Stereoselective synthesis of 2-spirocyclopropyl-indolin-3-ones through cyclopropanation of aza-aurones with tosylhydrazones

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A simple and efficient approach for the synthesis of 2-spirocyclopropyl-indolin-3-ones is herein described. The method involves a diasteroselective cyclopropanation of aza-aurones with tosylhydrazones, selected as versatile carbene sources, and represents a remarkable synthetic alternative to get access to this class of C2-spiropseudoindoxyl scaffolds. The reactions proceed in the presence of a base and catalytic amounts of benzyl triethylammonium chloride and well-tolerate a broad range of substituents on both aza-aurones and tosylhydrazones to afford a series of C2-spirocyclopropanated derivatives in high yields. In addition, selected functional groups transformations of the final products were explored demonstrating the synthetic potential of these indole-based derivatives.

Introduction

(*Z*)-2-ylideneindolin-3-ones, namely aza-aurones, represent an interesting class of heterocyclic enones showing a broad range of applications in medicinal chemistry and in material sciences. Therefore, aza-aurones demonstrated potential applications as antimalarial,[1,2] antituberculotic[3] and anticancer agents[4] and, because of their peculiar photochemical behaviour, they have recently been studied as photoswitching systems.[5–8] However, aza-aurones are also known as powerful synthetic building blocks for cycloaddition reactions both as heterocyclic dienes, furnishing a "four-atom" unit,[9–12] or by reacting at the exocyclic double bond, providing an easy access to 3-oxo-2-spiroannulated indolines (spiropseudoindoxyls) by [*n*+2] processes.[13,14] (Figure 1).

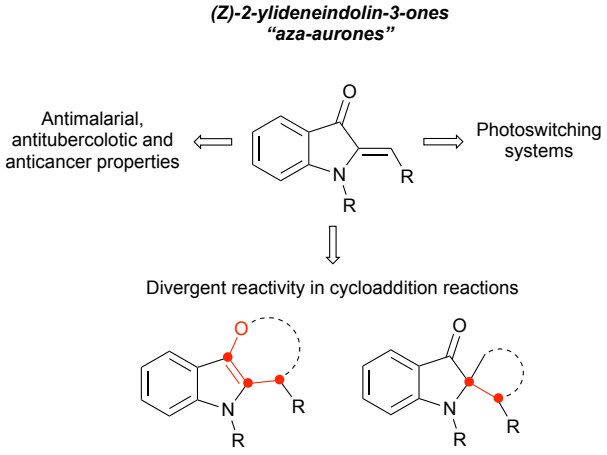

Figure 1 The importance of aza-aurones in different research area

In the latter case, the obtained spiropseudoindoxyls represent an important class of organic derivatives. They are in fact widely distributed in the core scaffold of various natural alkaloids,[15–17] and more recently they have also found useful applications as fluorescent dyes.[18] Despite these relevant properties, the synthesis of 3-oxo-2-spiroannulated indolines has been scarcely developed if compared to the C3-spirocyclic analogues (spiroxoindoles).[19] As recently described in the comprehensive review by Peng and Huang,[14] C2-spiropseudoindoxyl skeleton can be generated mainly from three different classes of substrates: nitrogen-containing phenylacetylenes, C2-functionalized indoles or indolines and, as reported before, from aza-aurones. However, most reported examples deal with the synthesis of spiroannulated systems containing the indole nucleus spirofused with five-membered ring systems[20,21] and the extension to larger or smaller rings is less common. For example, only few methods have been reported for the synthesis of 2-spirocyclopropane-indolin-3-ones.[14] Thus, the described syntheses are based on Krapcho decarboxylation-ring

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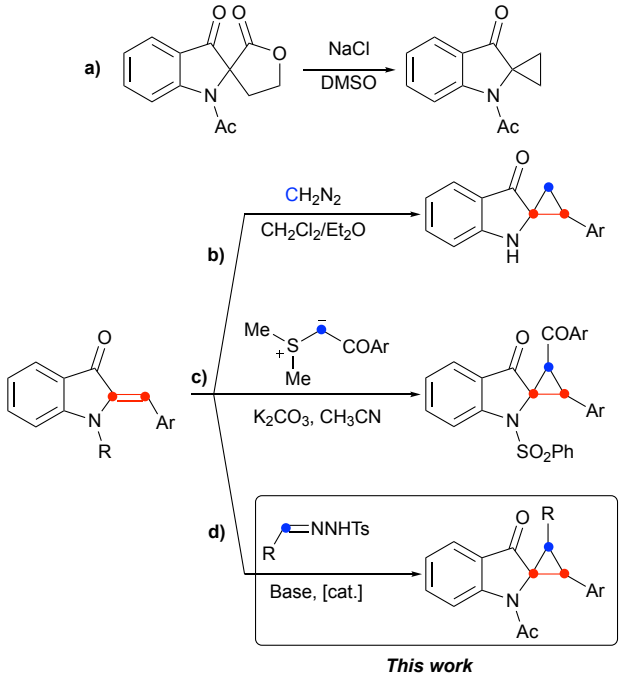
contraction reactions of spirocyclolactones in the presence of NaCl, (scheme 1a)[22,23] or, starting from aza-aurones, on the formal [2+1] cycloadditions with diazomethane[24] or sulfur ylides (Scheme 1b,c).[25] Therefore, taking into account these premises and our research program directed towards the synthesis and functionalisation of complex indole derivatives,[26–34] including C2-spiropseudoindoxyl derivatives,[35] we decided to explore an alternative strategy to synthetise 2-spirocyclopropane-indolin-3-ones, based on the direct cyclopropanation of aza-aurones with a suitable carbene source (Scheme 1d). To this scope, among the various possibilities,[36,37] tosylhydrazones were selected as carbene precursors. Tosylhydrazones are in fact readily accessible and highly stable molecules and represent a valuable alternative for the generation of an aryl diazo compound directly *in situ* by a base-mediate Bamford-Stevens reaction.[38] Therefore, the obtained diazo compounds can lead to the formation of a carbene intermediate by thermal decomposition or in the presence of a transition metal.[38–41] In addition, tosylhydrazones demonstrated to be particularly reactive in the cyclopropanation of electron-poor alkenes,[42–44] a process that is hardly achieved in the presence of diazo carbonyl compounds under metal catalysis.[45]

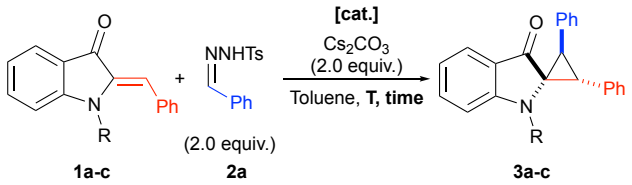


Scheme 1 Synthetic methods to obtain 2-spirocyclopropane-indolin-3-ones and our proposed approach.

Results and discussion

In order to verify the feasibility of our idea, we tested the reaction between aza-aurone **1a** and tosylhydrazone **2a** in the presence of Cs_2CO_3 as base and under different catalytic conditions. The obtained results are summarised in Table 1.

Table 1 Optimisation of reaction conditions[a]

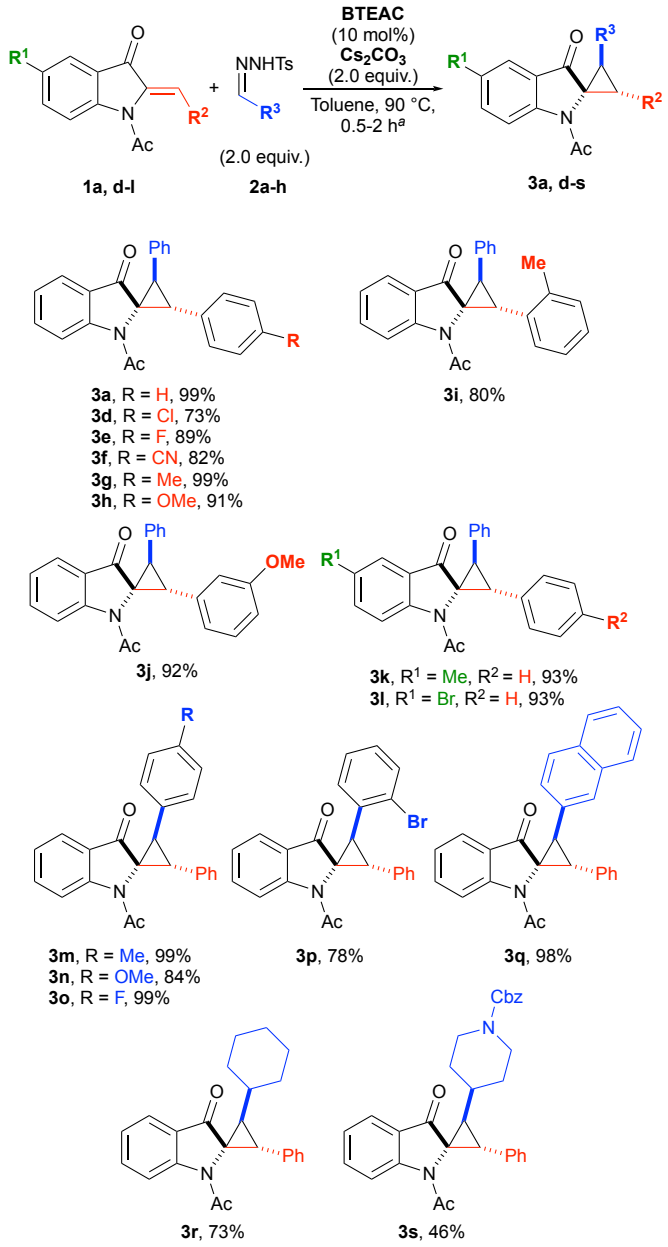


1a-c **2a** **3a-c**

Entry	R	Cat. (mol%)	T, °C	t, h	Yield, (%)[b,c]
1	Ac	$Rh_2(OAc)_4$ (2.5 mol%)	40	22	n.r.
2	Ac	BTEAC (10 mol%) $Rh_2(OAc)_4$ (2.5 mol%)	40	22	76
3	Ac	BTEAC (10 mol%)	40	22	57
4	Ac	BTEAC (10 mol%) $Rh_2(OAc)_4$ (2.5 mol%)	90	0.5	97
5	Ac	$Rh_2(OAc)_4$ (2.5 mol%)	90	1	99
6	Ac	$Rh_2(OAc)_4$ (1 mol%)	90	3	99
7	Ac	BTEAC (10 mol%)	90	0.5	99
8	Ac	BTEAC (10 mol%)[d]	90	22	<5
9	H	BTEAC (10 mol%)	90	22	n.r.
10	Bn	BTEAC (10 mol%)	90	22	n.r.

[a]Reaction conditions: **1a-c** (0.1 mmol), **2a** (0.2 mmol), catalyst (1-10 mol%), Cs_2CO_3 (0.2 mmol) in toluene (2 ml) at the stated temperature and reaction time. [b]Isolated yield. [c]dr > 20:1. [d]K_2CO_3 (0.2 mmol) was used as base.

At the outset, we performed our model reaction using $Rh_2(OAc)_4$ as catalyst, in toluene at 40 °C. However, no product was formed and unreacted **1a** was recovered unaltered even after 22 h (entry 1). Looking at the earlier reports on cyclopropanation of electron-poor systems with tosylhydrazones as carbene source,[42,44] 10 mol% of benzyltriethylammonium chloride (BTEAC), a phase transfer catalyst, were added to the reaction mixture under the previously reported conditions. In this way we were able to isolate 2-spirocyclopropyl-indolin-3-one **3a** in 76% yield as single diasteroisomer (entry 2). In addition, BTEAC demonstrated to be active as catalyst, even without rhodium(II), and the reaction proceed at the same temperature for 22 h to yield 57% of **3a** (entry 3). An increase of the temperature up to 90 °C, revealed to be beneficial for the formation of the product and, using $Rh_2(OAc)_4$ and BTEAC as catalysts, **3a** was isolated in 97% yield after 0.5 h (entry 4). The sole $Rh_2(OAc)_4$, employed in 2.5 or 1 mol%, worked efficiently at the same temperature, providing **3a** quantitatively even if after a prolonged reaction time of 1 and 3 hours, respectively (entries 5-6). Finally, a comparable quantitative yield was also obtained after 0.5 h with the only use of 10 mol% of BTEAC. The use of a different base than Cs_2CO_3 was also evaluated, however the employment of K_2CO_3 had a detrimental effect on the reaction outcome and only traces of product could be observed in ^{1}H-NMR of the crude. Finally, we tested the reactivity of NH free and N-benzyl aza-aurones **1b** and **1c** but, in both cases any cyclopropanation product **3b** or **3d** was formed and, after 22 h, a complex mixture of unidentifiable products was recovered. Therefore, the conditions reported in entry 7, were selected to explore the scope of the reaction between differently substituted aza-aurones **1a-i** and tosylhydrazones **2a-h** (Scheme 2).



Scheme 2 Scope of the reaction between aza-aurones **1a, d-l** and tosylhydrazones **2a-h**. Reaction conditions: **1a, d-l** (0.1 mmol), **2a-h** (0.2 mmol), BTEAC (10 mol%), Cs_2CO_3 (0.2 mmol), in toluene at 90 °C for 0.5-2 h. Isolated yields are reported. dr > 20:1. [a]For reaction times see ESI.

Modifications of aza-aurone were firstly evaluated and aza-aurones bearing electron-withdrawing or electron-donating groups on alkenyl aryl ring or on indole scaffold were prepared. The presence of a halogen atom in 4-position of the benzylidene group was tolerated and corresponding spirocyclopropyl indolin-3-ones **3d** and **3e** were obtained in slightly reduced yields of 73% and 89%, respectively. In addition, other electron-withdrawing groups such as a 4-ciano substituent could also be introduced to furnish product **3f** in 82% yield. Similarly, an electron-donating substituent, such as a methyl or a methoxy group, did not influence the reaction outcome and products **3g** and **3h** were obtained almost quantitatively. The introduction of these two last substituents in other positions of the benzylidene ring was also verified. In particular the reaction conducted using 2-methylbenzylidene indolin-3-one afforded spirocyclopropanated indoline **3i** in 80% yield even if after a longer reaction time (1h, see ESI), while 3-methoxybenzylidene derivative led to the formation of **3j** in 92% yield. 5-substituted aza-aurones were also tested under optimised conditions and, similarly to before, we confirmed the robustness of our methodology by isolating 5-methyl-spirocyclopropyl and 5-bromo-spirocyclopropyl derivatives **3k** and **3l** both in excellent 93% yield. Next, we focused our attention on the modification of tosylhydrazones and, **2b-h** were synthetised and used in the reaction with **1a**. The introduction of a substituent in 4-position of the tosylhydrazone phenyl ring did not produce any particular effect on the reaction result and 4-methyl and methoxy aryl substituted tosylhydrazones efficiently gave **3m** and **3n** in 99% and 84% yield, while 4-fluoro derivative led to the quantitative formation of **3o**. A slightly reduced yield was instead obtained when 2-bromo aryl substituted tosylhydrazone was employed, obtaining **3p** in 78% yield after 2 h. Other aromatic substituents, such a naphthyl ring, were also introduced leading to cyclopropanated indoline **3q** in 98% yield. Finally, we turned our attention in the employment of aliphatic tosylhydrazones. In particular cyclohexyl tosylhydrazone reacted with **1a** to yield **3r** with a lower, but still good, 73% yield, while spirocyclopropyl-indoline **3s**, substituted with a N-Cbz piperidine, was synthetised from the corresponding tosylhydrazone with moderate 46% yield.

In all the cases, synthetised spirocyclopropyl-indolin-3-ones were isolated as single diasteroisomer, which relative configuration was assigned on the base of 2D-NMR analyses of product **3r** and unambiguously confirmed by X-ray diffraction analysis of a single crystal performed on **3q** (Figure 2).

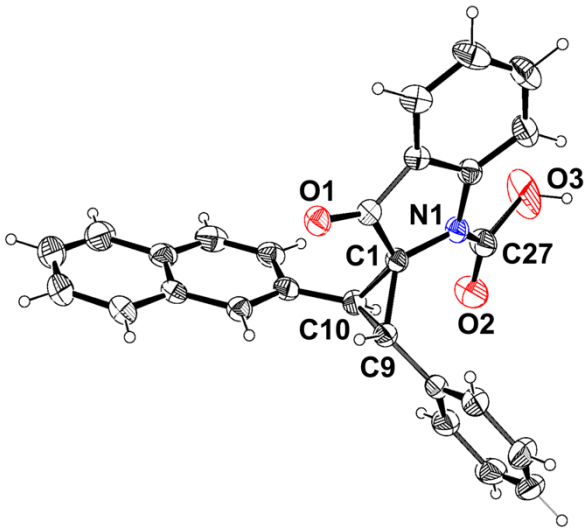
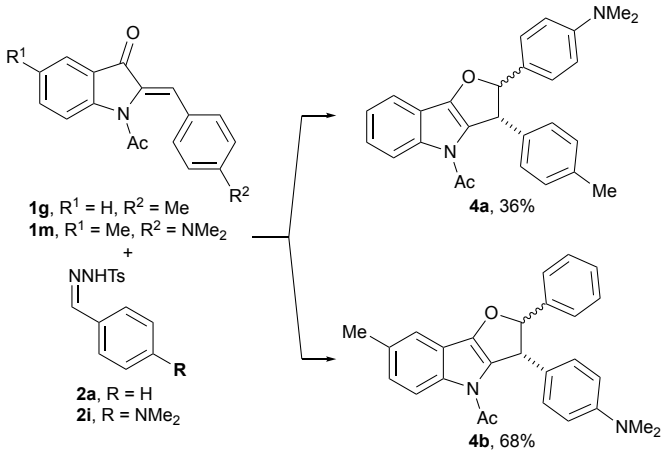
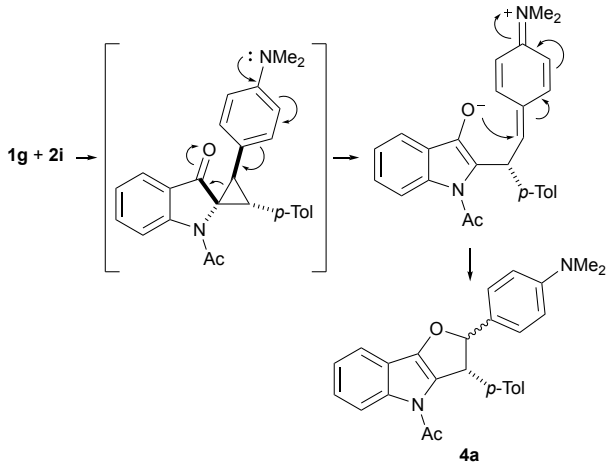


Figure 2 ORTEP representation of the X-ray crystal structure of **3q.** Ellipsoids drawn at 30% probability.

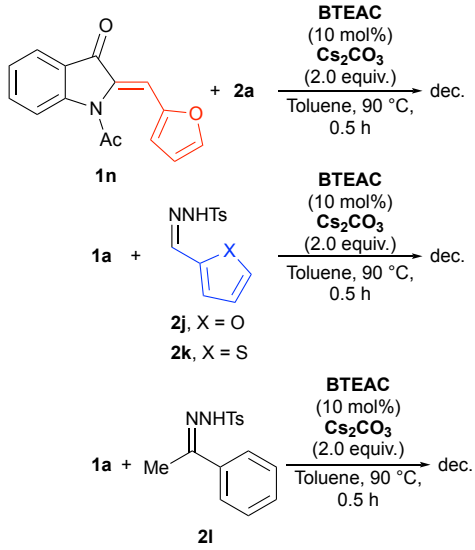
Despite the general robustness and good functional group tolerance of the proposed cyclopropanation reaction, some limitations regarding the nature of usable aza-aurones and tosylhydrazones were highlighted during the study of the reaction scope. In particular, with the aim of verifying the effect of other electron-donating groups, we synthetised dimethylamino-substituted aza-aurone **1m** and dimethylamino-substituted tosylhydrazone **2i** and we subjected them to a reaction, under optimised conditions, with **1g** or **2a**, respectively. Nevertheless, in both cases, instead of the corresponding cyclopropanated spirocyclic indolinones, unexpected dihydrofuroindolyl derivatives **4a** and **4b** were formed, probably through a mechanism that involves cyclopropanation reaction, followed by cyclopropane ring-opening induced by the presence of a strong electron-donating amino group. Then, nucleophilic attack of carbonyl anion on arylidene double bond, led to cyclisation and formation of the products (Scheme 3).[46,47] Dihydrofuroindoles **4a** and **4b** were isolated as single diastereoisomers, however the reciprocal positions of the substituents could not be assigned on the basis of 1D and 2D NMR analysis due to the lack of unambiguous. diagnostic signals.





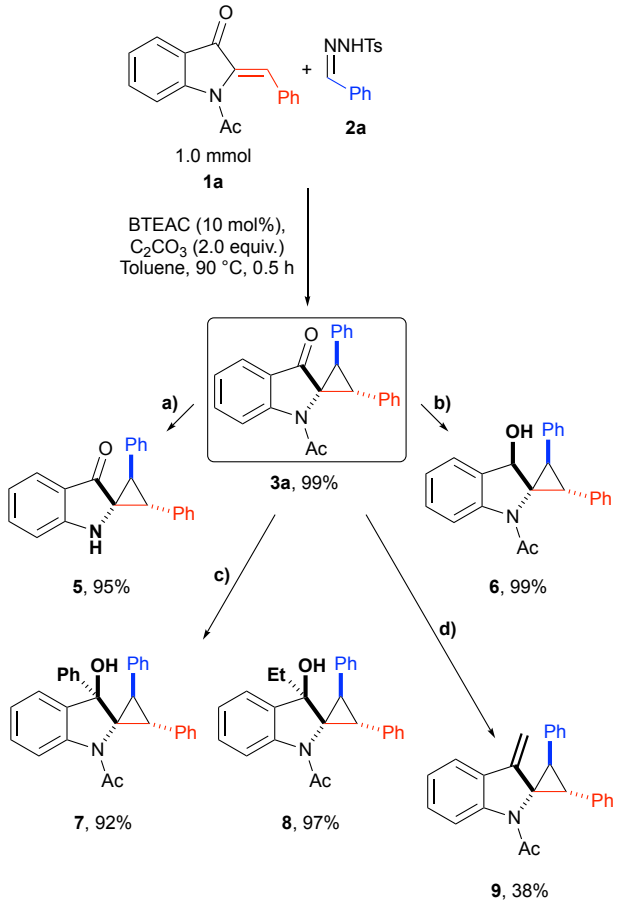
Scheme 3 Reaction with dimethylamino substituted aza-aurone **1m** or tosylhydrazone **2i.**

Furthermore, heterocyclic substituents both on aza-aurone and tosylhydrazones were not tolerated and any product arising from furyl-subsituted aza-aurone **1n** or furyl-/thiophenyl-derived tosylhydrazones **2j**,**k** could be detected at the end of the reaction. Similarly, tosylhydrazone **2l**, synthetised from the acetophenone, led to a complex mixture of decomposition products when employed under optimised conditions instead than **2a** (Scheme 4).



Scheme 4 Observed limitations of the proposed methodology employing heterocyclic substituted aza-aurone **1n** or tosylhydrazones **2j-2l**.

Having prepared a series of spirocyclopropyl-indolin-3-ones, we got interested in verifying their synthetic behaviour by realising some useful and selective transformations of their functional groups. To this scope we firstly prepared **3a**, selected as benchmark reagent, in 1.0 mmol scale and, even working on a ten times bigger scale, we isolated the product in quantitative yield. Then, **3a** was subjected to N-deacylation, reduction of the C-3 keto group, addition of Grignard reagents and Wittig reaction (Scheme 5).



Scheme 5 Scale-up of the reaction for the synthesis of **3a** and selected transformations performed on this product.

As first reaction, the removal of the N-protecting acyl group was performed under basic conditions, and employing NaOH in methanol, NH-free derivative **5** was isolated in 95% yield. The reduction of the ketone at C-3 position was then realised with sodium borohydride in EtOH at room temperature, obtaining the corresponding alcohol **6** in 99% yield as single diasteroisomer. With the aim to increase the molecular complexity of **3a** by the formation of new C-C bonds, we next tested the addition of Grignard reagents, such as phenyl or ethyl magnesium bromide, on the ketone moiety and we were able to prepare **7** and **8** in excellent 92% and 97% yield, respectively. Noteworthy, also in this case, products were isolated as single diasteroisomers. Thus, in order to establish the relative configuration of the newly formed hydroxy groups, both products **6** and **8** were subject to 2D-NMR analysis, which revealed selective NOE interactions between OH proton and one of the protons of the cyclopropane ring (Figure 3, see ESI for details). Finally, **3a** could also be employed in a Wittig reaction with methyltriphenylphosphonium bromide to afford the corresponding alkene **9** in modest 38% yield.

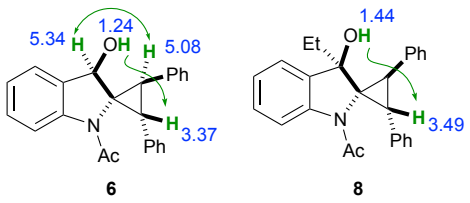
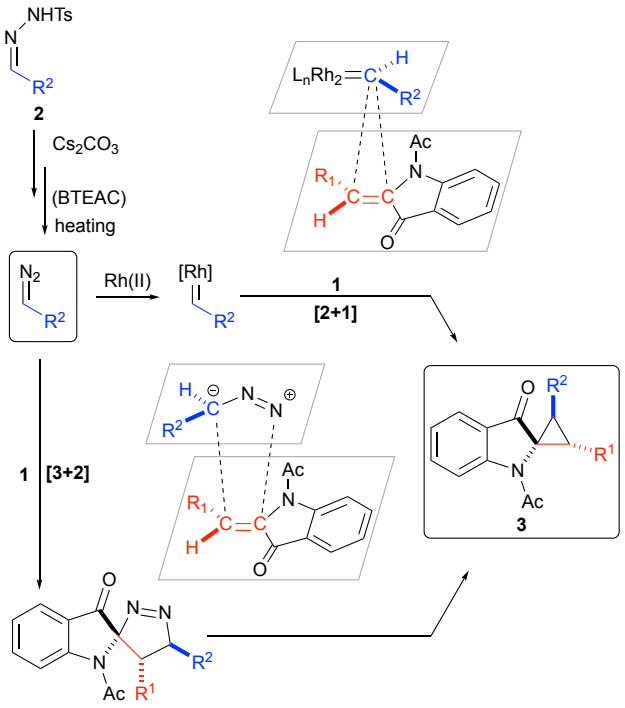


Figure 3 Diagnostic NOE interactions observed in products **6** and **8**.

Mechanistically, we believe that the synthesis of spirocyclopropyl-indolin-3-ones is in accordance with other reports on cyclopropanation of electron-poor alkenes with tosylhydrazones.[42] In particular, after deprotonation of tosylhydrazone by means of the base, the warming of the reaction mixture led to the *in situ* generation of the corresponding aryl diazo compound. In this step, addition of a phase transfer catalyst generally favours the passage of the anion from the solid to the liquid phase, allowing to operate under milder conditions and improving reaction performance.[38] Then, the formation of cyclopropanated product could be ascribed to two alternative mechanisms depending on the presence of metal catalyst or of sole BTEAC. In the rhodium catalysed reaction, the corresponding rhodium carbene is formed from diazo compound and the direct reaction of this species with the double bond of aza-aurone would lead to **3**. On the other hand, in the non-metal catalysed approach the formation of the product should proceed via diasteroselective [3+2] cycloaddition to give a pyrazoline intermediate followed by nitrogen extrusion. In both cases, the observed diasteroselectivity could be dictated by the relative approach of the alkene and of the carbene or of diazo compound aimed to minimise steric repulsion between bulkier groups (Scheme 6).



Scheme 6 Hypothesised reaction mechanism.

Conclusions

In summary, we designed a novel approach to synthetise spirocyclopropyl indolin-3-ones by direct diasteroselective cyclopropanation reaction at the exocyclic double bond of aza-aurones. This transformation was realised using tosylhydrazone as safer and convenient carbene source and proceeded in the presence of a base and of a phase transfer catalyst. The proposed method tolerated a broad range of substitutions on both of aza-aurones and tosylhydrazones affording a series of spirocyclopropyl-indolin-3-ones in high and reproducible yields. In addition, the synthetic utility of obtained products was verified by selective functional groups elaborations performed on a representative substrate, which yielded the desired products efficiently. Thus, we believe that this study provides an advantageous synthetic alternative to access highly functionalized C2-spirocyclopropanated scaffolds under easy-to-perform reaction conditions.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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