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## Accepted Article

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**To be cited as:** *Adv. Synth. Catal.* 10.1002/adsc.201800660

**Link to VoR:** <http://dx.doi.org/10.1002/adsc.201800660>

DOI: 10.1002/adsc.201((will be filled in by the editorial staff))

# Auto-Tandem Catalysis with Ruthenium: From *o*-Aminobenzamides and Allylic Alcohols to Quinazolinones via Redox Isomerization/Acceptorless Dehydrogenation

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Received: ((will be filled in by the editorial staff))

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/adsc.201#####>.

**Abstract:** A strategy for the synthesis of quinazolinones via Ru-catalyzed redox isomerization/acceptorless dehydrogenation was proposed and accomplished. In the presence of a commercially available [(*p*-cymene)RuCl<sub>2</sub>]<sub>2</sub>, a range of desirable products were obtained with *o*-aminobenzamides and allylic alcohols as starting materials in moderate to high yields. This strategy is attractive due to

high atom efficiency, and minimal consumption of chemicals and energy.

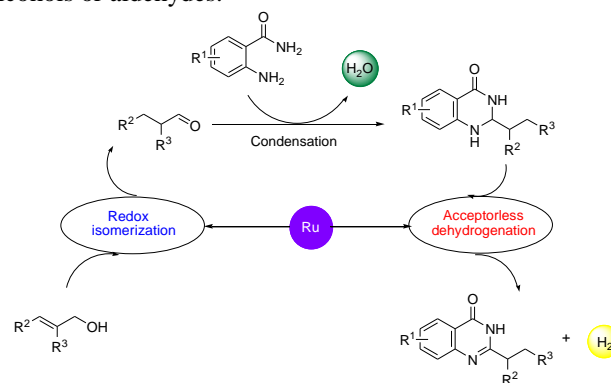
**Keywords:** redox isomerization; acceptorless dehydrogenation; quinazolinones; ruthenium; homogeneous catalysis

## Introduction

Against increasing environmental pollution, the development of catalytic transformations with high atom economy is one of the most urgent and important tasks for modern organic synthesis.<sup>[1]</sup> In recent years, transition metal-catalyzed redox-isomerization of readily available allylic alcohols has become a very useful methodology for the synthesis of carbonyl derivatives including ketones and aldehydes as alternative of traditional procedures, which involve a two-step sequential oxidation and reduction using stoichiometric amounts of reagents.<sup>[2,3]</sup> More recently, much attention has been devoted to the development of transition metal-catalyzed acceptorless dehydrogenative reactions accompanied by the liberation of hydrogen gas without the use of any oxidants, such as acceptorless dehydrogenation of alcohols<sup>[4]</sup> and N-containing heterocycles.<sup>[5,6]</sup> Such methodologies provide the clearest and most atom-economical processes instead of traditional oxidation using various oxidants. Although significant advances have been made in transition metal-catalyzed redox isomerization of allylic alcohols and acceptorless dehydrogenation, the design and development of an auto-tandem catalysis in which one catalyst activates above two mechanistically different reactions in a single reactor remains unexplored and is apparently highly desirable.<sup>[7]</sup>

Recently, we have developed a series of iridium-catalyzed environmentally friendly transformations based on hydrogen autotransfer process<sup>[8]</sup> or acceptorless dehydrogenation.<sup>[9]</sup> As part of our continuing effort in this field, we turned our attention to ruthenium-catalyzed reactions because ruthenium is far more cheap than iridium and its complexes were widely used as transition metal

catalysts. In this paper, we wish to report a strategy of the synthesis of quinazolinones *via* ruthenium-catalyzed auto-tandem redox isomerization/acceptorless dehydrogenation from *o*-aminobenzamides and allylic alcohols (Scheme 1). Such products are important structural units and key synthetic intermediates of many naturally occurring alkaloids<sup>[10]</sup> and other biologically active molecules.<sup>[11]</sup> Although a large number of methods have been developed,<sup>[12]</sup> most classical and versatile routes for the synthesis of quinazolinones rely on the condensation between *o*-aminobenzamides and aldehydes followed by the oxidation of the resulting aminal intermediates in the presence of stoichiometric amounts or a large excess of environmentally harmful oxidants.<sup>[13]</sup> They have been recently synthesized *via* iridium-catalyzed acceptorless dehydrogenative cyclization of *o*-aminobenzamides with alcohols or aldehydes.<sup>[14, 9c-e]</sup>



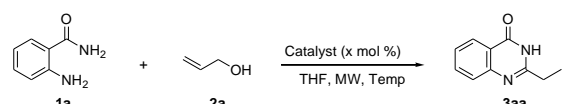
**Scheme 1.** Proposed strategy for the synthesis of quinazolinones through auto-tandem catalysis.

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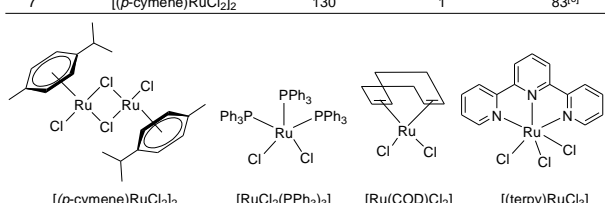
## Results and Discussion

To explore the feasibility of above proposal, the reaction of *o*-aminobenzamide (**1a**) and allylic alcohol (**2a**) was selected as a model (Table 1). In the presence of a commercially available ruthenium complex [(*p*-cymene)RuCl<sub>2</sub>]<sub>2</sub> (1 mol %), the reaction was performed at 130 °C in a focused, single mode microwave synthesizer (Discover CEM, USA, 300 W) to afford the desired product **3aa** in 89% yield (Table 1, entry 1). Using [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] or [Ru(cod)Cl<sub>2</sub>] with a same Ru loading amount as an alternative catalyst, the product **3aa** was obtained in 85% and 76% yields, respectively (Table 1, entries 2-3). However, none of product was detected when [(terpy)RuCl<sub>3</sub>] was examined (Table 1, entry 4). Attempt to decrease the reaction temperature and reduce the amount of catalyst loading resulted in relatively low yields (Table 1, entries 5-6). When the reaction of **1a** and **2a** was carried out under a magnetic stirrer for 12 h and the product **3aa** could be obtained in 83% yield (Table 1, entry 7).

**Table 1.** Reaction of *o*-aminobenzamide (**1a**) with allylic alcohol (**2a**) under various conditions.<sup>[a]</sup>



Entry	Catalyst	Temp [°C]	x	Yield [%] <sup>[b]</sup>
1	[( <i>p</i> -cymene)RuCl <sub>2</sub> ] <sub>2</sub>	130	1	89
2	[RuCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>3</sub> ]	130	2	85
3	[Ru(COD)Cl <sub>2</sub> ]	130	2	76
4	[(terpy)RuCl <sub>3</sub> ]	130	2	n.d.
5	[( <i>p</i> -cymene)RuCl <sub>2</sub> ] <sub>2</sub>	130	0.5	80
6	[( <i>p</i> -cymene)RuCl <sub>2</sub> ] <sub>2</sub>	120	1	81
7	[( <i>p</i> -cymene)RuCl <sub>2</sub> ] <sub>2</sub>	130	1	83 <sup>[c]</sup>



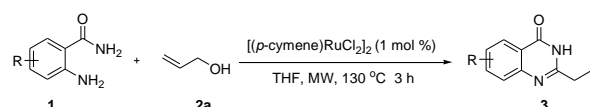
<sup>[a]</sup> Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), catalyst (x mol %), THF (1 mL), MW, 3 h.

<sup>[b]</sup> Isolated yield.

<sup>[c]</sup> Under a magnetic stirrer, 12 h.

Having established the most optimal catalyst and conditions (Table 1, entry 1), the scope of reaction with respect to *o*-aminobenzamides **1** was examined (Table 2). Reactions of *o*-aminobenzamides bearing one or two electron-donating groups, such as methyl, methoxy and dimethoxy, proceeded smoothly to give the desired products **3ba-3ca** in 83%-91% yields (Table 2, entries 1-4). Similarly, a series of *o*-aminobenzamides bearing one or two halogen atoms, such as fluorine, chlorine, dichlorine and bromide, were converted to the corresponding products **3da-3oa** in 82-91% yields (Table 2, entries 5-14). The stronger electron-withdrawing trifluoromethyl group was also tolerated and the desired product **3pa** was obtained in 88% yield (Table 2, entry 15). In the case of *o*-aminobenzamides bearing a substituent on N atom of amido group, the corresponding products **3qa** and **3ra** could be obtained, albeit in moderate yields (Table 2,

**Table 2.** Scope of reaction with respect to *o*-aminobenzamides.<sup>[a]</sup>



Entry	<i>o</i> -Aminobenzamide	Product	Yield [%] <sup>[b]</sup>
1	<b>1b</b>	<b>3ba</b>	89
2	<b>1c</b>	<b>3ca</b>	91
3	<b>1d</b>	<b>3da</b>	83
4	<b>1e</b>	<b>3ea</b>	86
5	<b>1f</b>	<b>3fa</b>	81
6	<b>1g</b>	<b>3ga</b>	89
7	<b>1h</b>	<b>3ha</b>	88
8	<b>1i</b>	<b>3ia</b>	91
9	<b>1j</b>	<b>3ja</b>	88
10	<b>1k</b>	<b>3ka</b>	82
11	<b>1l</b>	<b>3la</b>	90
12	<b>1m</b>	<b>3ma</b>	91
13	<b>1n</b>	<b>3na</b>	88
14	<b>1o</b>	<b>3oa</b>	83
15	<b>1p</b>	<b>3pa</b>	88

**Table 2.** (Continued).

Entry	<i>o</i> -Aminobenzamide	Product	Yield [%] <sup>[b]</sup>
16			78
17			74

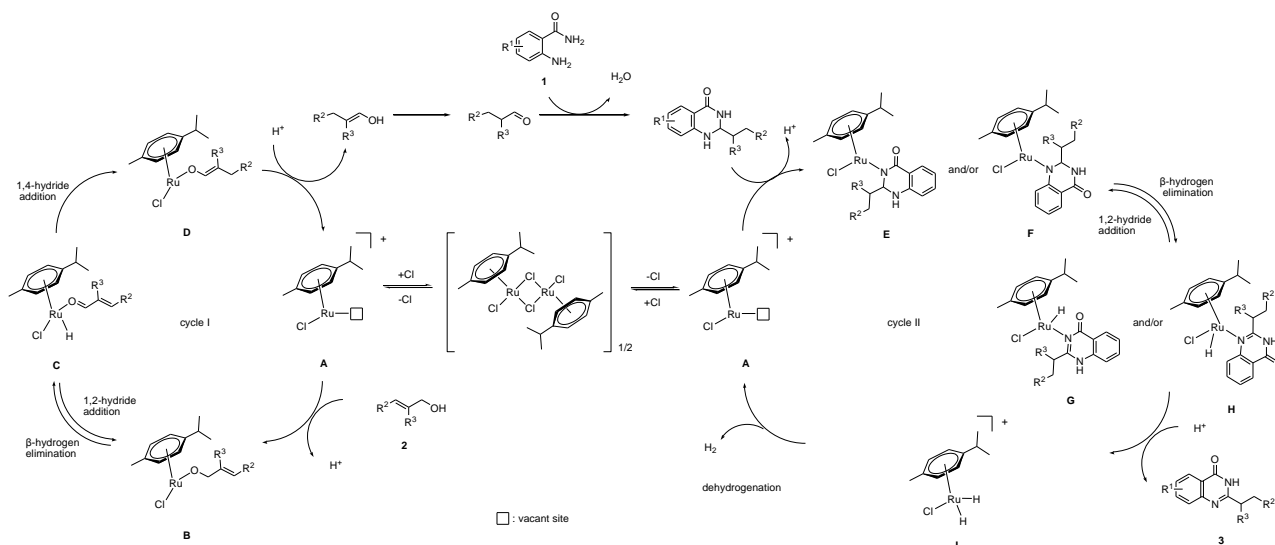
<sup>[a]</sup> Reaction conditions: **1** (0.5 mmol), **2a** (0.6 mmol), [(*p*-cymene)RuCl<sub>2</sub>]<sub>2</sub> (1 mol %), THF (1 mL), MW, 130 °C, 3 h.

<sup>[b]</sup> Isolated yield.

entries 16-17). However, no reaction occurred when *o*-aminobenzamides bearing same substituent groups on N atom of amino group were used as substrates.

The generality of reaction with respect to allylic alcohols **2** was then investigated (Table 3). Linear allylic alcohols, such as (*E*)-but-2-en-1-ol, (*E*)-pent-2-en-1-ol, (*E*)-hex-2-en-1-ol as (*E*)-but-2-en-1-ol, (*E*)-pent-2-en-1-ol, (*E*)-hex-2-en-1-ol and (*E*)-3-phenylprop-2-en-1-ol, were converted to the corresponding products **3ab-3ae** in 84-90% yields (Table 3, entries 1-4). Transformations of allylic alcohols bearing an a branched chain, such as 3-methylbut-2-en-1-ol, and 2-methylprop-2-en-1-ol gave the desired products **3af** and **3ag** in 53% and 91% yields, respectively (Table 3, entries 5-6). Interestingly, one of double bonds remained unreacted when (*E*)-3,7-dimethylocta-2,6-dien-1-ol was served as a substrate and the corresponding product **3ah** was obtained in 67% yield (Table 3, entry 7).

On the basis of experimental results and the previous knowledge, a plausible mechanism was proposed for the present auto-tandem catalysis (Scheme 2). The initial step of cycle I involves the deprotonation of allylic alcohols and the coordination of the resulting  $\alpha,\beta$ -unsaturated alkoxide to cationic unsaturated ruthenium species **A**, which were generated *via* the dissociation of ruthenium dimer and chlorine. Subsequent  $\beta$ -hydrogen elimination of the resulting species **B** gave enone-ruthenium-hydride species **C**, followed by 1,4-hydride addition resulted in the formation of ruthenium-oxo-allyl species **D**. Furthermore,

**Scheme 2.** Proposed reaction mechanism.**Table 3.** Scope of reaction with respect to allylic alcohols.<sup>[a]</sup>

Entry	Allylic Alcohol	Product	Yield [%] <sup>[b]</sup>
1			88
2			89
3			84
4			90
5			53
6			91
7			67

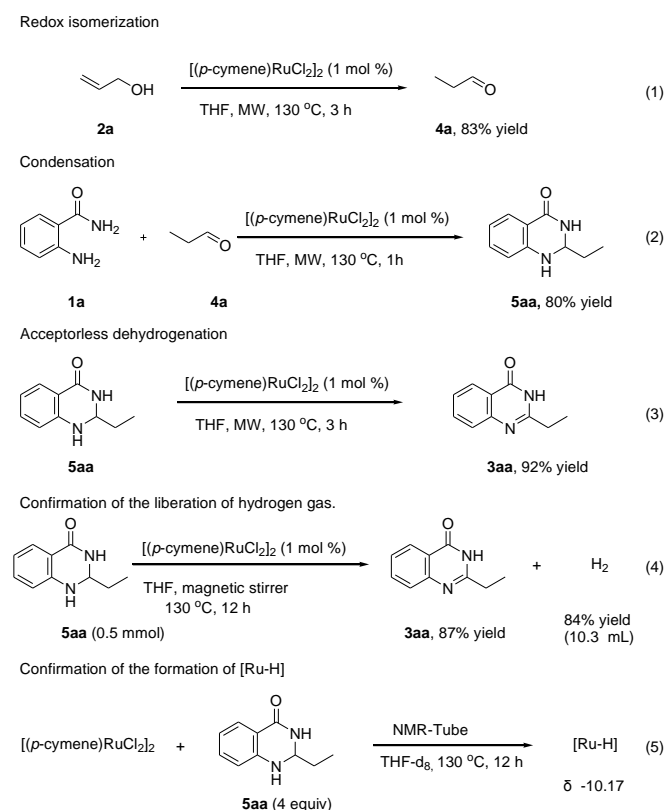
<sup>[a]</sup> Reaction conditions: **1** (0.5 mmol), **2a** (0.6 mmol), [(*p*-cymene)RuCl<sub>2</sub>]<sub>2</sub> (1 mol %), THF (1 mL), MW, 130 °C, 3 h.

<sup>[b]</sup> Isolated yield.

the protonation promoted the regeneration of catalytic species **A** and the liberation of enol intermediates, which were then converted to aldehydes. The condensation between the resulting aldehydes and *o*-aminobenzamides occurred to afford 2,3-dihydroquinazolinones. In cycle II, the

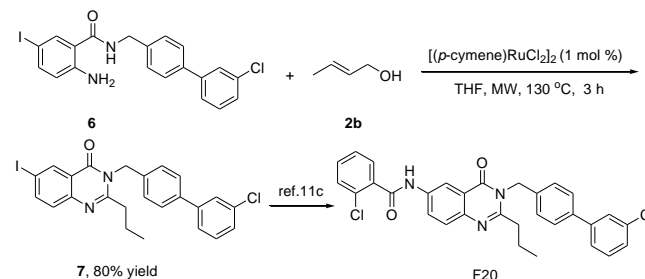
deprotonation of 2,3-dihydroquinazolinones and the coordination to cationic unsaturated ruthenium species **A**, occurred to give ruthenium species **E** and **F**. Subsequently,  $\beta$ -hydrogen elimination of the resulting ruthenium species **E** and **F** afford the ruthenium species **G** and **H**, which underwent the protonation and it resulted in the the generation of ruthenium species **I** and the liberation of quinazolinones as desirable products. Finally, catalytically active species **A** were regenerated through the liberation of hydrogen gas from ruthenium species **I**.

To support the proposed mechanism, a series of mechanistic experiments were undertaken (Scheme 3). In the presence of  $[(p\text{-cymene})\text{RuCl}_2]_2$  (1 mol %), the redox isomerization of **1a** was carried out for 3 h at 130 °C under microwave irradiation to afford propionaldehyde (**4a**) in 83% yield (Eq. 1). The condensation between **4a** and **2a** proceeded for 1 h to afford 2-ethyl-2,3-dihydroquinazolin-4(1H)-one (**5aa**) in 80% yield (Eq. 2). Furthermore, ruthenium-catalyzed acceptorless dehydrogenation of **5aa** was performed for 3 h to give the desired product **3aa** in 92% yield (Eq. 3). Same reaction was carried out for 12 h under magnetic stirrer, 12 h to give the product **3aa** in 87% yield accompanied by the generation of 10.3 mL of gas by water displacement. The collected gas was confirmed to be hydrogen gas by GC analysis and the yield of gas is calculated to be 84% (Eq. 4). In addition, a peak ( $\delta$  -10.17) was observed from  $^1\text{H}$  NMR spectrum of the substoichiometric reaction of  $[(p\text{-cymene})\text{RuCl}_2]_2$  with **5aa** (4 equiv) in  $\text{THF-d}_8$  at 130 °C for 10 min (Eq. 5). It was speculated to be a characteristic signal of  $[\text{Ru-H}]$ . Obviously, these experimental results supported the proposed mechanism shown in Scheme 2.



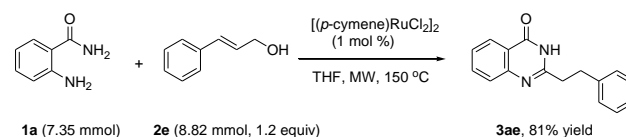
Scheme 3. Mechanistic experiments.

The present catalytic system was also applied to the synthesis of a key intermediate of a biologically active molecule FR20 (Inhibitors of human microsomal prostaglandin synthase 1) (Scheme 4). Under established conditions (Table 1, entry 1), the reaction of **6** with **2b** was carried out for 3 h to give the product **7** in 80% yield, which could be further converted to FR20 through Cu-catalyzed Ullmann cross-coupling according to a previous report.<sup>[11c]</sup>



Scheme 4. Application of synthetic strategy.

To demonstrate the practical potential of this methodology, a representative transformation on a preparative scale was undertaken. In the presence of  $[(p\text{-cymene})\text{RuCl}_2]_2$  (1 mol %), the reaction of **1a** (7.35 mmol) and **2e** (8.82 mmol, 1.2 equiv) was carried out under microwave irradiation at 150 °C for 3 h to give the corresponding product **3ae** in 81% yields (Scheme 5).



Scheme 5. Representative transformation on a preparative scale.

## Conclusion

We have demonstrated an approach for the direct synthesis of quinazolinones *via* ruthenium-catalyzed redox isomerization/acceptorless dehydrogenation. In the presence of a commercially available  $[(p\text{-cymene})\text{RuCl}_2]_2$  (1 mol %), a variety of *o*-aminobenzamides and allylic alcohols were converted to desirable products in 53%-91% yields. This strategy is attractive due to the readily available starting materials, high atom efficiency, and minimal consumption of chemicals and energy. Furthermore, a plausible mechanism was proposed and supported by a series of mechanistic experiments. The catalytic system was also applied to the synthesis of a key intermediate of a biologically active molecule. Notably, this research would facilitate the progress of auto-tandem catalysis.

## Experimental Section

**Experimental Details.** Melting points were measured on a micromelting apparatus. High-resolution mass spectra (HRMS) were obtained on a HPLC-Q-ToF MS(Micro) spectrometer and are reported as  $m/z$  (relative intensity). Accurate masses are reported for the molecular ion  $[\text{M}+\text{H}]^+$ . Proton nuclear magnetic resonance

(<sup>1</sup>H NMR) spectra were recorded at 500 MHz using a 500 spectrometer. Chemical shifts are reported in delta (δ) units, parts per million (ppm) downfield from tetramethylsilane or ppm relative to the center of the singlet at 7.26 ppm for CDCl<sub>3</sub> and 2.50 ppm for DMSO-d<sub>6</sub>. Coupling constants *J* values are reported in Hertz (Hz), and the splitting patterns were designated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; b, broad. Carbon-13 nuclear magnetic resonance (<sup>13</sup>C NMR) spectra were recorded at 125 MHz using a 500 spectrometer. Chemical shifts are reported in delta (δ) units, ppm relative to the center of the triplet at 77.0 ppm for CDCl<sub>3</sub> and 39.5 ppm for DMSO-d<sub>6</sub>. <sup>13</sup>C NMR spectra were routinely run with broadband decoupling.

**General procedure for catalytic redox isomerization/acceptorless dehydrogenation for the synthesis of quinazolinones from *o*-aminobenzamides and allylic alcohols.** *o*-Aminobenzamides (0.5 mmol), allylic alcohols (0.6 mmol, 1.2 equiv), [(*p*-cymene)RuCl<sub>2</sub>]<sub>2</sub> (3.1 mg, 0.005 mmol, 1 mol %) and THF (1 mL) were added to a microwave vial containing a stirrer bar. The vial was then placed in a focused, single-mode microwave synthesizer (Discover CEM, USA) at 130 °C for 3 h (300 W, sealed reaction vessel), and was then cooled to ambient temperature. The reaction mixture was concentrated under vacuum and purified by flash column chromatography with hexanes/ethyl acetate to afford the corresponding products.

**2-Ethylquinazolin-4(3H)-one (3aa).**<sup>[12c]</sup> White solid, 89% yield (77 mg); mp 230-232 °C; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>) δ 12.17 (br s, 1H), 8.07 (d, *J* = 7.8 Hz, 1H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 2.64-2.60 (q, *J* = 7.5 Hz, 2H), 1.26-1.23 (t, *J* = 7.5 Hz, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, DMSO-d<sub>6</sub>) δ 161.9, 158.4, 148.8, 134.2, 126.7, 125.9, 125.7, 120.8, 27.9, 11.3.

**2-Ethyl-6-methylquinazolin-4(3H)-one (3ba).**<sup>[15]</sup> White solid, 89% yield (84 mg); mp 224-226 °C; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>) δ 12.06 (br s, 1H), 7.85 (s, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 2.62-2.55 (q, *J* = 7.5 Hz, 2H), 2.39 (s, 3H), 1.25-1.22 (t, *J* = 7.5 Hz, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, DMSO-d<sub>6</sub>) δ 161.9, 157.5, 147.0, 135.6, 135.6, 126.7, 125.2, 120.6, 27.9, 20.8, 11.4.

**2-Ethyl-7-methylquinazolin-4(3H)-one (3ca).** White solid, 91% yield (86 mg); mp 219-221 °C; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>) δ 12.08 (br s, 1H), 7.87 (s, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.35 (d, *J* = 3.0 Hz, 1H), 3.85 (s, 3H), 2.62-2.57 (q, *J* = 7.5 Hz, 2H), 1.24-1.20 (t, *J* = 7.5 Hz, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, DMSO-d<sub>6</sub>) δ 161.8, 157.5, 146.8, 135.5, 135.5, 126.6, 125.0, 120.6, 55.5, 27.6, 11.3; HRMS (ESI) *m/z* calcd for C<sub>11</sub>H<sub>13</sub>N<sub>2</sub>O [M+H]<sup>+</sup> 189.10224, found 189.10207.

**2-Ethyl-6-methoxyquinazolin-4(3H)-one (3da).**<sup>[16]</sup> Light yellow solid, 83% yield (85 mg); mp 241-243 °C; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>) δ 12.10 (br s, 1H), 7.54 (d, *J* = 8.9 Hz, 1H), 7.46 (d, *J* = 3.1 Hz, 2H), 7.47 (d, *J* = 8.3 Hz, 2H), 2.63-2.58 (q, *J* = 7.5 Hz, 2H), 2.42 (s, 3H), 1.24-1.20 (t, *J* = 7.5 Hz, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, DMSO-d<sub>6</sub>) δ 161.7, 157.1, 155.9, 143.4, 128.3, 123.5, 121.5, 105.8, 27.8, 20.8, 11.3.

**2-Ethyl-6,7-dimethoxyquinazolin-4(3H)-one (3ea).** White solid, 86% yield (101 mg); mp 232-234 °C; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>) δ 12.02 (br s, 1H), 7.40 (s, 1H), 7.07 (s, 1H), 3.89 (s, 1H), 3.85 (s, 3H), 2.61-2.56 (q, *J* = 7.5 Hz, 2H), 1.29-1.20 (t, *J* = 7.5 Hz, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, DMSO-d<sub>6</sub>) δ 161.2, 156.7, 154.5, 148.0, 145.0, 113.6, 107.7, 104.9, 55.9, 55.6, 27.6, 11.3; HRMS (ESI) *m/z* calcd for C<sub>12</sub>H<sub>15</sub>N<sub>2</sub>O<sub>3</sub> [M+H]<sup>+</sup> 235.10772, found 235.10764.

**2-Ethyl-5-fluoroquinazolin-4(3H)-one (3fa).** White solid, 81% yield (78 mg); mp 208-210 °C; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>) δ 12.20 (br s, 1H), 7.72 (m, 1H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.17 (d, *J* = 8.4 Hz, 1H), 2.62-2.56 (q, *J* = 7.5 Hz, 2H), 1.24-1.21 (t, *J* = 7.5 Hz, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, DMSO-d<sub>6</sub>) δ 160.4 (d, *J*<sub>C-F</sub> = 312.1 Hz), 159.5, 151.2, 134.7 (d, *J*<sub>C-F</sub> = 10.5 Hz), 122.9, 112.3, 112.1, 110.3, 104.9, 55.9, 55.6, 27.7, 11.1; HRMS (ESI) *m/z* calcd for C<sub>10</sub>H<sub>10</sub>FN<sub>2</sub>O [M+H]<sup>+</sup> 193.07717, found 193.07716.

**2-Ethyl-6-fluoroquinazolin-4(3H)-one (3ga).**<sup>[17]</sup> White solid, 89% yield (86 mg); mp 227-229 °C; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>) δ 12.30 (br s, 1H), 7.73 (d, *J* = 8.9 Hz, 1H), 7.65 (m, 2H), 2.64-2.55 (q, *J* = 7.5 Hz, 2H), 1.25-1.21 (t, *J* = 7.5 Hz, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, DMSO-d<sub>6</sub>) δ 161.2, 159.6 (d, *J*<sub>C-F</sub> = 244.5 Hz), 157.7, 145.8, 129.5 (d, *J*<sub>C-F</sub> = 8.2 Hz), 122.6 (d, *J*<sub>C-F</sub> = 24.4 Hz), 121.9 (d, *J*<sub>C-F</sub> = 8.7 Hz), 110.2 (d, *J*<sub>C-F</sub> = 22.8 Hz), 27.7, 11.2.

**2-Ethyl-7-fluoroquinazolin-4(3H)-one (3ha).** White solid, 88% yield (85 mg); mp 229-231 °C; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>) δ 12.26 (br s, 1H), 8.12 (t, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 10.3 Hz, 1H), 7.30 (d, *J* = 8.7 Hz, 1H), 2.65-2.59 (q, *J* = 7.5 Hz, 2H), 1.25-1.22 (t, *J* = 7.5 Hz, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, DMSO-d<sub>6</sub>) δ 165.6 (d, *J*<sub>C-F</sub> = 250.8 Hz), 161.0, 159.9, 151.1 (d, *J*<sub>C-F</sub> = 13.5 Hz), 128.7 (d, *J*<sub>C-F</sub> = 10.9 Hz), 117.8, 114.3 (d, *J*<sub>C-F</sub> = 23.5 Hz), 111.8 (d, *J*<sub>C-F</sub> = 21.3 Hz), 27.8, 11.1; HRMS (ESI) *m/z* calcd for C<sub>10</sub>H<sub>10</sub>FN<sub>2</sub>O [M+H]<sup>+</sup> 193.07717, found 193.07698.

**6-Chloro-2-ethylquinazolin-4(3H)-one (3ia).**<sup>[17]</sup> White solid, 91% yield (95 mg); mp 218-220 °C; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>) δ 8.00 (s, 1H), 7.76 (d, *J* = 8.7 Hz, 1H), 7.60 (d, *J* = 8.8 Hz, 1H), 2.64-2.60 (q, *J* = 7.5 Hz, 2H), 1.25-1.21 (t, *J* = 7.5 Hz, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, DMSO-d<sub>6</sub>) δ 160.8, 158.9, 147.6, 134.2, 130.1, 129.0, 124.6, 122.1, 27.8, 11.1.

**7-Chloro-2-ethylquinazolin-4(3H)-one (3ja).**<sup>[17]</sup> White solid, 88% yield (92 mg); mp 205-207 °C; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>) δ 12.31 (br s, 1H), 8.06 (d, *J* = 8.5 Hz, 1H), 7.65 (d, *J* = 1.9 Hz, 1H), 7.48 (d, *J* = 1.8 Hz, 1H), 2.64-2.59 (q, *J* = 7.5 Hz, 2H), 1.25-1.20 (t, *J* = 7.5 Hz, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, DMSO-d<sub>6</sub>) δ 161.2, 160.0, 150.0, 138.8, 127.7, 126.1, 125.9, 119.6, 27.9, 11.1.

**8-Chloro-2-ethylquinazolin-4(3H)-one (3ka).**<sup>[17]</sup> White solid, 82% yield (86 mg); mp 223-225 °C; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>) δ 12.40 (br s, 1H), 8.03 (d, *J* = 7.5 Hz, 1H), 7.91 (d, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 2.68-2.63 (q, *J* = 7.3 Hz, 2H), 1.28-1.25 (t, *J* = 7.5 Hz, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, DMSO-d<sub>6</sub>) δ 161.3, 159.4, 145.3, 134.4, 130.4, 126.2, 124.9, 122.6, 28.1, 11.2.

**6,8-Dichloro-2-ethylquinazolin-4(3H)-one (3la).** White solid, 90% yield (109 mg); mp 228-230 °C; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>) δ 12.56 (br s, 1H), 8.06 (d, *J* = 2.5 Hz, 1H), 7.97 (d, *J* = 2.5 Hz, 1H), 2.67-2.62 (q, *J* = 7.6 Hz, 2H), 1.27-1.24 (t, *J* = 7.6 Hz, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, DMSO-d<sub>6</sub>) δ 160.3, 159.8, 144.2, 133.7, 131.8, 129.6, 123.9, 123.1, 28.0, 11.0; HRMS (ESI) *m/z* calcd for C<sub>10</sub>H<sub>9</sub>Cl<sub>2</sub>N<sub>2</sub>O [M+H]<sup>+</sup> 243.00864, found 243.00854.

**5-Bromo-2-ethylquinazolin-4(3H)-one (3ma).** White solid, 91% yield (115 mg); mp 218-219 °C; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>) δ 12.22 (br s, 1H), 7.65 (m, 1H), 7.57 (m, 2H), 2.61-2.56 (q, *J* = 7.5 Hz, 2H), 1.24-1.20 (t, *J* = 7.5 Hz, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, DMSO-d<sub>6</sub>) δ 160.0, 158.9, 151.3, 134.2, 132.0, 27.0, 119.9, 118.6, 27.5, 11.0; HRMS (ESI) *m/z* calcd for C<sub>10</sub>H<sub>10</sub>BrN<sub>2</sub>O [M+H]<sup>+</sup> 252.99710, found 252.99718.

**6-Bromo-2-ethylquinazolin-4(3H)-one (3na).**<sup>[18]</sup> White solid, 88% yield (111 mg); mp 227-229 °C; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>) δ 12.34 (br s, 1H), 8.14 (d, *J* = 2.1 Hz, 1H), 7.90 (dd, *J* = 8.6 Hz and 2.4 Hz, 2H), 7.54 (d, *J* = 8.9 Hz, 1H), 2.64-2.59 (q, *J* = 7.5 Hz, 2H), 1.25-1.22 (t, *J* = 7.5 Hz, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, DMSO-d<sub>6</sub>) δ 160.7, 159.1, 147.8, 137.0, 129.1, 127.8, 122.4, 118.2, 27.8, 11.1.

**7-Bromo-2-ethylquinazolin-4(3H)-one (3oa).**<sup>[19]</sup> White solid, 83% yield (105 mg); mp 212-214 °C; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>) δ 12.31 (br s, 1H), 7.97 (d, *J* = 8.5 Hz, 1H), 7.80 (s, 1H), 7.61 (d, *J* = 8.5 Hz, 1H), 2.64-2.59 (q, *J* = 7.5 Hz, 2H), 1.25-1.21 (t, *J* = 7.5 Hz, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, DMSO-d<sub>6</sub>) δ 161.3, 160.0, 150.0, 128.9, 128.9, 127.7, 119.9, 27.9, 11.1.

**2-Bthyl-7-(trifluoromethyl)quinazolin-4(3H)-one (3pa).** White solid, 88% yield (106 mg); mp 183-185 °C; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>) δ 12.47 (br s, 1H), 8.27 (d, *J* = 8.4 Hz, 1H), 7.91 (s, 1H), 7.75 (d, *J* = 8.3 Hz, 1H), 2.68-2.63 (q, *J* = 7.5 Hz, 2H), 1.27-1.24 (t, *J* = 7.5 Hz, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, DMSO-d<sub>6</sub>) δ 161.1, 160.3, 148.9, 134.0 (q, *J* = 32.0 Hz), 127.5, 123.6 (q, *J* =

273.1 Hz), 123.8, 123.7, 121.6, 27.9, 11.1; HRMS (ESI) *m/z* calcd for C<sub>11</sub>H<sub>10</sub>F<sub>3</sub>N<sub>2</sub>O [M+H]<sup>+</sup> 243.07397, found 243.07390.

**3-Benzyl-2-ethylquinazolin-4(3H)-one (3qa).**<sup>[20]</sup> White solid, 78% yield (103 mg); mp 122-124 °C; <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 8.15 (d, *J* = 8.1 Hz, 1H), 7.81 (t, *J* = 7.7 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.25 (d, *J* = 7.4 Hz, 1H), 7.16 (d, *J* = 7.4 Hz, 1H), 5.40 (s, 2H), 2.79-2.74 (q, *J* = 7.3 Hz, 2H), 1.20-1.17 (t, *J* = 7.4 Hz, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, DMSO-*d*<sub>6</sub>) δ 161.6, 158.1, 146.9, 136.7, 134.5, 128.8, 127.2, 126.9, 126.5, 126.4, 126.1, 119.8, 45.5, 27.3, 10.7.

**3-Butyl-2-ethylquinazolin-4(3H)-one (3ra).**<sup>[21]</sup> White solid, 74% yield (85 mg); mp 110-111 °C; <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 8.09 (d, *J* = 7.8 Hz, 1H), 7.77 (t, *J* = 7.7 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 4.05-4.01 (t, *J* = 7.8 Hz, 2H), 2.95-2.88 (q, *J* = 7.2 Hz, 2H), 1.41-1.33 (q, *J* = 7.5 Hz, 2H), 1.31-1.28 (t, *J* = 7.3 Hz, 2H), 0.95-0.91 (t, *J* = 7.3 Hz, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, DMSO-*d*<sub>6</sub>) δ 161.0, 157.6, 146.9, 133.9, 126.7, 126.0, 126.0, 119.9, 42.6, 39.5, 30.1, 27.0, 19.7, 13.5, 10.8.

**2-Propylquinazolin-4(3H)-one (3ab).**<sup>[12c]</sup> White solid, 88% yield (83 mg); mp 206-207 °C; <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 12.15 (br s, 1H), 8.07 (d, *J* = 7.8 Hz, 1H), 7.75 (t, *J* = 7.5 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 1H), 2.59-2.56 (t, *J* = 7.5 Hz, 1H), 1.78-1.70 (q, *J* = 7.5 Hz, 2H), 0.95-0.92 (t, *J* = 7.4 Hz, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, DMSO-*d*<sub>6</sub>) δ 161.8, 157.4, 148.8, 134.2, 126.7, 125.9, 125.7, 120.8, 36.3, 20.2, 13.5.

**2-Butylquinazolin-4(3H)-one (3ac).**<sup>[22]</sup> White solid, 89% yield (90 mg); mp 108-110 °C; <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 12.15 (br s, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 2.61-2.58 (t, *J* = 7.6 Hz, 1H), 1.73-1.67 (m, 2H), 1.38-1.31 (m, 2H), 0.92-0.89 (t, *J* = 7.4 Hz, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, DMSO-*d*<sub>6</sub>) δ 161.9, 157.5, 148.9, 134.1, 126.7, 125.8, 125.7, 120.8, 34.2, 28.9, 21.7, 13.6.

**2-Pentylquinazolin-4(3H)-one (3ad).**<sup>[23]</sup> White solid, 84% yield (91 mg); mp 153-154 °C; <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 12.15 (br s, 1H), 8.06 (d, *J* = 7.9 Hz, 1H), 7.75 (t, *J* = 7.7 Hz, 1H), 7.58 (d, *J* = 8.1 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 2.60-2.57 (t, *J* = 7.6 Hz, 1H), 1.75-1.69 (m, 2H), 1.34-1.29 (m, 4H), 0.88-0.85 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, DMSO-*d*<sub>6</sub>) δ 161.9, 157.5, 148.9, 134.1, 126.7, 125.8, 125.6, 120.8, 34.5, 30.7, 26.5, 21.8, 13.8.

**2-Phenethylquinazolin-4(3H)-one (3ae).**<sup>[12c]</sup> White solid, 90% yield (113 mg); mp 209-210 °C; <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 12.21 (br s, 1H), 8.07 (d, *J* = 7.8 Hz, 1H), 7.76 (t, *J* = 7.5 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.28 (m, 4H), 7.19 (m, 1H), 3.07-2.04 (t, *J* = 7.9 Hz, 1H), 2.91-2.87 (t, *J* = 7.9 Hz, 2H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, DMSO-*d*<sub>6</sub>) δ 161.8, 156.6, 140.8, 134.3, 128.3, 126.8, 126.1, 126.0, 125.7, 120.9, 36.3, 32.5.

**2-Isobutylquinazolin-4(3H)-one (3af).**<sup>[12c]</sup> White solid, 53% yield (54 mg); mp 194-196 °C; <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 12.15 (br s, 1H), 8.07 (d, *J* = 7.6 Hz, 1H), 7.76 (t, *J* = 7.5 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 2.47 (d, *J* = 7.3 Hz, 2H), 2.18 (m, 1H), 0.92 (d, *J* = 6.9 Hz, 6H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, DMSO-*d*<sub>6</sub>) δ 161.8, 156.7, 148.9, 134.2, 126.8, 125.9, 125.6, 120.7, 43.3, 27.0, 22.1.

**2-Isopropylquinazolin-4(3H)-one (3ag).**<sup>[12c]</sup> White solid, 91% yield (86 mg); mp 234-236 °C; <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 12.11 (br s, 1H), 8.07 (d, *J* = 7.9 Hz, 1H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 1H), 2.93-2.84 (m, 1H), 1.27-1.25 (d, *J* = 7.0 Hz, 2H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, DMSO-*d*<sub>6</sub>) δ 162.0, 161.6, 148.7, 134.2, 126.8, 125.9, 125.7, 120.9, 33.3, 20.3.

**2-(2,6-Dimethylhept-5-enyl)quinazolin-4(3H)-one (3ah).** White solid, 67% yield (91 mg); mp 124-125 °C; <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 12.17 (br s, 1H), 8.07 (d, *J* = 7.8 Hz, 1H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 1H),

5.07 (t, *J* = 6.8 Hz, 1H), 2.58 (dd, *J* = 6.5 Hz and 6.1 Hz, 1H), 2.38 (dd, *J* = 8.3 Hz and 8.1 Hz, 1H), 2.09-1.93 (m, 3H), 1.62 (s, 3H), 1.54 (s, 3H), 1.38-1.32 (m, 2H), 1.24-1.19 (m, 2H), 0.90-0.88 (d, *J* = 6.48 Hz, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, DMSO-*d*<sub>6</sub>) δ 161.8, 156.8, 148.9, 134.2, 130.6, 126.8, 125.9, 125.7, 124.4, 120.7, 41.8, 36.3, 31.3, 25.5, 24.9, 19.1, 17.5; HRMS (ESI) *m/z* calcd for C<sub>17</sub>H<sub>23</sub>N<sub>2</sub>O [M+H]<sup>+</sup> 271.18049, found 271.18011.

**Procedure for redox isomerization of allylic alcohol.** Allylic alcohol (**2a**) (29 mg, 0.5 mmol), [(*p*-cymene)RuCl<sub>2</sub>]<sub>2</sub> (3.1 mg, 0.005 mmol, 1 mol %) and THF (1 mL) were added to a microwave vial containing a stirrer bar. The vial was then placed in a focused, single-mode microwave synthesizer (Discover CEM, USA) at 130 °C for 3 h (300 W, sealed reaction vessel), and was then cooled to ambient temperature. The reaction mixture was concentrated under vacuum and the NMR yield was determined to be 83 % on the basis of the <sup>1</sup>H NMR spectrum of the crude reaction mixture.

**Propionaldehyde (4a).**<sup>[24]</sup> Yellow liquid, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.75 (s, 1H), 2.45-2.40 (m, *J* = 7.3 Hz, 2H), 1.08-1.05 (t, *J* = 7.4 Hz, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) δ 203.1, 37.3, 6.1.

**Procedure for the condensation between 4a and 2a:** *o*-Aminobenzamide (**1a**) (68 mg, 0.5 mmol), propionaldehyde (**4a**) (35 mg, 0.6 mmol, 1.2 equiv) and THF (1 mL) were added to a microwave vial containing a stirrer bar. The vial was then placed in a focused, single-mode microwave synthesizer (Discover CEM, USA) at 130 °C for 1 h (300 W, sealed reaction vessel), and was then cooled to ambient temperature. The reaction mixture was concentrated under vacuum and purified by flash column chromatography with hexanes/ethyl acetate to afford the corresponding product **5aa**.

**2-Ethyl-2,3-dihydroquinazolin-4(1H)-one (5aa).**<sup>[25]</sup> White solid, 80% yield (70 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.87 (d, *J* = 7.8 Hz, 1H), 7.29 (t, *J* = 7.7 Hz, 1H), 6.98 (s, NH, 1H), 6.84 (d, *J* = 7.5 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 4.83-4.81 (t, *J* = 5.6 Hz, 1H), 4.35 (s, NH, 1H), 1.83-1.77 (m, 2H), 1.05-1.01 (t, *J* = 7.5 Hz, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) δ 165.7, 147.6, 133.9, 128.6, 119.3, 116.0, 114.8, 66.5, 28.6, 8.4.

**Procedure for acceptorless dehydrogenation of 4aa.** **4aa** (88 mg, 0.5 mmol), [(*p*-cymene)RuCl<sub>2</sub>]<sub>2</sub> (3.1 mg, 0.005 mmol, 1 mol %) and THF (1 mL) were added to a microwave vial containing a stirrer bar. The vial was then placed in a focused, single-mode microwave synthesizer (Discover CEM, USA) at 130 °C for 3 h (300 W, sealed reaction vessel), and was then cooled to ambient temperature. The reaction mixture was concentrated under vacuum and purified by flash column chromatography with hexanes/ethyl acetate to afford the corresponding product **3aa** in 92% yield (80 mg).

**Procedure for the hydrogen evolution experiment.** **5aa** (88 mg, 0.5 mmol), [(*p*-cymene)RuCl<sub>2</sub>]<sub>2</sub> (3.1 mg, 0.005 mmol, 1 mol %) and THF (1 mL) were added into a 5 mL thick walled glass vessel fitted with a side arm and a rubber septum through a valve. The vessel was previously degassed three times. The vessel was connected to the gas collection apparatus (standard water displacement apparatus, using a graduated cylinder to determine volume) through a valve. The valve was closed and the reaction mixture was stirred vigorously at 130 °C for 12 h under sealed conditions. When reaction mixture was cooled to room temperature and the valve was turned on and the gas was collected by water displacement until gas evolution ceased.

The GC analysis was performed on a gas chromatograph with TCD detector. Injector temperature = 150 °C, column temperature = 80 °C, detector temperature (TCD) = 80 °C, carrier gas = N<sub>2</sub>, column flow = 20 mL/min, *t* = 0.42 min.

The volume of 1 mol of H<sub>2</sub> at 298.15 K, 100700 Pa was calculated according to the van der Waals equation as shown below

$$\left(p + \frac{n^2 a}{V^2}\right)(V-nb) = nRT$$

where  $R = 8.3145 \text{ m}^3 \text{ Pa} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ;  $T = 298.15 \text{ K}$ ;  $p = 100700 \text{ Pa}$ ;  $a = 0.002476 \text{ m}^6 \text{ Pa} \cdot \text{mol}^{-1}$ ;  $b = 0.02661 \times 10^{-3} \text{ m}^3 \cdot \text{mol}^{-1}$ ; thus,  $V (\text{H}_2, 298.15 \text{ K}, 100700 \text{ Pa}) = 24.6 \text{ L} \cdot \text{mol}^{-1}$ .

The collected volume of gas in this experiment above was 10.3 mL, which corresponds to 0.84 mmol of  $\text{H}_2$ .

**Confirmation of the formation of [Ru-H].** A *J*-Young NMR tube was charged with [(*p*-cymene)RuCl<sub>2</sub>]<sub>2</sub> (3.1 mg, 0.005 mmol), **5aa** (3.5 mg, 0.02 mmol, 4 equiv) and THF-*d*<sub>8</sub> (1 mL), and was then heated in oil bath at 130 °C for 10 min. The NMR tube was cooled and was put into the NMR probe. <sup>1</sup>H NMR (500 MHz, THF-*d*<sub>8</sub>)  $\delta$  -10.17.

**Procedure for the synthesis of 7: 6** (93 mg, 0.2 mmol), (*E*)-but-2-en-1-ol (17 mg, 0.24 mmol, 1.2 equiv), [(*p*-cymene)RuCl<sub>2</sub>]<sub>2</sub> (2.4 mg, 0.004 mmol, 1 mol %) and THF (1 mL) were added to a microwave vial containing a stirrer bar. The vial was then placed in a focused, single-mode microwave synthesizer (Discover CEM, USA) at 130 °C for 3 h (300 W, sealed reaction vessel), and was then cooled to ambient temperature. The reaction mixture was concentrated under vacuum and purified by flash column chromatography with hexanes/ethyl acetate to afford the corresponding product **7**.

Pale yellow oil, 80% yield (82 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.64 (d,  $J = 1.9 \text{ Hz}$ , 1H), 7.98 (dd,  $J = 8.7 \text{ Hz}$  and  $J = 2.0 \text{ Hz}$ , 1H), 7.51-7.49 (m, 3H), 7.42-7.39 (m, 2H), 7.35-7.28 (m, 2H), 7.23 (d,  $J = 8.1 \text{ Hz}$ , 2H), 5.42 (s, 2H), 2.74-2.70 (t,  $J = 7.6 \text{ Hz}$ , 2H), 1.86-1.78 (sext,  $J = 7.3 \text{ Hz}$ , 2H), 1.01-0.98 (t,  $J = 7.4 \text{ Hz}$ , 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  161.1, 157.6, 146.6, 143.0, 142.2, 139.3, 135.8, 135.6, 134.6, 130.0, 128.9, 127.6, 127.4, 127.1, 126.9, 125.1, 122.0, 90.6, 46.3, 37.0, 20.4, 13.8.

**Procedure for representative transformation of 1a and 2e on a preparative scale was undertaken.** *o*-Aminobenzamide **1a** (1.0 g, 7.35 mmol), (*E*)-3-phenylprop-2-en-1-ol **2e** (1.18 g, 8.82 mmol, 1.2 equiv), [(*p*-cymene)RuCl<sub>2</sub>]<sub>2</sub> (45 mg, 0.0735 mmol, 1 mol %) and THF (5 mL) were added to a microwave vial containing a stirrer bar. The vial was then placed in a focused, single-mode microwave synthesizer (Discover CEM, USA) at 150 °C for 3 h (300 W, sealed reaction vessel), and was then cooled to ambient temperature. The reaction mixture was concentrated under vacuum and purified by flash column chromatography with hexanes/ethyl acetate to afford the corresponding products.

2-phenethylquinazolin-4(3*H*)-one (**3ae**).<sup>[12c]</sup> White solid, 81% yield (1.48 g); mp 209-210 °C; <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  12.25 (br s, 1H), 8.09 (d,  $J = 7.9 \text{ Hz}$ , 1H), 7.78 (t,  $J = 7.7 \text{ Hz}$ , 1H), 7.62 (d,  $J = 8.0 \text{ Hz}$ , 1H), 7.47 (t,  $J = 7.6 \text{ Hz}$ , 1H), 7.31-7.27 (m, 4H), 7.22-7.17 (m, 1H), 3.06 (t,  $J = 8.0 \text{ Hz}$ , 2H), 2.90 (t,  $J = 8.0 \text{ Hz}$ , 2H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  161.7, 156.5, 148.8, 140.7, 134.2, 128.3, 126.8, 126.0, 126.0, 125.7, 120.8, 36.3, 32.4.

## Acknowledgements

Financial support by National Natural Science Foundation of China (21272115), Natural Science Foundation of Jiangsu Province (BK20161494) and the State Key Laboratory of Fine Chemicals (KF1704) is greatly appreciated.

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