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Rhodium(I)-Catalyzed Cycloisomerization of Nitrogen-Tethered Indoles and Alkylidenecyclopropanes: Convenient Access to Polycyclic Indole Derivatives

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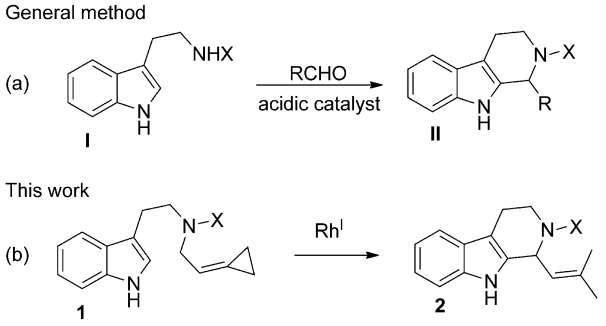
The indole moiety is a privileged structural motif in many biologically active and medicinally valuable molecules.[1] Polycyclic frameworks lead to relatively rigid structures that might be expected to show substantial selectivity in their interactions with enzymes or receptors.[2] Construction of polycyclic indoles usually requires multistep approaches.[3] The preparation of polyfunctional indoles is therefore an important research field.

The tetrahydro-β-carboline ring system, which belongs to the polycyclic indole family, is widely found in natural products and pharmaceuticals.[4] Representative examples, such as jafrine, mitragynine, and ajmalicine, all have tetrahydro-β-carboline structures (Figure 1). The Pictet–Spengler reaction has been recognized as one of the most direct and efficient methods for the construction of tetrahydro-β-carboline frameworks.[5] However, to date, most of the reported methods are accomplished by the treatment of tryptamine with a carbonyl functionality in the presence of an acidic catalyst (Scheme 1a).

Alkylidenecyclopropanes (ACPs), containing a coordinating double bond and a strained carbocycle, can undergo a number of interesting metal-assisted transformations,[6–8] and our group has developed a series of transformations of these *exo*-methylene three-membered carbocycles.[9] Herein, we report a new method of construction of polycyclic indoles by a rhodium(I)-catalyzed cycloisomerization reaction from alkylidenecyclopropanes toward tetrahydro-β-carboline derivatives (Scheme 1b).



Scheme 1. Construction of tetrahydro-β-carboline derivatives.

Initial studies by using indole–alkylidenecyclopropane **1a** (0.1 mmol) as the substrate in the presence of $[RhCl(PPh_3)_3]$ were aimed at determining the reaction outcome and subsequently optimizing the reaction conditions. To our delight, we found that an interesting tetrahydro-β-carboline derivative, **2a**, was formed by using the rhodium catalyst. Further examination of the reaction with [Rh(cod)(IPr)Cl] (cod = 1,5-cyclooctadiene, IPr = 1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene) revealed that the conjugated diene **3a** could be obtained in 76% yield (Scheme 2). After the catalyst and ligand screening and the investigation of solvent effects, reaction temperature, and concentration on the reaction outcome, we determined that the optimal reaction conditions involve carrying out the reaction in toluene (0.0125 M) at 110 °C by using $[RhCl(PPh_3)_3]$ (5 mol%)/PPh_3 (15 mol%) as the catalyst (Scheme 2, see Table SI-2 in the Supporting Information for details). The structure of compound **2a** was confirmed by use of NMR spectroscopic data and X-ray diffraction analysis (see the Supporting Information).[10]

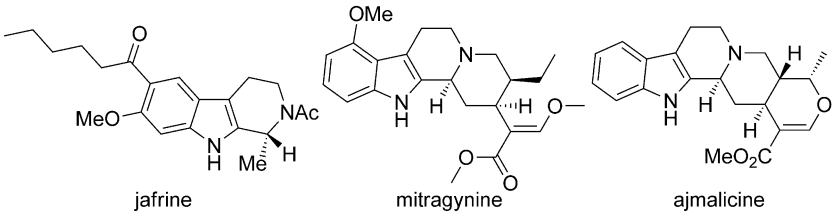


Figure 1. Selected naturally occurring compounds containing tetrahydro-β-carboline.

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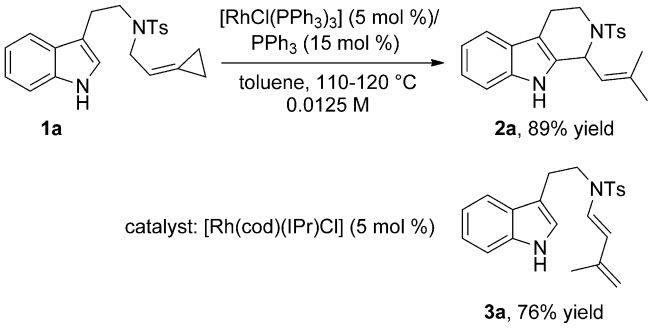
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201302331. It contains experimental procedures and spectral data for all new compounds, as well as X-ray crystal structures and data for **2a** and **5b**.



Scheme 2. Optimization of reaction conditions for rhodium(I)-catalyzed cyclization.

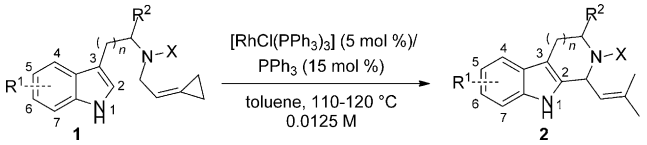
We next examined the generality of the reaction with respect to the substrate under the optimized conditions and the results are shown in Table 1. A variety of indole–alkylidenecyclopropanes **1b**–**1j**, having either electron-donating or -withdrawing groups as substituents at the 4-, 5-, 6-, or 7-position of the benzene ring of the indole, underwent the reactions smoothly, to give the corresponding products **2b**–**2j** in 52–95% yields (Table 1, entries 1–9). In the case of other *N*-sulfonated amines (X = Ns or Ms), the cycloisomerized compounds **2k** and **2l** were obtained in 85 and 73% yields, respectively (Table 1, entries 10 and 11). Examination of the reaction with substrate **1m** (R^2 = Me) revealed that the desired product **2m** could be formed in 73% yield with good diastereoselectivity (4.3:1; Table 1, entry 12). As for longer-chain substrate **1n**, the seven-membered heterocyclic compound **2n** was obtained in 68% yield (Table 1, entry 13). Only in the case of carbon-tethered alkylidenecyclopropane (**1o**), the corresponding conjugated diene **3o** was formed in 51% yield rather than the cyclized product (Table 1, entry 14). As for substrate **1p**, only 10% of the desired product **2p** was obtained and 64% of **1p** was recovered (Table 1, entry 15). The product structures of **2b**–**2p** were determined by use of NMR spectroscopic data, MS, and HRMS (see the Supporting Information).

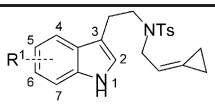
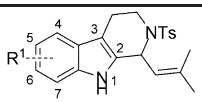
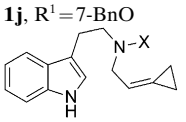
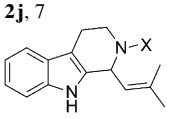
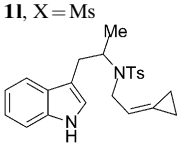
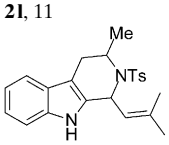
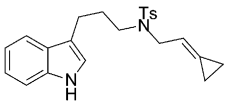
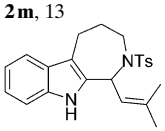
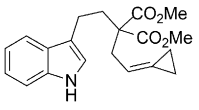
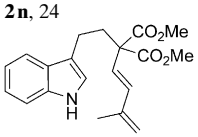
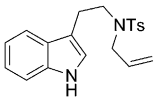
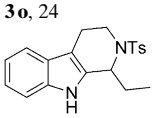
Further transformations of product **2a** are shown in Scheme 3. The 1,7-diene **4a** could be obtained in 84% yield by treatment with sodium hydride and allyl bromide, and subsequently gave the polycyclic indole **5a** in 67% yield in the presence of Grubbs first-generation catalyst (10 mol%). Meanwhile, we synthesized allene **4b** in excellent yield. By using [Au(*t*BuXPhos)(NCMe)][SbF_6] (XPhos = 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl) as the catalyst, tetracyclic compound **5b** could be formed smoothly in 79% yield. The structure of compound **5b** was confirmed by use of NMR spectroscopic data and X-ray diffraction analysis (see the Supporting Information).[11]

As shown in Scheme 4, carrying out the reaction of conjugated diene **3a** in the presence of [$RhCl(PPh_3)_3$] (5 mol%)/PPh_3 (15 mol%) in toluene (0.025 M) led to the desired product **2a** in 88% yield. It should be mentioned here that trifluoroacetic acid (TFA) can also promote this reaction, suggesting that the Rh complex may play a role as a Lewis acid in this cyclization process (see Table SI-3 in the Supporting Information for details). As for substrate **1q**, having a methyl group at the C2-position of indole, the corresponding conjugated diene **3q** was formed in 38% yield rather than the cyclized product.

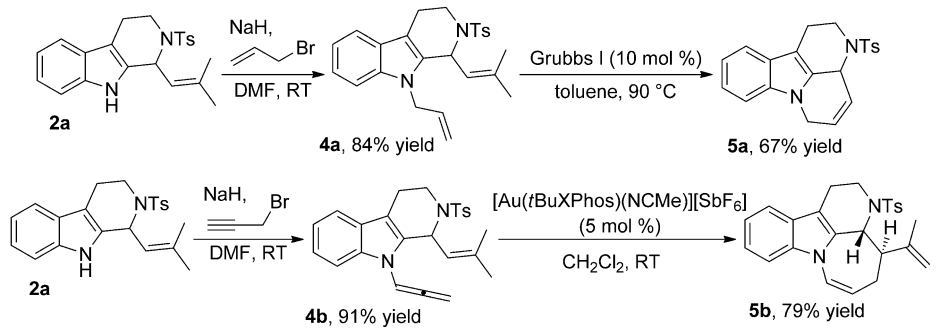
To elucidate the cycloisomerization mechanism, deuterium-labeling experiments were performed as shown in Scheme 5. Alkylidenecyclopropane [D_1]-**1a**, bearing a D atom at the indole C2-position, produced cyclized product

Table 1. Substrate scope of the rhodium(I)-catalyzed cycloisomerization reaction.[a]

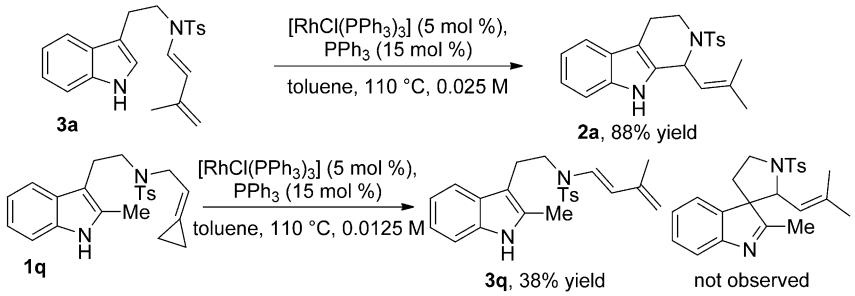


Entry	Substrate **1**	Product **2**, *t* [h]	Yield [%][b]
			
1	**1b**, R^1 = 5-MeO	**2b**, 8	95
2	**1c**, R^1 = 5-Me	**2c**, 7	82
3	**1d**, R^1 = 5-Br	**2d**, 9	76
4	**1e**, R^1 = 5-Cl	**2e**, 9	75
5	**1f**, R^1 = 6-Me	**2f**, 7	80
6	**1g**, R^1 = 6-F	**2g**, 7	52
7	**1h**, R^1 = 4-Me	**2h**, 8	56
8	**1i**, R^1 = 7-Me	**2i**, 7	91
9	**1j**, R^1 = 7-BnO	**2j**, 7	88
			
10	**1k**, X = Ns	**2k**, 12	85
11	**1l**, X = Ms	**2l**, 11	73
			
12	**1m**	**2m**, 13	73 (4.3:1)[c]
			
13	**1n**	**2n**, 24	68
			
14	**1o**	**3o**, 24	51
			
15	**1p**	**2p**, 24	10 (64)[d]

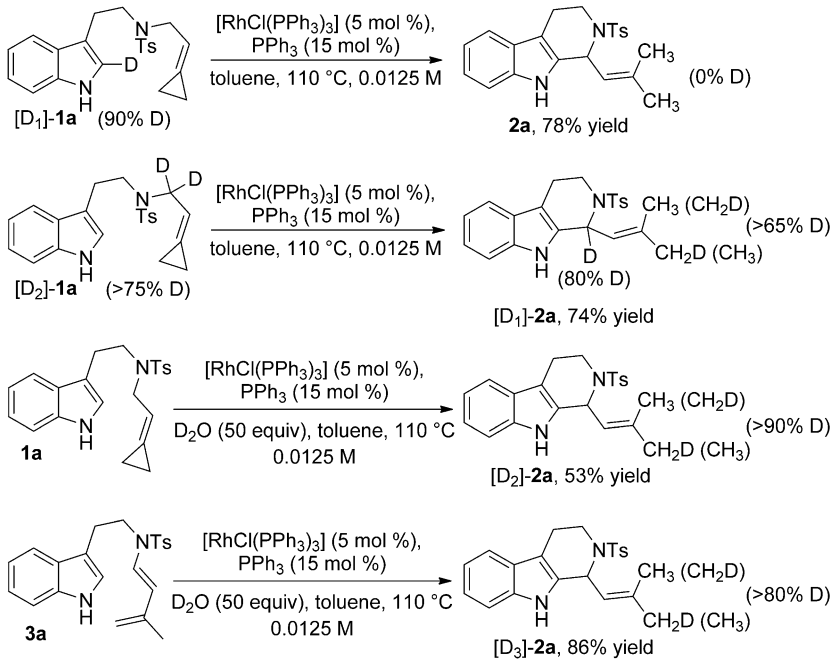
[a] All reactions were carried out by using **1** (0.1 mmol) in the presence of [$RhCl(PPh_3)_3$] (5 mol%)/PPh_3 (15 mol%) in toluene (8.0 mL) at 110–120 °C. The reactant concentration was 0.0125 M (Ts = 4-toluenesulfonyl, Ns = 4-nitrobenzenesulfonyl, Ms = methylsulfonyl, Bn = benzyl). [b] Yield of the isolated product. [c] The d.r. value was determined by ^{1}H NMR spectroscopy. [d] The amount of **1p** recovered is given in parentheses.



Scheme 3. Further transformations of product **2a**.



Scheme 4. Transformations of **3a** and **1q** in the presence of rhodium(I) catalysts.

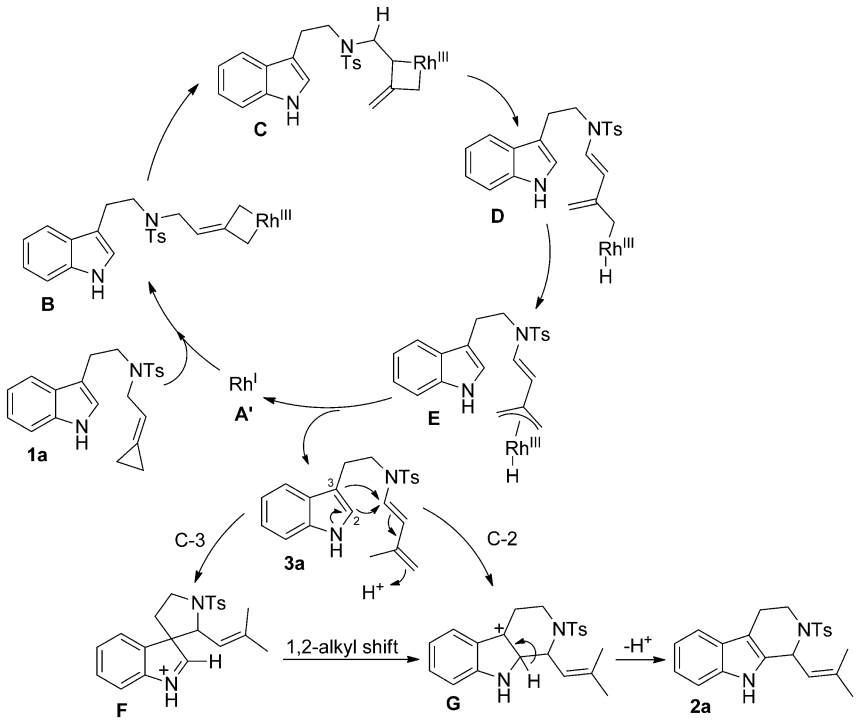


Scheme 5. Isotopic labeling experiments.

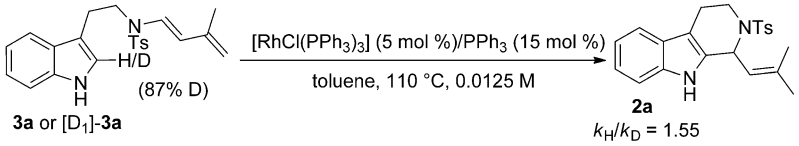
2a in 78% yield with 0% deuterium incorporation. As for substrate [D_2]-**1a**, containing two deuterium atoms at the allylic position, the desired product [D_1]-**2a** was obtained in 74% yield with >65% deuterium incorporation at its methyl carbon atom. Carrying out the reaction of indole derivatives **1a** or **3a** in the presence of D_2O (50 equiv) afforded the corresponding products [D_2]-**2a** and [D_3]-**2a** in 53% (>90% D) and 86% (>80% D) yields, respectively.

A plausible mechanism for this reaction is outlined in Scheme 6 on the basis of the aforementioned deuterium-labeling and control experiments.[12] Initial insertion of the metal at the distal position of alkylidenecyclopropane **1a** gives metallacyclobutene **B**, followed by isomerization to form intermediate **C** through a trimethylenemethane (TMM)-like transition state. The intermediate **C** undergoes β-H elimination to give rhodium–hydrogen species **D**, which can isomerize to produce π-allylic Rh^{III} complex **E**. Conjugated diene **3a** can be obtained from intermediate **E** through reductive elimination along with regeneration of the Rh^{I} complex. There are two competing pathways for cyclization in the Pictet–Spengler reaction, since both the indole C2- and C3-positions are nucleophilic.[13] Through indole C3-position attack on the conjugated diene, spiroindolenine intermediate **F** is formed, which can further undergo a 1,2-alkyl shift to afford the six-membered-ring intermediate **G**. Alternatively, nucleophilic attack of the indole C2-position on the diene moiety leads directly to intermediate **G**, followed by deprotonation to give **2a** (see Table SI-3 in the Supporting Information). Furthermore, we carried out a deuterium-labeling experiment by using alkylidenecyclopropane [D_1]-**3a**, in which the indole C2-position of **3a** was deuterated, as the substrate under the standard conditions (Scheme 7, for details, see Table SI-1 in the Supporting Information). The observed KIE ($k_H/k_D \approx 1.55$) was rather insignificant, indicating that the deprotonation step may not be the rate-limiting step.

To clearly understand the mechanism of the rhodium(I)-catalyzed reaction and subsequent cyclization step in the

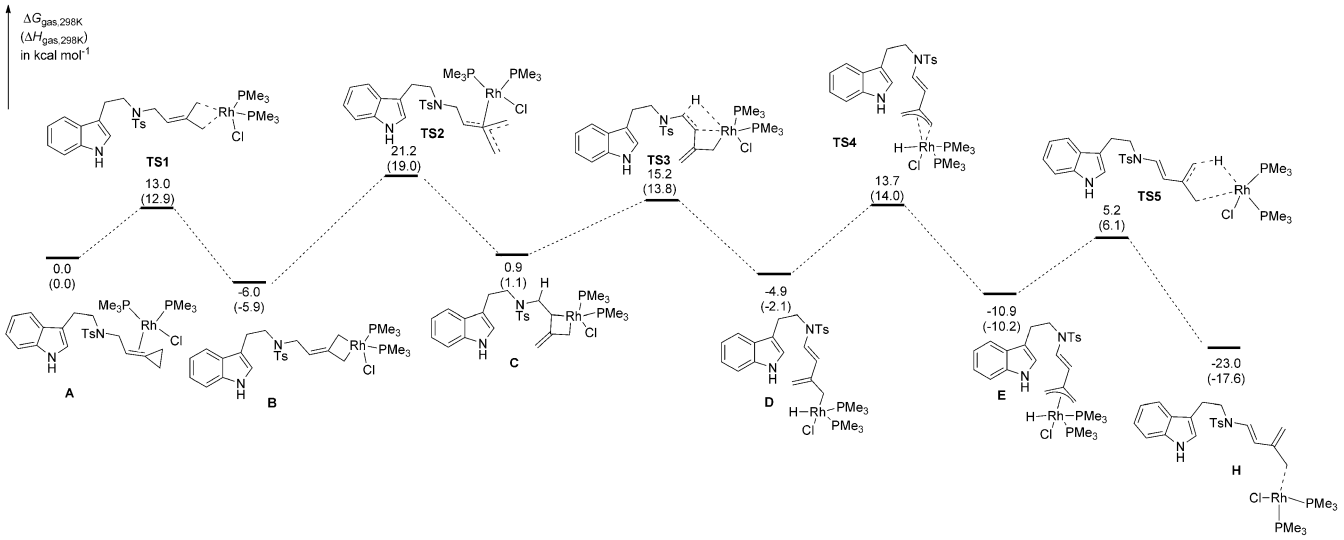


Scheme 6. A plausible reaction mechanism.



Scheme 7. Deuterium-labeling experiment for the rhodium(I)-catalyzed cycloisomerization of alkylidenepropanes **3a** and [D_1]-**3a**.

Pictet–Spengler reaction, we have theoretically investigated the reaction pathways, as shown in Scheme 8 and Scheme SI-1 in the Supporting Information, respectively. All calculations were performed at the B3LYP level with the Gaussian 09 program.[14] The LANL2DZ basis set and pseudopotential were used for the rhodium atom, and the 6-31G(d) basis set was used for all other atoms. The formation of reactant complex **A** promotes oxidative addition to afford square-pyramidal rhodacyclobutane **B**, which is 6.0 kcal mol^{-1} lower in energy than the reactant complex and has an associated transition state, **TS1**, at 13.0 kcal mol^{-1}. Intermediate **B** rearranges to afford intermediate **C** via transition state **TS2**, with an energy barrier of 27.2 kcal mol^{-1}. Passing through transition state **TS3** with an energy barrier of 14.3 kcal mol^{-1}, intermediate **C** undergoes β-H elimination to give rhodium–hydrogen species **D**. The rhodium-hydrogen species **D** can isomerize to produce π-allylic Rh^{III} complex **E** via **TS4** with an energy barrier of 18.6 kcal mol^{-1}. Passing through **TS5**, the π-allylic Rh^{III} complex **E** undergoes reductive elimination to yield the product complex **H** with an energy barrier of 16.1 kcal mol^{-1}. We also theoretically investigated the reaction mechanism via rhodium(I)-catalyzed allylic C–H activation (for details, see



Scheme 8. DFT studies on the rhodium(I)-catalyzed reaction.

Scheme SI-1 in the Supporting Information). However, the reaction mechanism via rhodium(I)-catalyzed allylic C–H activation involves a C–C bond-cleavage step with a very high reaction barrier. Thus, we suggest that the reaction pathway shown in Scheme 8 is more reasonable. The calculation results for the subsequent cyclization step in the Pictet–Spengler reaction suggest that the direct indole C2-attack is favored (for details, see Scheme SI-2 in the Supporting Information).

In conclusion, we have developed a new rhodium(I)-catalyzed cycloisomerization reaction of nitrogen-tethered indoles and alkylidenecyclopropanes to provide easy access to tetrahydro-β-carboline derivatives in good yields. The reaction mechanism is proposed on the basis of isotopic labeling and control experiments, and is also supported by DFT calculations. Further applications of this chemistry and more detailed mechanistic investigations are underway in our laboratory.

Experimental Section

General procedure for the rhodium(I)-catalyzed cycloisomerization of indole–alkylidenecyclopropanes: Under an argon atmosphere, indole–alkylidenecyclopropane **1** (0.1 mmol, 1.0 equiv) was dissolved in toluene (8.0 mL, 0.0125 M) in an Schlenk tube, and $[RhCl(PPh_3)_3]$ (5 mol%) and PPh_3 (15 mol%) were added. The reaction mixture was then stirred at 110 °C until the reaction was complete. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO_2) to give the corresponding product **2** in moderate to good yields.

Acknowledgements

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Keywords: alkylidenecyclopropanes · cycloisomerization · indoles · polycyclic indoles · rhodium · tetrahydrocarbolines

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