Highly Effective Ni-Catalyzed Alkynylation of Unactivated (Hetero)arene C-H Bonds with Alkynes

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1. General Information

Trimethylacetonitrile was dried by Sodium, distilled under reduced pressure and stored under nitrogen. Ni(OTf)$_2$ was prepared by reported procedure.$^{[1]}$ The other materials and solvents were purchased from Aladdin and other commercial suppliers and used without additional purification. NMR spectra were recorded on a Bruke Avance operating for $^1$H NMR at 400 MHz, $^{13}$C NMR at 100 MHz, and $^{19}$F NMR at 376 MHz, using TMS as internal standard. The peaks were internally referenced to TMS (0.00 ppm) or residual undeuterated solvent signal (77.16 ppm for $^{13}$C NMR). The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, b = broad. Mass spectroscopy data of the products were collected on an HRMS-TOF instrument or a low-resolution MS instrument using EI ionization.
2. Experimental Section

2.1 Praperation of Substrates

Compounds 1a-1e, 1g-1h, 1j-1m, 1o, 1q-1t, 1a-d5, 4b and 4d-4g were known compounds.[2, 3] Compounds 1f, 1i, 1n, 1p, 1u, 1v and 1ae were prepared following typical method A or method B.[3]

**General Procedure for the Preparation of Starting Materials (Method A):**

\[
\begin{align*}
R^1\text{O} & \rightarrow 1) \text{SOCl}_2, \text{reflux,2h} \\
& \rightarrow 2) \text{Et}_3\text{N, R}^2\text{NH}_2, \text{DCM, r.t.}
\end{align*}
\]

A solution of an acid (5 mmol) was refluxed in 5 mL SOCl\(_2\) for 2h and cooled to RT. The excess of SOCl\(_2\) was removed under vacuum to give corresponding acid chloride. The acid chloride was then re-dissolved in 5 mL dry CH\(_2\)Cl\(_2\) and added dropwiseto a 20 mL dry CH\(_2\)Cl\(_2\) solution containing amine (5 mmol) and Et\(_3\)N (10 mmol) at 0 °C. After stirring for 6h at ambient temperature, the resulting mixture was washed with brine, dried over MgSO\(_4\), filtered and concentrated under reduced pressure. The residue was purified by flash chromatography to give the desired product.

**General Procedure for the Preparation of Starting Materials (Method B):**

\[
\begin{align*}
R^1\text{O} & \rightarrow \text{EDCI, HOBT, DMF} \\
& \rightarrow \text{R}^2\text{NH}_2
\end{align*}
\]

A mixture of amine (5 mmol), 6-bromohexanoic acid (5 mmol), EDCI (5.5 mmol) and HOBT (5.5 mmol) in anhydrous DMF (20 mL) was stirred at room temperature overnight. Water was added and the mixture was extracted with diethyl ether. The combined organic layer was washed with brine, dried over MgSO\(_4\), filtered and concentrated under reduced pressure. The residue was purified by flash chromatography to give the desired product.
2-Chloro-N-(2-(pyridin-2-yl)propan-2-yl)benzamide 1f

The title compound 1f was prepared according to the general procedure (Method A). 

\[^1\text{H} \text{NMR (400 MHz, CDCl}_3\] \( \delta \) 8.49 (d, \( J = 4.0 \) Hz, 1H), 8.36 (br, 1H), 7.73 (td, \( J = 7.6, 2.0 \) Hz, 1H), 7.63 (dd, \( J = 7.6, 2.0 \) Hz, 1H), 7.47 (d, \( J = 8.0 \) Hz, 1H), 7.41 (dd, \( J = 7.6, 1.6 \) Hz, 1H), 7.36 - 7.28 (m, 2H), 7.19 (ddd, \( J = 7.6, 4.8, 0.8 \) Hz, 1H), 1.90 (s, 6H); 

\[^{13}\text{C} \text{NMR (100 MHz, CDCl}_3\] \( \delta \) 165.94, 164.34, 147.75, 137.25, 137.06, 130.99, 130.79, 129.75, 127.02, 122.04, 119.58, 57.63, 27.64; HRMS (EI-TOF) calcd for C\(_{15}\)H\(_{15}\)N\(_2\)OCl (M\(^+\)): 274.0873, found: 274.0874.

3-bromo-N-(2-(pyridin-2-yl)propan-2-yl)benzamide 1i

The title compound 1i was prepared according to the general procedure (Method A). 

\[^1\text{H} \text{NMR (400 MHz, CDCl}_3\] \( \delta \) 8.90 (br, 1H), 8.57 (d, \( J = 4.8 \) Hz, 1H), 8.05 (s, 1H), 7.81 (d, \( J = 7.6 \) Hz, 1H), 7.77 (td, \( J = 8.0, 1.6 \) Hz, 1H), 7.62 (d, \( J = 7.6 \) Hz, 1H), 7.46 (d, \( J = 8.0 \) Hz, 1H), 7.33 (t, \( J = 8.0 \) Hz, 1H), 7.24 (dd, \( J = 7.6, 6.0 \) Hz, 1H), 1.87 (s, 6H); 

\[^{13}\text{C} \text{NMR (100 MHz, CDCl}_3\] \( \delta \) 164.84, 164.54, 147.71, 138.23, 137.47, 134.13, 130.49, 130.12, 125.64, 122.83, 122.18, 119.66, 56.88, 27.53.

N-(2-(pyridin-2-yl)propan-2-yl)-2-naphthamide 1l

The title compound 1l was prepared according to the general procedure (Method A). 

\[^1\text{H} \text{NMR (400 MHz, CDCl}_3\] \( \delta \) 8.47 (ddd, \( J = 4.4, 2.0, 0.8 \) Hz, 1H), 8.39 (m, 1H), 8.34 (s, 1H), 7.91 (d, \( J = 8.0 \) Hz, 1H), 7.88 (m, 1H), 7.78 - 7.69 (m, 2H), 7.57 - 7.45
(m, 4H), 7.20 (ddd, J = 6.8, 5.6, 0.8 Hz, 1H), 1.98 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 168.89, 164.42, 147.67, 137.18, 135.94, 133.77, 130.35, 130.10, 128.22, 126.86, 126.22, 125.68, 124.86, 121.94, 119.49, 57.29, 27.67; HRMS (EI-TOF) calcd for C$_{15}$H$_{15}$N$_3$O$_3$ (M$^+$): 289.1419, found: 289.1425.

### 2-chloro-N-(2-(pyridin-2-yl)propan-2-yl)nicotinamide 1n

The title compound 1n was prepared according to the general procedure (Method B). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.75 (br, 1H), 8.48 (ddd, J = 6.8, 4.0, 1.6 Hz, 2H), 8.02 (dd, J = 7.6, 1.6 Hz, 1H), 7.76 (td, J = 8.0, 1.6 Hz, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.33 (dd, J = 7.6, 4.8 Hz, 1H), 7.22 (ddd, J = 7.6, 4.8, 0.8 Hz, 1H), 1.90 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.12, 163.90, 150.50, 147.67, 139.00, 137.41, 133.20, 122.68, 122.20, 119.54, 57.75, 27.46.

### 3-chloro-N-(2-(pyridin-2-yl)propan-2-yl)isonicotinamide 1p

The title compound 1p was prepared according to the general procedure (Method B). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.75 (br, 1H), 8.66 (d, J = 4.0 Hz, 1H), 8.57 (d, J = 4.8 Hz, 1H), 8.48 (d, J = 4.0 Hz, 1H), 7.76 (m, 1H), 7.54 (d, J = 4.0 Hz, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.23 (m, 1H), 1.90 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 163.67, 163.45, 150.46, 148.27, 147.59, 143.29, 137.49, 128.21, 123.26, 122.26, 119.52, 57.78, 27.46.
The title compound 1u was prepared according to the general procedure (Method B).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.76 (br, 1H), 8.54 (d, $J$ = 4.8 Hz, 1H), 7.76 (td, $J$ = 8.0, 1.6 Hz, 1H), 7.44 (d, $J$ = 8.0 Hz, 1H), 7.36 (d, $J$ = 4.0 Hz, 1H), 7.24 (ddd, $J$ = 7.6, 4.8, 0.8 Hz, 1H), 6.90 (d, $J$ = 4.0 Hz, 1H), 1.84 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.30, 160.12, 147.64, 139.89, 137.51, 134.57, 126.92, 126.79, 122.23, 119.63, 56.98, 27.66; HRMS (EI-TOF) calcd for C$_{13}$H$_{13}$ClN$_2$OS (M$^+$): 280.0437, found: 280.0436.

$\text{Br} \quad \text{O} \quad \text{S} \quad \text{N} \quad \text{H} \quad \text{N} \quad \text{O}$

5-bromo-N-(2-(pyridin-2-yl)propan-2-yl)thiophene-2-carboxamide 1v

The title compound 1v was prepared according to the general procedure (Method B).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.76 (br, 1H), 8.55 (d, $J$ = 4.8 Hz, 1H), 7.76 (td, $J$ = 8.0, 1.6 Hz, 1H), 7.44 (d, $J$ = 8.0 Hz, 1H), 7.33 (d, $J$ = 4.0 Hz, 1H), 7.24 (ddd, $J$ = 7.6, 4.8 Hz, 1H), 7.04 (d, $J$ = 4.0 Hz, 1H), 1.84 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.28, 160.03, 147.64, 139.89, 137.51, 130.60, 127.67, 122.23, 119.63, 117.20, 56.99, 27.65; HRMS (EI-TOF) calcd for C$_{13}$H$_{13}$BrN$_2$OS (M$^+$): 323.9932, found: 323.9939.

$\text{N} \quad \text{O} \quad \text{H} \quad \text{Ac} \quad \text{Br}$

4-acetyl-N-(2-(pyridin-2-yl)propan-2-yl)benzamide 1ae

The title compound 1ae was prepared according to the general procedure (Method A).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.06 (br, 1H), 8.56 (d, $J$ = 4.2 Hz, 1H), 8.04 (d, $J$ = 8.4 Hz, 2H), 7.99 (d, $J$ = 8.4 Hz, 2H), 7.78 (td, $J$ = 8.0, 1.7 Hz, 1H), 7.48 (d, $J$ = 8.0 Hz, 1H), 7.23 (s, 1H), 2.65 (s, 3H), 1.89 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 197.76, 165.33, 164.53, 147.67, 140.16, 139.01, 137.55, 128.61, 127.45, 122.25, 119.72, 56.91, 27.53, 26.97.
2.2 Optimization of Reaction Conditions

Screening of Ni Salts

![Reactivity Optimization Table]

<table>
<thead>
<tr>
<th>Entry&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Ni (10%)</th>
<th>Yield&lt;sup&gt;b&lt;/sup&gt; of 3a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ni(O Tf)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>28%</td>
</tr>
<tr>
<td>2</td>
<td>NiCl&lt;sub&gt;2&lt;/sub&gt;·6H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>trace</td>
</tr>
<tr>
<td>3</td>
<td>NiBr&lt;sub&gt;2&lt;/sub&gt;</td>
<td>N.D.</td>
</tr>
<tr>
<td>4</td>
<td>NiCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>trace</td>
</tr>
<tr>
<td>5</td>
<td>(dppe)NiCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>trace</td>
</tr>
<tr>
<td>6</td>
<td>(dppp)NiCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>trace</td>
</tr>
<tr>
<td>7</td>
<td>(PPh&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;NiCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>trace</td>
</tr>
<tr>
<td>8</td>
<td>Ni(cod)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>trace</td>
</tr>
<tr>
<td>9</td>
<td>(DME)NiCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>trace</td>
</tr>
<tr>
<td>10</td>
<td>NiCp&lt;sub&gt;2&lt;/sub&gt;</td>
<td>trace</td>
</tr>
<tr>
<td>11</td>
<td>Ni(acac)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>22%</td>
</tr>
<tr>
<td>12</td>
<td>Ni(OAc)&lt;sub&gt;2&lt;/sub&gt;·4H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>trace</td>
</tr>
</tbody>
</table>

<sup>a</sup>The reactions were carried out 1a (0.1 mmol), 2a (0.2 mmol), [Ni] (0.01 mmol), DME (0.02 mmol), Na<sub>2</sub>CO<sub>3</sub> (0.2 mmol), DCE (1 mL), N<sub>2</sub>, 140°C.  
<sup>b</sup>Yield of <sup>1</sup>H NMR. N.D. = No Detection.
**Screening of Ligands**

\[
\begin{align*}
\text{1a} + \text{Br} = \text{TIPS} & \rightarrow \frac{\text{Ni(OTf)}_2 (10\%), \text{L} (20\%)}{\text{Na}_2\text{CO}_3 (2.0), \text{DCE}, 140^\circ\text{C}, 12 \text{ h}}} \rightarrow \text{3a}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Entry(^a)</th>
<th>L (20%)</th>
<th>Yield(^b) of 3a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BINAP</td>
<td>trace</td>
</tr>
<tr>
<td>2</td>
<td>PCy(_3)</td>
<td>trace</td>
</tr>
<tr>
<td>3</td>
<td>DPPM</td>
<td>8%</td>
</tr>
<tr>
<td>4</td>
<td>DPPP</td>
<td>trace</td>
</tr>
<tr>
<td>5</td>
<td>DPPB</td>
<td>trace</td>
</tr>
<tr>
<td>6</td>
<td>BPy</td>
<td>N.D.</td>
</tr>
<tr>
<td>7</td>
<td>1,10-Phen</td>
<td>N.D.</td>
</tr>
<tr>
<td>8</td>
<td>BDMAE</td>
<td>15%</td>
</tr>
<tr>
<td>9</td>
<td>DME</td>
<td>60% (mono:di=3:1)</td>
</tr>
<tr>
<td>10</td>
<td>TMEDA</td>
<td>25%</td>
</tr>
</tbody>
</table>

\(^a\) The reactions were carried out 1a (0.1 mmol), 2a (0.2 mmol), Ni(OTf)$_2$ (0.01 mmol), Ligands (0.02 mmol), Na$_2$CO$_3$ (0.2 mmol), DCE (1 mL), N$_2$, 140$^\circ$C. \(^b\) Yield of $^1$H NMR. N.D. = No Detection.
Screening of Solvents

<table>
<thead>
<tr>
<th>Entry&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Solvent</th>
<th>Yield&lt;sup&gt;b&lt;/sup&gt; of 3a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DMF</td>
<td>11%</td>
</tr>
<tr>
<td>2</td>
<td>DMSO</td>
<td>15%</td>
</tr>
<tr>
<td>3</td>
<td>1,4-dioxane</td>
<td>18%</td>
</tr>
<tr>
<td>4</td>
<td>Toluene</td>
<td>trace</td>
</tr>
<tr>
<td>5</td>
<td>o-xylene</td>
<td>trace</td>
</tr>
<tr>
<td>6</td>
<td>Isobutynitrile</td>
<td>75%(mono:di=4:1)</td>
</tr>
<tr>
<td>7</td>
<td>DME</td>
<td>5%</td>
</tr>
<tr>
<td>8</td>
<td>DCM</td>
<td>trace</td>
</tr>
<tr>
<td>9</td>
<td>Acetonitrile</td>
<td>trace</td>
</tr>
<tr>
<td>10</td>
<td>Butynitrile</td>
<td>16%</td>
</tr>
<tr>
<td>11</td>
<td>Pivalonitrile</td>
<td>81%(mono:di=3:1)</td>
</tr>
</tbody>
</table>

<sup>a</sup> The reactions were carried out 1a (0.1 mmol), 2a (0.2 mmol), Ni(OTf)<sub>2</sub> (0.01 mmol), DME (0.02 mmol), Na<sub>2</sub>CO<sub>3</sub> (0.2 mmol), solvent (1.0 mL), N<sub>2</sub>, 140°C, 12 h.  
<sup>b</sup> Yield of <sup>1</sup>H NMR.
Screening of Bases

\[
\begin{array}{ccc}
1a & + & 2a \\
& & \xrightarrow{\text{Ni(OTf)}_2 (10\%), \text{DME (20\%)}} \\
& & 3a
\end{array}
\]

<table>
<thead>
<tr>
<th>Entry (^a)</th>
<th>Bases (2.0 eq.)</th>
<th>Yield(^b) of 3a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Li(_2)CO(_3)</td>
<td>8%</td>
</tr>
<tr>
<td>2</td>
<td>Na(_2)CO(_3)</td>
<td>81%(mono:di=3:1)</td>
</tr>
<tr>
<td>3</td>
<td>K(_2)CO(_3)</td>
<td>N.D.</td>
</tr>
<tr>
<td>4</td>
<td>Cs(_2)CO(_3)</td>
<td>N.D.</td>
</tr>
<tr>
<td>5</td>
<td>NaHCO(_3)</td>
<td>99%(mono:di=1:2)</td>
</tr>
<tr>
<td>6</td>
<td>KHCO(_3)</td>
<td>90%(mono:di=1:3)</td>
</tr>
<tr>
<td>7</td>
<td>K(_3)PO(_4)</td>
<td>37%</td>
</tr>
<tr>
<td>8</td>
<td>K(_2)HPO(_4)</td>
<td>25%</td>
</tr>
<tr>
<td>9</td>
<td>KH(_2)PO(_4)</td>
<td>N.D.</td>
</tr>
<tr>
<td>10</td>
<td>NaOAc</td>
<td>N.D.</td>
</tr>
</tbody>
</table>

\(^a\) The reactions were carried out 1a (0.1 mmol), 2a (0.2 mmol), Ni(OTf)_2 (0.002 mmol), DME (0.02 mmol), base (0.2 mmol), t-BuCN (1 mL), N\(_2\), 140 \(^\circ\)C, 24 h.

\(^b\) Yield of \(^1\)H NMR. N.D. = No detection.

Entry\(^a\) | Solvent | Yield\(^b\) of 3a |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5 mL</td>
<td>99%(mono:di=1:2.8)</td>
</tr>
<tr>
<td>2</td>
<td>2 mL</td>
<td>83%(mono:di=2:1)</td>
</tr>
<tr>
<td>3</td>
<td>4 mL</td>
<td>79%(mono:di=1.5:1)</td>
</tr>
<tr>
<td>4</td>
<td>6 mL</td>
<td>63%(mono:di=2:1)</td>
</tr>
<tr>
<td>5</td>
<td>8 mL</td>
<td>61%(mono:di=2:1)</td>
</tr>
<tr>
<td>6(^c)</td>
<td>0.5 mL</td>
<td>99%(mono:di=32:1)</td>
</tr>
</tbody>
</table>

\(^a\) The reactions were carried out 1a (0.4 mmol), 2a (0.8 mmol), Ni(OTf)_2 (0.002 mmol), DME (0.004 mmol), NaHCO\(_3\) (0.8 mmol), t-BuCN (x mL), N\(_2\), 150 \(^\circ\)C, 24 h. \(^b\) Yield of \(^1\)H NMR. \(^c\) 1a (0.8 mmol), 2a (0.4 mmol).
Screening of Directing Group

\[
\begin{align*}
\text{Standard condition} & \quad \text{Br$\equiv$TiPS} \\
\text{45\%(mono)+27\%(di)} & \\
\end{align*}
\]
2.3 General Procedure for the Alkynylation

**Condition A:**

To an oven-dried 50 mL screw-capped vial was added substrate 1a (x mmol), 2a (y mmol), Ni(OTf)$_2$ (0.8 mg, 0.002 mmol), NaHCO$_3$ (67.2 mg, 0.8 mmol), DME (0.004 mmol) in t-BuCN (0.5 mL). The mixture was stirred for 24 h at 150 °C under N$_2$ followed by cooling. The resulting mixture was filtered through a celite pad and concentrated in vacuo. The residue was purified by preparative TLC using hexane/EtOAc as the eluent to afford the product.

**Condition B:**

To an oven-dried 50 mL screw-capped vial was added substrate 1a (0.4 mmol), 2a (1.6 mmol), Ni(OTf)$_2$ (0.8 mg, 0.002 mmol), NaHCO$_3$ (67.2 mg, 0.8 mmol), DME (0.004 mmol) in t-BuCN (0.5 mL). The mixture was stirred for 24 h at 150 °C under N$_2$ followed by cooling. The resulting mixture was filtered through a celite pad and
concentrated in vacuum. The residue was purified by preparative TLC using hexane/EtOAc as the eluent to afford the product.

**Condition C:**

To an oven-dried 50 mL screw-capped vial was added substrate 1a (0.8 mmol), 2a (0.4 mmol), Ni(OTf)$_2$ (0.8 mg, 0.002 mmol), NaHCO$_3$ (67.2 mg, 0.8 mmol), DME (0.004 mmol) in t-BuCN (0.5 mL). The mixture was stirred for 24 h at 130 °C under N$_2$ followed by cooling. The resulting mixture was filtered through a celite pad and concentrated in vacuum. The residue was purified by preparative TLC using hexane/EtOAc as the eluent to afford the product.

**N-(2-(Pyridin-2-yl)propan-2-yl)-2-((triisopropylsilyl)ethynyl)benzamide 3a**

Following **Condition A:** 1a (0.8 mmol), 2a (0.4 mmol); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.51 (d, $J = 4.0$ Hz, 1H), 8.40 (br, 1H), 7.80 (dd, $J = 6.8$, 3.6 Hz, 1H), 7.68 (td, $J = 8.0$, 2.0 Hz, 1H), 7.58 – 7.55 (m, 1H), 7.47 (d, $J = 8.0$ Hz, 1H), 7.40 – 7.36 (m, 2H), 7.15 (dd, $J = 6.4$, 4.8 Hz, 1H), 1.87 (s, 6H), 1.07–1.02 (m, 21H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.19, 164.57, 148.04, 137.75, 136.81, 134.72, 129.78, 129.13, 128.68, 121.62, 120.13, 119.36, 105.36, 97.33, 57.68, 27.76, 18.65, 11.30; HRMS (EI-TOF) calcd for C$_{26}$H$_{36}$N$_2$OSi (M$^+$): 420.2597, found: 420.2599.

**N-(2-(pyridin-2-yl)propan-2-yl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide 4a**

Following **Condition B:** $^1$H NMR (400 MHz, CDCl$_3$) δ 8.42 (d, $J = 5.2$ Hz, 1H), 8.41 (br, 1H), 7.70 (t, $J = 7.2$ Hz, 1H), 7.48 - 7.42 (m, 3H), 7.24 (t, $J = 8.0$ Hz, 1H), 7.15
(dd, J = 6.4, 5.2 Hz, 1H), 1.92 (s, 6H), 1.03 – 0.97 (m, 42H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.03, 164.58, 147.41, 142.42, 137.13, 133.82, 128.18, 121.80, 121.59, 119.49, 104.25, 95.04, 57.29, 27.58, 18.74, 11.38; HRMS (EI-TOF) calcd for C$_{37}$H$_{56}$N$_2$O$_2$Si$_2$ (M$^+$): 600.3931, found: 600.3932.

2-Methyl-N-(2-(pyridin-2-yl)propan-2-yl)-6-((triisopropylsilyl)ethynyl)benzamid 3b

Following Condition A: 1b (0.4 mmol), 2a (0.8 mmol); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.43 (d, J = 4.8 Hz, 1H), 8.16 (br, 1H), 7.71 (td, J = 7.6, 1.6 Hz, 1H), 7.46 (d, J = 8.4 Hz, 1H), 7.37 (d, J = 6.4 Hz, 1H), 7.21-7.15 (m, 3H), 2.37 (s, 3H), 1.92 (s, 6H), 1.02-0.97 (m, 21H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.60, 164.38, 147.47, 140.14, 137.00, 135.43, 131.23, 130.38, 128.14, 121.77, 120.48, 119.42, 105.06, 93.91, 57.13, 27.43, 19.33, 18.61, 11.27; HRMS (EI-TOF) calcd for C$_{27}$H$_{38}$N$_2$O$_2$Si (M$^+$): 434.2753, found: 434.2755.

5-Methyl-N-(2-(pyridin-2-yl)propan-2-yl)-2-((triisopropylsilyl)ethynyl)benzamid 3c

Following Condition A: 1c (0.4 mmol), 2a (0.8 mmol); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.51 (dd, J = 4.0, 0.8 Hz, 1H), 8.36 (br, 1H), 7.69–7.64 (m, 2H), 7.46 (dd, J = 8.0, 3.6 Hz, 2H), 7.19–7.13 (m, 2H), 2.36 (s, 3H), 1.86 (s, 6H), 1.07–1.02 (m, 21H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.36, 164.82, 148.25, 139.21, 137.41, 136.84, 134.87, 130.78, 129.97, 121.67, 119.49, 117.24, 105.78, 96.68, 57.87, 27.95, 21.46, 18.79, 11.47; HRMS (EI-TOF) calcd for C$_{27}$H$_{38}$N$_2$O$_2$Si (M$^+$): 434.2753, found: 434.2752.
\[
N\text{-}(2\text{-}(\text{Pyridin-2-yl})\text{propan-2-yl})-2\text{-}(\text{trifluoromethyl})\text{-}6\text{-}((\text{triisopropylsilyl})\text{ethynyl})\text{benzamide 3d}
\]
Following **Condition A**: 1d (0.4 mmol), 2a (0.8 mmol); \[^1\text{H NMR}\] (400 MHz, CDCl\(_3\)) \(\delta\) 8.52 (br, 1H), 8.41 (d, \(J = 4.8\) Hz, 1H), 7.75-7.71 (m, 2H), 7.63 (d, \(J = 7.6\) Hz, 1H), 7.45-7.41 (m, 2H), 7.17 (dd, \(J = 6.8, 5.2\) Hz, 1H), 1.91 (s, 6H), 1.03–0.97 (m, 21H); \[^{13}\text{C NMR}\] (100 MHz, CDCl\(_3\)) \(\delta\) 164.73, 164.25, 147.37, 138.76, 137.40, 137.29, 128.56, 127.98 (q, \(J = 31.7\) Hz), 126.02 (q, \(J = 4.8\) Hz), 123.65 (q, \(J = 272.7\) Hz), 123.20, 121.98, 119.53, 103.41, 96.73, 57.49, 27.14, 18.71, 11.36; \[^{19}\text{F NMR}\] (376 MHz, CDCl\(_3\)) \(\delta\) 59.02; **HRMS** (EI-TOF) calcd for C\(_{27}\)H\(_{35}\)F\(_3\)N\(_2\)OSi (M\(^+\)) 488.2471, found: 488.2474.

\[
N\text{-}(2\text{-}(\text{Pyridin-2-yl})\text{propan-2-yl})-5\text{-}(\text{trifluoromethyl})\text{-}2\text{-}((\text{triisopropylsilyl})\text{ethynyl})\text{benzamide 3e}
\]
Following **Condition A**: 1e (0.4 mmol), 2a (0.8 mmol); \[^1\text{H NMR}\] (400 MHz, CDCl\(_3\)) \(\delta\) 8.57 (br, 1H), 8.50 (d, \(J = 4.4\) Hz, 1H), 8.06 (s, 1H), 7.71 (td, \(J = 7.6, 1.6\) Hz, 1H), 7.67 (d, \(J = 8.0\) Hz, 1H), 7.60 (d, \(J = 8.0\) Hz, 1H), 7.46 (d, \(J = 8.0\) Hz, 1H), 7.18 (dd, \(J = 7.2, 5.2\) Hz, 1H), 1.89 (s, 6H), 1.06–0.99 (m, 21H); \[^{13}\text{C NMR}\] (100 MHz, CDCl\(_3\)) \(\delta\) 165.14, 164.34, 148.08, 138.89, 137.10, 135.21, 130.59 (q, \(J = 33.0\) Hz), 126.41-126.23 (m), 123.92, 123.69 (q, \(J = 270.8\) Hz), 121.92, 119.54, 103.94, 100.56, 57.87, 27.69, 18.71, 11.37; \[^{19}\text{F NMR}\] (376 MHz, CDCl\(_3\)) \(\delta\) 62.96; **HRMS** (EI-TOF) calcd for C\(_{27}\)H\(_{35}\)F\(_3\)N\(_2\)OSi (M\(^+\)) 488.2471, found: 488.2473.
2-Chloro-N-(2-(pyridin-2-yl)propan-2-yl)-6-((triisopropylsilyl)ethynyl)benzamide 3f

Following **Condition A**: 1f (0.4 mmol), 2a (0.8 mmol);

\( ^1H \) NMR (400 MHz, CDCl₃)
\( \delta \) 8.44 (d, \( J = 4.8 \) Hz, 1H), 8.30 (br, 1H), 7.72 (td, \( J = 7.6, 1.6 \) Hz, 1H), 7.46 (d, \( J = 8.0 \) Hz, 1H), 7.43 (dd, \( J = 7.6, 0.8 \) Hz, 1H), 7.35 (d, \( J = 8.0 \) Hz, 1H), 7.23 (t, \( J = 8.0 \) Hz, 1H), 7.17 (dd, \( J = 7.2, 5.2 \) Hz, 1H), 1.92 (s, 6H), 1.06–0.98 (m, 21H);

\( ^{13}C \) NMR (100 MHz, CDCl₃) \( \delta \) 164.78, 164.32, 147.51, 139.64, 137.24, 132.22, 131.61, 129.77, 129.30, 122.96, 121.97, 119.56, 103.57, 95.94, 57.55, 27.51, 18.74, 11.38;

HRMS (EI-TOF) calcd for C₂₆H₃₅ClN₂OSi (M⁺): 454.2207, found: 454.2209.

5-chloro-N-(2-(pyridin-2-yl)propan-2-yl)-2-((triisopropylsilyl)ethynyl)benzamide 3g

Following **Condition A**: 1g (0.4 mmol), 2a (0.8 mmol);

\( ^1H \) NMR (400 MHz, CDCl₃)
\( \delta \) 8.50 (d, \( J = 4.0 \) Hz, 1H), 8.46 (br, 1H), 7.77 (d, \( J = 2.0 \) Hz, 1H), 7.69 (td, \( J = 8.0, 1.6 \) Hz, 1H), 7.47 (dd, \( J = 14.8, 8.0 \) Hz, 2H), 7.33 (dd, \( J = 8.0, 2.0 \) Hz, 1H), 7.17 (dd, \( J = 6.4, 4.8 \) Hz, 1H), 1.86 (s, 6H), 1.05 – 1.00 (m, 21H);

\( ^{13}C \) NMR (100 MHz, CDCl₃) \( \delta \) 165.04, 164.42, 148.13, 139.56, 137.02, 135.97, 134.94, 130.00, 129.34, 121.85, 119.45, 118.76, 104.26, 98.51, 57.84, 27.74, 18.74, 11.39;

HRMS (EI-TOF) calcd for C₂₆H₃₅ClN₂OSi (M⁺): 454.2207, found: 454.2203.

2-bromo-N-(2-(pyridin-2-yl)propan-2-yl)-6-((triisopropylsilyl)ethynyl)benzamide 3h

Following **Condition A**: 1h (0.4 mmol), 2a (0.8 mmol);

\( ^1H \) NMR (400 MHz, CDCl₃)
\( \delta \) 8.43 (d, \( J = 4.4 \) Hz, 1H), 8.35 (br, 1H), 7.72 (td, \( J = 8.0, 1.6 \) Hz, 1H), 7.47 – 7.42 (m, 2H), 7.34 (dd, \( J = 8.0, 0.8 \) Hz, 1H), 7.22 (t, \( J = 8.0 \) Hz, 1H), 7.17 (dd, \( J = 6.4, 4.8 \) Hz, 1H), 1.93 (s, 6H), 1.04 – 0.99 (m, 21H);

\( ^{13}C \) NMR (100 MHz, CDCl₃) \( \delta \) 64.69,
5-bromo-N-(2-(pyridin-2-yl)propan-2-yl)-2-((triisopropylsilyl)ethynyl)benzamide 3i

Following **Condition A**: 1i (0.4 mmol), 2a (0.8 mmol); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.50 (br, 2H), 7.92 (d, $J = 1.6$ Hz, 1H), 7.69 (t, $J = 6.8$ Hz, 1H), 7.49 -7.40 (m, 3H), 7.16 (dd, $J = 6.4$, 5.2 Hz, 1H), 1.87 (s, 6H), 1.05 – 1.00 (m, 21H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 164.84, 164.25, 147.98, 139.63, 136.95, 135.94, 132.78, 132.06, 122.92, 121.77, 119.34, 119.11, 104.20, 98.55, 57.71, 27.61, 18.65, 11.27; HRMS (EI-TOF) calcd for C$_{26}$H$_{35}$BrN$_2$OSi (M$^+$): 498.1702, found: 498.1705.

2-Fluoro-N-(2-(pyridin-2-yl)propan-2-yl)-6-((triisopropylsilyl)ethynyl)benzamide 3g

Following **Condition A**: 1g (0.4 mmol), 2a (0.8 mmol); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.45 (d, $J = 4.2$ Hz, 1H), 8.28 (br, 1H), 7.72 (td, $J = 8.0$, 1.6 Hz, 1H), 7.46 (d, $J = 8.0$ Hz, 1H), 7.34–7.25 (m, 2H), 7.17 (dd, $J = 6.8$, 5.2 Hz, 1H), 7.07 (t, $J = 8.0$ Hz, 1H), 1.90 (s, 6H), 1.07–0.99 (m, 21H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 164.30, 162.77, 159.37 (d, $J = 246.9$ Hz), 147.60, 137.24, 130.01(d, $J = 9.0$ Hz), 129.79 (d, $J = 3.2$ Hz), 128.73 (d, $J = 19.1$ Hz), 123.26 (d, $J = 5.0$ Hz), 121.96, 119.52, 116.22 (d, $J = 2.2$ Hz), 103.39, 96.10, 57.62, 27.64, 18.73, 11.38; $^{19}$F NMR (376 MHz, CDCl$_3$) δ 115.83; HRMS (EI-TOF) calcd for C$_{26}$H$_{35}$FN$_2$OSi (M$^+$): 438.2503, found: 438.2500.
N-(2-(Pyridin-2-yl)propan-2-yl)-5-((triisopropylsilyl)ethynyl)-2,3-dihydrobenzo[b][1,4]dioxine-6-carboxamide 3k

**1H NMR** (400 MHz, CDCl₃) δ 8.51 (d, J = 4.0 Hz, 1H), 8.35 (br, 1H), 7.64 (td, J = 7.6, 1.6 Hz, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.38 (d, J = 8.8 Hz, 1H), 7.13 (dd, J = 6.8, 5.2 Hz, 1H), 6.87 (d, J = 8.8 Hz, 1H), 4.30 (m, 4H), 1.83 (s, 6H), 1.09-1.04 (m, 21H);

**13C NMR** (100 MHz, CDCl₃) δ 165.65, 164.98, 148.29, 145.97, 145.17, 136.73, 131.07, 122.37, 121.56, 119.46, 117.56, 110.06, 103.94, 100.18, 64.47, 64.20, 57.88, 28.07, 18.73, 11.46; **HRMS** (EI-TOF) calcd for C₂₈H₃₈N₂O₃Si (M⁺): 478.2652, found: 478.2655.

N-(2-(pyridin-2-yl)propan-2-yl)-3-((triisopropylsilyl)ethynyl)-2-naphthamide 3l

Following **Condition A**: 1l (0.4 mmol), 2a (0.8 mmol); **1H NMR** (400 MHz, CDCl₃) δ 8.50 (s, 2H), 8.32 (br, 1H), 8.09 (s, 1H), 7.85 (d, J = 7.2 Hz, 1H), 7.79 (d, J = 7.6 Hz, 1H), 7.68 (td, J = 8.0, 1.6 Hz, 1H), 7.54 - 7.48 (m, 3H), 7.15 (dd, J = 6.4, 5.2 Hz, 1H), 1.91 (s, 6H), 1.12 – 1.06 (m, 21H); **13C NMR** (100 MHz, CDCl₃) δ 166.31, 164.74, 148.13, 136.90, 135.30, 134.48, 133.37, 132.45, 129.58, 128.73, 127.86, 127.50, 127.26, 121.71, 119.47, 117.44, 105.84, 96.49, 57.84, 27.89, 18.81, 11.47; **HRMS** (EI-TOF) calcd for C₃₀H₃₈N₂OSi (M⁺): 470.2753, found: 470.2759.

N-(2-(Pyridin-2-yl)propan-2-yl)-2-((triisopropylsilyl)ethynyl)-1-naphthamide 3m
Following **Condition A**: \(1m\) (0.4 mmol), \(2a\) (0.8 mmol); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.43 (br, 1H), 8.39 (d, \(J = 4.0\) Hz, 1H), 8.04 (d, \(J = 6.8\) Hz, 1H), 7.79 (m, 1H), 7.76 (d, \(J = 8.8\) Hz, 1H), 7.71 (td, \(J = 8.0, 1.6\) Hz, 1H), 7.50 (m, 4H), 7.14 (dd, \(J = 6.8, 5.2\) Hz, 1H), 2.02 (s, 6H), 1.05-1.00 (m, 21H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 167.26, 164.31, 147.56, 138.64, 137.16, 133.03, 130.25, 129.79, 128.64, 127.99, 127.35, 126.91, 125.90, 121.92, 119.52, 117.88, 105.44, 95.77, 57.56, 27.64, 18.75, 11.39; HRMS (EI-TOF) calcd for C\(_{30}\)H\(_{38}\)N\(_2\)OSi (M\(^+\)): 470.2753, found: 470.2757.

![2-chloro-N-(2-(pyridin-2-yl)propan-2-yl)-4-((triisopropylsilyl)ethynyl)nicotinamide](image)

Following **Condition A**: \(1n\) (0.4 mmol), \(2a\) (0.8 mmol); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.53 (br, 1H), 8.44 (d, \(J = 4.0\) Hz, 1H), 8.33 (d, \(J = 5.2\) Hz, 1H), 7.75 (t, \(J = 7.2\) Hz, 1H), 7.46 (d, \(J = 8.0\) Hz, 1H), 7.33 (d, \(J = 4.8\) Hz, 1H), 7.20 (dd, \(J = 6.4, 5.2\) Hz, 1H), 1.92 (s, 6H), 1.10 – 1.00 (m, 21H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 163.87, 163.21, 148.95, 148.65, 147.41, 137.41, 134.73, 131.86, 126.20, 122.13, 119.50, 102.40, 101.00, 57.57, 27.33, 18.64, 11.23; HRMS (EI-TOF) calcd for C\(_{25}\)H\(_{34}\)ClN\(_3\)OSi (M\(^+\)): 455.2160, found: 455.2158.

![5-methyl-N-(2-(pyridin-2-yl)propan-2-yl)-2-((triisopropylsilyl)ethynyl)nicotinamide](image)

Following **Condition A**: \(1o\) (0.4 mmol), \(2a\) (0.8 mmol); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.55-8.48 (m, 3H), 7.86 (s, 1H), 7.71 (td, \(J = 8.0, 5.2\) Hz, 1H), 7.45 (d, \(J = 8.0\) Hz, 1H), 7.18 (dd, \(J = 6.8, 4.8\) Hz, 1H), 2.36 (s, 3H), 1.88 (s, 6H), 1.07-1.01 (m, 21H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 165.32, 164.34, 151.75, 148.05, 137.14, 137.07, 136.54.
3-chloro-N-(2-(pyridin-2-yl)propan-2-yl)-5-((triisopropylsilyl)ethynyl)isonicotinamide 3p

Following **Condition A**: 1p (0.4 mmol), 2a (0.8 mmol); **1H NMR** (400 MHz, CDCl₃) δ 8.62 (s, 2H), 8.52 (br, 1H), 8.44 (d, J = 4.0 Hz, 1H), 7.75 (td, J = 8.0, 1.6 Hz, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.22 – 7.19 (m, 1H), 1.92 (s, 6H), 1.05 – 1.00 (m, 21H); **13C NMR** (100 MHz, CDCl₃) δ 163.55, 162.33, 152.03, 148.54, 147.32, 145.16, 137.36, 128.38, 122.09, 119.38, 118.66, 99.93, 99.80, 57.62, 27.35, 18.57, 11.15; **HRMS** (EI-TOF) calcd for C₂₅H₃₄ClN₃OSi (M⁺): 455.2160, found: 455.2159.

2-methyl-N-(2-(pyridin-2-yl)propan-2-yl)-5-((triisopropylsilyl)ethynyl)isonicotinamide 3q

Following **Condition A**: 1q (0.4 mmol), 2a (0.8 mmol); **1H NMR** (400 MHz, CDCl₃) δ 8.69 (s, 1H), 8.61 (br, 1H), 8.50 (d, J = 4.0 Hz, 1H), 7.71 (td, J = 8.0, 1.6 Hz, 1H), 7.50 (s, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.18 (dd, J = 6.4, 4.8 Hz, 1H), 2.58 (s, 3H), 1.88 (s, 6H), 1.07 – 1.01 (m, 21H); **13C NMR** (100 MHz, CDCl₃) δ 164.43, 163.94, 158.52, 154.48, 147.88, 144.48, 136.95, 121.78, 121.64, 119.23, 113.47, 102.09, 99.41, 57.68, 27.46, 24.30, 18.54, 11.16; **HRMS** (EI-TOF) calcd for C₂₆H₃₈N₃OSi (M+H)⁺: 436.2784, found: 436.2794.
2-chloro-N-(2-(pyridin-2-yl)propan-2-yl)-5-((triisopropylsilyl)ethynyl)isonicotinamide 3r

Following Condition A: 1r (0.4 mmol), 2a (0.8 mmol); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.67 (br, 1H), 8.55 (s, 1H), 8.49 (dd, $J = 4.0$, 0.8 Hz, 1H), 7.73 (td, $J = 8.0$, 1.6Hz, 1H), 7.34 (s, 1H), 7.43 (d, $J = 8.4$ Hz, 1H), 7.20 (ddd, $J = 7.6$, 5.2, 0.8 Hz, 1H), 1.86 (s, 6H), 1.05–0.99 (m, 21H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 163.85, 163.22, 155.03, 151.30, 148.00, 119.43, 115.79, 101.86, 100.67, 57.95, 27.54, 18.70, 11.33; HRMS (EI-TOF) calcd for C$_{25}$H$_{34}$ClN$_3$OSi (M$^+$): 455.2160, found: 455.2161.

![2-chloro-N-(2-(pyridin-2-yl)propan-2-yl)-5-((triisopropylsilyl)ethynyl)isonicotinamide](image)

2-bromo-N-(2-(pyridin-2-yl)propan-2-yl)-5-((triisopropylsilyl)ethynyl)isonicotinamide 3s

Following Condition A: 1s (0.4 mmol), 2a (0.8 mmol); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.72 (br, 1H), 8.52 (s, 1H), 8.49 (d, $J = 4.0$ Hz, 1H), 7.79 (s, 1H), 7.73 (t, $J = 7.6$ Hz, 1H), 7.45 (d, $J = 8.0$ Hz, 1H), 7.21 (dd, $J = 6.4$, 5.2 Hz, 1H), 1.87 (s, 6H), 1.05–1.00 (m, 21H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 163.62, 162.93, 155.01, 147.80, 146.89, 141.59, 137.21, 126.59, 122.02, 119.29, 116.00, 101.86, 100.53, 57.78, 27.37, 18.56, 11.15; HRMS (EI-TOF) calcd for C$_{25}$H$_{34}$BrN$_3$OSi (M$^+$): 499.1655, found: 499.1657.

![2-bromo-N-(2-(pyridin-2-yl)propan-2-yl)-5-((triisopropylsilyl)ethynyl)isonicotinamide](image)

N-(2-(pyridin-2-yl)propan-2-yl)-3-((triisopropylsilyl)ethynyl)thiophene-2-carboxamide 3t

Following Condition A: 1t (0.4 mmol), 2a (0.8 mmol); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.55 (d, $J = 4.0$ Hz, 1H), 8.14 (br, 1H), 7.64 (td, $J = 7.6$, 1.6 Hz, 1H), 7.45 (d, $J =
8.0 Hz, 1H), 7.34 (d, J = 5.2 Hz, 1H), 7.14-7.11 (m, 2H), 1.83 (s, 6H), 1.12–1.06 (m, 21); $^1$H NMR (100 MHz, CDCl$_3$) δ 164.51, 160.33, 148.61, 142.83, 136.61, 132.69, 128.64, 121.58, 120.09, 119.25, 101.04, 99.08, 58.19, 28.28, 18.71, 11.28; HRMS (EI-TOF) calcd for C$_{24}$H$_{34}$N$_2$OSSi (M$^+$): 426.2161, found: 426.2165.

5-chloro-N-(2-(pyridin-2-yl)propan-2-yl)-3-((triisopropylsilyl)ethynyl)thiophene-2-carboxamide 3u

Following Condition A: 1u (0.4 mmol), 2a (0.8 mmol); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.54 (d, J = 4.0 Hz, 1H), 8.06 (br, 1H), 7.65 (td, J = 8.0, 1.6 Hz, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.14 (dd, J = 7.2, 5.6 Hz, 1H), 6.94 (s, 1H), 1.81 (s, 6H), 1.10 – 1.05 (m, 21H); $^1$C NMR (100 MHz, CDCl$_3$) δ 164.35, 159.61, 148.74, 141.58, 136.75, 134.14, 131.29, 121.76, 119.62, 119.28, 100.13, 99.96, 58.33, 28.29, 18.75, 11.32; HRMS (EI-TOF) calcd for C$_{24}$H$_{33}$ClN$_2$OSSi (M$^+$): 460.1771, found: 460.1777.

5-bromo-N-(2-(pyridin-2-yl)propan-2-yl)-3-((triisopropylsilyl)ethynyl)thiophene-2-carboxamide 3v

Following Condition A: 1v (0.4 mmol), 2a (0.8 mmol); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.54 (d, J = 4.0 Hz, 1H), 8.05 (br, 1H), 7.65 (td, J = 8.0, 1.6 Hz, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.14 (td, J = 5.6, 1.6 Hz, 1H), 7.07 (s, 1H), 1.80 (s, 6H), 1.10 – 1.05 (m, 21H); $^1$C NMR (100 MHz, CDCl$_3$) δ 164.35, 159.54, 148.75, 144.35, 136.75, 134.90, 121.76, 120.48, 119.29, 116.98, 100.28, 99.69, 58.33, 28.29, 18.76, 11.33; HRMS (EI-TOF) calcd for C$_{24}$H$_{33}$BrN$_2$OSSi (M$^+$): 504.1266, found: 504.1269.
4-Methyl-N-(2-(pyridin-2-yl)propan-2-yl)-2-((triisopropylsilyl)ethynyl)benzamide 3w

Following **Condition A**: 1w (0.8 mmol), 2a (0.4 mmol); **1H NMR** (400 MHz, CDCl₃) δ 8.50 (d, J = 4.4 Hz, 1H), 8.35 (br, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.66 (td, J = 7.6, 1.6 Hz, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.36 (s, 1H), 7.18 (d, J = 8.0 Hz, 1H), 7.13 (dd, J = 6.8, 5.2 Hz, 1H), 2.35 (s, 3H), 1.85 (s, 6H), 1.08–1.03 (m, 21H); **13C NMR** (100 MHz, CDCl₃) δ 166.16, 164.87, 148.22, 140.18, 136.79, 135.18, 134.91, 129.77, 129.54, 121.62, 120.00, 119.45, 105.84 97.12, 57.82, 27.98, 21.12, 18.79, 11.45; **HRMS** (EI-TOF) calcd for C₂₇H₃₈N₂O₅Si: 434.2753, found: 434.2752.

4-methyl-N-(2-(pyridin-2-yl)propan-2-yl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide 4w

Following **Condition B**: **1H NMR** (400 MHz, CDCl₃) δ 8.41 (d, J = 4.0 Hz, 1H), 8.37 (br, 1H), 7.70 (t, J = 7.6 Hz, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.28 (s, 2H), 7.14 (dd, J = 6.4, 5.2 Hz, 1H), 2.31 (s, 3H), 1.91 (s, 6H), 1.03 – 0.98 (m, 42H); **13C NMR** (100 MHz, CDCl₃) δ 166.15, 164.60, 147.37, 139.92, 138.10, 137.08, 134.38, 121.75, 121.42, 119.47, 104.47, 94.41, 57.22, 27.55, 20.84, 18.72, 11.37; **HRMS** (EI-TOF) calcd for C₃₉H₅₈N₂O₂Si₂: 614.4088, found: 614.4093.
4-methoxy-N-(2-(pyridin-2-yl)propan-2-yl)-2-((triisopropylsilyl)ethynyl)benzamide 3x
Following **Condition A:** 1x (0.8 mmol), 2a (0.4 mmol); \(^1H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.54 (d, \(J = 4.0\) Hz, 1H), 8.37 (br, 1H), 7.85 (d, \(J = 8.8\) Hz, 1H), 7.67 (td, \(J = 8.0, 1.6\) Hz, 1H), 7.46 (d, \(J = 8.4\) Hz, 1H), 7.15 (dd, \(J = 7.2, 5.2\) Hz, 1H), 7.04 (d, \(J = 2.4\) Hz, 1H), 6.91 (dd, \(J = 8.8, 2.4\) Hz, 1H), 3.83 (s, 3H), 1.86 (s, 6H), 1.09–1.04 (m, 21H); \(^13C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 165.82, 164.72, 160.61, 148.32, 136.92, 131.63, 129.67, 121.68, 121.44, 119.74, 119.46, 114.63, 105.55, 97.88, 57.81, 55.50, 28.00, 18.72, 11.36; HRMS (EI-TOF) calcd for C\(_{27}\)H\(_{38}\)N\(_2\)O\(_2\)Si (M\(^+\)): 450.2703, found: 450.2704.

![Structural formula of 4-methoxy-N-(2-(pyridin-2-yl)propan-2-yl)-2-((triisopropylsilyl)ethynyl)benzamide 3x]

4-methoxy-N-(2-(pyridin-2-yl)propan-2-yl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide 4x
Following **Condition B:** \(^1H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.42 (d, \(J = 4.0\) Hz, 1H), 8.38 (br, 1H), 7.70 (t, \(J = 6.4\) Hz, 1H), 7.43 (d, \(J = 8.0\) Hz, 1H), 7.14 (dd, \(J = 7.0, 5.2\) Hz, 1H), 7.00 (s, 2H), 3.81 (s, 3H), 1.92 (s, 6H), 1.04 – 0.98 (m, 42H); \(^13C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 165.86, 164.54, 158.60, 147.31, 137.06, 135.82, 122.75, 121.71, 119.42, 119.25, 104.22, 94.72, 57.12, 55.55, 27.47, 18.65, 11.30; HRMS (EI-TOF) calcd for C\(_{38}\)H\(_{58}\)N\(_2\)O\(_2\)Si\(_2\) (M\(^+\)): 630.4037, found: 630.4036.

![Structural formula of 4-methoxy-N-(2-(pyridin-2-yl)propan-2-yl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide 4x]

4-Fluoro-N-(2-(pyridin-2-yl)propan-2-yl)-2-((triisopropylsilyl)ethynyl)benzamide 3y
Following **Condition A:** 1y (0.8 mmol), 2a (0.4 mmol); \(^1H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.51 (d, \(J = 4.0\) Hz, 1H), 8.38 (br, 1H), 7.80 (dd, \(J = 6.8, 4.0\) Hz, 1H), 7.68 (td, \(J = 8.0, 1.6\) Hz, 1H), 7.46 (d, \(J = 8.4\) Hz, 1H), 7.15 (dd, \(J = 7.2, 5.2\) Hz, 1H), 7.04 (d, \(J = 2.4\) Hz, 1H), 6.91 (dd, \(J = 8.8, 2.4\) Hz, 1H), 3.83 (s, 3H), 1.86 (s, 6H), 1.09–1.04 (m, 21H); \(^13C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 165.86, 164.54, 158.60, 147.31, 137.06, 135.82, 122.75, 121.71, 119.42, 119.25, 104.22, 94.72, 57.12, 55.55, 27.47, 18.65, 11.30; HRMS (EI-TOF) calcd for C\(_{38}\)H\(_{58}\)N\(_2\)O\(_2\)Si\(_2\) (M\(^+\)): 630.4037, found: 630.4036.
8.0, 1.6 Hz, 1H), 7.58–7.55 (m, 1H), 7.47 (d, \( J = 8.0 \) Hz, 1H), 7.38–7.36 (m, 2H),
7.17–7.14 (m, 1H), 1.87 (s, 6H), 1.07–1.02 (m, 21H); \(^1^3^C\) NMR (100 MHz, CDCl\(_3\)) \( \delta \)
165.42, 164.65, 163.03 (d, \( J = 249.3 \) Hz), 148.19, 136.97, 134.36, 131.75 (d, \( J = 9.1 \)
Hz), 122.38 (d, \( J = 9.7 \) Hz), 121.80, 121.07 (d, \( J = 22.9 \) Hz), 119.47, 116.30 (d, \( J =
21.3 \) Hz), 104.17, 98.99, 57.83, 27.84, 18.75, 11.41; \(^1^9^F\) NMR (376 MHz, CDCl\(_3\)) \( \delta \)
110.89; HRMS (EI-TOF) calcd for C\(_{26}\)H\(_{35}\)FN\(_2\)OSi (M\(^{+}\)): 438.2503, found: 438.24503.

4-fluoro-N-(2-(pyridin-2-yl)propan-2-yl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide 4y

Following Condition B: \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.51 (br, 1H), 8.42 (d, \( J = 4.4 \)
Hz, 1H), 7.71 (td, \( J = 8.0, 1.6 \) Hz, 1H), 7.43 (d, \( J = 8.0 \) Hz, 1H), 7.17 (d, \( J = 8.8 \) Hz,
3H), 1.93 (s, 6H), 1.03 – 0.98 (m, 42H); \(^1^3^C\) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 165.21,
164.30, 161.21 (d, \( J = 247.2 \) Hz), 147.29, 139.06 (d, \( J = 3.2 \) Hz), 137.18, 123.56 (d, \( J =
10.2 \) Hz), 121.84, 120.52 (d, \( J = 22.5 \) Hz), 119.41, 103.05 (d, \( J = 2.7 \) Hz), 96.47,
57.19, 27.44, 18.62, 11.27; \(^1^9^F\) NMR (376 MHz, CDCl\(_3\)) \( \delta \) 113.07; HRMS (EI-TOF)
calcd for C\(_{37}\)H\(_{57}\)FN\(_2\)OSi\(_2\) (M\(^{+}\)): 618.3837, found: 618.3842.

4-Chloro-N-(2-(pyridin-2-yl)propan-2-yl)-2-((triisopropylsilyl)ethynyl)benzamide 3z

Following Condition A: 1z (0.8 mmol), 2a (0.4 mmol); \(^1^H\) NMR (400 MHz, CDCl\(_3\))
\( \delta \) 8.50 (d, \( J = 4.4 \) Hz, 1H), 8.42 (br, 1H), 7.74–7.67(m, 2H), 7.51 (d, \( J = 2.0 \) Hz, 1H),
7.45 (d, \( J = 8.0 \) Hz, 1H), 7.34 (dd, \( J = 8.4, 2.0 \) Hz, 1H), 7.16 (dd, \( J = 6.8, 5.2 \) Hz, 1H),
1.86 (s, 6H), 1.06-1.01 (m, 21H); \(^1^3^C\) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 165.45, 164.53,
148.11, 137.04, 136.57, 135.76, 134.13, 130.73, 129.05, 121.94, 121.84, 119.48,
4-chloro-N-(2-(pyridin-2-yl)propan-2-yl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide 4z

Following **Condition B**: $^1$H NMR (400 MHz, CDCl$_3$) δ 8.53 (br, 1H), 8.41 (d, $J = 4.4$ Hz, 1H), 7.71 (t, $J = 6.8$ Hz, 1H), 7.44 - 7.41 (m, 3H), 7.16 (dd, $J = 7.2$, 5.2 Hz, 1H), 1.92 (s, 6H), 1.03 – 0.98 (m, 42H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.07, 164.20, 147.26, 140.82, 137.20, 133.68, 133.21, 123.14, 121.85, 119.37, 102.81, 96.67, 57.19, 27.43, 18.63, 11.25; HRMS (EI-TOF) calcd for C$_{37}$H$_{55}$ClN$_2$OSi$_2$ (M$^+$): 634.3541, found: 634.3546.

4-bromo-N-(2-(pyridin-2-yl)propan-2-yl)-2-((triisopropylsilyl)ethynyl)benzamide 3aa

Following **Condition A**: 1aa (0.8 mmol), 2a (0.4 mmol); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.49 (d, $J = 4.8$ Hz, 1H), 8.44 (br, 1H), 7.71-7.63 (m, 3H), 7.49 (dd, $J = 8.4$, 2.0 Hz, 1H), 7.44 (d, $J = 8.0$ Hz, 1H), 7.16 (dd, $J = 7.2$, 4.8 Hz, 1H), 1.86 (s, 6H), 1.06–1.01 (m, 21H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.50, 164.45, 148.06, 137.09, 136.99, 136.91, 131.91, 130.70, 123.77, 122.12, 121.80, 119.41, 103.75, 98.99, 57.75, 27.72, 18.72, 11.36; HRMS (EI-TOF) calcd for C$_{26}$H$_{33}$BrN$_2$OSi (M$^+$): 498.1702, found: 498.1705.
4-bromo-N-(2-(pyridin-2-yl)propan-2-yl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide 4aa

Following **Condition B**: \(^1H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.48 (br, 1H), 8.42 (d, \(J = 4.4\) Hz, 1H), 7.71 (td, \(J = 7.6, 1.6\) Hz, 1H), 7.59 (s, 2H), 7.41 (d, \(J = 8.0\) Hz, 1H), 7.16 (dd, \(J = 6.8, 5.2\) Hz, 1H), 1.90 (s, 6H), 1.02–0.97 (m, 42H); \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 165.19, 164.36, 147.39, 141.28, 137.23, 136.12, 123.36, 121.49, 119.45, 102.76, 96.88, 57.30, 27.53, 18.71, 11.35; HRMS (EI-TOF) calcd for C\(_{37}\)H\(_{55}\)BrN\(_2\)O\(_2\)Si\(_2\) (M\(^+\)): 678.3036, found: 678.3034.

2-Methyl-N-(2-(pyridin-2-yl)propan-2-yl)-6-((triisopropylsilyl)ethynyl)benzamide 3ab

Following **Condition A**: 1ab (0.8 mmol), 2a (0.4 mmol); \(^1H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.54 (br, 1H), 8.48 (d, \(J = 4.4\) Hz, 1H), 7.84 (d, \(J = 8.0\) Hz, 1H), 7.77 (s, 1H), 7.71 (td, \(J = 7.86, 1.6\) Hz, 1H), 7.60 (d, \(J = 8.4\) Hz, 1H), 7.45 (d, \(J = 8.0\) Hz, 1H), 7.18 (dd, \(J = 6.8, 4.8\) Hz, 1H), 1.88 (s, 6H), 1.06-1.01 (m, 21H); \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 165.41, 164.22, 147.88, 141.69, 137.07, 131.82 (q, \(J = 32.8\) Hz), 131.26 (q, \(J = 2.8\) Hz), 129.49, 127.48, 125.10 (q, \(J = 3.6\) Hz), 123.41 (q, \(J = 270.9\) Hz), 121.86, 121.20, 119.38, 103.48, 98.94, 57.68, 27.56, 18.63, 11.30; \(^{19}F\) NMR (376 MHz, CDCl\(_3\)) \(\delta\) 60.04; HRMS (EI-TOF) calcd for C\(_{27}\)H\(_{35}\)F\(_3\)N\(_2\)OSi (M\(^+\)): 488.2471, found: 488.2474.
N-(2-(pyridin-2-yl)propan-2-yl)-4-(trifluoromethyl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide 4ab

Following **Condition B**:

\[ ^1H \text{ NMR (400 MHz, CDCl}_3 \] \( \delta \) 8.53 (br, 1H), 8.32 (d, \( J = 4.0 \) Hz, 1H), 7.64 (td, \( J = 8.0, 1.2 \) Hz, 1H), 7.59 (s, 2H), 7.33 (d, \( J = 8.0 \) Hz, 1H), 7.08 (dd, \( J = 6.4, 4.8 \) Hz, 1H), 1.85 (s, 6H), 0.95 – 0.90 (m, 42H); \[ ^13C \text{ NMR (100 MHz, CDCl}_3 \] \( \delta \) 164.89, 164.10, 147.30, 145.06, 137.31, 130.87 (q, \( J = 33.4 \) Hz), 130.02 (q, \( J = 3.0 \) Hz), 123.17 (q, \( J = 271.2 \) Hz), 122.63, 121.96, 119.40, 102.64, 97.33, 57.32, 27.50, 18.66, 11.30; \[ ^19F \text{ NMR (376 MHz, CDCl}_3 \] \( \delta \) 63.12; \[ \text{HRMS (EI-TOF) calcd for C}_{38}\text{H}_{55}\text{F}_{3}\text{N}_{2}\text{O}_{3}\text{Si}_{2} (M^+) : 688.3805, found: 688.3804. \]

4-Nitro-N-(2-(pyridin-2-yl)propan-2-yl)-2-((triisopropylsilyl)ethynyl)benzamide 3ac

Following **Condition A**: 1ac (0.8 mmol), 2a (0.4 mmol); \[ ^1H \text{ NMR (400 MHz, CDCl}_3 \] \( \delta \) 8.66 (br, 1H), 8.48 (d, \( J = 4.4 \) Hz, 1H), 8.36 (d, \( J = 2.4 \) Hz, 1H), 8.18 (dd, \( J = 8.4, 2.0 \) Hz, 1H), 7.86 (d, \( J = 8.4 \) Hz, 1H), 7.74 (td, \( J = 8.0, 2.0 \) Hz, 1H), 7.46 (d, \( J = 8.10 \) Hz, 1H), 7.20 (dd, \( J = 7.2, 5.6 \) Hz, 1H), 1.89 (s, 6H), 1.06–1.01 (m, 21H); \[ ^13C \text{ NMR (100 MHz, CDCl}_3 \] \( \delta \) 164.94, 164.02, 148.20, 147.85, 144.22, 137.34, 130.08, 129.28, 123.15, 122.18, 122.09, 119.48, 102.55, 100.19, 57.79, 27.54, 18.69, 11.34; \[ \text{HRMS (EI-TOF) calcd for C}_{26}\text{H}_{35}\text{N}_{3}\text{O}_{3}\text{Si} (M^+) : 465.2448, found: 465.2446. \]
4-nitro-N-(2-(pyridin-2-yl)propan-2-yl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide 4ac

Following **Condition B**: ¹H NMR (400 MHz, CDCl₃) δ 8.73 (br, 1H), 8.42 (d, J = 4.4 Hz, 1H), 8.26 (s, 2H), 7.76 (t, J = 8.0 Hz, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.20 (dd, J = 6.4, 5.2 Hz, 1H), 1.95 (s, 6H), 1.05 – 1.00 (m, 42H); ¹³C NMR (100 MHz, CDCl₃) δ 164.16, 163.76, 147.18, 147.06, 147.00, 137.37, 127.79, 123.32, 122.00, 119.33, 101.78, 98.62, 57.32, 27.40, 18.56, 11.19; HRMS (EI-TOF) calcd for C₃₇H₅₅N₃O₃Si₂ (M⁺): 645.3782, found: 645.3775.

4-Cyano-N-(2-(pyridin-2-yl)propan-2-yl)-2-((triisopropylsilyl)ethynyl)benzamide 3ad

Following **Condition A**: 1ad (0.8 mmol), 2a (0.4 mmol); ¹H NMR (400 MHz, CDCl₃) δ 8.59 (br, 1H), 8.48 (d, J = 4.4 Hz, 1H), 7.82 (dd, J = 4.5, 3.1 Hz, 2H), 7.83–7.81 (m, 2H), 7.73 (td, 8.0, 1.6 Hz, 1H), 7.63 (dd, J = 8.0, 1.6 Hz, 1H), 7.45 (d, J = 8.4 Hz, 1H), 7.20 (dd, J = 7.6, 5.2 Hz, 1H), 1.88 (s, 6H), 1.05–1.00 (m, 21H); ¹³C NMR (100 MHz, CDCl₃) δ 165.03, 164.11, 147.90, 142.37, 138.10, 137.31, 131.56, 129.82, 122.06, 121.89, 119.51, 117.66, 113.90, 102.67, 100.26, 57.81, 27.59, 18.71, 11.35; HRMS (EI-TOF) calcd for C₂₇H₃₅N₃OSi (M⁺): 445.2549, found: 445.2551.
4-Cyano-N-(2-(pyridin-2-yl)propan-2-yl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide 4ad

Following **Condition B**: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.62 (br, 1H), 8.42 (d, $J$ = 4.8 Hz, 1H), 7.74 (td, $J$ = 7.6, 1.2 Hz, 1H), 7.71 (s, 2H), 7.42 (d, $J$ = 8.0 Hz, 1H), 7.18 (dd, $J$ = 7.6, 5.2 Hz, 1H), 1.91 (s, 6H), 1.06–0.97 (m, 42H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.40, 164.06, 147.35, 145.50, 137.38, 136.42, 123.25, 122.04, 119.44, 117.17, 112.99, 101.88, 98.61, 57.44, 27.52, 18.68, 11.32; **HRMS** (EI-TOF) calcd for C$_{38}$H$_{55}$N$_3$OSi$_2$ (M$^+$): 625.3884, found: 625.3882.

4-acetyl-N-(2-(pyridin-2-yl)propan-2-yl)-2-((triisopropylsilyl)ethynyl)benzamide 3ae

Following **Condition A**: 1ae (0.8 mmol), 2a (0.4 mmol); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.54 (br, 1H), 8.49 (d, $J$ = 4.0 Hz, 1H), 8.10 (s, 1H), 7.92 (dd, $J$ = 8.4, 1.6 Hz, 1H), 7.83 (d, $J$ = 8.4 Hz, 1H), 7.71 (td, $J$ = 8.0, 1.2 Hz, 1H), 7.46 (d, $J$ = 8.0 Hz, 1H), 7.18 (dd, $J$ = 6.4, 4.8 Hz, 1H), 2.63 (s, 3H), 1.89 (s, 6H), 1.13 – 1.01 (m, 21H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 196.93, 165.71, 164.29, 147.95, 142.19, 137.77, 137.07, 134.44, 129.35, 128.13, 121.87, 120.94, 119.41, 104.10, 98.23, 57.72, 27.63, 26.82, 18.70, 11.35; **HRMS** (EI-TOF) calcd for C$_{28}$H$_{38}$N$_2$O$_2$Si (M$^+$): 462.2703, found: 462.2712.
4-acetyl-N-(2-(pyridin-2-yl)propan-2-yl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide

Following Condition B: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.58 (br, 1H), 8.41 (d, $J = 4.4$ Hz, 1H), 8.00 (s, 2H), 7.73 (t, $J = 6.8$ Hz, 1H), 7.43 (d, $J = 8.4$ Hz, 1H), 7.17 (dd, $J = 6.4$, 5.2 Hz, 1H), 2.62 (s, 3H), 1.94 (s, 6H), 1.05 – 0.99 (m, 42H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 196.39, 165.20, 164.13, 147.27, 145.69, 137.25, 136.71, 133.16, 122.26, 121.90, 119.38, 103.14, 96.42, 57.27, 27.49, 26.78, 18.66, 11.29; HRMS (EI-TOF) calcd for C$_{39}$H$_{58}$N$_2$O$_2$Si$_2$ (M$^+$): 642.4037, found: 642.4036.

Methyl 4-((2-(pyridin-2-yl)propan-2-yl)carbamoyl)-3-((triisopropylsilyl)ethynyl)benzoate

Following Condition A: 1af (0.8 mmol), 2a (0.4 mmol); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.52 (br, 1H), 8.49 (d, $J = 4.8$ Hz, 1H), 8.20 (d, $J = 1.6$ Hz, 1H), 8.00 (dd, $J = 8.0$, 1.6 Hz, 1H), 7.80 (d, $J = 8.0$ Hz, 1H), 7.71 (td, $J = 8.0$, 1.6 Hz, 1H), 7.46 (d, $J = 8.0$ Hz, 1H), 7.19 – 7.16 (m, 1H), 3.94 (s, 3H), 1.89 (s, 6H), 1.07 – 1.01 (m, 21H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.91, 165.76, 164.30, 147.95, 142.18, 137.05, 135.73, 131.29, 129.39, 129.11, 121.84, 120.71, 119.41, 104.05, 98.07, 57.71, 52.50, 27.62, 18.69, 11.34; HRMS (EI-TOF) calcd for C$_{28}$H$_{38}$N$_2$O$_3$Si$_2$ (M$^+$): 478.2652, found: 478.2659.
methyl

4-((2-(pyridin-2-yl)propan-2-yl)carbamoyl)-3,5-bis((triisopropylsilyl)ethynyl)benzoate 4af

Following **Condition B**: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.58 (br, 1H), 8.41 (d, $J = 4.0$ Hz, 1H), 8.10 (s, 2H), 7.73 (t, $J = 6.4$ Hz, 1H), 7.43 (d, $J = 8.0$ Hz, 1H), 7.17 (dd, $J = 6.4$, 4.8 Hz, 1H), 3.95 (s, 3H), 1.94 (s, 6H), 1.04 – 0.99 (m, 42H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.46, 165.23, 164.12, 147.25, 145.64, 137.22, 134.40, 130.19, 122.05, 121.87, 119.36, 103.09, 96.24, 57.25, 52.55, 27.46, 18.63, 11.26; HRMS (El-TOF) calcd for C$_{39}$H$_{58}$N$_2$O$_3$Si$_2$ (M$^+$): 658.3986, found: 658.3988.

3-Fluoro-N-(2-(pyridin-2-yl)propan-2-yl)-2-((triisopropylsilyl)ethynyl)benzamide 3ag

Following **Condition A**: 1ag (0.8 mmol), 2a (0.4 mmol); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.50 (d, $J = 4.8$ Hz, 1H), 8.45 (br, 1H), 7.69 (td, $J = 8.0$, 1.6 Hz, 1H), 7.56 (d, $J = 7.6$ Hz, 1H), 7.45 (d, $J = 8.0$ Hz, 1H), 7.33 (td, $J = 8.0$, 5.6 Hz, 1H), 7.18-7.13 (m, 2H), 1.87 (s, 6H), 1.07–1.02 (m, 21H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.34 (d, $J = 2.9$ Hz), 164.52, 164.23 (d, $J = 251.1$ Hz), 162.98, 148.10, 140.31, 137.02, 129.69 (d, $J = 8.5$ Hz), 124.56 (d, $J = 3.3$ Hz), 121.83, 119.47, 116.91 (d, $J = 11.8$ Hz), 109.55 (d, $J = 17.2$ Hz, 2H), 104.09 (d, $J = 4.8$ Hz), 97.49, 57.81, 27.76, 18.67, 11.37; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ 107.44; HRMS (El-TOF) calcd for C$_{26}$H$_{35}$FN$_2$OSi (M$^+$): 438.2503, found: 438.2499.
3-Fluoro-N-(2-(pyridin-2-yl)propan-2-yl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide 4ag

Following **Condition B**: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.49 (br, 1H), 8.43 (d, $J$ = 4.0 Hz, 1H), 7.71 (td, $J$ = 8.0, 1.6 Hz, 1H), 7.46–7.42 (m, 2H), 7.16 (dd, $J$ = 6.4, 4.8 Hz, 1H), 7.02 (t, $J$ = 8.4 Hz, 1H), 1.92 (s, 6H), 1.03–0.97 (m, 42H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.84 (d, $J$ = 2.4 Hz), 164.40, 163.42 (d, $J$ = 254.6 Hz), 147.42, 144.40, 137.22, 135.20 (d, $J$ = 22.3 Hz), 110.88, 103.32, 101.87 (d, $J$ = 4.4 Hz), 96.62, 94.61, 57.37, 27.56, 18.73, 18.70, 11.40, 11.34; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ 105.83; HRMS (El-TOF) calcd for C$_{37}$H$_{55}$FN$_2$OSi$_2$ (M$^+$): 618.3837, found: 618.3839.

2-methyl-N-(2-(pyridin-2-yl)propan-2-yl)-6-((trimethylsilyl)ethynyl)benzamide 5a

Following **Condition C**: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.46 (d, $J$ = 4.0 Hz, 1H), 8.11 (br, 1H), 7.72 (td, $J$ = 8.0, 1.6 Hz, 1H), 7.49 (d, $J$ = 8.0 Hz, 1H), 7.34 (d, $J$ = 6.8 Hz, 1H), 7.21 – 7.17 (m, 3H), 2.38 (s, 3H), 1.92 (s, 6H), 0.10 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.63, 164.46, 147.64, 140.44, 137.15, 135.64, 130.74, 130.63, 128.34, 121.95, 120.22, 119.61, 103.04, 97.41, 57.30, 27.60, 19.50, -0.08; HRMS (El-TOF) calcd for C$_{21}$H$_{26}$N$_2$OSi (M$^+$): 350.1814, found: 350.1822.
2-(hex-1-yn-1-yl)-6-methyl-N-(2-(pyridin-2-yl)propan-2-yl)benzamide 5b
Following Condition C: $^1$H NMR (400 MHz, CDCl$_3$) δ 8.47 (d, $J = 4.8$ Hz, 1H), 7.98 (br, 1H), 7.72 (t, $J = 8.0$ Hz, 1H), 7.51 (d, $J = 8.0$ Hz, 1H), 7.27 – 7.25 (m, 1H), 7.19 -7.16 (m, 2H), 7.11 (d, $J = 7.2$ Hz, 1H), 2.37 (s, 3H), 2.31 (t, $J = 7.2$ Hz, 2H), 1.91 (s, 6H), 1.50 – 1.43 (m, 2H), 1.39 -1.33 (m, 2H), 0.82 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.23, 164.56, 147.69, 140.49, 137.15, 135.35, 129.92, 129.68, 128.32, 121.93, 121.18, 119.63, 93.59, 78.70, 57.30, 30.76, 27.65, 22.13, 19.44, 19.40, 13.70; HRMS (El-TOF) calcd for C$_{22}$H$_{26}$N$_2$O (M$^+$): 334.2045, found: 334.2047.

![Chemical Structure 5b](image)

2-methyl-6-(phenylethynyl)-N-(2-(pyridin-2-yl)propan-2-yl)benzamide 5c
Following Condition C: $^1$H NMR (400 MHz, CDCl$_3$) δ 8.44 (d, $J = 4.4$ Hz, 1H), 8.09 (br, 1H), 7.64 (td, $J = 8.0$, 1.6 Hz, 1H), 7.47 (d, $J = 8.4$ Hz, 1H), 7.42 – 7.36 (m, 3H), 7.26 – 7.23 (m, 4H), 7.19 (d, $J = 7.2$ Hz, 1H), 7.16 – 7.13 (m, 1H), 2.42 (s, 3H), 1.91 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.92, 164.44, 147.70, 140.53, 137.16, 135.57, 131.67, 130.54, 129.97, 128.49, 128.32, 123.34, 121.95, 120.42, 119.63, 92.22, 87.69, 57.44, 27.70, 19.45; HRMS (El-TOF) calcd for C$_{24}$H$_{22}$N$_2$O (M$^+$): 354.1732, found: 354.1732.

![Chemical Structure 5c](image)

2-methyl-N-(2-(pyridin-2-yl)propan-2-yl)-6-(p-tolylethynyl)benzamide 5d
Following Condition C: $^1$H NMR (400 MHz, CDCl$_3$) δ 8.43 (d, $J = 4.8$ Hz, 1H), 8.08 (br, 1H), 7.64 (td, $J = 8.0$, 1.6 Hz, 1H), 7.47 (d, $J = 8.0$ Hz, 1H), 7.39 (d, $J = 7.6$ Hz, 1H), 7.27 (d, $J = 8.4$ Hz, 2H), 7.22 (d, $J = 7.6$ Hz, 1H), 7.18 – 7.12 (m, 2H), 7.05 (d, $J = 7.6$ Hz, 2H), 2.41 (s, 3H), 2.31 (s, 3H), 1.90 (s, 6H); $^{13}$C NMR (100 MHz,
CDCl$_3$ δ 167.96, 164.41, 147.67, 140.40, 138.44, 137.12, 135.50, 131.53, 130.33, 129.90, 129.07, 128.44, 121.91, 120.57, 120.23, 119.61, 92.43, 87.00, 57.41, 27.68, 21.56, 19.42; HRMS (EI-TOF) calcd for C$_{25}$H$_{24}$N$_2$O (M$^+$): 368.1889, found: 368.1896.

![Chemical structure of 2-((4-methoxyphenyl)ethynyl)-6-methyl-N-(2-(pyridin-2-yl)propan-2-yl)benzamide 5e](image1.png)

2-((4-methoxyphenyl)ethynyl)-6-methyl-N-(2-(pyridin-2-yl)propan-2-yl)benzamide 5e

Following **Condition C**: $^1$H NMR (400 MHz, CDCl$_3$) δ 8.44 (d, $J = 4.4$ Hz, 1H), 8.06 (br, 1H), 7.64 (td, $J = 8.0$, 1.6 Hz, 1H), 7.48 (d, $J = 8.0$ Hz, 1H), 7.38 (d, $J = 7.6$ Hz, 1H), 7.31 (d, $J = 8.4$ Hz, 2H), 7.23 (t, $J = 7.6$ Hz, 1H), 7.17 – 7.13 (m, 2H), 6.77 (d, $J = 8.8$ Hz, 2H), 3.77 (s, 3H), 2.41 (s, 3H), 1.90 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.01, 164.42, 159.65, 147.68, 140.33, 137.12, 135.46, 133.09, 130.19, 129.80, 128.44, 121.92, 120.70, 119.61, 115.44, 113.95, 92.27, 86.35, 57.41, 55.35, 27.69, 19.42; HRMS (EI-TOF) calcd for C$_{25}$H$_{24}$N$_2$O$_2$ (M$^+$): 384.1838, found: 384.1836.

![Chemical structure of 2-((4-methoxyphenyl)ethynyl)-6-methyl-N-(2-(pyridin-2-yl)propan-2-yl)benzamide 5f](image2.png)

2-((4-(tert-butyl)phenyl)ethynyl)-6-methyl-N-(2-(pyridin-2-yl)propan-2-yl)benzamide 5f

Following **Condition C**: $^1$H NMR (400 MHz, CDCl$_3$) δ 8.43 (d, $J = 4.8$ Hz, 1H), 8.08 (br, 1H), 7.63 (t, $J = 7.6$ Hz, 1H), 7.48 (d, $J = 8.0$ Hz, 1H), 7.39 (d, $J = 7.6$ Hz, 1H), 7.32 (d, $J = 8.0$ Hz, 2H), 7.26 (d, $J = 8.8$ Hz, 2H), 7.22 (d, $J = 7.6$ Hz, 1H), 7.18 – 7.11 (m, 2H), 2.41 (s, 3H), 1.91 (s, 6H), 1.28 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.97, 164.40, 151.56, 147.67, 140.34, 137.11, 135.47, 131.37, 130.30, 129.97,
128.43, 125.29, 121.90, 120.59, 120.26, 119.61, 92.41, 87.02, 57.41, 34.83, 31.24, 27.70, 19.41; HRMS (EI-TOF) calcd for C_{28}H_{30}N_{2}O (M^+) 410.2358, found: 410.2359.

2-((4-chlorophenyl)ethynyl)-6-methyl-N-(2-(pyridin-2-yl)propan-2-yl)benzamide

5g

Following **Condition C**: {\textsuperscript{1}H NMR} (400 MHz, CDCl\textsubscript{3}) δ 8.44 (d, J = 4.4 Hz, 1H), 8.14 (br, 1H), 7.67 (td, J = 7.6, 1.6 Hz, 1H), 7.46 (d, J = 7.6 Hz, 1H), 7.30 (m, 3H), 7.25 (m, 3H), 7.16 (dd, J = 7.2, 4.8 Hz, 1H), 2.42 (s, 3H), 1.90 (s, 6H); {\textsuperscript{13}C NMR} (100 MHz, CDCl\textsubscript{3}) δ 167.85, 164.39, 147.68, 140.65, 137.24, 135.59, 134.35, 132.86, 130.78, 129.90, 128.69, 128.53, 122.03, 121.87, 120.11, 119.62, 91.02, 88.68, 57.41, 27.66, 19.43; HRMS (EI-TOF) calcd for C_{24}H_{21}ClN_{2}O (M^+) 388.1342, found: 388.1342.

2-methyl-6-((4-pentylphenyl)ethynyl)-N-(2-(pyridin-2-yl)propan-2-yl)benzamide

5h

Following **Condition C**: {\textsuperscript{1}H NMR} (400 MHz, CDCl\textsubscript{3}) δ 8.43 (d, J = 4.4 Hz, 1H), 8.07 (br, 1H), 7.62 (td, J = 8.0, 1.6 Hz, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.29 (d, J = 8.4 Hz, 2H), 7.23 (t, J = 7.6 Hz, 1H), 7.17 – 7.11 (m, 2H), 7.05 (d, J = 8.0 Hz, 2H), 2.55 (t, J = 7.6 Hz, 2H), 2.41 (s, 3H), 1.90 (s, 6H), 1.61 - 1.52 (m, 2H), 1.32 – 1.26 (m, 4H), 0.87 (t, J = 6.8 Hz, 3H); {\textsuperscript{13}C NMR} (100 MHz, CDCl\textsubscript{3}) δ 167.94, 164.40, 147.66, 143.46, 140.36, 137.10, 135.47, 131.53, 130.30, 129.91, 128.42, 128.39, 121.88, 120.58, 120.41, 119.60, 92.48, 87.01, 57.41, 35.92, 31.50,
30.95, 27.68, 22.58, 19.40, 14.09; **HRMS** (EI-TOF) calcd for C\textsubscript{29}H\textsubscript{32}N\textsubscript{2}O (M\textsuperscript{+}): 424.2515, found: 424.2514.

![Chemical structure image](image)

2-(dec-1-yn-1-yl)-6-methyl-N-(2-(pyridin-2-yl)propan-2-yl)benzamide 5i

Following **Condition C**: \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.46 (d, \(J = 4.0\) Hz, 1H), 7.98 (br, 1H), 7.72 (td, \(J = 8.0, 1.6\) Hz, 1H), 7.50 (d, \(J = 8.0\) Hz, 1H), 7.27 – 7.26 (m, 1H), 7.17 (t, \(J = 7.2\) Hz, 2H), 7.11 (d, \(J = 7.2\) Hz, 1H), 2.37 (s, 3H), 2.30 (t, \(J = 7.2\) Hz, 2H), 1.91 (s, 6H), 1.51 – 1.44 (m, 2H), 1.27 – 1.21 (m, 10H), 0.86 (t, \(J = 6.4\) Hz, 3H);

\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 168.19, 164.54, 147.69, 140.48, 137.08, 135.30, 129.89, 129.65, 128.29, 121.89, 121.16, 119.57, 93.64, 78.66, 57.29, 31.94, 29.22, 29.20, 29.07, 28.69, 27.64, 22.74, 19.69, 19.40, 14.20; **HRMS** (ESI-TOF) calcd for C\(_{26}\)H\(_{35}\)N\(_2\)O (M+H\(^{+}\)): 391.2744, found: 391.2747.

### 2.4 Gram-scale Reaction

To an oven-dried 100 mL screw-capped vial was added substrate 1a (6.0 mmol), 2a (12.0 mmol), Ni(OTf)\(_2\) (0.03 mmol), NaHCO\(_3\) (12 mmol), DME (0.06 mmol) in \textit{t}-BuCN (6 mL). The mixture was stirred for 36 h at 150 °C under \(N_2\) followed by cooling. The resulting mixture was filtered through a celite pad and concentrated in \textit{vacuo}. The residue was purified by chromatography on silica gel using hexane/EtOAc as the eluent to afford the product 3a (1.436 g, 57%) and 4a (657.9 mg, 18%).
2.5 Mechanistic Investigation

**Intrermolecular Competition KIE**

To an oven-dried 50 mL screw-capped vial was added substrate 1a (0.4 mmol), 2a (0.8 mmol), Ni(OTf)\(_2\) (0.8 mg, 0.002 mmol), NaHCO\(_3\) (67.2 mg, 0.8 mmol), DME (0.004 mmol) in t-BuCN (0.5 mL). The mixture was stirred for 4 h at 150 °C under N\(_2\) followed by cooling. The resulting mixture was filtered through a celite pad and concentrated in vacuo. The residue was purified by preparative TLC using hexane/EtOAc as the eluent to afford the product. The ratio of product 3a/d-3a was analyzed by \(^1\)H NMR.

**Radical Scavenger Reactions**

To an oven-dried 50 mL screw-capped vial was added substrate 1a (0.4 mmol), 2a (0.8 mmol), Ni(OTf)\(_2\) (0.8 mg, 0.002 mmol), NaHCO\(_3\) (67.2 mg, 0.8 mmol), additives (0.4 mmol), DME (0.004 mmol) in t-BuCN (0.5 mL). The mixture was stirred for 24 h at 150 °C under N\(_2\) followed by cooling. The resulting mixture was filtered through a celite pad and concentrated in vacuo. The yield of product 3a was analyzed by \(^1\)H NMR.
3. References:


4. NMR Spectra

1f

[Chemical structure and NMR spectra images]

S40
3f

S53
3g
3h
3k
3m
3p
3u
3w
4w

N
H
O

TIPS

Me
N
H
O

TIPS

S72
3y
TIPS

3z

S78
3aa
4ab
3ac
3ad
TIPS NC-
3ag
4ag
5a
5c
S100