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Raju Vaggu, Akhila Muraharikar, Yenamareddy Bhargav Kumar, Yarasi Soujanya, René Grée, et al.. Controlled Ru (II) and Rh (III) catalyzed [4+2] and [4+1] carbo-annulation via C–H Activation using Sulfoxonium ylide and Maleimide: Facile access to Fused Benzoisindole and Spiroindanone. *European Journal of Organic Chemistry*, 2024, 27 (47), pp.e202400885. 10.1002/ejoc.202400885 . hal-04822723

HAL Id: hal-04822723

<https://hal.science/hal-04822723v1>

Submitted on 17 Feb 2025

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Controlled Ru (II) & Rh (III) catalyzed [4+2] & [4+1] carbo-annulations via C–H Activation using Sulfoxonium ylide and Maleimide: Facile access to Fused Benzoisindole & Spiroindanone

Raju Vaggu,^{a,c} Akhila Muraharika,^a Yenamareddy Bhargav Kumar,^b Yarasi Soujanya,^{b,c} René Grée^d and Saibal Das^{a,c*}

^a Department of Organic Synthesis & Process Chemistry, CSIR-Indian Institute of Chemical Technology (CSIR-IICT), Hyderabad 500007, India.

^b Department of Polymers and Functional Materials, CSIR-Indian Institute of Chemical Technology, Hyderabad 500007, India.

^c Academy of Scientific and Innovative Research (AcSIR), Ghaziabad, 201002, India.

^d University of Rennes, CNRS, ISCR (Institute for Chemical Sciences in Rennes, UMR 6226), 35000 Rennes, France. [Phone: +91 40 2719 1887, E-mail: saibal@iict.res.in]

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#####>. ((Please delete if not appropriate))

Abstract. A well-ordered strategy of sulfoxonium ylides as a directing group as well as carbene source for the Ru-catalysed [4+2] and Rh-catalysed [4+1] carbo-annulations with maleimides has been described. These novel methodologies have been successfully established for the synthesis of complex spiroindanones and benzoisindoles containing compounds by the transition metal-mediated C-H activation/functionalization reactions. Further, Rh-catalysed [4+1] annulated compounds were obtained in the absence of any oxidant. A possible rationale for the remarkable divergent selectivity between the two catalysts has been proposed.

Keywords: C-H Activation; Carbo-annulation; Transition Metal Catalyst; Benzoisindole; Spiroindanone

Spiroindanones^[1] and benzoisindoles^[2] structures are present in bioactive molecules, as well as in drugs, which explains the special attention paid by synthetic chemists^[3,4,8d] to these structures. Molecules of this type show biological activities that include anti-tumor, antibiotic^[5] and α 1A-adrenoceptor antagonist activity^[6,7] (Figure 1).

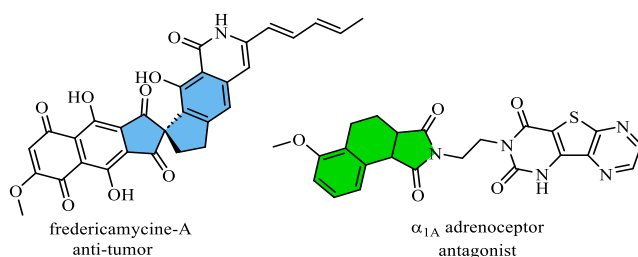
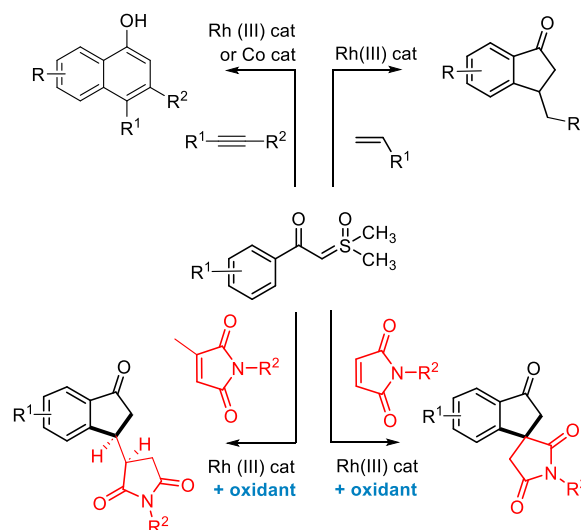


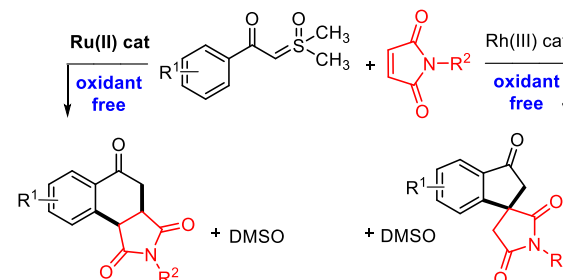
Figure 1. Representative examples of spiroindanone and fused benzoisindole bioactive molecules.

In the past decades, many groups have developed elegant strategies towards the synthesis of various types of spiroindanones^[8] and benzoisindoles^[9] by using transition metal catalysts.^[10]

Representative previous approaches:



Present work:



Scheme 1. Previous approaches and present work.

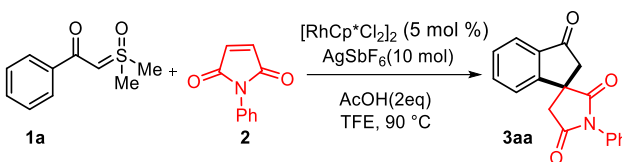
The weakly coordinating group sulfoxonium ylide^[11a] is a recent addition as a directing group for C-H activation and it can be used for further transition metal catalysed reactions.^[11] The first examples were reported few years back on the reactions of such ylides with various alkynes to afford naphthol derivatives (Scheme 1).^[11f] The Rh(III) catalysts were used first for this kind of [4+2] annulation for C-H activation of alkenes,^[12] and then air-stable Co-catalysts proved to be efficient as well. Reactions with activated alkenes^[13] have been developed more recently affording, under Rh(III) catalysis, the indanones via a [4+1] annulation strategy with acrylates and acrylamides.^[14a] And very recently, similar moiety was reported using stoichiometric amount of metal oxidant^[11d] for the synthesis of spiroindanones or indanolyrrolidine-2-5-diones. In parallel to these studies, various types of carbo- and heterocyclic structures have been prepared by similar approaches using sulfoxonium ylides and transition metal catalysts, mostly using Rh-catalysts with oxa/azabicyclic olefins,^[15a] allenolates,^[15c] anthranils,^[15f,15g] then using Ru-catalysts for homocouplings^[15d,15e] and Co(III) complexes with arenes^[15h] and dioxazolones.^[15i]

In extension to our previous studies,^[16] we have decided to explore the reaction of these sulfoxonium ylides with readily available maleimides as coupling partners. Therefore, the goal of this publication is to demonstrate that the less expensive Ru (II) catalyst can be used in [4+2] carbo-annulation reactions for a facile route to complex benzoisindoles. The protocol also allowed an improvement for efficient synthesis of spiroindanones via an Rh (III) catalysed C-H activation following a [4+1] carbo-annulation under oxidant free conditions. Further, we propose mechanisms for these reactions and an explanation for the selectivity difference between the two catalytic systems.

Initially, we started to explore our reaction (Table 1) with phenylsulfoxonium ylide **1a** and *N*-phenyl maleimide **2** in presence of 5 mol % of [Cp**Rh*Cl₂]₂ with 0.5 eq. of acetic acid and 10 mol% of AgSbF₆ in TFE as solvent at 90 °C for 10h^[14] and we obtained the desired adduct **3aa** in 20% yield (entry 1). Then, we investigated the role of the acetic acid (entries 2-4) and we found the best results with 2 equivalents, affording **3aa** with 75% yield (entry 4). Other silver salts, in 10 mol%, proved to be less efficient (entries 5-7). Increasing the quantity of AgSbF₆ (up to 30% mol) did not improve the yield of the reaction (entries 8-9). On the other hand, PivOH and NaOAc proved to have a low impact on the [4+1] carbo-annulation reaction furnishing the product **3aa** in 45% and 40% yield respectively (entries 10 and 11). Next, we investigated different solvents in which TFE demonstrated the best

yields (entries 12-17), although THF was another good possibility (entry 18). We studied also the role of the temperature and we found the best results at 90°C, affording **3aa** with 75% yield (entries 19-22). The reaction gave only poor yields in the absence of the silver salt (entry 23) or in the absence of acetic acid (entry 24). Finally, the yield was found to decrease (entry 25) in the absence of inert gas.

Table 1. Optimization of the reaction under Rh-catalysis^a

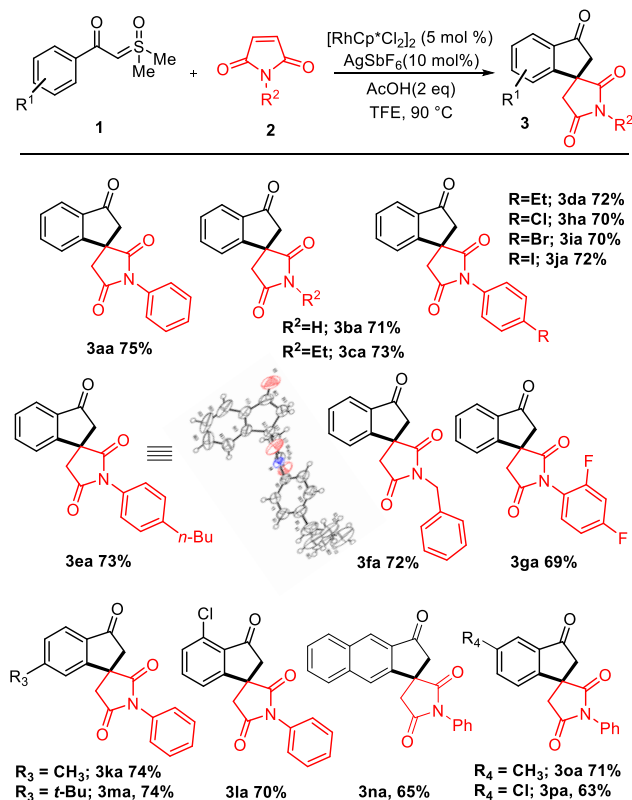


| Entry | Silver salt (10 mol %) | Additive (2 eq.) | Solvent | Temp (°C) | Yield (%) ^[b] |
|-----------------|-------------------------------|------------------|---------|-----------|--------------------------|
| 1 | AgSbF ₆ | AcOH (0.5 eq.) | TFE | 90 | 20 |
| 2 | AgSbF ₆ | AcOH (1.0 eq.) | TFE | 90 | 40 |
| 3 | AgSbF ₆ | AcOH (1.5 eq.) | TFE | 90 | 60 |
| 4 | AgSbF ₆ | AcOH (2.0 eq.) | TFE | 90 | 75 |
| 5 | AgBF ₄ | AcOH | TFE | 90 | 50 |
| 6 | AgOAc | AcOH | TFE | 90 | 20 |
| 7 | AgOTf | AcOH | TFE | 90 | 30 |
| 8 | AgSbF ₆ (20 mol %) | AcOH | TFE | 90 | 74 |
| 9 | AgSbF ₆ (30 mol %) | AcOH | TFE | 90 | 63 |
| 10 | AgSbF ₆ | PivOH | TFE | 90 | 45 |
| 11 | AgSbF ₆ | NaOAc | TFE | 90 | 40 |
| 12 | AgSbF ₆ | AcOH | DCE | 90 | 20 |
| 13 | AgSbF ₆ | AcOH | DMF | 90 | Trace |
| 14 | AgSbF ₆ | AcOH | EtOAc | 90 | 20 |
| 15 | AgSbF ₆ | AcOH | DMSO | 90 | No reaction |
| 16 | AgSbF ₆ | AcOH | PhCl | 90 | No reaction |
| 17 | AgSbF ₆ | AcOH | Toluene | 90 | 50 |
| 18 | AgSbF ₆ | AcOH | THF | 90 | 75 |
| 19 | AgSbF ₆ | AcOH | TFE | 100 | 70 |
| 20 | AgSbF ₆ | AcOH | TFE | 120 | 65 |
| 21 | AgSbF ₆ | AcOH | TFE | 80 | 65 |
| 22 | AgSbF ₆ | AcOH | TFE | 70 | 50 |
| 23 | None | AcOH | TFE | 90 | 25 |
| 24 | AgSbF ₆ | None | TFE | 90 | 20 |
| 25 ^c | AgSbF ₆ | AcOH | TFE | 90 | 30 |

Reaction conditions: ^a**1a**(0.25mmol), **2**(0.375 mmol), [Rh(Cp*Cl₂)₂] (5 mol%), AgSbF₆, (10 mol%), AcOH (2 eq.), N₂(g), TFE (1.5 ml), 90 °C, 12 to 22h. ^bIsolated yield, ^cAbsence of nitrogen gas.

We carried out the next investigations at optimal standard conditions (entry 8) to explore the scope of this [4+1] annulation reaction as regards to both the aryl sulfoxonium ylides and the maleimides (Scheme 2). The model ylide **1a** reacted with *N*-H maleimide to give the desired spiro-lactone **3ba** in 71% yield,

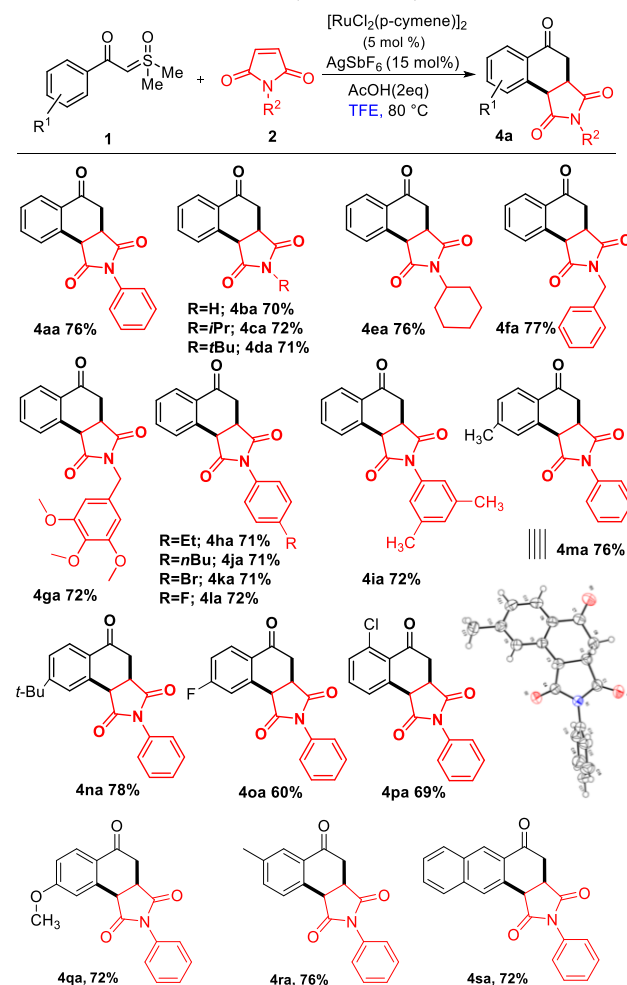
similar to the one obtained with the *N*-phenyl maleimide **3aa** (75%). Subsequently, we tried with *N*-alkyl substituted maleimide to give the desired product **3ca** in 73% yield. Then, we performed reactions with alkyl containing *N*-phenyl substituted maleimides and we were pleased to obtain the desired products **3da-3ea**, as well as the benzyl derivative **3fa** in 72%-73% yields. In the next series, we employed *N*-aryl substituted maleimides with halogens on the aromatic moiety. They similarly afforded the corresponding annulated spiro products **3ga-3ha-3ia** and **3ja** in fair yields (69% to 72%). We also explored the reaction of a sulfoxonium ylide with a methyl and *t*-butyl added in *para* position on the aromatic ring with *N*-phenyl maleimide, affording the annulated spiro product **3ka** in 74% yield and **3ma** in 74% yield. Satisfyingly, the sulfoxonium ylide with a chloro in *ortho* to the ketone reacted as well to give the desired annulated spiro-product **3la** in 70% yield. In addition, naphthol substitution furnished the anticipated spiro-product **3na** in 65% yield. The reactions with *meta*-substituted sulfoxonium ylide with electron donating and withdrawing groups furnished the desired spiro product **3oa** and **3pa** in 71% and 63% respectively. All these heterocycles have spectral and analytical data in agreement with the proposed structures. In addition, the structure of **3ea** has been confirmed by X-Ray crystallographic studies (see Supplementary Information).



Scheme 2. Synthesis of spiroindanones with sulfoxonium

ylides and maleimides via Rh (III) catalysed [4+1] carbonylation.

In parallel to previous studies, we have also explored the reaction of these two components, in the presence of a Ru (II) catalyst: $[\text{RuCl}_2(\text{p-cymene})]_2$. After optimization of the reaction conditions (see the Supporting Information for details), we were delighted to find that the reaction of the sulfoxonium ylide **1a** and *N*-phenyl maleimide in presence of 5 mol % Ru (II) catalyst with 2 eq. of acetic acid and 15 mol% of AgSbF_6 in TFE at 80 °C for 14h afforded in 76% yield the [4+2] annulated product **4aa**, fully characterized by its spectral and analytical data. Then, we explored the substrate scope of this [4+2] annulation reaction with several aryl sulfoxonium ylides and various *N*-substituted maleimides (Scheme 3).

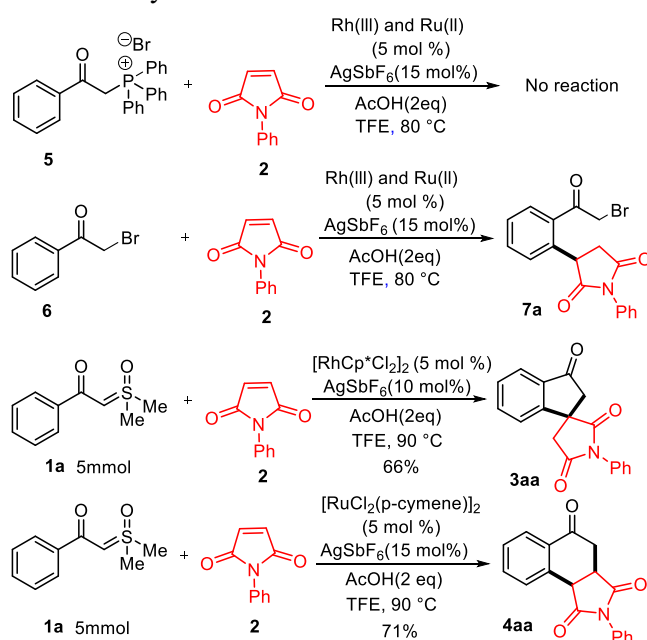


Scheme 3. Synthesis of benzoisindoles from sulfoxonium ylides and maleimides via Ru (II) catalysed [4+2] carbonylation.

First, sulfoxonium ylide **1a** reacted well with *N*-H maleimide affording **4ba** in 70% yield. Next, the same ylide reacted smoothly with two *N*-alkyl substituted maleimides to give the desired products **4ca** - **4da** in 72%-71% yield, and with the *N*-cyclohexyl derivative

affording **4ea** in 76% yield. The reaction of **1a** worked accordingly well with two *N*-benzyl maleimides to afford **4fa** and **4ga** in 77% and 72% yield respectively. Similarly, the reaction of **1a** went on smoothly with four different *N*-arylmaleimides to give **4ia**, **4ja**, **4ka**, and **4la** in 71%-72% yields. Finally, this annulation reaction was performed also with five other sulfoxonium ylides. For those bearing electron donating in *para* position of the aromatic group, the desired compounds **4ma**, **4na**, **4qa**, **4ra** and **4sa** were obtained in similar 72-78% yields. The structure of **4ma** was confirmed by X-Ray crystallography.^[18] For the ylides, possessing electron-withdrawing substituents in *para* position the awaited compounds **4oa** and **4pa** were obtained in slightly lower yields (60% and 69% respectively).

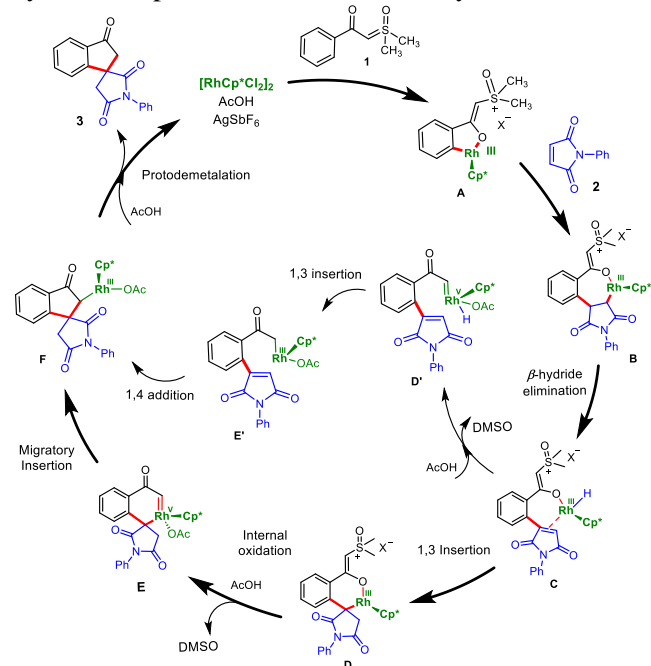
In the control experiments (Scheme 4), the sulfoxonium ylide proved to be a key directing group for the reaction with maleimide leading to the spiro-lactones and indanones. Similar reactions were performed starting with phosphonium derivative^[17] **5** and in that case, no reaction occurred (without any traces of **3aa** or **4aa**). Interestingly under our standard reaction conditions, phenacyl bromide **6** reacted with *N*-phenyl maleimide furnishing the phenacyl directed Rh (III) and Ru (II) catalyzed arene alkylation product **7a** in 60 % yield with no Heck type adduct formation. Again, no traces of **3aa** or **4aa** were observed during latter reactions. Finally, we demonstrated that the reaction can be performed on gram scale (5 mmol) too under standard conditions furnishing the spiro-compound **3aa** in 66% yield and the annulated product **4aa** in 71% yields.



Scheme 4. Control experiments

Based on the experiments and preceding literature^[13,14] on Rh(III) catalysis the following plausible

mechanism has been proposed (Scheme 5). The ylide **1** forms a five membered rhodacycle ring **A** after C-H activation followed by the concerted metalation deprotonation. Then, a seven membered rhodacycle **B** is formed by the insertion of maleimide onto **A** and the intermediate **C** is generated by the β -hydride elimination of **B**. At this point, two pathways appear possible to obtain the final product. In pathway-1 the intermediate **C** leads to the 6-membered rhodacycle **D** by the 1,3-insertion of hydride. Next, it leads to intermediate **E** by elimination of DMSO and internal oxidation of Rh (III) to Rh (V). Then, the intermediate **F** is generated by migratory insertion. In pathway-2, the intermediate **C** generates the hydride **D'** by elimination of DMSO and internal oxidation. Next, **D'** leads to the formation of **E'** by a 1,3-insertion, and an intramolecular 1,4-addition generates the intermediate **F**. In both pathways, the desired product **3** is generated by the final proto-demetalation of **F** by AcOH.

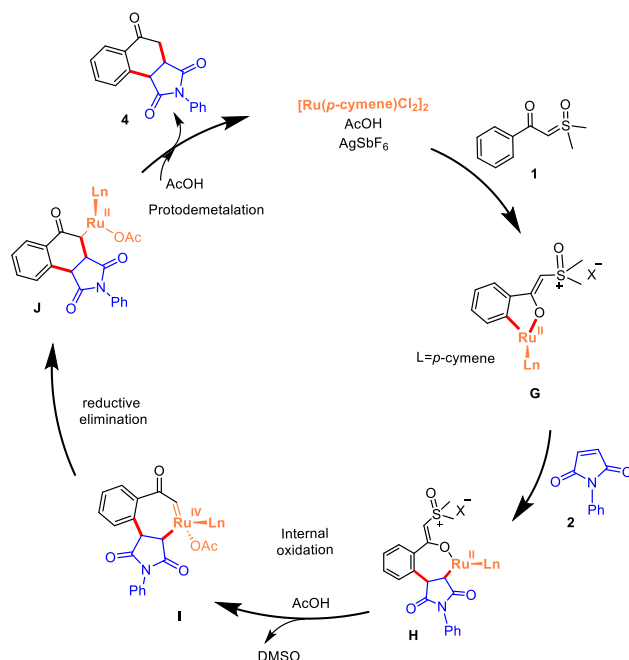


Scheme 5. Plausible mechanism for C-H activation followed by [4+1] carbo-annulation

In the case of Ru (II) we did not obtain the same [4+1] carbo-annulated products as before with the rhodium catalyst, but instead we obtained benzoisindole-type products through a [4+2] carbo-annulation and we can propose a mechanism for this process, as indicated in Scheme 6. The ylide **1** forms a five membered chelated intermediate **G** by a concerted metalation deprotonation process and then it leads to intermediate **H** by the insertion of maleimide. The internal oxidation of Ru (II) to Ru (IV) and the elimination of DMSO leads to the formation of intermediate **I**. Next, a reductive elimination gives **J** which, after proto-demetalation generate the final product **4**.

The preference of Rh (III) catalyst towards spiro product may be attributed to a greater Lewis acidity of

Rhodium with smaller ionic radius (0.665 Å) and therefore it is electron deficient compared to Ruthenium. Thus, *int-B* can undergo β -hydride elimination and Rh immediately gets attached to the carbon atom by 1,3 insertion leading to the formation of the spiro *int-F*. However, looking at the plausible mechanism of Ru catalysed annulation has offered no similar possibility.



Scheme 6. Plausible mechanism for C-H activation followed by [4+2] carbo-annulation

In conclusion, we have developed a new strategy to synthesize both complex spiroindanone-type molecules and benzoisindole derivatives by taking advantage of the capabilities of sulfoxonium ylide to act as directing group as well as carbene source in C-H activation/functionalization reactions, followed by transition metal-mediated carbo-annulations with maleimide derivatives. In the case of the Ru (II)-catalysed C-H activation the benzoisindole derivatives **4** were obtained in a [4+2] annulation process with *N*-phenyl maleimide. To the best of our knowledge, it is the first example of such a reaction of ruthenium-catalysed reaction with sulfoxonium ylides. On the other hand, the directed Rh (III)-catalysed [4+1] tandem annulation provided the complex spiro molecules **3**. Herein subsequently, rhodium-catalysed [4+1] carbo-annulation reaction with sulfoxonium ylides has been realized in the absence of any additional metal oxidant such Cu(OAc)₂, previously reported.^[11d] The divergent reactivities of Ru(II) and Rh(III) catalyst systems on similar substrates (sulfoxonium ylides and maleimides) furnishing very different scaffolds via C-H activation followed by [4+2] or [4+1] carbo-annulation has been projected establishing a comprehensive mechanistic pathways, highlighting the possible reasons for a fundamentally different behaviour of these catalytic cycles. Both annulation reactions have a broad scope and they are

performed under oxidant free and mild reaction conditions. In addition, this work not only expands the application of sulfoxonium ylides in C-H activation, but also provides a new strategy for switchable access to one-pot construction of polyheterocyclic scaffolds.

Experimental Section

General procedure for the synthesis of compounds (3aa-3la): An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with [Cp*₂Rh(Cl)₂]₂ (0.0125 mmol, 5 mol %), AgSbF₆ (0.025 mmol, 10 mol %), AcOH (2 equiv) in a small portion TFE (0.5 ml), **1** (0.25 mmol, 1.0 equiv), maleimide **2** (0.375 mmol, 1.5 equiv) followed by TFE (1.5 ml). The tube was then flushed several times with nitrogen gas, to ensure removal of moisture and placed in a pre-heated silicon oil bath at 90°C and the reaction mixture was stirred at the same temperature for 10-16 h under nitrogen atmosphere. After completion of the reaction (monitored by TLC), the reaction mixture was then allowed to cool down to room temperature and filtered through the short silica bed with (100-200 mesh) and concentrated under reduced pressure. The resulted crude mixture was purified by flash column chromatography ethyl acetate/hexane (30:70) on silica gel afforded **3** as white colour solid in 65-75% isolated yield.

General procedure for the synthesis of compounds (4aa-4pa): An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with [Ru(p-cymene)Cl₂]₂ (0.0125 mmol, 5 mol %), AgSbF₆ (0.025 mmol, 15 mol %), AcOH (2 equiv) in a small portion TFE (0.5 ml), **1** (0.25 mmol, 1.0 equiv), maleimide **2** (0.375 mmol, 1.5 equiv) followed by TFE (1.5 ml). The tube was then flushed several times with nitrogen gas, to ensure removal of moisture and placed in a pre-heated silicon oil bath at 80°C and the reaction mixture was stirred at the same temperature for 10-16 h under nitrogen atmosphere. After completion of the reaction (monitored by TLC), the reaction mixture was then allowed to cool down to room temperature and filtered through the short silica bed with (100-200 mesh) and concentrated under reduced pressure. The resulted crude mixture was purified by flash column chromatography, ethyl acetate/hexane (30:70) on silica gel afforded **4** as white colour solid in 60-78% isolated yields.

X-Ray Data: Deposition numbers CCDC 2314310 (for **3ea**), and CCDC 2314306 (for **4ma**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Acknowledgements

V. R. thank CSIR for fellowship. Y. B. K. thank CSIR-IICT for financial support. All the authors thanks the Indo-French "Joint Laboratory for Natural Products and Synthesis toward Affordable Health" program for the platform to carry out the finding jointly. We sincerely thank the Department of Analytical and Structural Chemistry at CSIR-IICT for all the analytical support and especially for X-ray crystal data. We gratefully acknowledge the overall support by CSIR-IICT to perform the research (IICT/Pubs./2024/124)

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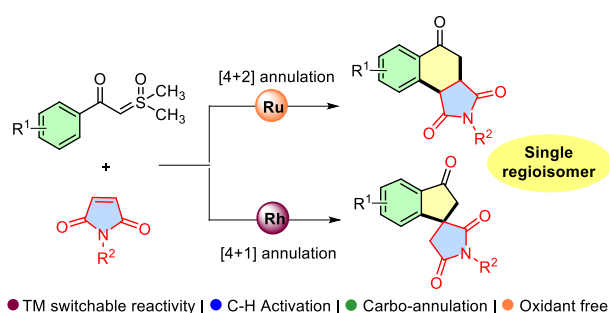
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COMMUNICATION

Controlled Ru (II) and Rh (III) catalysed [4+2] & [4+1] carbo-annulations via C–H Activation using Sulfoxonium ylides and Maleimides: Facile access to Fused Benzoisindoles and Spiroindanones

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Raju Vaggu,^{a,c} Akhila Muraharikar,^a Yenamareddy Bhargav Kumar,^b Yasari Soujanya,^{b,c} René Grée^d and Saibal Das^{a,c,*}



A new strategy has been developed to synthesize both complex spiroindanone-type molecules and benzoisindole derivatives by taking advantage of the capabilities of sulfoxonium ylide to act as directing group as well as carbene source in the C-H activation/functionalization reactions, followed by transition metal-mediated carbo-annulations in [4+2] or [4+1] with maleimide derivatives