Supporting Information

Platinum(II)-catalyzed dehydrative C3-benzylation of electron-deficient indoles with benzyl alcohols

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Scheme S1. Rates on the dehydrative coupling with stoichiometric amounts of water.

A mixture of 5-nitroindole 1a (165 mg, 1 mmol), PtCl₂(PhCN)₂ (23 mg, 0.05 mmol), benzhydrole 2a (221 mg, 1.2 mmol), and H₂O or D₂O (1 mmol) in 1,2-dichloroethane (4 mL) was heated at 60 °C under air. After the reaction mixture was cooled, 1,3,5-trimethoxybenzene (168 mg, 1 mmol, internal standard) was added to the reaction mixture, which was extracted with EtOAc. The organic layer was concentrated in vacuo. The residue was analyzed by ¹H-NMR spectroscopy.

Figure S1. Comparison of reaction rates in the presence of H₂O and D₂O.

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>[3a] (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>D₂O</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>0.005</td>
</tr>
<tr>
<td>2</td>
<td>0.0425</td>
</tr>
<tr>
<td>3</td>
<td>0.1025</td>
</tr>
<tr>
<td>4</td>
<td>0.15</td>
</tr>
<tr>
<td>5</td>
<td>0.21</td>
</tr>
<tr>
<td>6</td>
<td>0.2325</td>
</tr>
</tbody>
</table>

Figure S2. Isotope effect measured for the reactions.

K_SIE (k_H₂O/k_D₂O) = 0.3501/0.2353 = 1.5

A mixture of benzhydryl alcohols 2X (1 mmol), benzhydrol (2a) (186 mg, 1 mmol), 5-nitroindole (1a) (165 mg, 1 mmol), PtCl₂(PhCN)₂ (23.6 mg, 0.05 mmol) in 1,2-dichloroethane (4 mL) was heated at 90 °C for 5 h in a sealed tube under air. After cooling, the reaction mixture was poured into water and extracted with EtOAc. The organic layer was analyzed by ¹H-NMR spectroscopy.

<table>
<thead>
<tr>
<th>σᵢ</th>
<th>log(kᵢ/kᵢ₀)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OMe</td>
<td>-0.27</td>
</tr>
<tr>
<td>Me</td>
<td>-0.17</td>
</tr>
<tr>
<td>H</td>
<td>0</td>
</tr>
<tr>
<td>F</td>
<td>0.06</td>
</tr>
<tr>
<td>Cl</td>
<td>0.23</td>
</tr>
</tbody>
</table>

log(conversion X/conversion H) = log (0.89/1) = -0.051
Scheme S3: a $^1$H NMR study

A mixture of 5-nitroindole 1a (8.4 mg, 0.05 mmol), bis(benzonitrile)dichloroplatinum(II) (13.3 mg, 0.05 mmol) and CDCl$_3$ (4 mL) was heated at 60 °C under air. After cooling, the reaction mixture was analyzed by $^1$H-NMR spectroscopy.
**Scheme S4.** Scale-up experiment.

A mixture of 5-nitroindole 1a (1.14 g, 7 mmol), bis(benzonitrile)dichloroplatinum(II) (33 mg, 0.07 mmol), benzhydrol 2a (1.55 g, 8.4 mmol) and water (126 mg, 7 mmol) in 1,2-dichloroethane (28 mL) was heated at 60 °C for 36 h under air. After cooling, n-hexane was added to the reaction mixture. The precipitate was filtered to give desired product 3a as yellow solid (2.12 g, 92%).
3-Benzhydryl-5-nitro-1H-indole 3a

$\text{NMR (400 MHz, CDCl}_3\text{)}$

$\text{C NMR (100 MHz, CDCl}_3\text{)}$
3-Benzhydryl-4-nitro-1H-indole 3b

\[ \text{1H NMR (400 MHz, CDCl}_3\text{)} \]

\[ \text{13C NMR (100 MHz, CDCl}_3\text{)} \]
3-Benzhydryl-6-nitro-1H-indole 3c

$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}C$ NMR (100 MHz, CDCl$_3$)
3-Benzylhydrol-7-nitro-1H-indole 3d

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
3-Benzhydryl-1H-indole-5-carboxylic acid 3e

1H NMR (400 MHz, CDCl3)

13C NMR (100 MHz, CDCl3)
3-Benzhydryl-1H-indole-6-carboxylic acid 3f

$^1$H NMR (400 MHz, DMSO-$d_6$)

$^{13}$C NMR (100 MHz, DMSO-$d_6$)
3-Benzhydryl-1H-indole-7-carboxylic aci 3g

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
3-Benzhydryl-1H-indole-5-carbonitrile 3h

**1H NMR (400 MHz, CDCl₃)**

**13C NMR (100 MHz, CDCl₃)**
3-Benzhydryl-5-chloro-1H-indole 3i

**1H NMR (400 MHz, CDCl₃)**

**13C NMR (100 MHz, CDCl₃)**
3-Benzhydryl-1H-indole-2-carboxylic acid 3j

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
3-Benzhydryl-1-methyl-2-phenyl-1$H$-indole 3k

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
3-[Bis(4-methoxyphenyl)methyl]-5-nitro-1H-indole 3I

^1H NMR (400 MHz, CDCl₃)

^13C NMR (100 MHz, CDCl₃)

S17
3-[Bis(4-chlorophenyl)methyl]-5-nitro-1H-indole 3m

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
3-[Bis(4-fluorophenyl)methyl]-5-nitro-1H-indole 3n

^1^H NMR (400 MHz, CDCl_3)

^13^C NMR (100 MHz, CDCl_3)
3-[(4-Methoxyphenyl)(phenyl)methyl]-5-nitro-1H-indole 3o

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
5-Nitro-3-[phenyl(p-tolyl)methyl]-1H-indole 3p

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)

S21
3-[(4-Chlorophenyl)(phenyl)methyl]-5-nitro-1H-indole 3q

$^{13}$C NMR (100 MHz, CDCl$_3$)

$^{1}$H NMR (400 MHz, CDCl$_3$)
5-Nitro-3-\{phenyl[3-(trifluoromethyl)phenyl]methyl\}-1H-indole 3r

\(^1\)H NMR (400 MHz, DMSO-\(\text{d}_6\))

\(^1\)C NMR (100 MHz, DMSO-\(\text{d}_6\))
3-[1-(4-Methoxyphenyl)ethyl]-5-nitro-1H-indole 3s

\[ \text{H NMR (400 MHz, CDCl}_3\text{)} \]

\[ \text{C NMR (100 MHz, CDCl}_3\text{)} \]
5-Nitro-3-(1-phenylethyl)-1H-indole 3t

\[ \text{\(^1H\) NMR (400 MHz, CDCl}_3\) \]

\[ \text{\(^{13}C\) NMR (100 MHz, CDCl}_3\) \]

S25
(E)-3-(1,3-Diphenylallyl)-5-nitro-1H-indole 3u

**1H NMR (400 MHz, CDCl₃)**

**13C NMR (100 MHz, CDCl₃)**
5-Nitro-3-trityl-1H-indole 3v

\[ \text{1H NMR (400 MHz, CDCl}_3\text{)} \]

\[ \text{13C NMR (100 MHz, CDCl}_3\text{)} \]