Supporting Information for

Organoselenium-Catalyzed Aza-Wacker Reaction: Efficient Access to Isoquinolinium Imides and Isoquinoline-N-Oxides

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Contents

1. General Methods S2
2. Procedures for the Preparation of Substrates S3
4. Further Transformations of Isoquinolinium Imide 2e S14
5. Characterization Data for Products S15
6. NMR Spectra for Substrates and Products S23
1. General Methods

Unless otherwise stated, commercial reagents were purchased from Alfa, Aladdin, J&K, Energy or Adamas, and used without further purification. THF was distilled from sodium prior to use. MeCN was distilled from calcium hydride. All catalytic reactions carried out using pre-dried glassware without special care. Analytical thin layer chromatography was performed on 0.20 mm silica gel HSGF-254 plates (Huanghai, China), and visualized under 254 nm UV light or by staining with potassium permanganate. Preparative thin layer chromatography was performed on 0.9 mm-1.0 mm silica gel HSGF-254 plates (Huanghai, China). Column chromatography was performed on 200-300 mesh silica gel (Huanghai, China).

$^1$H, $^{13}$C{$^1$H} and $^{19}$F NMR spectra were recorded on Brucker ARX 400 MHz spectrometer at ambient temperature. All NMR spectra are referenced to the residual solvent signal. Data for $^1$H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), integration. Data for $^{13}$C{$^1$H} NMR and $^{19}$F NMR are reported as follows: chemical shift (δ ppm), multiplicity (d = doublet, t = triplet, q = quartet), coupling constant (Hz). High resolution mass spectra of new compounds were recorded on LTQ Orbitrap Elite LC/MS (ESI) at analytical center of Sun Yat-Sen University, and Guangzhou Micromon Technology Services CO. LTD.
2. Procedures for the Preparation of Substrates

![Chemical Structures]

Method A:

\[
\text{R}^1\text{C} = \text{C}
\]

\[
\text{R}^2\text{C} = \text{C} + \text{OH}
\]

\[
\text{Pd}(\text{PPh}_3)_4, \text{K}_2\text{CO}_3, \text{reflux}
\]

Toluene/EtOH/H_2O, 24 h

Step 1

Method B:

\[
\text{R}^1\text{C} = \text{C} + \text{Br}
\]

\[
\text{R}^2\text{C} = \text{C} + \text{OH}
\]

\[
\text{Pd}(\text{OAc})_2, \text{PPh}_3, \text{K}_2\text{CO}_3
\]

THF/H_2O, 24 h, 90 °C

Step 1

Method C:

\[
\text{R}^1\text{C} = \text{C} + \text{Br}
\]

\[
\text{R}^2\text{C} = \text{C} + \text{OH}
\]

\[
\text{Pd}(\text{OAc})_2, \text{K}_3\text{PO}_4
\]

DMF, 1 h, 140 °C

Step 1
Method A:
Step 1: In a 50-mL Schlenk flask equipped with a magnetic stir bar were subsequently added Pd(PPh$_3$)$_4$ (5 mol%), vinyl boronic acid (1.5 equiv), and K$_2$CO$_3$ (4.0 equiv). The flask was evacuated and flushed with nitrogen three times. Then, toluene-EtOH-H$_2$O (5:2:1, v/v/v) and aldehyde (1.0 equiv) were added. The mixture was refluxed for 24 h and then cooled to room temperature, in which the mixture was diluted with water and extracted with Et$_2$O (15 mL x 3). The combined organic layers were dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by chromatography on silica gel to afford the product for the next step.

Method B:
Step 1: In a 50-mL Schlenk flask equipped with a magnetic stir bar were subsequently added Pd(OAc)$_2$ (5.0 mol%), PPh$_3$ (15 mol%), and K$_2$CO$_3$ (1.3 equiv). The flask was evacuated and flushed with nitrogen three times. Then, THF-H$_2$O (1.0:1.5, v/v), aldehyde (1.0 equiv), and vinylboronate (1.2 equiv) were added. The resulting mixture was stirred at 90 °C for 24 h and then cooled to room temperature, in which the mixture was diluted with water and extracted with Et$_2$O (15 mL x 3). The combined organic layers were dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by chromatography on silica gel to afford the product for the next step.

Method C:
Step 1: In a 50-mL Schlenk flask equipped with a magnetic stir bar were subsequently added K$_3$PO$_4$ (1.5 equiv) and Pd(OAc)$_2$ (10 mol%). The flask was evacuated and flushed with nitrogen three times. Then, DMF, aldehyde (1.0 equiv), and styrene (10 equiv) were added. The resulting mixture was stirred at 140 °C for 1 h and then cooled to room temperature. Water was added. The mixture was extracted with ethyl acetate (15 mL x 3). The combined organic layers were dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by chromatography on silica gel to afford the product for the next step.

Step 2: To a stirred solution of pure 4-methylbenzenesulfonylhydrazide in methanol (0.5 M) was added aldehyde (1.0 equiv) at room temperature. The solution was stirred at room temperature for 3 h. Then, the solution was cooled to 0 °C. The product was crystallized from the solution. By filtration, the product was collected and used without further purification.
Compounds 1e<sup>5</sup> and 3<sup>6</sup> are known and prepared on the basis of the literature procedure.

\((E)-N'-(2-((E)-Styryl)benzylidene)benzohydrazide\) (1d)

\[
\text{Prepared by the Method A: (E)-styrylboronic acid (1.33 g, 1.5 equiv), Pd(PPh}_3)_4 (0.35 g, 5 mol%), and K}_2\text{CO}_3 (0.33 g, 4.0 equiv), toluene (18.0 mL), EtOH (7.0 mL), H}_2\text{O (4.0 mL), 2-bromobenzaldehyde (700 }\mu\text{L, 5 mmol, 1.0 equiv). }
\]

**Step 1:** The crude residue was purified by chromatography (eluent: PE/EA = 80:1 to 50:1, v/v). 1.03 g, 82% yield, a light yellow oil.

**Step 2:** 159.7 mg, 49% yield, a white solid.

\(^1\text{H NMR (400 MHz, d}_6\text{-DMSO) }\delta = 11.84 \text{ (s, 1H), 8.92 \text{ (s, 1H), 7.98 - 7.87 \text{ (m, 3H), 7.83 - 7.74 \text{ (m, 2H), 7.68 \text{ (d, } J = 7.6 \text{ Hz, 2H, 7.64 - 7.51 \text{ (m, 3H), 7.50 - 7.28 \text{ (m, 5H), 7.18 \text{ (d, } J = 16.1 \text{ Hz, 1H).}}}}
\]

\(^1\text{3C NMR (101 MHz, d}_6\text{-DMSO) }\delta = 163.01, 146.22, 137.05, 136.70, 133.42, 131.99, 131.78, 131.34, 129.99, 128.72, 128.50, 128.02, 127.78, 127.58, 126.78, 126.63, 125.02.\]

HR-ESI-MS m/z calcd for C\text{\textsubscript{22}}H\text{\textsubscript{18}}N\text{\textsubscript{2}}O\text{Na [M+Na]}\textsuperscript{+}: 349.1311, found: 349.1308.

\((E)-4-\text{Methyl-N'-(2-((E)-4-methylstyryl)benzylidene)benzenesulphonohydrazide}\) (1f)

\[
\text{Prepared by the Method B: (E)-4,4,5,5-tetramethyl-2-(4-methylstyryl)-1,3,2-dioxaborolane (966.8 mg, 1.2 equiv), 2-bromobenzaldehyde (385 }\mu\text{L, 3.3 mmol, 1.0 equiv), Pd(OAc)}_2 (37.0 mg, 5 mol%), PPh}_3 (129.8 mg, 15 mol%), K}_2\text{CO}_3 (592.9 mg, 1.3 equiv), THF (15.0 mL), H}_2\text{O (7.5 mL). }
\]

**Step 1:** The crude residue was purified by chromatography (eluent: PE/EA = 30:1, v/v). 482.6 mg, 66% yield, a light yellow oil.

**Step 2:** 558.1 mg, 66% yield, a white solid.

\(^1\text{H NMR (400 MHz, CDCl}_3) \delta = 8.10 \text{ (s, 1H), 7.84 \text{ (d, } J = 8.2 \text{ Hz, 2H), 7.67 \text{ (d, } J = 7.8 \text{ Hz, 1H), 7.55 - 7.44 \text{ (m, 2H), 7.42 - 7.31 \text{ (m, 3H), 7.25 - 7.13 \text{ (m, 5H), 6.85 \text{ (d, } J = 16.1 \text{ Hz, 1H), 2.36 \text{ (s, 6H).}}}
\]

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\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta = 147.17, 144.33, 138.20, 137.71, 135.39, 134.42, 132.89, 129.79, 129.61, 128.19, 128.12, 127.51, 127.08, 126.97, 126.85, 124.69, 21.71, 21.42.

HR-ESI-MS m/z calcd for C\(_{23}\)H\(_{22}\)N\(_2\)O\(_2\)S\(_2\)Na [M+Na]\(^+\): 413.1294, found: 413.1291.

\((E)\)-\(N'\)-(2-((\(E\))-4-Methoxystyryl)benzylidene)-4-methylbenzenesulfonohydrazide (1g)

Prepared by the Method B: Pd(OAc)\(_2\) (10.4 mg, 5 mol\%), PPh\(_3\) (46.0 mg, 15 mol\%), K\(_2\)CO\(_3\) (210.2 mg, 1.3 equiv), THF (4.0 mL), H\(_2\)O (6.0 mL), (\(E\))-2-(4-methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (363.7 mg, 1.2 equiv), 2-bromobenzaldehyde (137 \(\mu\)L, 1.2 mmol, 1.0 equiv).

**Step 1:** The crude residue was purified by chromatography (eluent: PE/EA = 30:1, v/v). 260.4 mg, 93% yield, a light yellow oil.

**Step 2:** 320.2 mg, 80% yield, a white solid.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 8.11 (s, 1H), 8.03 (s, 1H), 7.83 (d, \(J = 8.3\) Hz, 2H), 7.66 (d, \(J = 7.7\) Hz, 1H), 7.52 (d, \(J = 7.8\) Hz, 1H), 7.48 – 7.29 (m, 4H), 7.22 (d, \(J = 8.1\) Hz, 2H), 6.90 (d, \(J = 8.7\) Hz, 2H), 6.83 (d, \(J = 16.1\) Hz, 1H), 3.82 (s, 3H), 2.36 (s, 3H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta = 159.65, 147.18, 144.21, 137.73, 135.27, 132.33, 130.22, 130.09, 129.90, 129.65, 128.10, 128.07, 127.98, 127.20, 126.84, 123.43, 114.21, 55.35, 21.57.

HR-ESI-MS m/z calcd for C\(_{23}\)H\(_{22}\)N\(_2\)O\(_2\)S\(_2\)Na [M+Na]\(^+\): 429.1243, found: 429.1238.

\((E)\)-\(N'\)-(2-((\(E\))-4-Fluorostyryl)benzylidene)-4-methylbenzenesulfonohydrazide (1h)

Prepared by the Method B: (\(E\))-2-(4-fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (465.5 mg, 1.2 equiv), 2-bromobenzaldehyde (183 \(\mu\)L, 1.6 mmol, 1.0 equiv), Pd(OAc)\(_2\) (17.6 mg, 5 mol\%), PPh\(_3\) (61.8 mg, 15 mol\%), K\(_2\)CO\(_3\) (282.1 mg, 1.3 equiv), THF (4.0 mL), H\(_2\)O (6.0 mL).

**Step 1:** The crude residue was purified by chromatography (eluent: PE/EA = 30:1, v/v). 189.7 mg, 53% yield, a light yellow oil.

**Step 2:** 192.7 mg, 58% yield, a white solid.
\[ ^1H \text{ NMR (400 MHz, CDCl}_3 \] \delta = 8.13 (d, J = 9.7 Hz, 2H), 7.82 (d, J = 7.5 Hz, 2H), 7.64 (d, J = 7.3 Hz, 1H), 7.58 – 7.32 (m, 5H), 7.21 (d, J = 7.4 Hz, 2H), 7.05 (t, J = 7.9 Hz, 2H), 6.85 (d, J = 16.1 Hz, 1H), 2.36 (s, 3H).
\[ ^{13}C \text{ NMR (101 MHz, CDCl}_3 \] \delta = 162.71 (d, \ J_{C-F} = 247.9 \text{ Hz}), 147.27, 144.37, 137.36, 135.44, 133.47 (d, \ J_{C-F} = 2.9 \text{ Hz}), 131.48, 130.48, 130.37, 129.79, 128.55, 128.47, 128.09, 127.73, 127.08, 125.84 (d, \ J_{C-F} = 2.2 \text{ Hz}), 115.85 (d, \ J_{C-F} = 21.7 \text{ Hz}), 21.71.

HR-ESI-MS m/z calcd for C\textsubscript{22}H\textsubscript{20}FN\textsubscript{2}O\textsubscript{2}S [M+H\textsuperscript{+}]: 395.1224, found: 395.1215.

\( (E)-N'(2-((E)-4-Chlorostyryl)benzylidene)-4-methylbenzenesulfonohydrazide (\text{1i}) \)

\[
\begin{align*}
\text{Prepared by the Method B: (E)-2-(4-chlorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (315.5 mg, 1.2 equiv), 2-bromobenzaldehyde (116 \mu L, 1.0 \text{ mmol, 1.0 equiv), Pd(OAc)}_2 (11.2 \text{ mg, 5 mol\%), PPh}_3 (39.2 \text{ mg, 15 mol\%), K}_2\text{CO}_3 (178.8 \text{ mg, 1.3 equiv), THF (5.0 mL), H}_2\text{O (3.0 mL).}
\end{align*}
\]

**Step 1:** The crude residue was purified by chromatography (eluent: PE/EA = 50:1, v/v). 205.1 mg, 85% yield, a light yellow oil.

**Step 2:** 232.8 mg, 67% yield, a white solid.

\[ ^1H \text{ NMR (400 MHz, CDCl}_3 \] \delta = 8.40 (s, 1H), 8.14 (s, 1H), 7.82 (d, J = 7.6 Hz, 2H), 7.67 – 7.50 (m, 3H), 7.44 (d, J = 7.7 Hz, 2H), 7.39 – 7.27 (m, 3H), 7.22 – 7.16 (m, 2H), 6.83 (d, J = 16.1 Hz, 1H), 2.36 (s, 3H).
\[ ^{13}C \text{ NMR (101 MHz, CDCl}_3 \] \delta = 147.14, 144.26, 136.98, 135.65, 135.24, 133.58, 131.08, 130.44, 129.67, 128.69, 128.89, 128.47, 128.00, 127.93, 127.73, 126.90, 126.53, 21.58.

HR-ESI-MS m/z calcd for C\textsubscript{22}H\textsubscript{19}CIN\textsubscript{2}O\textsubscript{2}SNa [M+Na\textsuperscript{+}]: 433.0748, found: 433.0746.

\( (E)-N'(2-((E)-4-Bromostyryl)benzylidene)-4-methylbenzenesulfonohydrazide (\text{1j}) \)

\[
\begin{align*}
\text{Prepared by the Method B: (E)-2-(4-bromostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (255.4 mg, 1.2 equiv), 2-bromobenzaldehyde (94 \mu L, 0.8 \text{ mmol, 1.0 equiv), Pd(OAc)}_2 (9.0 \text{ mg, 5 mol\%), PPh}_3 (31.7 \text{ mg, 15 mol\%), K}_2\text{CO}_3 (144.8 \text{ mg, 1.3 equiv), THF (4.0 mL), H}_2\text{O (2.5 mL).}
\end{align*}
\]

**Step 1:** The crude residue was purified by chromatography (eluent: PE/EA = 50:1, v/v). 153.2 mg, 66% yield, a yellow oil.

**Step 2:** 95.3 mg, 39% yield, a yellow solid.
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 8.10\) (s, 2H), 7.81 (d, \(J = 7.9\) Hz, 2H), 7.66 – 7.58 (m, 2H), 7.54 (d, \(J = 7.6\) Hz, 1H), 7.46 (t, \(J = 10.0\) Hz, 2H), 7.41 – 7.17 (m, 5H), 6.82 (d, \(J = 16.1\) Hz, 1H), 2.37 (s, 3H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta = 147.07, 144.27, 136.97, 136.07, 135.25, 131.86, 131.19, 130.38, 129.66, 128.59, 128.27, 127.94, 127.77, 126.99, 126.72, 121.82, 21.59.

HR-ESI-MS m/z calcd for C\(_{22}\)H\(_{20}\)BrN\(_2\)O\(_3\)S\(^+\): 471.0378, found: 471.0369.

\((E)-4\)-Methyl-N\(^{-}\)-((2-(\((E)-4\)-trifluoromethyl)styryl)benzylidene)benzenesulfonohydrazide (1k)

Prepared by the Method B: (E)-4,4,5,5-tetramethyl-2-(4-(trifluoromethyl) styryl)-1,3,2-dioxaborolane (605.7 mg, 1.2 equiv), 2-bromobenzaldehyde (198 \(\mu\)L, 1.70 mmol, 1.0 equiv), Pd(OAc)$_2$ (19.1 mg, 5 mol%), PPh$_3$ (66.9 mg, 15 mol%), K$_2$CO$_3$ (305.4 mg, 1.3 equiv), THF (9.0 mL), H$_2$O (4.5 mL).

**Step 1:** The crude residue was purified by chromatography (eluent: PE/EA = 60:1, v/v). 448.6 mg, 96% yield, a light yellow solid.

**Step 2:** 561.6 mg, 78% yield, a white solid.

\(^1\)H NMR (400 MHz, CDCl$_3$) \(\delta = 8.11\) (s, 1H), 7.85 – 7.71 (m, 3H), 7.66 – 7.51 (m, 4H), 7.45 – 7.27 (m, 1H), 7.24 – 7.15 (m, 5H), 6.92 (d, \(J = 16.1\) Hz, 1H), 2.36 (s, 3H).

\(^{13}\)C NMR (101 MHz, d$_6$-DMSO) \(\delta = 189.31, 146.22, 143.42, 141.10, 136.20\) (d, \(J_{C-F} = 1.9\) Hz), 135.77, 130.98, 130.21, 129.96, 129.61, 128.29, 127.71, 127.42, 127.24, 127.16, 126.91, 125.53 (d, \(J_{C-F} = 3.6\) Hz), 124.21 (q, \(J_{C-F} = 259.2\) Hz), 20.95.


\((E)-4\)-Methyl-N\(^{-}\)-((2-((E)-2-methylstyryl)benzylidene)benzenesulfonohydrazide (1l)

Prepared by the Method B: (E)-4,4,5,5-tetramethyl-2-(2-methylstyryl) -1,3,2-dioxaborolane (649.1 mg, 1.2 equiv), 2-bromobenzaldehyde (284 \(\mu\)L, 2.43 mmol, 1.0 equiv), Pd(OAc)$_2$ (27.3 mg, 5 mol%), PPh$_3$ (95.6 mg, 15 mol%), K$_2$CO$_3$ (436.6 mg, 1.3 equiv), THF (13.0 mL), H$_2$O (6.5 mL).

**Step 1:** The crude residue was purified by chromatography (eluent: PE/EA = 50:1, v/v). 86.6 mg, 16% yield, a light yellow oil.

**Step 2:** 54.2 mg, 36% yield, a white solid.
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 8.12 (s, 1H), 7.91 – 7.80 (m, 3H), 7.70 (d, $J$ = 7.7 Hz, 1H), 7.63 – 7.47 (m, 2H), 7.42 – 7.05 (m, 8H), 2.41 (s, 3H), 2.38 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 146.95, 146.09, 144.33, 137.87, 136.26, 135.41, 133.14, 131.62, 130.95, 130.59, 130.40, 129.88, 128.11, 127.94, 127.74, 127.39, 127.05, 126.49, 125.86, 21.71, 20.03.

HR-ESI-MS m/z calcd for C$_{23}$H$_{33}$N$_2$O$_2$S [M+H]$^+$: 391.1475, found: 391.1472.

(E)-N$^\prime$-(2-((E)-3-Fluorostyryl)benzylidene)-4-methylbenzenesulfonohydrazide (1m)

Prepared by the Method B: (E)-2-(3-fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (324.9 mg, 1.2 equiv), 2-bromobenzaldehyde (127 $\mu$L, 1.0 mmol, 1.0 equiv), Pd(OAc)$_2$ (27.3 mg, 5 mol%), PPh$_3$ (11.2 mg, 15 mol%), K$_2$CO$_3$ (181.5 mg, 1.3 equiv), THF (6.0 mL), H$_2$O (3.0 mL).

**Step 1:** The crude residue was purified by chromatography (eluent: PE/EA = 50:1, v/v). 172.0 mg, 75% yield, a light yellow oil.

**Step 2:** 137.8 mg, 46% yield, a white solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 8.09 (s, 1H), 7.97 (s, 1H), 7.83 (d, $J$ = 8.0 Hz, 2H), 7.66 (d, $J$ = 7.6 Hz, 1H), 7.62 – 7.50 (m, 2H), 7.41 – 7.16 (m, 6H), 6.99 (t, $J$ = 7.7 Hz, 1H), 6.85 (d, $J$ = 16.1 Hz, 1H), 2.37 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 163.32 (d, $J_{C-F}$=246.3), 147.05, 144.46, 139.58 (d, $J_{C-F}$=8.0), 137.02, 135.40, 131.61, 130.57, 130.45, 130.43, 130.34, 129.83, 128.70, 128.11, 128.06, 127.38 (d, $J_{C-F}$=13.2), 122.81, 115.01 (d, $J_{C-F}$=21.7), 113.31 (d, $J_{C-F}$=22.0), 21.72.

HR-ESI-MS m/z calcd for C$_{22}$H$_{20}$FN$_2$O$_2$S [M+H]$^+$: 395.1224, found: 395.1227.

(E)-4-Methyl-N$^\prime$-(2-((E)-2-(thiophen-2-yl)vinyl)benzylidene)benzenesulfonohydrazide (1n)

Prepared by the Method B: (E)-4,4,5,5-tetramethyl-2-(2-(thiophen-2-yl)vinyl)-1,3,2-dioxaborolane (322.4 mg, 1.2 equiv), 2-bromobenzaldehyde (133 $\mu$L, 1.14 mmol, 1.0 equiv), Pd(OAc)$_2$ (12.8 mg, 5 mol%), PPh$_3$ (44.9 mg, 15 mol%), K$_2$CO$_3$ (204.8 mg, 1.3 equiv), THF (6.0 mL), H$_2$O (3.0 mL).

**Step 1:** The crude residue was purified by chromatography (eluent: PE/EA = 80:1, v/v). 177.2 mg, 73% yield, a light yellow solid.

**Step 2:** 221.9 mg, 68% yield, a light yellow solid.
1H NMR (400 MHz, CDCl3) δ = 8.09 (s, 2H), 7.87 (d, J = 8.2 Hz, 2H), 7.68 (d, J = 7.6 Hz, 1H), 7.49 (d, J = 7.8 Hz, 1H), 7.39 – 7.18 (m, 5H), 7.09 (d, J = 3.3 Hz, 1H), 7.06 – 6.97 (m, 2H), 2.37 (s, 3H).

13C NMR (101 MHz, CDCl3) δ = 146.59, 144.22, 142.41, 136.82, 135.28, 130.24, 130.19, 129.67, 128.04, 128.01, 127.72, 126.74, 126.72, 125.62, 125.11, 124.81, 21.59.

HR-ESI-MS m/z calcd for C20H18N2O2S2Na [M+Na]⁺: 405.0702, found: 405.0701.

(E)-N’-(2-((E)-Hex-1-en-1-yl)benzylidene)-4-methylbenzenesulfonylhydrazide (10)

Prepared by the Method B: (E)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (512.8 mg, 1.2 equiv), 2-bromobenzaldehyde (237 μL, 2.0 mmol), Pd(OAc)2 (22.8 mg, 5 mol%), PPh3 (79.9 mg, 15 mol%), K2CO3 (364.7 mg, 1.3 equiv), THF (6.0 mL), H2O (4.0 mL).

Step 1: The crude residue was purified by chromatography (eluent: PE/EA = 80:1, v/v). 346.7 mg, 91% yield, a light yellow oil.

Step 2: 162.2 mg, 25% yield, a white solid.

1H NMR (400 MHz, CDCl3) δ = 8.09 (s, 1H), 7.88 (d, J = 8.2 Hz, 2H), 7.71 (d, J = 7.6 Hz, 1H), 7.38 – 7.27 (m, 4H), 7.20 (t, J = 7.1 Hz, 1H), 6.64 (d, J = 15.6 Hz, 1H), 5.99 (dt, J = 15.5, 6.9 Hz, 1H), 2.41 (s, 3H), 2.20 (dt, J = 7.8, 4.0 Hz, 2H), 1.53 – 1.29 (m, 4H), 0.92 (t, J = 7.2 Hz, 3H).

13C NMR (101 MHz, CDCl3) δ = 147.00, 144.36, 138.23, 136.26, 135.51, 130.33, 129.81, 128.54, 128.11, 127.24, 127.13, 127.06, 126.27, 33.16, 31.52, 22.44, 21.73, 14.08.


(E)-4-Methyl-N’-(6-((E)-styryl)benzo[d][1,3]dioxol-5-yl)methylene)benzenesulfonohydrazide (1p)

Prepared by the Method B: (E)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (276.1 mg, 1.2 equiv), 6-bromobenzof[d][1,3]dioxole-5-carbaldehyde (229.0 mg, 1.0 mmol, 1.0 equiv), Pd(OAc)2 (11.2 mg, 5 mol%), PPh3 (39.3 mg, 15 mol%), K2CO3 (179.7 mg, 1.3 equiv), THF (6.0 mL), H2O (3.0 mL).

Step 1: The crude residue was purified by chromatography (eluent: PE/EA = 40:1 to 20:1, v/v). 158.1 mg, 63% yield, a yellow oil.

Step 2: 183.4 mg, 69% yield, a white solid.
$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 8.10$ (s, 1H), 7.97 (s, 1H), 7.84 (d, $J = 8.1$ Hz, 2H), 7.45 (d, $J = 7.4$ Hz, 2H), 7.39 – 7.29 (m, 4H), 7.28 – 7.21 (m, 2H), 6.96 (s, 1H), 6.77 (d, $J = 15.9$ Hz, 1H), 5.98 (s, 2H), 2.38 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 149.97$, 147.75, 146.31, 144.34, 137.06, 135.43, 133.07, 131.97, 129.81, 128.90, 128.16, 128.10, 126.77, 125.11, 124.56, 106.29, 106.12, 101.72, 21.72.

HR-ESI-MS m/z calcd for C$_{23}$H$_{20}$N$_2$O$_4$SNa [M+Na]$^+$: 443.1036, found: 443.1037.

$^{(E)}$-$^{N'}$-(2-Fluoro-6-((E)-styryl)benzylidene)-4-methylbenzenesulfonohydrazide (1q)

Prepared by the Method B: ($E$)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (276.1 mg, 1.2 equiv), 2-bromo-6-fluorobenzaldehyde (203.0 mg, 1.0 mmol, 1.0 equiv), Pd(OAc)$_2$ (11.2 mg, 5 mol%), PPh$_3$ (39.3 mg, 15 mol%), K$_2$CO$_3$ (179.7 mg, 1.3 equiv), THF (6.0 mL), H$_2$O (3.0 mL).

**Step 1:** The crude residue was purified by chromatography (eluent: PE/EA = 40:1, v/v). 202.3 mg, 89% yield, a light yellow oil.

**Step 2:** 251.6 mg, 71% yield, a white solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 8.14$ (s, 1H), 8.03 (d, $J = 16.3$ Hz, 1H), 7.73 (d, $J = 8.3$ Hz, 2H), 7.63 (d, $J = 7.4$ Hz, 2H), 7.47 – 7.39 (m, 3H), 7.36 – 7.28 (m, 2H), 7.05 (d, $J = 8.0$ Hz, 2H), 7.01 – 6.92 (m, 2H), 2.30 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 162.27$ (d, $J_{C,F} = 251.3$ Hz), 144.31, 141.95 (d, $J_{C,F} = 8.1$ Hz), 139.66, 137.37, 135.16, 132.47, 131.10 (d, $J_{C,F} = 10.0$ Hz), 129.68, 128.93, 128.27, 128.16, 127.81 (d, $J_{C,F} = 2.7$ Hz), 127.26, 123.04 (d, $J_{C,F} = 3.0$ Hz), 118.46 (d, $J_{C,F} = 8.8$ Hz), 114.22 (d, $J_{C,F} = 22.5$ Hz), 21.68.

HR-ESI-MS m/z calcd for C$_{22}$H$_{20}$FN$_2$O$_2$S [M+H]$^+$: 395.1224, found: 395.1213.

$^{(E)}$-$^{N'}$-(5-Chloro-2-((E)-styryl)benzylidene)-4-methylbenzenesulfonohydrazide (1r)

Prepared by the Method B: ($E$)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (276.1 mg, 1.2 equiv), 2-bromo-5-chlorobenzaldehyde (129 $\mu$L, 1.0 mmol, 1.0 equiv), Pd(OAc)$_2$ (11.2 mg, 5 mol%), PPh$_3$ (39.3 mg, 15 mol%), K$_2$CO$_3$ (179.7 mg, 1.3 equiv), THF (6.0 mL), H$_2$O (3.0 mL).

**Step 1:** The crude residue was purified by chromatography (eluent: PE/EA = 60:1, v/v). 143.2 mg, 59% yield, a light yellow oil.
Step 2: 223.0 mg, 92% yield, a white solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta =$ 8.22 (s, 1H), 8.07 (s, 1H), 7.84 (d, $J = 8.1$, 2H), 7.66 (d, $J = 1.7$, 1H), 7.52 – 7.42 (m, 3H), 7.41 – 7.19 (m, 6H), 6.87 (d, $J = 16.0$, 1H), 2.38 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta =$ 144.95, 144.33, 136.75, 135.69, 135.24, 133.46, 133.23, 131.84, 130.13, 129.72, 128.80, 128.30, 128.27, 127.96, 127.40, 126.84, 124.32, 21.60.

HR-ESI-MS m/z calcd for C$_{22}$H$_{18}$ClN$_2$O$_2$S$^+$ [M-H]$^+$: 409.0778, found: 409.0779.

$^{(E)}$-4-Methyl-$N'$-((1-((E)-styryl)naphthalen-2-yl)methylene)benzenesulfonohydrazone (1s)

Prepared by the Method B: $^{(E)}$-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (345.2 mg, 1.2 equiv), 1-bromo-2-naphthaldehyde (293.9 mg, 1.25 mmol, 1.0 equiv), Pd(OAc)$_2$ (14.0 mg, 5 mol%), PPh$_3$ (49.2 mg, 15 mol%), K$_2$CO$_3$ (224.6 mg, 1.3 equiv), THF (7.0 mL), H$_2$O (3.5 mL).

**Step 1:** The crude residue was purified by chromatography (eluent: PE/EA = 80:1, v/v). 180.1 mg, 56% yield, an orange oil.

**Step 2:** 309.5 mg, 90% yield, a light pink solid.

$^1$H NMR (400 MHz, d$_6$-DMSO) $\delta =$ 11.50 (s, 1H), 8.41 (s, 1H), 8.13 (d, $J = 6.9$ Hz, 1H), 7.96 – 7.83 (m, 3H), 7.78 (d, $J = 8.2$ Hz, 2H), 7.74 – 7.67 (m, 2H), 7.61 – 7.52 (m, 2H), 7.50 – 7.32 (m, 5H), 6.60 (d, $J = 16.4$ Hz, 1H), 2.35 (s, 3H).

$^{13}$C NMR (101 MHz, d$_6$-DMSO) $\delta =$ 146.53, 143.44, 137.95, 136.50, 136.26, 133.43, 131.58, 129.70, 128.69, 128.59, 128.29, 127.65, 127.17, 127.14, 126.92, 126.87, 125.49, 123.06, 122.36, 21.00.

HR-ESI-MS m/z calcd for C$_{26}$H$_{23}$N$_2$O$_2$S$^+$ [M+H]$^+$: 427.1475, found: 427.1483.

$^{(E)}$-4-Methyl-$N'$-((3-((E)-styryl)thiophen-2-yl)methylene)benzenesulfonohydrazone (1t)

Prepared by the Method B: $^{(E)}$-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (345.2 mg, 1.2 equiv), 3-bromothiophene-2-carbaldehyde (133 $\mu$L, 1.25 mmol, 1.0 equiv), Pd(OAc)$_2$ (14.0 mg, 5 mol%), PPh$_3$ (49.2 mg, 15 mol%), K$_2$CO$_3$ (224.6 mg, 1.3 equiv), THF (7.0 mL), H$_2$O (3.5 mL).

**Step 1:** The crude residue was purified by chromatography (eluent: PE/EA = 80:1, v/v). 248.6 mg, 93% yield, a yellow oil.
Step 2: 272.3 mg, 61% yield, a yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$) δ = 8.44 (s, 1H), 8.26 (s, 1H), 7.87 (d, J = 8.3 Hz, 2H), 7.46 (d, J = 7.4 Hz, 2H), 7.33 (t, J = 7.5 Hz, 2H), 7.28 – 7.18 (m, 5H), 6.93 (d, J = 16.1 Hz, 1H), 2.35 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ = 144.33, 142.33, 140.99, 136.75, 135.12, 132.75, 131.81, 129.69, 128.78, 128.43, 128.17, 126.65, 125.70, 119.85, 21.58.

HR-ESI-MS m/z calcd for C$_{20}$H$_{19}$N$_2$O$_2$S$_2$ [M+H]$^+$: 383.0882, found: 383.0873.

(E)-2-Nitro-N′-(2-((E)-styryl)benzylidene)benzenesulfonylhydrazide (1u)

Prepared by the Method B: (E)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (345.2 mg, 1.2 equiv), 2-bromobenzaldehyde (146 μL, 1.25 mmol, 1.0 equiv), Pd(OAc)$_2$ (14.0 mg, 5 mol%), PPh$_3$ (49.2 mg, 15 mol%), K$_2$CO$_3$ (224.6 mg, 1.3 equiv), THF (7.0 mL), H$_2$O (3.5 mL).

Step 1: The crude residue was purified by chromatography (eluent: PE/EA = 50:1, v/v). 208.3 mg, 80% yield, a light yellow oil.

Step 2: 105.8 mg, 26% yield, a white solid.

$^1$H NMR (400 MHz, CDCl$_3$) δ = 8.52 (s, 1H), 8.26 (s, 1H), 8.17 (d, J = 7.9 Hz, 1H), 7.79 (d, J = 7.9 Hz, 1H), 7.70 – 7.60 (m, 3H), 7.56 (d, J = 7.6 Hz, 3H), 7.48 (t, J = 7.7 Hz, 1H), 7.45 – 7.28 (m, 4H), 6.87 (d, J = 16.1 Hz, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ = 149.85, 148.29, 137.89, 137.22, 134.35, 133.28, 133.03, 132.82, 131.75, 130.80, 129.94, 129.01, 128.99, 128.38, 127.71, 127.43, 126.97, 126.19, 125.24.

HR-ESI-MS m/z calcd for C$_{21}$H$_{17}$N$_3$O$_4$SNa [M+Na]$^+$: 430.0832, found: 430.0832.

3. General Procedure for the Synthesis of Isoquinolinium Imides and Isoquinoline-$N$-Oxides via C–H Amination

Method D: In an oven-dried 20-mL vial were subsequently added substrate 1 (0.10 mmol), PhSeSePh (3.1 mg, 10 mol%), NFSI (0.12 mmol, 1.2 equiv), and acetonitrile (4.0 mL). The resulting mixture was stirred at room temperature for 12 h. After the reaction was completed, the resulting mixture was concentrated under reduced
pressure. The residue was directly purified by column chromatography (eluents: DCM and methanol) on silica gel to give the corresponding product 2.

4. Further Transformations of Isoquinolinium Imide 2e

4.1 Ag-catalyzed cycloaddition of 2e with alkyne

In an oven-dried 4-mL vial were subsequently added 2e (0.1 mmol, 1.0 equiv), AgOTf (2.6 mg, 10 mol%), DBU (37 μL, 2.5 equiv), alkyne (20 μL, 1.5 equiv), and CCl₄ (1.0 mL). The reaction mixture was stirred at room temperature for about 5 h. After completion of reaction as indicated by TLC, the mixture was diluted with CCl₄ and washed by water. The organic layer was dried over Na₂SO₄, filtered, and concentrated. The residue was purified by column chromatography (eluent: PE/EA = 50:1 to 30:1, v/v) on silica gel to afford the desired product 5 (28.5 mg, 81% yield) as a white solid. This product is known and its spectra are in accordance with those reported in the literature.⁷

¹H NMR (400 MHz, CDCl₃) δ = 8.12 (d, J = 7.1 Hz, 1H), 8.06 (d, J = 6.6 Hz, 2H), 7.95 (d, J = 8.7 Hz, 2H), 7.75 – 7.70 (m, 1H), 7.60 – 7.49 (m, 5H), 7.31 (s, 1H), 7.04 (s, 1H), 7.02 – 6.94 (m, 2H), 3.85 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ = 159.84, 152.18, 140.80, 138.43, 133.92, 129.73, 129.38, 129.25, 128.82, 128.22, 127.92, 127.75, 127.26, 126.26, 123.93, 123.55, 114.10, 112.24, 94.33, 55.37.

4.2 Reduction of 2e

In an oven-dried 4-mL vial were subsequently added 2e (0.1 mmol, 1.0 equiv), sodium borohydride (37.8 mg, 20 equiv), and absolute ethanol (0.3 mL). The resulting mixture was stirred at 0 °C for 7 h, and then allowed warm up to room temperature. Water (0.7 mL) was added. The mixture was extracted with DCM (10 mL x 3). The organic phases were combined, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by preparative thin layer chromatography to afford product 6 (21.0 mg, 60% yield) as a white solid.⁸

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1H NMR (400 MHz, CDCl3) δ = 7.72 (d, J = 8.2 Hz, 2H), 7.25 – 7.10 (m, 8H), 7.03 (d, J = 7.2 Hz, 2H), 6.96 (d, J = 7.1 Hz, 1H), 4.06 (t, J = 5.7 Hz, 1H), 3.91 (dd, J = 47.1, 15.6 Hz, 2H), 3.19 (ddd, J = 58.8, 17.1, 5.7 Hz, 2H), 2.44 (s, 3H).
13C NMR (101 MHz, CDCl3) δ = 143.82, 138.09, 135.62, 133.15, 132.40, 129.51, 128.56, 128.46, 128.42, 127.81, 127.22, 127.02, 126.42, 63.92, 55.50, 31.91, 21.74. HR-ESI-MS m/z calcd for C22H23N2O2S [M+H]+: 379.1475, found: 379.1468.

5. Characterization Data for Products

(3-Phenylisoquinolin-2-ium-2-yl)(tosyl)amide (2e)

Prepared by the method D. Column chromatography (eluent: DCM/methanol = 80:1, v/v) to afford 2e (35.7 mg, 97% yield) as a white solid. This product is known and its spectra are in accordance with those reported in the literature.9
1H NMR (400 MHz, CDCl3) δ = 9.70 (s, 1H), 8.16 (d, J = 8.3 Hz, 1H), 7.93 (d, J = 3.7 Hz, 2H), 7.85 – 7.77 (m, 2H), 7.37 – 7.28 (m, 3H), 7.25 – 7.19 (m, 2H), 7.03 (d, J = 8.1 Hz, 2H), 6.78 (d, J = 8.1 Hz, 2H), 2.27 (s, 3H).
13C NMR (101 MHz, CDCl3) δ = 150.83, 148.67, 140.43, 139.99, 135.48, 134.67, 132.35, 130.33, 130.10, 129.19, 128.90, 128.75, 127.65, 127.35, 126.75, 126.52, 125.84, 21.42.

(3-(p-Tolyl)isoquinolin-2-ium-2-yl)(tosyl)amide (2f)

Prepared by the method D. Column chromatography (eluent: DCM/methanol = 50:1, v/v) to afford 2f (41.2 mg, 97% yield) as a light yellow solid.
1H NMR (400 MHz, CDCl3) δ = 9.65 (s, 1H), 8.13 (d, J = 8.2 Hz, 1H), 7.92 (d, J = 3.5 Hz, 2H), 7.80 (s, 2H), 7.22 (d, J = 7.9 Hz, 2H), 7.04 (dd, J = 13.3, 7.9 Hz, 4H), 6.78 (d, J = 7.9 Hz, 2H), 2.38 (s, 3H), 2.29 (s, 3H).
13C NMR (101 MHz, CDCl3) δ = 150.59, 148.70, 140.24, 140.15, 139.22, 135.43, 134.45, 130.18, 129.83, 129.40, 128.58, 128.52, 128.18, 127.11, 126.63, 126.42, 125.48, 21.38, 21.33. HR-ESI-MS m/z calcd for C23H21N2O2S [M+H]+: 389.1318, found: 389.1325.

(4-(4-Methoxyphenyl)isoquinolin-2-ium-2-yl)(tosyl)amide (2g)

Prepared by the method D. Column chromatography (eluent: DCM/methanol = 60:1, v/v) to afford 2g (32.7 mg, 81% yield) as a white solid.

$^{1}$H NMR (400 MHz, CDCl$_3$) δ = 9.62 (s, 1H), 8.11 (d, $J = 8.3$ Hz, 1H), 7.89 (d, $J = 3.9$ Hz, 2H), 7.76 (s, 2H), 7.30 – 7.26 (m, 2H), 7.04 (d, $J = 7.9$ Hz, 2H), 6.78 (d, $J = 8.0$ Hz, 2H), 6.72 (d, $J = 8.7$ Hz, 2H), 3.83 (s, 3H), 2.26 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ = 160.37, 150.83, 148.48, 140.26, 140.19, 135.64, 134.56, 131.89, 129.79, 128.70, 128.62, 127.03, 126.64, 126.45, 125.29, 124.65, 113.05, 55.45, 21.40.

HR-ESI-MS m/z calcd for C$_{23}$H$_{21}$N$_{2}$O$_{3}$S [M+H]$^+$: 405.1267, found: 405.1261.

(3-(4-Fluorophenyl)isoquinolin-2-ium-2-yl)(tosyl)amide (2h)

Prepared by the method D. Column chromatography (eluent: DCM/methanol = 60:1, v/v) to afford 2h (36.9 mg, 95% yield) as a white solid.

$^{1}$H NMR (400 MHz, CDCl$_3$) δ = 9.68 (s, 1H), 8.18 (d, $J = 8.1$ Hz, 1H), 7.96 – 7.90 (m, 2H), 7.86 – 7.78 (m, 2H), 7.35 – 7.28 (m, 2H), 7.07 (d, $J = 7.7$ Hz, 2H), 6.91 (t, $J = 8.5$ Hz, 2H), 6.84 (d, $J = 8.0$ Hz, 2H), 2.30 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ = 163.28 (d, $J_{C-F} = 250.5$ Hz), 151.09, 147.71, 140.62, 140.24, 135.48, 134.80, 132.48 (d, $J_{C-F} = 8.6$ Hz), 130.24, 128.89, 128.85, 128.37 (d, $J_{C-F} = 2.9$ Hz), 127.45, 126.76, 126.47, 125.66, 114.76 (d, $J_{C-F} = 21.9$ Hz), 21.44.

HR-ESI-MS m/z calcd for C$_{22}$H$_{18}$FN$_{2}$O$_{2}$S [M+H]$^+$: 393.1068, found: 393.1068.

(4-(4-Chlorophenyl)isoquinolin-2-ium-2-yl)(tosyl)amide (2i)

Prepared by the method D. Column chromatography (eluent: DCM/methanol = 60:1, v/v) to afford 2i (35.9 mg, 87% yield) as a light yellow solid.

$^{1}$H NMR (400 MHz, CDCl$_3$) δ = 9.67 (s, 1H), 8.18 (d, $J = 8.2$ Hz, 1H), 8.00 – 7.91 (m, 2H), 7.88 – 7.77 (m, 2H), 7.28 – 7.23 (m, 2H), 7.18 (d, $J = 8.5$ Hz, 2H), 7.07 (d, $J = 7.9$ Hz, 2H), 6.85 (d, $J = 8.0$ Hz, 2H), 2.32 (s, 3H).

-S16-
$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 151.24, 147.59, 144.97, 140.70, 140.22, 135.70, 135.47, 134.86, 131.74, 130.64, 130.34, 128.89, 127.88, 127.53, 126.81, 126.47, 125.65, 21.49.$

HR-ESI-MS m/z calcd for C$_{22}$H$_{18}$ClN$_2$O$_2$S [M+H]$^+$: 409.0772, found: 409.0777.

**(3-(4-Bromophenyl)isoquinolin-2-ium-2-yl)(tosyl)amide (2j)**

Prepared by the method D. Column chromatography (eluent: DCM/methanol = 50:1, v/v) to afford 2j (37.6 mg, 84% yield) as a light yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 9.67$ (s, 1H), 8.19 (d, $J = 8.3$ Hz, 1H), 8.01 – 7.93 (m, 2H), 7.89 – 7.79 (m, 2H), 7.34 (d, $J = 8.4$ Hz, 2H), 7.19 (d, $J = 8.4$ Hz, 2H), 7.07 (d, $J = 8.0$ Hz, 2H), 6.86 (d, $J = 8.0$ Hz, 2H), 2.33 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 151.17, 147.48, 140.57, 140.07, 135.33, 134.74, 131.80, 130.95, 130.69, 130.22, 128.76, 128.71, 127.40, 126.67, 126.30, 125.45, 123.93, 21.37.

HR-ESI-MS m/z calcd for C$_{22}$H$_{18}$BrN$_2$O$_2$S [M+H]$^+$: 453.0267, found: 453.0267.

**Tosyl(3-(4-(trifluoromethyl)phenyl)isoquinolin-2-ium-2-yl)amide (2k)**

Prepared by the method D. Column chromatography (eluent: DCM/methanol = 50:1, v/v) to afford 2k (29.8 mg, 67% yield) as a light yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 9.69$ (s, 1H), 8.21 (d, $J = 8.3$ Hz, 1H), 7.99 (d, $J = 3.7$ Hz, 2H), 7.92 – 7.81 (m, 2H), 7.49 – 7.38 (m, 4H), 7.02 (d, $J = 7.7$ Hz, 2H), 6.78 (d, $J = 8.0$ Hz, 2H), 2.29 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 192.99, 151.52, 147.00, 140.67, 140.00, 135.62, 135.41, 135.09, 130.91$ (q, $J_{C-F} = 32.3$ Hz), 130.79, 130.63, 128.97, 127.68, 126.96, 126.31, 126.04, 124.42 (d, $J_{C-F} = 3.5$ Hz), 123.91 (q, $J_{C-F} = 272.6$ Hz), 21.29.

HR-ESI-MS m/z calcd for C$_{23}$H$_{18}$F$_3$N$_2$O$_2$S [M+H]$^+$: 443.1036, found: 443.1043.

**(3-(o-Tolyl)isoquinolin-2-ium-2-yl)(tosyl)amide (2l)**

Prepared by the method D. Column chromatography (eluent: DCM/methanol = 50:1,
v/v) to afford 2l (30.4 mg, 83% yield) as a white solid.

$^1$H NMR (400 MHz, CDCl$_3$) δ = 9.78 (s, 1H), 8.17 (d, $J = 8.3$ Hz, 1H), 7.99 – 7.92 (m, 2H), 7.83 (ddd, $J = 8.2, 5.8, 2.3$ Hz, 1H), 7.76 (s, 1H), 7.33 – 7.27 (m, 1H), 7.22 – 7.11 (m, 3H), 6.92 (d, $J = 8.0$ Hz, 3H), 6.59 (d, $J = 7.1$ Hz, 1H), 2.34 (s, 3H), 2.08 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ = 149.17, 148.54, 140.60, 140.53, 137.82, 134.63, 134.28, 132.40, 130.03, 129.98, 129.53, 129.16, 128.91, 128.45, 127.44, 126.64, 126.58, 125.98, 125.01, 21.34, 20.09.

HR-ESI-MS m/z calcd for C$_{23}$H$_{21}$N$_2$O$_2$S $[M+H]^+$: 389.1318, found: 389.1320.

(3-(3-Fluorophenyl)isoquinolin-2-i um-2-yl)(tosyl)amide (2m)

Prepared by the method D. Column chromatography (eluent: DCM/methanol = 40:1, v/v) to afford 2m (28.1 mg, 72% yield) as a light yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$) δ = 9.72 (s, 1H), 8.20 (d, $J = 8.3$ Hz, 1H), 8.05 – 7.91 (m, 2H), 7.86 (m, $J = 8.1, 5.9, 2.2$ Hz, 1H), 7.80 (s, 1H), 7.26 – 7.20 (m, 2H), 7.12 – 6.98 (m, 3H), 6.84 (d, $J = 8.0$ Hz, 2H), 6.74 (d, $J = 9.5$ Hz, 1H), 2.31 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ = 162.02 (d, $J_{C-F} = 246.4$ Hz), 151.17, 147.19, 140.78, 139.79, 135.23, 134.76, 133.90 (d, $J_{C-F} = 8.5$ Hz), 130.29, 128.97 (d, $J_{C-F} = 7.9$ Hz), 128.86, 128.80, 127.43, 126.72, 126.39, 125.78, 117.06 (d, $J_{C-F} = 23.6$ Hz), 116.00 (d, $J_{C-F} = 21.0$ Hz), 99.99, 21.21.

HR-ESI-MS m/z calcd for C$_{22}$H$_{18}$FN$_2$O$_2$S $[M+H]^+$: 393.1068, found: 393.1064.

(3-(Thiophen-2-yl)isoquinolin-2-i um-2-yl)(tosyl)amide (2n)

Prepared by the method D. Column chromatography (eluent: DCM/methanol = 40:1, v/v) to afford 2n (36.4 mg, 99% yield) as a light yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$) δ = 9.66 (s, 1H), 8.11 (s, 1H), 8.04 (d, $J = 8.3$ Hz, 1H), 7.95 – 7.82 (m, 2H), 7.74 (t, $J = 7.4$ Hz, 1H), 7.52 (d, $J = 5.0$ Hz, 1H), 7.48 (d, $J = 3.5$ Hz, 1H), 7.33 (d, $J = 8.1$ Hz, 2H), 7.00 – 6.95 (m, 1H), 6.89 (d, $J = 8.0$ Hz, 2H), 2.25 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ = 148.18, 142.25, 140.98, 139.03, 135.03, 134.20, 132.34, 132.11, 130.47, 129.73, 128.77, 128.23, 126.71, 126.64, 126.34, 126.03, 122.79, 77.35, 21.31.

HR-ESI-MS m/z calcd for C$_{20}$H$_{17}$N$_2$O$_2$S$_2$ $[M+H]^+$: 381.0726, found: 381.0728.

(4-Butylisoquinolin-2-i um-2-yl)(tosyl)amide (2o)
Prepared by the method D. Column chromatography (eluent: DCM/methanol = 50:1, v/v) to afford 2o (16.7 mg, 46% yield) as a white solid.

$^1$H NMR (400 MHz, CDCl$_3$) δ = 9.48 (s, 1H), 8.00 (d, $J$ = 8.1, 1H), 7.86 (s, 2H), 7.78 – 7.67 (m, 2H), 7.56 (d, $J$ = 7.7, 2H), 7.14 (d, $J$ = 7.8, 2H), 2.78 (t, 2H), 2.35 (s, 3H), 1.57 (dd, $J$ = 14.8, 7.5, 2H), 1.29 (dt, $J$ = 14.7, 7.4, 2H), 0.88 (t, $J$ = 7.2, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ = 160.44, 151.24, 148.65, 148.61, 141.27, 140.80, 135.06, 134.04, 129.28, 128.19, 126.58, 126.07, 122.90, 30.80, 29.58, 22.34, 21.37, 13.74.

HR-ESI-MS m/z calcd for C$_{20}$H$_{23}$N$_2$O$_2$S [M+H]$^+$: 355.1475, found: 355.1474.

(7-Phenyl-[1,3]dioxolo[4,5-g]isoquinolin-6-ium-6-yl)(tosyl)amide (2p)

Prepared by the method D. Column chromatography (eluent: DCM/methanol = 50:1, v/v) to afford 2p (39.6 mg, 99% yield) as a yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$) δ = 9.33 (s, 1H), 7.56 (s, 1H), 7.33 – 7.24 (m, 4H), 7.23 – 7.16 (m, 2H), 7.13 (s, 1H), 7.00 (d, $J$ = 8.0, 2H), 6.76 (d, $J$ = 8.0, 2H), 6.24 (s, 2H), 2.27 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ = 154.80, 150.78, 148.13, 147.43, 140.08, 139.96, 135.29, 132.36, 130.10, 128.84, 128.70, 127.44, 126.37, 125.03, 124.25, 103.41, 103.12, 102.64, 21.30.

HR-ESI-MS m/z calcd for C$_{23}$H$_{19}$N$_2$O$_4$S [M+H]$^+$: 419.1060, found: 419.1058.

(8-Fluoro-3-phenylisoquinolin-2-ium-2-yl)(tosyl)amide (2q)

Prepared by the method D. Column chromatography (eluent: DCM/methanol = 50:1, v/v) to afford 2q (38.3 mg, 99% yield) as a light yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$) δ = 9.84 (s, 1H), 7.93 – 7.82 (m, 2H), 7.74 (d, $J$ = 8.3 Hz, 1H), 7.44 (t, $J$ = 8.7 Hz, 1H), 7.38 – 7.29 (m, 3H), 7.27 – 7.19 (m, 2H), 7.13 – 7.05 (m, 2H), 6.81 (d, $J$ = 7.9 Hz, 2H), 2.29 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ = 158.35 (d, $J_{C,F} = 263.5$ Hz), 149.61, 145.24 (d, $J_{C,F}$ = 4.5 Hz), 140.57, 139.92, 135.92, 135.45 (d, $J_{C,F}$ = 8.4 Hz), 132.01, 130.25, 129.41, 128.94, 127.70, 126.49, 125.59 (d, $J_{C,F}$ = 1.8 Hz), 122.74 (d, $J_{C,F}$ = 4.7 Hz), 118.56 (d, $J_{C,F}$ = 15.5 Hz), 113.87 (d, $J_{C,F}$ = 18.2 Hz), 21.39.
HR-ESI-MS m/z calcd for C_{22}H_{18}FN_{2}O_{2}S [M+H]^+: 393.1068, found: 393.1061.

(7-Chloro-3-phenylisoquinolin-2-ium-2-yl)(tosyl)amide (2r)

Prepared by the method D. Column chromatography (eluent: DCM/methanol = 50:1, v/v) to afford 2r (39.4 mg, 97% yield) as a light yellow solid.

^1^H NMR (400 MHz, CDCl_3) δ = 9.64 (s, 1H), 8.12 (s, 1H), 7.90 (d, J = 8.8 Hz, 1H), 7.86 – 7.78 (m, 2H), 7.37 – 7.28 (m, 3H), 7.26 – 7.20 (m, 2H), 7.04 (d, J = 8.0 Hz, 2H), 6.79 (d, J = 8.0 Hz, 2H), 2.28 (s, 3H).

^13^C NMR (101 MHz, CDCl_3) δ = 149.32, 148.80, 140.49, 139.72, 136.21, 135.33, 133.44, 131.94, 130.18, 129.26, 128.84, 128.35, 127.88, 127.60, 126.85, 126.35, 125.64, 21.31.

HR-ESI-MS m/z calcd for C_{22}H_{18}FN_{2}O_{2}S [M+H]^+: 409.0772, found: 409.0782.

(2-Phenylbenzo[lf]isoquinolin-3-ium-3-yl)(tosyl)amide (2s)

Prepared by the method D. Column chromatography (eluent: DCM/methanol = 50:1, v/v) to afford 2s (17.9 mg, 42% yield) as a light pink solid.

^1^H NMR (400 MHz, CDCl_3) δ = 9.64 (s, 1H), 8.58 (d, J = 8.2 Hz, 1H), 8.52 (s, 1H), 8.04 (d, J = 8.4 Hz, 2H), 7.93 – 7.83 (m, 2H), 7.83 – 7.76 (m, 1H), 7.42 – 7.35 (m, 3H), 7.33 – 7.27 (m, 2H), 7.06 (d, J = 7.8 Hz, 2H), 6.79 (d, J = 8.0 Hz, 2H), 2.29 (s, 3H).

^13^C NMR (101 MHz, CDCl_3) δ = 149.90, 149.18, 140.29, 139.83, 135.65, 134.67, 132.58, 131.60, 131.10, 130.24, 129.50, 129.28, 128.81, 128.65, 127.66, 127.13, 126.78, 126.44, 123.98, 123.60, 121.43, 21.32.

HR-ESI-MS m/z calcd for C_{26}H_{21}N_{2}O_{2}S [M+H]^+: 425.1318, found: 425.1322.

(5-Phenylthieno[2,3-c]pyridin-6-ium-6-yl)(tosyl)amide (2t)

Prepared by the method D. Column chromatography (eluent: DCM/methanol = 50:1, v/v) to afford 2t (31.1 mg, 82% yield) as a light yellow solid.
1H NMR (400 MHz, CDCl$_3$) δ = 9.54 (s, 1H), 8.16 (d, J = 5.3 Hz, 1H), 7.77 (s, 1H), 7.50 (d, J = 5.3 Hz, 1H), 7.35 – 7.28 (m, 1H), 7.25 – 7.15 (m, 4H), 7.00 (d, J = 7.6 Hz, 2H), 6.76 (d, J = 8.0 Hz, 2H), 2.27 (s, 3H).

13C NMR (101 MHz, CDCl$_3$) δ = 149.82, 146.15, 144.09, 140.36, 139.84, 135.52, 132.55, 130.18, 129.18, 128.89, 127.63, 126.83, 126.50, 123.39, 121.26, 21.41.

HR-ESI-MS m/z calcd for C$_{20}$H$_{17}$N$_2$O$_2$S$_2$ [M+H]$^+$: 381.0726, found: 381.0724.

(2-Nitrophenyl)sulfonyl)(3-phenylisoquinolin-2-ium-2-yl)amide (2u)

Prepared by the method D. Column chromatography (eluent: DCM/methanol = 60:1, v/v) to afford 2u (35.0 mg, 98% yield) as a white solid.

1H NMR (400 MHz, CDCl$_3$) δ = 9.55 (s, 1H), 8.22 (d, J = 8.3 Hz, 1H), 8.01 – 7.96 (m, 2H), 7.91 (s, 1H), 7.89 – 7.83 (m, 1H), 7.47 – 7.43 (m, 1H), 7.35 (d, J = 7.2 Hz, 2H), 7.31 – 7.20 (m, 2H), 7.18 – 7.06 (m, 4H).

13C NMR (101 MHz, CDCl$_3$) δ = 151.01, 148.69, 147.91, 137.45, 136.17, 135.02, 132.30, 131.55, 130.66, 130.49, 130.42, 129.25, 129.23, 127.67, 126.85, 125.89, 122.14, 100.13.

HR-ESI-MS m/z calcd for C$_{21}$H$_{16}$N$_3$O$_4$S [M+H]$^+$: 406.0856, found: 406.0863.

Benzoyl(3-phenylisoquinolin-2-ium-2-yl)amide (2d)

Prepared by the method D (But change MeCN to MeNO$_2$) Column chromatography (eluent: DCM/methanol = 50:1, v/v) to afford 2d (16.8 mg, 53% yield) as a yellow liquid.

1H NMR (400 MHz, CDCl$_3$) δ = 9.58 (s, 1H), 8.09 (d, J = 8.1 Hz, 1H), 8.04 (s, 1H), 8.01 – 7.84 (m, 4H), 7.77 (t, J = 7.4 Hz, 1H), 7.72 – 7.65 (m, 2H), 7.44 (s, 3H), 7.39 – 7.28 (m, 3H).

13C NMR (101 MHz, CDCl$_3$) δ = 170.51, 148.03, 147.02, 137.37, 135.01, 133.74, 132.94, 129.86, 129.69, 129.59, 128.14, 128.03, 127.71, 127.28, 126.74, 125.61.

HR-ESI-MS m/z calcd for C$_{22}$H$_{17}$N$_2$O [M+H]$^+$: 325.1335, found: 325.1327.

3-Phenylisoquinoline 2-oxide (4)
Prepared by the method D. Column chromatography (eluent: DCM/methanol = 50:1, v/v) to afford 4 (13.9 mg, 63% yield) as a light yellow solid. This product is known and its spectra are in accordance with those reported in the literature.\textsuperscript{10}

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta = 8.94\) (s, 1H), 7.86 – 7.77 (m, 4H), 7.74 (d, \(J = 7.0\) Hz, 1H), 7.64 – 7.55 (m, 2H), 7.53 – 7.43 (m, 3H).

\textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta = 137.22, 132.82, 129.75, 129.45, 129.43, 129.38, 129.19, 129.09, 128.99, 128.23, 126.62, 124.85, 124.57.\)

6. NMR Spectra for Substrates and Products

$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) of 1f
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) of 1g
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) of 1h
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) of 1i
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) of 1j
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, d$_6$-DMSO) of 1k
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) of 11
$^1H$ NMR (400 MHz, CDCl$_3$) and $^{13}C$ NMR (101 MHz, CDCl$_3$) of 1m
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) of 1n
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) of 1o
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) of 1p
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) of 1q
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) of 1r
$^1$H NMR (400 MHz, d$_6$-DMSO) and $^{13}$C NMR (101 MHz, d$_6$-DMSO) of 1s
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) of 1t
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) of 1u
$^1$H NMR (400 MHz, d6-DMSO) and $^{13}$C NMR (101 MHz, d6-DMSO) of 1d
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) of 2e
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) of 2f
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) of 2g
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) of 2h
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) of 2i
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) of 2j
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) of 2k
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) of 2l
$^1$H NMR (400 MHz, CDCl₃) and $^{13}$C NMR (101 MHz, CDCl₃) of 2m
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) of 2n
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) of 2o
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) of 2p
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) of 2q
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) of 2r
\(^1\)H NMR (400 MHz, CDCl\textsubscript{3}) and \(^{13}\)C NMR (101 MHz, CDCl\textsubscript{3}) of 2s
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) of 2t
$^{1}H$ NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) of 2u


$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) of 2d
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) of 4
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) of 5
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) of 6