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# Ruthenium- and Rhodium-Catalyzed Dehydrogenative *ortho*-Alkenylation of Benzylamines *via* Free Amino Group Directed C–H Bond Cleavage

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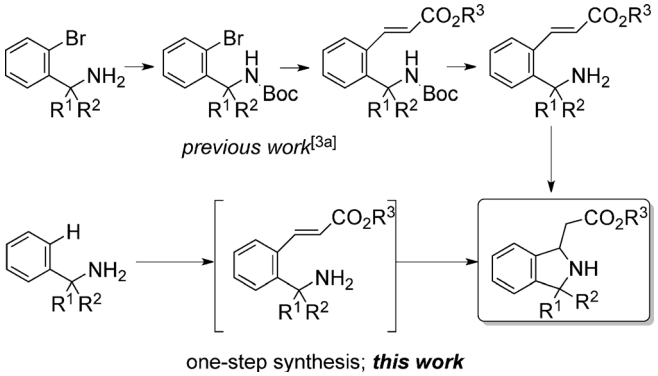
**Abstract:** The dehydrogenative direct coupling of α,α-disubstituted benzylamines with acrylates takes place efficiently at room temperature under ruthenium catalysis, accompanied by free amino group-directed *ortho*-alkenylation and successive cyclization to produce (isoindol-1-yl)acetic acid derivatives. The reactions using styrenes in place of acrylates proceed effectively in the presence of a rhodium catalyst rather than ruthenium.

**Keywords:** amines; C–C coupling; C–H activation; dehydrogenation; heterocycles




**Scheme 1.** Synthesis of (isoindol-1-yl)acetate derivatives.

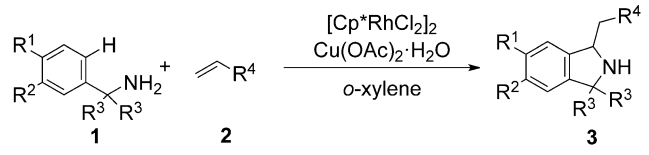
Isoindoline frameworks can be seen in a variety of biologically active compounds including pharmaceuticals.[1] In addition, isoindoline *N*-oxides are known to be utilizable as antioxidizing agents as well as EPR spin traps.[2] Therefore, development of effective methods for their preparation has attracted much attention in organic synthesis. Among such an important class of compounds, (isoindol-1-yl)acetic acids are of particular interest because of their applicability as melanocortin receptor ligands.[3] These molecules are usually synthesized from benzylamines through complicated multistep procedures including protection and deprotection steps on the amino nitrogen (for example, see Scheme 1). Unprotected amino functions, although they are ubiquitous in organic molecules, have been recognized to be too reactive toward various reagents and coordinate to transition metals too tightly to be involved in catalytic processes.

Defying this conventional wisdom, we recently found that 2-aminobiphenyls undergo ruthenium-catalyzed direct coupling with alkynes accompanied by free amino group-directed C–H bond cleavage.[4–6] In the context of our further studies of ruthenium-[7,8] as well as rhodium-catalyzed[9,10] C–H functionalization, we succeeded in finding that a one-step synthesis of (isoindol-1-yl)acetate derivatives can be achieved by rhuthenium- or rhodium-catalyzed dehydrogenative coupling of *N*-unsubstituted α,α-disubstituted benzylamines with acrylates through free amino-directed *ortho*-alkenylation and successive domino cyclization. In addition, the direct coupling of the amines with styrenes could be conducted under rhodium catalysis. The latter reaction proceeded unaccompanied by cyclization to produce the corresponding *ortho*-alkenylated benzylamines, which are structurally relevant to an antibiotic agent, fumimycin.[11] These new findings are described herein.

In an initial attempt, cumylamine (**1a**) (0.25 mmol) was treated with *n*-butyl acrylate (**2a**) (0.5 mmol) in the presence of $[Cp^*RhCl_2]_2$ (0.01 mmol) and $Cu(OAc)_2 \cdot H_2O$ (0.5 mmol) in *o*-xylene under $N_2$ at 80 °C for 2 h. As a result, an alkenylation/cyclization

**Table 1.** Rhodium-catalyzed reaction of α,α-disubstituted benzylamines **1** with alkenes **2**.[a]




**1** **2** **3**

| Entry | 1 | 2 | Time [h] | Product(s), Yield [%][b] |
|---|---|---|---|---|
| 1 | **1a** | **2a**: R = $CO_2$Bu-*n* | 2 | **3a**: R = $CO_2$Bu-*n*, 88 |
| 2[c] | | **2a**: R = $CO_2$Bu-*n* | 5 | **3a**: R = $CO_2$Bu-*n*, 48 |
| 3 | | **2b**: R = $CO_2$Bu-*i* | 4 | **3b**: R = $CO_2$Bu-*i*, 91 |
| 4 | | **2c**: R = $CO_2$Bu-*t* | 4 | **3c**: R = $CO_2$Bu-*t*, 91 |
| 5 | | **2d**: R = $CO_2$Cy | 4 | **3d**: R = $CO_2$Cy, 88 |
| 6 | | **2e**: R = $CO_2$Et | 4 | **3e**: R = $CO_2$Et, 81 |
| 7 | **1b** | **2a** | 4 | **3f**, 4[d] |
| 8 | **1c**: R = Me | **2a** | 4 | **3g**: R = Me, 63 |
| 9 | **1d**: R = Cl | | | **3h**: R = Cl, 5[d] |
| 10 | **1e** | **2a** | 24 | **3i**, 52 |

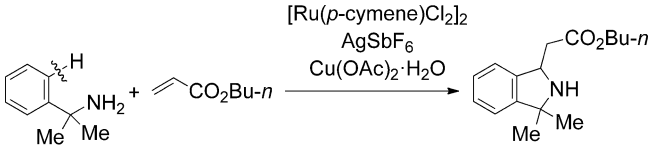
[a] *Reaction conditions:* **1a** (0.5 mmol), **2a** (2 equiv.), $[Cp^*RhCl_2]_2$ (2 mol%), $Cu(OAc)_2{\cdot}H_2O$ (2 equiv.) in *o*-xylene (3 mL) at 80 °C under $N_2$.
[b] Isolated yield.
[c] In dioxane (3 mL).
[d] GC yield.

product, butyl 2-(3,3-dimethylisoindolin-1-yl)acetate (**3a**), was formed in 88% yield (entry 1, Table 1). In dioxane, the **3a** yield significantly decreased (entry 2). In *o*-xylene, the reactions using isobutyl (**2b**), *tert*-butyl (**2c**), cyclohexyl (**2d**), and ethyl (**2e**) acrylates in place of **2a** also proceeded efficiently to produce the corresponding (isoindol-1-yl)acetates **3b–e** in 81–91% yields (entries 3–6). In contrast to reactive **1a**, tritylamine (**1b**) exhibited low reactivity in the reaction with **2a** to give **3f** in a low yield (entry 7). While the reaction of 3-(4-methylphenyl)pentan-3-amine (**1c**) gave **3g** in 63% yield (entry 8), 3-(4-chlorophenyl)-pentan-3-amine (**1d**) was found to be poorly reactive (entry 9). 3-(2-Naphthyl)pentan-3-amine (**1e**) coupled with **2a** to afford a tricyclic product, **3i**, in a moderate yield (entry 10).

Meanwhile, the reaction of **1a** with **2a** could also be carried out efficiently in the presence of a ruthenium catalyst in place of rhodium. Thus, treatment of **1a** (0.25 mmol) with **2a** (0.5 mmol) in the presence of $[Ru(p\text{-cymene})Cl_2]_2$ (0.0125 mmol), $AgSbF_6$ (0.05 mmol), and $Cu(OAc)_2{\cdot}H_2O$ (0.5 mmol) in dioxane under $N_2$ at 80 °C for 3 h gave **3a** in 97% yield (entry 1, Table 2). In other solvents such as *o*-xylene (entry 2), *t*-AmOH (entry 3), and DMF (entry 4), the product yield decreased slightly. In the absence of $AgSbF_6$, the reaction was sluggish (entry 5). It should be noted that the reaction proceed smoothly even at room temperature. Although an elongation of the reaction time (6 h) was needed, **3a** was obtained in quantitative yield (entry 6). In the case of decreasing the catalyst amount by half, the high product yield was maintained by further extension of the reaction time to 24 h (entry 7). Doubling the reaction scale with **1a** (0.5 mmol) did not affect the reaction efficiency (entry 8).

The coupling of various benzylamines and alkenes was next examined under ruthenium catalysis (Table 3). The reactions of **1a** using **2b–e** proceeded efficiently at room temperature to produce **3b–e** in slightly better yields, in comparison with those under rhodium catalysis (entries 1–4 in Table 2 *versus* en-

**Table 2.** Ruthenium-catalyzed reaction of cumylamine (**1a**) with *n*-butyl acrylate (**2a**).[a]

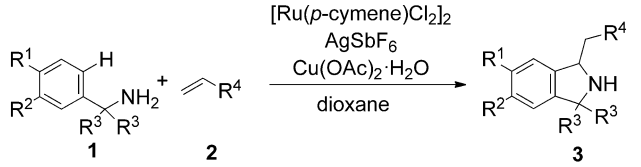



**1a** **2a** **3a**

| Entry | Solvent | Temp. [°C] | Time [h] | Yield of **3a** [%][b] |
|---|---|---|---|---|
| 1 | dioxane | 80 | 3 | 97 |
| 2 | *o*-xylene | 80 | 3 | 96 |
| 3 | *t*-AmOH | 80 | 3 | 92 |
| 4 | DMF | 80 | 3 | 87 |
| 5[c] | dioxane | 80 | 3 | 52 |
| 6 | dioxane | r. t. | 6 | 98 |
| 7[d] | dioxane | r. t. | 24 | 97 |
| 8[e] | dioxane | r. t. | 6 | 98 (92) |

[a] *Reaction conditions:* **1a** (0.25 mmol), **2a** (2 equiv.), $[Ru(p\text{-cymene})Cl_2]_2$ (5 mol%), $AgSbF_6$ (20 mol%), $Cu(OAc)_2{\cdot}H_2O$ (2 equiv.), solvent (3 mL) under $N_2$.
[b] GC yield based on the amount of **1a** used. Value in parentheses indicates yield after purification.
[c] Without $AgSbF_6$.
[d] With $[Ru(p\text{-cymene})Cl_2]_2$ (2.5 mol%) and $AgSbF_6$ (10 mol%).
[e] With **1a** (0.5 mmol).

**Table 3.** Ruthenium-catalyzed reaction of α,α-disubstituted benzylamines **1** with alkenes **2**.[a]




**1** **2** **3**

| Entry | 1 | 2 | Product(s), Yield [%][b] |
|---|---|---|---|
| 1 | **1a** | **2b**: R = $CO_2$Bu-*i* | **3b**: R = $CO_2$Bu-*i*, 93 |
| 2 | | **2c**: R = $CO_2$Bu-*t* | **3c**: R = $CO_2$Bu-*t*, 93 |
| 3 | | **2d**: R = $CO_2$Cy | **3d**: R = $CO_2$Cy, 92 |
| 4 | | **2e**: R = $CO_2$Et | **3e**: R = $CO_2$Et, 89 |
| 5[c] | | **2f** | **3j+4j**, 62 (76:24) |
| 6[c] | | **2g** | **3k+5k**, 53 (31:69) |
| 7[c] | **1b** | **2a** | **3f**, 78 |
| 8[c] | **1c**: R = Me | **2a** | **3g**: R = Me, 87 |
| 9[d] | **1d**: R = Cl | | **3h**: R = Cl, 89 |
| 10[d] | **1e** | **2a** | **3i**, 80 |
| 11 | **1f** | **2a** | **3l**, 51[e] |
| 12 | **1g** | **2a** | **5m**, 21 |

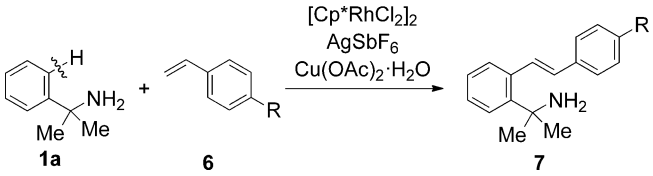
tries 3-6 in Table 1). *N-tert*-Butylacrylamide (**2f**) also reacted with **1a**, although the product **3j** was contaminated by a minor amount of (isoindolin-1-ylidene)acetate **4j** (entry 5). In the case of using acrylonitrile (**2g**), nucleophilic addition by the NH of **1a** was faster than the desired alkenylation to form **5k** predominantly along with a minor amount of **3k** (entry 6). In contrast to these reactive monosubstituted alkenes, disubstituted methyl crotonate did not react with **1a** at all. Meanwhile, **1b–d** coupled with **2a** effectively to form **3f–h** in 78–89% yields after 24–48 h (entries 7–9). It should be emphasized that the reaction efficiencies were dramatically improved by using the ruthenium catalyst, especially in cases with **1b** and **1d**. In the reaction of **1e**, the yield of tricyclic **3i** was also enhanced up to 80% (entry 10). In addition, an α-monosubstituted benzylamine, 1-phenylethan-1-amine (**1f**), underwent the coupling with **2a** to produce **3l** as a mixture of diastereomers (*cis*:*trans* = 2.2:1) (entry 11). However, in the case with a sterically less hindered amine, the α-unsubstituted benzylamine (**1g**), nucleophilic addition by its NH took place prior to alkenylation to give **5m** (entry 12).

In contrast to acrylates **2**, styrene (**6a**) did not react with **1a** at all under ruthenium catalysis (entry 1 in Table 4). It was, however, observed that **6a** could be coupled under rhodium catalysis. Thus, treatment of **1a** (0.5 mmol) with **6a** (1 mmol) in the presence of $[Cp^*RhCl_2]_2$ (0.01 mmol), $AgSbF_6$ (0.04 mmol), and $Cu(OAc)_2{\cdot}H_2O$ (1 mmol) in dioxane under $N_2$ at 80 °C for 4 h gave *ortho*-strylated product **7a** in 24% yield (entry 2). In *t*-AmOH, the reaction proceeded more smoothly to produce **7a** in 51% yield (entry 3). The yield of **7a** decreased in other solvents including *n*-BuOH, EtOH, DMF, *o*-xylene, DCE, PhCl, and $PhCF_3$ (entries 4–10). When the reaction was conducted in *t*-AmOH at 100 °C, the product yield was slightly reduced (entry 11). Even in *t*-AmOH at 80 °C, the reaction did not proceeded at all in the absence of $AgSbF_6$ (entry 12). Therefore, formation of a cationic Rh active species *in situ* seems to be essential for the reaction. Possible active species are probably $[Ru(OAc)]^+[SbF_6]^-$ and $[Cp^*Rh(OAc)]^+[SbF_6]^-$, which could be formed from anion exchange between the Rh catalyst precursor, $[Cp^*RhCl_2]_2$, and $AgSbF_6$. Under optimized conditions (entry 3), the reactions of methyl- (**6b**), methoxy- (**6c**), chloro- (**6d**), and trifluoromethyl- (**6e**) substituted styrenes with **1a** pro-

[a] *Reaction conditions:* **1** (0.5 mmol), **2** (2 equiv.), $[Ru(p\text{-cymene})Cl_2]_2$ (5 mol%), $AgSbF_6$ (20 mol%), $Cu(OAc)_2{\cdot}H_2O$ (2 equiv.) in dioxane (3 mL) at room temperature under $N_2$ for 6 h.
[b] Isolated yield.
[c] For 24 h.
[d] For 48 h.
[e] *cis*/*trans* = 2.2:1.

**Table 4.** Reaction of cumylamine (**1a**) with styrenes **6**.[a]




| Entry | R | 6 | Solvent | Time [h] | Product, Yield [%][b] |
|---|---|---|---|---|---|
| 1[c] | H | **6a** | dioxane | 3 | **7a**, 0 |
| 2 | H | **6a** | dioxane | 4 | **7a**, 24 |
| 3 | H | **6a** | *t*-AmOH | 4 | **7a**, 51 (50) |
| 4 | H | **6a** | *n*-BuOH | 4 | **7a**, 10 |
| 5 | H | **6a** | EtOH | 4 | **7a**, 17 |
| 6 | H | **6a** | DMF | 4 | **7a**, 3 |
| 7 | H | **6a** | *o*-xylene | 4 | **7a**, 9 |
| 8 | H | **6a** | DCE | 8 | **7a**, 39 |
| 9 | H | **6a** | PhCl | 4 | **7a**, 43 |
| 10 | H | **6a** | $PhCF_3$ | 8 | **7a**, 35 |
| 11[d] | H | **6a** | *t*-AmOH | 2 | **7a**, 43 |
| 12[e] | H | **6a** | *t*-AmOH | 4 | **7a**, 0 |
| 13 | Me | **6b** | *t*-AmOH | 6 | **7b**, (46) |
| 14 | OMe | **6c** | *t*-AmOH | 6 | **7c**, (41) |
| 15 | Cl | **6d** | *t*-AmOH | 6 | **7d**, (44) |
| 16 | $CF_3$ | **6e** | *t*-AmOH | 6 | **7e**, (48) |

[a] *Reaction conditions:* **1a** (0.5 mmol), **2a** (2 equiv.), $[Cp^*RhCl_2]_2$ (2 mol%), $AgSbF_6$ (8 mol%), $Cu(OAc)_2{\cdot}H_2O$ (2 equiv.), solvent (3 mL) at 80 °C under $N_2$.

[b] GC yield based on the amount of **1a** used. Value in parentheses indicates yield after purification.

[c] With **1a** (0.25 mmol), **2a** (2 equiv.), $[Ru(p\text{-cymene})Cl_2]_2$ (5 mol%), $AgSbF_6$ (20 mol%), and $Cu(OAc)_2{\cdot}H_2O$ (2 equiv.).

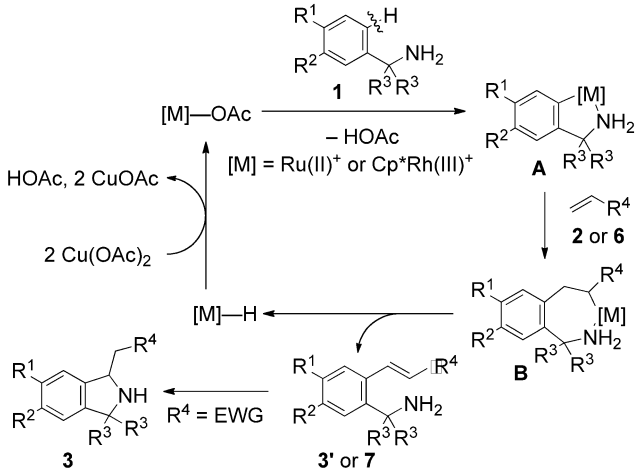
[d] At 100 °C.

[e] Without $AgSbF_6$.

ceeded to produce the corresponding stilbenes **7b–e** (entries 13–16). In contrast, an aliphatic alkene, 1-octene, did not undergo the coupling smoothly. Only trace amounts of unidentified products were formed.

A plausible mechanism for the dehydrogenative *ortho*-alkenylation of **1** is illustrated in Scheme 2. Coordination of the amino nitrogen of **1** toward the Ru or Rh center appears to be the key for the regioselective C–H bond cleavage at the *ortho*-position to form a five-membered metallacycle intermediate **A**. Then, alkene insertion into the resulting aryl-metal bond to form **B** and subsequent β-hydrogen elimination may take place to produce an *ortho*-alkenylated product. The resulting [M]–H species seems to be oxidized by a copper salt to regenerate an active [M]–X species. In the case of using an alkene possessing an electron-withdrawing group, the *ortho*-alkenylated product undergoes successive nucleophilic cyclization to construct an isoindoline framework.

In summary, we have demonstrated that the dehydrogenative *ortho*-alkenylation of α,α-disubstituted benzylamines with alkenes can be performed efficiently under ruthenium or rhodium catalysis. This is one of the rare examples for catalytic processes utilizing a free amino group as a directing group.




**Scheme 2.** A plausible pathway for the *ortho*-alkenylation of **1**.

## Experimental Section

### General Procedure for the Ruthenium-Catalyzed Reaction of α,α-Disubstituted Benzylamines 1 with Alkenes 2

A mixture of α,α-disubstituted benzylamine **1** (0.5 mmol), alkene **2** (1 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (0.025 mmol, 15 mg), $AgSbF_6$ (0.1 mmol, 35 mg), $Cu(OAc)_2{\cdot}H_2O$ (1.0 mmol, 200 mg), and 1-methylnaphthalene (*ca.* 30 mg) as internal standard was stirred in dioxane (3 mL) under $N_2$ at room temperature for 6–48 h. GC and GC-MS analyses of the mixtures confirmed formation of coupling product **3**. After cooling, the reaction mixture was poured into aqueous $NaHCO_3$ (40 mL) containing ethylenediamine (1 mL), extracted with ethyl acetate (40 mL), and washed with aqueous $NaHCO_3$ (40 mL, two times). The organic layer was dried over $Na_2SO_4$, and concentrated under vacuum. The desired product **3** was isolated by column chromatography on silica gel using hexane-ethyl acetate (2:1 v/v) as eluent. Characterization data of products are summarized in the Supporting Information.

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