl-2-(4-chlorophenyl)-1H-benzo[d]imidazole (7d).[17b] White solid, (0.202mg, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 7.96 Hz, 1H), 7.55 (d, J = 8.56 Hz, 2H), 7.35 (d, J = 8.56 Hz, 2H), 7.29-7.23 (m, 4H), 7.20-7.15 (m, 2H), 7.01 (d, J = 6.52 Hz, 2H), 5.36 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 143.2, 136.3, 136.3, 136.3, 130.7, 129.3, 129.2, 128.7, 128.1, 126.0, 123.4, 123.0, 120.2, 110.6, 48.5.

1-benzyl-2-(4-bromophenyl)-1H-benzo[d]imidazole (7e).[17b] White solid, (0.240mg, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 7.96 Hz, 1H), 7.59-7.53(m, 4H), 7.36-7.30(m, 4H), 7.27-7.21(2H), 7.08 (d, J = 6.52 Hz, 2H), 5.42 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 143.2, 136.3, 132.1, 130.8, 129.3, 129.1, 128.0, 126.0, 124.6, 123.5, 123.0, 120.2, 110.6, 48.5.

1-benzyl-2-(pyridin-2-yl)-1H-benzo[d]imidazole (7f).[30] White solid, (0.226mg, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, J = 4.72 Hz, 1H), 8.33 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 8.08 Hz, 1H), 7.69 (t, J = 7.92 Hz, 1H), 7.25-7.05 (m, 9H), 6.08 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 150.0, 148.7, 142.8, 137.5, 136.9, 136.9, 128.6, 127.4, 126.9,124.7, 123.9, 123.6, 122.9, 120.2, 110.8, 49.0.

2-phenyl-1H-benzo[d]imidazole (5a).[17c] Pale yellow solid, (0.149mg, 77% yield). ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.95 (br s, 1H), 8.19 (d, J = 7.14 Hz, 2H), 7.67(d, J = 6.96 Hz, 1H), 7.57-7.54 (m, 3H), 7.50-7.48 (m, 1H), 7.23-7.19 (m, 2H), ^{13}C NMR (150 MHz, DMSO-d_6) δ 151.3, 143.8, 135.0, 130.2, 129.9, 129.0, 126.5, 122.6, 121.8, 118.9, 111.4.

2-(4-methoxyphenyl)-1H-benzo[d]imidazole (5b).[17c] White solid, (0.184mg, 82% yield). ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.76 (s, 1H), 8.11 (d, J = 8.76 Hz, 2H), 7.61 (d, J = 7.5 Hz, 1H), 7.49 (d, J = 7.5 Hz, 1H), 7.19 - 7.14 (m, 2H), 7.11(d, J = 8.76 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 160.6, 151.4, 143.9, 135.0, 128.1, 122.7, 122.2, 121.5, 118.5, 114.4, 111.1, 55.4**.**

2-(3-methoxyphenyl)-1H-benzo[d]imidazole (5c).[17c] White solid, (0.189mg, 85% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.90 (s, 1H), 7.77-7.75 (m, 2H), 7.67 (d, J = 7.44 Hz, 1H), 7.53 (d, J = 7.36 Hz, 1H), 7.46 (t, J = 7.6 Hz, 1H), 7.24-7.17 (m, 2H), 7.07-7.05 (m, 1H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.7, 151.1, 143.7, 135.0, 131.5, 130.1, 122.6, 121.7, 118.9, 118.8, 115.9, 111.4, 111.3, 55.3.

2-(naphthalen-2-yl)-1H-benzo[d]imidazole (5d).[17c] Yellow solid, (0.179mg, 73% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.08 (s, 1H), 8.75 (s, 1H), 8.32 (d, J = 8.04 Hz, 1H), 8.09-7.99 (m, 3H), 7.70 (d, J = 6.64 Hz, 1H), 7.61-7.59 (m, 3H), 7.23 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 151.3, 143.9, 135.2, 133.5, 132.8, 128.6, 128.5, 127.8, 127.62, 127.1, 126.9, 125.8, 124.0, 122.7, 121.8, 118.9, 111.4.

2-(p-tolyl)-1H-benzo[d]imidazole (5e).[17c] White solid, (0.169mg, 81% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.82 (s, 1H), 8.07 (d, J = 8.12 Hz, 2H), 7.64 (d, J = 6.12 Hz, 1H), 7.51 (d, J = 6.24 Hz, 1H), 7.35 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 3.76 Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 151.4, 143.8, 139.6, 135.0, 129.5, 127.5, 126.4, 122.3, 121.6, 118.7, 111.2, 21.0.

2-(3-phenoxyphenyl)-1H-benzo[d]imidazole (5f).[31] Yellow solid, (0.246mg, 86% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.94 (s, 1H), 7.96 (d, J = 7.72 Hz, 1H), 7.81 (s, 1H), 7.65 (d, J = 7.6 Hz, 1H), 7.57 (t, J = 7.96 Hz, 1H), 7.52 (d, J = 7.56 Hz, 1H), 7.45 (t, J = 8.04 Hz, 2H), 7.24-7.11 (m, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 157.4, 156.3, 150.5, 143.6, 135.0, 132.0, 130.8, 130.2, 123.9, 122.7, 121.8, 121.4, 120.0, 119.0, 119.0, 116.0, 111.4.

2-(thiophen-2-yl)-1H-benzo[d]imidazole (5g).[17c] Yellow solid, (0.150mg, 75% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.94 (s, 1H), 7.83 (d, J = 3.6 Hz, 1H), 7.72 (d, J = 4.92 Hz, 1H), 7.55(s, 2H), 7.24-7.18 (m, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 147.0, 133.7, 128.8, 128.3, 126.7, 122.6, 122.5, 121.9, 118.5, 111.3, 111.1.

2-(pyridin-2-yl)-1H-benzo[d]imidazole (5h).[17c] Yellow solid, (0.176mg, 90% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.10 (s, 1H), 8.72 (d, J = 4.68 Hz, 1H), 8.33 (d, J = 7.88 Hz, 1H), 7.99 (dt, J = 7.76 Hz, 1.48 Hz, 1H), 7.70 (d, J = 7.6 Hz, 1H), 7.56-7.50 (m, 2H), 7.26-7.19 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 150.8, 149.4, 148.5, 143.9, 137.6, 134.9, 124.7, 123.2, 121.9, 121.4, 119.3, 112.1.

2-(4-bromophenyl)-1H-benzo[d]imidazole (5i).[17c] Yellow solid, (0.219mg, 80% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.99 (s, 1H), 8.12 (d, J = 8.48 Hz, 2H), 7.76 (d, J = 8.48 Hz, 2H), 7.67 (d, J = 6.96 Hz, 1H), 7.53 (d, J = 6.84 Hz, 1H),

7.22 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 150.2, 143.7, 135.0, 132.0, 129.4, 128.4, 123.3, 122.8, 121.9, 119.0, 111.4.

2-(4-chlorophenyl)-1H-benzo[d]imidazole (5*J*).[17c] White solid, (0.187mg, 82% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.99 (s, 1H), 8.19 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.56 Hz, 4H), 7.23-7.20 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 150.2, 143.7, 134.6, 129.1, 129.1, 128.2, 122.7, 122.1, 119.0, 111.5.

2-(4-fluorophenyl)-1H-benzo[d]imidazole (5k).[17c] Yellow solid, (0.151mg, 71% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.92 (s, 1H), 8.25-7.21 (m, 2H), 7.67 (d, J = 7.24 Hz, 1H), 7.53 (d, J = 7.28 Hz, 1H), 7.40 (t, J = 8.88 Hz, 2H), 7.24-7.17 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 162.6 (d, J=246 Hz), 150.4, 143.8, 135.0, 128.7 (d, J=9 Hz), 126.8 (d, J=3 Hz), 122.6, 121.7, 118.9, 116.0 (d, J=22 Hz), 111.3.

2-(2,5-difluorophenyl)-1H-benzo[d]imidazole (5l).[17f] Orange liquid, (0.143mg, 62% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.70 (s, 1H), 8.00-7.96 (m, 1H), 7.66 (s, 2H), 7.54-7.48 (m, 1H), 7.44-7.39 (m, 1H), 7.26-7.24 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 158.3 (dd, J= 239 Hz, 2 Hz), 155.9 (d, J= 245 Hz, 2 Hz), 145.3 (t, 3 Hz), 122.8-122.3 (m), 119.5 (dd, J=14.5, 9Hz), 118.7, 118.6, 118.6, 118.5, 118.5, 118.4, 118.3, 118.2, 115.8 (dd, J= 23 Hz, 3Hz).

5-methyl-2-(p-tolyl)-1H-benzo[d]imidazole (5m).[32] White solid, (0.162mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.08 Hz, 2H), 7.48 (d, J = 7.56 Hz, 1H), 7.34 (s, 1H), 7.17 (d, J = 8.0 Hz, 2H), 7.03 (d, J = 8.24 Hz, 1H), 2.42 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d$_6$) δ 151.2, 139.5, 131.3, 129.6, 127.6, 126.5, 126.4, 123.5, 117.9, 111.3, 21.4, 21.1.

2-(4-chlorophenyl)-5-methyl-1H-benzo[d]imidazole (5n).[32] White solid, (0.180mg, 74% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.16 (d, J = 8.12 Hz, 2H), 7.60 (d, J = 8.08 Hz, 2H), 7.51-7.31 (m, 2H), 7.03 (d, J = 6.96 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 149.8, 141.9, 135.3, 134.3, 132.1, 129.2, 129.0, 128.0, 123.5, 118.6, 111.1, 21.3.

5-methyl-2-(thiophen-2-yl)-1H-benzo[d]imidazole (5o).[24] White solid, (0.148mg, 69% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.79 (s, 1H), 7.81 (d, J = 3.24 Hz, 1H), 7.69 (d, J = 4.8 Hz, 1H), 7.47-7.29 (m, 2H), 7.21 (t, J = 4.72 Hz, 1H), 7.01 (s, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 146.6, 141.7, 135.0, 133.9, 132.0, 128.4, 128.2, 126.4, 123.3, 118.1, 110.8, 21.3.

5,6-dichloro-2-(4-methoxyphenyl)-1H-benzo[d]imidazole (5p).[32] White solid, (0.223mg, 76% yield). ^{1}HNMR (400 MHz, DMSO-d_6) δ 13.07 (s, 1H), 8.09 (d, J = 8.84 Hz, 2H), 7.78 (s, 2H), 7.11 (d, J = 8.88 Hz, 2H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.1, 154.0, 128.4, 124.1, 121.8, 114.5, 55.4.

5,6-dimethyl-2-(pyridin-2-yl)-1H-benzo[d]imidazole (5q).[33] Orange solid, (0.194mg, 87% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.85 (s, 1H), 8.68 (d, J = 4.68 Hz, 1H), 8.28 (d, J = 7.92 Hz, 1H), 7.96 (dt, J= 7.56 Hz, 1.52 Hz 1H), 7.46 (t, J = 6.16 Hz, 2H), 7.31 (s, 1H), 2.31 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 149.9, 149.3, 148.8, 142.6, 137.4, 133.5, 132.0, 130.3, 124.4, 121.2, 119.2, 112.0, 20.1, 20.1.

2-heptyl-1H-benzo[d]imidazole (5r).[18b] White solid, (0.076mg, 35% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.46 (m, 2H), 7.17-7.11 (m, 2H), 2.88(t, J = 7.8 Hz, 2H), 1.82-1.74 (m, 2H), 1.30-1.22 (m, 2H), 1.20-1.11 (m, 6H), 0.74 (t, J = 7.08 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 138.7, 122.2, 114.7, 31.8, 29.5, 29.4, 29.1, 28.5, 22.7, 14.1.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website

Copies of the ^{1}H NMR, ^{13}C NMR of all the compounds and HRMS, IR and crystallographic data of **1**. MS analysis of the crude reaction mixture of o-phenylenediamine and 4-methoxybenzyl alcohol (PDF)

X-ray crystallographic data (CCDC 1831616) for **1** (CIF)

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Notes

The authors declare no competing financial interest.

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