Supporting Information

for

Highly Efficient [3+2] Reaction of 3-Vinylindoles with 3-Indolylmethanols by Brønsted-Acid Catalysis

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General data

Unless otherwise noted, commercial reagents were used as received and all reactions were carried out directly in air atmosphere. All reactions were monitored by TLC with silica gel coated plates. \(^1\)H NMR and \(^{13}\)C NMR spectra were recorded on a Bruker Avance 300 spectrometer. HRMS (Bio TOF Q) spectra were recorded on P-SIMS-Gly of Bruker Daltonics Inc. Chemical shifts are reported in ppm from tetramethyl silane (TMS) with the solvent resonance as the internal standard. Proton signal multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad) or a combination of them. \(J\)-values are in Hz. The 3-indolylmethanol\(^{[1]}\) and 3-Vinylindoles \(^{[2]}\) were prepared according to the literature.

References:

2. Li, Q.; Jaeki; Ahn, Y.-H.; N., Joshua; K., E. Min; L., Rowena; K., H. Yun; J., Yong; W., Hueizhi; W., Thomas; Chang, Y.-T., \textit{ChemBioChem.}, 2007, 8, 1679.

I. General procedure.

A reaction tube was charged with catalyst 3g (0.25 mg, 0.001 mmol), 3-Vinylindole 2 (0.1 mmol) and DCM (1 mL). The solution was stirred at 0°C or -20°C for 15 minutes, then 3-Indolylmethanol 1 (0.1 mmol) was added. After the 3-indolylmethanol 1 and 3-Vinylindole 2 were consumed completely by TLC analysis, one drop of Et\(_3\)N was added. The mixture was subjected to silica gel column chromatography directly to afford the desired products 4 with using ethyl acetate/petroleum as eluent.
4a was obtained as a white solid in 95% yield after flash chromatography; m.p. 183-184°C; \( ^1H \) NMR (300 MHz, DMSO-\( d_6 \)): \( \delta \) (ppm) 11.04 (s, 1H), 10.97 (s, 1H), 7.29 (m, 12H), 7.16 (d, \( J = 2.1 \), 1H), 7.14-7.08 (m, 1H), 7.07-7.00 (m, 2H), 6.97-6.82 (m, 3H), 4.95 (d, \( J = 7.6 \), 1H), 4.66 (d, \( J = 8.0 \), 1H), 3.85 (t, \( J = 8.4 \), 1H); \( ^{13}C \) NMR (75 MHz, DMSO-\( d_6 \)): \( \delta \) (ppm) 145.36, 144.32, 142.72, 141.39, 137.22, 128.65, 127.74, 126.88, 126.66, 126.54, 124.16, 123.57, 121.32, 120.32, 119.11, 118.76, 118.12, 117.86, 114.72, 112.52, 112.03, 71.11, 53.11, 45.98; HRMS(ESI): calcd. for C31H24N2O(\( M^+ + Na \)): 447.1832, found: 447.1823.

4b was obtained as a white solid in 99% yield after flash chromatography; m.p. 155-156°C; \( ^1H \) NMR (300 MHz, DMSO-\( d_6 \)): \( \delta \) (ppm) 11.43 (s, 1H), 10.90 (s, 1H), 7.48-7.09 (m, 13H), 7.05-6.74 (m, 5H), 5.60 (s, 1H), 4.59 (s, 1H), 3.88 (s, 1H); \( ^{13}C \) NMR (75 MHz, DMSO-\( d_6 \)): \( \delta \) (ppm) 146.61, 144.41, 142.95, 141.34, 138.11, 128.56, 127.98, 126.72, 125.11, 123.98, 121.96, 120.19, 119.04, 118.16, 117.24, 116.03, 112.58, 111.23, 71.62, 53.25, 44.42; HRMS(ESI): calcd. for C31H23ClN2Na(\( M^+ + Na \)): 481.1442, found: 481.1434.

4c was obtained as a white solid in 87% yield after flash chromatography; m.p. 245-246°C; \( ^1H \) NMR (300 MHz, DMSO-\( d_6 \)): \( \delta \) (ppm) 11.19 (s, 1H), 11.05 (s, 1H), 7.38-7.30 (m, 2H), 7.30-7.20 (m, 6H), 7.20-7.07 (m, 7H), 7.02 (t, \( J = 7.4 \), 1H), 6.96-6.84 (m, 2H), 4.90 (d, \( J = 8.3 \), 1H), 4.63 (d, \( J = 7.6 \), 1H), 3.72 (t, \( J = 8.3 \), 1H); \( ^{13}C \) NMR (75 MHz, DMSO-\( d_6 \)): \( \delta \) (ppm) 144.85, 144.20, 142.63, 141.44, 135.79, 128.71, 128.43, 127.62, 127.02, 126.75, 125.11, 124.13, 123.83, 121.44, 120.51, 119.18, 118.08, 117.91, 114.78, 114.00, 112.58, 111.35, 71.29, 53.08, 45.82; HRMS (ESI): calcd. for C31H23BrN2Na(\( M^+ + Na \)): 525.0937, found: 525.0926.
**4d** was obtained as a white solid in 85.5% yield after flash chromatography; m.p. 204-205°C; $^1$H NMR (300 MHz, DMSO-$d_6$): δ (ppm) 11.08 (d, $J = 17.0$, 2H), 7.42-7.31 (m, 2H), 7.27 (t, $J = 7.6$, 5H), 7.23-7.14 (m, 6H), 7.10-6.99 (m, 2H), 6.90 (m, 2H), 6.78-6.68 (m, 1H), 4.93 (d, $J = 8.5$, 1H), 4.65 (d, $J = 7.4$, 1H), 3.79 (t, $J = 8.4$, 1H); $^{13}$C NMR (75 MHz, DMSO-$d_6$): δ (ppm) 160.70 and 157.59 (d, $J_{CF} = 233.25$), 145.07, 144.20, 142.53, 141.39, 137.11, 136.94, 128.68, 127.74, 126.82, 124.15, 123.39, 120.40, 120.03, 119.11, 118.07, 114.98, 112.55, 107.48, 107.16, 97.96, 71.27, 53.08, 45.87; HRMS(ESI): calcd. for C$_{31}$H$_{23}$FN$_2$Na (M$^+$/Na): 465.1737, found: 465.1733.

**4e** was obtained as a white solid in 86.1% yield after flash chromatography; m.p. 140-141°C; $^1$H NMR (300 MHz, DMSO-$d_6$): δ (ppm) 11.08 (s, 1H), 10.83 (s, 1H), 7.48-7.17 (m, 12H), 7.15 (d, $J = 1.8$, 1H), 7.05 (t, $J = 7.2$, 1H), 6.99-6.87 (m, 2H), 6.70 (dd, $J = 8.7$, 2.0, 1H), 6.45 (d, $J = 1.6$, 1H), 4.94 (d, $J = 8.1$, 1H), 4.66 (d, $J = 7.7$, 1H), 3.77 (t, $J = 8.2$, 1H), 3.47 (s, 3H); $^{13}$C NMR (75 MHz, DMSO-$d_6$): δ (ppm) 153.04, 145.12, 144.43, 143.17, 141.45, 132.22, 128.71, 128.65, 127.63, 126.78, 124.11, 123.79, 120.37, 119.07, 118.04, 114.96, 112.58, 112.50, 111.44, 100.89, 71.33, 55.24, 53.33, 46.04; HRMS(ESI): calcd. for C$_{32}$H$_{26}$N$_2$NaO (M$^+$/Na): 477.1937, found: 477.1931.

**4f** was obtained as a white solid in 96.8% yield after flash chromatography; m.p. 127-128 °C; $^1$H NMR (300 MHz, DMSO-$d_6$): δ (ppm) 10.99 (s, 1H), 10.75 (s, 1H), 7.59 (dd, $J = 27.6$, 11.0, 1H), 7.42 (dd, $J = 20.7$, 7.0, 1H), 7.30 (s, 2H), 7.21 (s, 3H), 7.16 (d, $J = 9.2$, 6H), 7.01 (s, 1H), 6.88 (d, $J = 11.0$, 3H), 6.63 (d, $J = 7.1$, 1H), 4.86 (d, $J = 7.7$, 1H), 4.60 (d, $J = 7.3$, 1H), 3.77 (t, $J = 7.6$, 1H), 2.31 (s, 3H); $^{13}$C NMR (75 MHz, DMSO-$d_6$): δ (ppm) 145.40, 144.37, 142.80, 141.41, 137.68, 130.36, 128.65, 127.74, 126.86, 125.86, 124.48, 124.16, 122.75, 120.55, 120.31, 118.93, 118.15, 117.87, 116.04, 114.66, 112.53, 111.81, 71.20, 53.14, 46.11, 21.75.; HRMS(ESI): calcd. for C$_{32}$H$_{26}$N$_2$Na (M$^+$/Na): 461.1988, found: 461.1978.
4g was obtained as a white solid in 95.5% yield after flash chromatography; m.p. 143-144°C; $^1$H NMR (300 MHz, DMSO-d$_6$): δ (ppm) 11.04 (s, 1H), 10.93 (s, 1H), 7.45-7.30 (m, 3H), 7.20 (t, $J = 12.3$, 6H), 7.05 (dt, $J = 15.2$, 8.2, 6H), 6.87 (dt, $J = 14.9$, 7.8, 3H), 5.02-4.83 (m, 2H), 3.91 (t, $J = 8.0$, 1H); $^{13}$C NMR (75 MHz, DMSO-d$_6$): δ (ppm) 162.48 and 159.24 (d, $J_{CF} = 243$ Hz), 145.46, 142.95, 141.39, 137.19, 130.90, 130.71, 129.58, 128.62, 128.19, 126.90, 126.55, 124.90, 123.90, 123.55, 121.35, 120.41, 119.17, 118.81, 117.84, 117.07, 115.68, 115.39, 114.79, 112.57, 112.03, 69.97, 45.86, 45.71; HRMS (ESI): calcd. for C$_{31}$H$_{23}$F$_2$N$_2$Na(M$^+$+Na): 465.1737, found: 465.1721.

4h was obtained as a white solid in 99% yield after flash chromatography; m.p. 109-110°C; $^1$H NMR (300 MHz, DMSO-d$_6$): δ (ppm) 11.05 (s, 1H), 10.94 (s, 1H), 7.37-7.29 (m, 2H), 7.28-7.09 (m, 7H), 7.08-6.96 (m, 5H), 6.96-6.85 (m, 3H), 6.81 (t, $J = 7.4$, 1H), 4.92 (d, $J = 8.3$, 1H), 4.64 (d, $J = 8.0$, 1H), 3.78 (t, $J = 8.3$, 1H); $^{13}$C NMR (75 MHz, DMSO-d$_6$): δ (ppm) 164.26 and 161.44 (d, $J_{CF} = 241.5$ Hz), 147.55, 145.61, 142.41, 141.42, 137.22, 130.64, 128.72, 127.02, 126.55, 124.00, 123.62, 121.37, 120.47, 119.22, 118.81, 118.05, 117.25, 114.59, 114.04, 113.64, 113.36, 112.63, 112.07, 71.04, 52.82, 45.92; HRMS(ESI): calcd. for C$_{31}$H$_{23}$F$_2$N$_2$Na(M$^+$+Na): 465.1737, found: 465.1727.

4i was obtained as a white solid in 85.1% yield after flash chromatography; m.p. 128-129°C; $^1$H NMR (300 MHz, DMSO-d$_6$): δ (ppm) 10.99 (s, 1H), 10.91 (s, 1H), 7.37-7.19 (m, 5H), 7.18-7.06 (m, 7H), 7.05-6.94 (m, 3H), 6.81 (m, 3H), 4.89 (d, $J = 8.4$, 1H), 4.59 (d, $J = 8.0$, 1H), 3.72 (t, $J = 8.1$, 1H); $^{13}$C NMR (75 MHz, DMSO-d$_6$): δ (ppm) 162.89 and 159.71 (d, $J_{CF} = 238.5$ Hz), 145.44, 142.38, 141.37, 140.33, 137.21, 129.44, 128.65, 126.95, 126.51, 124.04, 123.59, 121.33, 120.38, 119.13, 118.78, 118.03, 117.59, 115.54, 115.27, 114.57, 112.57, 112.04, 71.32, 52.34, 45.83; HRMS(ESI): calcd. for C$_{31}$H$_{23}$F$_2$N$_2$Na(M$^+$+Na): 465.1737, found: 465.1738.
**4j** was obtained as a white solid in 99% yield after flash chromatography; m.p. 138-139°C; $^1$H NMR (300 MHz, DMSO-d$_6$): δ (ppm) 11.14 (s, 1H), 11.01 (s, 1H), 7.58 (d, $J = 8.1$, 1H), 7.34 (dt, $J = 13.9$, 7.2, 6H), 7.20 (dd, $J = 14.7$, 8.6, 4H), 7.06 (t, $J = 6.3$, 3H), 6.96 (d, $J = 8.9$, 2H), 6.85 (t, $J = 7.2$, 1H), 4.98 (d, $J = 8.3$, 1H), 4.68 (d, $J = 7.9$, 1H), 3.77 (t, $J = 8.2$, 1H); $^{13}$C NMR (75 MHz, DMSO-d$_6$): δ (ppm) 145.77, 145.59, 141.94, 141.36, 137.16, 131.03, 129.51, 129.23, 128.76, 128.66, 128.13, 127.14, 126.52, 123.80, 123.65, 121.37, 120.55, 119.34, 119.01, 118.80, 117.94, 116.70, 114.37, 112.67, 112.07, 71.09, 52.20, 45.76; HRMS (ESI): calcd. for C$_{31}$H$_{22}$Cl$_2$N$_2$Na(M$^+$+Na): 515.1052, found: 515.1053.

**4k** was obtained as a white solid in 92.3% yield after flash chromatography; m.p. 235-236°C; $^1$H NMR (300 MHz, DMSO-d$_6$): δ (ppm) 11.10 (s, 1H), 10.96 (s, 1H), 7.48 (d, $J = 7.3$, 1H), 7.42-7.32 (m, 3H), 7.31-7.10 (m, 9H), 7.09-6.97 (m, 2H), 6.86 (t, $J = 5.9$, 3H), 5.12 (d, $J = 7.3$, 1H), 4.99 (d, $J = 7.7$, 1H), 3.90 (t, $J = 7.6$, 1H); $^{13}$C NMR (75 MHz, DMSO-d$_6$): δ (ppm) 145.58, 143.17, 141.62, 141.45, 137.15, 133.57, 129.55, 128.65, 128.23, 127.83, 126.94, 126.63, 123.77, 123.50, 121.40, 120.51, 119.21, 119.13, 118.89, 117.89, 115.05, 112.60, 112.06, 70.50, 49.22, 45.74; HRMS (ESI): calcd. for C$_{31}$H$_{23}$ClN$_2$Na (M$^+$+Na): 481.1442, found: 481.1434.

**4l** was obtained as a yellow solid in 79.4% yield after flash chromatography; m.p. 204-205°C; $^1$H NMR (300 MHz, DMSO-d$_6$): δ (ppm) 11.16 (s, 1H), 10.99 (s, 1H), 7.72 (t, $J = 7.8$, 2H), 7.64 (t, $J = 7.4$, 1H), 7.46-7.29 (m, 3H), 7.27-7.19 (m, 3H), 7.17 (d, $J = 2.0$, 1H), 7.15-7.09 (m, 3H), 7.08-6.99 (m, 2H), 6.97-6.82 (m, 3H), 5.12 (d, $J = 7.6$, 1H), 5.01 (d, $J = 8.1$, 1H), 3.88 (t, $J = 8.1$, 1H); $^{13}$C NMR (75 MHz, DMSO-d$_6$): δ (ppm) 150.65, 145.77, 141.90, 141.42, 137.56, 137.12, 133.27, 129.99, 128.74, 128.13, 127.98, 127.20, 126.60, 123.85, 123.61, 121.42, 120.64, 119.34, 119.90, 118.93, 117.83, 117.04, 114.61, 112.67, 112.07, 71.44, 47.36, 45.50; HRMS (ESI): calcd. for C$_{31}$H$_{23}$N$_2$O$_2$ (M$^+$+Na): 492.1682, found: 492.1673.
4m was obtained as a yellow solid in 92.5% yield after flash chromatography; m.p. 148-149°C; $^1$H NMR (300 MHz, DMSO-d$_6$): δ (ppm) 11.14 (s, 1H), 10.97 (s, 1H), 8.12-7.94 (m, 2H), 7.64-7.47 (m, 2H), 7.35 (d, $J = 8.0$, 2H), 7.29-7.13 (m, 6H), 7.11-6.97 (m, 3H), 6.91 (t, $J = 9.1$, 2H), 6.86-6.73 (m, 1H), 4.97 (d, $J = 8.3$, 1H), 4.79 (d, $J = 8.0$, 1H), 3.78 (t, $J = 8.2$, 1H); $^{13}$C NMR (75 MHz, DMSO-d$_6$): δ (ppm) 148.31, 146.74, 145.94, 141.94, 141.49, 137.24, 134.64, 130.31, 128.83, 128.70, 127.21, 126.56, 123.87, 123.69, 122.10, 121.95, 121.43, 120.64, 119.40, 119.09, 118.86, 118.00, 116.66, 114.42, 112.76, 112.12, 71.17, 52.73, 45.93; HRMS(ESI): calcd. for C$_{31}$H$_{23}$N$_3$NaO$_2$ (M$^+$+Na): 492.1682, found: 492.1671.

4n was obtained as a yellow solid in 98.3% yield after flash chromatography; m.p. 144-145°C; $^1$H NMR (300 MHz, DMSO-d$_6$): δ (ppm) 11.13 (s, 1H), 10.96 (s, 1H), 8.16 (d, $J = 8.6$, 2H), 7.41 (d, $J = 8.6$, 2H), 7.37 (d, $J = 3.3$, 1H), 7.34 (d, $J = 3.2$, 1H), 7.26 (q, $J = 6.1$, 3H), 7.17 (dd, $J = 8.0$, 5.0, 3H), 7.12-6.96 (m, 3H), 6.91 (t, $J = 8.0$, 1H), 4.98 (d, $J = 8.5$, 1H), 4.77 (s, 1H), 3.80 (t, $J = 8.4$, 1H); $^{13}$C NMR (75 MHz, DMSO-d$_6$): δ (ppm) 152.49, 146.66, 145.88, 141.84, 141.43, 137.22, 128.96, 128.79, 128.66, 127.18, 126.51, 124.06, 123.87, 123.37, 119.33, 119.11, 118.87, 118.00, 116.65, 114.27, 112.69, 112.07, 71.06, 53.00, 45.98; HRMS(ESI): calcd. for C$_{31}$H$_{23}$N$_3$NaO$_2$ (M$^+$+Na): 492.1682, found: 492.1666.

4o was obtained as a white solid in 90.7% yield after flash chromatography; m.p. 178-179°C; $^1$H NMR (300 MHz, DMSO-d$_6$): δ (ppm) 11.08 (s, 1H), 10.95 (s, 1H), 7.75-7.57 (m, 2H), 7.42-7.32 (m, 4H), 7.30-7.22 (m, 3H), 7.22-7.12 (m, 3H), 7.05 (dd, $J = 16.3$, 8.1, 3H), 6.90 (d, $J = 4.9$, 2H), 6.84 (dd, $J = 13.7$, 6.3, 1H), 4.95 (d, $J = 8.3$, 1H), 4.74 (d, $J = 8.0$, 1H), 3.79 (t, $J = 8.4$, 1H); $^{13}$C NMR (75 MHz, DMSO-d$_6$): δ (ppm) 149.16, 145.75, 142.14, 141.42, 137.21, 128.76, 128.66, 128.48, 127.66, 127.24, 127.08, 126.51, 125.68, 125.63, 123.94, 123.65, 121.36, 120.49, 119.27, 119.19, 118.83, 118.04, 116.88, 114.39, 112.62, 112.05, 71.05, 52.87, 45.04; HRMS(ESI): calcd. for C$_{32}$H$_{33}$F$_3$N$_2$Na (M$^+$+Na): 515.1706, found: 515.1694.
4p was obtained as a white solid in 56.3% yield after flash chromatography; m.p. 237-238°C; $^1$H NMR (300 MHz, DMSO-d$_6$): δ (ppm) 10.95 (s, 1H), 10.87 (s, 1H), 7.36-7.27 (m, 2H), 7.24 (d, $J$ = 5.1, 1H), 7.21 (s, 1H), 7.16 (s, 3H), 7.14-7.07 (m, 2H), 7.00 (t, $J$ = 7.4, 3H), 6.94 (d, $J$ = 6.2, 1H), 6.91-6.77 (m, 5H), 4.95 (d, $J$ = 7.0, 1H), 4.84 (d, $J$ = 7.3, 1H), 3.81 (t, $J$ = 7.3, 1H), 3.39 (s, 3H); $^{13}$C NMR (75 MHz, DMSO-d$_6$): δ (ppm) 157.56, 145.30, 144.65, 141.45, 137.14, 132.50, 128.39, 127.99, 127.61, 126.58, 126.49, 124.20, 123.34, 121.34, 120.79, 120.25, 119.19, 118.99, 118.75, 118.18, 118.11, 115.48, 112.46, 112.00, 111.33, 69.50, 55.35, 46.08, 45.93; HRMS(ESI): calcd. for C$_{32}$H$_{26}$N$_2$NaO(M$^+$+Na): 477.1937, found: 477.1925.

4q was obtained as a white solid in 99% yield after flash chromatography; m.p. 218-219°C; $^1$H NMR (300 MHz, DMSO-d$_6$): δ (ppm) 11.03 (s, 1H), 10.96 (s, 1H), 7.44-7.30 (m, 2H), 7.30-7.16 (m, 6H), 7.15-6.97 (m, 5H), 6.95-6.70 (m, 5H), 4.92 (d, $J$ = 8.1, 1H), 4.62 (d, $J$ = 7.8, 1H), 3.82 (t, $J$ = 8.2, 1H), 3.63 (s, 3H); $^{13}$C NMR (75 MHz, DMSO-d$_6$): δ (ppm) 159.55, 146.07, 145.36, 142.90, 141.41, 137.25, 129.69, 128.64, 126.89, 126.51, 124.17, 123.57, 121.35, 120.36, 120.04, 119.09, 118.75, 118.22, 117.75, 114.76, 113.48, 112.54, 112.07, 111.75, 70.85, 55.10, 53.13, 46.01; HRMS(ESI): calcd. for C$_{32}$H$_{26}$N$_2$NaO(M$^+$+Na): 477.1937, found: 477.1928.

II. Determination of the stereochemistry of 4d.
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**III. The spectrums of $^1$H NMR, $^{13}$C NMR.**
Electronic Supplementary Material (ESI) for RSC Advances
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