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ORIGINAL PAPER

Microwave-assisted synthesis and luminescent properties of triphenylamine substituted mono- and di- branched benzimidazole derivatives

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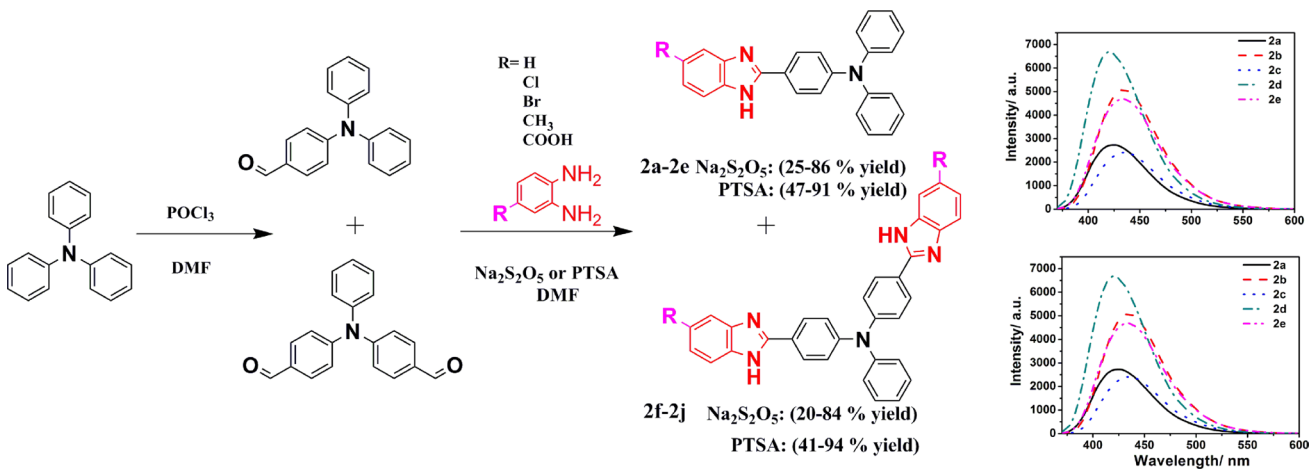
Abstract

In the present work, the synthesis of the target products using sodium metasulfite ($Na_2S_2O_5$) and *p*-toluenesulfonic acid (PTSA) separately as catalysts was studied. Herein, the liquid phase microwave method was chosen to synthesize triphenylamine substituted mono- and di-branched benzimidazole derivatives compared with the solid phase microwave method, and the reaction conditions were optimized using $Na_2S_2O_5$ as a catalyst in *N*,*N*-dimethylformamide (DMF) solvent. A possible reaction mechanism is discussed. Ten new triphenylamine-benzimidazole derivatives were successfully synthesized. On this basis, PTSA using a catalyst was introduced into the reaction, the yields of the target products were evidently increased (the yield was enhanced 5−22% using PTSA as a catalyst). It is found that PTSA only acted as a catalyst, while $Na_2S_2O_5$ acted as both a catalyst and an oxidant, and PTSA could effectively catalyze the synthesis of benzimidazoles. Further, the luminescent properties of the synthesized compounds were comparatively studied after the structures of the synthesized compounds were confirmed. The results showed that the fluorescence quantum yield and the intensity of the synthesized compounds were enhanced with the increase in the number of substituted benzimidazole on triphenylamine, and the different substituents on 5-position of benzimidazole also have significant effect on the luminescent properties of the compound.

Graphic Abstract



Keywords Triphenylamine-benzimidazole · Catalysis · Microwave chemistry · Reaction mechanisms · Luminescent property

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Introduction

In recent years, benzimidazole derivatives as fluorescent organic small molecules have attracted intensive attention because of their value in technological applications referring to fluorescent probes for detecting metal ion (Saluja et al. 2012; Wang et al. 2013; Jayabharathi et al. 2012), pH probes (Sevinoç et al. 2014), electrochromic devices (Sydam et al. 2013), sensors (Wannalerse et al. 2008) and organic semiconductor materials (Lai et al. 2008) and so on. Compared with metal and inorganic compounds, organic compounds were easily modified with various functional structures. Organic fluorescent molecules such as benzimidazole derivatives are a group of heterocyclic organic compounds consist of benzene/imidazole ring structure. According to the comprehensive reports from Yamamoto et al. on n-type π-conjugated units, benzimidazole is a potentially acceptor unit, displayed good electrochemical and optical features (Tanimoto and Yamamoto 2006; Ahn et al. 2001). Also, benzimidazole derivatives showed high electron transporting ability due to the electron-withdrawing imine (C=N) bonds on their molecular skeletons (Akpınar et al. 2010; Newkome et al. 1982; Tanimoto and Yamamoto 2004). Triphenylamine is a non-planar molecule having a larger conjugated structure (Janic and Kakas 1984). triphenylamine derivatives are widely used in organic optoelectronic functional materials (Salbeck et al. 1997; Tokito et al. 1998), OLEDs (Liu et al. 2014; Xia et al. 2009; Nguyen et al. 2014), organic dyes (Shang et al. 2016), solar cells (Chen et al. 2013; Le et al. 2018) and so on. Herein, we designed and synthesized novel D-A type organic small molecule compounds using triphenylamine as electron donor and benzimidazole-based moiety as electron acceptors, whose luminescence property were further studied.

So far, the developed synthesis of substituted benzimidazoles generally started from *o*-phenylenediamine or *o*-nitroaniline and carboxylic/aldehyde derivatives using diverse catalytic/oxidation system. The mainly used oxidation system including *p*-toluenesulfonic acid/air (Han et al. 2007), Oxone (Beaulieu et al. 2003), molecular iodine (Gogoi et al. 2006), bisulfite adduct (Weidner-Wells et al. 2001), $FeCl_3{\cdot}H_2O$ (Singh et al. 2000), air (Lin et al. 2005), sodium dithionite (Romero et al. 2013) and so on.

Moreover, microwave technique was widely applied in organic synthesis in recent years. The principal advantages of various reported microwave-assisted synthesis are simple work up procedure, fast reaction rate, high yield, well selectivity, environmentally friendly (Raner et al.1995; Gedye et al. 1986; Dariusz 1998; Srikrishna and Nagaraju 1992; Shi et al. 2019a). Sodium pyrosulfite ($Na_2S_2O_5$) is a non-toxic food additive, has been reported to be an efficient catalyst and oxidant used in the synthesis of benzimidazole derivatives under microwave-assisted condition (Bui et al. 2016; Gabriel et al. 2006). And another catalyst, PTSA as an acid catalyst was widely applied in the field of organic synthesis because it is an efficient, non-toxic, and inexpensive solid acid. Although PTSA has been used to synthesize simple structure 2-arylsubstituted benzimidazole, quinoline, quinoxaline and pyrimidine from amine and aldehyde condensation (Han et al. 2007; Chan et al. 2020; Shi et al. 2008; Jin et al. 2002), the synthesis of benzimidazole derivatives using PTSA as a catalyst in microwave radiation has not been reported. Especially, the synthesis of the larger steric hindrance triphenylamine substituted mono- and di- branched benzimidazole derivatives has not been reported.

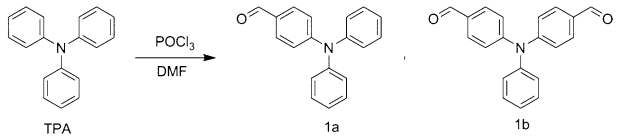
In the present work, we focus on the synthesis and luminescence property of new 5- substituted 4-(1*H*-benzoimidazole-2-yl)-*N*,*N*-diphenylaniline (triphenylamine substituted mono- branched benzimidazole) and 5- substituted *N*-(4-(1H-benzoimidazole-2-yl)phenyl)-4-(1H-benzoimidazole-2-yl)-*N*-phenylanline (triphenylamine substituted di- branched benzimidazole) bearing different electron-withdrawing and electron-donating substituents at 5- position of benzimidazole. Herein, $Na_2S_2O_5$ is used as a catalyst and oxidant to explore the synthesis of 2-substituted benzimidazole staring from high steric resistance triphenylamine aldehydes and substituted *o*-phenylenediamine by solid phase and liquid phase microwave-assisted method, respectively. On the basis of the obtained optimum synthesis process, the catalyst PTSA was introduced into the reaction, and the catalytic effects of $Na_2S_2O_5$ and PTSA were compared. The structures of the synthesized compounds were characterized by HRMS, FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopy. The luminescence property was studied by detecting their absorption and fluorescence spectrum. The results suggested that the catalysis of PTSA was superior to that of $Na_2S_2O_5$, and the maximum absorption wavelength and fluorescence quantum yield of the synthesized compounds are respectively red-shifted and obviously enhanced with increasing the number of substituted benzimidazole on triphenylamine.

Results and discussion

Synthesis condition optimization

It is known that Vilsmeier–Haack reaction is widely used to formylation reaction (Chakradhar et al. 2009). In general, *N*,*N*-dimethylformamide (DMF) and phosphorus oxychloride ($POCl_3$) are used to introducing an aldehyde group on the activated aromatic ring. In our present work, two kinds of target products were successfully prepared using triphenylamine (TPA) as a raw material by controlling the

Table 1 The synthesis of triphenylamine aldehydes



Entry	Compound	$n_{(POCl3)}/n_{(DMF)}$	Reaction time (h)	Yield (%)	M.P. (°C)
1	**1a**	1:3	2	82	132–134
2	**1b**	2:3	3	62	144–146

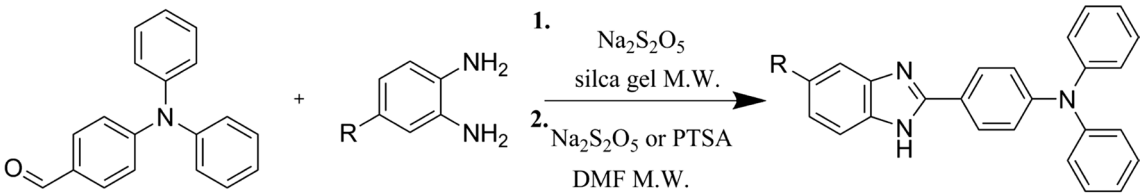
Table 2 The synthesis of compounds **2a**−**2e** under solvent- free and microwave irradiation conditions

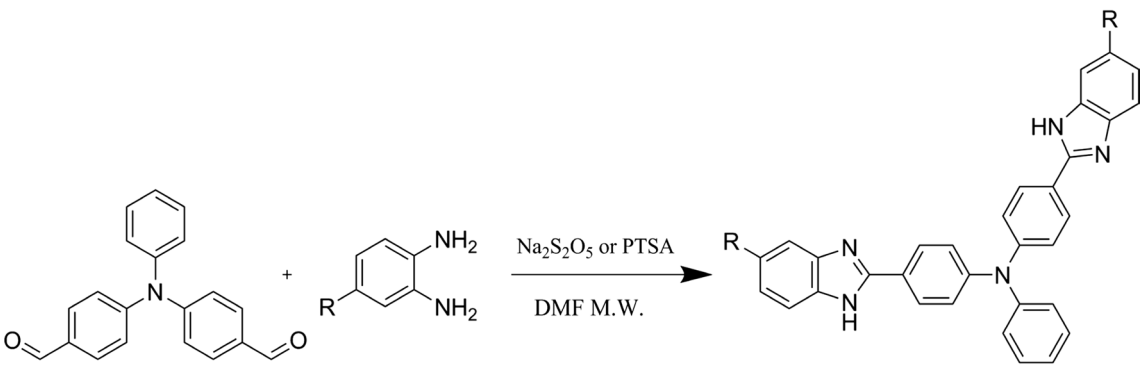
Entry	Compound	R	$n_{Catalyst}$ (mmol)	Time (min)	Yield[a] (%)
1	**2a**	H	1.0	20	68
2	**2b**	Cl	1.0	20	51
3	**2c**	Br	1.0	25	–
4	**2d**	CH_3	1.0	25	36
5	**2e**	COOH	1.0	25	11

[a]Isolated yield

feed mole ratio of $POCl_3$ and DMF (Table 1). As shown in Table 1, triphenylamine's monoaldehyde (**1a**), dialdehyde (**1b**) were respectively synthesized in 82% and 62% yields. Also, with the increase of the number of substituted aldehyde groups on triphenylamine, the mole ratio of $POCl_3$ to DMF was increased from 1:3 to 2:3, the reaction time was also increased from 2 to 3 h. However, the yield decreased from 82.3% (**1a**) to 62.4% (**1b**). It indicated that the formylation reaction become more difficult and melting point (M.P.) of the product enhanced with extending the substituted aldehyde group (Table 1).

In our previous work, we successfully synthesized 1,2,4,5-tetrasubstituted imidazoles (Shi et al. 2019a) and pyrazolone derivatives containing substituted isoxazole ring compounds by solvent-free microwave-assisted method in moderate to good yield (Zhang et al. 2016; Yan et al. 2017; Mi et al. 2018; Li et al. 2012). Herein, on the basis of our previous work (Shi et al. 2019b), the synthesis possibility of the desired products 2-*N*,*N*-diphenylaniline substituted benzimidazoles were investigated starting from 4-substitutied *o*-diphenylaniline and triphenylamine aldehydes using $Na_2S_2O_5$ as a catalyst and oxidant under solvent-free and microwave irradiation conditions (Table 2 and Scheme 1). As shown in Table 2, four of the desired compounds were synthesized in 11−68% yield. However, the target product **2c** was not obtained. Also, the yields of the obtained **2d** and **2e** were very low. The possible reason was that silica gel





Scheme 1 Synthetic routes to compound **2a**−**2j**

is good at dispersing the reactants while preventing them from touching each other and the catalytic oxidation of the catalyst could not be fully exploited. Additionally, the products were difficult to be separated resulting from the similar polarity and reciprocity between product and by-product mono-Schiff base. It was verified by HPLC–MS analysis of the reactants when the reaction for synthesizing product **2c** was over (Fig. 1a). Therefore, it was necessary to choose a solvent that could inhibit the interaction of mono-*Schiff* base and the product and promote the reactant dissolution.

It is known that DMSO and DMF are all-purpose solvent. At the beginning of the study, DMSO and DMF were chosen as solvents to investigate the synthesis of product **2c s**tarting from **1a** and 4-bromobenzene-1, 2-diamine. It is disappointing that the obtained **2c** in DMSO solvent was still hard to be separated efficiently. As a result, DMF as a solvent was introduced to the reaction in the presence of 1 equivalent $Na_2S_2O_5$. The desired product **2c** was firstly obtained in 37% yield (Table 4, entry **3**). Further, the HPLC–MS analysis of the crude product at the end point of the reaction under the same chromatographic conditions with Fig. 1a was measured (Fig. 1b). The result showed that only a few mono-Schiff base (*m*/*e* = 441) was produced, and the cross between product and mono-Schiff base was not formed. It suggested that the reactant solubility in DMF effectively inhibited the formation of by-products. Therefore, the liquid microwave method was more suitable for the reaction system. The reaction mechanism was inferred from the above HPLC–MS analysis and the simple tracking experiments (Scheme 2). Herein, gas produced in the reaction progress was monitored by the wet extensive pH indicator paper. The wet extensive pH indicator paper turned red first and then red disappearing, which is an evidence of SO_2 formation. The difference between this reaction and the previous synthesis of the small steric hindrance benzimidazoles is the production of no bi-*Schiff* base.

As shown in Scheme 2, the lone pair electron on a nitrogen atom of 4-substitutied *o*-diphenylaniline attacked the

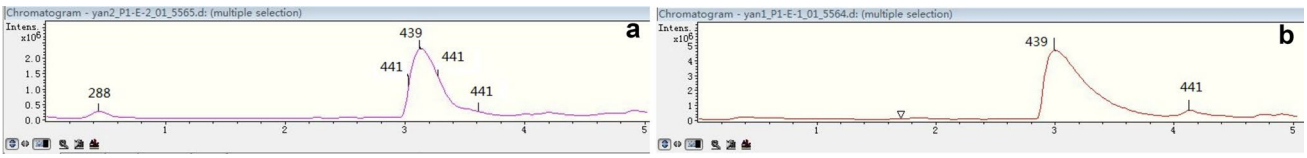
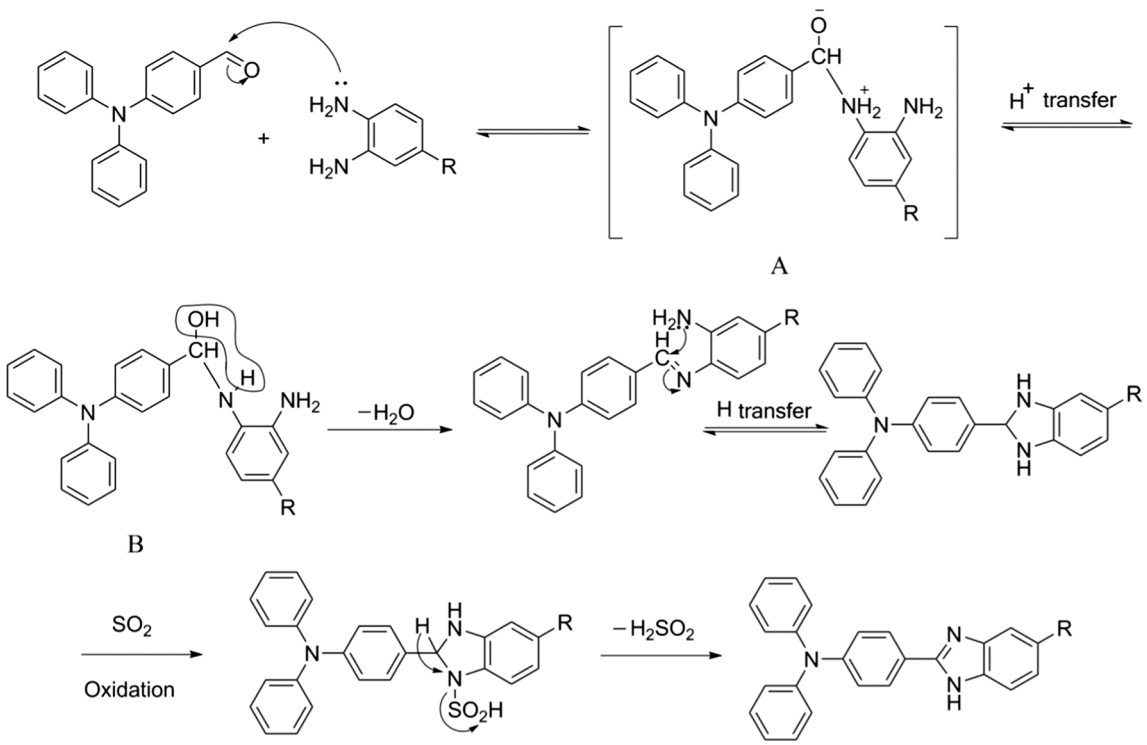


Fig. 1 The HRMS analysis of the obtained compound **2c** under solvent-free (**a**) and DMF as a solvent (**b**) microwave radialization conditions



Scheme 2 The inferred reaction mechanism to synthesize compounds **2a**–**2e**

carbonyl carbon of triphenylamine aldehyde by nucleophilic addition to form transitional state product **A**, further occurred H^+ transfer to obtain secondary alcohol amine **B**. Sequentially dehydrating to produce mono-*Schiff* base (See Fig. 1b). Then, the lone pair electrons on the other amino nitrogen atom continued to attack the imine carbon of mono-*Schiff* base, further occurred H transfer to cyclize to 4-(5-substitute-2,3-dihydro-1*H*-benzo[d]imidazol-2-yl)-*N*,*N*-diphenylaniline. Finally, 4-(5-substitute-2 ,3-dihydro-1*H*-benzo[d]imidazol-2-yl)-*N*,*N*-diphenylaniline was oxidized to the target product by SO_2 produced via the thermal decomposition of $Na_2S_2O_5$ (Romero et al. 2013).

To get a high yield, the synthesis conditions were investigated by employing 4-methylbenzene-1,2-diamine(**I**) and 4-(diphenylamino)benzaldehyde (**II**) using 1 equivalent $Na_2S_2O_5$ as a catalyst and oxidant under microwave irradiation condition in 15 mL DMF, and the reaction was monitored by TLC. The results are summarized in Table 3. As shown in Table 3, the yield of the obtained target product (**2a**) increased firstly and remained almost unchanged and then decreased with the molar ratio of **I** and **II** (n_I:n_{II}) decreasing from 1:1 to 1:1.05. **I** could be completely consumed when n_I:n_{II} was controlled at 1:1.05, and the yield of the obtained target product (**2a**) was the highest (86%).

Table 3 Optimization of reaction conditions

Entry	n_I:n_{II}	Reaction time (min)	Reaction temperature (°C)	Yield[a] (%)
1	1:1	20	98	84%
2	1:1.05	20	98	86%
3	1:1.1	20	98	85%
4	1:1.05	25	75	69%

[a]Isolated yield

However, it was found that the reactants could not be reacted completely and the reaction time was prolonged when the reaction temperature was decreased to 75 °C. Therefore, 1:1.05 molar ratios of the reactants, reaction time 20 min and reaction temperature 98 °C were chosen to carry out the liquid phase microwave reaction.

The application of the optimum conditions

Subsequently, the optimized reaction condition was extended to synthesize the designed compounds. Five desired products **2a–2e** were successfully synthesized in 25–86% yield at 98 °C using DMF as a solvent and under microwave irradiation condition (Table 4, entries **1**–**5**, method **A**). The yields were markedly improved compared to the solid phase microwave method (Table 2). Further, the liquid microwave-assisted method was extended to the synthesis of di-branched triphenylamine-benzimidazole derivatives, and five target products **2f**–**2j** were successfully prepared in 20–84% yield (Table 4, entries **6**–**10**, method **A**). The polarity of **2e, 2j** is too large, or the solubility of **2b** and **2g** in the eluent is too small to be hardly separated by column chromatography, further resulting in low yield and very long separation time (Table 4, entries **5** and **10**, **2** and **7**).

It is known that the first benzimidazole compound was synthesized by Hoebrecker under the strong acidic conditions in 1872. (Lu et al. 2002) and (Boufatah et al. 2004) also synthesized benzimidazole derivatives respectively using polyphosphoric acid and hydrochloric acid as the catalyst. By chance, when 0.1 equivalent PTSA replaced 1 equivalent $Na_2S_2O_5$ and was added to the reaction, the yield of product **2d** was significantly increased ($Na_2S_2O_5$ 56%; PTSA 77%) (Table 4**,** entry **4**). Similarly, the catalyst PTSA was expanded to catalyze the synthesis of the rest of benzimidazole derivatives using DMF as a solvent and under

Table 4 The synthesized compounds **2a**−**2j** under microwave irradiation and solvent as DMF

Entry	Compound	R	Method A[a]		Method B[b]		M.P. (°C)
			Time (min)	Yield[c] (%)	Time (min)	Yield[c] (%)	
1	**2a**	H	20	86	15	91	> 280
2	**2b**	Cl	20	84	15	89	216–218
3	**2c**	Br	20	37	15	57	242–244
4	**2d**	CH_3	20	56	15	77	245–247
5	**2e**	COOH	30	25	20	47	184–186
6	**2f**	H	20	84	15	94	> 280
7	**2g**	Cl	20	80	15	86	210–212
8	**2h**	Br	20	49	15	68	242–244
9	**2i**	CH_3	20	58	15	79	> 280
10	**2j**	COOH	30	20	20	41	> 280

[a]All the compounds were synthesized using $Na_2S_2O_5$ as a catalyst at 98 °C under microwave irradiation

[b]All the compounds were synthesized using PTSA as a catalyst at 120 °C under microwave irradiation

[c]Isolated yield

microwave irradiation condition, the desired products were successfully synthesized at 120 °C in 41–94% yield (Table 4, entries **1**–**3** and **5**–**10**, method **B**). The results showed that the yields of the obtained target products were improved and the reaction times were reduced comparing with using $Na_2S_2O_5$ as a catalyst. This result may be due to the protonation of the carbonyl group of triphenylamine aldehyde in the acid system enhanced the electropositivity of the carbonyl carbon which improved the activity of the carbonyl group and promoting the nucleophile attack of the amine. It is hypothesized that the formation of triphenylamine-benzimidazole could be occurred with the followed mechanism (Scheme 3).

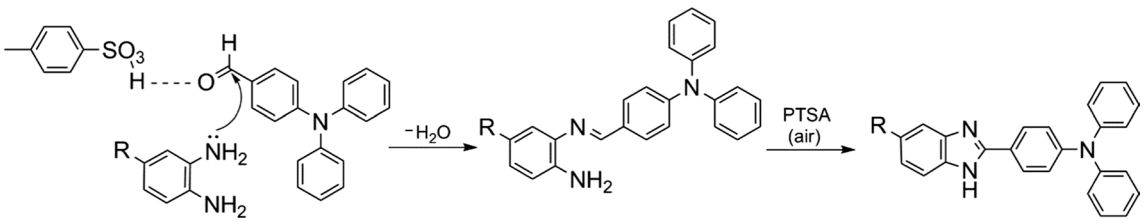
It was seen from Table 4, the better yields were obtained when no substituents was at 5-position of *o*-phenylenediamine (Table 4, entries **1** and **6**), and it was higher than that of the bearing electron-withdrawing substituent at 4-position of *o*-phenylenediamine (Table 4, entries **2** and **7**, **3** and **8**, **5** and **10**). The result may be due to the fact that the electron-withdrawing substituent on *o*-phenylenediamine reduced the electron cloud density of amino N, which was not conducive to amino N nucleophilic attack on carbonyl carbon. Moreover, the yield of the target product might also be controlled thermodynamics. The structures of the obtained compounds **2a**−**2j** were confirmed by FT-IR, ^{1}H and ^{13}C NMR and HRMS spectra analysis. The –C–NH–C– protons of imidazole ring exhibited resonances at δ 12.58–13.18 ppm using DMSO as the solvent. The resonances for carbon directly attached to 2-position carbon atom attached to NH on imidazole ring and carbon bearing on triphenylamine were respective observed peaks at δ 148.43–152.93 ppm and δ 146.54–149.55 ppm.

Luminescence properties

Further, the absorbance and fluorescence properties of compounds **2a–2f** (1.0×10^{-6} mol/L) were evaluated in ethanol solution. It is known that substituents had significant effects in spectroscopic shift of both absorption and fluorescence. In general, electron-donating groups could cause an increase molar absorption coefficient and enhance fluorescence efficiency, while electron-withdrawing groups reduced fluorescence quantum yield (Giri et al. 1988). Herein, compound **2a** was considered as the model compound to investigate the effects of different electron donating (**2b** and **2g**) and electron withdrawing (**2c–2e** and **2f–2j**) substituents on benzimidazole luminescence properties.

Figure 2 shows that the absorption spectra of compounds **2a–2e** and **2f–2j** in ethanol solution and their maximum absorption wavelengths are summarized in Table 5. Two primary bands, the absorption of these compounds around 284−305 nm (**2a–2e**) and 330−340 nm (**2f–2j**) was attributed to the locally excited π–π* transition centered on triphenylamine, while another absorption of longer wavelength around 345–368 nm (**2a–2e**) nm and 369–377 nm (**2f–2j**) could be associated with the charge transfer of the π–π* transition from the HOMO of the electron-donating triphenylamine moiety to the LUMO of the electron-accepting benzimidazole moiety (Ge et al. 2008; Gong et al. 2010; Pina et al. 2013). Besides, the band of the di-branched compounds **2f–2j** red-shifted 12–19 nm (Fig. 2 and Table 5) comparing with mono-branched compounds **2a–2e**. This might be because the interaction of electron-donor and electron-acceptor upon excitation enhanced π-electron delocalization (Lin et al. 2004; Wang et al. 2010). The synthesized mono-branched compounds **2b–2e** (Table 5: entries **2**–**5**) and di-branched compounds **2g–2i** (Table 5, entries **7**–**10**) containing different substituents except for **2g** had a slight red shift (1–6 nm) respectively comparing to their model compounds **2a** (Table 5, entry **1**) and **2f** (Table 5, entry **6**). It is likely that the introduction of $–CH_3$, –COOH and halogen groups slightly increased the degree of conjugation of the molecule, and further enhanced the conjugated system electron delocalized.

With respect to the emission spectrum, the maximum emission wavelength and fluorescence quantum yield of compounds **2a–2e** are shown in Fig. 3 and Table 5. The compound bearing electron-withdrawing substituent (Table 5, entries **2**, **3** and **5**) displayed a red-shift about 10 nm at a maximum emission wavelength comparing to that of compound **2a** (Table 5, entry **1**). However, when substituent was replaced with electron-donating group ($–CH_3$) (Table 5, entry **4**), a negligible blue-shift was observed. The main reason was that the electron-withdrawing groups (–Cl, –Br, –COOH) enhanced the electron-pulling strength of benzimidazole-based moiety acceptor (Lin et al. 2004). The



Scheme 3 The possible reaction mechanism to synthesis of compounds **2a**−**2e** using PTSA as a catalyst

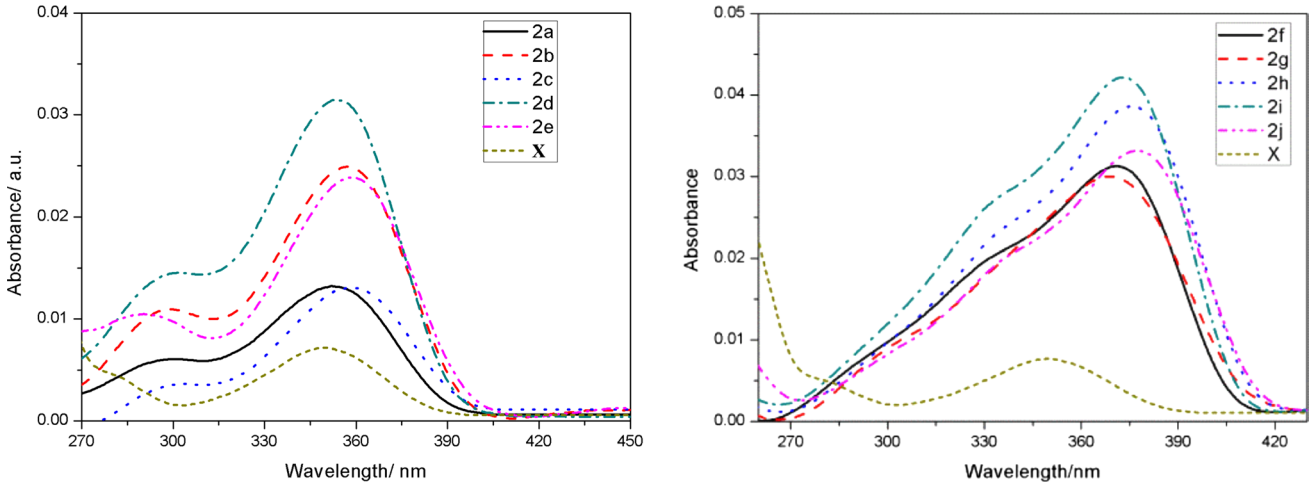


Fig. 2 The absorption spectrum of **2a**−**2e** and **2f**−**2j** (1.0×10^{-6} mol/L) containing different substituents in ethanol solvent (X: Quinine sulfate)

Table 5 Spectroscopic data (Absorption λ_{max}, fluorescence emission λ_{max}, and fluorescence quantum yield Φ) of compound **2a**−**2j** in ethanol solvent [1.0×10^{-6} mol/L ($\lambda_{ex}=310$ nm)]

Entry	Compound	λ_{max} (nm)	λ_{emmax} (nm)	Φ^a
1	**2a**	352	424	0.235
2	**2b**	357	435	0.258
3	**2c**	358	434	0.226
4	**2d**	353	421	0.132
5	**2e**	358	434	0.209
6	**2f**	371	415	0.562
7	**2g**	369	421	0.413
8	**2h**	375	422	0.393
9	**2i**	373	414	0.243
10	**2j**	377	432	0.437

[a]Φ was calculated by means of the equation, namely,$\Phi_x = \frac{n^2_x}{n^2_{std}} \times \frac{A_{std}}{A_x} \times \frac{F_X}{F_{std}} \times \Phi_{std}$, where x, represents sample to be tested, std represents standard sample (quinine sulfate), n represents the refractive index, A represents the absorbance, and F represents the fluorescence intensity

di-branched compounds **2f–2j** also followed the same rule as mono-branched compounds **2a**−**2e**. However, the emission wavelengths of compounds **2f–2j** were blue-shifted compared with that of the corresponding compounds **2a–2e.** This result may be due to the planarity of the synthesized compounds.

Besides, the fluorescence quantum yield (Φ) was measured and calculated using quinine sulfate as a standard according to the literatures (Gill et al. 1969; Fletcher 1969). The obtained fluorescence quantum yields of the products are listed in Table 5. The Φ of compound **2f** (Table 5, entry **6**) was highest ($\Phi=0.562$) among the synthesized compound **2a–2j**, and the Φ of the rest compounds were in the range of 0.132–0.437. Similarly, it could be seen from Fig. 3 and Table 5 that the fluorescence intensity and Φ of di-branched compounds **2f–2j** (Table 5, entry **6**–**10**) was higher than that of the corresponding mono-branched compound **2a–2e** (Table 5, entry **1**–**5**) bearing the same substitute. It is likely because the increases of the systematic conjugation and the coplanarity of the molecular structure were enhanced as the number of substituted benzimidazole in the structure increased. As shown in Fig. 3 and Table 5, the fluorescence intensity and Φ of **2b** and **2g** were higher than that of **2c** and **2h** when the hydrogen on benzene ring was respectively replaced with chlorine and bromine. It resulted from an introduction of a heavy atom (Cl and Br) into a molecule enhance the rate of S1-T1 spin-forbidden process (Chen et al. 2014; Chandra et al. 1978). Moreover, the fluorescence intensity of the compounds **2d** and **2i** bearing $-CH_3$ on 5-position of benzimidazole was the strongest, but Φ was the lowest. This possible reason was that the interaction between methyl group and triphenylanilyl group on benzimidazole in ethanol solvent increased the characteristic absorption peak intensity of coupounds 2**d** and 2**i**. That is, this interaction caused the absorbance of compounds 2**d** and 2**i** to increase (Fig. 2), which further led to Φ decreasing (Table 5, entries **4** and **9**). It is notable that although the synthesized compound **2f**, **2h**, **2j** had good fluorescence properties, the overall fluorescence quantum yield not reach the expectation. This maybe lied in the fact that the C–C bond from triphenylamine molecule to the imidazole ring increases the degree of rotational freedom of the molecule, resulting in triphenylamine twist out of benzimidazole plane (Zhao et al. 2006). Therefore, the poor coplanarity of benzimidazole ring and triphenylamine might decrease the degree of the conjugation of the molecule and prevent the circulation of π-electrons.

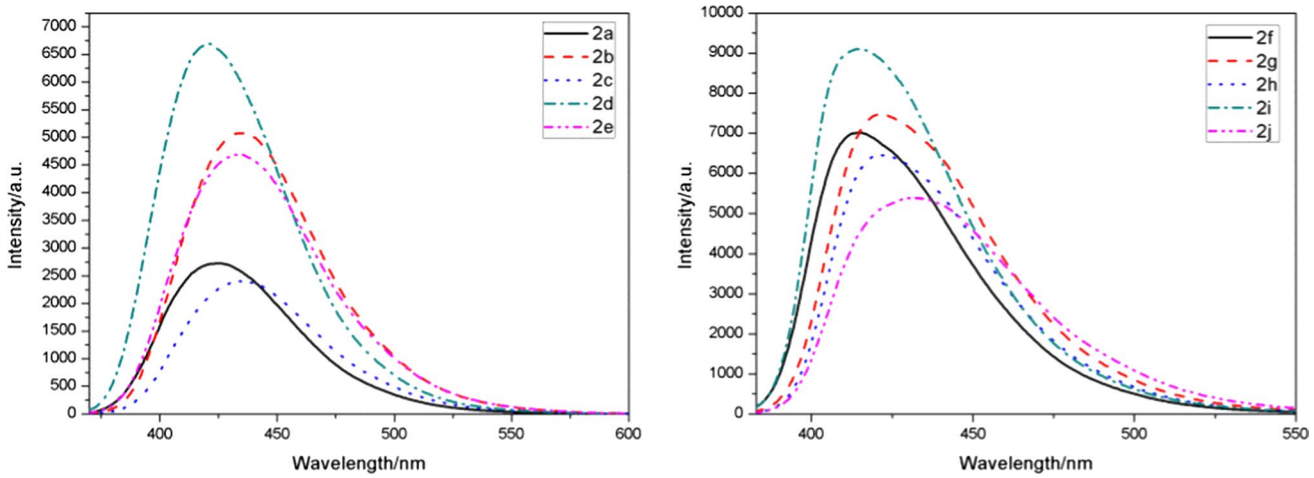


Fig. 3 The emission spectra of **2a**−**2e** and **2f**−**2j** in ethanol solvent (1.0×10^{-6} mol/L ($\lambda_{ex=}$ 310 nm))

Conclusions

In summary, the synthesis of triphenylamine substituted mono- and di-branched benzimidazole derivatives was investigated and compared under microwave irradiation solvent-free and solvent (DMF) conditions in the present of 1 equivalent $Na_2S_2O_5$. The results showed that the microwave-assisted liquid phase method had better selectivity and yield. Then, ten desired triphenylamine–benzimidazole derivatives were successfully synthesized in 20–86% yield. The possible reaction mechanism was proposed. And on this basis, the catalyst PTSA (0.1 equivalent) was introduced to catalyze the reaction. Not only the yields of the obtained target products were significantly increased (yield: 41–94%), but also the reaction time was obviously reduced. It suggested that PTSA was a highly efficient and environmentally friendly catalyst. Further, the luminescent properties of the synthesized compounds were compared. The results showed that di-branched compounds **2f**−**2i** were marked red-shifted 12–19 nm in absorption spectrum and displayed a significant enhancement (maximum increase is 0.327) for Φ when compared with mono-branched compounds **2a**−**2e**. It suggested that the successful introduction of multiple benzimidazole rings enhance the degree of conjugate of the molecule and improved fluorescence performance. Moreover, the design, synthesis and performance measurement of other benzimidazole derivatives are going.

Experimental section

Materials and methods

Triphenylamine and various substituted o-phenylenediamine were from Shanghai Darui Chemical Co., Ltd, China and Shanghai Aladdin Biochemical Technology Co., Ltd, and was not further purified before being used. The other solvents and reagents used were supplied by Tianjin Tiantai Chemical Co. Ltd (China) and Sinopharm Chemical Reagent Co., Ltd. All melting points were determined on an XT-4 melting point apparatus (China) and were uncorrected. HRMS was obtained using an US Agilent1290–micrOTOF Q II spectrometer. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker AVANCE-500 or 600 NMR spectrometer (Germany) and with TMS as an internal standard. FT-IR spectra were measured, KBr pellets as a reference, using a Shimadzu IRAffinity-1 instrument in the range of 500–4000 cm^{-1}. A XO-50 N microwave reactor with a thermocouple thermometer purchased from Nanjing Xianou instruments Manufacture Company was used to synthesize the target products. Fluorescence spectra were measured with a FLS920 spectrofluorimeter (Edinburgh Instruments. UK). The absorption spectra were measured by Shimadzu UV-3600 within the wavelength range from 270 to 450 nm.

Synthesis

General synthesis approach for triphenylamine's monoaldehyde, dialdehyde and trialdehyde (*1a*, *1b*)

Compounds **1a**, **1b** were prepared referring to literature (Chakradhar et al. 2009). Firstly, Phosphorus oxychloride (15 mL 0.16 mol) was added dropwise to *N*,*N*-dimethylformamide (DMF) according to a certain proportion ($n_{(POCl3)}/n_{(DMF)}=1{:}3,\ 2{:}3$) under an ice-water bath condition and continuous magnetic stirring. Then, triphenylamine (5.00 g 0.02 mol) was added to the above reaction mixture, and was stirred for 1 h at room temperature. Sequentially, the reaction mixture was then heated to 98 °C in oil bath until TLC indicated the reaction end. The residue was cooled to

room temperature and was poured slowly into iced water (150 mL). A large amount of solid particles were precipitated when the obtained mixture was adjust pH = 7 with sodium hydroxide solution. Finally, the crude products were filtered, washed, dried and then was further purified with column chromatography (silica gel, 200–300 mesh) to generate 4-(diphenylamino)benzaldehyde (**1a**, yield: 82%), 4,4′-(phenylazanediyl)dibenzaldehyde (**1b**, yield: 62%), respectively.

General synthesis approach for triphenylamine-benzimidazole under solvent-free and microwave irradiation conditions.

A mixture of dry silica gel (1.00 g), 3-(diphenylamino)benzaldehyde (1.05 mmol), substituted o-phenylenediamine (1.00 mmol), $Na_2S_2O_5$ (1.00 mmol) was fully ground in a mortar, then transferred to a 50 mL dried round-bottomed flask and heated with microwave irradiation for 20–25 min (the reaction heating power was 300 W). The reaction progress was monitored by TLC. When the microwave-assisted reaction was over, the residue was cooled to room temperature and purified by column chromatography (silica gel, 200–300 mesh, the eluant: petroleum ether/ethyl acetate = 8/1 (except for carboxyl substituted product, firstly, removal of impurities with the eluant: petroleum ether/ethyl acetate = 1/1. Then, the target product, the eluant: dichloromethane/methanol = 10/1.) to generate 4-(6-substituted-1*H*-benzo[d]imidazol-2-yl)-*N*,*N*-diphenylanilines.

General synthesis approach for triphenylamine-benzimidazole in DMF solvent under microwave irradiation

A mixture of 4-(diphenylamino)benzaldehyde (1.05 mmol) or 4,4′-(phenylazanediyl)dibenzaldehyde (1.05 mmol), and substituted *o*-phenylenediamine (1.00 mmol or 2.00 mmol) in DMF solvent (15 mL) was fully transferred to a 250 mL microwave reaction bottle equipped with a magnetic stir bar, reflux condenser and thermocouple thermo element. Then, $Na_2S_2O_5$ (1 mmol) was added to the above mixture for synthesizing compounds **2a**−**2e** while 2 mmol $Na_2S_2O_5$ was required for synthesizing compounds **2f**−**2j** and heated with microwaved at 98 °C for 20–30 min. However, when PTSA is used as a catalyst, only 0.1 mmol PTSA was added to the above mixture for synthesizing compounds **2a**−**2j** and heated with microwave irradiation at 120 °C for 15–25 min. The reaction was monitored by TLC. The residue was cooled to room temperature, and then poured into beaker filled with 80–100 mL of ice water to gain crude product until it was completely precipitated. Further, the crude product was collected by vacuum filtration, washed with water (3 × 25 mL) and dried. The slurry was extracted with ethyl acetate if the crude product didn't crystallize. Finally, the desired products **2a**−**2j** were obtained by purified with column chromatography (silica gel, 200–300 mesh, the eluant: petroleum ether/ethyl acetate = 3/1 (except for carboxyl substituted product, firstly, removal of impurities with the eluant: petroleum ether/ethyl acetate = 1/1. Then, the target product, the eluant: chloroform/methanol = 10/1.).

Characterization data of synthesized compounds

4-(1*H*-benzo[d]imidazol-2-yl)-*N*,*N*-diphenylaniline (2a)

^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm) 12.79 (s, 1H; N–H), 8.05 (d, J = 8.7 Hz, 2H; Ar–H), 7.55 (s, 2H; Ar–H), 7.37 (m, 4H; Ar–H), 7.17 (dd, J = 5.9, 3.1 Hz, 2H; Ar–H), 7.15–7.11 (m, 6H; Ar–H), 7.05 (d, J = 8.7 Hz, 2H; Ar–H); ^{13}C NMR (126 MHz, DMSO-d_6) δ (ppm) 151.62, 149.24, 147.08, 130.23, 128.14, 125.40, 124.43, 123.62, 122.31, 122.04, 40.00. IR (KBr) (ν/cm^{-1}) 3137, 3029, 1612, 1593, 1454, 1403, 1325, 1277, 839, 748, 694. HRMS (EI) *m/z* $[M+H]^+$ Calcd for $C_{25}H_{19}N_3$: 362.1657, found: 362.1695.

4-(5-chloro-1*H*-benzo[d]imidazol-2-yl)-*N*,*N*-diphenylaniline (2b)

^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm) 12.93 (s, 1H; N–H), 8.04 (d, J = 8.8 Hz, 2H; Ar–H), 7.66 (s, 1H; Ar–H), 7.51 (s, 1H; Ar–H), 7.37 (m, 4H; Ar–H), 7.21–7.10 (m, 7H; Ar–H), 7.04 (d, J = 8.8 Hz, 2H; Ar–H); ^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm) 149.07, 146.54, 129.75, 125.04, 122.67, 121.36, 39.59. IR (KBr) (ν/cm^{-1}) 3290, 3152, 3030, 1590, 1490, 1446, 1328, 1271, 1183, 1109, 835, 802, 750, 693. HRMS (EI): Calcd for $C_{25}H_{18}ClN_3$ $[M+H]^+$ 396.1268, found 396.1285.

4-(5-bromo-1*H*-benzo[d]imidazol-2-yl)-*N*,*N*-diphenylaniline (2c)

^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm) 12.94 (s, 1H; N–H), 8.04 (d, J = 8.8 Hz, 2H; Ar–H), 7.72 (dd, J = 5.7, 3.3 Hz, 1H; Ar–H), 7.67 (dd, J = 5.7, 3.3 Hz, 1H; Ar–H), 7.40–7.34 (m, 4H; Ar–H), 7.30 (dd, J = 8.5, 1.8 Hz, 1H; Ar–H), 7.17–7.07 (m, 6H; Ar–H), 7.04 (d, J = 8.8 Hz, 2H; Ar–H); ^{13}C NMR (151 MHz, DMSO-d_6) δ (ppm) 152.93, 149.55, 146.98, 130.26, 129.12, 128.31, 125.54, 125.06, 124.57, 122.98, 121.78. IR (KBr) (ν/cm^{-1}) 3322, 3112, 3031, 1587, 1484, 1325, 1287, 1183, 1119, 846, 753, 687, 510. HRMS (EI): Calcd for $C_{25}H_{18}BrN_3$ $[M+H]^+$ 440.0762, found 440.0793.

4-(5-methyl-1*H*-benzo[d]imidazol-2-yl)-*N*,*N*-diphenylaniline (2d)

^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm) 12.58 (s, 1H; N–H), 8.03 (d, J = 8.8 Hz, 2H; Ar–H), 7.49–7.27 (m, 6H;

Ar–H), 7.15–7.07 (m, 6H; Ar–H), 7.06–7.02 (m, 2H; Ar–H), 6.99 (d, $J = 8.2$ Hz, 1H; Ar–H), 2.41 (s, 3H; CH_3); ^{13}C NMR (151 MHz, DMSO-d_6) δ (ppm) 151.38, 149.01, 147.13, 130.20, 127.98, 125.28, 124.32, 124.07, 122.23, 40.14, 21.80. IR (KBr) (ν/cm^{-1}) 3146, 3034, 2961, 2870, 1587, 1487, 1443, 1394, 1325, 1277, 1192, 1110, 845, 743, 687. HRMS (EI): Calcd for $C_{26}H_{21}N_3[M+H]^+$ 376.1814, found 376.1839.

2-(4-(diphenylamino)phenyl)-1*H*-benzo[d] imidazole-5-carboxylicacid (2e)

^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm) 13.18 (s, 1H; N–H), 12.25 (s, 1H; COOH) 8.09 (d, $J = 8.8$ Hz, 2H), 7.82 (d, $J = 8.5$ Hz, 1H), 7.59 (s, 1H), 7.40–7.36 (m, 3H), 7.19–7.10 (m, 6H), 7.09–6.98 (m, 3H), 6.49 (d, $J = 8.1$ Hz, 1H); ^{13}C NMR (151 MHz, DMSO-d_6) δ (ppm) 168.59, 149.63, 146.99, 140.56, 134.13, 130.28, 128.46, 125.58, 124.60, 123.09, 121.73, 120.79, 115.78, 113.09. IR (KBr) (ν/cm^{-1}) 3132, 3019, 1677, 1614, 1587, 1487, 1327, 1287, 1193, 1147, 949, 830, 753, 697. HRMS (EI): Calcd for $C_{26}H_{19}N_3O_2$ $[M+H]^+$ 406.1556, found 406.1590.

N-(4-(1*H*-benzo[d]imidazol-2-yl)phenyl)-4-(1*H*-benzo[d] imidazol-2-yl)-*N*-phenylaniline (2f)

^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm) 12.84 (s, 2H; N–H), 8.16–8.10 (m, 4H; Ar–H), 7.61–7.54 (m, 4H; Ar–H), 7.43 (t, $J = 7.9$ Hz, 2H; Ar–H), 7.22–7.17 (m, 11H; Ar–H); ^{13}C NMR (126 MHz, DMSO-d_6) δ (ppm) 151.49, 148.61, 146.67, 130.44, 129.12, 128.30, 126.06, 125.11, 124.85, 123.67, 122.38. IR (KBr) (ν/cm^{-1}) 3131, 3029, 1590, 1492, 1398, 1321, 1276, 1168, 1114, 835, 742, 678. HRMS (EI): Calcd for $C_{21}H_{15}NO_3$ $[M+H]^+$ 478.2032, found 478.5335.

4-(5-chloro-1*H*-benzo[d] imidazol-2-yl)-*N*-(4-(6-chloro-1*H*-benzo[d]imidazol-2-yl) phenyl)-*N*-phenylaniline (2g)

^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm) 12.93 (s, 2H; N–H), 8.11 (d, $J = 8.7$ Hz, 2H; Ar–H), 8.02 (d, $J = 8.8$ Hz, 1H; Ar–H), 7.72 (dd, $J = 5.6$, 3.4 Hz, 1H; Ar–H), 7.67 (dd, $J = 5.6$, 3.4 Hz, 1H; Ar–H), 7.60–7.52 (m, 2H; Ar–H), 7.43 (t, $J = 7.8$ Hz, 1H; Ar–H), 7.36 (d, $J = 4.6$ Hz, 2H; Ar–H), 7.20 (td, $J = 5.7$, 3.3 Hz, 5H; Ar–H), 7.10 (t, $J = 7.8$ Hz, 2H; Ar–H), 7.01 (d, $J = 8.8$ Hz, 2H; Ar–H); ^{13}C NMR (151 MHz, DMSO-d_6) δ (ppm) 152.91, 148.84, 146.53, 132.47, 130.47, 128.46, 126.66, 125.29, 124.64, 124.36, 123.63, 122.57, 122.02. IR (KBr) (ν/cm^{-1}) 3333, 3147, 3030, 1595, 1492, 1325, 1277, 1183, 1120, 840, 796, 752, 694. HRMS (EI): Calcd for $C_{32}H_{21}Cl_2N_5$ $[M+H]^+$ 546.1252, found 546.1258.

4-(5-bromo-1*H*-benzo[d] imidazol-2-yl)-*N*-(4-(6-bromo-1*H*-benzo[d]imidazol-2-yl) phenyl)-*N*-phenylaniline (2h)

^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm) 13.01 (s, 2H; N–H), 8.11 (d, $J = 8.7$ Hz, 4H; Ar–H), 7.75 (s, 2H; Ar–H), 7.53 (d, $J = 8.5$ Hz, 2H; Ar–H), 7.43 (t, $J = 7.9$ Hz, 2H; Ar–H), 7.34–7.30 (m, 2H; Ar–H), 7.24–7.17 (m, 7H; Ar–H); ^{13}C NMR (126 MHz, DMSO-d_6) δ (ppm) 152.71, 148.88, 146.50, 130.49, 128.51, 126.25, 125.34, 124.22, 123.64, 123.25, 121.96, 114.55. IR (KBr) (ν/cm^{-1}) 3328, 3137, 3029, 1594, 1487, 1324, 1271, 1178, 1125, 840, 743, 694, 509. HRMS (EI): Calcd for $C_{32}H_{21}Br_2N_5$ $[M+H]^+$ 634.0242, found 634.0230.

4-(5-methyl-1*H*-benzo[d] imidazol-2-yl)-*N*-(4-(6-methyl-1*H*-benzo[d]imidazol-2-yl) phenyl)-*N*-phenylaniline (2i)

^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm) 12.65 (s, 2H; N–H), 8.11–8.08 (m, 4H; Ar–H), 7.51–7.30 (m, 6H; Ar–H), 7.21–7.13 (m, 7H; Ar–H), 7.01 (d, $J = 8.2$ Hz, 2H; Ar–H), 2.43 (s, 6H; CH_3); ^{13}C NMR (151 MHz, DMSO-d_6) δ (ppm) 148.43, 146.73, 130.40, 128.13, 125.91, 125.11, 124.97, 123.68, 39.99, 21.80. IR (KBr) (ν/cm^{-1}) 3298, 3029, 2961, 2857, 1609, 1590, 1481, 1443, 1389, 1320, 1277, 1184, 1119, 837, 753, 697. HRMS (EI): Calcd for $C_{34}H_{27}N_5$ $[M+H]^+$ 505.2266, found 505.2287.

2-(4-((4-(6-carboxy-1*H*-benzo[d]imidazol-2-yl) phenyl)(phenyl)amino)phenyl)-1*H*-benzo[d] imidazole-5-carboxylicacid (2j)

^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm) 8.17 (d, $J = 8.5$ Hz, 6H; Ar–H), 7.83 (d, $J = 8.0$ Hz, 2H; Ar–H), 7.55 (d, $J = 8.3$ Hz, 2H; Ar–H), 7.43 (t, $J = 7.8$ Hz, 2H; Ar–H), 7.20 (t, $J = 7.5$ Hz, 7H; Ar–H); ^{13}C NMR (126 MHz, DMSO-d_6) δ (ppm) 153.12, 148.72, 146.62, 130.45, 128.51, 126.14, 125.18, 124.76, 123.95, 123.62. IR (KBr) (ν/cm^{-1}) 3152, 1594, 1551, 1487, 1400, 1326, 1277, 1184, 1119, 959, 837, 781, 678. HRMS (EI): Calcd for $C_{34}H_{23}N_5O_4$ $[M+H]^+$ 566.1828, found 566.1801.

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