Supporting Information: Part-1

Highly chemo- and regio-selective allylic substitution with tautomerizable heteroarenes

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Table of Contents

1) General Methods ................................................................................................................................................. 3
2) Synthesis of authentic sample of 3a₁, 3a₂, and 3a₃ ................................................................................................. 3
3) Investigation of allylating reagents for selectivity control under base free condition ........................................... 5
4) Investigation of allylating reagents for selectivity control under basic condition ................................................. 6
5) Effect of solvents on the selectivity control ............................................................................................................. 7
6) Effect of different Pd-catalysts on the selectivity control ......................................................................................... 8
7) Effect of ligands on the selectivity control ............................................................................................................. 9
8) Effect of non-Pd transition metal catalysts on the selectivity control ................................................................. 10
9) Investigation of allylic disposition under reaction condition .................................................................................... 12
10) Investigation of allylic disposition from in-situ generated 3a₁ .............................................................................. 13
11) Investigation of allylic migration from 3a₁ in the presence of different catalysts under reaction conditions ..................... 13
12) Validation of route B-1 / B-2: Investigation of allylic migration from 4 ............................................................. 14
13) Preparation of substrates ........................................................................................................................................ 16
14) Spectra data of products (Table 6 & 7) .................................................................................................................. 21
15) Experimental procedure for inter-molecular competition study ........................................................................... 28
16) References: .......................................................................................................................................................... 29
1) General Methods

All commercially obtained reagents/solvents were purchased from Alfa Aesar®, Sigma-Aldrich®, Acros®, TCI America®, Mallinckrodt®, and Oakwood® Products, and used as received without further purification. Unless stated otherwise, reactions were conducted in oven-dried glassware under nitrogen atmosphere in glove box. Glassware was oven-dried for at least 1 h prior to use. Thin layer chromatography (TLC) was performed on silica gel Whatman-60F glass plates, and components were visualized by illumination with UV light or by staining with potassium permanganate solution. Chromatography was performed using silica E. Merck silica gel 60 (230-400 mesh). ¹H NMR and ¹³C NMR spectra were recorded on Bruker 400 MHz and 100 MHz spectrometers respectively using TMS as an internal standard. Both ¹H and ¹³C NMR chemical shifts were reported in parts per million downfield from tetramethylsilane (δ = 0). Data for ¹H NMR are reported as chemical shift (δ ppm) with the corresponding integration values. Coupling constants (J) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: s (singlet), br (broad), d (doublet), t (triplet), q (quartet) and m (multiplet). Data for ¹³C NMR spectra are reported in terms of chemical shift (δ ppm). GC-MS analyses were performed on Agilent technologies GC coupled with ELSI mass spectrometer. High-resolution mass spectra were obtained at a Bruker Daltronics BioTOF HRMS spectrometer in positive (ESI⁺) ion mode.

2) Synthesis of of authentic sample of 3a₁, 3a₂, and 3a₃

2a) Synthesis of 4-(allyloxy) quinazoline (3a₁)

Experimental procedure: In a glove box, to an oven dried 4 mL glass vial equipped with a stir bar, 4-hydroxy quinazoline 1a (0.146 g, 1 mmol), BOP [(1-Benzotriazol-1-yl)oxo tris (dimethylamino) phosphonium hexafluorophosphate] (0.885 g, 2 mmol, 2 equiv), Cs₂CO₃ (0.652 g, 2 mmol, 2 equiv) followed by dry THF (3 mL) was added and the reaction mixture was stirred at rt for 60 min. The resulting mixture was evaporated under reduced pressure, Cs₂CO₃ (0.652 g, 2 mmol, 2 equiv) and allyl alcohol 2d (1.16 g, 20 mmol, 20 equiv) were added followed by stirring at rt until TLC (5 h) indicated complete reaction. The reaction mixture was diluted with water (10 mL) and extracted with EtOAc (3 x 10 mL). The organic layer was dried over anhyd. Na₂SO₄ and concentrated under reduced pressure. The crude products were adsorbed on silica gel and pass through the column (eluent: Hexane/EtOAc) to get analytically pure product 3a₁ (0.130 g, 70%) as a yellowish liquid; ¹H NMR (400 MHz, CDCl₃): δ 8.79 (d, J = 2.9 Hz, 1H), 8.16 (t, J = 2.3 Hz, 1H), 7.92 (t, J = 3.7 Hz, 1H), 7.82-7.79 (m, 1H), 7.55-7.51 (m, 1H), 6.19-6.12 (m, 1H), 5.48 (dd, J = 17.2, 1.5 Hz), 5.34-5.31 (m, 1H),
5.09 (d, J = 0.9 Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): δ 166.3, 154.3, 151.0, 133.5, 132.3, 127.7, 127.0, 123.5, 118.4, 116.6, 67.5; MS (ESI) m/z: 186.1 M\(^+\).

2b) Synthesis of 3-allylquinazolín-4(3\(H\))-one (3a\(_2\))^2

\[
\begin{align*}
\text{CON} & \quad \text{NH} & \quad \text{CH(OEt)}_3 \\
\text{O} & \quad \text{O} & \\
\text{H} & \\
\text{CON} & \quad \text{NH} & \quad \text{CH(OEt)}_3 \\
\text{O} & \quad \text{O} & \\
\text{H} & & & \text{Neat, 120 °C} \\
& & & 5\ h
\end{align*}
\]

**Experimental procedure:** A mixture of isatoic anhydride (0.163 g, 1 mmol), allylamine (0.086 g, 1.5 mmol, 1.5 equiv), and triethyl orthoformate 3 (0.41 g, 2.5 mmol) were stirred magnetically at 120 °C (oil bath temp). After completion of the reaction (TLC, 5 h), the crude reaction mixture was recrystallized from EtOH to obtain analytically pure 3b (0.134 g, 72%) as white solid; \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 8.34 (d, J = 8.0 Hz, 1H), 8.04 (s, 1H), 7.80 - 7.72 (m, 2H), 7.55 - 7.50 (m, 1H), 6.07 - 5.97 (m, 1H), 5.31 (t, J = 10.1 Hz, 2H), 4.66 (d, J = 5.7 Hz, 2H); \(^{13}\)C NMR (100.6 MHz, CDCl\(_3\)): δ 160.8, 148.1, 146.2, 134.3, 131.9, 127.5, 127.3, 126.8, 122.1, 118.9, 48.3; MS (ESI) m/z: 186.1 M\(^+\).

2c) Synthesis of 1-allylquinazolín-4(1\(H\))-one (3a\(_3\))^3

\[
\begin{align*}
\text{CO} & \quad \text{H} & \quad \text{Br} \\
\text{N} & & & \text{DMF, rt, 5 h} \\
\text{CO} & \quad \text{H} & \quad \text{OH} \\
\text{N} & & & \text{NaOH, water rt-15 °C} \\
\text{CO} & \quad \text{H} & \quad \text{OAc} \\
\text{N} & & & \text{CH(OEt)}_3, 100 °C, 100 h
\end{align*}
\]

**Experimental procedure:** **Step 1:** To a solution of isatin (1.47 g, 10 mmol) in DMF (10 mL), potassium carbonate (1.65 g, 12 mmol, 1.2 equiv) and allyl bromide (3.62 g, 30 mmol, 3 equiv) were added. After reacting at rt for 5 h (monitored by TLC), the mixture was poured into ice water. The precipitate formed was filtered, dried and used as such without further purification.

**Step 2:** A solution of sodium hydroxide (0.84 g, 21 mmol) in water (10 mL) was cooled in an ice-water bath. N-allyl isatin (10 mmol) was then added and dissolved. While maintaining the temperature of below 15 °C, a 30% aqueous solution of hydrogen peroxide (1.8 g, 52.8 mmol) was added dropwise. Stirring was continued at 15–20 °C for 2 h (monitored by TLC). The mixture was cooled in an ice bath and pH was adjusted to 5–6 with glacial acetic acid. After several hours of standing in refrigerator, the precipitate formed was collected by filtration, washed with ice water three times, and dried in air to give the 2-(N-allyl amino) benzoic acid.
Step 3: A mixture of 2-(N-allyl amino) benzoic acid (0.53 g, 3 mmol), ammonium acetate (0.69 g, 9 mmol) and triethyl orthoformate (2.22 g, 15 mmol) was stirred at 100 °C for 10 h (monitored by TLC). Excess triethyl orthoformate was removed by rotary evaporation, and the residue was applied to a silica-gel column and eluted with DCM: MeOH (95:5) to give analytically pure 3c (0.379 g, 68%) as white solid; \(^{1}H\) NMR (400 MHz, CDCl\(_3\)): \(\delta 8.24-8.22\) (m, 2H), 7.67-7.62 (m, 1H), 7.41-7.37 (m, 1H), 7.29 (d, \(J = 8.4\) Hz 1H), 6.00 - 5.90 (m, 1H), 5.31-5.28 (m, 1H), 5.19-5.15 (m, 1H), 4.74 (d, \(J = 4.9\) Hz 2H); \(^{13}C\) NMR (100 MHz, CDCl\(_3\)): \(\delta 169.4, 153.3, 139.2, 133.8, 130.6, 128.7, 124.4, 120.4, 119.3, 115.4, 52.2\); MS(ESI) \(m/z\): 186.1 M\(^+\).

3) Investigation of allylating reagents for selectivity control under base free condition

Table 1: Reaction of 1a with different allylating reagents 2 in presence of Pd(PPh\(_3\))\(_4\) under base-free condition.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Allylating agent</th>
<th>% Conversion(^b) 3a(_1)</th>
<th>3a(_2)</th>
<th>3a(_3)</th>
<th>Selectivity 3a(_1) : 3a(_2) : 3a(_3)</th>
<th>Yield (%)(^c) 3a(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2a; Cl</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>N/A</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>2b; Br</td>
<td>0</td>
<td>76</td>
<td>0</td>
<td>00 : 100 : 00</td>
<td>62(^d)</td>
</tr>
<tr>
<td>3</td>
<td>2c; I</td>
<td>0</td>
<td>81</td>
<td>0</td>
<td>00 : 100 : 00</td>
<td>68(^d)</td>
</tr>
<tr>
<td>4</td>
<td>2d; OH</td>
<td>0</td>
<td>82</td>
<td>0</td>
<td>00 : 100 : 00</td>
<td>70(^d)</td>
</tr>
<tr>
<td>5</td>
<td>2e; OAc</td>
<td>0</td>
<td>85</td>
<td>0</td>
<td>00 : 100 : 00</td>
<td>71(^d)</td>
</tr>
<tr>
<td>6</td>
<td>2f; OCOCF(_3)</td>
<td>3</td>
<td>85</td>
<td>0</td>
<td>03 : 97 : 00</td>
<td>72(^d)</td>
</tr>
<tr>
<td>7</td>
<td>2g; OCO(_2)Me</td>
<td>0</td>
<td>95</td>
<td>0</td>
<td>00 : 100 : 00</td>
<td>88(^d)</td>
</tr>
<tr>
<td>8</td>
<td>2h; OPO(OEt)(_2)</td>
<td>0</td>
<td>100</td>
<td>0</td>
<td>00 : 100 : 00</td>
<td>86(^d)</td>
</tr>
<tr>
<td>9</td>
<td>2i; OPh</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>N/A</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>2j; NH(_2)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>N/A</td>
<td>0</td>
</tr>
<tr>
<td>11</td>
<td>2k; NCO</td>
<td>4</td>
<td>65</td>
<td>0</td>
<td>06 : 94 : 00</td>
<td>52(^d)</td>
</tr>
</tbody>
</table>
12 2l;  \( \text{NCS} \)  0 0 0 N/A  0
13 2m;  \( \text{NHCONH}_2 \)  6 60 0 10 : 90 : 00  49 \(^d\)
14 2n;  \( \text{Me} \)  0 26 0 00 : 100 : 00  15 \(^d\)
15 2o;  \( \text{SO}_2\text{Me} \)  0 38 0 00 : 25 : 00  25 \(^d\)
16 2p;  \( \text{CN} \)  0 0 0 N/A  0
17 2q;  \( \text{Ph} \)  0 0 0 N/A  0

\(^a\)1a (0.5 mmol) was treated with different allylating reagents 2 (2 equiv, 1 mmol) in PhMe (1 mL) at 100 °C in presence of Pd(PPh\(_3\))\(_4\) (10 mol \%) for 12 h. \(^b\)Based on GC-MS. \(^c\)Isolated yield of 3a\(_2\). \(^d\)No product formation was observed (1a was found intact) in absence of catalyst.

4) Investigation of allylating reagents for selectivity control under basic condition

Table 2: Reaction of 1a with different allylating reagents 2 in presence of Pd(PPh\(_3\))\(_4\) in the under basic condition.\(^a\)

\[
\begin{array}{|c|c|c|c|c|c|}
\hline
\text{Entry} & \text{Allylating agent} & \% \text{Conversion}\(^b\) & \text{Selectivity} & \text{Yield (%)}\(^c\) \\
& & \text{3a\(_1\)} & \text{3a\(_2\)} & \text{3a\(_3\)} & \text{3a\(_2\)} \\
\hline
1 & 2a;  \( \text{Cl} \) & 0 & 73 & 0 & 00 : 100 : 00 & 60 \\
2 & 2b;  \( \text{Br} \) & 0 & 100 & 0 & 00 : 100 : 00 & 89 \\
3 & 2c;  \( \text{I} \) & 0 & 100 & 0 & 00 : 100 : 00 & 88 \\
4 & 2d;  \( \text{OH} \) & 0 & 92 & 0 & 00 : 100 : 00 & 79 \(^d\) \\
5 & 2e;  \( \text{OAc} \) & 0 & 85 & 0 & 00 : 100 : 00 & 73 \(^d\) \\
6 & 2f;  \( \text{OCOCF}_3 \) & 3 & 92 & 0 & 03 : 97 : 00 & 79 \(^d\) \\
7 & 2g;  \( \text{OCO}_2\text{Me} \) & 0 & 100 & 0 & 00 : 100 : 00 & 90 \(^d\) \\
8 & 2h;  \( \text{OPO(OEt)}_2 \) & 0 & 100 & 0 & 00 : 100 : 00 & 91 \(^d\) \\
\hline
\end{array}
\]
5) Effect of solvents on the selectivity control

Table 3: Reaction of 1a with allyl alcohol 2d in different solvents under Pd(PPh₃)₄ catalysis.a

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>% Conversionb</th>
<th>Selectivity 3a₁ : 3a₂ : 3a₃</th>
<th>Yield (%)c</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MeOH</td>
<td>9 60 0</td>
<td>13 : 87 : 00</td>
<td>47</td>
</tr>
<tr>
<td>2</td>
<td>EtOH</td>
<td>5 90 0</td>
<td>05 : 95 : 00</td>
<td>78</td>
</tr>
<tr>
<td>3</td>
<td>TFE</td>
<td>2 97 0</td>
<td>02 : 98 : 00</td>
<td>81</td>
</tr>
<tr>
<td>4</td>
<td>1,4-Dioxane</td>
<td>0 97 0</td>
<td>00 : 100 : 00</td>
<td>84</td>
</tr>
<tr>
<td>5</td>
<td>THF</td>
<td>0 37 0</td>
<td>00 : 86 : 00</td>
<td>25</td>
</tr>
<tr>
<td>6</td>
<td>DMF</td>
<td>0 93 0</td>
<td>00 : 100 : 00</td>
<td>82</td>
</tr>
<tr>
<td>7</td>
<td>DMSO</td>
<td>0 96 0</td>
<td>00 : 100 : 00</td>
<td>85</td>
</tr>
</tbody>
</table>

*a1a (0.5 mmol) was treated with different allylating reagents 2 (2 equiv, 1 mmol) in PhMe (1 mL) at 100 °C in presence of Pd(PPh₃)₄ (10 mol %) and K₂CO₃ (2 equiv, 1 mmol) for 12 h. bBased on GC-MS. cIsolated yield of 3a₂. dNo product formation was observed (1a was found intact) in absence of catalyst except for entry 1-3 where mixture of 3a₁ and 3a₂ was formed.
<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>% Conversion</th>
<th>Selectivity</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>3a&lt;sub&gt;1&lt;/sub&gt;</td>
<td>3a&lt;sub&gt;2&lt;/sub&gt;</td>
<td>3a&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>1</td>
<td>PdCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0</td>
<td>21</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>Pd(OAc)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0</td>
<td>18</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>(PPh&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;4&lt;/sub&gt;Pd</td>
<td>0</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>(PPh&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;PdCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0</td>
<td>8</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>(TFA)&lt;sub&gt;2&lt;/sub&gt;Pd</td>
<td>0</td>
<td>41</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>[PdCl(C&lt;sub&gt;5&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;)]&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0</td>
<td>40</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>(C&lt;sub&gt;8&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;CN)&lt;sub&gt;2&lt;/sub&gt;PdCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0</td>
<td>13</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>Pd&lt;sub&gt;2&lt;/sub&gt;(dba)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0</td>
<td>12</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>Pd(dpdpf)Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0</td>
<td>5</td>
<td>0</td>
</tr>
</tbody>
</table>

<sup>a</sup>1a (0.5 mmol) was treated with 2d (2 equiv, 1 mmol) in DMC (1 mL) at 100 °C in presence of Pd(PPh<sub>3</sub>)<sub>4</sub> (10 mol%) for 12 h. <sup>b</sup>Based on GC-MS. <sup>c</sup>Isolated yield of 3a<sub>2</sub>.
7) **Effect of ligands on the selectivity control**

**Table 5**: Reaction of 1a with allyl alcohol 2d in presence of different ligands under (PPh\textsubscript{3})\textsubscript{4}Pd catalysis using DMC as solvent.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ligand</th>
<th>% Conversion\textsuperscript{b} 3a\textsubscript{1} 3a\textsubscript{2} 3a\textsubscript{3}</th>
<th>Selectivity 3a\textsubscript{1} : 3a\textsubscript{2} : 3a\textsubscript{3}</th>
<th>Yield (%)\textsuperscript{c} 3a\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PCy\textsubscript{3}</td>
<td>0 96 0</td>
<td>00 : 100 : 00</td>
<td>85</td>
</tr>
<tr>
<td>2</td>
<td>P(o-tol)\textsubscript{3}</td>
<td>0 87 0</td>
<td>00 : 100 : 00</td>
<td>76</td>
</tr>
<tr>
<td>3</td>
<td>TFP</td>
<td>0 91 0</td>
<td>00 : 100 : 00</td>
<td>78</td>
</tr>
<tr>
<td>4</td>
<td>dppp</td>
<td>3 70 0</td>
<td>04 : 96 : 00</td>
<td>67</td>
</tr>
<tr>
<td>5</td>
<td>BPhen</td>
<td>4 88 0</td>
<td>04 : 96 : 00</td>
<td>92</td>
</tr>
<tr>
<td>6</td>
<td>DPFF</td>
<td>0 95 0</td>
<td>00 : 100 : 00</td>
<td>83</td>
</tr>
<tr>
<td>7</td>
<td>XPhos</td>
<td>0 86 0</td>
<td>00 : 100 : 00</td>
<td>72</td>
</tr>
<tr>
<td>8</td>
<td>(DHQD)\textsubscript{2}AQN</td>
<td>5 93 0</td>
<td>05 : 95 : 00</td>
<td>84</td>
</tr>
<tr>
<td>9</td>
<td>TEP</td>
<td>5 82 0</td>
<td>06 : 94 : 00</td>
<td>70</td>
</tr>
</tbody>
</table>

\textsuperscript{a}1a (0.5 mmol) was treated with 2d (2 equiv, 1 mmol) in dimethyl carbonate (1 mL) at 100 °C in presence of Pd(PPh\textsubscript{3})\textsubscript{4} (10 mol%) and different ligands (20 mol%) for 12 h. \textsuperscript{b}Based on GC-MS. \textsuperscript{c}Isolated yield of 3a\textsubscript{2}.
8) Effect of non-Pd transition metal catalysts on the selectivity control

Table 6: Reaction of 1a with allyl alcohol 2d in presence of different non-palladium transition metal catalysts under ligand and base free condition.²

![Reaction Scheme]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>% Conversion[^b]</th>
<th>Selectivity</th>
<th>Yield (%)[^c]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>3a₁</td>
<td>3a₂</td>
<td>3a₃</td>
</tr>
<tr>
<td>1</td>
<td>[Ir(1,5-cod)Cl]₂</td>
<td>0</td>
<td>32</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>RhCl(PPh₃)₃</td>
<td>0</td>
<td>14</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>Ni(PPh₃)₄</td>
<td>0</td>
<td>15</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>[Ru(p-cymene)Cl₂]₂</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>Fe(acac)₃</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>(Ph₃P)AuCl</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>CuI(I)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>Zirconocene dichloride</td>
<td>0</td>
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</tr>
</tbody>
</table>

[^a]: 1a (0.5 mmol) was treated with 2d (2 equiv, 1 mmol) in DMC (1 mL) at 100 °C in presence of different non-palladium transition metal catalysts (10 mol%) for 12 h.[^b]: Based on GC-MS.[^c]: Isolated yield of 3a₂.
Table 7: Reaction of 1a with allyl alcohol 2d in presence of different non-palladium transition metal catalysts under basic condition.\(^a\)

![Chemical structure and reaction scheme]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>% Conversion(^b)</th>
<th>Selectivity (3a_1 : 3a_2 : 3a_3)</th>
<th>Yield (%)(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Ir(1,5-cod)Cl]₂</td>
<td>0</td>
<td>00 : 100 : 00</td>
<td>17</td>
</tr>
<tr>
<td>2</td>
<td>RhCl(PPh₃)₃</td>
<td>0</td>
<td>00 : 100 : 00</td>
<td>traces</td>
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<tr>
<td>3</td>
<td>Ni(PPh₃)₄</td>
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<td>00 : 100 : 00</td>
<td>36</td>
</tr>
<tr>
<td>4</td>
<td>[Ru(p-cymene)Cl]₂</td>
<td>0</td>
<td>00 : 100 : 00</td>
<td>12</td>
</tr>
<tr>
<td>5</td>
<td>Fe(acac)₃</td>
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<td>00 : 100 : 00</td>
<td>10</td>
</tr>
<tr>
<td>6</td>
<td>(Ph₃P)AuCl</td>
<td>0</td>
<td>00 : 100 : 00</td>
<td>10</td>
</tr>
<tr>
<td>7</td>
<td>CuI(I)</td>
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<td>00 : 100 : 00</td>
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</tr>
<tr>
<td>8</td>
<td>Zirconocene dichloride</td>
<td>0</td>
<td>N/A</td>
<td>0</td>
</tr>
</tbody>
</table>

\(^a\)1a (0.5 mmol) was treated with 2d (2 equiv, 1 mmol) in dimethyl carbonate (1 mL) at 100 °C in presence of different non-palladium transition metal catalysts (10 mol%) and K₂CO₃ (2 equiv) for 12 h. \(^b\)Based on GC-MS. \(^c\)Isolated yield of 3a₂.

Table 8: Reaction of 1a with allyl alcohol 2d under non-palladium transition metal catalysis in presence of bathophenanthroline (Bphen).\(^a\)

![Chemical structure and reaction scheme]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>% Conversion(^b)</th>
<th>Selectivity (3a_1 : 3a_2 : 3a_3)</th>
<th>Yield (%)(^c)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>[Ir(1,5-cod)Cl]₂</td>
<td>0</td>
<td>00 : 100 : 00</td>
<td>24</td>
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</tbody>
</table>
2 RhCl(PPh$_3$)$_3$ 0 25 0 00 : 100 : 00 18
3 Ni(PPh$_3$)$_4$ 0 32 0 00 : 100 : 00 21
4 [Ru(p-cymene)Cl$_2$]$_2$ 0 0 0 N/A 0
5 Fe(acac)$_3$ 0 0 0 N/A 0
6 (Ph$_3$P)AuCl 0 0 0 N/A 0
7 CuI(I) 0 0 0 N/A 0
8 Zirconocene 0 0 0 N/A 0

$dichloride$

$^{a}$1a (0.5 mmol) was treated with 2d (2 equiv, 1 mmol) in DMC (1 mL) at 100 °C in presence of different non-palladium transition metal catalysts (10 mol%) and BPhen (20 mol%) for 12 h. $^{b}$Based on GC-MS. $^{c}$Isolated yield of 3a$_2$.

9) Investigation of allylic disposition under reaction condition

Representative experimental procedure: In a glove box, to an oven dried 4 mL glass vial equipped with a stirring bar, 3a$_1$ (0.093 g, 0.5 mmol), Pd(PPh$_3$)$_4$ (0.578 g, 0.05 mmol, 10 mol%), followed by DMC (1 mL) was added and the reaction mixture was stirred at 100 °C for 12 h. Then the reaction mixture was cooled to rt, diluted with MeOH (2 x 10 mL) and passed through bed of celite to remove catalyst. An aliquot portion (100 μL) of the organic layer was taken out, diluted with MeOH and subjected to GCMS to observe the selectivity. The organic layer was dried over anhyd. Na$_2$SO$_4$ and concentrated under reduced pressure. The crude products were adsorbed on to silica gel and passed through the column (elucent: Hexane/EtOAc) to get analytically pure product 3a$_2$ as white solid (0.086 g, 93%).
10) Investigation of allylic disposition from in-situ generated 3a₁

Representative experimental procedure: In a glove box, to an oven dried 4 mL glass vial equipped with a stirring bar, 1a (0.731 g, 0.5 mmol), BOP reagent (0.442 g, 1 mmol, 2 equiv), Cs₂CO₃ (0.326 g, 1 mmol, 2 equiv) followed by dry Dioxane (2 mL) was added and the reaction mixture was stirred at rt for 60 min. The resulting mixture was evaporated under reduced pressure, Cs₂CO₃ (0.326 g, 1 mmol, 2 equiv) and allyl alcohol 2d (10 mmol, 20 equiv) were added followed by stirring at rt until TLC (5 h) indicated complete reaction. To the above resulting reaction mixture, Pd(PPh₃)₄ (0.578 g, 0.05 mmol, 10 mol%) followed by DMC (1 mL) was added and the resultant reaction mixture was stirred at 100 °C for 12 h. After stipulated time period, the reaction mixture was cooled to rt, diluted with water (10 mL) and extracted with EtOAc (3 x 10 mL). The organic layer was dried over anhyd. Na₂SO₄ and concentrated under reduced pressure. The crude products were adsorbed on to silica gel and passed through the column (eluent: Hexane/EtOAc) to get analytically pure product 3a₂ as white solid (0.067 g, 72%).

11) Investigation of allylic migration from 3a₁ in the presence of different catalysts under reaction conditions

Table 9: Treatment of 3a₁ in the presence of different catalysts under reaction conditions.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>% Conversionb</th>
<th>Selectivityb</th>
<th>Yield (%)c</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>None</td>
<td>0</td>
<td>N/A</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>K₂CO₃</td>
<td>0</td>
<td>N/A</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>In(OTf)₃</td>
<td>0</td>
<td>N/A</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>(PPh₃)₄Pd</td>
<td>100</td>
<td>100 : 00</td>
<td>93</td>
</tr>
</tbody>
</table>

s-13
a3a₁ (0.5 mmol) was subjected to under reaction condition in presence of different catalysts/additives in DMC (1 mL) at 100 °C for 12 h. b Based on GC-MS. b Isolated yield of 3a₂.

Representative experimental procedure: In a glove box, to an oven dried 4 mL glass vial equipped with a stirring bar, 3a₁ (0.093 g, 0.5 mmol), Pd(PPh₃)₄ (0.578 g, 0.05 mmol, 10 mol%) followed by DMC (1 mL) was added and the reaction mixture was stirred at 100 °C for 12 h. After stipulated time period, the reaction mixture was cooled to rt, diluted with MeOH (2 x 10 mL) and passed through bed of celite to remove catalyst. An aliquot portion (100 μL) of the organic layer was taken out, diluted with MeOH and subjected to GCMS to observe the selectivity. The organic layer was dried over anhyd. Na₂SO₄ and concentrated under reduced pressure. The crude products were adsorbed on silica gel and passed through the column (eluent: Hexane/EtOAc) to get analytically pure product 3a₂ as white solid (0.086 g, 93%).

12) Validation of route B-1 / B-2: Investigation of allylic migration from 4

12a) Synthesis of (E)-4-(but-2-en-1-yl oxy)quinazoline (4)

Experimental procedure: In a glove box, to an oven dried 10 mL glass vial equipped with a stirring bar, 4-hydroxy quinazoline 1a (0.292 g, 2 mmol), BOP reagent (1.77 g, 4 mmol, 2 equiv), Cs₂CO₃ (1.304 g, 2 mmol, 2 equiv) followed by dry Dioxane (6 mL) was added and the reaction mixture was stirred at rt for 60 min. The resulting mixture was evaporated under reduced pressure, Cs₂CO₃ (1.304 g, 4 mmol, 2 equiv) and 2-buten-1-ol (2.88 g, 40 mmol, 20 equiv) were added followed by stirring at the rt until TLC (5 h) indicated reaction completion. After stipulated time period, the reaction mixture was diluted with water (15 mL) and extracted with EtOAc (3 x 15 mL). The organic layer was dried over anhyd. Na₂SO₄ and concentrated under reduced pressure. The crude products were adsorbed on to silica gel and passed through the column (eluent: Hexane/EtOAc) to get analytically pure product 4 (0.288 g, 72%) as yellowish liquid; ¹H NMR (400 MHz, CDCl₃): δ 8.80 (s, 1H), 8.19 (dd, J = 8.2, 0.6 Hz, 1H), 7.95 (d, J = 8.4 Hz, 1H), 7.84-7.80 (m, 1H), 7.57-7.53 (m, 1H), 5.99-7.89 (m, 1H), 5.87-7.83 (m, 1H), 5.03 (dd, J = 6.2, 0.9 Hz, 1H), 1.78 (d, J = 0.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): 166.5, 154.4, 150.9, 133.4, 131.6, 127.6, 126.9, 125.2, 123.6, 116.7, 67.6, 17.8; HRMS (ESI-TOF) m/z: [M + H]^+ Calcd for C₁₂H₁₃N₂O 201.1028, Found 201.1031.
12b) Representative experimental procedure for the validation of route B-1 / B-2:

In a glove box, to an oven dried 4 mL glass vial equipped with a stirring bar, 4 (0.1 g, 0.5 mmol), Pd(PPh₃)₄ (0.578 g, 0.05 mmol, 10 mol%) followed by DMC (1 mL) was added and the reaction mixture was stirred at 100 °C for 12 h. After stipulated time period, the reaction mixture was cooled to rt, diluted with MeOH (2 x 10 mL) and passed through bed of celite to remove catalyst. An aliquot portion (100 µL) of the organic layer was taken out, diluted with MeOH and subjected to GCMS to observe the selectivity. The organic layer was dried over anhyd. Na₂SO₄ and concentrated under reduced pressure. The crude products were adsorbed on silica gel and passed through the column (eluent: Hexane/EtOAc) to get analytically pure product 5a as white solid (0.074 g, 74%); ¹H NMR (400 MHz, CDCl₃): δ 8.24 (td, J = 8.1, 1.4 Hz, 1H), 7.98 (s, 1H), 7.67-7.62 (m, 2H), 7.44-7.39 (m, 1H), 5.76-5.70 (m, 1H), 5.61-5.57 (m, 1H), 4.50 (td, J = 7.4, 2.3 Hz, 2H), 1.67-1.65 (m, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 160.9, 160.7, 148.0, 146.2, 146.1, 134.0, 131.0, 130.0, 127.3, 127.12, 127.10, 126.7, 126.6, 124.8, 123.9, 122.1, 47.8, 42.7, 17.6, 13.1; HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₁₂H₁₃N₂O 201.1028, Found 201.1030.
13) Preparation of substrates

1a and 1p-1w were purchased from Sigma-Aldrich and Alfa Aesar. Compounds 1b-1o and 1x were prepared according to literature report. All allyl alcohols were purchased from Sigma-Aldrich and used as such.

4-Hydroxy quinazolines:

Other tautomizerable heterocycles:

Allyl alcohols
(a) Representative experimental procedure for the synthesis of 1b, 1g, 1h:

\[
\begin{array}{c}
\text{X} = \text{H} / \text{Me} / \text{Cl} \\
\text{R} = \text{H} / \text{Me}
\end{array}
\]

\[
\begin{array}{c}
\text{RC(OEt)}_3 + \text{NH}_2\text{NH}_2 \rightarrow \text{HO} \\
\text{Neat, } 120 \degree \text{C} \\
\text{5 - 10 h}
\end{array}
\]

A mixture of isatoic anhydride (0.815 g, 5 mmol), ammonium acetate (0.578 g, 7.5 mmol, 1.5 equiv), and triethyl orthoacetate (1.22 g, 7.5 mmol, 1.5 equiv) were stirred magnetically at 120 °C (oil bath temp). After completion of the reaction (TLC, 5 h), the crude reaction mixture was recrystallized from EtOH to obtain analytically pure 1b (0.640 g, 80%) as white solid;\(^2\) \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 8.27 \text{ (dd, } J = 7.5, 1.2 \text{ Hz, 1H)}, 7.80-7.78 \text{ (m, 1H)}, 7.71 \text{ (d, } J = 7.7 \text{ Hz, 1H)}, 7.52-7.48 \text{ (m, 1H)}, 2.63 \text{ (s, 3H)}; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 164.8, 153.7, 149.8, 135.5, 127.3, 127.0, 126.5, 120.6, 22.6\).

**6-Chloro-quinazolin-4-ol**

**1g:** White solid (0.659 g, 73%); \(^1\)H NMR (400 MHz, DMSO): \(\delta 12.47 \text{ (s, bd, 1H)}, 8.12 \text{ (s, 1H)}, 8.03 \text{ (d, } J = 2.4 \text{ Hz, 1H)}, 7.82-7.79 \text{ (m, 1H)}, 7.67 \text{ (d, } J = 8.6 \text{ Hz, 1H}); \(^{13}\)C NMR (100 MHz, DMSO): \(\delta 160.2, 147.9, 146.4, 134.8, 131.5, 129.9, 125.3, 124.3\).

(b) Experimental procedure for the synthesis of 1i:

\[
\begin{array}{c}
\text{R} \text{NO} \text{H} \\
\text{NH} \text{Me} \text{2}
\end{array}
\]

\[
\begin{array}{c}
\text{140 °C, 12 h}
\end{array}
\]

A solution of 2-amino-5-nitrobenzoic acid (1g, mmol) in formamide (1.7 mol) was heated under reflux at 140 °C for 4 h. Solvent was removed under reduced pressure and the crude solid was recrystallized from EtOH to yield analytically pure 1q (0.831 g, 87%); Yellow solid; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta 12.76 \text{ (br, 1H)}, 8.80 \text{ (d, } J = 1.6 \text{ Hz, 1H)}, 8.56-8.53 \text{ (m, 1H)}, 8.32 \text{ (s, 1H)}, 7.86 \text{ (d, } J = 8.9 \text{ Hz, 1H)}.

(c) Representative experimental procedure for the synthesis 1c, 1d, 1e, 1f, 1j-1o:

\[
\begin{array}{c}
\text{1} \text{OH} \\
\text{R}
\end{array}
\]

\[
\begin{array}{c}
\text{Open air} \\
\text{DMSO, 140 °C, 12 h}
\end{array}
\]
Anthranilamide (5.0 mmol) and an aldehyde (6 mmol, 1.2 equiv) were dissolved in DMSO (10 mL). Then, the reaction mixture was stirred at 100 °C in an open flask and monitored by TLC. After complete consumption of the starting materials (12-36 h), the reaction mixture was cooled to rt. When water (100 mL) was added to the reaction mixture, the precipitate was formed and collected by filtration. Recrystallization in ethanol afforded 4-hydroxy quinazolines.

2-Cyclohexyl-quinazolin-4-ol

![Image of 2-Cyclohexyl-quinazolin-4-ol]

**1c;** White solid (0.913 g, 80%); $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 12.72 (br, 1H), 8.08 (d, $J = 7.5$ Hz, 1H), 7.76 (t, $J = 7.1$ Hz, 1H), 7.59 (d, $J = 8.1$ Hz, 1H), 7.45 (t, $J = 7.4$Hz, 1H), 2.61-2.51 (m, 2H), 1.92-1.77 (m, 4H), 1.69-1.54 (m, 3H), 1.34-1.20 (m, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ 162.4; 161.26, 149.29, 134.7, 127.3, 126.4, 126.1, 121.4, 43.3, 30.6, 25.9, 25.8.

2-Phenyl-quinazolin-4-ol

![Image of 2-Phenyl-quinazolin-4-ol]

**1d;** White solid (0.911 g, 82%); $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 12.51 (br, 1H), 8.16 (d, $J = 7.5$ Hz, 3H), 7.85 (t, $J = 7.3$ Hz, 1H), 7.78 (d, $J = 8.4$ Hz, 1H), 7.66-7.55 (m, 4H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ 162.5, 152.4, 149.6, 134.7, 132.6, 131.4, 128.8, 127.5, 127.4, 126.7, 125.7, 120.7.

2-Furan-2-yl-quinazolin-4-ol

![Image of 2-Furan-2-yl-quinazolin-4-ol]

**1e;** White solid (0.859 g, 81%); $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 12.50 (br, 1H), 8.13 (d, $J = 7.4$ Hz, 1H), 8.01-7.80 (m, 2H), 7.70-7.64 (m, 2H), 7.50 (t, $J = 7.4$ Hz, 1H), 6.76 (q, $J = 1.5$ Hz, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ 162.0, 149.1, 147.1, 146.6, 144.5, 135.1, 127.7, 126.9, 126.4, 121.6, 114.9, 112.9.

2-Styryl-quinazolin-4-ol

![Image of 2-Styryl-quinazolin-4-ol]

**1f;** White solid; (0.307 g, 62%); $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 8.32 (d, $J = 7.9$ Hz, 1H), 7.99 (d, $J = 15.3$ Hz, 1H), 7.82 (d, $J = 3.5$ Hz, 2H) 7.64-7.55 (m, 3H), 7.52-7.49 (m, 1H), 7.35-7.29 (m, 7H), 6.40 (d, $J = 15.6$ Hz, 1H); $^{13}$C NMR (100 MHz, DMSO): δ 162.7, 152.3, 149.7, 138.9, 135.6, 135.1, 130.4, 129.6, 128.2, 127.7, 126.7, 126.5, 121.8.
2-(4-Dimethylamino-phenyl)-quinazolin-4-ol

\[ \text{1j; Brown solid (0.968 g, 73%); } ^1\text{H NMR (400 MHz, DMSO-}d_6) : \delta 12.18 \text{ (br, 1H), 8.09-8.14 (m, 3H), 7.75-7.79 (m, 1H), 7.65 (d, } J = 7.6 \text{ Hz, 1H), 7.40-7.44 (m, 1H), 6.78 (d, } J = 9.1 \text{ Hz, 2H), 3.00 (s, 6H); } ^{13}\text{C NMR (100 MHz, DMSO-}d_6) : \delta 162.9, 152.71, 152.70, 149.8, 134.9, 129.3, 127.5, 126.3, 125.8, 120.9, 119.3, 111.7, 66.5, 40.1. \]

2-(4-Trifluoromethyl-phenyl)-quinazolin-4-ol

\[ \text{1k; White solid (1.16 g, 80%); } ^1\text{H NMR (400 MHz, DMSO-}d_6) : \delta 12.75 \text{ (br, 1H), 8.38 (d, } J = 8.1 \text{ Hz, 1H), 8.18 (dd, } J = 7.9, 1.2 \text{ Hz, 1H), 7.92 (d, } J = 8.3 \text{ Hz, 2H), 7.85-7.89 (m, 1H), 7.78 (dd, } J = 8.1 \text{ 0.6 Hz, 1H), 7.54-7.59 (m, 1H); } ^{13}\text{C NMR (100 MHz, DMSO-}d_6) : \delta = 162.6, 151.6, 148.9, 137.1, 135.2, 131.6 (q, } J = 1.33 \text{ Hz), 129.2, 128.2, 127.6, 126.4, 125.9 (q, } J = 14.8), 123.1, 121.7. \]

4-(4-Hydroxy-quinazolin-2-yl)-benzonitrile

\[ \text{1l; White solid (0.964 g, 78%); } ^1\text{H NMR (400 MHz, DMSO-}d_6) : \delta 12.7 \text{ (br, 1H), 7.35 (d, } J = 7.0 \text{ Hz, 2H), 8.18 (d, } J = 7.7 \text{ Hz, 1H), 8.05 (d, } J = 6.7 \text{ Hz, 2H), 7.86 (t, } J = 7.5 \text{ Hz, 1H), 7.77 (d, } J = 8.4 \text{ Hz, 1H), 7.58 (dd, } J = 7.5, 7.1 \text{ Hz, 1H); } ^{13}\text{C NMR (100 MHz, DMSO-}d_6) : \delta 162.5, 160.2, 148.5, 136.9, 135.2, 132.8, 128.9, 127.7, 127.5, 126.2, 121.5, 118.6, 113.8. \]

4-(4-Hydroxy-quinazolin-2-yl)-benzaldehyde

\[ \text{1m; White solid (0.950 g, 76%); } ^1\text{H NMR (400 MHz, DMSO-}d_6) : \delta 12.72 \text{ (br, 1H), 10.12 (s, 1H), 8.38 (d, } J = 8.3 \text{ Hz, 1H), 8.18 (dd, } J = 7.9, 1.0 \text{ Hz, 1H), 8.07 (d, } J = 8.3 \text{ Hz, 2H), 7.89-7.85 (m, 1H), 7.79 (d, } J = 8.0 \text{ Hz, 2H), 7.58-7.55 (m, 1H); } ^{13}\text{C NMR (100 MHz, DMSO-}d_6) : \delta 193.3, 162.6, 151.9, 148.9, 138.25, 138.19, 135.2, 129.9, 129.0, 129.2, 127.6, 126.4, 121.7. \]

1-[4-(4-Hydroxy-quinazolin-2-yl)-phenyl]-ethanone

\[ \text{1n; White solid (0.924 g, 70%); } ^1\text{H NMR (400 MHz, DMSO-}d_6) : \delta 12.69 \text{ (br, 1H), 8.32 (d, } J = 8.5 \text{ Hz, 2H), 8.18 (dd, } J = 7.9, 1.1 \text{ Hz, 1H), 8.10 (d, } J = 8.4 \text{ Hz, 2H), 7.85-7.89 (m, 1H), 7.78 (d, } J = 7.8 \text{ Hz, 1H), 7.54-7.59 (m, 1H), 2.66 (s, 3H); } ^{13}\text{C NMR} \]

S-19
10 MHz, DMSO-d6): δ 198.1, 162.6, 151.9, 149.0, 139.0, 135.2, 128.8, 128.6, 128.2, 127.5, 121.6, 27.4.

2-Benz[1,3]dioxol-5-yl-quinazolin-4-ol

10: Gray solid (1.13 g, 85%); 1H NMR (400 MHz, DMSO-d6): δ 12.36 (br, 1H), 8.16 (d, J = 7.6 Hz, 1H), 7.85-7.72 (m, 4H), 7.53 (t, J = 7.8 Hz, 1H), 7.12 (d, J = 8.6 Hz, 1H), 6.18 (s, 2H); 13C NMR (100 MHz, DMSO-d6): δ 163.7, 147.9, 147.5, 135.8, 134.8, 133.5, 127.6, 125.9, 123.2, 120.5, 177.4, 114.5, 108.2, 107.7, 101.9.

(d) Experimental procedure for the synthesis of 1x:

To a round bottom flask containing a magnetic stir bar was added benzhydrazide (2.0 g, 14.7 mmol), CH2Cl2 (300 mL) and DIPEA (5.1 mL, 29 mmol, 2 equiv). The flask was fitted with a rubber septum containing two needles: one connected to a positive pressure N2 line, the other open to air. Triphosgene (1.75 g, 5.9 mmol, 0.4 equiv) and CH2Cl2 (10 mL) were added to a 40 mL vial; the vial was sonicated until the triphosgene had dissolved. Using a syringe, the triphosgene/CH2Cl2 solution was added drop wise to the stirred solution of benzhydrazide. The solution was stirred at room temperature; by TLC analysis, the reaction was nearly complete within 20 minutes (hexanes/EtOAc). The reaction mixture was concentrated by rotary evaporation; the crude product was purified by chromatography on silica (gradient elution from hexanes to EtOAc) affording 1x (0.689 g, 72%) as a white solid; 1H NMR (400 MHz, DMSO-d6): δ 12.51 (br, 1H), 7.85-7.73 (m, 2H), 7.62-7.53 (m, 3H); 13C NMR (100 MHz, DMSO-d6): δ 154.7, 154.1, 131.6, 129.5, 125.5, 124.2.
14) Spectra data of products (Table 6 & 7)

3-Cinnamyl-2-methylquinazolin-4(3H)-one (3c; Entry 2, Table 6)

White solid (0.126 g, 91%); MP 127-128 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.33 - 8.28 (m, 1H), 7.74 - 7.62 (m, 2H), 7.47 - 7.45 (m, 1H), 7.43 - 7.21 (m, 5H), 6.55 (dt, J = 16.0, 1.6 Hz, 1H), 6.30 (dt, J = 16.0, 5.2 Hz, 1H), 4.92 (dd, J = 5.9, 1.6 Hz, 2H), 2.69 (s, 3H); ¹³C NMR (101 MHz, CDCl₃): δ 161.9, 154.3, 147.4, 136.0, 134.3, 132.9, 128.6, 128.1, 126.9, 126.7, 126.49, 126.47, 122.9, 120.5, 45.9, 23.2; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for C₁₈H₁₇N₂O 277.1341, Found 277.1339.

3-Cinnamyl-2-cyclohexylquinazolin-4(3H)-one (3d; Entry 3, Table 6)

Colorless viscous liquid (0.146 g, 85%); ¹H NMR (400 MHz, CDCl₃): δ 8.34 - 8.31 (m, 1H), 7.74 - 7.69 (m, 2H), 7.47 - 7.42 (m, 1H), 7.39 - 7.25 (m, 5H), 6.53 (dt, J = 16.0, 1.6 Hz, 1H), 6.35 (dt, J = 16.0, 5.5 Hz, 1H), 5.01 (dd, J = 5.6, 1.7 Hz, 2H), 2.93 - 2.86 (m, 1H), 1.98 - 1.79 (m, 7H), 1.43 - 1.38 (m, 3H); ¹³C NMR (101 MHz, CDCl₃): δ 162.4, 160.6, 147.66, 136.2, 134.1, 132.4, 128.6, 127.9, 127.2, 126.9, 126.5, 126.2, 124.08, 120.4, 44.7, 42.3, 31.7, 26.2, 25.8; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for C₂₃H₂₅N₂O 345.1967, Found 345.1962.

3-Cinnamyl-2-phenylquinazolin-4(3H)-one (3e; Entry 4, Table 6)

White solid (0.149 g, 88%); MP 105-106 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.44 - 8.36 (m, 1H), 7.85 - 7.75 (m, 2H), 7.63 - 7.49 (m, 6H), 7.37 - 7.19 (m, 5H), 6.30 - 6.14 (m, 2H), 4.79 (d, J = 5.1 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃): δ 162.1, 156.2, 147.3, 136.2, 135.4, 134.5, 133.6, 130.0, 128.7, 128.5, 128.1, 127.9, 127.6, 127.1, 126.9, 126.5, 123.3, 120.9, 47.9; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for C₂₃H₁₉N₂O 339.1497, Found 339.1497.

3-Cinnamyl-2-(furan-2-yl)quinazolin-4(3H)-one (3f; Entry 5, Table 6)

Light yellow solid (0.138 g, 84%); MP 98-100 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.34 (dt, J = 7.9, 1.0 Hz, 1H), 7.83 - 7.73 (m, 2H), 7.67 (dd, J = 1.8, 0.9 Hz, 1H), 7.54 - 7.50 (m, 1H), 7.38 - 7.11 (m, 6H), 6.64 - 6.42 (m, 2H), 6.33 (dt, J = 15.9, 5.9 Hz, 1H), 5.11 (dd, J = 5.9, 1.5 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃): δ 162.1, 147.5, 147.4, 146.1, 144.5, 136.3, 134.5, 133.1, 128.5, 127.9, 127.6, 127.2, 127.0, 126.5, 123.69, 120.7, 115.5, 112.0, 46.9; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for C₂₁H₁₇N₂O₂ 329.1290, Found 329.1295.

3-Cinnamyl-2-((E)-styryl)quinazolin-4(3H)-one (3g; Entry 6, Table 6)

S-21
Light yellow solid (0.131 g, 72%); MP 180-182 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.35 (dt, J = 8.0, 1.1 Hz, 1H), 8.02 (d, J = 15.4 Hz, 1H), 7.80 - 7.76 (m, 2H), 7.62 - 7.59 (m, 2H), 7.51 - 7.47 (m, 1H), 7.46 - 7.38 (m, 5H), 7.35 - 7.30 (m, 2H), 7.28 - 7.26 (m, 1H), 7.21 (d, J = 15.4 Hz, 1H), 6.65 (dt, J = 16.0, 1.7 Hz, 1H), 6.41 (dt, J = 16.0, 5.6 Hz, 1H), 5.10 (dd, J = 5.5, 1.7 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃): δ 162.0, 152.4, 147.7, 141.2, 136.1, 135.5, 134.4, 132.9, 129.8, 128.9, 128.6, 128.1, 127.8, 127.4, 127.0, 126.5, 126.3, 126.3, 123.4, 120.6, 119.3, 45.5; HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₂₅H₂₀N₂O 365.1654, Found 365.1658.

6-Chloro-3-cinnamylquinazolin-4(3H)-one (3h; Entry 7, Table 6)

Off white solid (0.133 g, 90%); MP 120-121 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.34 - 8.28 (m, 1H), 8.10 (s, 1H), 7.72 - 7.66 (m, 2H), 7.40 - 7.25 (m, 5H), 6.69 (dt, J = 16.0, 1.5 Hz, 1H), 6.34 (dt, J = 15.8, 6.5 Hz, 1H), 4.80 (dd, J = 6.5, 1.4 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃): δ 159.9, 146.6, 146.3, 135.7, 134.9, 134.7, 133.2, 129.2, 128.7, 128.4, 126.6, 126.2, 123.2, 122.4, 48.3; HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₁₇H₁₄ClN₂O 297.0795, Found 297.0792.

3-Cinnamyl-6-methoxyquinazolin-4(3H)-one (3i; Entry 8, Table 6)

White solid (0.123 g, 84%); MP 172-173 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.02 (s, 1H), 7.71 - 7.63 (m, 2H), 7.39 - 7.33 (m, 3H), 7.31 - 7.26 (m, 3H), 6.67 (dt, J = 15.9, 1.5 Hz, 1H), 6.36 (dt, J = 15.9, 6.4 Hz, 1H), 4.80 (dd, J = 6.5, 1.4 Hz, 2H), 3.94 (s, 3H); ¹³C NMR (101 MHz, CDCl₃): δ 160.8, 158.8, 144.0, 142.7, 135.8, 134.4 129.1, 128.6, 128.2, 126.6, 124.5, 123.0, 122.9, 106.1, 55.8, 48.2; HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₁₈H₁₇N₂O₂ 293.1290, Found 293.1293.

3-Cinnamyl-6-nitroquinazolin-4(3H)-one (3j; Entry 9, Table 6)

Yellow solid (0.126 g, 82%); MP 145-146 °C; ¹H NMR (400 MHz, CDCl₃): δ 9.22 (d, J = 2.6 Hz, 1H), 8.57 (dd, J = 8.9, 2.6 Hz, 1H), 8.26 (s, 1H), 7.87 (d, J = 8.9 Hz, 1H), 7.42 - 7.29 (m, 5H), 6.71 (d, J = 15.8 Hz, 1H), 6.39 - 6.31 (m, 1H), 4.76 (dd, J = 6.6, 1.2 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃): δ 159.8, 152.1, 149.0, 146.1, 135.6, 135.4, 129.3, 128.8, 128.6, 128.4, 126.7, 123.5, 122.4, 121.7, 48.7; HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₁₇H₁₄N₃O₃ 308.1035, Found 308.1033.
3-Cinnamyl-2-(4-(dimethylamino)phenyl)quinazolin-4(3H)-one (3k; Entry 10, Table 6)

White semisolid (0.162 g, 85%); 1H NMR (400 MHz, DMSO-d6): δ 8.19 - 8.17 (m, 1H), 7.85 - 7.81 (m, 1H), 7.68 - 7.66 (m, 1H), 7.55 - 7.48 (m, 3H), 7.37 - 7.20 (m, 5H), 6.80 - 6.77 (m, 2H), 6.36 - 6.23 (m, 2H), 4.77 - 4.73 (m, 2H), 2.97 (s, 6H); 13C NMR (101 MHz, DMSO-d6) δ 162.0, 157.2, 151.5, 147.7, 136.6, 134.9, 131.6, 129.9, 129.0, 128.1, 127.6, 126.9, 126.7, 126.7, 125.3, 122.7, 120.5, 111.5, 48.0, 36.7, 24.8; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for C25H24N3O 382.1919, Found 382.1923.

3-Cinnamyl-2-(4-(trifluoromethyl)phenyl)quinazolin-4(3H)-one (3l; Entry 11, Table 6)

White solid (0.175 g, 86%); MP 138-140 °C; 1H NMR (400 MHz, CDCl3): δ 8.40 (dd, J = 8.0, 1.4 Hz, 1H), 7.84 - 7.72 (m, 6H), 7.60 - 7.56 (m, 1H), 7.34 - 7.24 (m, 5H), 6.27 - 6.18 (m, 2H), 4.76 (d, J = 5.2 Hz, 2H); 13C NMR (101 MHz, CDCl3): δ 161.8, 154.8, 147.1, 138.7 (q, JF-CCC = 1.33 Hz), 135.8, 134.7, 133.7, 132.14 (q, JF-CC = 33.23 Hz) 128.8, 128.6, 128.2, 127.6, 127.5, 127.0, 126.5, 125.7 (q, JF-CCC = 3.73 Hz) 123.7 (q, JF-C = 272.38 Hz), 122.8; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for C24H18F3N3O 407.1371, Found 407.1368.

4-(3-Cinnamyl-4-oxo-3,4-dihydroquinazolin-2-yl)benzonitrile (3m; Entry 12, Table 6)

White solid (0.154 g, 85%); MP 110-111 °C; 1H NMR (400 MHz, CDCl3): δ 8.39 (dd, J = 7.7, 1.5 Hz, 1H), 7.84 - 7.81 (m, 3H), 7.76 - 7.71 (m, 3H), 7.60 - 7.56 (m, 1H), 7.34 - 7.25 (m, 6H), 6.25 - 6.13 (m, 2H), 4.74 (d, J = 5.3 Hz, 2H); 13C NMR (101 MHz, CDCl3): δ 161.7, 154.3, 146.9, 139.4, 135.8, 134.8, 133.6, 132.5, 129.2, 128.7, 128.3, 127.7, 127.6, 127.0, 126.5, 122.8, 120.9, 118.0, 114.0, 48.0; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for C24H18N3O 364.1450, Found 364.1443.

(E)-4-(3-Cinnamyl-4-oxo-3,4-dihydroquinazolin-2-yl)benzaldehyde (3n; Entry 13, Table 6)

Colorless liquid (0.165 g, 90%); 1H NMR (400 MHz, CDCl3): δ 10.2 (s, 1H), 8.40 (dd, J = 8.1, 1.0 Hz, 1H), 8.06 (dd, J = 6.5, 1.8 Hz, 1H), 7.85 - 7.77 (m, 4H), 7.60 - 7.56 (m, 1H), 7.33 - 7.23 (m, 5H), 6.26 - 7.14 (m, 2H), 4.76 (d, J = 5.0 Hz 2H); 13C NMR (101 MHz, CDCl3): δ 191.4, 161.9, 154.9, 147.1, 140.7, 137.2, 135.9, 134.7, 133.7, 129.9, 129.1, 128.6, 128.2,
127.63, 127.58, 126.5, 122.9, 120.1, 47.9; HRMS (ESI-TOF) m/z: [M + H]^+ Calcd for C_{24}H_{19}N_2O_2 367.1447, Found 367.1448.

2-(4-Acetylphenyl)-3-cinnamylquinazolin-4(3H)-one (3o; Entry 14, Table 6)

Colorless semisolid (0.162 g, 85%); ^1H NMR (400 MHz, CDCl₃): δ 8.39 - 8.37 (m, 1H), 8.12 - 8.10 (m, 2H), 7.86 - 7.74 (m, 2H), 7.71 - 7.69 (m, 2H), 7.57 - 7.53 (m, 1H), 7.32 - 7.21 (m, 5H), 6.25 - 6.15 (m, 2H), 4.75 (d, J = 4.5 Hz, 2H), 2.68 (s, 3H); ^13C NMR (101 MHz, CDCl₃): δ 197.2, 161.2, 155.2, 147.1, 139.5, 138.1, 135.9, 134.6, 133.6, 128.6, 128.6, 128.1, 127.6, 127.5, 126.9, 126.5, 123.0, 120.9, 47.9, 26.8; HRMS (ESI-TOF) m/z: [M + H]^+ Calcd for C_{25}H_{21}N_2O_2 381.1603, Found 381.1610.

2-(Benzo[d][1,3]dioxol-5-yl)-3-cinnamylquinazolin-4(3H)-one (3p; Entry 15, Table 6)

White solid (0.159 g, 83%); MP 142-143 °C; ^1H NMR (400 MHz, CDCl₃): δ 8.38 - 8.36 (m, 1H), 7.81 - 7.70 (m, 2H), 7.55 - 7.51 (m, 1H), 7.40 - 7.22 (m, 6H), 7.10 - 7.06 (m, 2H), 6.95 (d, J = 7.8 Hz, 1H), 6.33 - 6.22 (m, 2H), 6.08 (s, 2H), 4.82 (d, J = 4.7 Hz, 2H); ^13C NMR (101 MHz, CDCl₃): δ 162.2, 155.7, 149.1, 147.9, 147.2, 136.2, 134.5, 133.5, 129.0, 128.6, 127.9, 127.5, 127.1, 126.9, 126.5, 123.4, 122.5, 120.9, 108.8, 108.5, 101.7, 48.2; HRMS (ESI-TOF) m/z: [M + H]^+ Calcd for C_{24}H_{19}N_2O_2 383.1396, Found 383.1401.

1-Cinnamylpyridin-2(1H)-one (3q; Entry 16, Table 6)

Pale brown liquid (0.085 g, 81%); ^1H NMR (400 MHz, CDCl₃): δ 7.39 - 7.24 (m, 7H), 6.63 - 6.57 (m, 2H), 6.33 (dt, J = 15.9, 6.5 Hz, 1H), 6.19 (td, J = 6.7, 1.4 Hz, 1H), 4.73 (dd, J = 6.5, 1.4 Hz, 2H); ^13C NMR (101 MHz, CDCl₃): δ 162.5, 139.5, 139.6, 136.0, 128.63, 128.5, 128.1, 126.6, 123.6, 121.2, 106.2, 50.7; HRMS (ESI-TOF) m/z: [M + Na]^+ Calcd for C_{14}H_{13}N_2ONa 234.0895, Found 234.0895.

3-Cinnamylpyrimidin-4(3H)-one (3r; Entry 17, Table 6)

White solid (0.089 g, 84%); MP 138-140 °C; ^1H NMR (400 MHz, CDCl₃): δ 8.18 (s, 1H), 7.92 (d, J = 6.8 Hz, 1H), 7.41 - 7.30 (m, 5H), 6.67 (d, J = 16.0 Hz, 1H), 6.51 (dd, J = 6.4, 0.4 Hz, 1H), 6.36-6.29 (m, 1H), 4.73 (dd, J = 6.8, 1.4 Hz, 1H); ^13C NMR (101 MHz, CDCl₃): δ 160.7, 153.4, 150.9, 135.6, 135.2, 128.7, 128.4, 126.7, 122.1, 116.1, 48.5; HRMS (ESI-TOF) m/z: [M + Na]^+ Calcd for C_{13}H_{12}N_2ONa 235.0847, Found 235.0845.
1-Cinnamylpyrazine-2(1H)-one (3s; Entry 18, Table 6)

White solid (0.089 g, 84%); MP 59-60 °C; 1H NMR (400 MHz, CDCl3) δ 8.21 (d, J = 1.2 Hz, 3H), 7.44 - 7.25 (m, 19H), 7.19 (dd, J = 4.4, 1.2 Hz, 3H), 6.68 (dt, J = 15.8, 1.4 Hz, 3H), 6.27 (dt, J = 15.8, 6.7 Hz, 3H), 4.69 (dd, J = 6.7, 1.4 Hz, 6H); 13C NMR (101 MHz, CDCl3) δ 156.0, 149.7, 135.8, 135.5, 128.7, 128.5, 127.8, 126.7, 124.0, 121.6, 50.3. HRMS (ESI-TOF) m/z: [M + Na]+ Calcd for C13H12N2ONa 235.0847, Found 235.0844.

2-Cinnamylphthalazin-1(2H)-one (3t; Entry 19, Table 6)

White solid (0.117 g, 89%); MP 64-65 °C; 1H NMR (400 MHz, CDCl3): δ 8.46 (dd, J = 7.5, 1.8 Hz, 1H), 8.19 (s, 1H), 7.81 - 7.73 (m, 2H), 7.68 (dd, J = 7.6, 1.6 Hz, 1H), 7.40 - 7.30 (m, 2H), 7.29 - 7.26 (m, 2H), 7.24 - 7.20 (m, 1H), 6.72 (dt, J = 15.8, 1.4 Hz, 1H), 6.47 (dt, J = 15.8, 6.6 Hz, 1H), 5.02 (dd, J = 6.5, 1.3 Hz, 2H); 13C NMR (101 MHz, CDCl3): δ 159.2, 138.1, 136.5, 133.7, 133.1, 131.7, 129.7, 128.5, 128.0, 127.8, 126.7, 126.6, 126.1, 123.7, 53.2; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for C17H15N2O 263.1184, Found 263.1186.

1-Cinnamylquinolin-2(1H)-one (3u; Entry 20, Table 6)

White solid (0.112 g, 86%); MP 45-46 °C; 1H NMR (400 MHz, CDCl3): δ 7.74 (d, J = 9.5 Hz, 1H), 7.65 - 7.51 (m, 2H), 7.45 (d, J = 8.6 Hz, 1H), 7.35 - 7.20 (m, 6H), 6.78 (d, J = 9.5 Hz, 1H), 6.57 (dt, J = 15.9, 1.8 Hz, 1H), 6.34 (dt, J = 16.0, 5.5 Hz, 1H), 5.14 (dd, J = 5.8, 1.7 Hz, 2H); 13C NMR (101 MHz, CDCl3): δ 162.1, 139.4, 139.4, 136.3, 132.5, 130.7, 128.94, 128.92, 128.6, 128.5, 127.7, 126.4, 123.5, 122.2, 121.7, 120.9, 114.7, 44.2; HRMS (ESI-TOF) m/z: [M + Na]+ Calcd for C18H15NO 284.1051, Found 284.1047.

1-Cinnamylquinoxalin-2(1H)-one (3v; Entry 21, Table 6)

Light yellow solid (0.118 g, 90%); MP 91-93 °C; 1H NMR (400 MHz, CDCl3): δ 8.38 (s, 1H), 7.93 (dd, J = 8.0, 1.5 Hz, 1H), 7.59 (m, 1H), 7.44 (dd, J = 8.5, 1.2 Hz, 1H), 7.41 - 7.22 (m, 7H), 6.63 (dt, J = 16.1, 1.6 Hz, 1H), 6.29 (dt, J = 16.0, 5.8 Hz, 1H), 5.08 (dd, J = 5.8, 1.6 Hz, 2H); 13C NMR (101 MHz, CDCl3): δ 154.7, 150.3, 135.9, 133.7, 133.6, 132.5, 131.1, 130.7, 128.6, 128.1, 126.5, 123.8, 121.8, 114.3, 43.8; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for C17H15N2O 263.1184, Found 263.1181.

3-Cinnamylbenzo[d]thiazol-2(3H)-one (3w; Entry 22, Table 6)

Light yellow solid (0.115 g, 86%); MP 46-47 °C; 1H NMR (400 MHz, CDCl3): δ 7.46 (dd, J = 7.8, 1.2 Hz, 1H), 7.38 - 7.25 (m, 6H), 7.21 - 7.13 (m, 2H), 6.65 (dt, J = 15.9, 1.6 Hz, 1H), 6.26 (dt, J = 15.9, 6.0 Hz, 1H), 4.76 (dd, J = 6.0, 1.6 Hz, 2H); 13C NMR (101 MHz, CDCl3): δ 158.1, 150.3, 135.9, 133.7, 133.6, 132.5, 131.1, 130.7, 128.6, 128.1, 126.5, 123.8, 121.8, 114.3, 43.8; HRMS (ESI-TOF) m/z: [M + Na]+ Calcd for C17H15N2O 263.1184, Found 263.1181.
3-Cinnamylbenzo[d]oxazol-2(3H)-one (3x; Entry 23, Table 6)

Light brown solid (0.113 g, 90%); MP 100-102 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.48 - 7.00 (m, 10H), 6.71 (dt, J = 15.9, 1.6 Hz, 1H), 6.28 (dt, J = 15.9, 6.2 Hz, 1H), 4.64 (dd, J = 6.2, 1.6 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃): δ 154.4, 142.7, 135.8, 134.2, 131.0, 128.7, 128.3, 126.6, 123.9, 122.5, 121.7, 110.1, 108.9, 44.4; HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₁₆H₁₄NOS 268.0796, Found 268.0792.

3-Cinnamyl-5-phenyl-1,3,4-oxadiazol-2(3H)-one (3y; Entry 24, Table 6)

White solid (0.119 g, 86%); MP 49-50 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.90 - 7.64 (m, 2H), 7.54 - 7.42 (m, 5H), 7.37 - 7.27 (m, 3H), 6.74 (dt, J = 15.9, 1.4 Hz, 1H), 6.33 (dt, J = 15.8, 6.5 Hz, 1H), 4.59 (dd, J = 6.6, 1.4 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃): δ 148.7, 148.6, 131.2, 130.0, 126.8, 124.2, 123.9, 123.5, 121.9, 121.0, 119.1, 117.01, 43.2; HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₁₇H₁₅N₂O₂ 279.1133, Found 279.1136.

3-Allyl-quinazolin-4(3H)-one (3a; Entry 1, Table 7)

White solid (0.084 g, 91%); MP 65-66 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.34 (d, J = 8.0 Hz, 1H), 8.04 (s, 1H), 7.80-7.72 (m, 2H), 7.55-7.50 (m, 1H), 6.07-5.97 (m, 1H), 5.31 (t, J = 10.1 Hz, 2H), 4.66 (d, J = 5.7 Hz, 2H); ¹³C NMR (100.6 MHz, CDCl₃): δ 160.8, 148.1, 146.2, 134.3, 131.9, 127.5, 127.3, 126.8, 122.1, 118.9, 48.3; MS (ESI) m/z: 186.1 M⁺.

3-(1-Methylallyl)quinazolin-4(3H)-one (5a; Entry 4, Table 7)

White semi-solid (0.082 g, 82%); ¹H NMR (400 MHz, CDCl₃): δ 8.24 (td, J = 8.1, 1.4 Hz, 1H), 7.98 (s, 1H), 7.67-7.62 (m, 2H), 7.44-7.39 (m, 1H), 5.76-5.70 (m, 1H), 5.61-5.57 (m, 1H), 4.50 (td, J = 7.4, 2.3 Hz, 2H), 1.67-1.65 (m, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 160.9, 160.7, 148.0, 146.2, 146.1, 134.0, 131.0, 130.0, 127.3, 127.12, 127.10, 126.7, 126.6, 124.8, 123.9, 122.1, 47.8, 42.7, 17.6, 13.1; HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₁₂H₁₃N₂O 201.1028, Found 201.1030.

3-(2-Methylallyl)quinazolin-4(3H)-one (6a; Entry 6, Table 7):
Colorless liquid (0.085 g, 85%); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.25-8.28 (m, 1H), 7.96 (s, 1H), 7.65-7.72 (m, 2H), 7.43-7.47 (m, 1H), 4.94 (t, $J = 1.2$ Hz, 1H), 4.94 (d, $J = 0.7$ Hz, 1H), 4.53 (s, 2H), 1.74 (d, $J = 0.5$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 160.8, 148.0, 146.4, 139.8, 134.2, 127.5, 127.2, 126.8, 122.0, 113.5, 50.9, 20.1; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for C$_{12}$H$_{13}$N$_2$O 201.1028, Found 201.1031.

3-(Cyclohex-2-en-1-yl)quinazolin-4(3H)-one (6b; Entry 7, Table 7):

Colorless liquid (0.088 g, 78%); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.32-8.35 (m, 1H), 8.19 (s, 1H), 7.70-7.76 (m, 2H), 7.49-7.53 (m, 1H), 6.22-6.27 (m, 1H), 5.65-5.69 (m, 1H), 5.55-5.66 (m, 1H), 2.10-2.67 (m, 3H), 1.68-1.82 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 160.9, 144.7, 134.6, 134.1, 127.4, 127.1, 126.9, 125.2, 121.9, 49.9, 29.8, 24.6, 19.6; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for C$_{14}$H$_{14}$N$_2$ONa 249.1004, Found 249.1006.

3-(1,3-Diphenyl-allyl)-3H-quinazolin-4-one (6c; Entry 8, Table 7):

White solid (0.120g, 71%); MP 100-101 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.43 - 8.36 (m, 1H), 8.19 (s, 1H), 7.81 - 7.71 (m, 2H), 7.52 (ddd, $J = 8.2$, 5.8, 2.6 Hz, 1H), 7.47 - 7.24 (m, 11H), 6.99 (d, $J = 5.9$ Hz, 1H), 6.76 - 6.58 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 160.7, 147.7, 145.2, 138.2, 135.7, 135.4, 134.4, 129.2, 128.8, 128.5, 127.9, 127.6, 127.4, 127.2, 126.8, 125.8, 122.0, 58.5; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for C$_{23}$H$_{18}$N$_2$ONa 361.1317, Found 361.1318.

(E)-3-(buta-1,3-dien-1-yl)quinazolin-4(3H)-one(6d; Entry 9, Table 7):

White solid (0.081g, 82%); MP 92-93 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.33 (d, $J = 7.8$ Hz, 1H), 8.28 (s, 1H), 7.72-7.80 (m, 2H), 7.53 (t, $J = 7.5$ Hz, 1H), 7.38 (d, $J = 13.2$ Hz, 1H), 6.49-6.57 (m, 2H), 5.45 (d, $J = 15.9$ Hz, 1H), 5.32 (d, $J = 9.4$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 159.6, 147.3, 142.5, 134.6, 133.3, 127.76, 127.14, 125.9, 123.1,121.6, 120.1; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for C$_{12}$H$_{13}$N$_2$O 199.0871, Found 199.0876.
15) Experimental procedure for inter-molecular competition study

Typical procedure for Inter-molecular competition study involving two different tautomerizable heteroarenes:

In a glove box, to an oven dried 4 mL glass vial equipped with a stirring bar, 4-hydroxy quinazoline 1a (0.036 g, 0.25 mmol), 2-hydroxy pyridine 1p (0.024 g, 0.25 mmol, 1 equiv), cinnamyl alcohol 2da (0.034 g, 0.25 mmol, 1 equiv), and Pd(PPh₃)₄ (0.015 g, 0.013 mmol, 5 mol%) followed by DMC (1 mL) was added and the resulted reaction mixture was stirred at 100 °C for 12 h. After stipulated time period, the reaction mixture was then cooled to rt, diluted with MeOH (2 x 5 mL) and passed through bed of celite to remove catalyst. An aliquot portion (100 μL) of the organic layer was taken out, diluted with MeOH and subjected to GCMS to observe the selectivity, which reflected an 82:18 selectivity in favor of 1a.

Typical procedure for Inter-molecular competition study involving two different allyl alcohols

In a glove box, to an oven dried 4 mL glass vial equipped with a stirring bar, 4-hydroxy quinazoline 1a (0.036 g, 0.25 mmol), allyl alcohol 2d (0.029 g, 0.5 mmol, 2 equiv), cinnamyl alcohol 2da (0.067 g, 0.5 mmol, 2 equiv), and Pd(PPh₃)₄ (0.015 g, 0.013 mmol, 5 mol%) followed by DMC (1 mL) was added and the resulting reaction mixture was stirred at 100 °C for 12 h. After stipulated time period, the reaction mixture was cooled to rt, diluted with MeOH (2 x 5 mL) and passed through bed of celite to remove catalyst. An aliquot portion (100 μL) of the organic layer was taken out, diluted with MeOH and subjected to GCMS to observe the selectivity, which reflected a 61:39 selectivity in favor of 2d.
16) References:

6) M. Golfier, R. Milcent, Synthesis, 1979, 946-948