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Rhodium catalyzed regioselective arene homologation of aryl urea *via* double C–H bond activation and migratory insertion of alkyne

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ABSTRACT

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Keywords: Urea Directing group C-H Activation Arene homologation Asymmetric alkynes Oxidative cyclization A convenient rhodium catalyzed oxidative arene homologation of aniline derivatives with symmetrical or unsymmetrical alkynes using $Cu(OAc)_2$ as oxidant is described. Urea group is shown to be effective as a directing group for initial *ortho* C–H activation. Two migratory insertion events of alkyne into Rh–C bond occur successively, both with complete regioselectivity. This method is particularly useful for synthesis of polyarenes with different substituents, which has not been reported with conventional protocol. A mechanism has been proposed to explain the observed data.

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1. Introduction

Great advancement has been made in transition metal catalyzed C-H bond activation and functionalization in the past 20 years [1–4]. The merits of direct C–H bond functionalization could reach its full extension only when site selective is achieved because there are almost always multiple C-H bonds in any organic substrate. The most common and successful strategy to address this selective challenge is using substrates containing coordinating ligands, namely directing groups [5,6]. By coordinate to transition metal, the directing group could deliver the catalytic center to a proximal C-H bond and therefore force the C-H bondactivating event to occur in a controlled manner. A plenty of directing groups have been devised for this purpose, and due to its vast structural diversity, the N-containing directing groups constitute the major and most important part. These N-containing directing groups span from various aromatic N-heterocycles, amines, amides, imides and imines to hydrazones, oximes, triazoles, and ureas, etc.[7-40].

Polycyclic aromatic compounds have been found increasing applications in functional materials in virtue of their excellent

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electro- and photo-chemical properties [41–45], which very often 28 could be modulated through the introduction of multiple 29 substituents on the arene core [46–49]. Metal catalyzed coupling 30 of arene with two fold internal alkynes provides an efficient arene 31 homologation method for poly-substituted polycyclic aromatic 32 compounds [50-61]. Direct site selective homologation of un-33 preactivated arenes, which involves double C-H activation is 34 highly appreciated as this method can provide polycyclic aromatic 35 compounds in both efficient and controlled manner from easily 36 accessible un-functionalized arenes [62-65]. Here, we would like 37 to report a urea group directed arene homologation catalyzed by 38 Rh(III) complex employing either symmetric or unsymmetrical 39 internal alkynes as coupling partners. 40

2. Experimental 41

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2.1. General

¹H NMR and ¹³C NMR spectra were recorded using Bruker AV-43 300/AV-400/AV-500 spectrometers. Analytical thin layer chroma-44 tography was performed on 0.25 mm extra hard silica gel plates 45 with UV254 fluorescent indicator and/or by exposure to phos-46 phomolybdic acid followed by brief heating with a heat gun. Liquid 47 chromatography (flash chromatography) was performed on 60 Å 48 49 $(40-60 \,\mu\text{m})$ mesh silica gel (SiO₂). All reactions were carried out under nitrogen or argon with anhydrous solvents in flame-dried 50

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glassware, unless otherwise noted. All reagents were commerciallyobtained and, where appropriate, purified prior to use.

53 2.2. General procedure for the homologation of aryl ureas

54 A mixture of the diphenylacetylene 2 (1.0 mmol, 2.5 eq.), 1 55 (0.4 mmol), [Cp*RhCl₂]₂ (6.2 mg, 0.01 mmol, 2.5 mol%), Cu(OAc)₂ 56 (188 mg, 1 mmol, 2.5 eq.), and AgSbF₆ (28 mg, 0.08 mmol, 57 20.0 mmol %) were weighted into a Schlenk tube equipped with 58 a stir bar. t-AmOH (2 mL) was added and the mixture was stirred at 59 120 °C for 24 h under N₂ atmosphere. The reaction mixture was 60 extracted with DCM for three times, and the combined organic 61 layers were then dried over anhydrous Na₂SO₄, filtered, and the 62 solvent was removed under reduced pressure. The crude product 63 was purified by column chromatography on silica gel, eluted by 64 hexane/EtOAc = 3:1 then 2:1 to afford the desired product **3**.

Characterization and spectra for new compounds are compiled in Supporting information.

67 3. Results and discussion

68 Our study commenced with urea 1a and diphenyl acetylene 2a 69 (Table 1). Using an effective protocol disclosed by Fagnou team, 70 several popular transition metal catalysts for oxidative C-H 71 functionalization were explored. Pd(OAc)₂ and [RuCl₂(P-Cym-72 ene)]₂ failed to promote any reaction (entries 1–3). (Cp*RhCl₂)₂ 73 activated by AgSbF₆ did catalyze the desired arene homologation 74 reaction and t-AmOH is the solvent of choice for good yield (entries 75 4 and 5). It was also found that $Cu(OAc)_2$ was a necessary oxidant

Table 1

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Condition optimization for oxidative condensation of phenyl urea with alkyne.



and $AgSbF_6$ was a critical additive for this reaction to proceed smoothly (entries 5–7).

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With the optimal conditions in hand, an array of urea substrates **1** were submitted to the reaction with diphenyl acetylene **2a** (Table 2). *Meta* substituted ureas, such as **1b** and **1c** were feasible substrates to give 5, 6, 7, 8-tetraphenyl naphthalene **3ba** and **3ca** in yields of more than 60% (entries 2–3). On the other hand, *ortho*and *para*- substituents decreased the yield dramatically, as both tetraphenyl naphthalenes **3 da** and **3ea** were obtain from **1d** to **1e** in less than 20% yields (entries 4–5). *N*,*N*-diphenyl urea **1f** condensed with diphenyl acetylene to give rise to **3fa** in 27% yield (entry 6). These outcomes may be the results of collective steric effects of both aryl substituents and bulky Cp* ligand on metal center, which will be discussed later on.

Further studies using unsymmetrical alkynes as the homologation partners highlight the virtue of this protocol (Table 3). Condensation of phenyl methyl acetylene **2b** with urea **1a**, **1b**, **1c** gave related 5,8-dimethyl-6,7-diphenyl naphthalenes **3ab**, **3bb**, **3cb** in 60–70% yields. The structure of **3ab** was established by extensive NMR experiments including, 2D ¹H–¹H Noesy experiments. The selectivity demonstrated by these reactions is amazing as only one single regioisomer is produced out of four possible isomers. Moreover, to our delight, *ortho* substituted phenyl urea **1e** achieved a much higher yield for 5,8-dimethyl-6,7-diphenyl naphthale **3eb** (Table 3, entry 4, 63%) than the yield for 5,6,7,8tetraphenyl naphthalene **3ea** (Table 2, entry 5, 18%). Methoxymethyl phenyl acetylene **2c** is also condensed with **1a** to give **3ac** in 51% yield with exclusive regioselectivity, while alkynes **2d** and **2e** are not feasible coupling partners for this reaction.

	Suu Pr	1			
Entry	Catalyst	Oxidant	Additive	Solvent	Yield (%) ^b
1	$Pd(OAc)_2$	$Cu(OAc)_2$	-	t-AmOH	_
2	$[RuCl_2(p-Cym)]_2$	$Cu(OAc)_2$	_	t-AmOH	-
3	$[RuCl_2(p-Cym)]_2$	$Cu(OAc)_2$	_	DCE	-
4	[Cp*RhCl ₂] ₂	$Cu(OAc)_2$	AgSbF ₆	toluene	20
5	[Cp*RhCl ₂] ₂	$Cu(OAc)_2$	AgSbF ₆	t-AmOH	50
6	[Cp*RhCl ₂] ₂	Air	AgSbF ₆	t-AmOH	-
7	[Cp*RhCl ₂] ₂	$Cu(OAc)_2$	-	t-AmOH	complex

^a Reaction conditions: **1a** (0.4 mmol, 1.0 eq.), **2a** (1.0 mmol, 2.5 eq.), oxidant air or Cu(OAc)₂ (1 mmol, 2.5 eq.) and catalyst (0.01 mmol, 2.5 mol%) in *t*-AmOH (2.5 mL) was heated to 120 °C in a Schlenk tube for 24 h;

^b Isolated yield.

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Table 2

Arene homologation of aryl ureas with dipenyl acetylene.ª

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$R^{2}HN \qquad NR^{1}$ $R^{3} \qquad I$	Ph Ph 2a [Cp*RhCl ₂] ₂ Cu(OAc) ₂ , AgSbF ₆	$R^{2}HN \xrightarrow{NR^{1}} Ph$ $R^{3} \xrightarrow{Ph} Ph$				
Entry	1	R ¹	R ²	R ³	Product	Yield (%) ^b
1	1a	Me	Me	Н	3aa	50
2	1b	Me	Me	3-Me	3ba	61
3	1c	Me	Me	3-Cl	3ca	63
4	1d	Me	Me	4-Me	3 da	17
5	1e	Me	Me	2-Cl	3ea	18
6	1f	Ph	Pr	Н	3fa	27

^a Reaction conditions: **1** (0.4 mmol, 1.0 eq.), **2a** (1.0 mmol, 2.5 eq.), Cu(OAc)₂ (1 mmol, 2.5 eq.), AgSbF₆ (0.02 mmol, 5 mol%), and [Cp*RhCl₂]₂ (0.01 mmol, 2.5 mol%) in *t*-AmOH (2.5 mL) was heated to 120 °C in a Schlenk tube for 24 h under N₂;

^b Isolated yield.

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Table 3

Arene homologation of aryl ureas with unsymmetrical acetylenes.^a

$R_3 \xrightarrow{\Pi}_{U} \qquad \qquad$	$Me = \frac{\frac{[Cp*RhCl_2]_2}{Cu(OAc)_2, AgSbF_6}}{Ph - R_4}$	MeHN NMe R ₄ R ₃ Ph 3 R ₄				
Entry	1	R ₃	2	R ₄	Product	Yield (%) ^b
1	1a	Н	2b	Me	3ab	60
2	1b	3-Me	2b	Me	3bb	69
3	1c	3-Cl	2b	Me	3cb	65
4	1e	2-Cl	2b	Me	3eb	63
5	1a	Н	2c	CH ₂ OMe	3ac	51
6	1c	3-Cl	2d	COOMe	-	
7	1a	Н	2e	CH ₂ OH	-	

^a Reaction conditions: 1 (0.4 mmol, 1.0 eq.), 2 (1.0 mmol, 2.5 eq.), Cu(OAc)₂ (1 mmol, 2.5 eq.), AgSbF₆ (0.02 mmol, 5 mol%) and [Cp*RhCl₂]₂ (0.01 mmol, 2.5 mol%) in t-AmOH (2.5 mL) was heated to 120 °C in a Schlenk tube for 24h under N₂.

^b Isolated yield.

105 Based on previous studies [11,66–70] and the data collected in 106 this research, a mechanism has been proposed as shown in Scheme 107 1. Pre-catalyst [RhCp*Cl₂]₂ is initially converted into an active cationic Rhodium species **A** by the action of AgSbF₆. **A** is directed to 108 109 activate the ortho C-H bond in urea 1 to finish aryl Cp*Rh(III) 110 species **B** which coordinates with alkyne **2** followed by migratory 111 insertion giving alkenyl Cp*Rh(III) intermediate C. A second C-H 112 bond activation event then took place intramolecularly leading to 113 Rhodacycle **D**. A second insertion of alkyne molecule provide two possible Rhodacycles E or/and F and consequent reductive 114 115 elimination delivers the homologated arene **3** and the reduced Cp*Rh(I) species is oxidized by Cu(II) to regenerate Cp*Rh(III) 116 complex A ready for a second catalytic circle. 117

According to this mechanism, it can be deduced from the product structure of **3ab-3eb** that **D** is formed favorably over **D'** from **B** and this is also in line with Fagnou's observations [11], where electronic effect was raised to explain this intrinsic 121 regioselectivity. For the same reason, the second alkyne insertion 122 will take place at one of the two C-Rh bonds of **D** to give 123 preferentially **E** over **E'** and **F** over **F'**, respectively. After reductive 124 elimination, rhodacycle E will give the observed naphthalene **3aa**, 125 whereas F will give its regioisomer 3'aa which is not detected, 126 disproving the intermediacy of rhodacycle F (Scheme 2). These 127 analyses support a pathway **B-C-D-E** as the operating pathway 128 shown in Scheme 1. 129

The low yield associated with *meta-* and *para-substituted* 130 phenyl ureas when diphenyl acetylene **2a** was used as condensation partner may derive from the serious steric repulsions in the 132 intermediates along the pathway, such as indicated in **G** and **H** 133 (Fig. 1). Those steric interactions can be relieved when diphenyl acetylene **2a** was replaced by methyphenyl acetylene **2b** to afford 135 increased yield. 136



 $\label{eq:scheme1} \textbf{Scheme1.} Proposed mechanism for the arene homologation (R_S stands for small group, R_L stands for large group).$

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Scheme 2. Discrimination of two possible pathways.



Fig. 1. The steric repulsions in intermediates G and H leading to low yields.

137 4. Conclusion

In summary, we have established a facile method for arene
homologation of aryl urea with internal alkyne. This rhodium
catalyzed transformation features a double C–H activation process
and two successive completely regioselctive migratory insertions
of unsymmetrical alkynes into Rhodium–carbon bonds enable this
method particularly useful for poly-substituted polyarenes.
Furthermore, a mechanism proposal has been discussed.

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152 Appendix A. Supplementary data

Supplementary data associated with this article can be found, in
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