Supporting Information

for

Cobalt-Catalyzed Cross-Dehydrogenative Coupling between N-(2-pyridyl) and Free Indoles for the Synthesis of Unsymmetrical 2,2'-Biindoles

Table of Contents

1. General Information S2
2. Synthesis of Unsymmetrical 2,2'-Biindoles S3
3. X-ray of Compound 3kf S17
4. Removal of the Pyridine Directing Group S19
5. Mechanistic studies. S21
6. NMR Spectra for New Compounds S23
1. General Information

Ethyl acetate (ACS grade), hexanes (ACS grade) and diethyl ether (ACS grade) were purchased from Fisher Scientific and used without further purification. Anhydrous dichloromethane (HPLC grade) was purified by distillation over calcium hydride. Anhydrous tetrahydrofuran from Aldrich was used directly without further purification. Commercially available reagents were used without further purification. Reactions were monitored by thin layer chromatography (TLC) using whatman precoated silica gel plates. Flash column chromatography was performed over silacycle silica gel (230-400 mesh). $^1$H NMR and $^{13}$C NMR spectra were recorded on a Varian 400 MHz Unity plus spectrometer using residue solvent peaks as internal standards. Infrared spectra were recorded with a Perkin Elmer FT-IR spectrum 2000 spectrometer and are reported in reciprocal centimeter (cm$^{-1}$). Mass spectra were recorded with Waters micromass ZQ detector using electron spray method. $N$-(2-pyridyl) indoles were prepared following literatures reports.
2. Synthesis of Unsymmetrical 2,2'-Biindoles

**General Procedure A:**

A suspension of 1 (0.20 mmol), 2 (0.40 mmol), [Cp*Co(CO)]_2 (2.5 mol%), AgSbF_6 (10 mol%), HOPiv (20 mol%), Ag_2O (2.0 equiv) and NaOAc (1.0 equiv) in DCE (2 mL) was stirred at 110 °C for 12 h. Then the solvent was removed in vacuo and the remaining residue was purified by column chromatography on silica gel to afford the desired product 3.

1-(pyridin-2-yl)-1'H,1'H-2,2'-biindole (3aa)

Compound 3aa was obtained as purple solid in 86% yield according to general procedure A.

**1H NMR** (400 MHz, CDCl_3) δ 8.95 (br, 1H), 8.73 (d, J = 3.6 Hz, 1H), 7.78 (td, J = 7.8, 1.7 Hz, 1H), 7.71 – 7.64 (m, 1H), 7.53 (d, J = 7.8 Hz, 1H), 7.48 – 7.41 (m, 1H), 7.36 (dd, J = 7.0, 5.2 Hz, 1H), 7.32 (d, J = 8.1 Hz, 1H), 7.27 (d, J = 8.1 Hz, 1H), 7.24 – 7.19 (m, 2H), 7.17 (t, J = 7.4 Hz, 1H), 7.08 (t, J = 7.4 Hz, 1H), 6.94 (s, 1H), 6.37 (s, 1H).

**13C NMR** (101 MHz, CDCl_3) δ 151.88, 149.24, 138.81, 138.49, 136.38, 132.61, 129.85, 128.53, 128.46, 123.27, 122.74, 122.45, 122.38, 121.53, 120.70, 120.60, 120.11, 111.10, 110.89, 105.25, 103.28.

**HRMS** m/z (ESI) Calcd for C_{21}H_{15}N_3Na [M+Na]^+ 332.1158, found: 332.1161.

4'-methyl-1-(pyridin-2-yl)-1'H,1'H-2,2'-biindole (3ab)
Compound 3ab was obtained as purple solid in 71% yield according to general procedure A.

**H NMR** (400 MHz, CD$_2$Cl$_2$) δ 8.81 (br, 1H), 8.68 (d, $J = 3.5$ Hz, 1H), 7.78 (td, $J = 7.8$, 1.8 Hz, 1H), 7.66 – 7.59 (m, 1H), 7.36 (dd, $J = 6.4$, 5.3 Hz, 2H), 7.31 (d, $J = 8.0$ Hz, 1H), 7.26 (d, $J = 8.0$ Hz, 1H), 7.18 – 7.13 (m, 2H), 7.09 (s, 1H), 6.88 (s, 1H), 6.85 (d, $J = 8.1$ Hz, 1H), 6.19 (s, 1H), 2.38 (s, 3H).

**13C NMR** (101 MHz, CD$_2$Cl$_2$) δ 151.73, 149.29, 138.79, 138.48, 136.81, 132.82, 132.39, 129.06, 128.46, 126.23, 122.93, 122.86, 122.34, 121.83, 121.29, 120.43, 119.98, 110.93, 110.66, 104.28, 102.75, 21.34.

**HRMS m/z (ESI)** Calcd for C$_{22}$H$_{17}$N$_3$Na [M+Na$^+$] 346.1315, found: 346.1312.

5'-methyl-1-(pyridin-2-yl)-1'H,1'H-2,2'-biindole (3ac)

Compound 3ac was obtained as purple solid in 85% yield according to general procedure A.

**H NMR** (400 MHz, CDCl$_3$) δ 8.79 (br, 1H), 8.72 (d, $J = 3.7$ Hz, 1H), 7.75 (td, $J = 7.8$, 1.7 Hz, 1H), 7.71 – 7.61 (m, 1H), 7.49 – 7.44 (m, 1H), 7.34 (dd, $J = 6.9$, 5.3 Hz, 1H), 7.32 (s, 1H), 7.25 – 7.17 (m, 4H), 6.99 (d, $J = 8.1$ Hz, 1H), 6.91 (s, 1H), 6.27 (d, $J = 0.8$ Hz, 1H), 2.42 (s, 3H).

**13C NMR** (101 MHz, CDCl$_3$) δ 151.92, 149.20, 138.77, 138.42, 134.75, 132.73, 129.87, 129.34, 128.75, 128.56, 124.11, 123.20, 122.65, 122.34, 121.49, 120.65, 120.18, 111.12, 110.55, 105.05, 102.83, 21.37.

**HRMS m/z (ESI)** Calcd for C$_{22}$H$_{17}$N$_3$Na [M+Na$^+$] 346.1315, found: 346.1312.
6'-methyl-1-(pyridin-2-yl)-1H,1'H-2,2'-biindole (3ad)

![Structure of 3ad](image)

Compound 3ad was obtained as purple solid as purple solid in 72% yield according to general procedure A.

\( ^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.93 (br, 1H), 8.68 – 8.58 (m, 1H), 7.66 (td, \( J = 7.8, 1.9 \) Hz, 1H), 7.59 (dd, \( J = 6.3, 2.6 \) Hz, 1H), 7.45 – 7.37 (m, 1H), 7.25 (dd, \( J = 6.7, 5.0 \) Hz, 1H), 7.17 – 7.13 (m, 3H), 7.06 (d, \( J = 8.1 \) Hz, 1H), 6.99 (d, \( J = 8.0 \) Hz, 1H), 6.84 (s, 1H), 6.81 (d, \( J = 7.0 \) Hz, 1H), 6.34 (d, \( J = 1.2 \) Hz, 1H), 2.41 (s, 3H).

\( ^{13}C \) NMR (101 MHz, CDCl\(_3\)) \( \delta \) 151.85, 149.10, 138.68, 138.45, 136.08, 132.72, 130.09, 129.22, 128.56, 128.37, 123.18, 122.63, 122.55, 122.31, 121.49, 120.65, 120.15, 111.10, 108.50, 105.28, 101.86, 18.63.

HRMS m/z (ESI) Calcd for C\(_{22}\)H\(_{17}\)N\(_3\)Na \([M+Na^+]\) 346.1315, found: 346.1312.

7'-methyl-1-(pyridin-2-yl)-1H,1'H-2,2'-biindole (3ae)

![Structure of 3ae](image)

Compound 3ae was obtained as purple solid in 77% yield according to general procedure A.

\( ^1\)H NMR (400 MHz, DMSO) \( \delta \) 11.27 (br, 1H), 8.83 – 8.71 (m, 1H), 8.04 (td, \( J = 7.7, 1.9 \) Hz, 1H), 7.82 – 7.72 (m, 1H), 7.60 (ddd, \( J = 7.5, 4.9, 0.9 \) Hz, 1H), 7.43 (d, \( J = 7.9 \) Hz, 1H), 7.37 – 7.32 (m, 1H), 7.31 (s, 1H), 7.27 – 7.19 (m, 3H), 6.95 – 6.87 (m, 2H), 5.71 (d, \( J = 2.0 \) Hz, 1H).

\( ^{13}C \) NMR (101 MHz, DMSO) \( \delta \) 151.72, 149.95, 139.47, 139.04, 136.48, 133.14, 130.00, 128.34, 128.22, 123.93, 123.32, 123.07, 122.99, 121.55, 121.04, 120.91, 120.07, 118.13, 111.29, 104.57, 102.23, 17.50.

HRMS m/z (ESI) Calcd for C\(_{22}\)H\(_{17}\)N\(_3\)Na \([M+Na^+]\) 346.1315, found: 346.1312.
Compound 3ag was obtained as purple solid in 82% yield according to general procedure A.

\(^1\)H NMR (400 MHz, DMSO) \(\delta\) 11.76 (br, 1H), 8.71 (d, \(J = 3.6\) Hz, 1H), 8.02 (td, \(J = 7.7, 1.8\) Hz, 1H), 7.72 (dd, \(J = 5.4, 3.2\) Hz, 1H), 7.58 (dd, \(J = 6.9, 5.1\) Hz, 1H), 7.46 – 7.40 (m, 2H), 7.38 (d, \(J = 8.6\) Hz, 1H), 7.30 (dd, \(J = 5.8, 2.8\) Hz, 1H), 7.24 – 7.12 (m, 3H), 7.09 (dd, \(J = 8.6, 1.9\) Hz, 1H), 5.66 (d, \(J = 1.1\) Hz, 1H).

\(^{13}\)C NMR (101 MHz, DMSO) \(\delta\) 151.42, 150.05, 139.61, 139.14, 135.41, 132.53, 131.71, 129.62, 128.21, 124.39, 124.09, 123.65, 123.00, 122.28, 121.68, 121.12, 119.66, 113.06, 111.32, 104.59, 101.01.

HRMS m/z (ESI) Calcd for C\(_{21}\)H\(_{14}\)ClN\(_3\)Na \([M+Na^+]\) 366.0768, found: 366.0772.

Compound 3ah was obtained as purple solid in 88% yield according to general procedure A.

\(^1\)H NMR (400 MHz, DMSO) \(\delta\) 11.71 (br, 1H), 8.71 (d, \(J = 4.7\) Hz, 1H), 8.03 (t, \(J = 7.7\) Hz, 1H), 7.74 – 7.65 (m, 1H), 7.58 (dd, \(J = 6.9, 5.4\) Hz, 1H), 7.43 (d, \(J = 7.9\) Hz, 1H), 7.38 (d, \(J = 8.5\) Hz, 2H), 7.32 – 7.23 (m, 1H), 7.23 – 7.14 (m, 3H), 6.96 (d, \(J = 8.4\) Hz, 1H), 5.69 (d, \(J = 0.9\) Hz, 1H).

\(^{13}\)C NMR (101 MHz, DMSO) \(\delta\) 151.44, 150.07, 139.63, 139.15, 137.35, 132.57, 131.16, 128.22, 127.29, 126.94, 124.12, 123.61, 123.03, 121.92, 121.66, 121.08, 120.21, 111.29, 111.10, 104.42, 101.42.

HRMS m/z (ESI) Calcd for C\(_{21}\)H\(_{14}\)ClN\(_3\)Na \([M+Na^+]\) 366.0768, found: 366.0772.
6'-fluoro-1-(pyridin-2-yl)-1'H,1'H-2,2'-biindole (3ai)

![Chemical Structure](image)

Compound 3ai was obtained as purple solid in 81% yield according to general procedure A.

**1H NMR** (400 MHz, DMSO) δ 11.58 (br, 1H), 8.72 (d, J = 3.2 Hz, 1H), 8.02 (t, J = 7.5 Hz, 1H), 7.67 – 7.55 (m, 1H), 7.51 (d, J = 9.2 Hz, 1H), 7.47 – 7.32 (m, 3H), 7.27 (dd, J = 8.5, 4.1 Hz, 1H), 7.19 – 7.07 (m, 2H), 7.02 (t, J = 9.0 Hz, 1H), 6.95 (t, J = 7.2 Hz, 1H), 5.67 (s, 1H).

**13C NMR** (101 MHz, DMSO) δ 151.40, 150.06, 139.66, 137.03, 135.76, 134.80, 129.60, 128.80 (d, J = 8.6 Hz), 128.40, 124.22, 123.05, 122.57, 120.67, 119.90, 112.45 (d, J = 9.5 Hz), 111.67, 111.32 (d, J = 26.4 Hz), 105.82, 105.62, 103.90 (d, J = 5.1 Hz), 101.71.

**HRMS** m/z (ESI) Calcd for C_{21}H_{14}FN_3Na [M+Na]^+ 350.1064, found: 350.1063.

methyl 1'(pyridin-2-yl)-1'H,1'H-[2,2'-biindole]-5-carboxylate (3aj)

![Chemical Structure](image)

Compound 3aj was obtained as purple solid in 50% yield according to general procedure A.

**1H NMR** (400 MHz, DMSO) δ 11.95 (br, 1H), 8.71 (d, J = 3.6 Hz, 1H), 8.07 (s, 1H), 8.03 (td, J = 7.8, 1.8 Hz, 1H), 7.77 – 7.70 (m, 2H), 7.59 (dd, J = 7.1, 5.1 Hz, 1H), 7.45 (dd, J = 8.2, 3.9 Hz, 2H), 7.30 (d, J = 6.8 Hz, 1H), 7.24 – 7.17 (m, 3H), 5.81 (s, 1H), 3.82 (s, 3H).

**13C NMR** (101 MHz, DMSO) δ 167.51, 151.37, 150.07, 139.63, 139.53, 139.17, 132.38, 131.86, 128.19, 128.12, 124.13, 123.71, 123.31, 123.13, 123.02, 121.69, 121.43, 121.16, 111.52, 111.32, 104.67, 102.49, 52.08.
HRMS m/z (ESI) Calcd for C_{23}H_{17}O_{2}N_{3}H [M+H^+ ] 368.1394, found: 368.1389.

5'-methoxy-1-(pyridin-2-yl)-1'H,1'H-2,2'-biindole (3ak)

Compound 3ak was obtained as purple solid in 76% yield according to general procedure A.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.84 (s, 1H), 8.70 (d, $J = 3.7$ Hz, 1H), 7.76 (t, $J = 6.9$ Hz, 1H), 7.68 – 7.63 (m, 1H), 7.46 – 7.39 (m, 1H), 7.34 (dd, $J = 6.8$, 5.3 Hz, 1H), 7.24 – 7.16 (m, 3H), 6.96 (s, 1H), 6.89 (s, 1H), 6.81 (dd, $J = 8.7$, 2.1 Hz, 1H), 6.27 (s, 1H), 3.81 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 154.47, 151.90, 149.20, 138.77, 138.48, 132.67, 131.64, 130.49, 128.89, 128.55, 123.22, 122.71, 122.37, 121.52, 120.67, 112.92, 111.62, 111.09, 105.08, 103.05, 102.18, 55.84.

HRMS m/z (ESI) Calcd for C$_{22}$H$_{17}$ON$_3$Na [M+Na$^+$] 362.1264, found: 362.1262.

3-methyl-1-(pyridin-2-yl)-1'H,1'H-2,2'-biindole (3ba)

Compound 3ba was obtained as purple solid in 71% yield according to general procedure A.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.97 (br, 1H), 8.60 (d, $J = 3.7$ Hz, 1H), 7.65 – 7.56 (m, 4H), 7.29 (d, $J = 8.1$ Hz, 1H), 7.24 – 7.15 (m, 4H), 7.13 – 7.09 (m, 1H), 7.03 (d, $J = 8.0$ Hz, 1H), 6.60 (d, $J = 1.2$ Hz, 1H), 2.46 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 152.22, 148.68, 148.32, 137.64, 136.37, 129.53, 128.94, 128.44, 128.33, 123.63, 122.20, 121.81, 121.26, 121.07, 120.53, 119.93, 119.12, 114.92, 111.30, 110.91, 104.99, 9.82.

HRMS m/z (ESI) Calcd for C$_{22}$H$_{17}$N$_3$Na [M+Na$^+$] 346.1315, found: 346.1312.
3,5'-dimethyl-1-(pyridin-2-yl)-1H,1'H-2,2'-biindole (3bc)

Compound 3bc was obtained as purple solid in 71% yield according to general procedure A.

$^1$H NMR (400 MHz, DMSO)  $\delta$ 11.01 (br, 1H), 8.59 (d, $J = 4.8$ Hz, 1H), 7.78 – 7.71 (m, 1H), 7.68 (dd, $J = 10.4, 4.3$ Hz, 2H), 7.37 (d, $J = 8.0$ Hz, 1H), 7.31 (dd, $J = 6.9, 5.4$ Hz, 1H), 7.26 – 7.19 (m, 2H), 7.12 (s, 1H), 6.96 (d, $J = 8.1$ Hz, 1H), 6.83 (d, $J = 8.1$ Hz, 1H), 6.25 (s, 1H), 2.43 (s, 3H), 2.38 (s, 3H).

$^{13}$C NMR (101 MHz, DMSO)  $\delta$ 151.98, 149.19, 138.73, 137.60, 137.43, 131.10, 129.43, 129.30, 128.47, 126.24, 123.74, 122.23, 121.48, 121.30, 120.69, 120.21, 119.35, 113.70, 112.09, 111.68, 103.90, 21.87, 9.92.

HRMS m/z (ESI) Calcd for C_{23}H_{19}N_{3}H [M+H$^+$] 338.1652, found: 338.1657

5'-chloro-3-methyl-1-(pyridin-2-yl)-1H,1'H-2,2'-biindole (3bf)

Compound 3bf was obtained as purple solid in 71% yield according to general procedure A.

$^1$H NMR (400 MHz, DMSO)  $\delta$ 11.34 (br, 1H), 8.62 – 8.56 (m, 1H), 7.76 (td, $J = 7.8, 1.9$ Hz, 1H), 7.71 – 7.66 (m, 2H), 7.51 (d, $J = 8.4$ Hz, 1H), 7.36 – 7.31 (m, 2H), 7.27 – 7.21 (m, 2H), 7.02 – 6.98 (m, 2H), 6.41 – 6.33 (m, 1H), 2.44 (s, 3H).

$^{13}$C NMR (101 MHz, DMSO)  $\delta$ 151.78, 149.31, 138.88, 137.53, 137.48, 130.39, 129.34, 128.57, 127.10, 126.62, 124.04, 122.39, 121.87, 121.40, 120.75, 120.08, 119.53, 114.30, 112.05, 111.41, 104.11, 9.91.

HRMS m/z (ESI) Calcd for C_{22}H_{16}N_{3}ClNa [M+Na$^+$] 380.0925, found: 380.0930.
5-fluoro-1-(pyridin-2-yl)-1'H,1'H-2,2'-biindole (3ca)

![Chemical structure of 3ca]

Compound 3ca was obtained as purple solid in 71% yield according to general procedure A.

1H NMR (400 MHz, CDCl3) δ 9.08 (br, 1H), 8.72 (d, J = 3.4 Hz, 1H), 7.82 (dd, J = 10.8, 4.5 Hz, 1H), 7.67 (dd, J = 6.1, 2.5 Hz, 1H), 7.43 (d, J = 7.1 Hz, 1H), 7.41 – 7.36 (m, 1H), 7.30 (d, J = 7.9 Hz, 1H), 7.22 (dt, J = 8.1, 7.1 Hz, 3H), 7.16 (dd, J = 9.5, 2.0 Hz, 1H), 6.98 – 6.78 (m, 2H), 6.33 (s, 1H).

13C NMR (101 MHz, CDCl3): δ 157.2, 151.8, 149.3, 138.8, 138.6, 132.9, 132.3, 131.7, 128.8 (d, J_C-F = 10.0 Hz), 128.5, 123.4, 122.9, 122.4, 121.6, 120.8, 111.5 (d, J_C-F = 9.0 Hz), 111.1, 110.8 (d, J_C-F = 26.4 Hz), 105.6, 105.2 (d, J_C-F = 23.7 Hz), 103.2, 103.1.


5-methyl-1-(pyridin-2-yl)-1'H,1'H-2,2'-biindole (3da)

![Chemical structure of 3da]

Compound 3da was obtained as purple solid in 71% yield according to general procedure A.

1H NMR (400 MHz, DMSO) δ 11.52 (br, 1H), 8.70 (d, J = 3.5 Hz, 1H), 8.00 (td, J = 7.7, 1.7 Hz, 1H), 7.55 (dd, J = 7.0, 5.2 Hz, 1H), 7.49 (s, 1H), 7.36 (t, J = 9.3 Hz, 3H), 7.19 (d, J = 8.4 Hz, 1H), 7.09 (t, J = 7.5 Hz, 1H), 7.05 (s, 1H), 7.01 (d, J = 8.3 Hz, 1H), 6.94 (t, J = 7.4 Hz, 1H), 5.65 (s, 1H), 2.42 (s, 3H).

13C NMR (101 MHz, DMSO) δ 151.77, 149.94, 139.46, 137.60, 136.94, 133.07, 130.31, 130.16, 128.57, 128.50, 124.90, 123.85, 122.90, 122.30, 120.52, 119.78, 111.57, 111.04, 103.77, 101.24, 21.50.

5,5'-dimethyl-1-(pyridin-2-yl)-1H,1'H-2,2'-biindole (3dc)

Compound 3dc was obtained as purple solid in 71% yield according to general procedure A.

$^1$H NMR (400 MHz, DMSO) $\delta$ 11.38 (br, 1H), 8.70 (d, $J = 4.2$ Hz, 1H), 8.03 – 7.91 (m, 1H), 7.54 (dd, $J = 7.3, 5.0$ Hz, 1H), 7.47 (s, 1H), 7.35 (d, $J = 7.9$ Hz, 1H), 7.26 (d, $J = 8.2$ Hz, 1H), 7.19 (d, $J = 8.4$ Hz, 1H), 7.12 (s, 1H), 7.03 (s, 1H), 7.00 (d, $J = 8.4$ Hz, 1H), 6.91 (d, $J = 8.2$ Hz, 1H), 5.55 (s, 1H), 2.41 (s, 3H), 2.31 (s, 3H).

$^{13}$C NMR (101 MHz, DMSO) $\delta$ 151.81, 149.90, 139.41, 137.54, 135.32, 133.24, 130.28, 130.14, 128.76, 128.60, 128.27, 124.81, 123.93, 123.79, 122.89, 120.48, 120.06, 111.28, 111.02, 103.57, 100.86, 21.55, 21.50.

HRMS m/z (ESI) Calcd for C$_{23}$H$_{19}$N$_3$Na [M+Na$^+$] 360.1471, found: 360.1478.

5-chloro-1-(pyridin-2-yl)-1H,1'H-2,2'-biindole (3ea)

Compound 3ea was obtained as purple solid in 71% yield according to general procedure A.

$^1$H NMR (400 MHz, DMSO) $\delta$ 11.76 (s, 1H), 8.71 (d, $J = 3.6$ Hz, 1H), 8.02 (td, $J = 7.7, 1.8$ Hz, 1H), 7.72 (dd, $J = 5.4, 3.2$ Hz, 1H), 7.58 (dd, $J = 6.9, 5.1$ Hz, 1H), 7.48 – 7.40 (m, 2H), 7.38 (d, $J = 8.6$ Hz, 1H), 7.30 (dd, $J = 5.8, 2.8$ Hz, 1H), 7.23 – 7.13 (m, 3H), 7.09 (dd, $J = 8.6, 1.9$ Hz, 1H), 5.66 (d, $J = 1.1$ Hz, 1H).

$^{13}$C NMR (101 MHz, DMSO) $\delta$ 151.42, 150.05, 139.61, 139.14, 135.41, 132.53, 131.71, 129.62, 128.21, 124.39, 124.09, 123.65, 123.00, 122.28, 121.68, 121.12, 119.66, 113.06, 111.32, 104.59, 101.01.

HRMS m/z (ESI) Calcd for C$_{21}$H$_{14}$ClN$_3$Na [M+Na$^+$] 366.0768, found: 366.0772.
5,5'-dichloro-1-(pyridin-2-yl)-1H,1'H-2,2'-biindole (3ee)

Compound 3ee was obtained as purple solid in 78% yield according to general procedure A.

\(^1\)H NMR (400 MHz, DMSO) \(\delta\) 11.83 (br, 1H), 8.71 (s, 1H), 8.03 (s, 1H), 7.81 (s, 1H), 7.59 (s, 1H), 7.42 (d, \(J = 20.5\) Hz, 2H), 7.39 (d, \(J = 8.3\) Hz, 1H), 7.29 (d, \(J = 8.3\) Hz, 1H), 7.26 – 7.07 (m, 3H), 5.68 (s, 1H).

\(^{13}\)C NMR (101 MHz, DMSO) \(\delta\) 150.99, 150.13, 139.77, 137.56, 135.50, 134.01, 131.09, 129.51, 129.40, 126.18, 124.50, 124.39, 123.51, 122.98, 122.55, 120.27, 119.81, 113.17, 112.92, 103.97, 101.47.

HRMS m/z (ESI) Calcd for C\(_{21}\)H\(_{13}\)N\(_3\)Cl\(_2\)Na \([\text{M+Na}^+]\) 400.0378, found: 400.0384.

5-chloro-5'-methyl-1-(pyridin-2-yl)-1H,1'H-2,2'-biindole (3ec)

Compound 3ec was obtained as purple solid in 66% yield according to general procedure A.

\(^1\)H NMR (400 MHz, DMSO) \(\delta\) 11.47 (s, 1H), 8.72 (d, \(J = 3.7\) Hz, 1H), 8.02 (td, \(J = 7.8, 1.7\) Hz, 1H), 7.78 (d, \(J = 1.6\) Hz, 1H), 7.60 (dd, \(J = 7.0, 5.0\) Hz, 1H), 7.41 (d, \(J = 7.9\) Hz, 1H), 7.27 (d, \(J = 8.3\) Hz, 2H), 7.20 – 7.13 (m, 2H), 7.10 (s, 1H), 6.93 (d, \(J = 8.1\) Hz, 1H), 5.55 (s, 1H), 2.31 (s, 3H).

\(^{13}\)C NMR (101 MHz, DMSO) \(\delta\) 151.21, 150.08, 139.68, 137.49, 135.44, 134.79, 129.54, 129.36, 128.63, 128.45, 126.04, 124.34, 124.30, 123.13, 123.11, 120.21, 120.04, 112.79, 111.38, 103.12, 101.43, 21.53.

HRMS m/z (ESI) Calcd for C\(_{22}\)H\(_{16}\)N\(_3\)Cl\(_2\)Na \([\text{M+Na}^+]\) 380.0925, found: 380.0930.

1-(6-methylpyridin-2-yl)-1H,1'H-2,2'-biindole (3ga)
Compound 3ga was obtained as purple solid in 52% yield according to general procedure A.

$^1$H NMR (400 MHz, DMSO) $\delta$ 11.52 (br, 1H), 7.89 (t, $J = 7.7$ Hz, 1H), 7.73 – 7.67 (m, 1H), 7.44 (d, $J = 7.6$ Hz, 1H), 7.40 – 7.35 (m, 2H), 7.30 – 7.25 (m, 1H), 7.17 (ddd, $J = 10.2$, 6.4, 5.1 Hz, 3H), 7.12 (s, 1H), 7.11 – 7.00 (m, 1H), 6.98 – 6.92 (m, 1H), 5.68 (d, $J = 1.8$ Hz, 1H), 2.57 (s, 3H).

$^{13}$C NMR (101 MHz, DMSO) $\delta$ 158.84, 150.90, 139.61, 139.15, 136.95, 133.06, 130.06, 128.48, 128.25, 123.31, 122.35, 121.47, 120.87, 120.57, 119.96, 119.80, 111.57, 111.41, 103.77, 101.33, 24.34.

HRMS m/z (ESI) Calcd for C$_{22}$H$_{17}$N$_3$Na [M+Na$^+$] 346.1315, found: 346.1312.

3-methyl-1-(3-methylpyridin-2-yl)-1H,1’H-2,2’-biindole (3ha)

Compound 3ha was obtained as purple solid in 62% yield according to general procedure A.

$^1$H NMR (400 MHz, DMSO) $\delta$ 11.18 (s, 1H), 8.41 (s, 1H), 7.68 (dd, $J = 6.3$, 1.9 Hz, 1H), 7.58 (dd, $J = 7.1$, 4.6 Hz, 2H), 7.49 (d, $J = 7.8$ Hz, 1H), 7.34 (d, $J = 8.1$ Hz, 1H), 7.24 – 7.18 (m, 2H), 7.08 (dd, $J = 11.1$, 4.0 Hz, 1H), 6.99 (t, $J = 7.5$ Hz, 1H), 6.92 (dd, $J = 8.2$, 2.5 Hz, 1H), 6.28 (s, 1H), 2.43 (s, 3H), 2.31 (s, 3H).

$^{13}$C NMR (101 MHz, DMSO) $\delta$ 149.68, 149.27, 139.20, 137.63, 137.11, 131.69, 129.29, 129.26, 129.25, 128.32, 123.67, 121.91, 121.12, 120.50, 120.42, 119.65, 119.36, 113.47, 111.91, 103.96, 100.00, 17.83, 9.91.

HRMS m/z (ESI) Calcd for C$_{23}$H$_{19}$N$_3$Na [M+Na$^+$] 360.1471, found: 360.1478.

1-(pyrimidin-2-yl)-1H,1’H-2,2’-biindole (3ia)
Compound 3ia was obtained as purple solid in 71% yield according to general procedure A.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.27 (s, 1H), 8.78 (d, $J = 4.6$ Hz, 2H), 8.12 (d, $J = 8.2$ Hz, 1H), 7.67 (d, $J = 7.6$ Hz, 1H), 7.61 (d, $J = 7.8$ Hz, 1H), 7.35 (dd, $J = 19.8$, 8.1 Hz, 2H), 7.29 (t, $J = 7.3$ Hz, 1H), 7.21 (dd, $J = 10.0$, 5.7 Hz, 2H), 7.13 (t, $J = 7.4$ Hz, 1H), 6.98 (s, 1H), 6.56 (s, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 158.37, 157.97, 138.13, 136.40, 132.53, 130.58, 129.09, 128.43, 123.96, 122.40, 122.33, 120.73, 120.60, 120.01, 118.10, 113.30, 110.95, 109.31, 104.06.

HRMS m/z (ESI) Calcd for C$_{20}$H$_{14}$N$_4$Na [M+Na$^+$] 333.1110, found: 333.1109.

2-(1-(pyridin-2-yl)-1H-pyrrol-2-yl)-1H-indole (3ja)

Compound 3ja was obtained as purple solid in 46% yield according to general procedure A.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.04 (br, 1H), 8.47 (s, 1H), 7.57 (t, $J = 6.9$ Hz, 1H), 7.47 (d, $J = 7.8$ Hz, 1H), 7.24 (dd, $J = 8.1$, 0.7 Hz, 1H), 7.18 - 7.10 (m, 2H), 7.09 - 6.97 (m, 3H), 6.53 (d, $J = 3.3$ Hz, 1H), 6.32 (s, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 148.40, 138.46, 136.05, 130.51, 128.58, 125.91, 123.85, 121.98, 121.85, 120.31, 119.89, 119.00, 113.32, 110.82, 110.51, 102.05.

HRMS m/z (ESI) Calcd for C$_{17}$H$_{13}$N$_3$Na[M+Na$^+$] 282.1002, found: 282.1001.

2-(5-methyl-1-(pyridin-2-yl)-1H-pyrrol-2-yl)-1H-indole (3ka)
Compound 3ka was obtained as purple solid in 76% yield according to general procedure A.

\[ ^{1}H \text{ NMR} \ (400 \text{ MHz, CDCl}_3) \delta 8.71 – 8.65 \ (m, 1H), \ 8.34 \ (s, 1H), \ 7.74 \ (td, J = 7.7, 1.9 \text{ Hz, 1H}), \ 7.42 \ (d, J = 7.8 \text{ Hz, 1H}), \ 7.38 – 7.33 \ (m, 1H), \ 7.23 \ (d, J = 8.1 \text{ Hz, 1H}), \ 7.18 \ (d, J = 7.9 \text{ Hz, 1H}), \ 7.08 \ (dd, J = 11.1, 4.0 \text{ Hz, 1H}), \ 7.02 \ (t, J = 7.4 \text{ Hz, 1H}), \ 6.46 \ (d, J = 3.5 \text{ Hz, 1H}), \ 6.13 \ (d, J = 3.4 \text{ Hz, 1H}), \ 5.86 \ (d, J = 1.3 \text{ Hz, 1H}), \ 2.20 \ (s, 3H). \]

\[ ^{13}C \text{ NMR} \ (101 \text{ MHz, CDCl}_3) \delta 152.21, \ 149.20, \ 138.28, \ 135.75, \ 132.26, \ 130.96, \ 128.72, \ 126.29, \ 123.27, \ 121.49, \ 120.02, \ 119.71, \ 110.43, \ 109.30, \ 108.48, \ 100.08, \ 13.02. \]

HRMS m/z (ESI) Calcd for C_{18}H_{15}N_{3}Na [M+Na\(^{+}\)] 296.1158, found: 296.1154.

5-methyl-2-(5-methyl-1-(pyridin-2-yl)-1H-pyrrol-2-yl)-1H-indole (3kc)

Compound 3kc was obtained as purple solid in 72% yield according to general procedure A.

\[ ^{1}H \text{ NMR} \ (400 \text{ MHz, CDCl}_3) \delta 8.71 – 8.64 \ (m, 1H), \ 8.19 \ (br, 1H), \ 7.73 \ (td, J = 7.7, 1.9 \text{ Hz, 1H}), \ 7.35 \ (ddd, J = 7.5, 4.9, 1.0 \text{ Hz, 1H}), \ 7.20 \ (s, 1H), \ 7.18 – 7.15 \ (m, 1H), \ 7.12 \ (d, J = 8.2 \text{ Hz, 1H}), \ 6.92 \ (dd, J = 8.2, 1.1 \text{ Hz, 1H}), \ 6.44 \ (d, J = 3.5 \text{ Hz, 1H}), \ 6.12 \ (dd, J = 3.5, 0.8 \text{ Hz, 1H}), \ 5.83 – 5.70 \ (m, 1H), \ 2.39 \ (s, 3H), \ 2.19 \ (s, 3H). \]

\[ ^{13}C \text{ NMR} \ (101 \text{ MHz, CDCl}_3) \delta 152.25, \ 149.17, \ 138.23, \ 134.09, \ 132.16, \ 131.03, \ 129.00, \ 128.89, \ 126.44, \ 123.26, \ 123.20, \ 123.07, \ 119.71, \ 110.09, \ 109.11, \ 108.42, \ 99.71, \ 21.33, \ 13.01. \]

HRMS m/z (ESI) Calcd for C_{19}H_{17}N_{3}Na [M+Na\(^{+}\)] 310.1315, found: 310.1319.
5-chloro-2-(5-methyl-1-(pyridin-2-yl)-1H-pyrrol-2-yl)-1H-indole (3kf)

Compound 3kf was obtained as purple solid in 62% yield according to general procedure A.

\(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.67 (d, \(J = 3.8\) Hz, 1H), 8.43 (s, 1H), 7.77 (dd, \(J = 10.8, 4.6\) Hz, 1H), 7.38 (dd, \(J = 6.8, 5.5\) Hz, 1H), 7.35 (s, 1H), 7.18 (d, \(J = 7.9\) Hz, 1H), 7.10 (d, \(J = 8.5\) Hz, 1H), 7.01 (dd, \(J = 8.5, 1.6\) Hz, 1H), 6.45 (d, \(J = 3.3\) Hz, 1H), 6.11 (d, \(J = 2.5\) Hz, 1H), 5.74 (s, 1H), 2.18 (s, 3H).

\(^1^3^C\) NMR (101 MHz, CDCl\(_3\)) \(\delta\) 152.08, 149.27, 138.40, 134.08, 132.61, 132.44, 129.84, 125.79, 125.33, 123.44, 123.25, 121.63, 119.31, 111.33, 109.68, 108.65, 99.44, 13.00.

HRMS m/z (ESI) Calcd for C\(_{19}\)H\(_{14}\)ClN\(_3\)Na \([M+Na^+]\) 330.0768, found: 330.0771.
3. X-ray of Compound 3kf

![Ortep drawing of compound 3kf.](image)

**Figure S1.** Ortep drawing of compound 3kf.

**Table S1:** Crystallographic Details for 3kf

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4. Removal of the Pyridine Directing Group

General Procedure B:

Methyl trifluoromethanesulfonate (0.24 mmol) was added dropwise to a solution of 3 (0.20 mmol) in dry CH₂Cl₂ (5.0 mL) at 0 °C, and the resulting solution was stirred for 6 h at room temperature. Then the solvent was removed under vacuum, and Pd(OH)₂/C (8 mg, 10 wt.-%) and ammonium formate (126 mg, 2.00 mmol, 10.0 equiv) were added. The mixture was diluted with MeOH (2.0 mL, 0.1 M) and stirred at 60 °C for 6 h. The solvents were removed, and the resulting residue was extracted with CH₂Cl₂ (2 × 10 mL). The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by flash chromatography, affording the desired product 4.

1H,1’H-2,2’-biindole (4a)

Compound 4a was obtained as purple solid in 71% yield according to general procedure B.

1H NMR (400 MHz, DMSO): δ 11.54 (br, 1H), 7.56 (d, J = 8.5 Hz, 1H), 7.40 (d, J = 8.5 Hz, 1H), 7.11 (t, J = 8.1 Hz, 1H), 7.02 (d, J = 7.6 Hz, 1H), 6.92 (d, J = 0.2 Hz, 1H);

13C NMR (101 MHz, DMSO): δ 136.88, 131.37, 128.41, 121.66, 120.00, 119.38, 111.03, 98.38.

HRMS m/z (ESI) Calcd for C₁₆H₁₂N₂Na [M+Na⁺] 255.0893, found: 255.0891.

2-(1H-pyrrol-2-yl)-1H-indole (4b)
Compound 4b was obtained as purple solid in 74% yield according to general procedure B.

$^1$H NMR (400 MHz, DMSO) $\delta$ 11.03 (br, 1H), 10.90 (br, 1H), 7.17 (s, 1H), 7.04 (s, 1H), 6.94 – 6.50 (m, 3H), 6.38 – 6.19 (m, 2H), 5.85 (s, 1H).

$^{13}$C NMR (101 MHz, DMSO) $\delta$ 136.49, 132.83, 129.04, 125.26, 120.76, 119.51, 119.40, 119.30, 110.89, 108.97, 105.88, 95.28.

HRMS m/z (ESI) Calcd for C$_{12}$H$_{10}$N$_2$Na [M+Na$^+$] 205.0736, found: 205.07367.
5. Mechanistic studies.

1a (0.2 mmol) or [D-1]-1a (0.2 mmol) was allowed to react with 2a in two paralleled dried Schlenk tube under standard conditions for 2 h. After cooling to room temperature, the mixture was diluted with ethyl acetate, filtrated through celite. After concentration, the yield of the resulting product of 3aa was collected to calculate the KIE.

2a (0.2 mmol) or [D-1]-2a (0.2 mmol) was allowed to react with 1a in two paralleled dried Schlenk tube under standard conditions for 2 h. After cooling to room temperature, the mixture was diluted with ethyl acetate, filtrated through celite. After concentration, the yield of the resulting product of 3aa was collected to calculate the KIE.

2a (0.2 mmol) or [D-2]-2a (0.2 mmol) was allowed to react with 1a in two paralleled dried Schlenk tube under standard conditions for 2 h. After cooling to room temperature, the mixture was diluted with ethyl acetate, filtrated through celite. After concentration, the yield of the resulting product of 3aa was collected to calculate the KIE.

1a (0.2 mmol) was allowed to react with 2a in one dried Schlenk tube in the presence
of 20 equiv D$_2$O under standard conditions for 2 h. After cooling to room temperature, the mixture was diluted with ethyl acetate, filtrated through celite. After purification, the NMR of [D-2]-1a and [D-3]-2a was collected.