Supporting Information

Visible-light-induced condensation cyclization to synthesize benzimidazoles using fluorescein as photocatalyst

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General Information

All starting materials and the reagents were purchased from TCI and J&K Chemical Company, and the reagents were used without further purification unless specified. The reactions were monitored by thin layer chromatography (TLC), and the products were purified by column chromatography on silica gel (300 ~ 400 mesh). 1H NMR, 13C NMR and 19F NMR spectra were recorded on a Bruker Ultrashield™ 400 spectrometer operating at 400 MHz and 100 MHz in DMSO or CDCl3. 1H NMR and 13C NMR were reported in ppm with tetramethylsilane (TMS) as internal standard. 19F NMR was reported in ppm with trifluoroacetic acid (TFA) as internal standard. The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, m = multiple. Coupling constants (J) were reported in Hertz (Hz). Room temperature fluorescence spectra (PL) of the synthesized compounds were taken using a Shimadzu RF-5301PC fluorescence spectrophotometer. Cyclic voltammetric (CV) measurements were carried out on the Chi 1200A system in a conventional three-electrode cell with a glass carbon working electrode, a platinum-wire counter electrode and a Ag/AgCl reference electrode with
ferrocene as the internal standard referenced in anhydrous chloromethane solution of C_{16}H_{36}ClNO_4 (0.10 M) at a sweeping rate of 100 mV s\(^{-1}\) at room temperature.

**Figure S1** Stern-Volmer fluorescence quenching experiments

**Figure S2** Cyclic voltammetry (CV) curves of intermediate B

**Optimum catalytic system comparison**

In order to further evaluate the efficiency of the catalyst system, we chose
benzaldehyde and o-phenylenediamine as representative substrates. The comparison results between the catalyst system and the earlier reported systems are summarized in Table S1. Although their photocatalysts are reusable and the catalytic system is highly efficient, their time requirements are relatively long. And our system has high catalytic performance to obtain the target product under relatively mild conditions without metal presence in a short reaction time. Therefore, the use of fluorescein as a photocatalyst to obtain benzimidazole is more practical and efficient than the previous method.

**Table S1** Comparisons of optimal protocol with earlier reports

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**1H NMR spectra and analysis of products**

Figure S3 1H NMR spectrum of 2-phenyl-1H-benzo[d]imidazole (3a)

1H NMR (400 MHz, DMSO) δ = 12.88 (s, 1H), 8.24 – 8.14 (m, 2H), 7.64 – 7.47 (m, 5H), 7.27 – 7.15 (m, 2H).

Figure S4 1H NMR spectrum of 2-(2-bromophenyl)-1H-benzo[d]imidazole (3b)

1H NMR (400 MHz, DMSO) δ = 12.74 (s, 1H), 7.85 – 7.74 (m, 2H), 7.60 (d, J=17.5, 2H), 7.55 (d, J=7.6, 1H), 7.49 – 7.44 (m, 1H), 7.24 (dd, J=6.0, 3.1, 2H).
Figure S5 $^1$H NMR spectrum of 2-(2-chlorophenyl)-1H-benzo[d]imidazole\(^3\) (3c)

$^1$H NMR (400 MHz, DMSO) $\delta$ = 12.72 (s, 1H), 7.93 (s, 1H), 7.62 (d, $J$=44.9, 5H), 7.27 (s, 2H).

Figure S6 $^1$H NMR spectrum of 2-(2-fluorophenyl)-1H-benzo[d]imidazole\(^5\) (3d)

$^1$H NMR (400 MHz, DMSO) $\delta$ = 12.39 (s, 1H), 8.25 (s, $J$=7.6, 1H), 7.60 (dd, $J$=23.0, 15.8, 3H), 7.49 – 7.36 (m, 2H), 7.25 (s, 2H).
Figure S7 $^{13}$C NMR spectrum of 2-(2-fluorophenyl)-1H-benzo[d]imidazole$^5$ (3d)

$^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 158.69, 146.86, 143.52, 135.49, 132.35, 132.27, 130.69, 125.56, 125.53, 123.23, 122.31, 119.39, 118.63, 118.52, 117.09, 116.87, 112.39.

Figure S8 $^{19}$F NMR spectrum of 2-(2-fluorophenyl)-1H-benzo[d]imidazole$^5$ (3d)

$^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 158.69, 146.86, 143.52, 135.49, 132.35, 132.27, 130.69, 125.56, 125.53, 123.23, 122.31, 119.39, 118.63, 118.52, 117.09, 116.87, 112.39.
Figure S9 $^1$H NMR spectrum of 2-(o-tolyl)-1H-benzo[d]imidazole (3e)

$^1$H NMR (400 MHz, DMSO) $\delta$ = 12.62 (s, 1H), 7.73 (dd, J=24.3, 6.6, 2H), 7.54 (d, J=6.8, 1H), 7.40 (s, 3H), 7.28 – 7.17 (m, 2H), 2.63 (s, 3H).

Figure S10 $^1$H NMR spectrum of 2-(3-chlorophenyl)-1H-benzo[d]imidazole (3f)

$^1$H NMR (400 MHz, DMSO) $\delta$ = 13.00 (s, 1H), 8.14 (d, J=7.2, 2H), 7.78 (d, J=7.3, 2H), 7.62 (d, J=7.5, 2H), 7.24 (s, 2H).
Figure S11 $^1$H NMR spectrum of 2-(3-nitrophenyl)-1H-benzo[\textit{d}]imidazole$^3$ (3g)

$^1$H NMR (400 MHz, DMSO) \( \delta = 9.03 \text{ (s, 1H)}, 8.61 \text{ (d, } J=7.8, 1\text{H)}, 8.37 \text{ (d, } J=8.1, 1\text{H)}, 7.89 \text{ (t, } J=8.0, 1\text{H)}, 7.70 \text{ (dd, } J=6.0, 3.1, 2\text{H)}, 7.33 \text{ (dd, } J=6.0, 3.1, 2\text{H}).$

Figure S12 $^1$H NMR spectrum of 2-(3-fluorophenyl)-1H-benzo[\textit{d}]imidazole$^5$ (3h)

$^1$H NMR (400 MHz, DMSO) \( \delta = 13.03 \text{ (s, 1H)}, 8.05 \text{ (d, } J=7.8, 2\text{H)}, 7.98 \text{ (d, } J=10.2, 2\text{H)}, 7.62 \text{ (dd, } J=13.9, 7.4, 3\text{H)}, 7.35 \text{ (t, } J=8.2, 3\text{H)}, 7.24 \text{ (dd, } J=5.8, 3.0, 1\text{H}).$
Figure S13 $^{13}$C NMR spectrum of 2-(3-fluorophenyl)-1H-benzo[d]imidazole$^5$ (3h)

$^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 164.14, 161.72, 150.45, 150.42, 133.02, 132.94, 131.65, 131.57, 123.00, 122.98, 117.16, 116.95, 113.69, 113.37.

Figure S14 $^{19}$F NMR spectrum of 2-(3-fluorophenyl)-1H-benzo[d]imidazole$^5$ (3h)

$^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 164.14, 161.72, 150.45, 150.42, 133.02, 132.94, 131.65, 131.57, 123.00, 122.98, 117.16, 116.95, 113.60, 113.37.
**Figure S15** $^1$H NMR spectrum of 2-(m-tolyl)-1H-benzo[d]imidazole\(^3\) (3i)

$^1$H NMR (400 MHz, DMSO) $\delta$ = 12.85 (s, 1H), 8.06 – 7.94 (m, 2H), 7.59 (s, 2H), 7.44 (t, J=7.6, 1H), 7.31 (d, J=7.5, 1H), 7.20 (dd, J=5.8, 2.9, 2H), 2.42 (s, 3H).

**Figure S16** $^1$H NMR spectrum of 2-(4-chlorophenyl)-1H-benzo[d]imidazole\(^3\) (3j)

$^1$H NMR (400 MHz, DMSO) $\delta$ = 12.99 (s, 1H), 8.21 (d, J=8.5, 2H), 7.73 – 7.51 (m, 4H), 7.24 (d, J=6.7, 2H).
Figure S17 $^1$H NMR spectrum of 2-(4-fluorophenyl)-1H-benzo[d]imidazole$^3$ (3k)

$^1$H NMR (400 MHz, DMSO) $\delta$ = 8.25 (dd, $J$=8.7, 5.4, 2H), 7.74 (dd, $J$=5.9, 3.0, 2H), 7.52 (t, $J$=8.7, 2H), 7.43 – 7.36 (m, 2H).

Figure S18 $^{13}$C NMR spectrum of 2-(4-fluorophenyl)-1H-benzo[d]imidazole$^3$ (3k)

$^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 149.83, 136.22, 130.29, 130.20, 124.48, 117.10, 116.88, 115.10.
Figure S19 $^{19}$F NMR spectrum of 2-(4-fluorophenyl)-1H-benzo[d]imidazole$^3$ (3k)

Figure S20 $^1$H NMR spectrum of 2-(4-methoxyphenyl)-1H-benzo[d]imidazole$^7$ (3l)

$^1$H NMR (400 MHz, DMSO) $\delta$ = 12.75 (s, 1H), 8.14 (d, $J$=8.0, 2H), 7.58 (d, $J$=5.2.4, 2H), 7.26 – 7.02 (m, 4H), 3.85 (s, 3H).
Figure S21 $^1$H NMR spectrum of 2-([1,1'-biphenyl]-4-yl)-1H-benzo[d]imidazole\(^8\) (3m)

$^1$H NMR (400 MHz, DMSO) $\delta$ = 12.99 (s, 1H), 8.31 (d, $J$=8.2, 2H), 7.89 (d, $J$=8.2, 2H), 7.78 (d, $J$=7.3, 2H), 7.71 (d, $J$=5.4, 1H), 7.58 (d, $J$=5.7, 1H), 7.51 (t, $J$=7.4, 3H), 7.45 – 7.38 (m, 1H), 7.24 (s, 2H).

Figure S22 $^1$H NMR spectrum of 2-(3,5-dimethoxyphenyl)-1H-benzo[d]imidazole\(^9\) (3n)

$^1$H NMR (400 MHz, DMSO) $\delta$ = 12.89 (s, 1H), 7.69 (d, $J$=7.2, 1H), 7.55 (d, $J$=7.1, 1H), 7.40 (s, 2H), 7.22 (t, $J$=7.5, 2H), 6.63 (s, 1H), 3.86 (s, 6H).
Figure S23 $^1$H NMR spectrum of 2-(pyridin-2-yl)-1H-benzo[d]imidazole$^{10}$ (3o)

$^1$H NMR (400 MHz, DMSO) $\delta$ = 13.09 (s, 1H), 8.74 (d, $J$=4.2, 1H), 8.34 (d, $J$=7.9, 1H), 8.01 (td, $J$=7.7, 1.7, 1H), 7.72 (d, $J$=7.6, 1H), 7.58 – 7.49 (m, 2H), 7.29 – 7.18 (m, 2H).

Figure S24 $^1$H NMR spectrum of 2-(furan-2-yl)-1H-benzo[d]imidazole$^{11}$ (3p)

$^1$H NMR (400 MHz, DMSO) $\delta$ = 12.90 (s, 1H), 7.94 (s, 1H), 7.62 (s, 1H), 7.50 (s, 1H), 7.19 (d, $J$=3.3, 3H), 6.76 – 6.70 (m, 1H).
Figure S25 $^1$H NMR spectrum of 1H-benzo[d]imidazole$^5$ (3q)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.55 (dd, $J$=5.9, 3.2, 2H), 7.24 – 7.19 (m, 2H), 2.64 (s, 3H).

Figure S26 $^1$H NMR spectrum of 2-cyclohexyl-1H-benzo[d]imidazole$^{12}$ (3r)

$^1$H NMR (400 MHz, DMSO) $\delta$ = 12.11 (s, 1H), 7.60 (dd, $J$=5.9, 3.2, 2H), 7.12 – 7.17 (m, 2H), 2.79 (tt, $J$=10.8, 3.5, 1H), 2.00 (d, $J$=8.3, 2H), 1.77 (d, $J$=11.7, 2H), 1.72 – 1.51 (m, 3H), 1.46 – 1.15 (m, 3H).
Figure S27 $^1$H NMR spectrum of 5-methyl-2-phenyl-1H-benzo[d]imidazole$^3$ (3s)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 8.06 (dd, $J$=6.5, 3.0, 2H), 7.52 (d, $J$=7.8, 1H), 7.46 – 7.35 (m, 4H), 7.08 (d, $J$=8.2, 1H), 2.45 (s, 3H).

Figure S28 $^1$H NMR spectrum of 5-chloro-2-phenyl-1H-benzo[d]imidazole$^5$ (3t)

$^1$H NMR (400 MHz, DMSO) $\delta$ = 13.13 (s, 1H), 8.20 (dd, $J$=5.2, 1.5, 2H), 7.77 – 7.50 (m, 5H), 7.25 (s, 1H).
Figure S29: $^1$H NMR spectrum of 2-phenylquinazolin-4(3$H$)-one (3u)

$^1$H NMR (400 MHz, DMSO) $\delta$ = 12.55 (s, 1H), 8.19 (dd, $J$=9.7, 8.2, 3H), 7.68 – 7.82 (m, 1H), 7.76 (d, $J$=8.0, 1H), 7.63 – 7.51 (m, 4H).

Figure S30: $^1$H NMR spectrum of 2-phenyl-3-(quinolin-8-yl)quinazolin-4(3$H$)-one (3v)

$^1$H NMR (400 MHz, DMSO) $\delta$ = 8.05 (dd, $J$=4.1, 1.5 Hz), 7.7 (d, $J$=4.1, 1.5 Hz, 3H), 8.23 – 8.27 (m, 3H), 8.00 – 8.10 (m, 3H), 7.52 (d, $J$=7.9 Hz, 1H), 7.51 – 7.43 (m, 4H), 7.25 – 7.27 (m, 2H), 7.12 (d, $J$=7.5 Hz, 1H), 7.07 (d, $J$=7.5 Hz, 2H, 2H).
$^1$H NMR spectra and analysis of intermediates

Figure S31 $^1$H NMR spectrum of intermediate A$^{13}$

Figure S32 $^1$H NMR spectrum of intermediate B$^{14}$
References