Supporting Information

Metal-free regioselective cascade sulfonylation-cyclization of 3-aza-1,5-enynes with sulfur dioxide and aryldiazonium tetrafluoroborates to construct 1,2-dihydropyridines

Ran Ding,* a, b Yu-Hang Deng,† a Shan Luo,† a Xue-Feng Tang,† a Lei Liu, a Pei-Long Wang * b, c

a College of Chemistry and Materials Engineering, Anhui Science and Technology University, Bengbu, Anhui, 233000, P. R.China.
b Key Laboratory of Green and Precise Synthetic Chemistry and Applications, Ministry of Education, School of Chemistry and Materials Science, Huai Bei Normal University, Huai Bei, Anhui 235000, P. R. China
c Information College, Huai Bei Normal University, Huai Bei, Anhui, 235000, P. R. China

Table of Contents

1. General information ...................................................................................................2

2. Procedure for the synthesis of compound 3a – 3t, 4a – 4l ........................................3

3. Procedures for the formation of 5q .........................................................................4

4. Analysis on the radical trapping reaction residue ....................................................4

5. Characterization Data of 3a – 3t, 4a – 4l, 5q ..........................................................4

6. NMR spectra for the products ..................................................................................19
1. General information

Unless otherwise noted, DABSO and solvents were purchased from commercial suppliers and used without further purification. Aiazonium salts were freshly prepared according to the literature.\textsuperscript{1} \textsuperscript{1}H-NMR and \textsuperscript{13}C-NMR spectra were recorded at 25 ºC on Bruker Advance 600M or 400M NMR spectrometers (CDCl\textsubscript{3} as solvent). Chemical shifts for \textsuperscript{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from SiMe\textsubscript{4} (δ 0.0) and relative to the signal of SiMe\textsubscript{4} (δ 0.00 singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); dt (doublet of triplets); m (multiplets) and etc. Coupling constants are reported as a \textit{J} value in Hz. \textsuperscript{13}C NMR spectra are reported as δ in units of parts per million (ppm) downfield from SiMe\textsubscript{4} (δ 0.0) and relative to the signal of chloroform-d (δ 77.00 triplet). High resolution mass spectral analysis (HRMS) was performed on WaterXEVOG2 Q-TOF (Waters Corporation). Flash chromatography was performed using 200-300 mesh silica gel with the indicated solvent system.
2. Procedure for the synthesis of compound 3a – 3t, 4a – 4l.

A dry 25-mL Schlenk tube containing a magnetic stirring bar was charged with
N-propargyl enamides 1 (0.1 mmol), aryldiazonium tetrafluoroborates 2 (0.2 mmol),
DABSO (0.15 mmol), DCE (1 mL), Then the mixture was charged with N₂ and heated
at 70 °C oil bath. After finishing, the reaction mixture was concentrated on a rotary
 evaporator and the residue was directly subjected to flash column chromatography on
silica gel with (10-40% EtOAc/Petroleum ether) as eluate to furnish the desired
product.

3. Procedures for the formation of compound 5q.

MnO₂ (10 equiv) was added to the mixture of 3q (0.2 mmol) and DCE (8 mL)
under O₂ atmosphere at 80 °C. After the reaction finished as indicated by TLC, the
reaction mixture was diluted with water and extracted with 10 mL CH₂Cl₂ for 3
times. The combined organic layers were washed with water, saturated brine, dried
over MgSO₄, concentrated in vacuo and purified by chromatography on silica gel
with (30% EtOAc/Petroleum ether) as eluate to furnish the desired product 5q.
4. The radical trapping reaction residue was analyzed by high resolution mass spectrometry (HRMS).

\[
\begin{align*}
\text{HRMS (ESI, m/z): Calcd. For } & C_{16}H_{25}NSO_3H [M+H]^+ \quad 312.1628, \text{ found: 312.1627.}
\end{align*}
\]
5. Characterization Data

1-(6-(naphthalen-2-yl)-4-phenyl-3-tosylpyridin-1(2H)-yl)ethanone (3a)

Yellow solid; mp 82.7-83.9 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 8.00 – 7.94 (m, 1H), 7.88 (dd, \(J = 8.7\), 3.5 Hz, 2H), 7.56 – 7.49 (m, 5H), 7.47 – 7.43 (m, 1H), 7.39 – 7.34 (m, 3H), 7.24 (d, \(J = 6.5\) Hz, 2H), 7.19 (d, \(J = 8.1\) Hz, 2H), 6.04 (s, 1H), 5.16 (s, 2H), 2.39 (s, 3H), 1.51 (s, 3H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 170.41, 144.95, 144.04, 142.61, 138.40, 135.97, 134.19, 133.72, 130.45, 130.29, 129.52, 129.43, 128.96, 128.54, 128.37, 127.98, 127.85, 127.66, 127.61, 126.54, 125.36, 123.87, 121.17, 43.42, 23.89, 21.63.

HRMS (ESI, m/z): Calcd. For C\(_{30}\)H\(_{25}\)NSO\(_3\)Na \([\text{M+Na}]^+\) 502.1447, found: 502.1454.

1-(6-(4-fluorophenyl)-4-phenyl-3-tosylpyridin-1(2H)-yl)ethanone (3b)

Yellow solid; mp 80.1-82.2 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.44 – 7.37 (m, 4H), 7.36 (d, \(J = 7.2\) Hz, 1H), 7.32 (t, \(J = 7.3\) Hz, 2H), 7.15 (t, \(J = 7.4\) Hz, 4H), 7.07 (t, \(J = 8.2\) Hz, 2H), 6.05 (s, 1H), 4.96 (s, 2H), 2.37 (s, 3H), 1.74 (s, 3H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 170.96, 163.54 (J = 251 Hz), 162.71, 145.05, 144.04, 143.11, 138.29, 135.75, 132.15, 129.41, 129.80, 128.57, 128.39, 127.94, 127.54, 126.89, 116.16 (J = 23 Hz), 43.71, 23.93, 21.57. \(^{19}\)F NMR (565 MHz, CDCl\(_3\)) \(\delta\) -109.64.

HRMS (ESI, m/z): Calcd. For C\(_{26}\)H\(_{22}\)FNSO\(_3\)H \([\text{M+H}]^+\) 470.1197, found: 470.120.

1-(6-(4-chlorophenyl)-4-phenyl-3-tosylpyridin-1(2H)-yl)ethanone (3c)
Yellow solid; mp 84.0-85.7 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.34 (d, \(J = 7.1\) Hz, 2H), 7.30 – 7.21 (m, 7H), 7.07 (d, \(J = 6.6\) Hz, 4H), 6.01 (s, 1H), 4.88 (s, 2H), 2.29 (s, 3H), 1.66 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 170.93, 145.05, 144.13, 142.89, 138.19, 135.87, 135.66, 134.41, 129.46, 129.36, 128.65, 128.42, 128.21, 128.00, 127.57, 119.37, 43.40, 23.98, 21.63.

HRMS (ESI, m/z): Calcd. For C\(_{26}\)H\(_{22}\)NSO\(_3\)ClNa [M+Na]\(^+\) 486.0901, found: 486.0906.

1-(6-(4-bromophenyl)-4-phenyl-3-tosylpyridin-1(2H)-yl)ethanone (3d)

Yellow solid; mp 80.3-82.5 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.41 (d, \(J = 8.1\) Hz, 2H), 7.33 (d, \(J = 7.3\) Hz, 2H), 7.24 (dd, \(J = 12.8, 5.5\) Hz, 3H), 7.19 (d, \(J = 8.0\) Hz, 2H), 7.06 (dd, \(J = 7.3, 3.4\) Hz, 4H), 6.01 (s, 1H), 4.87 (s, 2H), 2.28 (s, 3H), 1.66 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 170.93, 145.02, 144.15, 143.10, 138.17, 135.63, 134.87, 132.30, 129.47, 128.66, 128.43, 128.00, 127.56, 124.09, 119.40, 43.76, 23.94, 21.64.

HRMS (ESI, m/z): Calcd. For C\(_{26}\)H\(_{22}\)NSO\(_3\)BrNa [M+Na]\(^+\) 530.0396, found: 530.0399.

1-(4-phenyl-3-tosyl-6-(4-(trifluoromethyl)phenyl)pyridin-1(2H)-yl)ethanone (3e)

Yellow solid; mp 45.1-47.2 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.62 (d, \(J = 6.9\) Hz, 2H), 7.52 (d, \(J = 7.4\) Hz, 2H), 7.46 – 7.30 (m, 5H), 7.15 (t, \(J = 7.0\) Hz, 4H), 6.17 (s, 1H), 4.96 (s, 2H), 2.37 (s, 3H), 1.74 (s, 3H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 170.73,
144.73, 144.24, 139.27, 138.00, 135.45, 131.36, 129.47, 128.73, 128.42, 128.04, 127.61, 127.14, 126.00, 123.73 (J = 272 Hz), 120.68, 44.34, 23.51, 21.59. $^{19}$F NMR (565 MHz, CDCl$_3$) δ -62.74.

HRMS (ESI, m/z): Calcd. For C$_{27}$H$_{22}$NSO$_3$F$_3$Na [M+Na]$^+$ 520.1165, found: 520.1168.

1-(6-(2-chlorophenyl)-4-phenyl-3-tosylpyridin-1(2H)-yl)ethanone (3f)

Yellow solid; mp 106.8-107.6 °C; $^1$H NMR (600 MHz, CDCl$_3$) δ 7.45 (s, 2H), 7.37 (dd, J = 16.0, 7.3 Hz, 3H), 7.34 – 7.27 (m, 4H), 7.17 (dd, J = 12.9, 7.7 Hz, 4H), 5.88 (s, 1H), 4.92 (s, 2H), 2.38 (s, 3H), 1.67 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 169.50, 144.09, 138.15, 135.65, 135.22, 130.61, 130.20, 129.48, 128.59, 128.43, 127.92, 127.60, 127.35, 121.46, 42.82, 23.39, 21.59.

HRMS (ESI, m/z): Calcd. For C$_{26}$H$_{22}$NSO$_3$ClNa [M+Na]$^+$ 486.0901, found: 486.0906.

1-(6-(3-bromophenyl)-4-phenyl-3-tosylpyridin-1(2H)-yl)ethanone (3g)

Yellow solid; mp 71.0-72.1 °C; $^1$H NMR (600 MHz, CDCl$_3$) δ 7.54 (s, 1H), 7.49 (d, J = 7.4 Hz, 1H), 7.42 (s, 2H), 7.36 (d, J = 7.0 Hz, 1H), 7.33 (d, J = 6.9 Hz, 3H), 7.24 (s, 1H), 7.15 (d, J = 7.4 Hz, 4H), 6.10 (s, 1H), 4.96 (s, 2H), 2.37 (s, 3H), 1.72 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 170.84, 144.13, 138.11, 137.94, 135.54, 132.70, 130.54, 129.75, 129.66, 129.43, 128.64, 128.38, 127.99, 127.57, 126.04, 125.58, 123.26, 119.98, 43.74, 24.01, 21.58.

HRMS (ESI, m/z): Calcd. For C$_{26}$H$_{22}$NSO$_3$BrNa [M+H]$^+$ 530.0396, found: 530.0402.

1-(4-phenyl-6-p-tolyl-3-tosylpyridin-1(2H)-yl)ethanone (3h)
Yellow solid; mp 59.5-62.4 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.44 (d, \(J = 6.4\) Hz, 2H), 7.38 - 7.28 (m, 5H), 7.16 (dd, \(J = 15.6, 8.0\) Hz, 6H), 6.05 (s, 1H), 4.98 (s, 2H), 2.36 (s, 3H), 2.36 (s, 3H), 1.68 (s, 3H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 171.19, 145.32, 144.26, 143.89, 140.34, 138.50, 136.02, 133.22, 129.83, 129.37, 128.45, 128.39, 127.88, 127.53, 127.02, 118.23, 43.64, 24.11, 21.57, 21.34.

HRMS (ESI, m/z): Calcd. For C\(_{27}\)H\(_{25}\)NSO\(_3\)Na [M+Na]^+ 466.1447, found: 466.1446.

**1-(4-phenyl-6-o-tolyl-3-tosylpyridin-1(2H)-yl)ethanone (3i)**

Yellow solid; mp 54.5-56.2 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.48 (d, \(J = 7.7\) Hz, 2H), 7.34 (dt, \(J = 14.2, 7.0\) Hz, 3H), 7.28 (d, \(J = 7.4\) Hz, 2H), 7.19 (dd, \(J = 15.6, 7.9\) Hz, 6H), 5.80 (s, 1H), 5.00 (s, 2H), 2.38 (s, 3H), 2.29 (s, 3H), 1.61 (s, 3H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 170.24, 144.82, 143.97, 143.77, 138.39, 136.19, 135.96, 135.42, 131.02, 129.69, 129.46, 129.41, 128.48, 128.33, 127.91, 127.59, 126.57, 120.30, 42.84, 23.91, 21.59, 20.18.

HRMS (ESI, m/z): Calcd. For C\(_{27}\)H\(_{25}\)NSO\(_3\)Na [M+Na]^+ 466.1447, found: 466.1446.

**1-(6-(3-methoxyphenyl)-4-phenyl-3-tosylpyridin-1(2H)-yl)ethanone (3j)**

Yellow solid; mp 63.2-65.1 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.44 (d, \(J = 7.7\) Hz, 2H), 7.37 - 7.29 (m, 3H), 7.27 (d, \(J = 6.3\) Hz, 1H), 7.16 (t, \(J = 7.1\) Hz, 4H), 6.98 (d, \(J = 7.6\) Hz, 1H), 6.91 (d, \(J = 5.5\) Hz, 2H), 6.08 (s, 1H), 4.99 (s, 2H), 3.78 (s, 3H), 2.36
(s, 3H), 1.72 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 171.25, 160.12, 145.00, 144.05, 138.34, 137.48, 135.87, 130.26, 129.45, 128.55, 128.40, 127.96, 127.55, 119.63, 119.13, 115.44, 112.50, 55.46, 43.49, 24.04, 21.63.

HRMS (ESI, m/z): Calcd. For C$_{27}$H$_{25}$NSO$_4$Na [M+Na]$^+$ 482.1397, found: 482.1399.

1-(6-(4-methoxyphenyl)-4-phenyl-3-tosylpyridin-1(2H)-yl)ethanone (3k)

![Chemical structure of 3k](image)

Yellow solid; mp 69.5-71.5 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.44 (d, $J$ = 7.7 Hz, 2H), 7.33 (t, $J$ = 8.1 Hz, 5H), 7.16 (t, $J$ = 7.6 Hz, 4H), 6.89 (d, $J$ = 8.2 Hz, 2H), 6.01 (s, 1H), 4.97 (s, 2H), 3.82 (s, 3H), 2.36 (s, 3H), 1.71 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 171.37, 161.07, 145.52, 143.89, 138.57, 136.11, 129.39, 128.61, 128.47, 128.42, 127.90, 127.51, 117.40, 114.56, 55.45, 43.83, 24.16, 21.61.

HRMS (ESI, m/z): Calcd. For C$_{27}$H$_{25}$NSO$_4$Na [M+Na]$^+$ 482.1397, found: 482.1399.

1-(6-(naphthalen-1-yl)-4-phenyl-3-tosylpyridin-1(2H)-yl)ethan-1-one (3l)

![Chemical structure of 3l](image)

Yellow solid; mp 156.8-158.3 °C; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.99 – 7.94 (m, 1H), 7.87 (dd, $J$ = 8.8, 3.4 Hz, 2H), 7.53 – 7.49 (m, 5H), 7.45 (t, $J$ = 7.7 Hz, 1H), 7.38 – 7.34 (m, 3H), 7.24 (d, $J$ = 6.5 Hz, 2H), 7.19 (d, $J$ = 8.1 Hz, 2H), 6.03 (s, 1H), 5.17 (s, 2H), 2.38 (s, 3H), 1.51 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 170.38, 144.94, 144.02, 142.65, 138.38, 135.94, 134.14, 133.68, 130.42, 130.26, 129.49, 128.94, 128.51, 128.34, 127.95, 127.82, 127.62, 126.51, 125.33, 123.83, 121.13, 43.33, 23.86, 21.60.

1-(6-tert-butyl-4-phenyl-3-tosylpyridin-1(2H)-yl)ethanone (3m)

Amorphous solid; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.30 (t, $J$ = 8.4 Hz, 3H), 7.28 (dt, $J$ = 16.2, 7.8 Hz, 6H), 7.24 (d, $J$ = 7.5 Hz, 2H), 7.08 (t, $J$ = 6.4 Hz, 4H), 5.98 (s, 1H), 4.47 (s, 2H), 2.35 (s, 3H), 2.24 (s, 3H), 1.25 (s, 9H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 172.63, 160.29, 145.91, 143.92, 138.15, 135.92, 129.34, 128.53, 128.41, 127.78, 127.43, 127.34, 120.09, 46.96, 37.58, 31.01, 22.42, 21.52.

HRMS (ESI, m/z): Calcd. For C$_{24}$H$_{27}$NSO$_3$H [M+H]$^+$ 410.1784, found: 410.1784.

1-(5-ethyl-4,6-diphenyl-3-tosylpyridin-1(2H)-yl)ethanone (3n)

Yellow solid; mp 48.9-50.8 °C; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.36 (dd, $J$ = 19.8, 7.4 Hz, 6H), 7.33 – 7.25 (m, 4H), 7.09 (d, $J$ = 6.0 Hz, 4H), 4.98 (s, 2H), 2.35 (s, 3H), 2.06 (dd, $J$ = 14.5, 7.2 Hz, 2H), 1.90 – 1.13 (m, 3H), 0.58 (t, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 170.95, 147.55, 143.72, 138.79, 135.91, 134.20, 131.05, 130.07, 129.62, 129.23, 129.02, 128.61, 128.42, 128.27, 127.54, 127.41, 43.43, 23.84, 21.56, 21.51, 14.62.

HRMS (ESI, m/z): Calcd. For C$_{28}$H$_{27}$NSO$_3$Na [M+Na]$^+$ 480.1604, found: 480.1606.

1-(5-methyl-4,6-diphenyl-3-tosylpyridin-1(2H)-yl)ethan-1-one (3o)

Yellow solid; mp 167.2-169.0 °C; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.42 – 7.29 (m, 10H), 7.11 (d, $J$ = 8.0 Hz, 2H), 7.04 (d, $J$ = 7.2 Hz, 2H), 5.00 (s, 2H), 2.36 (s, 3H),
1.51 (d, $J = 59.5$ Hz, 6H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 171.02, 147.84, 143.82, 139.35, 138.74, 136.12, 134.56, 129.97, 129.28, 129.19, 129.01, 128.58, 128.40, 128.19, 128.01, 127.97, 127.73, 127.48, 123.65, 42.55, 23.81, 21.57, 16.42.

HRMS (ESI, m/z): Calcd. For C$_{27}$H$_{25}$NSO$_3$Na [M+Na]$^+$ 466.1447, found: 466.1445.

1-(4-methyl-6-phenyl-3-tosylpyridin-1(2H)-yl)ethanone (3p)

Yellow solid; mp 173.1-174.3 °C; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.84 (d, $J = 8.0$ Hz, 2H), 7.39 (s, 5H), 7.33 (d, $J = 8.0$ Hz, 2H), 6.00 (s, 1H), 4.80 (s, 2H), 2.42 (s, 3H), 2.32 (s, 3H), 1.56 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 171.01, 144.24, 142.25, 138.90, 136.12, 129.87, 129.13, 127.13, 127.01, 119.66, 43.09, 24.02, 21.63, 17.59.

HRMS (ESI, m/z): Calcd. For C$_{21}$H$_{21}$NSO$_3$Na [M+Na]$^+$ 390.1134, found: 390.1133.

1-(4,6-diphenyl-3-tosylpyridin-1(2H)-yl)ethanone (3q)

Yellow solid; mp 63.0-65.2 °C; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.45 (d, $J = 5.4$ Hz, 2H), 7.36 (dd, $J = 31.5, 9.7$ Hz, 8H), 7.20 – 7.12 (m, 4H), 6.09 (s, 1H), 4.99 (s, 2H), 2.37 (s, 3H), 1.68 (s, 2H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 171.07, 144.98, 144.21, 143.96, 138.38, 136.09, 135.89, 129.92, 129.39, 129.11, 128.50, 128.38, 127.91, 127.55, 127.06, 119.04, 43.50, 24.12, 21.58.

HRMS (ESI, m/z): Calcd. For C$_{26}$H$_{23}$NSO$_3$Na [M+Na]$^+$ 452.1291, found: 452.1290.

2-(1-acetyl-6-phenyl-3-tosyl-1,2-dihydropyridin-4-yl)benzonitrile (3r)
Yellow solid; mp 46-45.2 °C; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.66 (tt, $J = 8.1$, 4.1 Hz, 1H), 7.62 (d, $J = 7.6$ Hz, 1H), 7.52 (td, $J = 15.9$, 7.6 Hz, 4H), 7.45 (d, $J = 7.8$ Hz, 2H), 7.41 – 7.36 (m, 3H), 7.23 (d, $J = 8.0$ Hz, 2H), 6.05 (s, 1H), 5.39 (s, 1H), 4.67 – 4.49 (m, 1H), 2.39 (s, 3H), 1.64 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 171.61, 145.45, 144.64, 141.11, 139.82, 137.29, 135.79, 132.30, 132.24, 130.80, 130.37, 129.69, 129.22, 128.89, 127.59, 127.48, 125.74, 116.94, 116.70, 111.33, 43.16, 24.10, 21.64.

HRMS (ESI, m/z): Calcd. For C$_{27}$H$_{22}$N$_2$SO$_3$Na [M+Na]$^+$ 477.1243, found: 477.1244.

1-(6-phenyl-4-m-tolyl-3-tosylpyridin-1(2H)-yl)ethanone (3s)

Yellow solid; mp 54.7-55.2 °C; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.44 (d, $J = 5.8$ Hz, 2H), 7.41 (dd, $J = 6.7$, 3.1 Hz, 2H), 7.38 (s, 3H), 7.22 (t, $J = 7.6$ Hz, 1H), 7.17 – 7.12 (m, 3H), 6.99 (d, $J = 7.5$ Hz, 1H), 6.85 (s, 1H), 6.09 (s, 1H), 5.01 (s, 2H), 2.37 (s, 3H), 2.31 (s, 3H), 1.68 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 171.12, 145.23, 143.86, 138.53, 137.53, 136.07, 135.77, 129.88, 129.29, 129.18, 129.10, 128.71, 127.87, 127.57, 127.04, 125.50, 119.09, 43.50, 24.12, 21.55, 21.32.

HRMS (ESI, m/z): Calcd. For C$_{27}$H$_{25}$NSO$_3$Na [M+Na]$^+$ 466.1447, found: 466.1450.

1-(6-phenyl-4-(thiophen-2-yl)-3-tosylpyridin-1(2H)-yl)ethan-1-one (3t)
Yellow solid; mp 114.5-116.2 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.38 (d, $J = 7.8$ Hz, 2H), 7.33 (ddd, $J = 13.4$, 8.1, 3.9 Hz, 7H), 7.05 (d, $J = 8.1$ Hz, 2H), 6.98 – 6.93 (m, 1H), 6.06 (s, 1H), 4.96 (s, 2H), 2.27 (s, 3H), 1.61 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 171.08, 144.77, 144.02, 138.14, 138.00, 135.81, 135.41, 131.45, 130.14, 129.35, 129.17, 127.98, 127.40, 127.21, 127.15, 118.81, 44.11, 24.09, 21.63.

HRMS (ESI, m/z): Calcd. For C$_{24}$H$_{21}$NS$_{2}$O$_{3}$Na $[M+Na]^+$ 458.0855, found: 458.0859.

1-(3-(4-iodophenylsulfonyl)-4,6-diphenylpyridin-1(2H)-yl)ethanone (4a)

Yellow solid; mp 170.5-172.1 °C; $^1$H NMR (600 MHz, CDCl$_3$) δ 7.68 (d, $J = 8.1$ Hz, 2H), 7.40 (dd, $J = 16.6$, 7.1 Hz, 6H), 7.33 (t, $J = 7.1$ Hz, 2H), 7.20 (s, 2H), 7.13 (d, $J = 7.1$ Hz, 2H), 6.08 (s, 1H), 5.04 (s, 2H), 1.69 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 171.19, 146.06, 144.78, 141.14, 137.95, 135.93, 135.60, 130.20, 129.23, 128.81, 128.78, 128.44, 128.07, 127.21, 118.84, 100.90, 43.43, 24.22.

HRMS (ESI, m/z): Calcd. For C$_{25}$H$_{20}$NISO$_{3}$Na $[M+Na]^+$ 564.0101, found: 564.0101.

1-(3-((4-bromophenyl)sulfonyl)-4,6-diphenylpyridin-1(2H)-yl)ethan-1-one (4b)

Yellow solid; mp 125.2-126.9 °C; $^1$H NMR (600 MHz, CDCl$_3$) δ 7.46 (d, $J = 8.4$ Hz, 2H), 7.44 – 7.31 (m, 10H), 7.13 (d, $J = 7.2$ Hz, 2H), 6.09 (s, 1H), 5.04 (s, 2H), 1.70 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 171.15, 146.00, 144.69, 140.44, 135.91, 135.57, 131.94, 130.15, 129.19, 128.97, 128.75, 128.42, 128.21, 128.04, 127.17, 118.80, 77.25, 77.04, 76.83, 43.22, 24.16.

HRMS (ESI, m/z): Calcd. For C$_{25}$H$_{20}$NBrSO$_{3}$Na $[M+Na]^+$ 516.0239, found: 516.0241.
1-(3-((4-chlorophenyl)sulfonyl)-4,6-diphenylpyridin-1(2H)-yl)ethan-1-one (4c)

Yellow solid; mp 136.4-138.1 °C; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.41 (dq, $J = 25.6, 7.6$ Hz, 8H), 7.33 (t, $J = 7.4$ Hz, 2H), 7.30 (d, $J = 8.3$ Hz, 2H), 7.14 (d, $J = 7.3$ Hz, 2H), 6.09 (s, 1H), 5.04 (s, 2H), 1.66 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 171.19, 146.01, 144.73, 139.91, 139.64, 135.93, 135.60, 130.17, 129.22, 128.98, 128.93, 128.78, 128.45, 128.07, 127.20, 118.83, 43.46, 24.13. HRMS (ESI, m/z): Calcd. For C$_{25}$H$_{20}$NClSO$_3$Na [M+Na]$^+$ 472.0745, found: 472.0747.

1-(3-((4-fluorophenyl)sulfonyl)-4,6-diphenylpyridin-1(2H)-yl)ethan-1-one (4d)

Yellow solid; mp 90.5-92.1 °C; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.52 (s, 2H), 7.45 – 7.36 (m, 6H), 7.34 (t, $J = 7.3$ Hz, 2H), 7.15 (d, $J = 7.2$ Hz, 2H), 7.00 (t, $J = 8.3$ Hz, 2H), 6.09 (s, 1H), 5.04 (s, 2H), 1.69 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 175.24, 171.23, 165.325 ($J = 253.5$), 145.77, 144.46, 137.41, 135.92, 135.65, 130.35, 130.27 ($J = 10.5$), 129.21, 128.74, 128.45, 128.06, 127.17, 118.87, 115.96 ($J = 22.5$), 43.45, 24.15. $^{19}$F NMR (565 MHz, CDCl$_3$) $\delta$ -104.32. HRMS (ESI, m/z): Calcd. For C$_{25}$H$_{20}$NF$_3$O$_3$H [M+Na]$^+$ 456.1040, found: 456.1041.

1-(4,6-diphenyl-3-(4-(trifluoromethyl)phenylsulfonyl)pyridin-1(2H)-yl)ethanone (4e)
Yellow solid; mp 138.4-139.9 °C; $^1$H NMR (600 MHz, CDCl$_3$) δ 7.60 (s, 2H), 7.57 (d, $J = 7.8$ Hz, 2H), 7.40 (t, $J = 13.2$ Hz, 6H), 7.31 (t, $J = 7.3$ Hz, 2H), 7.11 (d, $J = 7.3$ Hz, 2H), 6.09 (s, 1H), 5.09 (s, 2H), 1.72 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 171.18, 146.68, 145.28, 145.00, 135.84, 135.40, 134.46 ($J = 33$ Hz), 130.28, 129.24, 128.87, 128.45, 128.10, 127.97, 127.24, 125.72 ($J = 3$ Hz), 123.17 ($J = 273$ Hz), 118.63, 43.39, 24.13. $^{19}$F NMR (565 MHz, CDCl$_3$) δ -63.19.

HRMS (ESI, m/z): Calcd. For C$_{26}$H$_{20}$F$_3$NSO$_3$Na [M+Na]$^+$ 506.1008, found: 506.1006.

1-(3-(4-nitrophensulfonyl)-4,6-diphenylpyridin-1(2H)-yl)ethanone (4f)

Yellow solid; mp 166.5-168.0 °C; $^1$H NMR (600 MHz, CDCl$_3$) δ 8.14 (d, $J = 8.4$ Hz, 2H), 7.65 (d, $J = 8.0$ Hz, 2H), 7.46 – 7.38 (m, 6H), 7.33 (t, $J = 7.4$ Hz, 2H), 7.13 (d, $J = 7.6$ Hz, 2H), 6.11 (s, 1H), 5.10 (s, 2H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 171.21, 150.08, 147.40, 147.06, 145.59, 135.71, 135.21, 130.45, 129.29, 129.10, 128.70, 128.51, 128.16, 127.30, 123.77, 118.56, 43.28, 24.16.

HRMS (ESI, m/z): Calcd. For C$_{25}$H$_{20}$N$_2$SO$_5$Na [M+Na]$^+$ 483.0985, found: 483.0984.

4-((1-acetyl-4,6-diphenyl-1,2-dihydropyridin-3-yl)sulfonyl)benzonitrile (4g)

Yellow solid; mp 152.3-153.7 °C; $^1$H NMR (600 MHz, CDCl$_3$) δ 7.60 (d, $J = 7.7$ Hz, 4H), 7.41 (dt, $J = 11.6, 7.6$ Hz, 6H), 7.33 (t, $J = 7.5$ Hz, 2H), 7.12 (d, $J = 7.3$ Hz, 2H), 6.10 (s, 1H), 5.08 (s, 2H), 1.69 (d, $J = 22.0$ Hz, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 171.22, 147.20, 145.55, 135.75, 135.27, 132.38, 130.43, 129.29, 129.04, 128.52, 128.16, 128.03, 127.30, 118.59, 118.59, 117.32, 116.49, 43.36, 24.17.
1-(4-((1-acetyl-4,6-diphenyl-1,2-dihydropyridin-3-yl)sulfonyl)phenyl)ethan-1-one (4h)

Yellow solid; mp 112.4-114.2 °C; \( ^1H \text{NMR (600 MHz, CDCl}_3 \) δ 7.89 (d, \( J = 8.1 \text{ Hz}, 2H), 7.61 (d, \( J = 7.0 \text{ Hz}, 2H), 7.46 - 7.36 (m, 6H), 7.32 (t, \( J = 7.4 \text{ Hz}, 2H), 7.14 (d, \( J = 7.3 \text{ Hz}, 2H), 6.10 (s, 1H), 5.06 (s, 2H), 2.61 (s, 3H), 1.68 (s, 3H). \( ^13C \text{NMR (151 MHz, CDCl}_3 \) δ 196.87, 171.16, 146.61, 145.24, 144.97, 140.10, 135.88, 135.50, 130.24, 129.23, 128.84, 128.48, 128.06, 127.77, 127.23, 118.80, 43.38, 26.92, 24.05.

HRMS (ESI, m/z): Calcd. For C\(_{27}\)H\(_{23}\)NSO\(_4\)H [M+H]\(^+\) 458.1421, found: 458.1426.

1-(3-(4-methoxyphenylsulfonyl)-4,6-diphenylpyridin-1(2H)-yl)ethanone (4i)

Yellow solid; mp 47.5-49.2 °C; \( ^1H \text{NMR (400 MHz, CDCl}_3 \) δ 7.47 (d, \( J = 8.0 \text{ Hz}, 2H), 7.36 (dd, \( J = 16.7, 6.6 \text{ Hz}, 8H), 7.17 (d, \( J = 7.2 \text{ Hz}, 2H), 6.81 (d, \( J = 8.5 \text{ Hz}, 2H), 6.08 (s, 1H), 5.00 (s, 2H), 3.81 (s, 3H), 1.67 (s, 3H). \( ^13C \text{NMR (101 MHz, CDCl}_3 \) δ 171.16, 163.29, 144.64, 143.96, 136.05, 135.97, 132.90, 129.96, 129.74, 129.16, 128.54, 128.43, 127.99, 127.09, 119.10, 114.02, 55.68, 43.54, 24.18.

HRMS (ESI, m/z): Calcd. For C\(_{27}\)H\(_{23}\)NO\(_4\)Na [M+Na]\(^+\) 468.1240, found: 468.1242.

1-(3-((4-(methylthio)phenyl)sulfonyl)-4,6-diphenylpyridin-1(2H)-yl)ethan-1-one (4j)
Yellow solid; mp 144.1-146.3 °C; $^1$H NMR (600 MHz, CDCl$_3$) δ 7.46 – 7.31 (m, 10H), 7.15 (dd, $J = 19.0$, 7.6 Hz, 4H), 6.09 (s, 1H), 5.02 (s, 2H), 2.48 (s, 3H), 1.68 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 171.13, 146.35, 145.16, 144.27, 137.06, 136.02, 135.85, 129.97, 129.14, 128.56, 128.40, 127.97, 127.77, 127.10, 124.96, 119.01, 43.45, 24.16, 14.76.

HRMS (ESI, m/z): Calcd. For C$_{26}$H$_{23}$NS$_2$O$_3$Na [M+Na]$^+$ 484.1015, found: 484.1015.

1-(3-(3-chlorophenylsulfonyl)-4,6-diphenylpyridin-1(2H)-yl)ethanone (4k)

Yellow solid; mp 51.0-52.9 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.49 – 7.37 (m, 9H), 7.37 – 7.31 (m, 2H), 7.29 (d, $J = 9.0$ Hz, 1H), 7.15 (d, $J = 7.4$ Hz, 2H), 6.11 (s, 1H), 5.06 (s, 2H), 1.73 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 171.20, 146.41, 145.00, 143.01, 135.90, 135.32, 134.82, 133.12, 130.23, 130.08, 129.24, 128.97, 128.43, 128.09, 127.70, 127.21, 125.52, 118.71, 43.41, 24.21.

HRMS (ESI, m/z): Calcd. For C$_{25}$H$_{20}$NCISO$_3$Na [M+Na]$^+$ 472.0745, found: 472.0746.

1-(3-(2-chlorophenylsulfonyl)-4,6-diphenylpyridin-1(2H)-yl)ethanone (4l)

Yellow solid; mp 80.2-81.7 °C; $^1$H NMR (600 MHz, CDCl$_3$) δ 7.44 (d, $J = 3.2$ Hz, 2H), 7.41 (d, $J = 7.9$ Hz, 4H), 7.30 (t, $J = 8.2$ Hz, 2H), 7.18 (t, $J = 7.2$ Hz, 1H), 7.11 (t, $J = 7.4$ Hz, 2H), 7.04 (d, $J = 7.2$ Hz, 2H), 6.97 (t, $J = 6.9$ Hz, 1H), 6.09 (s, 1H), 5.14 (s, 2H), 1.72 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 171.29, 145.14, 138.04, 136.22,
2,4-diphenyl-5-tosylpyridine (5q)

White solid; mp 147.2-148.9 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 9.54 (s, 1H), 8.05 (dd, \(J = 7.4\), 2.2 Hz, 2H), 7.56 (s, 1H), 7.48 (dd, \(J = 8.6\), 3.1 Hz, 3H), 7.41 (t, \(J = 7.5\) Hz, 1H), 7.30 (t, \(J = 7.7\) Hz, 2H), 7.19 (d, \(J = 8.3\) Hz, 2H), 7.08 (d, \(J = 7.2\) Hz, 2H), 7.03 (d, \(J = 8.1\) Hz, 2H), 2.34 (s, 3H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 160.96, 150.85, 149.61, 144.02, 137.59, 137.37, 136.24, 134.35, 130.45, 129.26, 129.18, 128.99, 128.63, 127.98, 127.68, 127.48, 123.00, 21.56.

HRMS (ESI, m/z): Calcd. For C\(_{24}\)H\(_{19}\)NSO\(_2\)H [M+H]\(^+\) 386.1209, found: 386.1217.
References


6. NMR spectra