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**Title:** Synthesis of 2-(3-Arylallylidene)-3-oxindoles via Dirhodium(II)-Catalyzed Reaction of 3-Diazoindolin-2-imines with 1-Aryl-Substituted Allylic Alcohols and Computational Insights

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# Synthesis of 2-(3-Arylallylidene)-3-oxindoles via Dirhodium(II)-Catalyzed Reaction of 3-Diazoindolin-2-imines with 1-Aryl-Substituted Allylic Alcohols and Computational Insights

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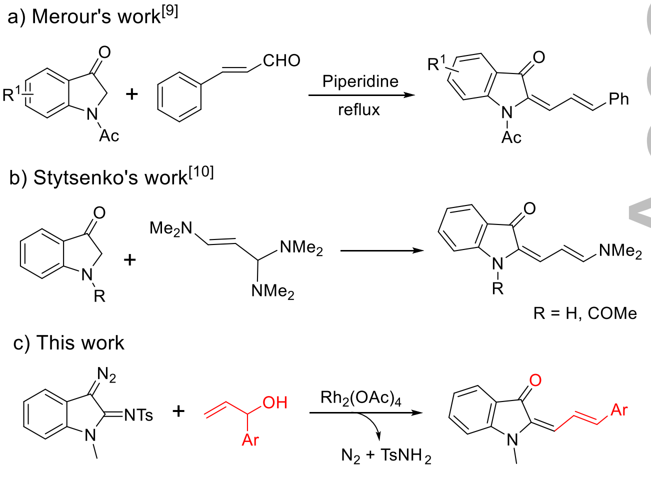
**Abstract.** A straightforward approach for the synthesis of 2-(3-arylallylidene)-3-oxindoles has been achieved by the dirhodium(II)-catalyzed reaction of 3-diazoindolin-2-imines with 1-aryl-substituted allylic alcohols. This protocol employs easily accessible feedstocks to produce oxindole derivatives, which might be applicable in the dye industry. DFT calculations were carried out to gain a mechanistic insight into the reaction.

**Keywords:** Rhodium catalysis; α-Imino carbene; Oxindole; DFT calculation.

Indoline and oxindole skeletons exist widely in natural products, bioactive molecules, and industrially useful compounds.[1] Thus, significant research attention has been devoted to developing new synthetic methods to functionalize indole scaffolds in a concise and efficient manner.[2] Recently, the employment of 3-diazoindolin-2-imine, which can be produced by direct 1,3-dipolar cycloaddition of indoles with tosyl azide, has emerged as a powerful tool to synthesize indole derivatives via transition metal carbene chemistry. In comparison with diazo compounds being commonly employed as precursors to generate transition metal carbene intermediates,[3] using 3-diazoindolin-2-imine as precursor can lead to the formation of α-imino transition metal carbenoid, which could further convert to N-containing heterocycles with appropriate nucleophiles. For instance, Wang and co-workers[4] reported that 3-diazoindolin-2-imines could be easily transferred to α-imino rhodium carbene intermediates in the presence of appropriate rhodium catalyst and subsequently react with alkynes, furans, indoles, and others, enabling efficient construction of the molecular complexity for cyclic compounds. Lee *et al*.[5] described that 3-diazoindolin-2-imines could be employed as rhodium carbene precursors to couple with 1,3-dienes, azirines and sulfoximines. Li and co-workers[6] successfully utilized 3-diazoindolin-2-imines to react with aryl imidates through Rh(III)-catalyzed C−H activation and C−C/C−N coupling processes. Moreover, Jiang's group[7] realized an efficient copper-catalyzed P−H insertions of α-imino carbenes using 3-diazoindolin-2-imines as carbene precursors.

In particular, 2-(3-arylallylidene)-3-oxindoles, being important oxindole derivatives present in merocyanine dyes, are often applied in the dye industry.[8] The reported methodology to construct 2-allylidene-3-oxindoles usually employs indolin-3-one as feedstock (Scheme 1).[9,10] Nevertheless, the development of the synthetic approach in a more efficient manner with readily available reagents is still desirable. Inspired by the chemistry of 3-diazoindolin-2-imine, herein we report a convenient approach to synthesize 2-(3-arylallylidene)-3-oxindoles via the $Rh(II)_2$-catalyzed reaction of 3-diazoindolin-2-imine with 1-aryl-substituted allylic alcohols, which may undergo sequential hydroxyl addition, Claisen rearrangement,[11] and the elimination of $TsNH_2$[5b] to finally afford the desired product.



**Scheme 1.** Synthesis of 2-(3-arylallylidene)-3-oxindoles.

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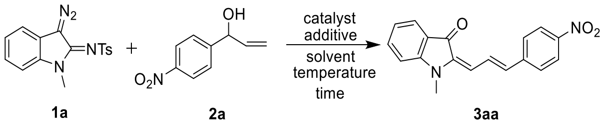
Initially, substrates 3-diazoindolin-2-imine (**1a)** and 1-(4-nitrophenyl)prop-2-en-1-ol (**2a**) were used to obtain the optimized reaction conditions (Table 1). A variety of dirhodium(II) catalysts were screened, such as $Rh_2(TFA)_4$, $Rh_2(Oct)_4$, $Rh_2(OAc)_4$ and $Rh_2(OPiv)_4$ in toluene at 85 °C for 6 hours. Among these catalysts, $Rh_2(OAc)_4$ demonstrates better efficiency in catalyzing this reaction to afford the product **3aa** (entries 1-4). The structure of **3aa** was confirmed by single-crystal X-ray diffraction analysis.[12] Next, the temperature of the reaction was screened (entries 5-8). However, the yield was not improved by either lowering or increasing temperature. When reaction time was extended to 13 hours, the yield can be improved slightly to 54%. However, further prolonging reaction time cannot lead to higher yield (entries 9-10). Subsequently, the amount of **1a** was increased to 2.8 equiv, and the yield can be improved slightly to 60%. Further increasing **1a** to 5 equiv, however, no any improvement of the yield was found (entries 11-12). Moreover, the addition of additives, such as base, acid, and 4Å molecular sieves, was also tried. Unfortunately, the yield was not improved further (entries 13-17). Furthermore, other solvent, such as DCE, PhCl, and THF, was screened. However, no any improvement of the yield was obtained (entries 18-20). In addition, the yield was not enhanced when the reaction was performed under nitrogen or argon atmosphere (entries 21-22). The yield remained at 59% when **1a** was added in portions in three batches (entry 23). When palladium catalysts such as $Pd(OAc)_2$, $[Pd(PPh_3)_2Cl_2]_2$, $PdCl_2$, and $Pd(PPh_3)_4$ were tried, the yield was in the range of 28-41% (entry 24-27). No desired product was detected when $Cu(OTf)_2$, $[Cu(MeCN)_4]BF_4$, AgOTf (entries 28-30), and other catalysts[13] were used. It turned out that the $Rh_2(OAc)_4$ catalyst shows the best performance in driving this reaction.

**Table 1.** Optimization of the reaction conditions. [a]

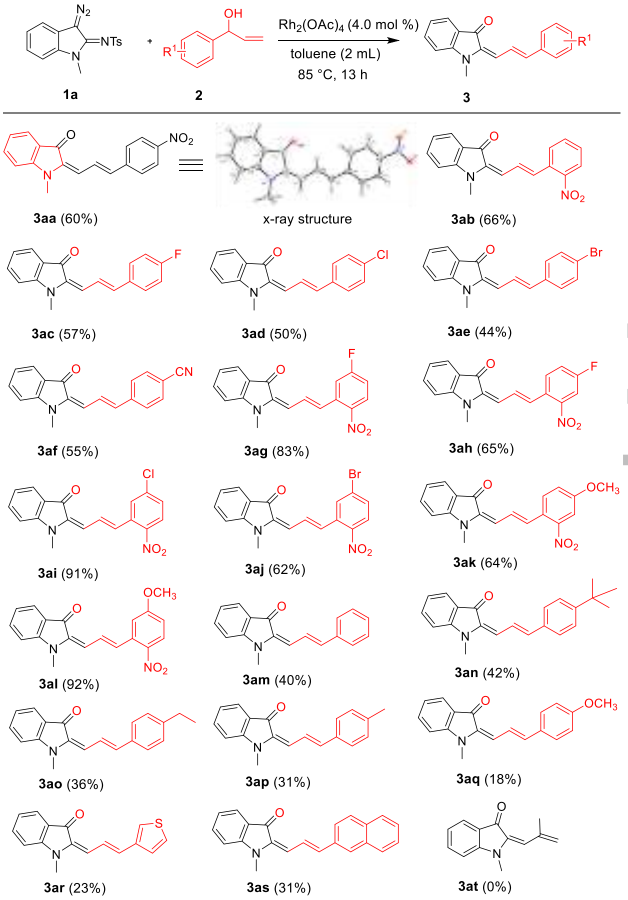


1a 2a 3aa

| entry | catalyst | additive | solvent | temp (°C) | time (h) | yield(%) |
|---|---|---|---|---|---|---|
| 1 | $Rh_2(TFA)_4$ | - | toluene | 85 | 6 | 8% |
| 2 | $Rh_2(Oct)_4$ | - | toluene | 85 | 6 | 10% |
| 3 | $Rh_2(OAc)_4$ | - | toluene | 85 | 6 | 48% |
| 4 | $Rh_2(OPiv)_4$ | - | toluene | 85 | 6 | 22% |
| 5 | $Rh_2(OAc)_4$ | - | toluene | 50 | 6 | trace |
| 6 | $Rh_2(OAc)_4$ | - | toluene | 70 | 6 | 14% |
| 7 | $Rh_2(OAc)_4$ | - | toluene | 110 | 6 | 33% |
| 8 | $Rh_2(OAc)_4$ | - | toluene | 95 | 6 | 44% |
| 9 | $Rh_2(OAc)_4$ | - | toluene | 85 | 13 | 54% |
| 10 | $Rh_2(OAc)_4$ | - | toluene | 85 | 48 | 40% |
| 11 | **$Rh_2(OAc)_4$** | - | toluene | **85** | **13** | **60%** [b] |
| 12 | $Rh_2(OAc)_4$ | - | toluene | 85 | 13 | 58% [c] |
| 13 | $Rh_2(OAc)_4$ | $NaHCO_3$ | toluene | 85 | 13 | n.d. |
| 14 | $Rh_2(OAc)_4$ | $CH_3COONa$ | toluene | 85 | 13 | n.d. |
| 15 | $Rh_2(OAc)_4$ | $CH_3COOH$ | toluene | 85 | 13 | 24% |
| 16 | $Rh_2(OAc)_4$ | HCOOH | toluene | 85 | 13 | 15% |
| 17 | $Rh_2(OAc)_4$ | 4 A MS | toluene | 85 | 13 | 28% |
| 18 | $Rh_2(OAc)_4$ | - | DCE | 85 | 13 | 40% |
| 19 | $Rh_2(OAc)_4$ | - | PhCl | 85 | 13 | 48% |
| 20 | $Rh_2(OAc)_4$ | - | THF | 85 | 13 | n.d. |
| 21 | $Rh_2(OAc)_4$ | - | toluene | 85 | 13 | 56% [d] |
| 22 | $Rh_2(OAc)_4$ | - | toluene | 85 | 13 | 54% [e] |
| 23 | $Rh_2(OAc)_4$ | - | toluene | 85 | 13 | 59% [f] |
| 24 | $Pd(OAc)_2$ | - | toluene | 85 | 13 | 30% |
| 25 | $[Pd(PPh_3)_2Cl_2]_2$ | - | toluene | 85 | 13 | 28% |
| 26 | $PdCl_2$ | - | toluene | 85 | 13 | 40% |
| 27 | $Pd(PPh_3)_4$ | - | toluene | 85 | 13 | 41% |
| 28 | $Cu(OTf)_2$ | - | toluene | 85 | 13 | n.d. |
| 29 | $[Cu(MeCN)_4]BF_4$ | - | toluene | 85 | 13 | n.d. |
| 30 | AgOTf | - | toluene | 85 | 13 | n.d. |

[a] Reaction conditions: **1a** (0.14 mmol, 1.4 equiv), **2a** (0.1 mmol), catalyst (4 mol%), toluene (2 mL), isolated yield. [b] **1a** (0.28 mmol, 2.8 equiv), **2a** (0.1 mmol). [c] **1a** (0.5 mmol, 5 equiv), **2a** (0.1 mmol). [d] Under $N_2$ atmosphere. [e] Under Argon atmosphere. [f] **1a** was added in portions in three batches. n. d. = not detected.

**Table 2.** Substrate scope of 1-aryl-substituted allylic alcohols.[a]

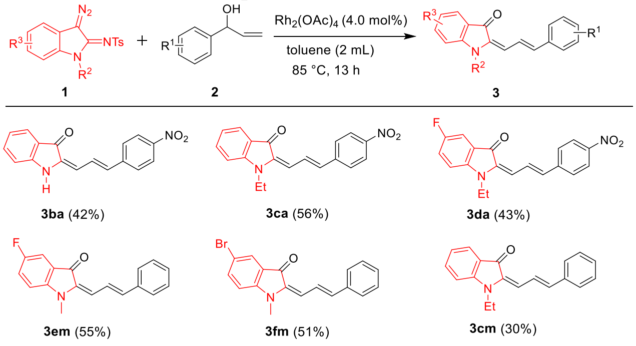


[a] Reaction conditions: **1a** (0.28 mmol, 2.8 equiv) and **2** (0.1 mmol), toluene (2 mL), 4 mol% $Rh_2(OAc)_4$, 85 °C, 13 h. The yields were given in isolated yields.

With the optimal reaction conditions in hand, we next explored the scope of the substrates. Firstly, the allylic alcohols with various substituents at the aryl moiety were examined (Table 2). When the nitro group is present at the *ortho*-position of phenyl moiety of the 1-aryl-substituted allylic alcohols (**2b**), the yield of the desired product (**3ab**) is 66%. For substrates with other electron-withdrawing substituents at the *para*-position, such as, –F (**2c**, 57%), –Cl (**2d**, 50%), –Br (**2e**, 44%), and –CN (**2f**, 55%), moderate yields of the desired product were obtained (**3ab~3af**). Substrates with multiple substituents on the phenyl moiety were also considered in this reaction. When halogen group is present with the $–NO_2$ group at the aryl moiety , such as 5-fluoro-2-nitro- (**2g**), 4-fluoro-2-nitro- (**2h**), 5-chloro-2-nitro- (**2i**), 5-bromo-2-nitro-(**2j**), 4-methoxy-2-nitro- (**2k**) and 5-methoxy-2-nitro- (**2l**), moderate to excellent yields (**3ag~3al**) were obtained. A gram-scale reaction for the $Rh(II)_2$-catalyzed reaction of **1a** with **2l** was tested and 61% yield of **3al** was obtained.[14] For substrate **2m**, in which no any substituent is present on the phenyl ring, lower yield of **3am** (40%) was obtained. When the electron-donating groups are attached to the phenyl moiety at the *para*-position, such as *para*-$^t$butyl (**3an**, 42%), *para*-ethyl (**3ao**, 36%), *para*-methyl (**3ap**, 31%) and *para*-methoxy (**3aq**, 18%), the yields of the desired product are not good. A possible reason responsible for the low yield for substrate with electron-donating group was provided based on computational studies (see below). In addition, heterocyclic substituted groups including thienyl (**3ar**) and naphthyl (**3as**) were also tested, giving yields of 23% and 31%, respectively. No desired product (**3at**) was observed for 2-alkyl-substituted allylic alcohol.

Subsequently, the substrate scope of 3-diazoindolin-2-imines (**1**) were investigated under the optimal reaction conditions (Table 3). For **1b** ($R^2$=H; $R^3$=H), the $Rh(II)_2$-catalyzed reaction with **2a** is less reactive and only 42% yield of the product (**3ba**) is obtained. When **1c** is employed ($R^2$=Et and $R^3$=H), moderate yield of the desired product **3ca** is obtained by 56%. For 3-Diazoindolin-2-imine derivatives with 5-F and 5-Br substituted groups, moderate yields of the corresponding products **3da**, **3em** and **3fm** are isolated in 43%, 55% and 51% yields, respectively. Only 30% yield of the desired product (**3cm**) is isolated when **1c** is used to react with **2m**.

**Table 3.** Substrate scope of 3-diazoindolin-2-imine. [a]



[a] Reaction conditions: **1** (0.28 mmol, 2.8 equiv) and **2a** (0.1 mmol), toluene (2 mL), 4 mol% $Rh_2(OAc)_4$, 85 °C, 13 h. The yields were given in isolated yields.

Computational studies[15] were carried out to gain a mechanistic insight into the dirhodium(II)-catalyzed reaction of **1a** with **2a** (Figure 1). The reaction may start with the coordination of **1a** with the catalyst, $Rh_2(OAc)_4$, to form an initial complex **INT1**. Subsequently, the $Rh(II)_2$-catalyzed decomposition of **INT1** via the extrusion of $N_2$ to form the key intermediate **INT2** may occur and the transition state was located as **TS1**. The predicted free energy barrier is 16.1 kcal/mol. After the formation of **INT2**, the intermolecular nucleophilic attack of substrate **2a** to the carbenoid moiety may follow. Both the additions of hydroxyl group and alkenyl group of **2a** to the carbene site of **INT2** were considered. Computational results show that the nucleophilic addition of hydroxyl group via **TS2** to form an ylide intermediate **INT5** is much more favorable than the [2+1] cycloaddition with the alkenyl group (Figure 1). Next, the formed **INT5** could undergo intramolecular proton migration from O atom to N atom via **TS3** to form intermediate **INT6** and regenerate the catalyst. It should be noteworthy that **INT6** could undergo Claisen rearrangement via **TS4** to afford intermediate **INT7**. The predicted free energy barrier for this step is 24.9 kcal/mol. Finally, the elimination of $TsNH_2$ from **INT7** was considered, which might proceed in the assistance of the rhodium(II) catalyst. The allylic $sp^3$ C-H bond could be activated by one of the acetate groups of $Rh_2(OAc)_4$ to form **INT9**. The β-elimination of the amido group of **INT9** might follow to yield the desired product **3aa** and the formed amido moiety is ready to be protonated from the yielded acetic acid to form a complex **INT10**. The catalyst can be regenerated after the release of $TsNH_2$. A plausible mechanistic pathway is shown in Scheme 2.

Computational results suggested that the rate-limiting step for the formation of the desired product is the allylic C−H bond activation of **INT7**, leading to the elimination of $TsNH_2$. When a substrate with electro-withdrawing group at the *para* position of the aryl moiety, such as **2a**, was employed, it is relatively advantageous for the formed complex **INT8** to undergo such C−H bond activation. The formed allylic carbon centered anion could be stabilized by the electro-withdrawing group at the *para* position of the aryl moiety via conjugated effect. For the substrate with electron-donating group, such as OMe at the *para* position (**2q**), the corresponding C−H bond activation, however, becomes more challenging because of the destabilizing effect caused by the electron-donating group to the formed carbon anion. The calculated $\Delta G^{\ddagger}$ of the rate-limiting step for **2q** is ca. 2 kcal/mol higher than that of **2a** (Figure S2). Thus, the 1-aryl-substituted allylic alcohols with electron-donating group are less reactive than those with electro-withdrawing group in the dirhodium(II)-catalyzed reaction with **1a**, which might account for, at least partially, the low yield of the product **3aq**.

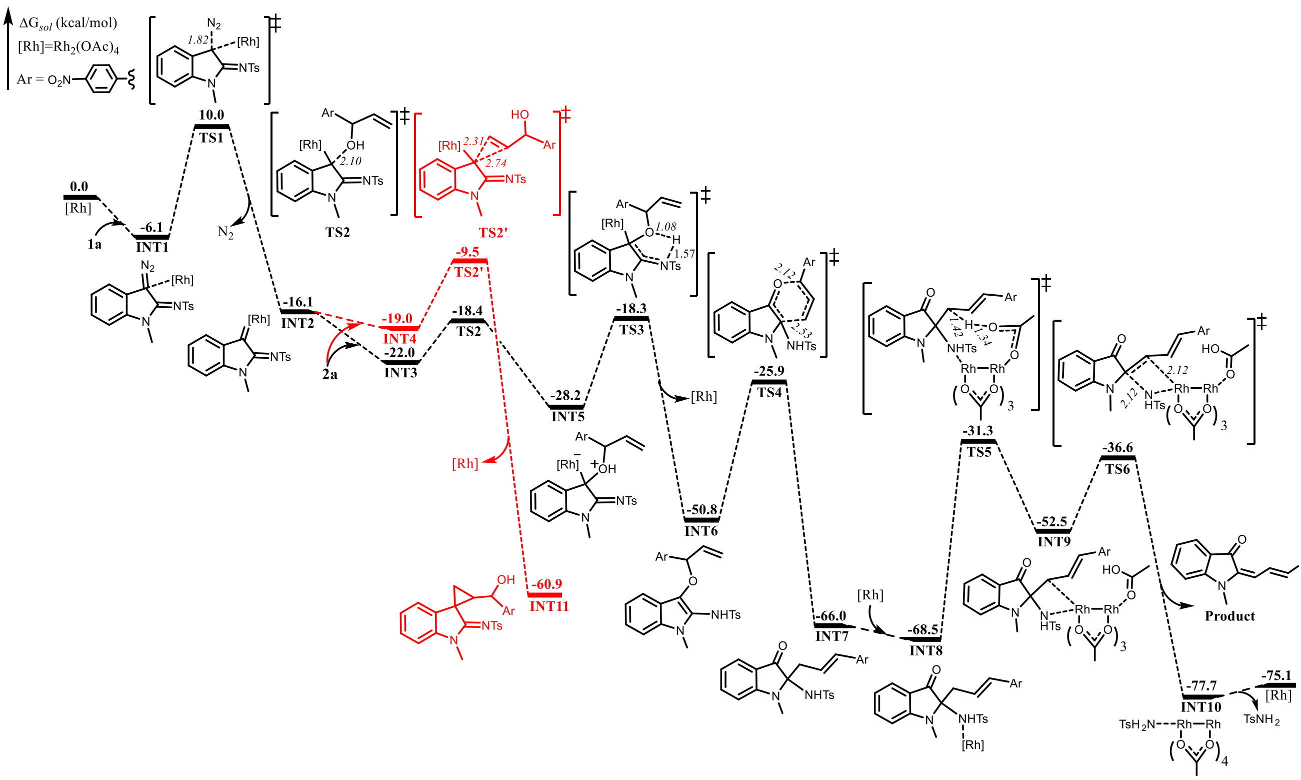
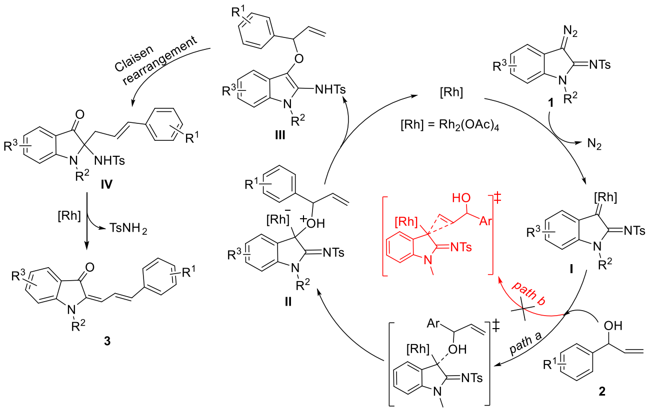


**Figure 1.** Energy profile for the formation of the final product **3aa**. Bond lengths are shown in Å.



**Scheme 2.** Proposed reaction mechanism.

Subsequently, the photophysical properties of **3aa** were investigated by UV/vis and photoluminescence (PL) spectroscopy at room temperature. The normalized UV/vis absorption and emission spectra of **3aa** in various organic solvents are shown in Figure 2. Compound **3aa** features two low-energy absorption bands centered at ~540 and ~380 nm, respectively. With increasing solvent polarity, slight red-shift for the absorption band centered at ca. 540 nm was observed. Interestingly, **3aa** exhibits solvent-dependent emission spectrum. The emission bands of **3aa** in DMSO demonstrate two peaks centered at ca. 420 and 450 nm while these emissive regions are not observed in AcOEt. By contrast, a strong emission band of **3aa** centered at ca. 600 nm is found in AcOEt while such emission band is absent in DMSO. The formation of an excimer, which is more likely in less polar solvent, is tentatively proposed to account for the solvent-dependent emission spectrum. More details about the photophysical properties of the synthesized compounds and potential applications are currently being working on in our lab.

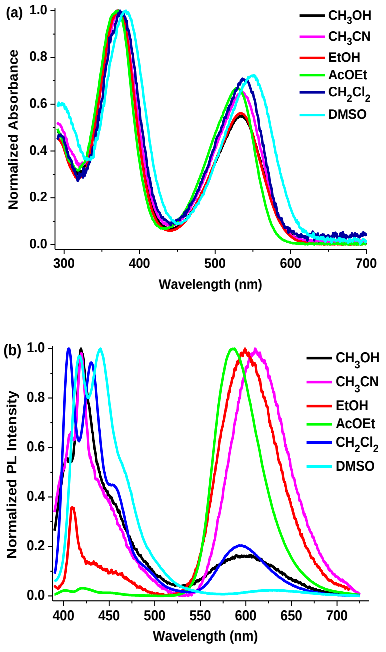


**Figure 2.** The normalized UV/vis absorption (a) and emission spectra (b) of **3aa** ($10^{-5}$ M) in various organic solvents.

In conclusion, we disclosed a reaction of dirhodium(II)-catalyzed 3-diazoindolin-2-imine with 1-aryl-substituted allylic alcohols to synthesize 2-(3-arylallylidene)-3-oxindoles. This methodology provides a convenient approach from easily accessible feedstock to synthesize oxindole derivatives, which might be applicable in the dye industry. DFT calculations suggest that the reaction may proceed via the hydroxyl addition of allylic alcohols to the formed Rh-carbenoid intermediate followed by sequential Claisen rearrangement and the elimination of $TsNH_2$ to afford the desired product.

## Experimental Section

### General procedure

To a 10-mL oven-dried test tube was added in a magnetic stirring stone. Then, 4.0 mol% $Rh_2(OAc)_4$, 0.28 mmol 3-diazoindolin-2-imine compound **1**, 0.1 mmol 1-aryl-substituted allylic alcohols compound **2** and 2 mL toluene were added. The reaction mixture was stirred for 13 hours at 85 °C. After the reaction finished, 2 mL EtOAc was added. Then, adding 1g silicon gel and evaporating the solvent *in vacuo*. The residue was purified by flash column chromatography on silica gel. (gradient eluent: Petroleum ether/EtOAc/ Dichloromethane = 30:1:1~8:1:1)

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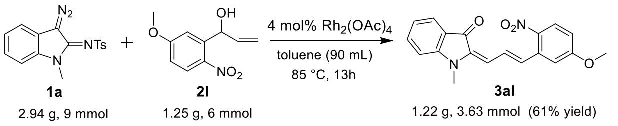
[12] CCDC-1947908 (3aa) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[13] More catalysts screening was shown in Table S1.

[14] The Rh(II)-catalyzed reaction of **1a** with **2l** could be scaled up to gram scale with 61% yield of **3al**.



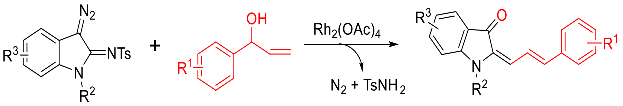
[15] See Supporting Information for computational details.

[16] A distortion/interaction analysis for TS2 and TS2' was performed to gain an insight on the chemo-selectivity (Figure S1).

[17] Molecular orbitals of **3aa** are shown in Figure S3.

COMMUNICATION

# Synthesis of 2-(3-Arylallylidene)-3-oxindoles via Dirhodium(II)-Catalyzed Reaction of 3-Diazoindolin-2-imines with 1-Aryl-Substituted Allylic Alcohols and Computational Insights



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