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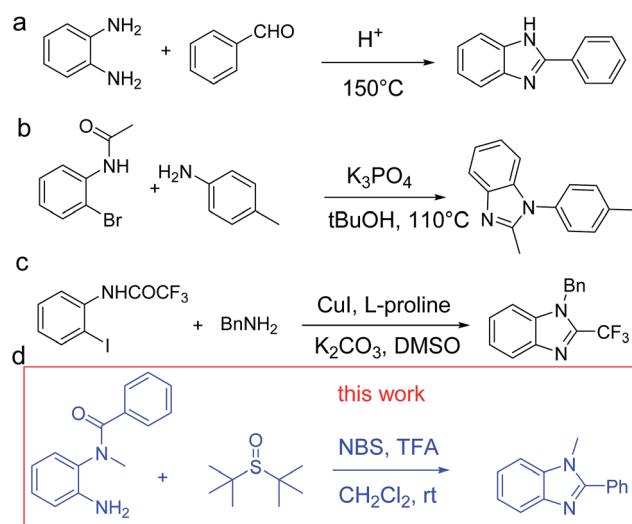
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Introduction

In recent years, molecules based on 1,2-disubstituted benzimidazole have attracted extensive attention due to their wide applications in new drugs, including antihypertensive drugs, GABA_A receptor agonists and the hepatitis C virus (HCV) NS5B polymerase inhibitors.^{1–3} We have witnessed great progress in the development of benzimidazole derivatives in recent decades. One of the key improvements is the effective synthesis of these functional benzimidazole compounds. The reported methods for the synthesis of 1,2-disubstituted benzimidazoles mostly include condensation of anilines with aldehydes under relatively harsh conditions (Scheme 1a),⁴ direct oxidative coupling of amines to imines (Scheme 1b)⁵ and transition metal-catalyzed intramolecular cyclization (Scheme 1c).⁶ However, the reported methods mostly employ harsh and strict conditions or expensive catalysts. Considering that harsh conditions could possibly cause decomposition of substrates or products, it is significant to explore milder conditions for the synthesis of 1,2-disubstituted benzimidazoles.

The synthesis of benzimidazoles involves the construction of C–N bond, an important class of transformation in organic synthesis.^{7,8} Of all C–N bond forming reactions, Schiff base represents an attractive and robust approach to the synthesis of nitrogen-containing compounds.^{9,10} However, in some cases, the activity of Schiff base reactions is not high enough. In this regard, assistant groups are introduced to enhance the activity.

Our group recently successfully established an effective C–S functionalization strategy, and various useful Wittig-like processes have been developed based on these investigations. For example, the synthesis of 3-substituted aryl^{4,5} isothiazoles through an all-



Scheme 1 The synthetic methods of 1,2-disubstituted benzimidazoles.

heteroatom Wittig-equivalent process offers a novel approach for isothiazoles.¹¹ Based on this discovery, we were interested in investigating the possibility to construct C–N bond in order to synthesize substituted benzimidazoles with the help of an aza-Wittig-equivalent process.¹² In this respect, the reaction presents extremely mild conditions compared with the reported methods. In this work, we use derivatives of *o*-phenylenediamine with the help of *tert*-butanesulfoxide and NBS in acid conditions to synthesize 1,2-disubstituted benzimidazoles, which demonstrates a novel synthetic route for functional benzimidazoles.

Results and discussion

The reaction details are outlined in Table 1. Our research initially began with the reaction of *o*-phenylenediamine

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Table 1 Exploration of optimal conditions for synthesizing 1,2-disubstituted benzimidazoles

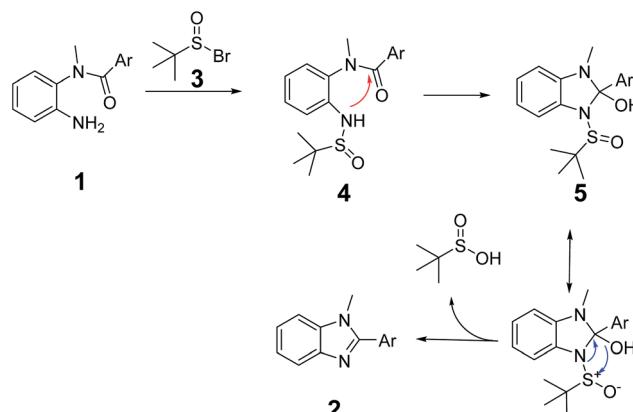
Entry	Acid	Solvent	N-Halogen succinamide	Yield 5a (%)	
				1h	2h
1	TFA	CH ₂ Cl ₂	NBS	84	
2	TFA	THF	NBS	52	
3	TFA	Tol	NBS	34	
4	TFA	DMF	NBS	60	
5	TFA	DMSO	NBS	25	
6	PTSA	CH ₂ Cl ₂	NBS	64	
7	AcOH	CH ₂ Cl ₂	NBS	43	
8	PhCOOH	CH ₂ Cl ₂	NBS	48	
9	CCl ₃ COOH	CH ₂ Cl ₂	NBS	72	
10	TFA	CH ₂ Cl ₂	NCS	66	
11	TFA	CH ₂ Cl ₂	NIS	75	
12 ^a	TFA	CH ₂ Cl ₂	NBS	36	
13 ^b	TFA	CH ₂ Cl ₂	NBS	50	
14 ^c	TFA	CH ₂ Cl ₂	NBS	68	

^a The reaction was treated at -20°C . ^b The reaction was treated at 0°C . ^c The reaction was treated at 40°C .

derivatives **1** using *tert*-butanesulfoxide and NBS with the catalysis of TFA in CH₂Cl₂. After 1 h, the conversion of the starting material (**1**) was up to 95% and the product 1,2-disubstituted benzimidazole (**2**) was obtained in a 84% yield (entry 1). By prolonging the reaction time to 4 h, the conversion would be close to 100%, and the yield could slightly increase. To optimize the reaction conditions, we firstly screened the solvents (entry 1–5). The results demonstrated that CH₂Cl₂ is the best solvent. As shown in Table 1, other polar or non-polar solvents are not optimal for this reaction. When THF, toluene and DMF were introduced as the reaction media, the yields dramatically decreased, reagent ratio (**1**/addition/acid = 1/2/1.5).

To further improve the reaction efficiency, we examined the influences of the acids in this reaction (entry 6–9). The results indicated that TFA with the appropriate acidity shows the best catalysis, while stronger acid or weaker acid would decrease the yields. It is possible that weaker acids are not suitable to form the sulfinyl halide, while stronger acids would decompose the intermediates. Furthermore, the *N*-halogen succinamide in this reaction could be NBS, NCS or NIS (entry 10–11), which helps to convert *tert*-butanesulfoxide to sulfinyl halogen. The results indicated that NBS is the best reagent while NCS and NIS could also play a similar role with the slightly decreased yields. Moreover, when the reaction was carried out at -20°C , 0°C or 40°C , respectively, all yields would decrease compared with that at 25°C (entry 12–14).

According to our previous works, as shown in Scheme 2, a possible mechanism is based on the aza-Wittig-equivalent



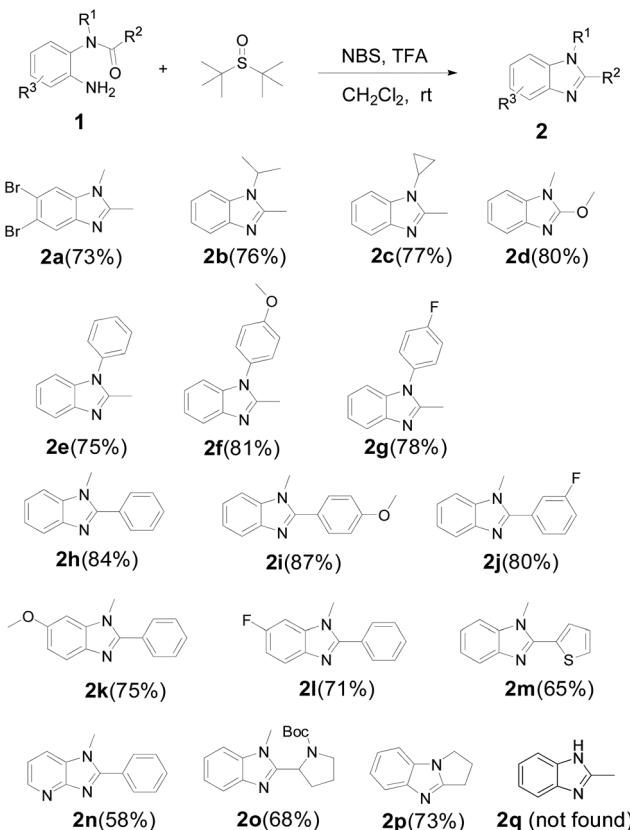
Scheme 2 The possible mechanism of forming benzimidazole.

process. In the beginning, *tert*-butanesulfoxide reacted with NBS to afford *tert*-butanesulfinic bromine (3). Subsequently, *tert*-butanesulfinic bromine reacted with the substrate (**1**) to form *tert*-butanesulfinamide (**4**). Then the sulfinyl amide attacks the carbonyl group to form the intermediate (**5**). In the end, by intramolecular rearrangements and charge transfer, accompanied by the elimination of *tert*-butanesulfinic acid, 1,2-disubstituted benzimidazole (**2**) can be formed. Consistent with this mechanism, the intermediate (**4**) could be detected by NMR and HRMS (see ESI†). From the mechanism, we can clearly see that one of the key steps is the formation and stability of intermediate (**5**). When the substrate is less reactive to form **5** or **5** is more inclined to decomposition rather than rearrangements, the product (**2**) could not be successfully synthesized. It is worth to note that by treating intermediate (**4**) in the optimized condition, the yield of benzimidazole could be effectively enhanced.

With the optimized reaction conditions in hand, a collection of starting materials (**1**) bearing various functional or electronic effecting groups were subjected to the NBS/TFA/CH₂Cl₂ protocol to produce **2**. As shown in Scheme 3, as expected, when R₁ and R₂ are alky or alkoxy groups (**2a–2d**), the reactions proceed smoothly and the yields are satisfying (73–80%). It is worthy to note that for **2a**, we obtained the dibromo substituted product, which is possibly related to the high activity of **1a**.

Furthermore, substrates with substituent (R¹), regardless of an electron-withdrawing or electron-donating group, could react smoothly to afford the desired product in high yields (75–81%) (**2e–2g**). This reaction also tolerated a range of electronic effect groups in the substituent (R²) (80–87%), which enabled potential applications of the final products in further functionalization (**2h–2j**). The substituents (R³) on aromatic ring present few influence with the reaction (**2k–2l**), and the yields are excellent. On the other hand, apart from introducing benzene units to benzimidazoles, we have successfully synthesized heterocycle fused products (**2m–2o**). However, the yields are slightly lower than the benzo analogues. Interestingly, the fused ring product was also obtained in a good yield (**2p**), which affords a new route to synthesize novel benzimidazoles. In comparison, **2k**, **2l** and **2n** could also be obtained without using





Scheme 3 Additional examples of 1,2-disubstituted benzimidazoles synthesis. Reaction conditions: a mixture of 1 (0.5 mmol), NBS (1.0 mmol), TFA (0.75 mmol), and CH₂Cl₂ (5 mL) was stirred at room temperature for 2 h under a nitrogen atmosphere.

the aza-Wittig process, but the yields were dramatically decreased (see ESI†), indicating that our new aza-Wittig protocol may be a very useful complement to the existing methods of benzimidazole synthesis. However, *N*-mono-substituted amide could not be transformed to corresponding benzimidazole (**2q**).

Experimental

Materials and instrumentation

All the reactions were performed in oven-dried reaction vessels under N₂. Commercially available solvents and reagents were used without further purification unless otherwise mentioned. CH₂Cl₂, THF, toluene, DMF, DMSO were dried before using. Thin-layer chromatography (TLC) was carried out on aluminum sheets coated with silica gel 60 F254 (MERCK). ¹H NMR spectra were obtained using a Bruker AM 400 spectrometer, and chemical shifts were reported relative to DMSO-*d*₆ (δ = 2.52), MeOD (δ = 3.34) and CDCl₃ (δ = 7.26) in ppm. ¹³C NMR spectra were recorded at 100 MHz (Bruker AM 400) and chemical shifts were reported relative to DMSO-*d*₆ (δ = 40.4), MeOD (δ = 49.8) and CDCl₃ (δ = 77.00) in ppm. The characterization data of **2b**, **2c**, **2d**, **2e**, **2f**, **2g**, **2h**, **2i**, **2j**, **2k**, **2m**, **2n**, **2p** could be found in the previous literature.¹³

General procedure for 2a-2o

In a 25 mL vial along with a stirring bar, to a mixture of *tert*-butanesulfoxide (1.0 mmol), TFA (0.75 mmol) and NBS (1.0 mmol) in CH₂Cl₂ (5 mL) under N₂. A CH₂Cl₂ (5 mL) solution of **1** (0.5 mmol) was added to the mixture and the reaction was stirred at RT for additional 1 h. The reaction mixture was washed with water; dried over anhydrous Na₂SO₄ and evaporated *in vacuo*. The residue was purified by silica-gel column chromatography with CH₂Cl₂/PE as an eluent. Recrystallization from CH₂Cl₂/hexane gave the white solid **2**.

2a. ¹H NMR (400 MHz, MeOD) δ 8.19 (m, 1H), 7.99 (m, 1H), 4.00 (s, 3H), 2.91 (s, 3H). ¹³C NMR (100 MHz, MeOD) δ 154.1, 134.3, 131.4, 129.5, 118.7, 115.0, 106.4, 62.8, 31.0, 10.5. HRMS [M + H⁺] *m/z* = 302.9126, calcd for C₉H₉N₂Br₂ = 302.9127.

2b. ¹H NMR (400 MHz, DMSO) δ 8.12–7.95 (m, 1H), 7.85–7.71 (m, 1H), 7.57–7.39 (m, 2H), 4.95 (s, 1H), 2.82 (s, 3H), 1.64 (d, *J* = 6.9 Hz, 6H). ¹³C NMR (101 MHz, DMSO) δ 125.2, 124.9, 115.3, 114.2, 49.9, 20.8, 13.1.

2c. ¹H NMR (400 MHz, DMSO) δ 7.51 (d, *J* = 8.8 Hz, 2H), 7.23–7.08 (m, 2H), 3.35–3.23 (m, 1H), 2.58 (s, 3H), 1.18 (dd, *J* = 6.8, 2.0 Hz, 2H), 1.07–0.95 (m, 2H). ¹³C NMR (100 MHz, DMSO) δ 154.0, 142.4, 136.5, 121.9, 121.6, 118.7, 110.6, 40.4, 24.8, 14.8. HRMS [M + H⁺] *m/z* = 173.1075, calcd for C₁₁H₁₃N₂ = 173.1073.

2d. ¹H NMR (400 MHz, MeOD) δ 7.62–7.50 (m, 2H), 7.49 (d, *J* = 2.8 Hz, 2H), 3.85 (s, 3H), 3.38–3.30 (m, 3H). ¹³C NMR (100 MHz, MeOD) δ 129.7, 128.3, 123.6, 52.8, 36.7.

2e. ¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, *J* = 7.8 Hz, 1H), 7.58–7.41 (m, 3H), 7.31 (d, *J* = 7.4 Hz, 2H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 7.8 Hz, 1H), 2.49 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 129.9, 128.8, 127.0, 122.6, 122.4, 118.9, 109.9, 14.3.

2f. ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, *J* = 6.2 Hz, 1H), 7.27 (t, *J* = 7.8 Hz, 3H), 7.20 (s, 1H), 7.09 (t, *J* = 7.8 Hz, 3H), 3.91 (s, 3H), 2.51 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 160.1, 128.3, 122.6, 118.8, 115.1, 110.0, 29.8.

2g. ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, *J* = 7.8 Hz, 1H), 7.41–7.34 (m, 2H), 7.29 (dd, *J* = 10.2, 6.2 Hz, 3H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.10 (d, *J* = 7.8 Hz, 1H), 2.52 (s, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 162.4, 152.8, 150.0, 141.3, 135.3, 131.6, 129.0, 128.9, 126.2, 122.8, 120.5, 119.0, 117.1, 111.9, 109.7, 30.4, 24.5.

2h. ¹H NMR (400 MHz, DMSO) δ 8.07 (dd, *J* = 6.2, 2.8 Hz, 1H), 8.02 (d, *J* = 6.8 Hz, 2H), 7.93–7.87 (m, 1H), 7.78 (dq, *J* = 14.4, 7.2 Hz, 3H), 7.69–7.62 (m, 2H), 4.06 (s, 3H). ¹³C NMR (100 MHz, DMSO) δ 150.3, 133.8, 133.1, 131.5, 130.8, 129.7, 126.7, 126.2, 123.3, 114.9, 113.6, 33.2.

2i. ¹H NMR (400 MHz, DMSO) δ 7.81 (d, *J* = 8.8 Hz, 2H), 7.67 (d, *J* = 7.4 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.26 (dd, *J* = 9.4, 7.8 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 3.86 (d, *J* = 1.8 Hz, 6H). ¹³C NMR (100 MHz, DMSO) δ 160.8, 153.4, 142.9, 137.0, 131.2, 122.9, 122.4, 122.2, 119.2, 114.5, 110.8, 55.8, 32.1.

2j. ¹H NMR (400 MHz, DMSO) δ 8.07 (d, *J* = 7.4 Hz, 1H), 7.97–7.85 (m, 3H), 7.80 (dd, *J* = 13.8, 7.6 Hz, 1H), 7.66 (dd, *J* = 9.2, 6.8 Hz, 3H), 4.06 (s, 3H). ¹³C NMR (101 MHz, DMSO) δ 163.4, 161.0, 149.0, 133.9, 132.0, 127.2, 126.7, 126.3, 120.1, 119.9, 118.0, 117.7, 115.2, 113.5, 33.1.



2k. ^1H NMR (400 MHz, DMSO) δ 7.83 (dd, J = 7.8, 1.6 Hz, 2H), 7.59–7.49 (m, 4H), 7.18 (d, J = 2.2 Hz, 1H), 6.87 (dd, J = 8.8, 2.4 Hz, 1H), 3.86 (s, 6H). ^{13}C NMR (100 MHz, DMSO) δ 156.6, 152.6, 137.7, 137.3, 130.8, 129.7, 129.5, 129.0, 119.9, 94.4, 32.1.

2l. ^1H NMR (400 MHz, DMSO) δ 7.84 (s, 2H), 7.75–7.66 (m, 1H), 7.59–7.33 (m, 4H), 7.10 (s, 1H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 160.5, 158.1, 154.4, 139.5, 137.3, 130.4, 129.67 (s), 129.1, 120.4, 110.5, 97.9, 32.3. HRMS [M + H $^+$] m/z = 227.0981, calcd for $\text{C}_{14}\text{H}_{12}\text{N}_2\text{F}$ = 227.0979.

2m. ^1H NMR (400 MHz, DMSO) δ 8.12 (d, J = 4.7 Hz, 2H), 7.90 (d, J = 7.6 Hz, 1H), 7.78 (d, J = 7.2 Hz, 1H), 7.56–7.35 (m, 3H), 4.12 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 132.8, 129.1, 125.0, 116.4, 112.4, 32.8.

2n. ^1H NMR (400 MHz, CDCl_3) δ 8.62 (d, J = 4.0 Hz, 1H), 7.84 (dd, J = 6.8, 2.8 Hz, 2H), 7.74 (d, J = 7.8 Hz, 1H), 7.59–7.53 (m, 3H), 7.27 (dd, J = 7.2, 4.0 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 155.9, 151.9, 135.4, 130.2, 130.0, 129.7, 129.2, 128.7, 127.3, 117.9, 31.6, 27.0.

2o. ^1H NMR (400 MHz, DMSO) δ 7.58 (d, J = 7.2 Hz, 1H), 7.52 (d, J = 7.8 Hz, 1H), 7.19 (dd, J = 13.4, 7.2 Hz, 2H), 5.24–4.92 (m, 1H), 3.82 (d, J = 18.8 Hz, 3H), 3.58 (d, J = 6.0 Hz, 1H), 3.45 (d, J = 7.2 Hz, 1H), 2.43–2.04 (m, 2H), 2.05–1.83 (m, 2H), 1.36 (s, 4H), 1.01 (s, 5H). ^{13}C NMR (100 MHz, DMSO) δ 156.9, 156.3, 153.4, 142.5, 135.9, 122.0, 121.8, 118.9, 110.2, 78.6, 32.9, 28.61, 28.1, 24.2, 23.5. HRMS [M + H $^+$] m/z = 302.1863, calcd for $\text{C}_{17}\text{H}_{24}\text{N}_3\text{O}_2$ = 302.1869.

2p. ^1H NMR (400 MHz, CDCl_3) δ 7.57 (d, J = 1.6 Hz, 1H), 7.43 (d, J = 1.6 Hz, 1H), 4.13 (t, J = 7.2 Hz, 2H), 3.12 (t, J = 7.8 Hz, 2H), 2.81–2.72 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 162.4, 133.3, 127.4, 114.7, 112.0, 43.2, 26.0, 23.5.

Synthesis of intermediate 4

In a 25 mL vial along with a stirring bar, to a mixture of *tert*-butanesulfoxide (1.0 mmol), TFA (0.75 mmol) and NBS (1.0 mmol) in CH_2Cl_2 (5 mL) under N_2 . A CH_2Cl_2 (5 mL) solution of **1h** (0.5 mmol) was added to the mixture and the reaction was stirred at RT for additional 10 min. The reaction mixture was washed with water; dried over anhydrous Na_2SO_4 and evaporated *in vacuo*. The residue was purified by silica-gel column chromatography with $\text{CH}_2\text{Cl}_2/\text{PE}$ as an eluent. Recrystallization from $\text{CH}_2\text{Cl}_2/\text{hexane}$ gave the white solid **4**.

4. ^1H NMR (400 MHz, CDCl_3) δ 7.32 (t, J = 11.6 Hz, 2H), 7.21–7.00 (m, 2H), 5.54 (m, 1H), 3.20 (m, 3H), 1.86 (s, 3H), 1.33 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 171.9, 171.5, 138.8, 133.6, 133.2, 129.6, 128.5, 123.9, 123.5, 118.9, 118.1, 36.0, 31.9, 29.8, 29.3, 22.6, 22.3, 14.0.

Conclusions

In summary, by treating the derivatives of *o*-phenylenediamine with the help of *tert*-butanesulfoxide and NBS in the acid condition, we have demonstrated an effectively intramolecular cyclization sequence to construct substituted benzimidazoles containing various alky or aromatic groups, which reveals a new approach for aza-Wittig-equivalent process. This synthetic method involves mild conditions instead of reported harsh

conditions and the yields are excellent. Furthermore, a series of substituted benzimidazoles containing diverse electronic effect groups have been successfully obtained based on this method. Further work towards expanding the use of photoredox catalysis in the construction of heterocyclic products is underway.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

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