Supporting Information

for

Synthesis of Fused-benzimidazoles via Successive Nucleophilic Additions of Benzimidazole Derivatives to Arynes under Transition Metal-free Conditions

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1、General information

All chemicals were purchased from Adamas Reagent, Ltd, energy chemical company, J&K Scientific Ltd, Alfa Aesa chemical company and so forth. All reagents and solvents were purchased from commercial suppliers and used without further purification. All air and moisture sensitive reactions were conducted under a nitrogen atmosphere in a glove box. CH₃CN was dried by CaH prior to use. Tetrahydrofuran (THF) and Toluene were dried over Na. Unless otherwise stated, all experiments were conducted in a sealed tube with magnetic stirring under air atmosphere. Reactions were monitored by TLC or GC-MS analysis. Flash column chromatography was performed over silica gel (200-300 mesh). ¹H NMR spectra were recorded on a Bruker AVIII-500M spectrometers, Chemical shifts (in ppm) were referenced to DMSO-d₆ (δ = 2.50 ppm) as an internal standard. ¹³C NMR spectra were obtained by using the same NMR spectrometers and were calibrated with DMSO- d₆ (δ = 40.45 ppm).

2、Optimization of the Reaction Conditions

Table S1. Optimization of reaction conditions for (1H-indol-2-yl)(phenyl)methanone (1q) with 2-(trimethylsilyl)aryl triflate (2a).¹

<table>
<thead>
<tr>
<th>entry</th>
<th>Fluoride(3 equiv)</th>
<th>Solvent(2 mL)</th>
<th>Base(2 equiv)</th>
<th>T(°C)</th>
<th>time(h)</th>
<th>yield(%)²</th>
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<tbody>
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<td>CsF</td>
<td>CH₃CN</td>
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<td>Cs₂CO₃</td>
<td>50</td>
<td>12</td>
<td>59</td>
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¹ Reaction conditions: [1q]=0.1 mmol; [2a]=0.15 mmol.
² Yields of isolated products are reported.
**Table S2.** Optimization of reaction conditions for (3a,7a-dihydro-1H-indazol-3-yl)(phenyl)methanone (1r) with 2-(trimethylsilyl)aryl triflate (2a).a

<table>
<thead>
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<th>Flouride (3 equiv)</th>
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<th>Base (2 equiv)</th>
<th>T (°C)</th>
<th>time (h)</th>
<th>yield (%)b</th>
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<td>trace</td>
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<tr>
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<td>CH₃CN</td>
<td>Cs₂CO₃</td>
<td>50</td>
<td>12</td>
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a Reaction conditions: [1r]=0.1 mmol; [2a]=0.15 mmol.
b Yields of isolated products are reported.

**Table S3.** Optimization of reaction conditions for (1H-benzo[d]imidazol-2-yl)(p-tolyl)methanone (1a) with 4,5-dimethyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (2b).a

<table>
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<th>Flouride (3 equiv)</th>
<th>Solvent (2 mL)</th>
<th>Base (2 equiv)</th>
<th>T (°C)</th>
<th>time (h)</th>
<th>yield (%)b</th>
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<td>63</td>
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</tbody>
</table>

a Reaction conditions: [1a]=0.1 mmol; [2b]=0.15 mmol.
b Yields of isolated products are reported.
3. Experimental procedures

3.1. General procedure for the synthesis of 2-aryloylbenzimidazoles 1a-1p

Benzimidazole S1 (20 mmol) was completely dissolved in pyridine (6 mL) then added trimethylamine (6 mL). A suitable benzylocetyl chloride S2 (40 mmol, 2 equiv) was gently and slowly dropped to the reaction media during the solution was stirred in ice bath under atmosphere with nitrogen gas. Then the mixture was stirred in room temperature without nitrogen atmosphere during a day. NaOH solution (7.5 N, 6 g NaOH and 20 mL water) was added to the mixture and refluxed for an hour. The reaction media was poured into ice-water and kept in a refrigerator for two days. The residue was filtered and washed with water. The raw product was recrystallized from ethanol.

3.2. General procedure for the synthesis of (1H-indol-2-yl)(phenyl)methanone 1q

To a flame dried 100 mL three necked round bottom flask equipped with a stir bar was added o-Nitrochalcone S3 (5 mmol), then B2pin2 (10 mmol, 2 equiv) was added to a mixture of Na2CO3 (12.5 mmol, 2.5 equiv) in MeOH (50 mL) under N2. The mixture was stirred at 100 °C for 12 hours. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatograph (silica gel, petroleum ether: AcOEt = 10:1, v/v) to give the desired product 1q.
3.3. General procedure for the synthesis of 1r-1t

![Chemical Reaction Diagram]

To a flame dried 100 mL round bottom flask equipped with a stir bar was added \( \text{S4} \) (10 mmol) in 10 mL THF until dissolved. 30 mL of ice water was added and mixture was stirred until it formed slush. Slowly, 20 mL of concentrated HCl was added and the resulting solution was allowed to stir for 15 min. More ice was added as needed to keep the mixture at 0 °C. A solution of NaNO\(_2\) in water (15 mmol in 7.5 mL) was slowly added and the mixture was stirred for 15 min resulting in several color changes varying from deep red to bright orange. Then, add some water into the mixture and keep the mixture at 25 °C to stir for 5 min. Upon completion of the reaction, aqueous layers was extracted with ethyl acetate (20 mL) thrice. The combine organic layers were dried over anhydrous Na\(_2\)SO\(_4\). The solvents were removed via rotary evaporator and the residue was purified with flash chromatography (silica gel).

3.4. General procedure for the synthesis of 2b

![Chemical Reaction Diagram]

2-Bromo-4,5-xylenol (S7)

To a solution of 3,4-xylenol \( \text{S6} \) (20 mmol) in CH\(_2\)Cl\(_2\) (125 mL) and Et\(_2\)O (10 mL) was added a solution of bromine (20 mmol) in CH\(_2\)Cl\(_2\) (40 mL) dropwise at 0 °C. After the addition was completed, the reaction was quenched with sat. Na\(_2\)SO\(_3\) aq. At 0°C and this mixture was warmed to room temperature. The layers were separated, and then the aqueous layer was extracted with CH\(_2\)Cl\(_2\). The combined organic layers were washed with water and brine then dried over MgSO\(_4\). The solvent was removed.
in vacuo, and the residue was recrystallized from pentane to afford 2-bromo-4,5-xylenol S7 as a white solid.

4,5-Dimethyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (2b)

To a solution of 2-bromo-4,5-xylenol (10 mmol) in THF (15 mL) was added HMDS (10.5 mmol) under argon atmosphere. The reaction mixture was refluxed for 3 h to give S8. After cooling to room temperature, the solvent was removed in vacuo. The residue was dissolve in THF (30 mL) under argon atmosphere and cooled to -78 °C. To the solution was added n-vutylithium (11 mmol, 2.65 M solution in hexane) dropwise. After stirring at -78 °C for 1 h, Tf₂O (11.9 mmol) was added to reaction mixture dropwise at -78 °C. After stirring at -78 °C for 2 h, the reaction mixture was quenched with sat. NaHCO₃ aq. at -78 °C and this mixture was warmed to room temperature. The layers were separated, and then the equeous layer was extracted with Et₂O twice. The combined organic layers were washed with brine and then dried over Na₂SO₄. The solvent was removed in vacuo, and the residue was purified by silica gel column chromatography with hexane to afford 4,5-dimethyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate 2b as a colorless liquid.

3.5. General procedure for the synthesis of 2c⁴

\[
\begin{align*}
\text{S9} & \xrightarrow[\text{bromine (0.9 equiv)}]{\text{AcOH, 0 °C}} \text{S10} & \xrightarrow[\text{THF, HMDS}]{\text{67 °C, relux, 2 h}} \text{S11} \\
1) \text{THF, n-BuLi, -78 °C, 1.5 h} & \text{2c} & 2) \text{Tf₂O, -78 °C, 2 h}
\end{align*}
\]

5-Bromosesamol (S10)

To a solution of sesamol (21.7 mmol) in AcOH (7 mL) was added a solution of bromine (19.4 mmol) in AcOH (4 mL) dropwise at 0 °C and the reaction mixture was stirred for 30 min at this temperature. This mixture was poured into ice and filtered
The residual solid was washed with water and dried to afford 5-bromosesamol as a faint green solid.

6-(Trimethylsilyl)benzo[d][1,3]dioxol-5-yl trifluoromethanesulfonate (2c)

To a solution of 3-bromo-2-sesamo (5.58 mmol) in THF (20mL) was added HMDS (5.65 mmol) under argon atmosphere. The reaction mixture was refluxed for 2 h. After cooling to room temperature, the solvent was removed in vacuo. The residue was dissolved in THF (30 mL) under argon atmosphere and cooled to -78 °C. To the solution was added n-butyllithium (1.6 M solution in hexane) dropwise. After stirring at -78 °C for 1.5 h, Tf₂O (5.84 mmol) was added to reaction mixture dropwise at -78 °C. After stirring at -78 °C for 2 h, the reaction mixture was quenched with sat. NaCHO₃ aq. At -78 °C and this mixture was warmed to room temperature. The layers were separated, and then the aqueous layer was extracted with Et₂O three times. The combined organic layers were dried over Na₂SO₄. The solvent was removed in vacuo, and the residue was purified by silica gel column chromatography with hexane to afford 6-(trimethylsilyl)benzo[d][1,3]dioxol-5-yl trifluoromethanesulfonate (2c) as a colorless liquid.

4. Characterization data for products

11-(p-tolyl)-11H-benzo[4,5]imidazo[1,2-a]indol-11-ol (3a)

The reaction was performed following general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether: AcOEt = 10:1– 5:1, v/v) to give the product as a yellow solid (55.9 mg, 90 %). ¹H NMR (500 MHz, DMSO) δ 8.13 (d, J = 8.0 Hz, 1H), 7.93 (d, J = 7.8 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.50 (td, J = 7.7, 1.1 Hz, 1H), 7.45 – 7.35 (m, 2H), 7.35 – 7.28 (m, 1H), 7.28 – 7.21 (m, 3H), 7.13 (d, J = 8.1 Hz, 2H), 7.01 (s, 1H), 2.26 (s, 3H). ¹³C NMR (126 MHz, DMSO) δ
HRMS (ESI, m/z) calcd for C_{21}H_{17}N_{2}O^{+} ([M+H]^{+}): 313.1335; found: 313.1335.

11-(m-tolyl)-11H-benzo[4,5]imidazo[1,2-a]indol-11-ol (3b)

The reaction was performed following general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether: AcOEt = 10:1–5:1, v/v) to give the product as a white solid (50.4 mg, 81 %). ¹H NMR (500 MHz, DMSO) δ 8.13 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 7.8 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.51 (td, J = 7.7, 1.1 Hz, 1H), 7.44 – 7.36 (m, 2H), 7.32 (m, 1H), 7.24 (m, 1H), 7.20 m, 2H), 7.14 (d, J = 8.2 Hz, 1H), 7.10 (d, J = 7.7 Hz, 1H), 7.03 (s, 1H), 2.25 (s, 3H). ¹³C NMR (126 MHz, DMSO) δ 164.4, 148.5, 142.7, 142.3, 138.4, 137.9, 130.7, 130.1, 129.3, 129.2, 126.9, 126.0, 124.7, 123.6, 121.3, 112.4, 112.3, 76.3, 22.1.

HRMS (ESI, m/z) calcd for C_{21}H_{17}N_{2}O^{+} ([M+H]^{+}): 313.1335; found: 313.1338.

11-phenyl-11H-benzo[4,5]imidazo[1,2-a]indol-11-ol (3c)

The reaction was performed following general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether: AcOEt = 10:1–5:1, v/v) to give the product as a yellow solid (54.1 mg, 91 %). ¹H NMR (500 MHz, DMSO) δ 8.13 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 7.8 Hz, 1H), 7.71 (d, J = 8.1 Hz, 1H), 7.52 (td, J = 7.7, 0.8 Hz, 1H), 7.46 – 7.35 (m, 4H), 7.35 – 7.28 (m, 4H), 7.25 (t, J = 7.5 Hz, 1H), 7.07 (s, 1H). ¹³C NMR (126 MHz, DMSO) δ 164.3, 148.5, 142.7, 142.2, 137.9, 130.8, 130.1, 129.3, 129.2, 128.7, 126.6, 126.5, 126.0, 124.8, 123.7, 121.3, 112.5, 112.4, 76.3.
HRMS (ESI, m/z) calcd for C_{20}H_{16}N_{2}O^{+} ([M+H]^+): 299.1179; found: 299.1180.

11-(4-methoxyphenyl)-11H-benzo[4,5]imidazo[1,2-a]indol-11-ol (3d)

\[
\begin{align*}
&\text{The reaction was performed following general procedure. The residue was purified by} \\
&\text{flash column chromatograph (silica gel, petroleum ether: AcOEt = 10:1– 5:1, v/v) to} \\
&\text{give the product as a white solid (53.9 mg, 82 %).} \\
&\text{^1H NMR (500 MHz, DMSO) } \delta \text{ 8.11 (d, } J = 8.0 \text{ Hz, 1H), 7.92 (d, } J = 7.8 \text{ Hz, 1H), 7.70 (d, } J = 8.0 \text{ Hz, 1H), 7.55 –} \\
&7.47 \text{ (m, 1H), 7.40 (t, } J = 6.4 \text{ Hz, 1H), 7.31 (t, } J = 7.7 \text{ Hz, 1H), 7.25 (t, } J = 7.5 \text{ Hz,} \\
&1H), 6.96 (s, 1H), 6.92 – 6.85 \text{ (m, 1H), 3.71 (s, 1H).} \\
&\text{^13C NMR (126 MHz, DMSO) } \delta \text{ 164.5, 159.8, 148.5, 142.3, 137.8, 134.6, 130.7, 130.1, 127.9, 126.6, 126.0, 124.7,} \\
&123.6, 121.3, 114.6, 76.0, 60.8, 56.1. \\
&\text{HRMS (ESI, m/z) calcd for } C_{21}H_{17}N_{2}O_{2}^{+} ([M+H]^+): 329.1285; \text{ found: 329.1285.}
\end{align*}
\]

11-(4-(trifluoromethyl)phenyl)-11H-benzo[4,5]imidazo[1,2-a]indol-11-ol (3e)

\[
\begin{align*}
&\text{The reaction was performed following general procedure. The residue was purified by} \\
&\text{flash column chromatograph (silica gel, petroleum ether: AcOEt = 10:1– 5:1, v/v) to} \\
&\text{give the product as a white solid (64.7 mg, 88 %).} \\
&\text{^1H NMR (500 MHz, DMSO) } \delta \text{ 8.15 (d, } J = 8.0 \text{ Hz, 1H), 7.97 (d, } J = 7.8 \text{ Hz, 1H), 7.71 (m, 3H), 7.59 (d, } J = 8.2 \text{ Hz,} \\
&2H), 7.54 (td, } J = 7.7, 1.2 \text{ Hz, 1H), 7.43 (td, } J = 7.8, 1.0 \text{ Hz, 1H), 7.41 – 7.37 \text{ (m, 1H),} \\
&7.36 – 7.30 \text{ (m, 2H), 7.26 (td, } J = 7.6, 0.8 \text{ Hz, 1H).} \\
&\text{^13C NMR (126 MHz, DMSO) } \delta \text{ 163.8, 148.5, 147.4, 141.6, 138.0, 131.3, 130.2, 129.4 (d, } J = 31.9 \text{ Hz), 127.5, 126.7,} \\
&126.4, 126.4, 126.3, 125.1, 123.9, 121.5, 112.6, 76.1. \\
&\text{HRMS (ESI, m/z) calcd for } C_{21}H_{17}F_{3}N_{2}O^{+} ([M+H]^+): 367.1053; \text{ found: 367.1068.}
\end{align*}
\]

11-(4-nitrophenyl)-11H-benzo[4,5]imidazo[1,2-a]indol-11-ol (3f)
The reaction was performed following general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether: AcOEt = 10:1– 5:1, v/v) to give the product as a white solid (58.1 mg, 85 %). \(^1\)H NMR (500 MHz, DMSO) \(\delta\) 8.24 – 8.14 (m, 3H), 7.99 (d, \(J = 7.8\) Hz, 1H), 7.73 (d, \(J = 8.1\) Hz, 1H), 7.67 – 7.61 (m, 1H), 7.55 (td, \(J = 7.7, 1.0\) Hz, 1H), 7.47 – 7.42 (m, 1H), 7.38 (d, \(J = 7.2\) Hz, 1H), 7.36 – 7.31 (m, 1H), 7.26 (t, \(J = 7.6\) Hz, 1H). \(^{13}\)C NMR (126 MHz, DMSO) \(\delta\) 163.4, 150.1, 148.5, 148.0, 141.3, 138.0, 131.4, 130.1, 128.0, 126.6, 126.3, 125.1, 124.6, 123.9, 121.5, 112.7, 112.6, 76.1.

HRMS (ESI, m/z) calcd for \(\text{C}_{20}\text{H}_{14}\text{N}_3\text{O}_3^+\) ([M+H]^+): 344.1030; found: 344.1029.

\textbf{11-(3-fluorophenyl)-11\textit{H}-benzo[4,5]imidazo[1,2-\textit{a}]indol-11-ol (3g)}

The reaction was performed following general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether: AcOEt = 10:1– 5:1, v/v) to give the product as a yellow solid (46.8 mg, 74 %). \(^1\)H NMR (500 MHz, DMSO) \(\delta\) 8.19 – 8.09 (m, 1H), 7.95 (d, \(J = 7.8\) Hz, 1H), 7.76 – 7.67 (m, 1H), 7.53 (td, \(J = 7.7, 1.2\) Hz, 1H), 7.47 – 7.39 (m, 2H), 7.38 – 7.28 (m, 3H), 7.28 – 7.21 (m, 2H), 7.18 – 7.10 (m, 1H), 7.02 (m, 1H). \(^{13}\)C NMR (126 MHz, DMSO) \(\delta\) 163.81, 163.1 (d, \(J = 243.8\) Hz), 148.5, 141.7, 138.0, 131.5 (d, \(J = 8.3\) Hz), 131.1, 130.2, 126.7, 126.2, 125.0, 123.8, 122.7 (d, \(J = 2.5\) Hz), 121.5, 115.7 (d, \(J = 20.9\) Hz), 113.6 (d, \(J = 23.0\) Hz), 112.6 (d, \(J = 5.2\) Hz), 76.0, 76.0.

HRMS (ESI, m/z) calcd for \(\text{C}_{20}\text{H}_{14}\text{FN}_2\text{O}^+\) ([M+H]^+): 317.1085; found: 317.1089.
11-(4-fluorophenyl)-11H-benzo[4,5]imidazo[1,2-a]indol-11-ol (3h)

The reaction was performed following general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether: AcOEt = 10:1−5:1, v/v) to give the product as a white solid (41.8 mg, 66%). $^1$H NMR (500 MHz, DMSO) $\delta$ 8.13 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 7.8 Hz, 1H), 7.71 (d, J = 8.1 Hz, 1H), 7.52 (td, J = 7.7, 0.8 Hz, 1H), 7.46 – 7.37 (m, 4H), 7.31 (m, 1H), 7.26 (t, J = 7.5 Hz, 1H), 7.21 – 7.07 (m, 3H). $^{13}$C NMR (126 MHz, DMSO) $\delta$ 164.1, 162.6 (d, J = 244.0 Hz), 148.5, 141.9, 138.9, 138.9, 137.9, 131.0, 130.1, 128.7 (d, J = 8.4 Hz), 126.6, 126.1, 124.9, 123.7, 121.4, 116.1 (d, J = 21.5 Hz), 112.5 (d, J = 7.1 Hz), 75.9.

HRMS (ESI, m/z) calcd for C$_{20}$H$_{14}$FN$_2$O$^+$ ([M+H]$^+$): 317.1085; found: 317.1085.

11-(3-chlorophenyl)-11H-benzo[4,5]imidazo[1,2-a]indol-11-ol (3i)

The reaction was performed following general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether: AcOEt = 10:1−5:1, v/v) to give the product as a white solid (27.7 mg, 42 %). $^1$H NMR (500 MHz, DMSO) $\delta$ 8.14 (d, J = 7.9 Hz, 1H), 7.96 (d, J = 7.8 Hz, 1H), 7.72 (d, J = 7.8 Hz, 1H), 7.58 – 7.50 (m, 2H), 7.42 (m, 2H), 7.40 – 7.36 (m, 1H), 7.36 – 7.30 (m, 2H), 7.29 – 7.23 (m, 2H), 7.19 (dd, J = 7.6, 1.2 Hz, 1H). $^{13}$C NMR (126 MHz, DMSO) $\delta$ 163.7, 148.5, 145.2, 141.5, 138.0, 134.1, 131.3, 131.1, 130.1, 128.8, 126.6, 126.4, 126.2, 125.3, 124.9, 123.8, 121.4, 116.1, 75.9.

HRMS (ESI, m/z) calcd for C$_{20}$H$_{14}$ClN$_2$O$^+$ ([M+H]$^+$): 333.0789; found: 333.0787.
11-(4-chlorophenyl)-11H-benzo[4,5]imidazo[1,2-a]indol-11-ol (3j)

The reaction was performed following general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether: AcOEt = 10:1 – 5:1, v/v) to give the product as a white solid (61 mg, 92 %). \(^1\)H NMR (500 MHz, DMSO) \(\delta\) 8.13 (d, \(J = 8.0\) Hz, 1H), 7.94 (d, \(J = 7.8\) Hz, 1H), 7.71 (d, \(J = 8.1\) Hz, 1H), 7.53 (td, \(J = 7.7, 1.0\) Hz, 1H), 7.45 – 7.36 (m, 6H), 7.35 – 7.29 (m, 1H), 7.25 (t, \(J = 7.5\) Hz, 1H), 7.18 (s, 1H). \(^{13}\)C NMR (126 MHz, DMSO) \(\delta\) 163.9, 148.5, 141.8, 141.7, 137.9, 133.4, 131.0, 130.1, 129.3, 128.5, 126.6, 126.2, 124.9, 123.8, 121.4, 112.5, 112.5, 75.9.

HRMS (ESI, m/z) calcd for \(C_{20}H_{14}ClN_2O^+ ([M+H]^+)\): 333.0789; found: 333.0792.

11-(4-bromophenyl)-11H-benzo[4,5]imidazo[1,2-a]indol-11-ol (3k)

The reaction was performed following general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether: AcOEt = 10:1 – 5:1, v/v) to give the product as a white solid (70 mg, 93 %). \(^1\)H NMR (500 MHz, DMSO) \(\delta\) 8.22 (d, \(J = 8.0\) Hz, 1H), 8.03 (d, \(J = 7.8\) Hz, 1H), 7.79 (d, \(J = 8.0\) Hz, 1H), 7.61 (dd, \(J = 7.4, 5.3\) Hz, 3H), 7.55 – 7.44 (m, 2H), 7.40 (t, \(J = 7.4\) Hz, 3H), 7.33 (t, \(J = 7.5\) Hz, 1H), 7.25 (s, 1H). \(^{13}\)C NMR (126 MHz, DMSO) \(\delta\) 163.8, 148.5, 142.2, 141.7, 137.9, 132.2, 131.0, 130.1, 128.8, 126.6, 126.1, 124.8, 123.7, 122.0, 121.4, 112.5, 112.4, 75.9.

HRMS (ESI, m/z) calcd for \(C_{20}H_{14}BrN_2O^+ ([M+H]^+)\): 377.0284; found: 377.0284.

The reaction was performed following general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether: AcOEt = 10:1– 5:1, v/v) to give the product as a white solid (61.2 mg, 94 %). $^1$H NMR (500 MHz, DMSO) $\delta$ 8.11 (d, $J = 8.0$ Hz, 1H), 7.92 (d, $J = 7.8$ Hz, 1H), 7.71 (d, $J = 8.0$ Hz, 1H), 7.50 (td, $J = 7.7$, 1.2 Hz, 1H), 7.45 – 7.35 (m, 2H), 7.35 – 7.28 (m, 1H), 7.24 (td, $J = 7.5$, 0.8 Hz, 1H), 6.97 (s, 3H), 6.91 (s, 1H), 2.19 (s, 6H).

$^{13}$C NMR (126 MHz, DMSO) $\delta$ 163.3, 148.4, 143.8, 141.1, 138.0, 132.1, 131.6, 131.3, 130.1, 128.57, 127.1, 126.6, 126.2, 125.0, 123.8, 121.4, 112.6, 75.5

HRMS (ESI, m/z) calcd for $\text{C}_{22}\text{H}_{19}\text{N}_{2}\text{O}^+$ ([M+H]⁺): 327.1492; found: 327.1494.

11-(3,4-dichlorophenyl)-11H-benzo[4,5]imidazo[1,2-a]indol-11-ol (3m)

The reaction was performed following general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether: AcOEt = 10:1– 5:1, v/v) to give the product as a white solid (61.2 mg, 94 %). $^1$H NMR (500 MHz, DMSO) $\delta$ 8.14 (d, $J = 8.0$ Hz, 1H), 7.96 (d, $J = 7.8$ Hz, 1H), 7.71 (m, 2H), 7.63 – 7.50 (m, 2H), 7.43 (m, 2H), 7.37 – 7.29 (m, 2H), 7.26 (t, $J = 7.5$ Hz, 1H), 7.20 (dd, $J = 8.5$, 2.1 Hz, 1H). $^{13}$C NMR (126 MHz, DMSO) $\delta$ 163.3, 148.4, 143.8, 141.1, 138.0, 132.1, 131.6, 131.3, 130.1, 128.57, 127.1, 126.6, 126.2, 125.0, 123.8, 121.4, 112.6, 75.5

HRMS (ESI, m/z) calcd for $\text{C}_{20}\text{H}_{13}\text{Cl}_{2}\text{N}_{2}\text{O}^+$ ([M+H]⁺): 367.0399; found: 367.0403.
11-(benzo[\(d\)][1,3]dioxol-5-yl)-11\(H\)-benzo[4,5]imidazo[1,2-\(a\)]indol-11-ol (3n)

The reaction was performed following general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether: AcOEt = 10:1– 5:1, v/v) to give the product as a yellow solid (58.7 mg, 86 %). \(^1\)H NMR (500 MHz, DMSO) \(\delta\) 8.11 (d, \(J = 8.0\) Hz, 1H), 7.92 (d, \(J = 7.8\) Hz, 1H), 7.71 (d, \(J = 8.0\) Hz, 1H), 7.51 (td, \(J = 7.7, 1.0\) Hz, 1H), 7.45 – 7.37 (m, 2H), 7.35 – 7.29 (m, 1H), 7.25 (t, \(J = 7.5\) Hz, 1H), 7.04 (d, \(J = 1.7\) Hz, 1H), 7.01 (s, 1H), 6.81 (d, \(J = 8.2\) Hz, 1H), 6.71 (m, 1H), 5.99 (s, 2H). \(^{13}\)C NMR (126 MHz, DMSO) \(\delta\) 164.2, 148.5, 148.3, 147.8, 142.0, 137.8, 136.6, 130.8, 130.1, 126.6, 126.0, 124.7, 123.6, 121.3, 119.8, 112.4, 112.3, 108.8, 107.4, 102.1, 76.1

HRMS (ESI, m/z) calcd for \(C_{21}H_{15}N_2O_3^+ ([M+H]^+)\): 343.1077; found: 343.1076.

11-(naphthalen-2-yl)-11\(H\)-benzo[4,5]imidazo[1,2-\(a\)]indol-11-ol (3o)

The reaction was performed following general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether: AcOEt = 10:1– 5:1, v/v) to give the product as a white solid (52 mg, 75 %). \(^1\)H NMR (500 MHz, DMSO) \(\delta\) 8.17 (d, \(J = 8.1\) Hz, 1H), 8.04 (s, 1H), 7.98 (d, \(J = 7.8\) Hz, 1H), 7.94 – 7.89 (m, 1H), 7.89 – 7.86 (m, 1H), 7.83 (d, \(J = 8.7\) Hz, 1H), 7.72 (d, \(J = 8.1\) Hz, 1H), 7.56 – 7.52 (m, 1H), 7.52 – 7.48 (m, 2H), 7.45 – 7.41 (m, 2H), 7.36 (dd, \(J = 8.7, 1.8\) Hz, 1H), 7.35 – 7.30 (m, 1H), 7.25 (t, \(J = 7.5\) Hz, 1H), 7.22 (s, 1H). \(^{13}\)C NMR (126 MHz, DMSO) \(\delta\) 164.3, 148.6, 142.1, 140.1, 138.0, 133.5, 133.4, 130.9, 130.14, 129.0, 129.0, 128.4, 127.3, 127.2, 126.7, 126.1, 124.9, 124.87, 124.8, 123.7, 121.4, 112.5, 112.4, 76.4

HRMS (ESI, m/z) calcd for \(C_{24}H_{17}N_2O^+ ([M+H]^+)\): 349.1335; found: 349.1337

The reaction was performed following general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether: AcOEt = 10:1– 5:1, v/v) to give the product as a white solid (44.3 mg, 68 %). $^1$H NMR (500 MHz, DMSO) $\delta$ 7.92 (s, 1H), 7.88 (d, $J = 7.8$ Hz, 1H), 7.48 (m, 2H), 7.32 (m, 6H), 7.21 (t, $J = 7.5$ Hz, 1H), 7.02 (s, 1H), 2.37 (d, $J = 37.5$ Hz, 6H). $^{13}$C NMR (126 MHz, DMSO) $\delta$ 163.5, 147.1, 143.1, 142.3, 138.0, 133.6, 132.1, 130.7, 129.3, 128.6, 128.6, 126.6, 126.5, 125.7, 121.3, 112.5, 112.1, 76.3, 32.1, 30.8, 21.0, 20.9. HRMS (ESI, m/z) calcd for $C_{22}H_{19}N_2O^+$ ([M+H]$^+$): 327.1492; found: 327.1496.

10-phenyl-10H-indolo[1,2-a]indol-10-ol (3q)

The reaction was performed following general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether: AcOEt = 10:1– 5:1, v/v) to give the product as a yellow solid (35.2 mg, 59 %). $^1$H NMR (500 MHz, DMSO) $\delta$ 8.01 (dd, $J = 8.2$, 0.6 Hz, 1H), 7.84 (d, $J = 7.8$ Hz, 1H), 7.62 (d, $J = 7.9$ Hz, 1H), 7.48 – 7.37 (m, 4H), 7.34 – 7.28 (m, 4H), 7.24 (m, 1H), 7.18 – 7.13 (m, 1H), 7.13 – 7.08 (m, 1H), 6.76 (s, 1H), 6.49 (s, 1H). $^{13}$C NMR (126 MHz, DMSO) $\delta$ 150.4, 145.5, 143.1, 140.0, 133.8, 131.4, 130.4, 129.9, 129.6, 129.1, 128.2, 126.4, 126.29, 124.3, 123.8, 122.6, 121.6, 112.2, 111.7, 99.1, 77.4. HRMS (ESI, m/z) calcd for $C_{21}H_{16}NO^+$ ([M+H]$^+$):298.1226; found: 298.1223.

11-phenyl-11H-indolo[1,2-b]indazol-11-ol (3r)
The reaction was performed following general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether: AcOEt = 10:1–5:1, v/v) to give the product as a yellow solid (27 mg, 91 %). $^1$H NMR (500 MHz, CDCl$_3$) δ 8.29 (dd, J = 8.1, 1.2 Hz, 1H), 8.06 (dd, J = 8.0, 1.5 Hz, 2H), 7.79 – 7.59 (m, 6H), 7.52 (t, J = 7.4 Hz, 1H), 7.48 – 7.39 (m, 3H), 7.22 (d, J = 8.7 Hz, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 169.9, 146.0, 143.0, 142.0, 135.1, 134.9, 134.8, 131.0, 130.9, 130.4, 129.8, 129.5, 129.4, 128.9, 128.1, 128.0, 128.0, 126.4, 126.3, 125.1, 117.8.

HRMS (ESI, m/z) calcd for C$_{20}$H$_{15}$N$_2$O$^+$ ([M+H]$^+$): 299.1179; found: 299.1171.

11-($p$-tolyl)-11$H$-indolo[1,2-$b$]indazol-11-ol (3s)

The reaction was performed following general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether: AcOEt = 10:1–5:1, v/v) to give the product as a yellow solid (28.7 mg, 92 %). $^1$H NMR (500 MHz, DMSO) δ 8.38 (d, J = 8.1 Hz, 1H), 8.20 (d, J = 8.1 Hz, 2H), 7.84 (m, 3H), 7.63 (t, J = 7.8 Hz, 2H), 7.60 – 7.54 (m, 1H), 7.48 (m, 2H), 7.35 (d, J = 8.0 Hz, 2H), 2.38 (s, 3H). $^{13}$C NMR (126 MHz, DMSO) δ 188.4, 144.3, 143.7, 140.3, 139.8, 135.6, 131.4, 130.8, 129.9, 129.2, 129.1, 125.6, 125.4, 124.4, 123.5, 112.1, 22.2.

HRMS (ESI, m/z) calcd for C$_{21}$H$_{17}$N$_2$O$^+$ ([M+H]$^+$): 313.1335; found: 313.1339.

11-(4-fluorophenyl)-11$H$-indolo[1,2-$b$]indazol-11-ol (3t)

The reaction was performed following general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether: AcOEt = 10:1–5:1, v/v) to give the product as a yellow solid (28.4 mg, 90 %). $^1$H NMR (500 MHz, DMSO) δ 8.28 (dd, J = 8.1, 1.2 Hz, 1H), 8.18 – 8.11 (m, 2H), 7.78 – 7.59 (m, 6H), 7.57 – 7.50 (m, 1H), 7.27 (m, 2H), 7.22 (d, J = 8.7 Hz, 1H). $^{13}$C NMR (126 MHz, DMSO) δ 169.8,
163.4 (d, $J = 246.3$ Hz), 144.9, 143.0, 142.0, 134.9, 131.6 (d, $J = 8.3$ Hz), 131.6, 131.6, 130.9, 130.4, 128.0, 126.4 (d, $J = 10.0$ Hz), 125.1, 117.8, 115.8 (d, $J = 21.4$ Hz).

HRMS (ESI, m/z) calcd for $C_{20}H_{14}FN_2O^+$ ([M+H]$^+$): 317.1085; found: 317.1082.

2,3-dimethyl-11-($p$-tolyl)-11$H$-benzo[4,5]imidazo[1,2-$a$]indol-11-ol (3u)

![Structure of 3u](image)

The reaction was performed following general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether: AcOEt = 10:1– 5:1, v/v) to give the product as a yellow solid (21.5 mg, 63 %). $^1$H NMR (500 MHz, DMSO) $\delta$ 8.11 (d, $J = 8.0$ Hz, 1H), 7.75 (s, 1H), 7.68 (d, $J = 8.1$ Hz, 1H), 7.39 (t, $J = 7.7$ Hz, 1H), 7.28 (t, $J = 7.3$ Hz, 1H), 7.23 (d, $J = 8.2$ Hz, 2H), 7.15 – 7.08 (m, 3H), 6.88 (s, 1H), 2.35 (s, 3H), 2.23 (d, $J = 19.4$ Hz, 6H). $^{13}$C NMR (126 MHz, DMSO) $\delta$ 164.8, 148.4, 140.1, 139.7, 139.1, 137.8, 135.9, 133.8, 130.0, 129.7, 127.4, 126.4, 124.5, 123.4, 121.2, 113.3, 112.3, 76.3, 21.6, 20.7, 20.3

HRMS (ESI, m/z) calcd for $C_{23}H_{21}N_2O^+$ ([M+H]$^+$): 341.1648; found: 341.1650.


![Structure of 3v](image)

The reaction was performed following general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether: AcOEt = 10:1– 5:1, v/v) to give the product as a yellow solid (34.2 mg, 96 %). $^1$H NMR (500 MHz, DMSO) $\delta$ 8.14 (d, $J = 8.1$ Hz, 1H), 7.74 (s, 1H), 7.67 (d, $J = 8.1$ Hz, 1H), 7.36 (m, 1H), 7.27 (m, 3H), 7.12 (d, $J = 8.3$ Hz, 2H), 6.92 (d, $J = 6.6$ Hz, 2H), 6.09 (dd, $J = 16.4$, 0.8 Hz, 2H), 2.26 (s, 3H). $^{13}$C NMR (126 MHz, DMSO) $\delta$ 164.8, 149.2, 148.1, 145.4, 139.9, 137.9, 134.8, 132.3, 129.9, 129.8, 126.5, 124.5, 123.3, 121.2, 112.2, 107.5, 102.7, 95.9, 76.3, 21.6
HRMS (ESI, m/z) calcd for C_{22}H_{17}N_{2}O_{3}^+ ([M+H]^+): 357.123; found: 357.1239.


The reaction was performed following general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether: AcOEt = 10:1– 5:1, v/v) to give the product as a yellow solid (28.6 mg, 87 %). $^1$H NMR (500 MHz, DMSO) $\delta$

$\begin{array}{l}
8.22 (d, J = 8.0 Hz, 1H), 8.10 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 8.5 Hz, 1H), 7.69 (dd, J = 8.0, 2.3 Hz, 2H), 7.51 (d, J = 2.2 Hz, 1H), 7.41 – 7.35 (m, 8H), 7.36 – 7.26 (m, 12H), 7.11 (s, 2H), 7.05 (dd, J = 8.6, 2.6 Hz, 2H), 6.95 (d, J = 3.2 Hz, 3H), 6.78 (dd, J = 8.4, 2.3 Hz, 1H), 3.90 (s, 3H), 3.76 (s, 4H). $^1$C NMR (126 MHz, DMSO) $\delta$

$\begin{array}{l}
165.1, 164.3, 161.9, 158.1, 148.4, 148.2, 143.8, 143.1, 142.8, 139.1, 134.0, 131.5, 130.0, 129.9, 129.3, 129.2, 128.7, 128.6, 127.4, 126.6, 126.5, 124.7, 124.6, 123.7, 123.3, 121.3, 114.9, 113.4, 113.0, 112.7, 112.2, 110.5, 100.5, 99.6, 76.6, 75.9, 56.9, 56.7. HRMS (ESI, m/z) calcd for C_{21}H_{17}N_{2}O_{2}^+ ([M+H]^+) 329.1285; found: 329.1283.
\end{array}$
5. Crystal Data of 3b

Crystallographic data for compound 3b (CCDC-1828308) has been deposited with the Cambridge Crystallographic Data Centre, Copies of the data can be obtained, free of charge, on application to CCDC (Email: deposit@ccdc.cam.ac.uk).

Table 1 Crystal data and structure refinement for exp_3993.

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F(000) 416.0
Crystal size/mm\(^3\) 0.09 \times 0.08 \times 0.07
Radiation MoK\(\alpha\) (\(\lambda = 0.71073\))
2\(\Theta\) range for data collection/° 5.7 to 52.74
Index ranges \(-11 \leq h \leq 11, -12 \leq k \leq 11, -14 \leq l \leq 11\)
Reflections collected 7650
Independent reflections 4214 [\(R_{int} = 0.0504, R_{sigma} = 0.0778\)]
Data/restraints/parameters 4214/0/274
Goodness-of-fit on F\(^2\) 1.059
Final R indexes [I>=2\(\sigma\) (I)] \(R_1 = 0.1274, wR_2 = 0.3304\)
Final R indexes [all data] \(R_1 = 0.1661, wR_2 = 0.3582\)
Largest diff. peak/hole / e Å\(^{-3}\) 0.47/-0.37
6. NMR Spectroscopic Data

11-((p-tolyl)-11\textit{H}-benzo[4,5]imidazo[1,2-\textit{a}]indol-11-ol (3a)
11-\((m\text{-}\text{tolyl})\)-11\(H\)-benzo[4,5]imidazo[1,2-\(a\)]indol-11-ol (3b)
11-phenyl-11$H$-benzo[4,5]imidazo[1,2-$a$]indol-11-ol (3c)
11-(4-methoxyphenyl)-11$H$-benzo[4,5]imidazo[1,2-$a$]indol-11-ol (3d)
11-(4-(trifluoromethyl)phenyl)-11H-benzo[4,5]imidazo[1,2-a]indol-11-ol (3e)
11-(4-nitrophenyl)-11H-benzo[4,5]imidazo[1,2-a]indol-11-ol (3f)
11-(3-fluorophenyl)-11H-benzo[4,5]imidazo[1,2-a]indol-11-ol (3g)
11-(4-fluorophenyl)-11H-benzo[4,5]imidazo[1,2-a]indol-11-ol (3h)
11-(3-chlorophenyl)-11\textit{H}-benzo[4,5]imidazo[1,2-\textit{a}]indol-11-ol (3i)
11-(4-chlorophenyl)-11$H$-benzo[4,5]imidazo[1,2-$a$]indol-11-ol (3j)
11-(4-bromophenyl)-11\textit{H}-benzo[4,5]imidazo[1,2-\textit{a}]indol-11-ol (3k)
11-(3,4-dichlorophenyl)-11H-benzo[4,5]imidazo[1,2-a]indol-11-ol (3m)
11-([benzo][d][1,3]dioxol-5-yl)-11\textit{H}-benzo[4,5]imidazo[1,2-\textit{a}]indol-11-ol (3n)
11-(naphthalen-2-yl)-11H-benzo[4,5]imidazo[1,2-a]indol-11-ol (3o)
10-phenyl-10H-indolo[1,2-a]indol-10-ol (3q)
11-phenyl-11H-indolo[1,2-b]indazol-11-ol (3r)
11-(p-tolyl)-11H-indolo[1,2-b]indazol-11-ol (3s)
11-(4-fluorophenyl)-11H-indolo[1,2-b]indazol-11-ol (3t)
2,3-dimethyl-11-(p-tolyl)-11H-benzo[4,5]imidazo[1,2-a]indol-11-ol (3u)
11-\((p\text{-tolyl})\)\(11H\)-benzo[4,5]imidazo[1,2-\(a\)][1,3]dioxolo[4,5-f]indol-11-ol (3v)
Reference


