Supplementary Information

A cascade process for direct converting nitriles (RCN) to cyanamide (RNHCN) via SO$_2$F$_2$-activated Tiemann rearrangement

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I. General Information

Reactions, unless otherwise stated, were carried out with magnetic stirring under an air or SO$_2$F$_2$ atmosphere in oven-dried glassware. Reagents were used as received without further purification, unless otherwise noted. All reaction solvents prior to use were distilled according to standard laboratory methods. Analytical thin-layer chromatography (TLC) was performed on 0.2 mm coated silica gel plates (HSGF 254) and visualized using a UV light (254 or 365 nm). Flash column chromatography was performed employing silica gel (200–300 mesh) at an increased pressure. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker Avance III HD 500 and 126 MHz NMR spectrometer in CDCl$_3$ or DMSO-$d_6$, respectively. Chemical shifts $\delta$ are reported in parts per million (ppm) relative to a residual undeuterated solvent as an internal reference ($^1$H $\delta$ 7.26 for CDCl$_3$, $\delta$ 2.50 for DMSO-$d_6$; $^{13}$C $\delta$ 77.16 for CDCl$_3$, $\delta$ 39.52 for DMSO-$d_6$). The following abbreviations were used to explain NMR peak multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad signal. High-resolution mass spectrometry was performed on an Agilent 6210 TOF-MS equipped with an ESI source of HR-MS System ESI spectrometer. Analytical and spectral data of all those known compounds are exactly matching with the reported values.
II. General procedure for the synthesis of benzamidoxime 2a<sup>1</sup>

To the solution of benzonitrile 1a (1.0 g, 10 mmol) in EtOH (50 mL, 0.2 M) was added 50 wt% aqueous hydroxylamine solution (1.0 g, 15 mmol, 1.5 equiv). The mixture was stirred at reflux temperature for 3 h under nitrogen. After cooling to room temperature, the reaction mixture was concentrated under reduced pressure and the residue was purified by recrystallization to give benzamidoxime 2a (white solid, 1.12 g, 8.10 mmol, 81%). <sup>1</sup>H NMR (500 MHz, DMSO-<em>d</em><sub>6</sub>): δ 9.65 (s, 1H), 7.76–7.63 (m, 2H), 7.38 (p, <em>J</em> = 3.7 Hz, 3H), 5.82 (s, 2H); <sup>13</sup>C NMR (126 MHz, DMSO-<em>d</em><sub>6</sub>): δ 150.86, 133.38, 128.88, 128.10, 125.40; HRMS [ESI] calcd for C<sub>7</sub>H<sub>9</sub>N<sub>2</sub>O [M+H]<sup>+</sup>: 137.0709, found: 137.0715.

Reference

III. General procedure for converting benzamidoxime 2a to N-phenylcyanamide 3a with SO$_2$F$_2$

\[
\begin{align*}
\text{N} & \quad \text{OH} \\
\text{2a} & \quad \text{SO}_2\text{F}_2 (\text{balloon}) \\
\text{Et}_3\text{N} (2.0 \text{ eq.}) & \quad \text{CH}_2\text{Cl}_2 (0.1 \text{ M}, \text{r.t.}) \\
\text{r.t.} & \quad 2.0 \text{ h} \\
\text{3a} & \quad \text{CN} \\
\end{align*}
\]

Benzamidoxime 2a (68.0 mg, 0.5 mmol), CH$_2$Cl$_2$ (5.0 mL, 0.1 M) and Et$_3$N (140 uL, 1.0 mmol) were added into a 35 mL Schlenk flask equipped with magnetic stirrer and rubber stopper. Then the SO$_2$F$_2$ gas was introduced into the stirring reaction mixture by slow bubbling through a SO$_2$F$_2$ balloon, and the reaction mixture was stirred at room temperature for 2.0 h. After the reaction, the mixture was concentrated under reduced pressure and the residue was purified by flashcolumn chromatography on silica gel (200-300 mesh) with hexane and ethyl acetate (Hex / EtOAc = 4 : 1, Rf = 0.20) to give N-phenylcyanamide 3a (yellow solid, 56.6 mg, 0.48 mmol, 96% isolated yield). $^1$H NMR (500 MHz, Chloroform-d): $\delta$ 7.34–7.28 (m, 2H), 7.08–6.88 (m, 3H); $^{13}$C NMR (126 MHz, Chloroform-d): $\delta$ 135.84, 129.79, 128.95, 116.74, 111.09; HRMS [ESI] calcd for C$_7$H$_5$N$_2$ [M-H]: 117.0458, found: 117.0458.
IV. Screening the optimized reaction conditions

**Table S1.** Screening the bases.$^{a}$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base (eq.)</th>
<th>Yield (%)$^{b}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DBU (2.0)</td>
<td>47</td>
</tr>
<tr>
<td>2</td>
<td>DIPEA (2.0)</td>
<td>73</td>
</tr>
<tr>
<td>3</td>
<td>Et$_3$N (2.0)</td>
<td>94</td>
</tr>
<tr>
<td>4$^c$</td>
<td>K$_2$CO$_3$ (2.0)</td>
<td>7</td>
</tr>
<tr>
<td>5$^c$</td>
<td>Na$_2$CO$_3$ (2.0)</td>
<td>$&gt;$1</td>
</tr>
<tr>
<td>6$^c$</td>
<td>t-BuONa (2.0)</td>
<td>13</td>
</tr>
<tr>
<td>7</td>
<td>Et$_3$N (1.5)</td>
<td>66</td>
</tr>
<tr>
<td>8</td>
<td>Et$_3$N (3.0)</td>
<td>93</td>
</tr>
<tr>
<td>9</td>
<td>-</td>
<td>nr</td>
</tr>
</tbody>
</table>

$^a$ Reaction conditions: benzamidoxime 2a (0.5 mmol), base, CH$_2$Cl$_2$ (2.5 mL, 0.2 M), and SO$_2$F$_2$ balloon, room temperature, 2.0 h. $^b$ Isolated yield. $^c$ 5.0 h.

**Table S2.** Screening the solvents.$^{a}$
$$\text{NH}_2 \xrightarrow{\text{SO}_2\text{F}_2 \text{ (balloon)}} \text{Et}_3\text{N (2.0 eq.)} \xrightarrow{\text{solvent, r.t.}} 2.0 \text{ h} \quad \text{NH} \text{CN}$$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Yield (%)$^b$</th>
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<tbody>
<tr>
<td>1</td>
<td>CH$_2$Cl$_2$</td>
<td>94</td>
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<tr>
<td>2</td>
<td>CH$_3$CN</td>
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</tr>
<tr>
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<td>7</td>
<td>CH$_3$OH</td>
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<tr>
<td>8$^c$</td>
<td>CH$_2$Cl$_2$</td>
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<tr>
<td>9$^d$</td>
<td>CH$_2$Cl$_2$</td>
<td>90</td>
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</tbody>
</table>

$^a$ Reaction conditions: benzamidoxime 2a (0.5 mmol), Et$_3$N (1.0 mmol, 2.0 eq.), solvent (2.5 mL, 0.2 M), and SO$_2$F$_2$ balloon, room temperature, 2.0 h. $^b$ Isolated yield. $^c$ 5.0 mL of CH$_2$Cl$_2$ (0.1 M). $^d$ 10 mL of CH$_2$Cl$_2$ (0.05 M).

Table S3. Screening the reaction time.$^a$
<table>
<thead>
<tr>
<th>Entry</th>
<th>Time (h)</th>
<th>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
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<td>96</td>
</tr>
<tr>
<td>2</td>
<td>3.0</td>
<td>95</td>
</tr>
<tr>
<td>3</td>
<td>1.5</td>
<td>94</td>
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<tr>
<td>4</td>
<td>1.0</td>
<td>86</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>43</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reaction conditions: benzamidoxime 2a (0.5 mmol), Et<sub>3</sub>N (1.0 mmol, 2.0 eq.), CH<sub>2</sub>Cl<sub>2</sub> (5.0 mL, 0.1 M), and SO<sub>2</sub>F<sub>2</sub> balloon, room temperature, 2.0 h. <sup>b</sup>Isolated yield.
Nitrile 1 (1.0 mmol, 1.0 eq.), 50 wt% aqueous hydroxylamine solution (0.1 g, 1.5 mmol, 1.5 eq.) and EtOH (10 mL, 0.1 M) were added into an oven-dried reaction tube (50 mL) equipped with a stirring bar, and the reaction mixture reacted at reflux temperature for 3.0 h. The reaction was monitored by TLC. After the nitrile was completely consumed, the reaction mixture was concentrated under reduced pressure to give the crude amidoxime 2. The crude amidoxime 2 (without any purification), CH₂Cl₂ (10 mL, 0.1 M) and Et₃N (280 uL, 2.0 mmol, 2.0 eq.) were added into a 50 mL Schlenk flask equipped with magnetic stirrer and rubber stopper. Then the SO₂F₂ gas was introduced into the stirring reaction mixture by slow bubbling through a SO₂F₂ balloon, and the reaction mixture was stirred at room temperature for 2.0 h. After the reaction, the mixture was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (300-400 mesh) with hexane and ethyl acetate to give cyanamide 3.
Characterization datas

\(N\text{-phenylcyanamide (3a)}\)

![Chemical structure](image)

Yellow solid, 112.0 mg, 95% isolated yield. \(^1\)H NMR (500 MHz, Chloroform-\(d\)): \(\delta\) 7.34–7.28 (m, 2H), 7.08–6.88 (m, 3H); \(^{13}\)C NMR (126 MHz, Chloroform-\(d\)): \(\delta\) 135.84, 129.79, 128.95, 116.74, 111.09; HRMS [ESI] calcd for \(C_{7}H_{5}N_{2}\) [M-H]: 117.0458, found: 117.0458.

\(N\text{-}(4\text{-Methylphenyl})cyanamide (3b)\)

![Chemical structure](image)

Yellow solid, 113.5 mg, 86% isolated yield. \(^1\)H NMR (500 MHz, Chloroform-\(d\)): \(\delta\) 7.15 (d, \(J = 8.1\) Hz, 2H), 6.98–6.87 (m, 2H), 6.38 (s, 1H), 2.32 (s, 3H); \(^{13}\)C NMR (126 MHz, Chloroform-\(d\)): \(\delta\) 134.60, 133.32, 130.24, 115.37, 111.53, 20.64; HRMS [ESI] calcd for \(C_{8}H_{8}N_{2}Na\) [M+Na]^+: 155.0580, found: 155.0586.

\(N\text{-}(4\text{-Methoxyphenyl})cyanamide (3c)\)

![Chemical structure](image)

Brown solid, 115.4 mg, 78% isolated yield. \(^1\)H NMR (500 MHz, Chloroform-\(d\)): \(\delta\) 7.01–6.94 (m, 2H), 6.92–6.85 (m, 2H), 6.72 (s, 1H), 3.79 (s, 3H); \(^{13}\)C NMR (126 MHz, Chloroform-\(d\)): \(\delta\) 156.04, 130.34, 116.87, 115.04, 112.27, 55.64; HRMS [ESI] calcd for \(C_{8}H_{7}N_{2}O\) [M-H]: 147.0564, found: 147.0560.

\(N\text{-}(4\text{-tert-Butylphenyl})cyanamide (3d)\)
Yellow solid, 148.0 mg, 85% isolated yield. $^1$H NMR (500 MHz, Chloroform-$d$): $\delta$ 7.42–7.33 (m, 2H), 7.07 (s, 1H), 6.99 (d, $J$ = 8.6 Hz, 2H), 1.32 (s, 9H); $^{13}$C NMR (126 MHz, Chloroform-$d$): $\delta$ 146.61, 134.66, 126.53, 115.17, 111.99, 34.26, 31.32; HRMS [ESI] calcd for C$_{11}$H$_{13}$N$_2$ [M-H]: 173.1084, found: 173.1076.

$N$-(4-Fluorophenyl)cyanamide (3e)

White solid, 118.3 mg, 87% isolated yield. $^1$H NMR (500 MHz, Chloroform-$d$): $\delta$ 7.09–7.02 (m, 2H), 7.02–6.97 (m, 2H), 6.75 (s, 1H); $^{13}$C NMR (126 MHz, Chloroform-$d$): $\delta$ 133.23, 116.95, 116.89, 116.66, 116.47, 111.45; HRMS [ESI] calcd for C$_7$H$_4$FN$_2$ [M-H]: 135.0364, found: 135.0365.

$N$-(4-Chlorophenyl)cyanamide (3f)

White solid, 129.7 mg, 85% isolated yield. $^1$H NMR (500 MHz, Chloroform-$d$): $\delta$ 7.58–7.51 (m, 3H), 7.49 (d, $J$ = 2.9 Hz, 1H), 7.19 (s, 1H); $^{13}$C NMR (126 MHz, Chloroform-$d$): $\delta$ 129.61, 129.50, 128.93, 128.80, 126.81; HRMS [ESI] calcd for C$_7$H$_4$ClN$_2$ [M-H]: 151.0068, found: 151.0064.

$N$-(4-Bromophenyl)cyanamide (3g)
**N-(4-Iodophenyl)cyanamide (3h)**

White solid, 205.0 mg, 84% isolated yield. $^1$H NMR (500 MHz, Chloroform-$d$): $\delta$ 7.69–7.61 (m, 2H), 6.84–6.77 (m, 2H), 6.68 (s, 1H); $^{13}$C NMR (126 MHz, Chloroform-$d$): $\delta$ 138.64, 137.11, 117.44, 110.57, 86.39; HRMS [ESI] calcd for C$_7$H$_4$IN$_2$ [M-H]: 242.9425, found: 242.9433.

**Methyl 4-cyanamidobenzoate (3i)**

Yellow solid, 114.2 mg, 82% isolated yield. $^1$H NMR (500 MHz, Chloroform-$d$): $\delta$ 8.13 (d, $J$ = 8.1 Hz, 2H), 7.89 (d, $J$ = 8.5 Hz, 2H), 3.96 (s, 3H); $^{13}$C NMR (126 MHz, Chloroform-$d$): $\delta$ 171.21, 137.17, 133.28, 129.93, 127.43, 114.92, 53.44; HRMS [ESI] calcd for C$_9$H$_7$N$_2$O$_2$ [M-H]: 175.0513, found: 175.0517.

**N-([1,1'-Biphenyl]-4-yl)cyanamide (3j)**
Yellow solid, 182.4 mg, 94% isolated yield. \(^1\)H NMR (500 MHz, DMSO-\(d_6\)): \(\delta\) 10.26 (s, 1H), 7.71–7.65 (m, 2H), 7.64–7.59 (m, 2H), 7.45 (t, \(J = 7.7\) Hz, 2H), 7.33 (t, \(J = 7.4\) Hz, 1H), 7.10–7.02 (m, 2H); \(^{13}\)C NMR (126 MHz, DMSO-\(d_6\)): \(\delta\) 139.39, 138.06, 134.52, 128.89, 127.99, 127.06, 126.19, 115.44, 111.95; HRMS [ESI] calcd for C\(_{13}\)H\(_9\)N\(_2\) [M-H]: 193.0771, found: 193.0771.

\(N\)-(4-Trifluoromethylphenyl)cyanamide (3k)

White solid, 161.8 mg, 87% isolated yield. \(^1\)H NMR (500 MHz, Chloroform-\(d\)): \(\delta\) 7.61 (d, \(J = 8.6\) Hz, 2H), 7.31 (s, 1H), 7.13 (d, \(J = 8.5\) Hz, 2H); \(^{13}\)C NMR (126 MHz, Chloroform-\(d\)): \(\delta\) 140.41, 127.21, 127.19, 127.16, 127.12, 115.41, 110.41; HRMS [ESI] calcd for C\(_8\)H\(_4\)F\(_3\)N\(_2\) [M-H]: 185.0332, found: 185.0334.

\(N\)-(4-Trifluoromethoxyphenyl)cyanamide (3l)

White solid, 181.8 mg, 90% isolated yield. \(^1\)H NMR (500 MHz, Chloroform-\(d\)): \(\delta\) 7.36 (s, 1H), 7.21 (d, \(J = 8.7\) Hz, 2H), 7.05 (d, \(J = 2.2\) Hz, 1H), 7.04 (d, \(J = 2.2\) Hz, 1H); \(^{13}\)C NMR (126 MHz, Chloroform-\(d\)): \(\delta\) 172.10, 145.04, 136.10, 122.72, 121.48, 119.44, 116.55, 111.18; HRMS [ESI] calcd for C\(_8\)H\(_4\)F\(_3\)N\(_2\)O [M-H]: 201.0281, found: 201.0275.

\(N\)-(4-Nitrophenyl)cyanamide (3m)
Yellow solid, 109.2 mg, 67% isolated yield. $^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ 8.32–8.28 (m, 2H), 8.15–8.05 (m, 2H), 7.71 (s, 1H); $^{13}$C NMR (126 MHz, DMSO-$d_6$): $\delta$ 166.16, 149.04, 139.98, 128.88, 123.38; HRMS [ESI] calcd for C$_7$H$_4$N$_3$O$_2$ [M-H]: 162.0309, found: 162.0310.

$N$-(4-Cyanamidophenyl)acetamide (3n)

Yellow solid, 119.0 mg, 68% isolated yield. $^1$H NMR (500 MHz, Chloroform-$d$): $\delta$ 7.66 (d, $J$ = 8.7 Hz, 2H), 7.62 (s, 2H), 7.61 (s, 1H), 7.53 (s, 1H), 2.23 (s, 3H); $^{13}$C NMR (126 MHz, Chloroform-$d$): $\delta$ 171.17, 141.95, 133.30, 126.20, 119.42, 60.40, 53.43; HRMS [ESI] calcd for C$_9$H$_7$N$_3$O [M-H]: 174.0564, found: 174.0558.

$N$-(4-Dimethylaminophenyl)cyanamide (3o)

Yellow solid, 135.2 mg, 84% isolated yield. $^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ 6.83 (d, $J$ = 8.9 Hz, 2H), 6.74 (d, $J$ = 9.0 Hz, 2H), 2.83 (s, 6H); $^{13}$C NMR (126 MHz, DMSO-$d_6$): $\delta$ 146.82, 128.19, 116.07, 113.96, 113.20, 40.63; HRMS [ESI] calcd for C$_9$H$_{10}$N$_3$ [M-H]: 160.0880, found: 160.0876.

$N$-(4-Aminophenyl)cyanamide (3p)
Brown solid, 107.7 mg, 81% isolated yield. $^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ 9.44 (s, 1H), 6.69–6.64 (m, 2H), 6.58–6.53 (m, 2H), 4.85 (s, 2H); $^{13}$C NMR (126 MHz, DMSO-$d_6$): $\delta$ 144.39, 127.36, 116.24, 114.96, 113.47; HRMS [ESI] calcd for C$_7$H$_6$N$_3$ [M-H]: 132.0567, found: 132.0566.

**4-Cyanamidophenyl sulfurofluoridate (3q)**

Yellow liquid, 162.0 mg, 75% isolated yield. $^1$H NMR (500 MHz, Chloroform-$d$): $\delta$ 7.36 (d, $J$ = 8.7 Hz, 2H), 7.15–7.10 (m, 2H); $^{13}$C NMR (126 MHz, Chloroform-$d$): $\delta$ 145.63, 137.66, 122.59, 116.82; HRMS [ESI] calcd for C$_7$H$_4$FN$_2$O$_3$S [M-H]: 215.1905, found: 215.2017.

**N-(m-Tolyl)cyanamide (3r)**

Yellow solid, 114.8 mg, 87% isolated yield. $^1$H NMR (500 MHz, Chloroform-$d$): $\delta$ 7.22 (t, $J$ = 7.8 Hz, 1H), 6.90 (d, $J$ = 7.5 Hz, 1H), 6.87–6.81 (m, 2H), 2.35 (s, 3H); $^{13}$C NMR (126 MHz, Chloroform-$d$): $\delta$ 139.94, 137.19, 129.51, 124.39, 115.97, 112.52, 111.67, 21.35; HRMS [ESI] calcd for C$_8$H$_7$N$_2$ [M-H]: 131.0615, found: 131.0611.

**N-(3-Bromophenyl)cyanamide (3s)**
White solid, 174.4 mg, 89% isolated yield. $^1$H NMR (500 MHz, Chloroform-$d$): $\delta$ 7.23 (q, $J$ = 7.7 Hz, 3H), 6.98 (dt, $J$ = 6.9, 2.1 Hz, 1H), 6.64 (s, 1H); $^{13}$C NMR (126 MHz, Chloroform-$d$): $\delta$ 138.52, 131.10, 126.91, 123.46, 118.59, 114.08, 110.36; HRMS [ESI] calcd for C$_7$H$_4$BrN$_2$ [M-H]: 194.9563, found: 194.9570.

**N-(3-Trifluoromethylphenyl)cyanamide (3t)**

White solid, 163.7 mg, 88% isolated yield. $^1$H NMR (500 MHz, Chloroform-$d$): $\delta$ 7.49 (t, $J$ = 7.9 Hz, 1H), 7.44 (s, 1H), 7.36 (d, $J$ = 7.8 Hz, 1H), 7.26–7.22 (m, 1H); $^{13}$C NMR (126 MHz, Chloroform-$d$): $\delta$ 138.00, 132.48, 132.22, 131.96, 130.49, 124.59, 122.42, 120.48, 118.61, 112.36, 110.73; HRMS [ESI] calcd for C$_8$H$_4$F$_3$N$_2$ [M-H]: 185.0332, found: 185.0334.

**N-(o-Tolyl)cyanamide (3u)**

Yellow solid, 114.8 mg, 87% isolated yield. $^1$H NMR (500 MHz, Chloroform-$d$): $\delta$ 7.29–7.20 (m, 2H), 7.17 (d, $J$ = 7.5 Hz, 1H), 7.03 (td, $J$ = 7.4, 1.1 Hz, 1H), 6.44 (s, 1H), 2.26 (s, 3H); $^{13}$C NMR (126 MHz, Chloroform-$d$): $\delta$ 135.56, 131.00, 127.49, 124.28, 123.68, 115.46, 111.76, 17.01; HRMS [ESI] calcd for C$_8$H$_7$N$_2$ [M-H]: 131.0615, found: 131.0621.

**N-(2-Bromophenyl)cyanamide (3v)**
White solid, 176.4 mg, 90% isolated yield. $^1$H NMR (500 MHz, Chloroform-$d$): $\delta$ 7.59–7.50 (m, 1H), 7.41–7.34 (m, 1H), 7.31 (dd, $J$ = 8.1, 1.4 Hz, 1H), 6.99 (td, $J$ = 7.9, 1.5 Hz, 1H), 6.51 (s, 1H); $^{13}$C NMR (126 MHz, Chloroform-$d$): $\delta$ 135.22, 132.87, 131.59, 129.07, 124.74, 116.05, 109.76; HRMS [ESI] calcd for C$_7$H$_4$BrN$_2$ [M-H]: 194.9563, found: 194.9573.

$N$-(2-Trifluoromethylphenyl)cyanamide (3w)

White solid, 145.1 mg, 78% isolated yield. $^1$H NMR (500 MHz, Chloroform-$d$): $\delta$ 7.66–7.57 (m, 2H), 7.46 (d, $J$ = 8.5 Hz, 1H), 7.22 (t, $J$ = 7.7 Hz, 1H), 6.51 (s, 1H); $^{13}$C NMR (126 MHz, Chloroform-$d$): $\delta$ 135.11, 133.82, 127.02, 126.98, 126.95, 126.90, 124.87, 123.62, 122.70, 117.24, 109.32; HRMS [ESI] calcd for C$_8$H$_4$F$_3$N$_2$ [M-H]: 185.0332, found: 185.0338.

$N$-(3,4-Dimethoxyphenyl)cyanamide (3x)

White solid, 147.6 mg, 83% isolated yield. $^1$H NMR (500 MHz, Chloroform-$d$): $\delta$ 6.83 (d, $J$ = 8.6 Hz, 1H), 6.61 (d, $J$ = 2.7 Hz, 1H), 6.55 (dd, $J$ = 8.5, 2.6 Hz, 1H), 6.10 (s, 1H), 3.89 (s, 3H), 3.87 (s, 3H); $^{13}$C NMR (126 MHz, Chloroform-$d$): $\delta$ 150.15, 145.67, 130.73, 112.40, 111.57, 107.16, 100.42, 56.40, 56.09; HRMS [ESI] calcd for C$_9$H$_9$N$_2$O$_2$ [M-H]: 177.067, found: 177.0661.

$N$-(2,4-Dichlorophenyl)cyanamide (3y)
White solid, 135.8 mg, 73% isolated yield. $^1$H NMR (500 MHz, Chloroform-$d$): $\delta$ 7.39 (d, $J$ = 2.2 Hz, 1H), 7.30 (dd, $J$ = 8.7, 2.2 Hz, 1H), 7.22 (d, $J$ = 8.6 Hz, 1H); $^{13}$C NMR (126 MHz, Chloroform-$d$): $\delta$ 171.23, 133.12, 129.47, 128.95, 128.51, 127.77, 116.90; HRMS [ESI] calcd for C$_7$H$_3$Cl$_2$N$_2$: 184.9679, found: 184.9680.

$N$-(Benzo[d][1,3]dioxol-5-yl)cyanamide (3z)

Yellow solid, 147.4 mg, 91% isolated yield. $^1$H NMR (500 MHz, Chloroform-$d$): $\delta$ 6.75 (d, $J$ = 8.3 Hz, 1H), 6.58 (d, $J$ = 2.3 Hz, 1H), 6.53 (d, $J$ = 16.6 Hz, 1H), 6.47 (dd, $J$ = 8.3, 2.4 Hz, 1H), 5.97 (s, 2H); $^{13}$C NMR (126 MHz, Chloroform-$d$): $\delta$ 148.71, 144.12, 131.66, 108.72, 108.05, 101.60, 98.16, 53.43; HRMS [ESI] calcd for C$_8$H$_5$N$_2$O$_2$: 161.0357, found: 161.0349.

$N$-(1H-Indol-5-yl)cyanamide (3aa)

Yellow solid, 120.9 mg, 77% isolated yield. $^1$H NMR (500 MHz, Chloroform-$d$): $\delta$ 8.24 (s, 1H), 7.37 (d, $J$ = 8.6 Hz, 1H), 7.30 (d, $J$ = 1.9 Hz, 1H), 7.26 (d, $J$ = 2.7 Hz, 1H), 6.90 (dd, $J$ = 8.6, 2.2 Hz, 1H), 6.51 (s, 1H), 5.80 (s, 1H); $^{13}$C NMR (126 MHz, Chloroform-$d$): $\delta$ 132.88, 130.03, 128.56, 125.95, 112.16, 112.08, 111.41, 106.97, 102.41; HRMS [ESI] calcd for C$_9$H$_6$N$_3$: 156.0567, found: 156.0567.

$N$-(Pyridin-3-yl)cyanamide (3ab)
Yellow liquid, 90.5 mg, 87% isolated yield. $^1$H NMR (500 MHz, Chloroform-$d$): $\delta$ 7.86–7.60 (m, 1H), 7.17–6.82 (m, 3H), 6.78–6.64 (m, 1H); $^{13}$C NMR (126 MHz, Chloroform-$d$): $\delta$ 143.38, 127.65, 126.27, 119.25, 118.73, 114.64; HRMS [ESI] calcd for C$_6$H$_4$N$_3$ [M-H]: 118.0411, found: 118.0412.

N-(Pyridin-2-yl)cyanamide (3ac)

Yellow liquid, 95.2 mg, 80% isolated yield. $^1$H NMR (500 MHz, Chloroform-$d$): $\delta$ 7.76–7.68 (m, 1H), 7.64 (ddd, $J$ = 8.9, 7.0, 1.8 Hz, 1H), 7.12 (d, $J$ = 8.9 Hz, 1H), 6.68–6.55 (m, 1H); $^{13}$C NMR (126 MHz, Chloroform-$d$): $\delta$ 160.31, 142.12, 136.49, 118.48, 117.57, 111.56; HRMS [ESI] calcd for C$_6$H$_4$N$_3$ [M-H]: 118.0411, found: 118.0409.

N-(Thiophen-2-yl)cyanamide (3ad)

Brown liquid, 64.5 mg, 52% isolated yield. $^1$H NMR (500 MHz, Chloroform-$d$): $\delta$ 7.52–7.47 (m, 1H), 7.08–7.02 (m, 1H), 6.96–6.84 (m, 2H); $^{13}$C NMR (126 MHz, Chloroform-$d$): $\delta$ 161.40, 155.11, 129.95, 128.25, 110.79; HRMS [ESI] calcd for C$_5$H$_3$N$_2$S [M-H]: 123.0022, found: 123.0023.

N-(Naphthalen-1-yl)cyanamide (3ae)
Yellow solid, 105.8 mg, 63% isolated yield. $^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ 10.23 (s, 1H), 8.11–8.06 (m, 1H), 7.99–7.93 (m, 1H), 7.66 (d, $J$ = 8.2 Hz, 1H), 7.63–7.56 (m, 2H), 7.52 (t, $J$ = 7.9 Hz, 1H), 7.25 (d, $J$ = 7.2 Hz, 1H); $^{13}$C NMR (126 MHz, DMSO-$d_6$): $\delta$ 134.34, 133.86, 128.38, 126.70, 126.15, 126.01, 123.22, 123.16, 120.98, 112.63, 111.15; HRMS [ESI] calcd for C$_{11}$H$_7$N$_2$ [M-H]: 167.0615, found: 167.0615.

$N$-(Naphthalen-2-yl)cyanamide (3af)

Yellow solid, 141.1 mg, 84% isolated yield. $^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ 10.37 (s, 1H), 7.93 (d, $J$ = 8.8 Hz, 1H), 7.86 (d, $J$ = 8.9 Hz, 2H), 7.49 (ddd, $J$ = 8.2, 6.9, 1.1 Hz, 1H), 7.43–7.36 (m, 2H), 7.20 (dd, $J$ = 8.8, 2.4 Hz, 1H); $^{13}$C NMR (126 MHz, DMSO-$d_6$): $\delta$ 136.42, 133.65, 129.87, 129.33, 127.69, 126.99, 126.62, 124.44, 116.27, 112.05, 110.02; HRMS [ESI] calcd for C$_{11}$H$_7$N$_2$ [M-H]: 167.0615, found: 167.0616.

$N$-(Phenylethynyl)cyanamide (3ag)

Yellow solid, 103.6 mg, 73% isolated yield. $^1$H NMR (500 MHz, Chloroform-$d$): $\delta$ 7.72 (dd, $J$ = 6.7, 3.0 Hz, 2H), 7.47–7.37 (m, 3H), 4.82 (s, 1H); $^{13}$C NMR (126 MHz, Chloroform-$d$): $\delta$ 169.11, 163.82, 129.67, 128.66, 126.52, 78.02; HRMS [ESI] calcd for C$_9$H$_5$N$_2$ [M-H]: 141.0531, found: 141.0530.

$N$-Benzylcyanamide (3ah)
Yellow liquid, 84.5 mg, 64 % isolated yield. $^1$H NMR (500 MHz, Chloroform-$d$): $\delta$ 7.45–7.31 (m, 5H), 4.21 (d, $J$ = 5.5 Hz, 2H), 4.15 (s, 1H); $^{13}$C NMR (126 MHz, Chloroform-$d$): $\delta$ 136.18, 128.95, 128.49, 127.82, 116.01, 50.22; HRMS [ESI] calcd for C$_8$H$_7$N$_2$ [M-H]: 131.0615, found: 131.0610.

**N-Phenethylcyanamide (3ai)**

Yellow liquid, 89.2 mg, 61 % isolated yield. $^1$H NMR (500 MHz, Chloroform-$d$): $\delta$ 7.35 (t, $J$ = 7.4 Hz, 2H), 7.30–7.25 (m, 1H), 7.22 (d, $J$ = 7.1 Hz, 2H), 3.74 (s, 1H), 3.41–3.27 (m, 2H), 2.92 (t, $J$ = 7.0 Hz, 2H); $^{13}$C NMR (126 MHz, Chloroform-$d$): $\delta$ 137.21, 128.84, 128.81, 126.99, 115.87, 47.39, 35.87; HRMS [ESI] calcd for C$_9$H$_9$N$_2$ [M-H]: 145.0771, found: 145.077.

**N-(tert-Butyl)cyanamide (3aj)**

Yellow liquid, 82.4 mg, 84 % isolated yield. $^1$H NMR (500 MHz, Chloroform-$d$): $\delta$ 4.54 (s, 1H), 1.25 (s, 9H); $^{13}$C NMR (126 MHz, Chloroform-$d$): $\delta$ 115.24, 53.10, 28.94; HRMS [ESI] calcd for C$_5$H$_{11}$N$_2$ [M+H]: 99.0844, found: 99.0843.

VI. Reproductions of $^1$H NMR and $^{13}$C NMR spectra

**N-phenylcyanamide (3a)**
N-(4-Methylphenyl)cyanamide (3b)
$N$-(4-Methoxyphenyl)cyanamide (3c)
N-(4-tert-Butylphenyl)cyanamide (3d)
N-(4-Fluorophenyl)cyanamide (3e)
$N$-(4-Chlorophenyl)cyanamide (3f)
$N$-(4-Bromophenyl)cyanamide (3g)
N-(4-Iodophenyl)cyanamide (3h)
Methyl 4-cyanamidobenzoate (3i)
N-([1,1′-biphenyl]-4-yl)cyanamide (3j)
N-(4-Trifluoromethylphenyl)cyanamide (3k)
N-(4-Trifluoromethoxyphenyl)cyanamide (3l)
N-(4-Nitrophenyl)cyanamide (3m)
**N-(4-Cyanamidophenyl)acetamide (3n)**
N-(4-Dimethylaminophenyl)cyanamide (3o)
$N$-(4-Aminophenyl)cyanamide (3p)
4-Cyanamidophenyl sulfurofluoridate (3q)
$N$-(m-Tolyl)cyanamide (3r)
$N$-(3-Bromophenyl)cyanamide (3s)
$N$-(3-Trifluoromethylphenyl)cyanamide (3t)
$N$-$(o$-Tolyl)$cyanamide (3u)$
N-(2-Bromophenyl)cyanamide (3v)
N-(2-Trifluoromethylphenyl)cyanamide (3w)
\( \text{N-(3,4-Dimethoxyphenyl)cyanamide (3x)} \)
N-(2,4-Dichlorophenyl)cyanamide (3y)
$N$-(Benzo[d][1,3]dioxol-5-yl)cyanamide (3z)
$N$-(1H-Indol-5-yl)cyanamide (3aa)
N-(Pyridin-3-yl)cyanamide (3ab)
N-(Pyridin-2-yl)cyanamide (3ac)
N-(Thiophen-2-yl)cyanamide (3ad)
N-(Naphthalen-1-yl)cyanamide (3ae)
N-(Naphthalen-2-yl)cyanamide (3af)
N-(Phenylethynyl)cyanamide (3ag)
N-Benzylcyanamide (3ah)
N-Phenethylcyanamide (3ai)
$N$-(tert-Butyl)cyanamide (3aj)