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Solvent-free and room temperature microwave-assisted direct C7 allylation of indolines *via* sequential C−H and C−C activation†

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A Ru or Rh-catalyzed efficient and atom-economic C7 allylation of indolines with vinylcyclopropanes was developed *via* sequential C−H and C−C activation. A wide range of substrates were well tolerated to afford the corresponding allylated indolines in high yields and *E/Z* selectivities under microwave irradiation. The obtained allylated indolines could further undergo transformations to afford various value-added chemicals. Importantly, this reaction proceeded at room temperature under solvent-free conditions.

The development of sustainable methodologies is attractive for access to complex molecular architectures in organic chemistry.[1] In recent years, various non-conventional techniques, such as microwave irradiation, sonochemistry, mechanical grinding and photochemistry, have achieved remarkable success.[2] In particular, microwaves have shown unique advantages with regards to reaction times, energy efficiency, temperature, and reaction media.[3] On the other hand, transition-metal-catalyzed activation of C−H[4] and C−C[5] bonds has been considered as an ideal method for the formation of C−C and C−X bonds. Nevertheless, transition-metal-catalyzed C−H or C−C bond activation under the above non-conventional techniques remains to be explored. It is thus highly imperative to develop a practical strategy in combination of C−H or C−C activation and microwave irradiation.[6]

Recently, there have significant advances in C−H activation technology by merging C−H functionalization with challenging C−C cleavage strategies.[7] Since the pioneering work by Bergman and co-workers[8] on the sequential C−H and C−C bond activation, many research groups, including Dong,[9] Ackermann,[10] Li,[11] Cramer,[12] and others[13] have contributed to C−H/C−C activation. In this content, certain small strained rings are often utilized as an effective synthons to undergo ring-opening reactions driven by strain-release energy.[14] Very recently, VCPs (vinylcyclopanes) have been reported as allyl reagents to access various (hetero)aromatic derivatives through sequential C−H and C−C activation (Scheme 1a–d).[15]

As a continuation of our interest in chelation-directed reactions and novel methods for C−H functionalization,[16] we herein report a Ru or Rh-catalyzed C-7 allylation of indolines under

microwave irradiation using VCPs as the allylating agents (Scheme 1e). This transformation possesses great synthetic potential from the viewpoint of green and sustainable chemistry. Notable features of our protocol include (1) C−H/C−C activation with VCPs by microwave irradiation, (2) broad substrate scope with good regio- and *E/Z* selectivities, (3) high atom economy, and (4) high efficiency (2 h) at room temperature under solvent-free conditions.

We initiated our investigation by choosing indoline **1a** and VCP **2a** as model substrates under microwave irradiation conditions (Table 1). To our delight, the allylated product **3aa**
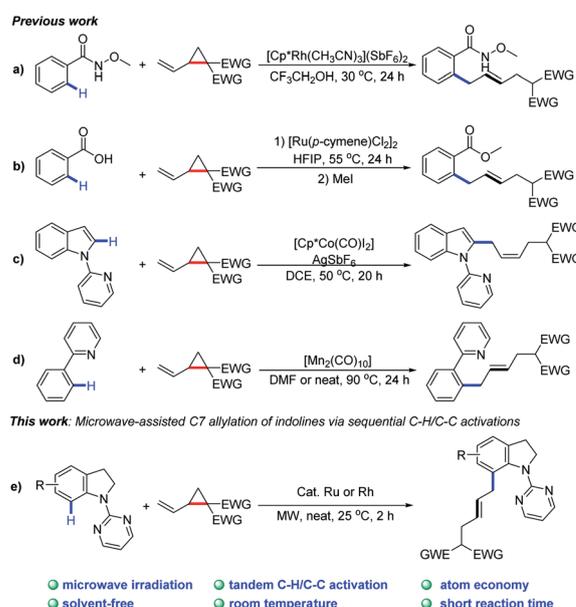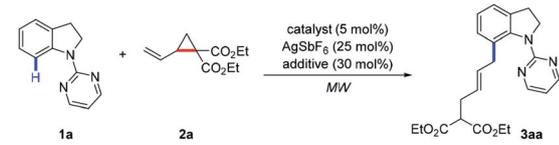

Scheme 1 Sequential C−H/C−C activations using VCPs.

College of Chemistry, Zhengzhou University, No. 100 of Science Road, Zhengzhou, Henan 450001, P. R. China. E-mail: zhuxinju@zzu.edu.cn; mpsong@zzu.edu.cn

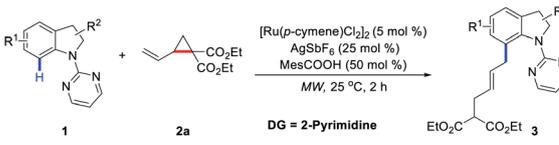† Electronic supplementary information (ESI) available. See DOI: 10.1039/d0ra02016h

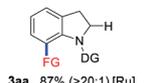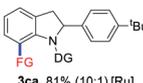**Table 1** Optimization of the reaction conditions[a]

Scheme: **1a** + **2a** (vinyl cyclopropane with CO$_2$Et, CO$_2$Et) → catalyst (5 mol%), AgSbF$_6$ (25 mol%), additive (30 mol%), MW → **3aa** (EtO$_2$C, CO$_2$Et)

Entry	Catalyst (mol%)	Additive (mol%)	T (°C)	Yield (%)
1	[Ru(p-cymene)Cl$_2$]$_2$	AdCOOH	90	40
2	RuCl$_3$·3H$_2$O	AdCOOH	90	N.R
3	[Cp*RuCl$_2$]$_2$	AdCOOH	90	N.R
4	[Ru(p-cymene)Cl$_2$]$_2$	MesCOOH	90	47
5	[Ru(p-cymene)Cl$_2$]$_2$	AcOH	90	40
6	[Ru(p-cymene)Cl$_2$]$_2$	NaOAc	90	20
7	[Ru(p-cymene)Cl$_2$]$_2$	PivONa·H$_2$O	90	21
8	[Ru(p-cymene)Cl$_2$]$_2$	DABCO	90	Trace
9[b]	[Ru(p-cymene)Cl$_2$]$_2$	MesCOOH	90	57
10[b]	[Ru(p-cymene)Cl$_2$]$_2$	MesCOOH	70	68
11[b]	[Ru(p-cymene)Cl$_2$]$_2$	MesCOOH	50	83
12[b]	[Ru(p-cymene)Cl$_2$]$_2$	MesCOOH	25	65
13[b,c]	[Ru(p-cymene)Cl$_2$]$_2$	MesCOOH	25	87 (>20 : 1)[e]
14[c,d]	[Cp*Rh(CH$_3$CN)$_3$](SbF$_6$)$_2$	AdCOOH	80	78 (10 : 1)[e]

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), [Ru(p-cymene)Cl$_2$]$_2$ (5 mol%), additive (30 mol%), MW, 1 h, 90 °C. [b] MesCOOH (50 mol%). [c] t = 2 h. [d] [Cp*Rh(CH$_3$CN)$_3$](SbF$_6$)$_2$ (8 mol%). [e] The E : Z ratio was determined by ^{1}H NMR analysis. MW = microwave irradiation.

Table 2 Substrate scope of indolines[a,b]

Scheme: **1** (R^1, R^2 substituted indoline with pyrimidine DG) + **2a** (vinyl cyclopropane CO$_2$Et, CO$_2$Et) → [Ru(p-cymene)Cl$_2$]$_2$ (5 mol %), AgSbF$_6$ (25 mol %), MesCOOH (50 mol %), MW, 25 °C, 2 h, DG = 2-Pyrimidine → **3** (EtO$_2$C, CO$_2$Et)
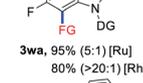
Product	Yield [Ru]	Yield [Rh]
3aa (H)	87% (>20:1) [Ru]	78% (10:1) [Rh]
3ba (Me)	96% (>20:1) [Ru]	92% (11:1) [Rh]
3ca (^{t}Bu-phenyl)	81% (10:1) [Ru]	68% (6:1) [Rh]
3da (Ph)	90% (7:1) [Ru]	81% (5:1) [Rh]
3ea (Cl-phenyl)	65% (5:1) [Ru]	58% (4:1) [Rh]
3fa (Br-phenyl)	75% (3:1) [Ru]	52% (3:1) [Rh]
3ga (Me)	91% (>20:1) [Ru]	90% (8:1) [Rh]
3ha (Me)	90% (>20:1) [Ru]	91% (13:1) [Rh]
3ia (OMe)	92% (>20:1) [Ru]	86% (13:1) [Rh]
3ja (OBn)	93% (>20:1) [Ru]	74% (>20:1) [Rh]
3ka (F)	94% (>20:1) [Ru]	72% (>20:1) [Rh]
3la (Cl)	96% (>20:1) [Ru]	76% (>20:1) [Rh]
3ma (Br)	54% (>20:1) [Ru]	56% (14:1) [Rh]
3na (Me)	86% (11:1) [Ru]	84% (11:1) [Rh]
3oa (MeO)	90% (>20:1) [Ru]	76% (14:1) [Rh]
3pa (BnO)	80% (>20:1) [Ru]	87% (>17:1) [Rh]
3qa (F)	91% (10:1) [Ru]	81% (>20:1) [Rh]
3ra (Cl)	90% (>20:1) [Ru]	84% (>20:1) [Rh]
3sa (Br)	73% (>20:1) [Ru]	54% (13:1) [Rh]
3ta (MeO$_2$C)	60% (4:1) [Ru]	71% (>20:1) [Rh]
3ua (Me, Ph)	82% (5:1) [Ru]	70% (6:1) [Rh]
3va (Cl, Ph)	89% (>20:1) [Ru]	72% (>20:1) [Rh]
3wa (F)	95% (5:1) [Ru]	80% (>20:1) [Rh]
3xa (Cl)	91% (14:1) [Ru]	71% (>20:1) [Rh]
3ya (Br)	78% (>20:1) [Ru]	65% (>20:1) [Rh]
3za (tetrahydroquinoline)	71% (3:1) [Ru]	64% (4:1) [Rh]
3a'a (carbazole)	78% (10:1) [Ru]	59% (13:1) [Rh]
3b'a (pyridyl DG)	84% (3:1) [Ru]	59% (5:1) [Rh]
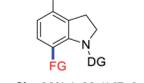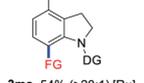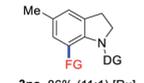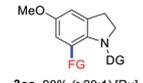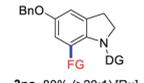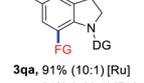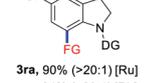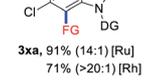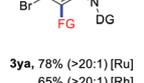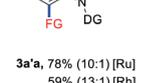
[a] Reaction conditions [Ru]: **1** (0.2 mmol), **2a** (0.4 mmol), [Ru(p-cymene)Cl$_2$]$_2$ (5 mol%), MesCOOH (50 mol%), AgSbF$_6$ (25 mol%), MW, 25 °C, 2 h; [Rh]: **1** (0.2 mmol), **2a** (0.4 mmol), [Cp*Rh(CH$_3$CN)$_3$](SbF$_6$)$_2$ (8 mol%), AdCOOH (30 mol%), AgSbF$_6$ (20 mol%), MW, 80 °C, 2 h. [b] The E : Z ratio was determined by ^{1}H NMR analysis. MW = microwave.

was isolated in 40% yield in the presence of [Ru(p-cymene)Cl$_2$]$_2$ (5 mol%), AgSbF$_6$ (25 mol%), and AdCOOH (30 mol%) at 25 °C for 1 h (Table 1, entry 1). Other ruthenium salts, such as [Cp*RuCl$_2$]$_2$ and RhCl$_3$·3H$_2$O, were also investigated, which showed no catalytic reactivity (Table 1, entries 2 and 3). Subsequently, the effects of various additives, including MesCOOH, AcOH, NaOAc, PivONa·H$_2$O, and DABCO, were screened, which indicates that MesCOOH was the best choice to afford **3aa** in 47% yield (Table 1, entry 4). Increasing the loading of MesCOOH from 30 mol% to 50 mol% resulted in an increased yield (57%) of **3aa** (Table 1, entry 9). To improve reaction efficiency, the temperature range was evaluated (Table 1, entries 10–12). It was found that product **3aa** was obtained in 83% yield at 50 °C (Table 1, entry 11) and a comparable result could still be achieved at 25 °C (Table 1, entry 12). Finally, the reactivity could be further increased when the reaction was performed at 25 °C for 2 h to deliver the desired product **3aa** in 87% yield with excellent E/Z selectivity (Table 1, entry 13). To demonstrate the unique reactivity of Ru catalyst in this protocol, [Cp*Rh(CH$_3$CN)$_3$](SbF$_6$)$_2$ was also tested to give a slightly lower yield with decreased E/Z selectivity at higher temperature (Table 1, entry 14).

Under the optimized reaction conditions with the ruthenium catalyst, the substrate scope of indolines **1** was investigated (Table 2). C2-alkyl and aryl substituted indolines were initially examined to give products **3ba–fa** in 65–96% yields. Indoline bearing methyl group at the C3 position was also tolerated to afford product **3ga** in 91% yield. For C4 and C5 substituted indolines, both electron-donating (Me, OMe, and OBn) and electron-withdrawing (F and Cl) groups were well compatible to provide the corresponding allylated products **3ha–la** and **3na–ra** in 80–96% yields. The presence of bromo and ester functionalities on substrates led to products **3ma** (54%), **3sa** (73%), and **3ta** (60%) in slightly decreased yields. In addition, disubstituted indolines were also tested to deliver products **3ua** and **3va** in 82% and 89% yields, respectively. Notably, C6-halogen substituted indolines exhibited high activity to afford products **3wa–ya** in 78–95% yield. However, C6-methyl substituted substrate turned to be unsuccessful probably due to steric hindrance effect. Moreover, quinoline and carbazole substrates were also employed to afford the allylated products **3za** and **3a'a** in 71% and 78% yields. Finally, a series of other directing groups such as acetyl, pyridyl, and others were also tried (see in

the ESI†). While **3b′a** was obtained in 84% yield, others failed to give the coupling products. Overall, indolines with a variety of functionalities ranging from C2 to C6 positions could react with VCP **2a** to afford the allylated products in good yields with high *E*/*Z* selectivities under the [Ru(*p*-cymene)Cl₂]₂ catalytic system. On the other hand, when [RhCp*(CH₃CN)₃](SbF₆)₂ was employed as the catalyst instead of Ru analogue, decreased yields accompanied with lower *E*/*Z* selectivities was observed in most cases.

Encouraged by the above results, the scope of VCPs **2** was also explored to further examine the generality of the current C–C/C–H activation strategy with the ruthenium catalyst (Table 3). Various ester-substituted VCPs, including CO₂Me, *t*BuCO₂, *i*PrCO₂, and BnCO₂ groups, were successfully coupled with indoline **1a** to afford products **3ab–ad** in 74–90% yields with up to 20 : 1 *E*/*Z* selectivity. For VCPs having CF₃CH₂CO₂ and lactone activating groups, products **3af** and **3ag** were isolated in decreased yields. When CN and PhSO₂ functionalities were introduced into VCP moiety, the corresponding products **3ah–ak** were obtained in 56–78% yields with decreased *E*/*Z* values. Furthermore, the substituted indolines could also furnish the corresponding products (**3fe**, **3kc**, and **3sc**) in 74–90% yields. Finally, Rh catalytic system could give the corresponding products in comparable yields and *E*/*Z* ratios.

To evaluate the practical utility of the current methodology, a gram-scale reaction between **1a** (6.0 mmol) and **2a** (12.0 mmol) was performed under standard conditions, which delivered the allylated product **3aa** in 74% yield (Scheme 2).

Table 3 Substrate scope of VCPs[a,b]

[a] Reaction conditions [Ru]: **1** (0.2 mmol), **2a** (0.4 mmol), [Ru(*p*-cymene)Cl₂]₂ (5 mol%), MesCOOH (50 mol%), AgSbF₆ (25 mol%), MW, 25 °C, 2 h; [Rh]: **1** (0.2 mmol), **2a** (0.4 mmol), [Cp*Rh(CH₃CN)₃](SbF₆)₂ (8 mol%), AdCOOH (30 mol%), AgSbF₆ (20 mol%), MW, 80 °C, 2 h. [b] The *E* : *Z* ratio was determined by ¹H NMR analysis. [c] 40 °C. [d] [Ru] CH₂Cl₂ (0.5 mL), 40 °C; [Rh] : MeOH (0.5 mL). MW = microwave.
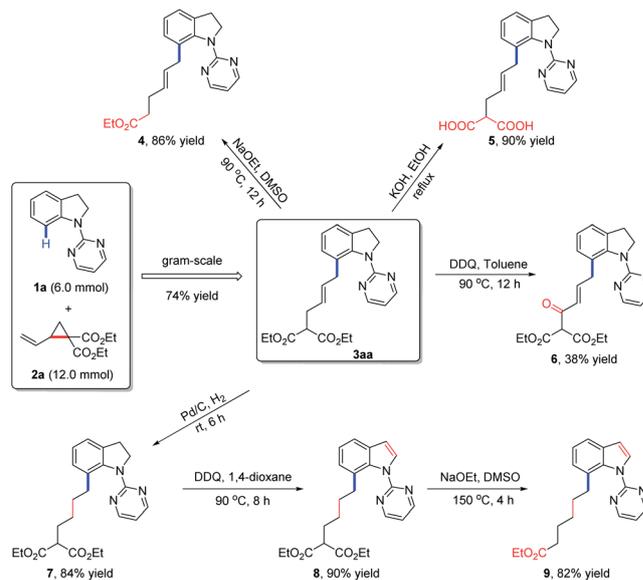

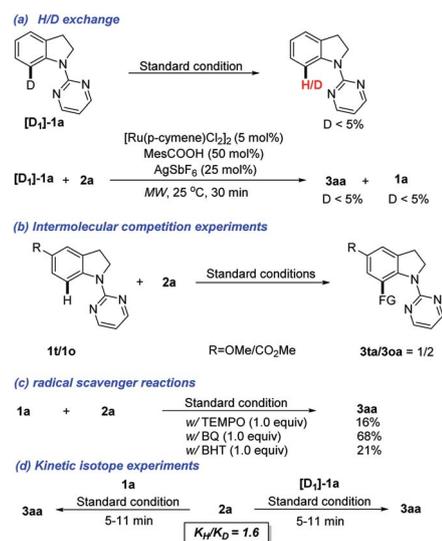**Scheme 2** Gram-scale reaction and further derivatization of product **3aa**.

Meanwhile, the derivatizations of **3aa** were also conducted to highlight the synthetic importance of allylated indolines. Firstly, **3aa** could undergo decarboxylation in the presence of NaOEt in DMSO to afford compound **4** in 86% yield. Under the condition of KOH in EtOH, the hydrolysis product **5** was obtained in 90% yield. Secondly, in the presence of DDQ in toluene, product **3aa** could be oxidized to compound **6** in 38% yield. Thirdly, hydrogenation of **3aa** under Pd–C/H₂ conditions would afford a reduced product **7**, which could further undergo oxidation and decarboxylation transformations to give indole derivatives **8** and **9** in 90% and 82% yields, respectively.

To gain insights into the reaction mechanism, a series of control experiments were conducted (Scheme 3). In the H/D
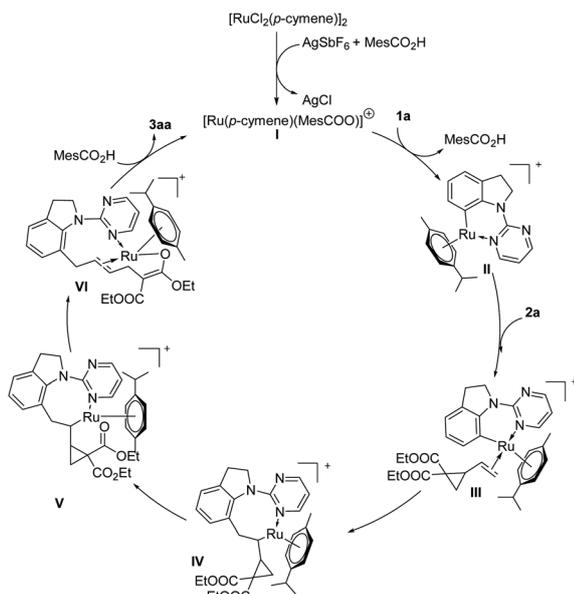

Scheme 3 Control experiments.

Scheme 4   Proposed reaction mechanism.

exchange experiment, the deuterated [D]-1a was prepared and subjected to the standard conditions. It was found that only negligible amount of deuterium was detected for retrieved 1a. When 2a reacted with [D]-1a for 30 min, a similar result with a distinct D/H exchange was also observed (Scheme 3a). Next, the intermolecular competition experiment between substituted indolines 1o and 1t was conducted. Methoxyl-substituted allylated indoline 3oa was isolated as the major product, indicating that indolines bearing electron-donating groups are more reactive (Scheme 3b). When a radical quencher, such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), 2,6-di-*tert*-butyl-4-methylphenol (BHT), or benzoquinone (BQ), was added, the allylation reaction was suppressed with product 3aa obtained in a decreased yield (Scheme 3c). These results could't indicate that a non-radical mediated reaction pathway. Finally, the KIE values observed in parallel reactions suggest that the C–H bond cleavage is not involved in the limiting step (Scheme 3d).

On the basis of above discussion and related reports,[17] a plausible catalytic cycle was proposed (Scheme 4). A pyrimidine-directed C–H activation between indoline 1a and an *in situ*-generated Ru cationic complex I gives a six-membered ruthenacycle II. Coordination of intermediate II with VCP 2a provides intermediate III, which undergoes 1,2-migratory insertion to afford an ruthenium intermediate IV. Then oxygen coordinates to Ru metal center to form intermediate V. After C–C cleavage of VCP 2a, intermediate VI will be generated, followed by protonation to deliver the desired product 3aa and regenerate the active catalyst species I.

Conclusions

In summary, we have successfully demonstrated a [Ru(*p*-cymene)Cl$_2$]$_2$-catalyzed C7 allylation of indolines with VCPs as the allylating reagents *via* a sequential C–H/C–C process. This protocol is applicable to broad substrate scope with good functional group compatibility and high *E/Z* selectivity. The practical applications of allylation transformation are highlighted through gram-scale production and multiple derivatizations. Notably, the use of microwave irradiation under room temperature and solvent-free conditions makes this protocol more valuable and operational convenience, which provides a new insight for the formation of indoline derivatives.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Notes and references

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