Supporting Information

Ruthenium(II)-Catalyzed C-H Alkynylation of Heterocycles under Chelation-Assistance

Yanping Liu\textsuperscript{a}, Feng Chang\textsuperscript{a}, Qiaojuan Jiang\textsuperscript{a}, Zhiwei Ma\textsuperscript{b}, Congjun Liu\textsuperscript{*a}

\textsuperscript{a} College of Chemical Engineering and Food Technology, Zhengzhou Institute of Technology, Zhengzhou, Henan 450000, China.
\textsuperscript{b} Department of Fundamental Courses, Henan University of Animal Husbandry and Economy, Zhengzhou, Henan 450000, China.
Tel./fax: 037168229693; E-mail address: 20053002@zhzhu.edu.cn

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1. General Information:

Unless otherwise noted, all reagents and solvents were obtained from commercial suppliers and used without any purification. Substituted indoles,[1] ethynyl benziodoxolones,[2] 2-(1H-pyrrol-1-yl)pyrimidine[1], 2-(benzofuran-2-yl)pyridine[3], 2-(5-methylthiophen-2-yl)pyridine[4], 2-(1-methyl-1H-pyrrol-2-yl)pyridine[5] were prepared according to the literature. Purifications of reaction products were carried out by chromatography using silica gel (200-300 mesh). Melting points were recorded on a BÜCHI B-540 melting point apparatus. NMR spectra were recorded for $^1$H NMR at 400 MHz and for $^{13}$C NMR at 100 MHz. For $^1$H NMR, tetramethylsilane (TMS) served as internal standard ($\delta=0$) and data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constant(s) in Hz. For $^{13}$C NMR, TMS ($\delta=0$) or CDCl$_3$ ($\delta=77.26$) was used as internal standard and spectra were obtained with complete proton decoupling.
2. Experiment Section

2.1 General Procedure for the Alkynylation

1-(pyrimidin-2-yl)-1H-indole 1 (0.1 mmol, 1.0 equiv), hypervalent iodine-alkyne 2 (0.12 mmol, 1.2 equiv), [Ru(cy-mene)Cl₂]₂ (5 mol %), AgSbF₆ (0.02 mmol, 20 mol %), NaOAc (0.1 mmol, 1.0 equiv) and 1,2-DCE (1 mL) were charged into a pressure tube under argon. The reaction mixture was stirred for 24 h at 80 °C under Ar atmosphere, and then the mixture was cooled to room temperature. The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using EA/PE to afford the alkynylation product 3.

Characterization data of compounds

1-(pyrimidin-2-yl)-2-((triisopropylsilyl)ethynyl)-1H-indole (3a)[6]

This compound was obtained according to the general procedure as a white solid, 85%; ¹H NMR (400 MHz, CDCl₃) δ 8.79 (d, J = 4.8 Hz, 2H), 8.28 (d, J = 7.7 Hz, 1H), 7.57 (d, J = 7.7 Hz, 1H), 7.34–7.29 (m, 1H), 7.25–7.19 (m, 1H), 7.17 (t, J = 4.8 Hz, 1H), 7.08 (s, 1H), 1.14 (s, 21H); ¹³C NMR (100 MHz, CDCl₃) δ 158.1, 157.4, 136.2, 128.6, 124.8, 122.4, 121.0, 120.7, 117.5, 115.7, 114.1, 98.8, 97.9, 18.7, 11.4.

5-methoxy-1-(pyrimidin-2-yl)-2-((triisopropylsilyl)ethynyl)-1H-indole (3b) [6]
This compound was obtained according to the general procedure as a white solid, 65%; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.75 (d, $J = 4.8$ Hz, 2H), 8.23 (d, $J = 9.0$ Hz, 1H), 7.14 (t, $J = 4.8$ Hz, 1H), 7.02–6.95 (m, 3H), 3.85 (s, 3H), 1.13 (s, 21H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.0, 157.3, 155.7, 131.1, 129.3, 121.3, 117.3, 115.6, 115.3, 114.5, 102.2, 98.9, 97.8, 55.6, 18.7, 11.4; HRMS (ESI$^+$): m/z calcd for [C$_{24}$H$_{31}$N$_3$OSi+H]$^+$: 406.2309; found [M+H]$^+$: 406.2312.

5-benzoxy-1-(pyrimidin-2-yl)-2-((triisopropylsilyl)ethynyl)-1H-indole (3c)

This compound was obtained according to the general procedure as a white solid, 65%; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.74 (d, $J = 4.8$ Hz, 2H), 8.23 (d, $J = 9.0$ Hz, 1H), 7.46 (d, $J = 7.2$ Hz, 1H), 7.38 (t, $J = 7.2$ Hz, 1H), 7.31 (t, $J = 7.2$ Hz, 1H), 7.13 (t, $J = 4.8$ Hz, 1H), 7.07 (d, $J = 2.4$ Hz, 1H), 7.05–7.01 (m, 1H), 6.97 (s, 1H), 5.11 (s, 2H), 1.13 (s, 21H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.0, 157.3, 154.9, 137.4, 131.3, 129.3, 128.6, 127.9, 127.6, 121.4, 122.4, 117.4, 115.7, 115.3, 115.2, 103.8, 98.9, 97.90, 70.6, 18.7, 11.4; HRMS (ESI$^+$): m/z calcd for [C$_{30}$H$_{35}$N$_3$OSi + H]$^+$: 482.2622; found [M + H]$^+$: 482.2624.

5-chloro-1-(pyrimidin-2-yl)-2-((triisopropylsilyl)ethynyl)-1H-indole (3d) $^{[7]}$

This compound was obtained according to the general procedure as a white solid,
78%; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.78 (d, \(J = 4.8\) Hz, 2H), 8.21 (d, \(J = 8.9\) Hz, 1H), 7.52 (d, \(J = 0.2\) Hz, 1H), 7.24–7.27 (m, 1H), 7.18–7.24 (m, 1H), 6.98 (s, 1H), 1.12 (s, 21H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 158.2, 157.1, 134.5, 129.7, 127.9, 124.9, 122.2, 119.9, 117.9, 114.8, 106.2, 98.9, 98.2, 18.7, 11.4; HRMS (ESI\textsuperscript{+}): m/z calc'd for [C\textsubscript{23}H\textsubscript{28}ClN\textsubscript{3}Si+H]\textsuperscript{+}: 410.1814; found [M+H]\textsuperscript{+}: 410.1821.

\textbf{1-(pyrimidin-2-yl)-2-((triisopropylsilyl)ethynyl)-1H-indole-5-carbonitrile (3e)}

This compound was obtained according to the general procedure as a white solid, 86%; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.66–8.62 (m, 1H), 7.84–7.77 (m, 1H), 7.76–7.70 (m, 3H), 7.67 (d, \(J = 8.1\) Hz, 1H), 7.65 (d, \(J = 7.9\) Hz, 1H), 7.32–7.21 (m, 2H), 7.19–7.11 (m, 1H), 7.00 (s, 1H), 1.05 (s, 21H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 158.4, 156.7, 137.6, 128.3, 127.4, 124.5, 119.9, 118.6, 114.9, 114.7, 105.7, 100.2, 97.3, 18.6, 11.3; HRMS (ESI\textsuperscript{+}): m/z calc'd for [C\textsubscript{24}H\textsubscript{28}N\textsubscript{4}Si + H]\textsuperscript{+}: 401.2156; found [M + H]\textsuperscript{+}: 401.2158.

\textbf{5-bromo-1-(pyrimidin-2-yl)-2-((triisopropylsilyl)ethynyl)-1H-indole (3f)}\textsuperscript{[6]}

This compound was obtained according to the general procedure as a yellow solid, 65%; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.78 (d, \(J = 4.8\) Hz, 2H), 8.17 (d, \(J = 8.9\) Hz, 1H), 7.69 (d, \(J = 1.8\) Hz, 1H), 7.42–7.35 (m, 1H), 7.20 (t, \(J = 5.2\) Hz, 1H), 6.98 (s, 1H), 1.12 (s, 21H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 158.2, 157.1, 134.8, 130.2, 127.5, 123.1, 122.1, 117.9, 115.8, 115.6, 114.6, 98.9, 98.1, 18.7, 11.4; HRMS (ESI\textsuperscript{+}): m/z calc'd for [C\textsubscript{23}H\textsubscript{28}BrN\textsubscript{3}Si + H]\textsuperscript{+}: 454.1309; found [M + H]\textsuperscript{+}: 454.1316, 456.1298.

\textbf{4-methyl-1-(pyrimidin-2-yl)-2-((triisopropylsilyl)ethynyl)-1H-indole (3g)}\textsuperscript{[7]}

This compound was obtained according to the general procedure as a yellow solid, 65%; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.78 (d, \(J = 4.8\) Hz, 2H), 8.17 (d, \(J = 8.9\) Hz, 1H), 7.69 (d, \(J = 1.8\) Hz, 1H), 7.42–7.35 (m, 1H), 7.20 (t, \(J = 5.2\) Hz, 1H), 6.98 (s, 1H), 1.12 (s, 21H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 158.2, 157.1, 134.8, 130.2, 127.5, 123.1, 122.1, 117.9, 115.8, 115.6, 114.6, 98.9, 98.1, 18.7, 11.4; HRMS (ESI\textsuperscript{+}): m/z calc'd for [C\textsubscript{23}H\textsubscript{28}BrN\textsubscript{3}Si + H]\textsuperscript{+}: 454.1309; found [M + H]\textsuperscript{+}: 454.1316, 456.1298.
This compound was obtained according to the general procedure as a white solid, 65%; \( ^1H \text{ NMR (400 MHz, CDCl}_3 \) \( \delta 8.78 \text{ (d, } J = 4.8 \text{ Hz, 2H), 8.09 \text{ (d, } J = 8.4 \text{ Hz, 1H), 7.21 \text{ (t, } J = 8.4 \text{ Hz, 1H), 7.16 \text{ (t, } J = 8.4 \text{ Hz, 1H), 7.10 \text{ (s, 1H), 7.01 \text{ (d, } J = 7.7 \text{ Hz, 1H), 2.54 \text{ (s, 3H), 1.13 \text{ (s, 21H); }} \) \( ^{13} \text{CNMR (100 MHz, CDCl}_3 \) \( \delta 158.1, 157.5, 136.1, 130.2, 128.3, 124.9, 122.6, 120.4, 117.5, 114.2, 111.6, 99.0, 97.6, 18.7, 18.5, 11.4; HRMS (ESI\(^{+}\)) \): m/z calced for [C\(_{24}\)H\(_{31}\)N\(_3\)Si\(+\)H\(^+\)]\(^{+}\): 390.2360; found [M+H\(^+\)]\(^{+}\): 390.2363.

Methyl-1-(pyrimidin-2-yl)-2-((triisopropylsilyl)ethynyl)-1H-indole-4-carboxylate (3h)

This compound was obtained according to the general procedure as a white solid, 67%; \( ^1H \text{ NMR (400 MHz, CDCl}_3 \) \( \delta 8.80 \text{ (d, } J = 4.8 \text{ Hz, 2H), 8.47 \text{ (d, } J = 8.4 \text{ Hz, 1H), 7.98 \text{ (d, } J = 6.8 \text{ Hz, 1H), 7.72 \text{ (s, 1H), 7.35 \text{ (t, } J = 8.2 \text{ Hz, 1H), 7.21 \text{ (d, } J = 4.8 \text{ Hz, 1H), 4.00 \text{ (s, 3H), 1.13 \text{ (s, 21H); }} \) \( ^{13} \text{CNMR (100 MHz, CDCl}_3 \) \( \delta 167.4, 158.2, 157.1, 136.8, 128.3, 125.5, 122.9, 121.5, 118.7, 118.0, 116.1, 99.4, 98.3, 51.9, 18.7, 18.5, 11.4; HRMS (ESI\(^{+}\)) \): m/z calced for [C\(_{25}\)H\(_{31}\)N\(_3\)O\(_2\)Si \(+\)H\(^+\)]\(^{+}\): 434.2258; found [M+H\(^+\)]\(^{+}\): 434.2265.

4-chloro-1-(pyrimidin-2-yl)-2-((triisopropylsilyl)ethynyl)-1H-indole (3i)

This compound was obtained according to the general procedure as a white solid, 54%; \( ^1H \text{ NMR (400 MHz, CDCl}_3 \) \( \delta 8.79 \text{ (d, } J = 4.8 \text{ Hz, 2H), 8.18–8.14 \text{ (m, 1H), } \)
7.26–7.18 (m, 3H), 7.16 (s, 1H), 1.13 (s, 21H); $^{13}$CNMR (100 MHz, CDCl$_3$) δ 158.2, 157.1, 134.8, 130.2, 127.5, 123.1, 122.1, 117.9, 115.8, 115.6, 114.6, 98.9, 98.1, 18.7, 11.4; HRMS (ESI$^+$): m/z calcd for [C$_{23}$H$_{28}$ClN$_3$Si + H]$^+$: 410.1814; found [M+H]$^+$: 410.1818.

6-bromo-1-(pyrimidin-2-yl)-2-((triisopropylsilyl)ethynyl)-1H-indole (3j)

This compound was obtained according to the general procedure as a white solid, 68%; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.80 (d, $J$ = 4.8 Hz, 2H), 8.49 (s, 1H), 7.42 (d, $J$ = 8.4 Hz, 1H), 7.36–7.30 (m, 1H), 7.21 (t, $J$ = 4.8 Hz, 1H), 7.01 (s, 1H), 1.12 (s, 21H); $^{13}$CNMR (100 MHz, CDCl$_3$) δ 158.2, 157.0, 136.7, 127.4, 125.7, 121.7, 121.6, 118.6, 117.9, 117.2, 115.4, 98.7, 98.2, 18.7, 11.4; HRMS (ESI$^+$): m/z calcd for [C$_{23}$H$_{28}$BrN$_3$Si + H]$^+$: 454.1309; found [M + H]$^+$: 454.1391, 456.1372.

6-fluorine-1-(pyrimidin-2-yl)-2-((triisopropylsilyl)ethynyl)-1H-indole (3k)

This compound was obtained according to the general procedure as a white solid, 65%; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.79 (d, $J$ = 4.8 Hz, 2H), 8.07 (dd, $J$ = 8.6 Hz, 1H), 7.52–7.44 (m, 1H), 7.19 (t, $J$ = 4.8 Hz, 1H), 7.03 (s, 1H), 7.01–6.94 (m, 1H), 1.13 (s, 21H); $^{13}$CNMR (100 MHz, CDCl$_3$) δ 161.5 (d, $J$=238.6 Hz), 158.1, 157.2, 136.3 (d, $J$=13.0 Hz), 124.9, 121.5, 121.4 (d, $J$=9.9 Hz), 117.8, 115.5, 111.1 (d, $J$=24.6 Hz), 101.4 (d, $J$ =28.8 Hz), 98.5, 98.0, 18.7, 11.4; $^{19}$FNMR (376 MHz, CDCl$_3$): HRMS (ESI$^+$): m/z calcd for [C$_{23}$H$_{28}$FN$_3$Si + H]$^+$: 394.2019; found [M + H]$^+$: 394.2117.

3-methyl-1-(pyrimidin-2-yl)-2-((triisopropylsilyl)ethynyl)-1H-indole (3l) [6]
This compound was obtained according to the general procedure as a white solid, 62%; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.74 (d, $J = 8.4$ Hz, 2H), 8.34 (d, $J = 8.4$ Hz, 1H), 7.55 (d, $J = 8.4$ Hz, 1H), 7.37–7.30 (m, 1H), 7.26–7.20 (m, 1H), 7.11 (t, $J = 4.8$ Hz, 1H), 2.47 (s, 3H), 1.15 (s, 21H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 157.9, 157.5, 135.9, 129.5, 125.1, 125.1, 122.0, 119.0, 118.8, 117.0, 114.3, 110.8, 98.4, 18.7, 11.4, 9.9; HRMS (ESI$^+$): m/z calcd for [C$_{24}$H$_{31}$N$_3$Si+H]$^+$: 390.2360; found [M+H]$^+$: 390.2362.

2-((tert-butyldimethylsilyl)ethynyl)-1-(pyrimidin-2-yl)-1H-indole (3m)

This compound was obtained according to the general procedure as a white solid, 27%; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.80 (d, $J = 4.8$ Hz, 2H), 8.28 (d, $J = 8.5$ Hz, 1H), 7.58 (d, $J = 7.8$ Hz, 1H), 7.37–7.28 (m, 1H), 7.26–7.14 (m, 2H), 7.06 (s, 1H), 0.99 (s, 9H), 0.19 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 158.1, 157.3, 136.2, 128.5, 124.9, 122.4, 120.8, 120.7, 117.6, 115.7, 114.1, 99.6, 97.6, 26.2, 16.9, -4.7; HRMS (ESI$^+$): m/z calcd for [C$_{20}$H$_{23}$N$_3$Si+H]$^+$: 334.1734; found [M + H]$^+$: 334.1738.

1-(pyrimidin-2-yl)-2-((tert-butyldimethylsilyl)ethynyl)-1H-indole-5-carbonitrile (3n)

This compound was obtained according to the general procedure as a white solid, 72%; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.84 (d, $J = 4.8$ Hz, 2H), 8.33 (d, $J = 8.7$ Hz,
1H, 7.92 (s, 1H), 7.54 (dd, J = 7.2 Hz, 1H), 7.29 (t, J = 4.8 Hz, 1H), 7.08 (s, 1H), 0.98 (s, 9H); 0.19 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 158.3, 137.6, 128.3, 127.5, 125.87, 123.2, 119.9, 118.6, 115.0, 114.8, 105.7, 101.8, 96.2, 29.7, 26.1, 16.9, -4.7; HRMS (ESI$^+$): m/z calcd for [C$_{21}$H$_{23}$N$_4$Si + H]$^+$: 359.1686; found [M + H]$^+$: 359.1688.

6-fluorine-1-(pyridin-2-yl)-2-((tert-butyldimethylsilyl)ethynyl) -1H-indole (3o)

This compound was obtained according to the general procedure as a white solid, 65%; $^1$HNMR (400 MHz, CDCl$_3$) δ 8.79 (d, J = 4.8 Hz, 2H), 8.09–8.05 (m, 1H), 7.53–7.44 (m, 1H), 7.20 (t, J = 4.8 Hz, 1H), 7.03 (s, 1H), 7.04–6.92 (m, 1H), 0.99 (s, 9H), 0.19 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 161.6 (d, J = 238.6 Hz), 158.1, 157.2, 136.3 (d, J = 12.87 Hz), 124.8, 121.5 (d, J = 10.0 Hz), 121.2, 117.8, 115.6, 111.1 (d, J = 24.6 Hz), 101.5 (d, J = 28.8 Hz), 99.7, 97.3, 26.1, 16.9, -4.7; $^{19}$FNMR (376 MHz, CDCl$_3$): m/z calcd for [C$_{20}$H$_{22}$FN$_3$Si + H]$^+$: 352.1640; found [M + H]$^+$: 352.1645.

1-(pyridin-2-yl)-2-((triisopropylsilyl)ethynyl)-1H-indole (3r) [7]

This compound was obtained according to the general procedure as a white solid, 70%; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.79 (d, J = 4.8 Hz, 2H), 8.28 (d, J = 7.7 Hz, 1H), 7.57 (d, J = 7.7 Hz, 1H), 7.37–7.28 (m, 1H), 7.27–7.17 (m, 1H), 7.17 (t, J = 4.8 Hz, 1H), 7.08 (s, 1H),1.14 (s, 21H); $^{13}$CNMR (100 MHz, CDCl$_3$) δ 151.2, 148.9, 137.8, 136.7, 127.7, 124.4, 121.7, 121.6, 120.9, 120.7, 120.7, 112.5, 112.1, 98.5, 98.3, 18.6, 11.3; HRMS (ESI$^+$): m/z calcd for [C$_{24}$H$_{30}$N$_2$Si + H]$^+$: 375.2251; found [M + H]$^+$: 375.2261.

5-bromo-1-(pyridin-2-yl)-2-((tert-butyldimethylsilyl)ethynyl) -1H-indole (3s)

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This compound was obtained according to the general procedure as a white solid, 81%; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.65 – 8.62 (m, 1H), 7.88–7.70 (m, 1H), 7.72 (d, $J = 1.8$ Hz, 1H), 7.65 (t, $J = 8.0$ Hz, 2H), 7.37– 7.26 (m, 2H), 6.92 (s, 1H), 0.90 (s, 9H), 0.13 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 150.8, 148.9, 137.8, 135.3, 129.3, 127.2, 123.2, 122.1, 121.6, 120.5, 114.8, 113.8, 111.5, 101.2, 96.6, 26.0, 16.7, -4.9; HRMS (ESI$^+$): m/z calcd for [C$_{21}$H$_{23}$BrN$_2$Si+H]$^+$: 411.0887; found [M+H]$^+$: 411.0886, 413.1891.

2-(N-methyl-3-((triisopropylsilyl)ethynyl)Pyrrole)pyridine (4a)

This compound was obtained according to the general procedure as a brown liquid; 46%; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.65–8.60 (m, 1H), 8.15 (d, $J = 8.0$ Hz, 1H), 7.69–7.60 (m, 1H), 7.17–7.10 (m, 1H), 6.60 (d, $J = 2.8$ Hz, 1H), 6.34 (d, $J = 2.8$ Hz, 1H), 3.90 (s, 3H), 1.09 (s, 21H); $^{13}$CNMR (100 MHz, CDCl$_3$) δ 151.0, 148.6, 135.9, 135.0, 124.7, 124.5, 121.1, 112.4, 105.8, 103.4, 90.6, 37.0, 18.7, 11.5; HRMS (ESI$^+$): m/z calcd for [C$_{21}$H$_{30}$N$_2$Si+H]$^+$: 339.2251; found [M+H]$^+$: 339.2254.

2-(3-((triisopropylsilyl)ethynyl)Benzoxazole)pyridine (4b)

This compound was obtained according to the general procedure as a white solid, 54%; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.83–8.74 (m, 1H), 8.66 (d, $J = 8.1$ Hz, 1H), 7.79–7.72 (m, 1H), 7.74–7.66 (m, 1H), 7.63 (d, $J = 8.0$ Hz, 1H), 7.44–7.23 (m, 3H),
1.22 (s, 21H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 155.4, 153.9, 150.0, 148.5, 136.4, 129.8, 126.3, 123.7, 123.3, 122.2, 120.8, 111.9, 102.8, 101.1, 97.8, 18.7, 11.4; HRMS (ESI$^+$): m/z calcd for [C$_{24}$H$_{29}$NOSi+H]$^+$: 376.2091; found [M+H]$^+$: 376.2095.

2-(5-methyl-3-((triisopropylsilyl)ethynyl)Thiophene)pyridine (4c)

This compound was obtained according to the general procedure as a yellow liquid; 71%; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.65 (d, $J = 8.1$ Hz, 1H), 8.58–8.50 (m, 1H), 7.67–7.57 (m, 1H), 7.17–7.10 (m, 1H), 6.83 (s, 1H), 2.45 (s, 3H), 1.15 (s, 21H); $^{13}$CNMR (100 MHz, CDCl$_3$) δ 152.2, 149.2, 144.6, 140.4, 136.2, 130.9, 121.9, 119.9, 118.7, 102.9, 95.7, 18.7, 15.3, 11.4; HRMS (ESI$^+$): m/z calcd for [C$_{21}$H$_{29}$NSSi+H]$^+$: 356.1863; found [M+H]$^+$: 356.1864.

2-(2,5-bis((triisopropylsilyl)ethynyl)-1H-pyrrol-1-yl)pyrimidine (4d)$^{[6]}$

This compound was obtained according to the general procedure as a white solid; 65%; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.80 (d, $J = 4.8$ Hz, 2H), 7.32–7.26 (m, 1H), 6.55 (s, 2H), 1.03–0.97 (m, 42H); $^{13}$CNMR (100 MHz, CDCl$_3$) δ 157.8, 156.1, 118.9, 117.1, 116.9, 97.3, 94.7, 18.0, 10.8; HRMS (ESI$^+$): m/z calcd for [C$_{30}$H$_{47}$N$_3$Si$_2$+H]$^+$: 506.3381; found [M+H]$^+$: 506.3385.

2.2 Gram-Scale Experiment

1-(pyrimidin-2-yl)-1H-indole 1a (5.0 mmol, 1.0 equiv), TIPS-EBX 2a (6.0 mmol, 1.2 equiv), [Ru(cy-mene)Cl$_2$]$_2$ (5 mol %), AgSbF$_6$ (20 mol %), NaOAc (5.0 mmol, 1.0
equiv) and 1,2-DCE (50 mL) were charged into a pressure tube under argon. The reaction mixture was stirred for 24 h at 80 °C under Ar atmosphere, and then the mixture was cooled to room temperature. The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using EA/PE to afford the alkynylation product 3a in 65% yield.

2.3 H/D Exchange Experiment

1-(pyrimidin-2-yl)-1H-indole 1 (0.1 mmol, 1.0 equiv), TIP-EBX 2a (0.12 mmol, 1.2 equiv), [Ru(cy-mene)Cl2]₂ (5 mol %), AgSbF6 (0.02 mmol, 20 mol %), NaOAc (0.1 mmol, 1.0 equiv) and 1,2-DCE (1 mL)/D2O (0.25 mL) were charged into a pressure tube under argon. The reaction mixture was stirred for 24 h at 80 °C under Ar atmosphere, and then the mixture was cooled to room temperature. The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using EA/PE to afford the deuterated product.

2.4 Competition Experiment
5-Methoxy-1-(pyrimidin-2-yl)-1H-indole (0.12 mmol, 1.0 equiv), 1-(pyrimidin-2-yl)-1H-indole-5-carbonitrile (0.12 mmol, 1.0 equiv), TIP-EBX 2a (0.1 mmol, 1.0 equiv), \([\text{Ru}(\text{cy-mene})\text{Cl}_2]_2\) (5 mol %), \(\text{AgSbF}_6\) (0.02 mmol, 20 mol %), \(\text{NaOAc}\) (0.1 mmol, 1.0 equiv) and 1,2-DCE (1 mL) were charged into a pressure tube under argon. The reaction mixture was stirred for 24 h at 80 °C under Ar atmosphere, and then the mixture was cooled to room temperature. The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using EA/PE afford the product 3b in 43% yield and 3e in 35% yield.

3. References

4. Spectra