Supporting Information

Acetic acid-promoted rhodium(III)-catalyzed hydroarylation of terminal alkynes

Chang-Lin Duan,‡a,b Xing-Yu Liu,‡b,d Yun-Xuan Tan,b Rui Ding,c Shi-Ping Yang,*a Ping Tian*b,c and Guo-Qiang Lin*b,c

aDepartment of Chemistry, Shanghai Normal University, 100 Guilin Road, Shanghai 200234, China. Email: shipingy@shnu.edu.cn;

bCAS Key Laboratory of Synthetic Chemistry of Natural Substances, Center for Excellence in Molecular Synthesis, Shanghai Institute of Organic Chemistry, University of Chinese Academy of Sciences, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China. Email: tianping@sioc.ac.cn lingq@sioc.ac.cn

cInnovation Research Institute of Traditional Chinese Medicine, Shanghai University of Traditional Chinese Medicine, 1200 Cailun Road, Shanghai 201203, China. Email: tianping@shutcm.edu.cn;

dSchool of Physical Science and Technology, ShanghaiTech University, 100 Haike Road, Shanghai 201210, China

‡These authors contributed equally to this work.
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1. GENERAL INFORMATION

All solvents were dried before use following the standard procedures. Unless otherwise indicated, all the arylpyridines purchased from commercial suppliers were used without further purification. The $^1$H and $^{13}$C NMR spectra were recorded on Bruker AV-400 MHz in the indicated solvents. Chemical shifts are reported in $\delta$ (ppm) referenced to an internal TMS standard for $^1$H NMR and CDCl$_3$ ($\delta = 77.10$ ppm) for $^{13}$C NMR. Coupling constants ($J$) are quoted in Hz. ESI mass spectra were recorded on Agilent1200/G6100A.

2. SUBSTRATE PREPARATION

The synthesis of the 6-arylpurines was according to reported literatures\(^1\).

9-(Cyclopropylmethyl)-6-phenyl-9H-purine (1t)

White solid, m.p.: 97-99 °C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 9.03 (s, 1H), 8.79 (d, $J = 7.6$ Hz, 2H), 8.24 (s, 1H), 7.61 – 7.50 (m, 3H), 4.18 (d, $J = 7.3$ Hz, 2H), 1.44 – 1.34 (m, 1H), 0.75 – 0.68 (m, 2H), 0.55 – 0.46 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) 154.7, 152.5, 152.3, 144.0, 135.8, 131.1, 130.9, 129.8, 128.7, 48.5, 11.1, 4.4.

ESI-MS: [M+H]$^+$ 251.0; HRMS (DART): [M+H]$^+$ calcd for C$_{15}$H$_{15}$N$_4$ 251.1291, found 251.1290.

9-Allyl-6-phenyl-9H-purine (1u)

Pale yellow solid, m.p.: 100-102 °C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 9.04 (s, 1H), 8.79 (d, $J = 7.0$ Hz, 2H), 8.13 (s, 1H), 7.65 – 7.49 (m, 3H), 6.19 – 6.01 (m, 1H), 5.42 – 5.20 (m, 2H), 4.94 (d, $J = 5.5$ Hz, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) 155.0, 152.6, 144.2, 135.7, 131.6, 131.1, 129.9, 128.8, 119.5, 45.9.

ESI-MS: [M+H]$^+$ 237.1; HRMS (DART): [M+H]$^+$ calcd for C$_{14}$H$_{13}$N$_4$ 237.1135, found 237.1133.

\(^1\) Ali, M, A.; Yao, X.; Sun, H.; Lu, H. Org. Lett. 2015, 17, 1513
3. Scope of the Substrates

General Procedure: To a dried Schlenk tube was equipped with a magnetic stir bar. \([\text{Cp}^*\text{RhCl}_2]_2\) (0.005 mmol, 2.5 mol %, 3.1 mg), AgSbF\(_6\) (0.03 mmol, 15 mol %, 10.3 mg), substrate 1 (0.2 mmol or 0.4 mmol), HOAc (1 ml), substrate 2 (0.24 mmol or 0.2 mmol) were added sequentially under argon. The tube was stirred at room temperature or 80 °C for 12 h. After completion of the reaction, the mixture was diluted with EtOAc (10 mL), filtered through a short pad of silica gel and washed with EtOAc (30 mL). The filtrate was pre-absorbed on silica gel and concentrated by rotary evaporation. The crude product was purified by flash silica gel (300-400 mesh) chromatography to afford the desired products product 3.

\((E)-2-(2-\text{Styrylphenyl})\text{pyridine (3aa)}\)

The product was purified by flash silica gel (300-400 mesh) chromatography (PE/EA = 9/1), yellow oil, 48.3 mg, 94% yield.

\(^1\text{H NMR (400 MHz, CDCl}_3\) δ (ppm) 8.76 (d, \(J = 4.4 \text{ Hz}, 1\text{H}), 7.80 – 7.71 (m, 2\text{H}), 7.56 (d, \(J = 6.5 \text{ Hz}, 1\text{H}), 7.48 – 7.36 (m, 5\text{H}), 7.34 – 7.19 (m, 5\text{H}), 7.06 (d, \(J = 16.2 \text{ Hz}, 1\text{H}).\)

\(^{13}\text{C NMR (100 MHz, CDCl}_3\) δ (ppm) 158.8, 149.4, 139.4, 137.6, 136.2, 135.7, 130.3, 130.2, 128.7, 128.6, 127.7, 127.6, 127.5, 126.6, 126.3, 125.1, 121.9.

\(2-(2,6-\text{di((E)-styryl)phenyl})\text{pyridine (3aa’)}\)

The product was purified by flash silica gel (300-400 mesh) chromatography (PE/EA = 9/1), yellow oil. 39.1 mg, 55% yield.

\(^1\text{H NMR (400 MHz, CDCl}_3\) δ (ppm) 8.82 (d, \(J = 4.3 \text{ Hz}, 1\text{H}), 7.79 (td, \(J = 7.7, 1.6 \text{ Hz}, 1\text{H}), 7.70 (d, \(J = 7.8 \text{ Hz}, 2\text{H}), 7.48 – 7.42 (m, 1\text{H}), 7.38 – 7.31 (m, 2\text{H}), 7.28 – 7.24 (m, 9\text{H}), 7.23 – 7.17 (m, 2\text{H}), 6.98 (d, \(J = 16.2 \text{ Hz}, 2\text{H}), 6.76 (d, \(J = 16.2 \text{ Hz}, 2\text{H}).\)

\(^{13}\text{C NMR (100 MHz, CDCl}_3\) δ (ppm) 158.3, 149.7, 138.7, 137.5, 136.7, 136.2, 130.2, 128.6, 127.6, 127.2, 126.6, 126.5, 124.9, 122.2.
(E)-2-(2-(4-Methylstyryl)phenyl)pyridine (3ab)

The product was purified by flash silica gel (300-400 mesh) chromatography (PE/EA = 10/1), green oil, 48.7 mg, 90% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 8.75 (d, $J = 4.3$ Hz, 1H), 7.77 – 7.68 (m, 2H), 7.55 (d, $J = 7.5$ Hz, 1H), 7.46 – 7.33 (m, 3H), 7.31 – 7.22 (m, 3H), 7.17 (d, $J = 16.2$ Hz, 1H), 7.11 (d, $J = 7.9$ Hz, 2H), 7.03 (d, $J = 16.2$ Hz, 1H), 2.32 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 158.9, 149.5, 139.4, 137.5, 136.1, 135.9, 134.9, 130.3, 130.1, 129.4, 128.7, 127.5, 126.6, 126.6, 126.2, 125.2, 121.9, 21.3.

(E)-2-(2-(4-Methoxystyryl)phenyl)pyridine (3ac)

The product was purified by flash silica gel (300-400 mesh) chromatography (PE/EA = 9/1), green oil, 53.3 mg, 93% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 8.74 (d, $J = 4.2$ Hz, 1H), 7.72 (ddd, $J = 9.5$, 6.0, 2.1 Hz, 2H), 7.56 – 7.51 (m, 1H), 7.40 (ddd, $J = 16.2$, 10.3, 7.2 Hz, 3H), 7.32 (d, $J = 8.7$ Hz, 2H), 7.25 (dd, $J = 7.0$, 5.4 Hz, 1H), 7.10 (d, $J = 16.2$ Hz, 1H), 7.00 (d, $J = 16.2$ Hz, 1H), 6.84 (d, $J = 8.7$ Hz, 2H), 3.78 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 159.3, 159.0, 149.5, 139.3, 136.0, 136.0, 130.4, 130.2, 129.6, 128.7, 127.8, 127.3, 126.0, 125.4, 125.1, 121.8, 114.1, 55.3.

(E)-4-(2-(Pyridin-2-yl)styryl)benzaldehyde (3ad)

The product was purified by flash silica gel (300-400 mesh) chromatography (PE/EA = 6/1), yellow oil, 52.4 mg, 92% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 9.96 (s, 1H), 8.76 (d, $J = 4.2$ Hz, 1H), 7.83 – 7.75 (m, 4H), 7.57 (dd, $J = 7.2$, 1.7 Hz, 1H), 7.52 (d, $J = 8.2$ Hz, 2H), 7.48 – 7.40 (m, 4H), 7.31 (ddd, $J = 7.4$, 4.9, 0.9 Hz, 1H), 7.10 (d, $J = 16.2$ Hz, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 191.7, 158.7, 149.5, 143.7, 140.0, 136.4, 135.3, 135.0, 131.2, 130.4, 130.2, 128.8, 128.6, 128.5, 127.0, 126.4, 125.0, 122.1.
Methyl (E)-4-(2-(pyridin-2-yl)styryl)benzoate (3ae)

The product was purified by flash silica gel (300-400 mesh) chromatography (PE/EA = 9/1), green oil, 58.8 mg, 93% yield.

\[ \text{H NMR (400 MHz, CDCl}_3\text{)} \delta (\text{ppm}) 8.75 (d, J = 4.3 \text{ Hz, 1H}), 7.97 (d, J = 8.3 \text{ Hz, 2H}), 7.81 - 7.71 (m, 2H), 7.56 (dd, J = 7.2, 1.2 \text{ Hz, 1H}), 7.47 - 7.34 (m, 6H), 7.32 - 7.24 (m, 1H), 7.07 (d, J = 16.2 \text{ Hz, 1H}), 3.89 (s, 3H). \]

\[ \text{C NMR (100 MHz, CDCl}_3\text{)} \delta (\text{ppm}) 166.8, 158.8, 149.5, 142.1, 139.8, 136.2, 135.2, 130.3, 130.1, 130.0, 128.9, 128.8, 128.7, 128.2, 126.4, 126.4, 125.0, 122.0, 52.0. \]

(E)-2-(2-(4-Fluorostyryl)phenyl)pyridine (3af)

The product was purified by flash silica gel (300-400 mesh) chromatography (PE/EA = 9/1), green oil, 50.6 mg, 92% yield.

\[ \text{H NMR (400 MHz, CDCl}_3\text{)} \delta (\text{ppm}) 8.75 (d, J = 4.2 \text{ Hz, 1H}), 7.80 - 7.70 (m, 2H), 7.55 (dd, J = 7.5, 1.2 \text{ Hz, 1H}), 7.48 - 7.31 (m, 5H), 7.31 - 7.24 (m, 1H), 7.15 (d, J = 16.2 \text{ Hz, 1H}), 7.05 - 6.96 (m, 3H). \]

\[ \text{C NMR (100 MHz, CDCl}_3\text{)} \delta (\text{ppm}) 162.3 (d, J_{C-F} = 247.3), 158.9, 149.5, 139.5, 136.2, 135.6, 133.8 (d, J_{C-F} = 3.3 \text{ Hz}), 130.3, 128.9, 128.8, 128.1 (d, J_{C-F} = 8.0 \text{ Hz}), 127.8, 127.4, 126.2, 125.1, 122.0, 115.6 (d, J_{C-F} = 21.6 \text{ Hz}). \]

(E)-2-(2-(4-Chlorostyryl)phenyl)pyridine (3ag)

The product was purified by flash silica gel (300-400 mesh) chromatography (PE/EA = 10/1), green oil, 57.2 mg, 98% yield.

\[ \text{H NMR (400 MHz, CDCl}_3\text{)} \delta (\text{ppm}) 8.75 (d, J = 4.1 \text{ Hz, 1H}), 7.79 - 7.71 (m, 2H), 7.54 (dd, J = 7.4, 1.4 \text{ Hz, 1H}), 7.47 - 7.35 (m, 3H), 7.32 - 7.24 (m, 5H), 7.21 (d, J = 16.2 \text{ Hz, 1H}), 6.99 (d, J = 16.2 \text{ Hz, 1H}). \]

\[ \text{C NMR (100 MHz, CDCl}_3\text{)} \delta (\text{ppm}) 158.8, 149.5, 139.6, 136.2, 136.1, 135.4, 133.1, 130.3, 128.8, 128.8, 128.2, 127.9, 127.8, 126.3, 125.0, 122.0. \]

(E)-2-(2-(4-Bromostyryl)phenyl)pyridine (3ah)

The product was purified by flash silica gel (300-400 mesh) chromatography (PE/EA = 9/1), green oil, 63.1 mg, 94% yield.

\[ \text{H NMR (400 MHz, CDCl}_3\text{)} \delta (\text{ppm}) 8.75 (d, J = 4.1 \text{ Hz, 1H}), 7.79 - 7.71 (m, 2H), 7.55 (dd, J = 7.4, 1.5 \text{ Hz, 1H}), 7.46 - 7.36 (m, 3H). \]
5H), 7.31 – 7.27 (m, 1H), 7.23 (dd, $J = 13.5, 5.1$ Hz, 3H), 6.98 (d, $J = 16.2$ Hz, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) 158.8, 149.5, 139.6, 136.6, 136.3, 135.4, 131.8, 130.3, 128.8, 128.8, 128.4, 128.1, 128.0, 126.3, 125.0, 122.0, 121.3.

(E)-2-(2-(2-Methylstyrlyl)phenyl)pyridine (3ai)

The product was purified by flash silica gel (300-400 mesh) chromatography (PE/EA = 15/1), green oil, 52.5 mg, 97% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 8.73 (d, $J = 4.7$ Hz, 1H), 7.76 (d, $J = 7.7$ Hz, 1H), 7.70 (td, $J = 7.7, 1.7$ Hz, 1H), 7.55 (d, $J = 7.4$ Hz, 1H), 7.47 – 7.35 (m, 4H), 7.29 – 7.20 (m, 2H), 7.16 – 7.09 (m, 4H), 2.40 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) 158.8, 149.5, 139.6, 136.6, 136.3, 135.4, 131.8, 130.3, 128.8, 128.7, 128.0, 127.7, 127.5, 126.5, 126.1, 125.5, 125.0, 121.9, 20.0.

(E)-2-(2-(3-Methylstyrlyl)phenyl)pyridine (3aj)

The product was purified by flash silica gel (300-400 mesh) chromatography (PE/EA = 15/1), green oil, 51.2 mg, 95% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 8.75 (d, $J = 4.2$ Hz, 1H), 7.77 – 7.69 (m, 2H), 7.56 (dd, $J = 7.3, 1.1$ Hz, 1H), 7.47 – 7.34 (m, 3H), 7.29 – 7.17 (m, 5H), 7.07 – 6.99 (m, 2H), 2.32 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) 158.9, 149.5, 139.6, 136.6, 136.1, 136.1, 135.8, 130.4, 130.3, 128.8, 128.7, 128.0, 127.7, 127.5, 126.5, 126.1, 125.5, 125.0, 121.9, 21.5.

(E)-2-(2-(2-(Thiophen-3-yl)vinyl)phenyl)pyridine (3ak)

The product was purified by flash silica gel (300-400 mesh) chromatography (PE/EA = 6/1), green oil, 48.6 mg, 92% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 8.73 (dd, $J = 4.8, 0.8$ Hz, 1H), 7.74 – 7.66 (m, 2H), 7.53 (dd, $J = 7.4, 1.3$ Hz, 1H), 7.46 – 7.31 (m, 3H), 7.27 – 7.20 (m, 2H), 7.18 (dd, $J = 2.8, 1.1$ Hz, 1H), 7.13 (dd, $J = 5.0, 1.1$ Hz, 1H), 7.07 (s, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) 158.8, 149.4, 140.4, 139.3, 136.1, 135.7, 130.2, 128.7, 127.5, 127.4, 126.1, 126.0, 125.1, 125.0, 124.2, 122.4, 121.9.
(E)-2-(2-(Naphthalen-2-yl)vinyl)phenyl)pyridine (3a)

The product was purified by flash silica gel (300-400 mesh) chromatography (PE/EA = 6/1), black oil, 48.5 mg, 79% yield.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 8.76 (d, \(J = 4.7\ Hz, 1H\), 7.84 – 7.68 (m, 6H), 7.56 (t, \(J = 8.7\ Hz, 2H\), 7.49 – 7.33 (m, 6H), 7.30 – 7.16 (m, 2H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm) 158.9, 149.6, 139.6, 136.1, 135.8, 135.1, 133.7, 133.0, 130.3, 130.2, 128.7, 128.3, 128.0, 127.9, 127.8, 127.7, 126.7, 126.3, 126.3, 125.9, 125.1, 123.6, 121.9.

(3a)

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(E)-2-(2-(Pyren-2-yl)vinyl)phenyl)pyridine (3am)

The product was purified by flash silica gel (300-400 mesh) chromatography (PE/EA = 9/1), Brown solid, 69.4 mg, 91% yield, m.p.: 125-128 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 8.77 (d, \(J = 4.2\ Hz, 1H\), 8.42 (d, \(J = 9.3\ Hz, 1H\), 8.15 – 7.99 (m, 6H), 7.98 – 7.92 (m, 4H), 7.70 (t, \(J = 7.7\ Hz, 1H\), 7.60 (d, \(J = 7.5\ Hz, 1H\), 7.53 – 7.48 (m, 2H), 7.47 – 7.41 (m, 2H), 7.28 – 7.21 (m, 1H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm) 158.9, 149.5, 139.7, 136.2, 136.2, 132.2, 131.5, 130.9, 130.8, 130.7, 130.4, 128.9, 128.4, 127.9, 127.6, 127.4, 127.3, 127.3, 126.6, 126.0, 125.3, 125.2, 125.1, 125.0, 125.0, 124.9, 123.8, 123.1, 122.0.

ESI-MS: [M+H]\(^+\) 382.1; HRMS (DART): [M+H]\(^+\) calcd for C\(_{29}\)H\(_{20}\)N\(^+\) 382.1590, found 382.1590.

(3am)

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(E)-2-(2-(2-(Cyclohex-1-en-1-yl)vinyl)phenyl)pyridine (3an)

The product was purified by flash silica gel (300-400 mesh) chromatography (PE/EA = 9/1), yellow oil, 44.9 mg, 86% yield.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 8.78 – 8.67 (m, 1H), 7.71 (td, \(J = 7.7, 1.8\ Hz, 1H\), 7.63 (d, \(J = 7.6\ Hz, 1H\), 7.50 (dd, \(J = 7.5, 1.3\ Hz, 1H\), 7.44 (d, \(J = 7.9\ Hz, 1H\), 7.36 (td, \(J = 7.4, 1.1\ Hz, 1H\), 7.30 (td, \(J = 7.4, 1.2\ Hz, 1H\), 7.27 – 7.21 (m, 1H), 6.71 (d, \(J = 16.1\ Hz, 1H\), 6.55 (d, \(J = 16.1\ Hz, 1H\), 5.88 (s, 1H), 2.16 (d, \(J = 3.6\ Hz, 2H\), 2.05 (d, \(J = 11.4\ Hz, 2H\), 1.67 – 1.55 (m, 4H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm) 159.1, 149.4, 139.1, 136.4, 136.2, 135.8, 134.0, 130.8, 130.1, 128.6, 127.0, 126.0, 125.1, 123.5, 121.8, 26.1, 24.5, 22.5, 22.5.

(3an)
(E)-3-(2-(Pyridin-2-yl)phenyl)allyl benzoate (3ao)

The product was purified by flash silica gel (300-400 mesh) chromatography (PE/EA = 6/1), yellow oil, 50.8 mg, 84% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 8.70 (dd, $J = 4.8$, 0.7 Hz, 1H), 8.06 – 7.99 (dd, 2H), 7.75 – 7.64 (m, 2H), 7.58 – 7.49 (m, 2H), 7.45 – 7.35 (m, 5H), 7.27 – 7.22 (m, 1H), 6.88 (d, $J = 15.9$ Hz, 1H), 6.37 (dt, $J = 15.8$, 6.0 Hz, 1H), 4.93 (dd, $J = 6.0$, 1.3 Hz, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 166.3, 158.6, 149.3, 139.5, 136.3, 134.6, 133.0, 132.3, 130.2, 130.2, 129.7, 128.7, 128.4, 128.1, 126.5, 125.0, 124.6, 121.9, 65.5.

(3aq)

(E)-2-(2-(6-Chlorohex-1-en-1-yl)phenyl)pyridine (3ap)

The product was purified by flash silica gel (300-400 mesh) chromatography (PE/EA = 9/1), yellow oil, 52.1 mg, 96% yield (3aq/3aq = 17:1).

$^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 8.72 (d, $J = 4.3$ Hz, 1H), 7.74 (td, $J = 7.7$, 1.4 Hz, 1H), 7.57 (d, $J = 7.4$ Hz, 1H), 7.50 – 7.44 (m, 1H), 7.42 (d, $J = 7.8$ Hz, 1H), 7.38 – 7.29 (m, 2H), 7.26 (t, $J = 6.1$ Hz, 1H), 6.47 (d, $J = 15.7$ Hz, 1H), 6.19 – 6.05 (m, 1H), 3.52 (t, $J = 6.7$ Hz, 2H), 2.18 (q, $J = 6.9$ Hz, 2H), 1.84 – 1.72 (m, 2H), 1.64 – 1.51 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 159.0, 149.2, 138.6, 136.1, 136.0, 131.6, 130.0, 129.1, 128.6, 127.1, 126.3, 125.0, 121.8, 44.9, 32.2, 32.0, 26.4.

(3aq)

(E)-2-(2-(2-(triisopropylsilyl)vinyl)phenyl)pyridine (3aq)

The product was purified by flash silica gel (300-400 mesh) chromatography (PE/EA = 10/1), yellow oil, 3aq: 3aq’ = 2.9:1, 31 mg, 31% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 8.70 (d, $J = 4.3$ Hz, 1H), 7.73 – 7.62 (m, 2H), 7.56 – 7.51 (m, 1H), 7.44 – 7.32 (m, 3H), 7.23 (ddd, $J = 5.8$, 5.3, 1.2 Hz, 1H), 7.02 (d, $J = 19.3$ Hz, 1H), 6.36 (d, $J = 19.3$ Hz, 1H), 1.09 – 0.96 (m, 21H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 158.7, 149.4, 144.8, 138.9, 137.8, 135.8, 129.8, 128.6, 127.8, 126.5, 126.2, 125.2, 121.8, 18.7, 11.0.
2-(2-(1-(triisopropylsilyl)vinyl)phenyl)pyridine (3aq’)

\[\text{Si(IPr)}_{\text{3aq'}}\]

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 8.65 (d, \(J = 4.8\) Hz, 1H), 7.60 (td, \(J = 7.7\), 1.8 Hz, 1H), 7.55 – 7.51 (m, 1H), 7.46 (d, \(J = 7.9\) Hz, 1H), 7.33 – 7.28 (m, 2H), 7.16 (ddd, \(J = 7.4\), 4.9, 1.1 Hz, 1H), 7.13 – 7.08 (m, 1H), 5.86 (d, \(J = 3.1\) Hz, 1H), 5.73 (d, \(J = 3.1\) Hz, 1H), 1.09 – 1.03 (m, 3H), 0.90 – 0.86 (m, 18H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm) 159.6, 149.8, 149.3, 144.8, 138.4, 135.2, 132.6, 130.3, 129.1, 127.7, 126.5, 126.1, 121.4, 18.7, 11.3.

\((E)\)-2-(4-Methyl-2-styrylphenyl)pyridine (3ba)

The product was purified by flash silica gel (300-400 mesh) chromatography (PE/EA = 6/1), green oil, 51.2 mg, 95% yield.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 8.77 – 8.68 (m, 1H), 7.69 (td, \(J = 7.7\), 1.8 Hz, 1H), 7.57 (s, 1H), 7.47 (d, \(J = 7.8\) Hz, 1H), 7.42 (d, \(J = 7.9\) Hz, 1H), 7.39 (d, \(J = 13.6\), 5.8 Hz, 2H), 7.25 – 7.16 (m, 4H), 7.05 (d, \(J = 16.2\) Hz, 1H), 2.43 (s, 3H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm) 158.9, 149.5, 138.4, 137.7, 136.9, 136.0, 135.5, 130.2, 129.8, 128.6, 126.8, 127.7, 126.0, 126.6, 125.1, 121.7, 21.4.

\((E)\)-2-(4-Methoxy-2-styrylphenyl)pyridine (3ca)

The product was purified by flash silica gel (300-400 mesh) chromatography (PE/EA = 6/1), green oil, 51 mg, 89% yield.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 8.72 (dd, \(J = 4.0\), 0.8 Hz, 1H), 7.69 (td, \(J = 7.7\), 1.8 Hz, 1H), 7.52 (d, \(J = 8.5\) Hz, 1H), 7.43 – 7.37 (m, 3H), 7.35 – 7.18 (m, 6H), 7.05 (d, \(J = 16.2\) Hz, 1H), 6.94 (dd, \(J = 8.5\), 2.3 Hz, 1H), 3.89 (s, 3H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm) 159.9, 158.6, 149.4, 137.5, 137.1, 136.0, 132.7, 131.7, 130.2, 128.7, 127.7, 126.7, 125.0, 121.5, 113.7, 111.2, 55.5.

\((E)\)-2-(4-Fluoro-2-styrylphenyl)pyridine (3da)

The product was purified by flash silica gel (300-400 mesh) chromatography (PE/EA = 9/1), green oil, 54.4 mg, 99% yield.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 8.74 (d, \(J = 4.8\) Hz, 1H), 7.74 (td, \(J = 7.7\), 1.8 Hz, 1H), 7.53 (dd, \(J = 8.5\), 6.0 Hz, 1H), 7.47 – 7.37 (m, 4H), 7.35 – 7.22 (m, 4H), 7.19 (d, \(J = 16.2\) Hz, 1H), 7.10 – 7.02
(m, 2H).

**13C NMR** (100 MHz, CDCl₃) δ (ppm) 164.3 (d, J₇₋₈F = 247.1 Hz), 158.0, 149.6, 138.0 (d, J₇₋₈F = 8.0 Hz), 137.1, 136.3, 135.7 (d, J₇₋₈F = 2.9 Hz), 132.2 (d, J₇₋₈F = 8.6 Hz), 131.2, 128.7, 128.0, 126.8, 126.5 (d, J₇₋₈F = 2.3 Hz), 125.1, 122.1, 114.7 (d, J₇₋₈F = 21.7 Hz), 112.6 (d, J₇₋₈F = 22.2 Hz).

**(E)-2-(4-Chloro-2-styrylphenyl)pyridine (3ea)**

The product was purified by flash silica gel (300-400 mesh) chromatography (PE/EA = 9/1), green oil, 53 mg, 91\% yield.

**1H NMR** (400 MHz, CDCl₃) δ (ppm) 8.75 (d, J = 4.2 Hz, 1H), 7.78 – 7.70 (m, 2H), 7.50 (d, J = 8.3 Hz, 1H), 7.43 (d, J = 7.9 Hz, 1H), 7.39 (d, J = 7.3 Hz, 2H), 7.36 – 7.22 (m, 5H), 7.17 (d, J = 16.2 Hz, 1H), 7.06 (d, J = 16.2 Hz, 1H).

**13C NMR** (100 MHz, CDCl₃) δ (ppm) 157.8, 149.7, 137.8, 137.5, 137.1, 136.3, 134.7, 131.7, 131.3, 128.7, 128.0, 127.7, 126.8, 126.3, 126.2, 125.1, 122.2.

**(E)-2-(4-Bromo-2-styrylphenyl)pyridine (3fa)**

The product was purified by flash silica gel (300-400 mesh) chromatography (PE/EA = 9/1), green solid, 62.3 mg, 93\% yield.

**1H NMR** (400 MHz, CDCl₃) δ (ppm) 8.74 (d, J = 4.1 Hz, 1H), 7.88 (d, J = 1.8 Hz, 1H), 7.72 (td, J = 7.7, 1.7 Hz, 1H), 7.48 (dd, J = 8.2, 1.9 Hz, 1H), 7.45 – 7.34 (m, 4H), 7.33 – 7.21 (m, 4H), 7.16 (d, J = 16.2 Hz, 1H), 7.04 (d, J = 16.2 Hz, 1H).

**13C NMR** (100 MHz, CDCl₃) δ (ppm) 157.8, 149.7, 138.3, 137.7, 137.0, 136.2, 131.9, 131.3, 130.5, 129.1, 128.7, 128.0, 126.8, 126.1, 125.0, 123.0, 122.2.

**(E)-2-(2-Styryl-4-(trifluoromethyl)phenyl)pyridine (3ga)**

The product was purified by flash silica gel (300-400 mesh) chromatography (PE/EA = 9/1), green oil, 63.7 mg, 98\% yield.

**1H NMR** (400 MHz, CDCl₃) δ (ppm) 8.76 (d, J = 4.5 Hz, 1H), 7.99 (s, 1H), 7.75 (td, J = 7.7, 1.7 Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.45 (d, J = 7.8 Hz, 1H), 7.39 (d, J = 7.3 Hz, 2H), 7.34 – 7.28 (m, 3H), 7.27 – 7.19 (m, 2H), 7.11 (d, J = 16.2 Hz, 1H).
\( ^{13} \text{C NMR} \) (100 MHz, CDCl\(_3\)) \( \delta \) (ppm) 157.5, 149.8, 142.5, 137.0, 136.5, 136.4, 131.7, 130.9, 130.8 (q, \( J_{C-F} = 32.3 \) Hz), 128.8, 128.1, 126.8, 126.2, 125.0, 124.2 (d, \( J_{C-F} = 272.5 \) Hz) 124.0 (q, \( J_{C-F} = 3.7 \) Hz), 123.2 (q, \( J_{C-F} = 3.8 \) Hz), 122.6.

\( (E)-4\)-(Pyridin-2-yl)-3-styrylbenzaldehyde (3ha) \)

The product was purified by flash silica gel (300-400 mesh) chromatography (PE/EA = 6/1), green oil, 47.3 mg, 83% yield.

\( ^{1} \text{H NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \) (ppm) 10.11 (s, 1H), 8.83 - 8.74 (m, 1H), 8.26 (s, 1H), 7.86 (dd, \( J = 7.9, 1.1 \) Hz, 1H), 7.78 (td, \( J = 7.7, 1.3 \) Hz, 1H), 7.72 (d, \( J = 7.9 \) Hz, 1H), 7.49 (d, \( J = 7.8 \) Hz, 1H), 7.40 (d, \( J = 7.4 \) Hz, 2H), 7.33 (dd, \( J = 13.0, 5.8 \) Hz, 3H), 7.29 - 7.21 (m, 2H), 7.18 (d, \( J = 16.2 \) Hz, 1H).

\( ^{13} \text{C NMR} \) (100 MHz, CDCl\(_3\)) \( \delta \) (ppm) 192.1, 157.6, 149.8, 144.8, 137.0, 136.8, 136.3, 136.3, 131.7, 131.1, 128.7, 128.4, 128.1, 127.8, 126.8, 126.1, 125.0, 122.7.

ESI-MS: [M+H]\(^{+}\) 286.0; HRMS (DART): [M+H]\(^{+}\) calcd for C\(_{20}\)H\(_{16}\)NO\(^{+}\) 286.1226, found 286.1226.

\( (E)-3\)-Methyl-2-(2-styrylphenyl)pyridine (3ia) \)

The product was purified by flash silica gel (300-400 mesh) chromatography (PE/EA = 6/1), green oil, 49.9 mg, 92% yield.

\( ^{1} \text{H NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \) (ppm) 8.57 (d, \( J = 4.7 \) Hz, 1H), 7.77 (d, \( J = 7.8 \) Hz, 1H), 7.58 (d, \( J = 7.6 \) Hz, 1H), 7.44 - 7.39 (m, 1H), 7.35 (t, \( J = 7.4 \) Hz, 1H), 7.31 - 7.15 (m, 7H), 7.00 (d, \( J = 16.3 \) Hz, 1H), 6.76 (d, \( J = 16.2 \) Hz, 1H), 2.10 (s, 3H).

\( ^{13} \text{C NMR} \) (100 MHz, CDCl\(_3\)) \( \delta \) (ppm) 158.8, 146.9, 139.7, 137.9, 137.5, 135.5, 132.3, 130.0, 129.4, 128.6, 128.3, 127.6, 126.6, 126.4, 125.4, 122.5, 19.3.

\( (E)-4\)-Methyl-2-(2-styrylphenyl)pyridine(3ja) \)

The product was purified by flash silica gel (300-400 mesh) chromatography (PE/EA = 9/1), green oil, 48.2 mg, 89% yield.

\( ^{1} \text{H NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \) (ppm) 8.50 (d, \( J = 5.0 \) Hz, 1H), 7.67 (d, \( J = 7.6 \) Hz, 1H), 7.42 (d, \( J = 7.3 \) Hz, 1H), 7.29 (qt, \( J = 7.4, 3.9 \) Hz, 4H), 7.23 - 7.17 (m, 3H), 7.16 - 7.07 (m, 2H), 7.00 (dd, \( J = 5.0, 0.7 \) Hz, 1H), 6.96 (d, \( J = 16.3 \) Hz, 1H), 2.28 (s, 3H).
13C NMR (100 MHz, CDCl3) δ (ppm) 158.8, 149.2, 147.2, 139.7, 137.7, 135.7, 130.2, 129.8, 128.6, 128.6, 127.6, 127.6, 127.5, 126.6, 126.1, 125.9, 122.9, 21.2.

(E)-4-Phenyl-2-(2-styrylphenyl)pyridine (3ka)

![Structure of 3ka]

The product was purified by flash silica gel (300-400 mesh) chromatography (PE/EA = 6/1), green oil, 60.6 mg, 91% yield, m.p.: 112-114 °C.

1H NMR (400 MHz, CDCl3) δ (ppm) 8.78 (d, J = 5.2 Hz, 1H), 7.79 (d, J = 7.4 Hz, 1H), 7.70 (d, J = 0.9 Hz, 1H), 7.65 – 7.59 (m, 3H), 7.50 (dd, J = 5.2, 1.7 Hz, 1H), 7.48 – 7.36 (m, 7H), 7.34 – 7.18 (m, 4H), 7.09 (d, J = 16.2 Hz, 1H).

13C NMR (100 MHz, CDCl3) δ (ppm) 159.4, 149.9, 148.6, 139.5, 138.1, 137.6, 135.9, 130.2, 130.2, 129.2, 129.2, 128.8, 128.7, 127.8, 127.7, 127.6, 127.1, 126.6, 126.3, 123.1, 120.0.


(E)-5-Methyl-2-(2-styrylphenyl)pyridine (3la)

![Structure of 3la]

The product was purified by flash silica gel (300-400 mesh) chromatography (PE/EA = 9/1), green oil, 52.5 mg, 97% yield.

1H NMR (400 MHz, CDCl3) δ (ppm) 8.57 (s, 1H), 7.74 (d, J = 7.3 Hz, 1H), 7.53 (td, J = 7.4, 1.5 Hz, 2H), 7.42 – 7.25 (m, 7H), 7.26 – 7.18 (m, 2H), 7.05 (d, J = 16.2 Hz, 1H), 2.39 (s, 3H).

13C NMR (100 MHz, CDCl3) δ (ppm) 155.9, 149.9, 148.6, 139.5, 138.1, 137.6, 135.9, 130.2, 129.9, 128.6, 128.5, 127.7, 127.6, 127.5, 126.6, 126.2, 124.6, 18.3.

(E)-2-(3-Styrylthiophen-2-yl)pyridine (3ma)

![Structure of 3ma]

The product was purified by flash silica gel (300-400 mesh) chromatography (PE/EA = 9/1), yellow oil, 50.3 mg, 96% yield.

1H NMR (400 MHz, CDCl3) δ (ppm) 8.67 (dd, J = 4.8, 0.7 Hz, 1H), 7.69 (td, J = 7.8, 1.7 Hz, 1H), 7.59 – 7.44 (m, 4H), 7.39 (d, J = 5.3 Hz, 1H), 7.36 – 7.30 (m, 3H), 7.27 – 7.21 (m, 1H), 7.20 – 7.15 (m, 1H), 7.05 (d, J = 16.3 Hz, 1H).

13C NMR (100 MHz, CDCl3) δ (ppm) 153.1, 149.8, 139.4, 137.4, 136.9, 136.6, 130.8, 128.7, 127.6, 126.9, 126.5, 126.3, 123.0, 122.6, 121.8.
(E)-1-(Pyridin-2-yl)-2-styryl-1H-indole (3na)

The product was purified by flash silica gel (300-400 mesh) chromatography (PE/EA = 6/1), yellow oil, 55.7 mg, 94% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 8.70 – 8.62 (m, 1H), 7.76 (td, $J = 7.9, 1.9$ Hz, 1H), 7.65 – 7.57 (m, 1H), 7.52 – 7.46 (m, 1H), 7.34 (dd, $J = 13.7, 8.0$ Hz, 3H), 7.30 – 7.12 (m, 6H), 7.10 – 7.03 (m, 2H), 6.95 (s, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) 151.2, 149.6, 138.3, 138.0, 137.8, 137.1, 130.5, 128.7, 128.6, 127.7, 126.5, 122.9, 122.0, 121.4, 121.3, 120.5, 118.3, 110.9, 102.3.

(3na)

(E)-1-(Pyrimidin-2-yl)-2-styryl-1H-indole (3oa)

The product was purified by flash silica gel (300-400 mesh) chromatography (PE/EA = 6/1), yellow oil, 49.9 mg, 83% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 8.79 (d, $J = 4.8$ Hz, 2H), 8.29 (d, $J = 8.0$ Hz, 1H), 7.69 (d, $J = 16.2$ Hz, 1H), 7.60 (d, $J = 7.5$ Hz, 1H), 7.48 (d, $J = 7.9$ Hz, 2H), 7.33 (t, $J = 7.4$ Hz, 2H), 7.29 – 7.09 (m, 5H), 7.00 (s, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) 158.3, 158.1, 138.3, 138.0, 137.5, 137.4, 129.7, 129.4, 128.7, 127.6, 126.7, 123.6, 122.4, 120.7, 120.4, 117.3, 114.1, 105.3.

(E)-1-(2-Styrylphenyl)isoquinoline (3pa)

The product was purified by flash silica gel (300-400 mesh) chromatography (PE/EA = 6/1), green oil, 55.9 mg, 91% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 8.66 (d, $J = 5.8$ Hz, 1H), 7.87 (d, $J = 8.1$ Hz, 2H), 7.72 – 7.67 (m, 2H), 7.67 – 7.61 (m, 1H), 7.53 – 7.47 (m, 1H), 7.46 – 7.37 (m, 3H), 7.18 – 7.07 (m, 5H), 7.02 (d, $J = 16.2$ Hz, 1H), 6.73 (d, $J = 16.2$ Hz, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) 160.6, 142.1, 138.2, 137.3, 136.4, 136.3, 130.5, 130.3, 130.0, 128.8, 128.4, 127.8, 127.7, 127.5, 127.3, 127.3, 126.9, 126.6, 126.5, 125.4, 120.2.

(E)-1-(2-Styrylphenyl)-1H-pyrazole (3qa)

The product was purified by flash silica gel (300-400 mesh) chromatography (PE/EA = 8/1), yellow oil, 32.1 mg, 65% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 7.77 (d, $J = 7.7$ Hz, 2H), 7.65
(d, \( J = 2.2 \) Hz, 1H), 7.47 – 7.35 (m, 5H), 7.35 – 7.21 (m, 3H), 7.05 (d, \( J = 16.3 \) Hz, 1H), 6.94 (d, \( J = 16.3 \) Hz, 1H), 6.47 (t, \( J = 2.0 \) Hz, 1H).

\( ^{13} \text{C NMR} \) (100 MHz, CDCl\(_3\)) \( \delta \) (ppm) 140.81, 138.81, 137.07, 133.06, 131.59, 131.30, 128.71, 128.46, 128.18, 128.01, 126.75, 126.63, 126.39, 123.96, 106.65, 77.42, 77.10, 76.78.

\((E)-2-(2\text{-styrylphenyl})\text{pyrimidine}(3ra)\)

The product was purified by flash silica gel (300-400 mesh) chromatography (PE/EA = 6/1), yellow oil, 25.8 mg, 50% yield.

\( ^{1} \text{H NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \) (ppm) 8.88 (d, \( J = 4.9 \) Hz, 2H), 7.89 (dd, \( J = 7.7, 1.1 \) Hz, 1H), 7.80 (d, \( J = 7.7 \) Hz, 1H), 7.67 (d, \( J = 16.2 \) Hz, 1H), 7.50 – 7.38 (m, 4H), 7.32 (t, \( J = 7.5 \) Hz, 2H), 7.29 – 7.20 (m, 2H), 7.07 (d, \( J = 16.2 \) Hz, 1H).

\( ^{13} \text{C NMR} \) (100 MHz, CDCl\(_3\)) \( \delta \) (ppm) 167.2, 157.1, 157.8, 137.3, 136.8, 131.0, 130.1, 129.9, 128.6, 128.1, 127.7, 127.5, 126.8, 126.8, 118.8.

\(2-(2,6\text{-di((E)-styrylphenyl})\text{pyrimidine}(3ra')\)

The product was purified by flash silica gel (300-400 mesh) chromatography (PE/EA = 6/1), yellow solid, 68.5 mg, 95% yield.

\( ^{1} \text{H NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \) (ppm) 8.92 (d, \( J = 4.9 \) Hz, 2H), 7.69 (d, \( J = 7.8 \) Hz, 2H), 7.46 (t, \( J = 7.8 \) Hz, 1H), 7.32 (t, \( J = 4.9 \) Hz, 1H), 7.30 – 7.22 (m, 8H), 7.22 – 7.16 (m, 2H), 6.98 (d, \( J = 16.1 \) Hz, 2H), 6.75 (d, \( J = 16.1 \) Hz, 2H).

\( ^{13} \text{C NMR} \) (100 MHz, CDCl\(_3\)) \( \delta \) (ppm) 167.5, 157.2, 157.4, 137.3, 136.4, 130.9, 129.1, 128.6, 127.7, 126.6, 126.6, 125.2, 119.2.

\((E)-9\text{-Isopropyl-6-(2\text{-styrylphenyl})-9H-purine (3sa)\)

The product was purified by flash silica gel (300-400 mesh) chromatography (PE/EA = 2/1), yellow oil, 65.4 mg, 96% yield.

\( ^{1} \text{H NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \) (ppm) 9.09 (s, 1H), 8.16 (s, 1H), 7.93 – 7.81 (m, 2H), 7.53 – 7.41 (m, 3H), 7.36 (d, \( J = 7.4 \) Hz, 2H), 7.26 (dd, \( J = 8.3, 6.7 \) Hz, 2H), 7.19 (t, \( J = 7.2 \) Hz, 1H), 7.11 (d, \( J = 16.2 \) Hz, 1H), 4.99 (dt, \( J = 13.5, 6.7 \) Hz, 1H), 1.68 (d, \( J = 6.8 \) Hz, 6H).
\[ ^{13} \text{C NMR} \ (100 \text{ MHz, CDCl}_3 \ \delta \ (\text{ppm}) \ 157.9, \ 151.8, \ 151.7, \ 142.5, \ 137.6, \ 136.6, \ 134.1, \ 132.8, \ 131.5, \ 130.1, \ 129.9, \ 128.5, \ 127.5, \ 127.4, \ 127.3, \ 126.6, \ 126.4, \ 47.5, \ 22.5. \]

\((E)-9-(\text{Cyclopropylmethyl})-6-(2-\text{styrylphenyl})-9\text{H}-\text{purine} \ (3ta)\)

The product was purified by flash silica gel (300-400 mesh) chromatography (PE/EA = 2/1), yellow oil, 67.7 mg, 96% yield.

\[ ^{1} \text{H NMR} \ (400 \text{ MHz, CDCl}_3 \ \delta \ (\text{ppm}) \ 9.09 \ (s, \ 1H), \ 8.19 \ (s, \ 1H), \ 7.87 \ (t, \ J = 6.6 \text{ Hz, } 2H), \ 7.53 - 7.40 \ (m, \ 3H), \ 7.35 \ (d, \ J = 7.5 \text{ Hz, } 2H), \ 7.25 \ (t, \ J = 6.4 \text{ Hz, } 2H), \ 7.17 \ (t, \ J = 6.8 \text{ Hz, } 1H), \ 7.10 \ (d, \ J = 16.2 \text{ Hz, } 1H), \ 4.21 - 4.03 \ (m, \ 2H), \ 1.44 - 1.29 \ (m, \ 1H), \ 0.67 \ (d, \ J = 6.1 \text{ Hz, } 2H), \ 0.47 \ (s, \ 2H). \]

\[ ^{13} \text{C NMR} \ (100 \text{ MHz, CDCl}_3 \ \delta \ (\text{ppm}) \ 157.7, \ 152.0, \ 151.9, \ 144.5, \ 137.5, \ 136.6, \ 133.9, \ 132.3, \ 131.5, \ 130.0, \ 129.9, \ 128.4, \ 127.4, \ 127.3, \ 126.6, \ 126.3, \ 48.5, \ 11.0, \ 4.4. \]

\text{ESI-MS:} \ [\text{M+H}]^\circ \ 353.1; \ \text{HRMS (DART):} \ [\text{M+H}]^\circ \ \text{calcd for C}_{23}\text{H}_{21}\text{N}_4^\circ \ 353.1761, \ \text{found} \ 353.1758. \]

\((E)-9-\text{Allyl}-6-(2-\text{styrylphenyl})-9\text{H}-\text{purine} \ (3ua)\)

The product was purified by flash silica gel (300-400 mesh) chromatography (PE/EA = 2/1), yellow oil, 62.9 mg, 93% yield.

\[ ^{1} \text{H NMR} \ (400 \text{ MHz, CDCl}_3 \ \delta \ (\text{ppm}) \ 9.10 \ (s, \ 1H), \ 8.09 \ (d, \ J = 1.6 \text{ Hz, } 1H), \ 7.87 \ (t, \ J = 7.1 \text{ Hz, } 2H), \ 7.55 - 7.39 \ (m, \ 3H), \ 7.34 \ (d, \ J = 7.6 \text{ Hz, } 2H), \ 7.26 \ (t, \ J = 7.4 \text{ Hz, } 2H), \ 7.18 \ (t, \ J = 6.8 \text{ Hz, } 1H), \ 7.10 \ (d, \ J = 16.2 \text{ Hz, } 1H), \ 6.18 - 6.00 \ (m, \ 1H), \ 5.29 \ (dd, \ J = 38.2, \ 13.5 \text{ Hz, } 2H), \ 4.91 \ (s, \ 2H). \]

\[ ^{13} \text{C NMR} \ (100 \text{ MHz, CDCl}_3 \ \delta \ (\text{ppm}) \ 157.9, \ 152.2, \ 151.9, \ 144.6, \ 137.6, \ 136.6, \ 133.9, \ 132.3, \ 131.5, \ 131.4, \ 130.1, \ 130.0, \ 128.5, \ 127.5, \ 127.4, \ 127.3, \ 126.6, \ 126.4, \ 119.4, \ 45.8. \]

\text{ESI-MS:} \ [\text{M+H}]^\circ \ 339.2; \ \text{HRMS (DART):} \ [\text{M+H}]^\circ \ \text{calcd for C}_{22}\text{H}_{19}\text{N}_4^\circ \ 339.1604, \ \text{found} \ 339.1601. \]
4. MECHANISTIC STUDIES

4.1 Cp*Rh(III)-Complex 4 catalyzed alkenylation reaction

The Cp*Rh(III)-Complex 4 was prepared according to the reported literature[1].

Procedure: In a dried Schlenk tube, the Cp*Rh(III)-Complex (0.01 mol, 4.3 mg, 5 mol %), AgSbF₆ (0.03 mmol, 10 mg), 1a (0.2 mmol), HOAc (1 ml), 2a (0.24 mmol) were added sequentially under the argon. The reaction mixture was stirred at room temperature for 12 h, then diluted with EtOAc (10 mL), filtered through a short pad of silica gel and washed with EtOAc (30 mL). The crude product was purified by flash silica gel (300-400 mesh) chromatography to afford the 3aa at the 88% yield.

4.2 Synthesis of 2-(pentadeuteriophenyl)pyridine[2]

Procedure: To a solution of bromobenzene-d₅ (6 mmol) in dried THF (20 ml) was added dropwise n-BuLi (1.6 M in hexane, 8 mmol, 5 ml) at -78 °C and stirred for 1 h. B(OMe)₃ (1.7 ml, 15 mmol) was then added. The resulting mixture was stirred at -78 °C for a further 1 h and then allowed to warm to room temperature. The solution was acidified with 10% HCl solution and extracted with ethyl ether. The combined organic layer was dried over magnesium sulfate and concentrated by rotary evaporation to give off-white solid which was used without further purification.

To a stirred solution of phenylboronic acid-d₅ (0.64 g, 5 mmol), Pd(PPh₃)₄ (0.25 g, 0.25 mmol) and Na₂CO₃ (3.3 g, 31 mmol,) in toluene (20 ml), water (20 ml) and ethanol (2 ml) was added 2-bromopyridine (1.0 g, 4.2 mmol) under nitrogen. The reaction was refluxed for 12 h and cooled to room temperature. Water was added and the mixture was extracted with dichloromethane. The combined organic layer was dried over magnesium sulfate. The solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography to afford 2-(pentaduteriophenyl)pyridine (0.5 g, 63% yield, 99% D).

¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.70 (d, J = 4.8 Hz, 1H), 7.78 – 7.70 (m, 2H), 7.25 – 7.20 (m, 1H).

4.3 H/D exchange experiment

**Procedure:** [Cp*RhCl$_2$]$_2$ (3.1 mg, 0.005 mmol), AgSbF$_6$ (10 mg, 0.03 mmol), $d_5$-2-phenylpyridine (29 μL, 0.2 mmol), HOAc (1.0 ml) was added stepwise into the 25 ml schlenk tube under the atmosphere of argon. Then the mixture was stirred at room temperature for 12 h. After removing the rest solvent under reduced pressure, the residue was purified by flash column chromatography (PE/EA = 20:1 – 10:1) to give the corresponding product.
4.4 Deuterium labeling experiments

4.4.1 Synthesis of deuterated 6-chloro-1-hexyne

**Procedure:** Under argon atmosphere, (1 mmol, 0.13 ml) 6-chloro-1-hexyne, THF(5 ml) was added stepwise into the reaction tube, then cooled the reaction system to -78 °C. n-BuLi (2.5 M in hexane, 1 ml) was added in slowly and stirred under -78 °C for 1 h. The reaction mixture was quenched by water and extracted by DCM (10 ml) dried by Na₂SO₄, removing the solvent under reduced pressure to afford the desired product (99 mg, 80% yield).

\(^1\)H NMR (400 MHz, CDCl₃) δ (ppm) 3.57 (t, \(J = 6.5\) Hz, 2H), 2.24 (t, \(J = 7.0\) Hz, 2H), 1.95 – 1.84 (m, 2H), 1.69 (dt, \(J = 14.1, 7.0\) Hz, 2H).
4.4.2 Deuterium labeling experiment

**Procedure (1):** To a dried Schlenk tube was equipped with a magnetic stir bar, [Cp*RhCl₂]₂ (0.005 mmol, 2.5 mol %, 3.1 mg), AgSbF₆ (0.03 mmol, 15 mol %, 10.3 mg), 1a (0.2 mmol, 29 µL), CH₃COOD (1 ml), 2q (0.24 mmol) were added sequentially under argon. The tube was stirred at room temperature for 5 h. After completion of the reaction, diluted with EtOAc (10 mL), filtered through a short pad of silica gel and washed with EtOAc (30 mL). The filtrate was pre-absorbed on silica gel and concentrated by rotary evaporation. The crude product was purified by flash silica gel (300-400 mesh) chromatography to afford the desired products product 3aq.

^1^H NMR (400 MHz, CDCl₃) δ (ppm) 8.72 (d, J = 4.1 Hz, 1H), 7.74 (td, J = 7.7, 1.8 Hz, 1H), 7.58 (d, J = 7.7 Hz, 1H), 7.46 (dd, J = 7.4, 1.5 Hz, 1H), 7.42 (d, J = 7.8 Hz, 1H), 7.34 (dtd, J = 18.5, 7.3, 1.4 Hz, 2H), 7.25 (d, J = 1.0 Hz, 1H), 3.53 (t, J = 6.7 Hz,
Procedure (2): To a dried Schlenk tube was equipped with a magnetic stir bar, [Cp*RhCl₂]₂ (0.005 mmol, 2.5 mol %, 3.1 mg), AgSbF₆ (0.03 mmol, 15 mol %, 10.3 mg), 1a (0.2 mmol, 29 µL), CH₃COOH (1 ml), deuterated 2q (0.24 mmol) were added sequentially under argon. The tube was stirred at room temperature for 5 h. After completion of the reaction, diluted with EtOAc (10 mL), filtered through a short pad of silica gel and washed with EtOAc (30 mL). The filtrate was pre-absorbed on silica gel and concentrated by rotary evaporation. The crude product was purified by flash silica gel (300-400 mesh) chromatography to afford the desired product product 3aq.

¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.72 (d, J = 4.2 Hz, 1H), 7.74 (t, J = 7.5 Hz, 1H), 7.57 (d, J = 7.4 Hz, 1H), 7.49 – 7.27 (m, 5H), 6.47 (d, J = 15.7 Hz, 1H), 6.19 – 6.07 (m, 1H), 3.53 (t, J = 6.6 Hz, 2H), 2.19 (dd, J = 14.1, 7.0 Hz, 2H), 1.88 – 1.73 (m, 2H), 1.59 (d, J = 6.4 Hz, 2H).
4.5 KIE determined from intermolar competition

**Procedure:** [Cp*RhCl₂]₂ (0.005 mmol, 2.5 mol %, 3.1 mg), AgSbF₆ (0.03 mmol, 15 mol %, 10.3 mg), 1a (0.2 mmol, 29 µL), deuterated 1a (0.2 mmol, 29 µL) CH₃COOH (1 ml), 2q (0.24 mmol) were added sequentially under argon. Then the mixture was stirred at room temperature for 10 min. After remove the rest solvent under reduced pressure, the total yield of the product was determined by the 1H NMR, and the residue was purified by flash column chromatography to give the corresponding product.
5. $^1$H NMR and $^{13}$C NMR
$^{13}$C NMR
Solvent: CDCl$_3$
3aa'

$^1$H NMR

Solvent: CDCl$_3$
$^{13}$C NMR
Solvent: CDCl$_3$
3ab
$^1$H NMR
Solvent: CDCl$_3$
$^{13}$C NMR
Solvent: CDCl$_3$
$3_{ac}$

$^1$H NMR

Solvent: CDCl$_3$
$^{13}\text{C NMR}$

Solvent: CDCl$_3$
$^{13}$C NMR
Solvent: CDCl$_3$
$^{13}$C NMR
Solvent: CDCl$_3$
$^1$H NMR
Solvent: CDCl$_3$
$^{13}$C NMR
Solvent: CDCl$_3$
$^1$H NMR
Solvent: CDCl$_3$
$^{13}$C NMR
Solvent: CDCl$_3$
3ah

$^1$H NMR

Solvent: CDCl$_3$
3ah
$^{13}$C NMR
Solvent: CDCl$_3$
$^1$H NMR
Solvent: CDCl$_3$
$^{13}$C NMR
Solvent: CDCl$_3$

3ai
$\text{3aj}$

$^{13}\text{C NMR}$

Solvent: CDCl$_3$
$3ak$

$^1$H NMR

Solvent: CDCl$_3$
$^{13}$C NMR
Solvent: CDCl$_3$
3al

$^1$H NMR

Solvent: CDCl$_3$
$^{1}H$ NMR
Solvent: CDCl$_3$
$^{13}$C NMR

Solvent: CDCl$_3$
$^{13}$C NMR
Solvent: CDCl$_3$
$^1$H NMR
Solvent: CDCl$_3$
$^{13}$C NMR

Solvent: CDCl$_3$
$^{1}$H NMR
Solvent: CDCl$_3$
$^{13}$C NMR
Solvent: CDCl$_3$
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$^{13}$C NMR
Solvent: CDCl$_3$
$\text{OMe}$

3ca

$^1\text{H NMR}$

Solvent: CDCl$_3$
$^{1}$H NMR

Solvent: CDCl$_3$
$^{13}$C NMR
Solvent: CDCl$_3$
3ea

$^{13}$C NMR
Solvent: CDCl$_3$
$^{1}H$ NMR
Solvent: CDCl$_3$
$^{13}$C NMR
Solvent: CDCl$_3$
$^{1}H$ NMR
Solvent: CDCl$_3$
$^{13}$C NMR
Solvent: CDCl$_3$
$^1$H NMR
Solvent: CDC$_3$
3ia
$^{13}$C NMR
Solvent: CDCl$_3$
$^1$H NMR
Solvent: CDCl$_3$
$^{13}$C NMR
Solvent: CDCl$_3$
3ka

$^1$H NMR

Solvent: CDCl$_3$
$^{1}$H NMR
Solvent: CDCl$_3$
$^{13}$C NMR
Solvent: CDCl$_3$
$^{13}$C NMR
Solvent: CDCl$_3$
3na

$^1$H NMR

Solvent: CDCl$_3$
$^1$H NMR
Solvant: CDCl$_3$
$^{13}$C NMR
Solvent: CDCl$_3$
3pa

$^1$H NMR

Solvent: CDCl$_3$
$^{13}$C NMR
Solvent: CDCl$_3$
$^{13}$C NMR
Solvent: CDCl$_3$
3ra

$^1$H NMR
Solvent: CDCl$_3$
$\text{H NMR}$

Solvent: CDCl$_3$
$^{13}$C NMR
Solvent: CDCl$_3$
$^{13}$C NMR
Solvent: CDCl$_3$