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REGULAR ARTICLE

Regioselective synthesis of pyrrole and indole-fused isocoumarins catalysed by N^O chelate ruthenium(II) complex

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Abstract. Heterocyclic compounds containing pyrrole and indole-fused isocoumarins were obtained from a one-pot synthesis *via* annulations of N-heterocyclic carboxylic acids and alkynes with N^O chelate ruthenium(II) complex, [RuCl($PySO_3$)(*p*-cymene)] ($PySO_3$ = 2-pyridinesulfonate) in the presence of $Cu(OAc)_2H_2O$. The reaction proceeds efficiently in DMF but can also be performed in other solvents such as dichloroethane, ^{t}AmOH, and water. The annulations reaction is regioselective when performed 1-methylpyrrole-2-carboxylic acid with 1-phenyl-1-propyne.

Keywords. Annulation reaction; isocoumarins; alkynes; ruthenium(II) catalyst; regioselection.

1. Introduction

Pyrrole and indole-fused N-heterocyclic compounds are found in several pharmacophores and bioactive compounds.[1,2] They are widely distributed in terrestrial and marine organisms and show various biological properties such as anti-microbial, antibiotic, antioxidant, anticancer and antitumor activities.[3–7] Interest for the development of synthetic methodologies of these heterocyclic scaffolds is inspired by their promising biological activities. There are several methods available for the synthesis of N-heterocyclic compounds. Among them, the transition metal-catalysed C–H bond functionalization of N-heterocyclic ring has emerged as an attractive and environmentally benign method for a ready accessing to various heterocyclic compounds.[8–11] Over the decades, tremendous progress has been made on the metal-catalysed direct C–C bond formation of aromatic compounds involving the activation of a normally unreactive aromatic C–H bond, specifically in terms of synthesis efficiency and minimizing chemical waste.[12] A wide range of functional groups such as ketones,[13,14] amines,[15] carboxylic acids[16] and amides[17,18] have been successfully used as a directing group in transition metal-catalysed C–H bond functionalization leading to various functional molecules. Initially, catalysts based on transition metals such as Pd and Rh have been used in these C–H bond functionalization of heterocycles.[19–24]

In recent years, sp^2-C–H bond functionalization using less expensive ruthenium(II) compounds were rapidly developed and their utility in several reactions such as arylation,[24–27] alkenylation[13,14,28] and annulation[29–35] reactions have been explored. Annulations reaction involving C–H/N–H and C–H/O–H bond cleavage resulting in varieties of the heterocyclic compounds have been reported with Cu,[36] Pd,[37] Rh[38–40] and Ru.[29–35] Specifically, Ackerman[29] and Jeganmohan's[10] groups have studied ruthenium(II)-catalysed annulations of amide or carboxylic acid with alkynes but the catalyst used was mainly based on [(*p*-cymene)$RuCl_2$]$_2$ and requires additives such as KPF_6 or $AgSbF_6$.

Notably, as mentioned above, ruthenium-catalysed annulations of N-heterocyclic acids and alkynes were based on [(*p*-cymene)$RuCl_2$]$_2$ catalyst and the reactions have employed organic solvents, although a few reports mentioned also in water.[32] Carboxylate assisted catalysis is well documented in arene ruthenium(II) systems[30,41–43] involving mostly [$RuCl_2$(*p*-cymene)]$_2$ catalysts. A limited number of reports describe on C-H bond functionalization catalysed by ruthenium(II)

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compounds containing a sulfonate ligand.[44] Herein, we wish to explore annulations of 1-methylpyrrole-2-carboxylic acid (**2**) or 1-methylindole-3-carboxylic acid (**3**) and substituted alkynes (**4a–e**) using ruthenium(II) catalyst containing a pyridine sulfonate ligand, [RuCl($PySO_3$)(*p*cymene)](**1**) ($PySO_3$ = 2-pyridinesulfonate) without additive but in the presence of an oxidant. Spectroscopic characterization of [RuCl($PySO_3$)(*p*-cymene)] (**1**) and regioselective annulations of 1-methylpyrrole-2-carboxylic acid (**2**) or 1-methylindole-3-carboxylic acid (**3**) with unsymmetrical alkyne has been described.

2. Experimental

2.1 *General remarks*

All reactions were performed under air in closed Schlenck tubes unless otherwise noted. The solvent used were of analytical grade and used as received. $RuCl_3 3 \cdot H_2O$ was purchased from Arrora Matthey Ltd., India. Diphenylacetylene, 1-phenyl-1-propyne, 3-hexyne, 4-octyne, 2-butyne, 1-methylpyrrole-2-carboxylic acid, 1-methylindole-3-carboxylic acid, $Cu(OAc)_2H_2O$, KOAc and Pivalic acid were obtained from Sigma Aldrich, India. Distilled water was degassed with nitrogen prior to use. NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer at 300.13 (^{1}H), 75.47 MHz (^{13}C) with $SiMe_4$ as internal references and coupling constants were given in Hertz. Mass spectra were recorded using QSTAR-TOF MS/MS of Applied Biosystems instrument or Waters UPLC-MSMS(Xevo TQD) mass spectrometers. Microanalysis (CHNS) was performed using Vario micro Cube Elemental Analyser. The precursor complex [$RuCl_2$(*p*-cymene)]$_2$ was prepared according to a published procedure.[45]

2.2 *Crystal structure analysis and refinement*

X-ray quality crystals of the complex **1** were grown by slow diffusion of hexane into a dichloromethane solution of 1. The X-ray diffraction data were collected at 100(2)°K on a Nonius Kappa CCD FR590 single crystal X-ray diffractometer, using MoKα radiation (λ = 0.71073 Å). Crystal-to-detector distance was 30 mm and exposure time was 20 seconds per degree. Data collection was 99.6% complete to 25° in θ. The structure was solved by direct methods (SHELXS, SIR97),[46] and refined by full matrix least-squares base on F^2 using (SHELXL 97).[47] All non-hydrogen atoms were refined anisotropically while hydrogen atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with C–H distances in the range 0.95–1.0 Å. Refinement converged at a final R = 0.0165 (for observed data F), and wR_2 = 0.0415 (for unique data F^2). The data collection parameters, selected bond lengths and angles are presented in Table S1 and Table S2 (Supplementary Information), respectively.

2.3 *Preparation of [RuCl (p-cymene)($PySO_3$)](**1**)*

A dried Schlenck tube was charged with pyridine sulfonic acid ($PySO_3H$, 0.342 mmol) and KO^{t}Bu (0.342 mmol). After addition of methanol, the reaction mixture was allowed to stir for 30 min then [$RuCl_2$(*p*-cymene)]$_2$ (0.1 g, 0.163 mmol) was added. The reaction mixture was stirred under nitrogen for 24 h. The yellow suspension became a clear red solution within a few minutes. As the reaction progress, the solution became cloudy then an orange-yellow solid appeared. The solid was centrifuged and washed with diethyl ether (2 x 10 mL). The additional compound was obtained from the supernatant by subsequently drying, then dissolving the residue in dichloromethane followed by precipitation with hexane.

Orange yellow solid; yield: 106 mg (76%); Anal. Calcd. for $C_{15}H_{18}ClNO_3RuS$: C 41.96; H 4.22; N 3.26; S 7.45. Found: C 41.86; H 4.11; N 3.58; S 7.24. FTIR (KBr, cm^{-1}): 3051, 2974, 1591, 1288, 1436; ^{1}H NMR ($CDCl_3$, δ): 8.76 (d, 1H, J = 5.1), 8.01 (m, 1H), 7.88 (d, 1H, J = 7.5), 7.57 (t, 1H), 5.78 (d, 1H, J = 5.7), 5.69 (d, 1H, J = 5.7), 5.59 (d, 1H, J 6.0), 5.49 (d, 1H, J = 6.0), 3.05 (m, 1H), 2.22 (s, 3H), 1.36 (t, 6H, J = 7.2); ^{13}C NMR ($CDCl_3$, δ): 157.34, 153.57, 140.57, 127.84, 122.79, 103.97, 97.65, 82.10, 81.92, 81.64, 80.54, 30.96, 22.91, 21.65, 18.39; ESI-MS: 394.0051 (M-Cl)$^+$ calculated for $C_{15}H_{18}NO_3RuS$, found 394.0026.

2.4 *General procedure for ruthenium(II)-catalysed annulations of 1-methylpyrrole-2- carboxylic acid or 1-methylindole-3-carboxylic acid with alkynes in DMF*

A dried Schlenck tube was loaded with [RuCl(*p*-cymene)($PySO_3$)] (0.022 g, 0.05 mmol, 10 mol%), heterocyclic acid (**2** or **3**) (0.5 mmol), alkyne (0.65 mmol), $Cu(OAc)_2H_2O$ (0.149g, 0.75 mmol). The reaction mixture was stirred in DMF at 80 °C for 16 h under air. After which the reaction mixture was rotary evaporated. The residue was purified over silica gel column using petroleum ether and ethyl acetate as eluant to give the compounds **5** and **6** in up to 80% of isolated yield. Spectroscopic data of the compounds **5** and **6** are in accordance with those reported values.[23,32,34]

2.5 *General procedure for ruthenium(II)-catalysed annulations of 1-methylpyrrole-2- carboxylic acid or 1-methylindole-3-carboxylic acid with alkynes in water*

A dried Schlenck tube was loaded with [RuCl (*p*-cymene)($PySO_3$)] (0.022 g, 0.05 mmol), heterocyclic acid **2** or **3** (0.5 mmol), alkyne (1 mmol), $Cu(OAc)_2H_2O$ (0.199g, 1.0 mmol). The reaction mixture was stirred in water at 100 °C for 20 h under nitrogen. After which the reaction mixture was extracted with ethyl acetate (3 x 20 mL). The organic fractions were combined and treated with sodium sulfate and filtered, then dried in a rotary evaporator. The residue was purified over silica gel column using petroleum ether and ethyl acetate as eluant to give the compound **5** or **6**.

3. Results and Discussion

Annulations of *N*-methylpyrrole-2-carboxylic (**2**) acid and *N*-methylindole-3-carboxylic acid (**3**) with substituted alkynes (**4a–e**) was carried out using ruthenium(II) catalyst, [RuCl($PySO_3$)(*p*-cymene)] (**1**) in the presence of an oxidant, $Cu(OAc)_2H_2O$. Complex **1** was obtained in 76% yield by the reaction of $[RuCl_2(p\text{-cymene})]_2$ with 2-pyridinesulfonic acid in the presence of KO^{t}Bu (Scheme 1). Complex **1** was fully characterized by NMR spectroscopy, ESI-MS data and its solid state structure has been established by single crystal X-ray crystallography (Figure 1). The ^{1}H-NMR spectrum of **1** shows signals for a pyridine ring in the region of 7.88–8.75 ppm in addition to the signals for the coordinated *p*-cymene ligand. ESI-MS spectrum of **1** showed a peak at m/z 394.0026 corresponding to $[M\text{-}Cl]^+$. An ORTEP diagram of complex **1** is shown in Figure 1. Complex **1** crystallizes in triclinic space group $P\bar{1}$ and adopts the well-known piano stool configuration. The geometry around the ruthenium atom is regarded as pseudo-octahedral with the *p*-cymene ligand occupying three coordinate sites while the remaining three coordination sites are occupied by nitrogen, oxygen and chlorine atoms.

The annulations of **2** or **3** with various alkynes have been performed in both DMF and water as a solvent and the efficiency of the ruthenium(II) complex **1** was compared to that of $[RuCl_2(p\text{-cymene})]$.[32] When the reaction was performed using 1-methylpyrrole-2-carboxylic acid **2** (0.5 mmol), complex **1** (10 mol%), diphenylacetylene (1.1 equiv), and $Cu(OAc)_2H_2O$ (1.5 equiv.) in DMF under air afforded the desired product, 1-methyl-4,5-diphenylpyrano[3,4-*b*]pyrrol-7(1H)-one (**5a**) in 60% isolated yield (Table 1, entry 3). Under the similar reaction condition, the reaction performed with KOAc (20 mol%) gave a lower yield (Table 1, entry 4). Employing silver salt such as $AgSbF_6$ as additive did not boost the efficacy of the reaction, instead of decreased the catalytic efficacy (Table 1, entry 2). The presence of $Cu(OAc)_2H_2O$ as oxidant is essential since attempting the reaction with another oxidant such as $(NH_4)_2S_2O_8$ did not give any desired product

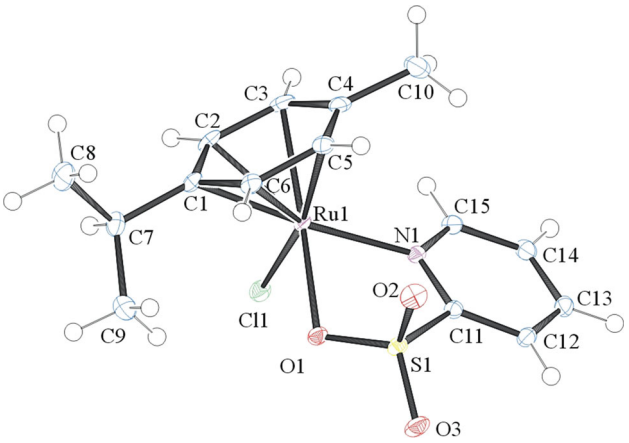
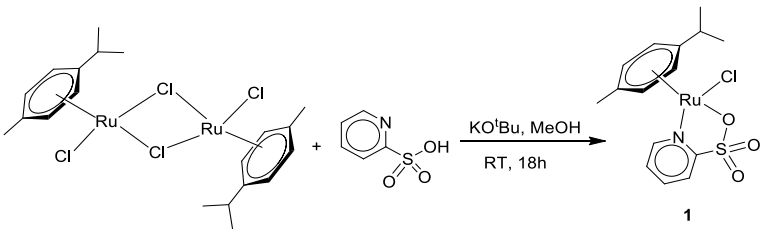


Figure 1. ORTEP diagram of [RuCl(*p*-cymene)($PySO_3$)] (**1**) with thermal ellipsoid at 50% probability.

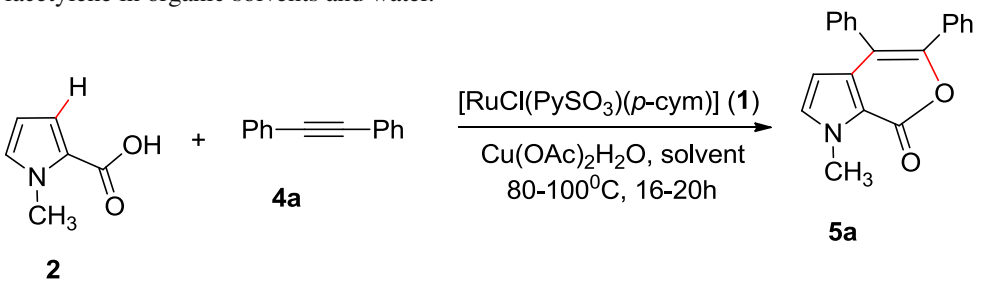
(Table 1, entry 6) indicating the reaction proceeds through carboxylate assisted ruthenium(II)-catalysed route.[33] The reaction performed in other organic solvents such as DCE and ^{t}AmOH, gave the desired product in lower yields (Table 1, entries 1 & 5).

Notably, the majority of annulations of alkynes and heterocyclic acids were performed in organic solvents using an additive.[10,29] Recently, we have reported annulations between heterocyclic acid and alkyne in water using the $[RuCl_2(p\text{-cymene})]_2$ as catalyst which proves to be highly efficient and regioselective.[32] This prompted us to evaluate efficacy of this ruthenium(II) complex, [RuCl($PySO_3$)(*p*-cymene)] (**1**) towards the annulations of heterocyclic acids and alkynes in water. In order to find the optimized reaction condition, we have tested the reaction for various reaction parameters in water (Table 1, entries 7–11). When the reaction was carried out using complex **1** (5 mol%) as catalyst, 1-methylpyrrole-2-carboxylic acid (0.5 mmol), alkyne (1.2 equiv.) and $Cu(OAc)_2H_2O$ (1.5 equiv.) in water (2 mL) under air for 20 h, gave the desired product **5a** in 25% isolated yield (Table 1, entry 7). An increased in catalyst loading to 10 mol% with 2 equiv. of diphenylacetylene boost the reaction giving upto 58% of **5a** (Table 1, entry 11). However, employing additives such as PivOH or KOPiv (20 mol%) did not make any significant change in the yield of the product (Table 1, entries 9



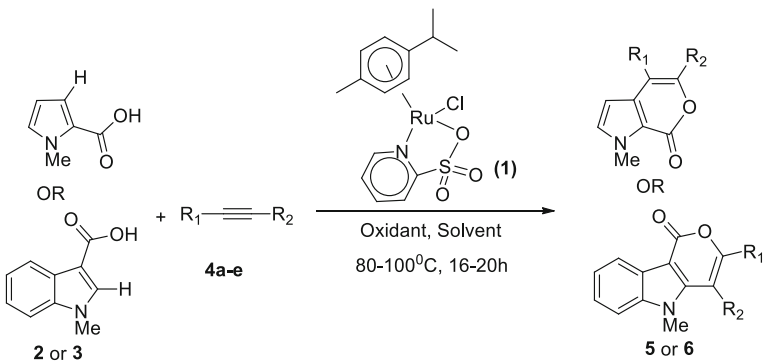
Scheme 1. Reaction pathway for the synthesis of complex 1.

Table 1. Optimization of reaction for ruthenium (II)-catalysed annulation of 1-methylpyrrole-2-carboxylic acid and diphenylacetylene in organic solvents and water.[a]



Entry	Oxidant	Additive	Solvent	Yield[b]
[1]	$Cu(OAc)_2H_2O$	$AgSbF_6$	DCE	54
[2]	$Cu(OAc)_2H_2O$	$AgSbF_6$	DMF	20
[3]	**$Cu(OAc)_2H_2O$**	**—**	**DMF**	**60**
[4]	$Cu(OAc)_2H_2O$	KOAc	DMF	58
[5]	$Cu(OAc)_2H_2O$	—	^tAmOH	35
[6]	$(NH_4)_2S_2O_8$	—	DMF	NR
[7][c]	$Cu(OAc)_2H_2O$	—	H_2O	25
[8]	$Cu(OAc)_2H_2O$	—	H_2O	54
[9]	$Cu(OAc)_2H_2O$	PivOH	H_2O	53
[10]	$Cu(OAc)_2H_2O$	KOPiv	H_2O	35
[11][d]	**$Cu(OAc)_2H_2O$**	**—**	**H_2O**	**58**
[12]	$Cu(OAc)_2H_2O$	$AgSbF_6$	H_2O	27

[a]Reaction conditions: Substrate (0.5 mmol), catalyst (0.05 mmol), diphenylacetylene (0.65 mmol, 1.2 equiv.), $Cu(OAc)_2.H_2O$ (1.5 equiv.), Additive (0.1 mmol), Solvent (2 mL), Temp. 80 °C/16 h (organic solvents) and 100 °C/20 h (water), under air. [b]Isolated yield after column chromatography; [c]Reaction performed using 5 mol% of catalyst **1**; [d]Reaction performed under N_2 atmosphere and 2 equiv. of diphenylacetylene.

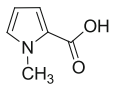
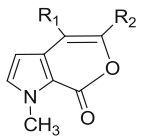
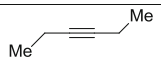
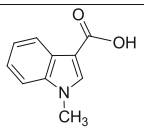
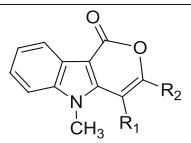
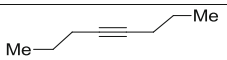
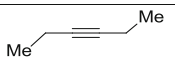


Scheme 2. Annulation of 2 or 3 with substituted alkynes into isocoumarins 5 or 6.

& 10). Even use of silver salt did not boost the reaction as in DMF instead, decreased the yield of the desired product (Table 1, entry 12). Thus, the optimized reaction conditions in DMF and water are as follows: a) [Ru-Cat] (10 mol%), substrate (0.5 mmol), $Cu(OAc)_2H_2O$ (1.5 equiv.), alkyne (1.1 equiv.), DMF (2 mL) at 80 °C for 16 h under air; and b) [Ru-Cat] (10 mol%), substrate (0.5 mmol), $Cu(OAc)_2H_2O$ (2 equiv.), alkyne (2 equiv.), water (2 mL) at 100 °C for 20 h under nitrogen.

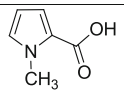
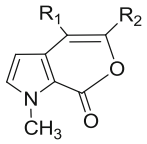
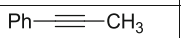
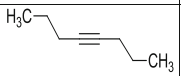
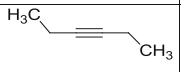
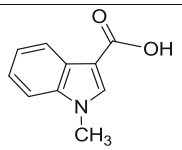
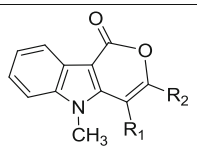
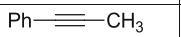
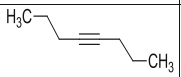
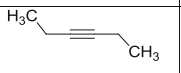
We have carried out the annulations of 1 -methylpyrrole-2-carboxylic acid (**2**) or 1-methylindole-3-carboxylic acid (**3**) with various alkynes in the presence of **1** under the optimized condition as found for **5a** and evaluated the catalytic efficacy of **1** first in DMF then in water (Scheme 2; Table 2 & 3). Thus, annulations of **2** with 4-octyne, 3-hexyne, and 2-butyne gave 41, 50 and 48% of the desired products, respectively (Table 2, entries 4–6). On the other hand, **3** gave

Table 2. Ruthenium(II)-catalysed annulations of 1-methylpyrrole-2-carboxylic acid or 1-methylindole-3-carboxylic acid with alkynes in DMF.[a]

Entry	Substrates 2 & 3	Alkynes	Products	Isolated Yield (%) [b]
	 **2**	R_1—≡—R_2	 **5a – e**	
1	**2**	Ph—≡—Ph	$R_1 = R_2$ = Ph (**5a**)	60
2	**2**	Ph—≡—CH_3	R_1 = Me; R_2 = Ph (**5b**)	80
3[c]	**2**	Ph—≡—CH_3	R_1 = Me; R_2 = Ph (**5b**)	53
4	**2**		R_1 = Pr; R_2 = Pr (**5c**)	41
5	**2**		R_1 = Et; R_2 = Et (**5d**)	50
6	**2**	Me—≡—Me	R_1 = Me; R_2 = Me (**5e**)	48
	 **3**	R_1—≡—R_2	 **6a–e**	
7	**3**	Ph—≡—Ph	$R_1 = R_2$ = Ph (**6a**)	69
8	**3**	Ph—≡—CH_3	R_1 = Me, R_2 = Ph (**6ba**) R_1 = Ph, R_2 = Me (**6bb**)	7 21
9	**3**		$R_1 = R_2$ = Pr (**6c**)	45
10	**3**		$R_1 = R_2$ = -Et (**6d**)	64
11	**3**	Me—≡—Me	$R_1 = R_2$ = -CH_3 (**6e**)	Traces

[a]Reaction conditions: Substrate (0.5 mmol), catalyst (0.05 mmol), alkynes (0.65 mmol, 1.2 equiv.), $Cu(OAc)_2H_2O$ (1.5 equiv.), DMF (2 mL), Temp. 80 °C, Time 16 h; [b]Isolated yield after column chromatography; [c]Reaction performed in the presence of KOAc.

Table 3. Ruthenium (II)-catalyzed annulations of *N*-methylpyrrole-2-carboxylic acid and *N*-methylindole-3-carboxylic acid in water[a].

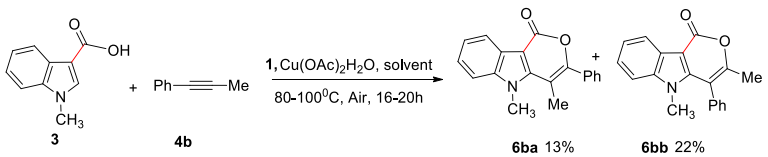
Entry	Substrates **2&3**	Alkynes	Products	Isolated Yield (%)[b]
	 **2**		 **5a–c**	
1	**2**		$R_1 = R_2 =$ Ph (**5a**)	58
2	**2**		R_1 = Me; R_2 = Ph (**5b**)	86
3	**2**		$R_1 = R_2 = -(CH_2)_2CH_3$ (**5c**)	12
4	**2**		$R_1 = R_2 = -(CH_2)CH_3$ (**5d**)	16
	 **3**		 **6a–c**	
5	**3**		$R_1 = R_2 =$ Ph (**6a**)	42
6	**3**		R_1 = Me, R_2 = Ph (**6ba**) R_1 = Ph, R_2 = Me (**6bb**)	13 22
7	**3**		$R_1 = R_2 = -(CH_2)_2CH_3$ (**6c**)	23
8	**3**		$R_1 = R_2 = -(CH_2)CH_3$ (**6d**)	20

[a]Reaction conditions: Substrate (0.5 mmol), catalyst (0.05 mmol), alkynes (1.0, mmol, 2 equiv.), $Cu(OAc)_2H_2O$ (2 equiv.), Water (2 mL), under N_2 atmosphere, Temp., 100 °C, Time 20 h; [b]Isolated yield after column chromatography.

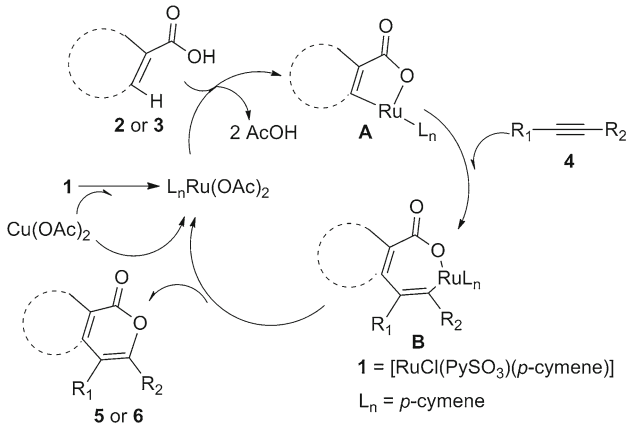
an isolated yield of 45% and 64% with 4-octyne and 3-hexyne, respectively but only a trace product with 2-butyne (Table 2, entries 9–11).

Annulation of *N*-methylpyrrole-2-carboxylic acid (**2**) with 1-phenyl-1-propyne is highly regioselective forming **5b**, as the only product in 80% isolated yield (Table 2, entry 2). Regioselectivity is also observed when performed in water as well where the desired product **5b** was formed with 86% yield, in the reaction of **2** with 1-phenyl-1-propyne (Table 3, entry 2). However, the reaction of 1-phenyl-1-propyne with *N*-methylindole-3-carboxylic (**3**) acid resulted in two products, **6ba** and **6bb** in low yields giving 7% and 21%, respectively in DMF (Scheme 3, Table 2, entry 9). Interestingly, **6bb** was formed with the **1** in favour of isomer **6ba** irrespective of the solvent used in contrast to $[RuCl_2(p\text{-cymene})]_2$ in which **6ba** was formed as the favour isomer[32] (Table 2, entry 9 and Table 3, entry 6).

Several ruthenium(II)-catalysed reactions were performed in water and in some cases catalyst activity enhances in water.[25,26] As many of ruthenium(II) catalysts tolerate water, the efficacy of **1** towards annulations



Scheme 3. Reaction pathway for the annulation of 1-methylindole-3-carboxylic acid with 1-phenyl-1-propyne, producing **6ba** and **6bb**.



Scheme 4. Plausible reaction mechanism for the formation of **5** and **6.**

of **2** or **3** with alkynes was tried as well in water. The reactions in water were not as competitive as in DMF except in the case of diphenylacetylene and 1-phenyl-1-propyne which gave isolated yields of 58% and 86%, respectively (Table 3, entries 1 & 2) for the substrate **2** but a modest yield of 42% with **3** and diphenylacetylene, whereas, two products **6ba** and **6bb** occurred in 13 and 22% when 1-phenyl-1-propyne was employed in the annulation with **3** (Table 3, entries 5 & 6). However, annulations of all the other tested alkynes *viz.,* 4-octyne and 3-hexyne with **3** gave low yields, 23 and 20%, respectively, when performed in water (Table 3, entries 7 & 8). Thus, the complex **1** is not as productive and effective as $[RuCl_2(p\text{-cymene})]_2$ in water.[32]

Since the $Cu(OAc)_2H_2O$ is essential for the reaction, the annulations are expected to occur via carboxylate directed reaction by formation of $RuL_n(OAc)_2$ (Scheme 4). The reaction probably initiated by the deprotonation of ortho C–H bond of the substrate (**2** or **3**) with acetate arising from $Cu(OAc)_2H_2O$[48] resulting in the formation of cyclometalate A. Coordinated insertion of alkyne into Ru^{II}–C bond expected to give intermediate B which then undergoes reductive elimination leading to products **5** and **6**. The produced ruthenium(0) species is then reoxidized by $Cu(OAc)_2H_2O$ into the active ruthenium(II) catalyst, $RuL_n(OAc)_2$ (Scheme 4).

4. Conclusions

Annulations of 1-methylpyrrole-2-carboxylic acid and 1-methylindole-3-carboxylic acid with alkynes in the presence of ruthenium(II) complex, $[RuCl(PySO_3)(p\text{-cymene})]$ (**1**) as a catalyst, and $Cu(OAc)_2H_2O$ as oxidant but without an additive is described. Reactions were performed in DMF giving excellent to modest yields of the desired products and even the reaction could be performed in water, though proved to be less effective then catalyst $[RuCl_2(p\text{-cymene})]_2$, but competitive for certain alkynes such as diphenylacetylene and 1-phenyl-1-propyne. The reaction is regioselectively forming exclusively (**5b**) in the annulation of 1-phenyl-1-propyne with **2** irrespective of solvent used. However, regioselectivity is less significant when performed **3** with 1-phenyl-1-propyne for which two isomers **6ba** and **6bb** were formed in low yields. Thus, **1** is efficient for catalytic sp^2C–H bond annulations of 1-methylpyrrole-2-carboxylic acid and 1-methylindole-3-carboxylic acid with alkynes in DMF in the presence of $Cu(OAc)_2H_2O$.

Supplementary Information (SI)

CCDC No. 1055202 contains the supplementary crystallography data for this paper. Copies of this information may be obtained free of charge from the Cambridge Crystallography Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Additional information pertaining to preparation and characterization of compounds (^{1}H, ^{13}C NMR and ESI-MS spectral data), copies of ^{1}H and ^{13}C-NMR spectra of all the compounds are available as supplementary information at www.ias.ac.in/chemsci.

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