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Ruthenium(II) Catalyzed Regiospecific C−H/O−H Annulations of Directing Arenes via Weak Coordination

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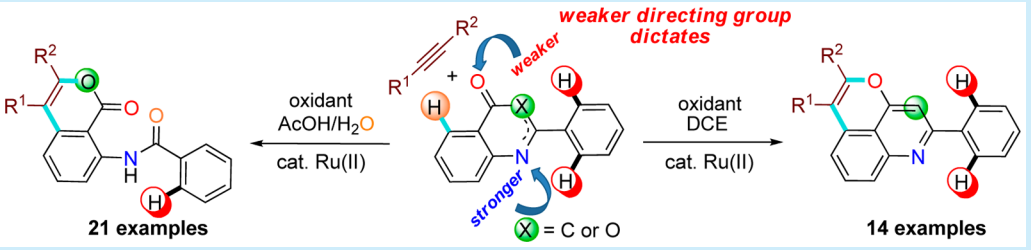
Supporting Information

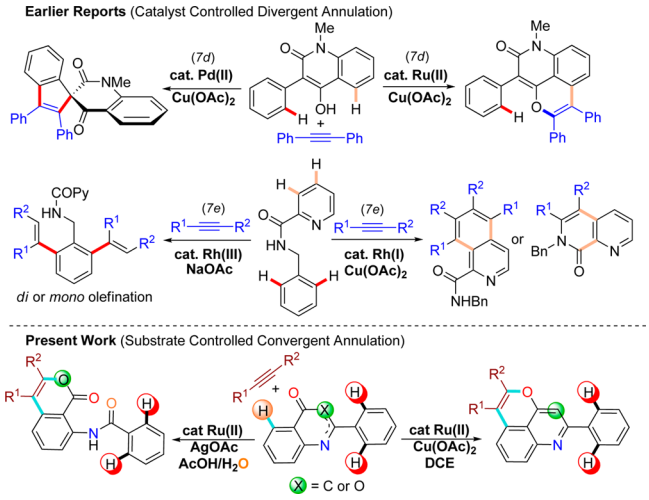


ABSTRACT: Ruthenium(II) catalyzed oxidative C−H/O−H annulations have been demonstrated using two different directing arenes viz. 2-arylquinolinone and 2-arylbenzoxazinone with internal alkynes. Regiospecific annulations have been observed for both directing arenes via the assistance of weaker carbonyl oxygen in the presence of a stronger nitrogen-directing site. In this substrate-controlled convergent protocol the weaker directing group dictates the annulation path.

Controlling site selective C−H activation in substrates possessing more than one type of C−H bond is an inherent and long-standing challenge in organic chemistry. One possible solution to this problem is either via catalyst or substrate control. Despite fast-paced progress in catalytic C−H bond functionalizations, strategies for preferential site selectivities are limited.[1] The ability to induce site-selectivity in substrates having multiple C−H's has tremendous importance in the field of diversity oriented synthesis of complex molecules.[2] Oxidative C−H annulation is one such powerful atom and step economical strategy, applied for the synthesis of bioactive complex polycyclic molecules.[3] In this context site selective annulation of substrates enable the construction of diverse molecular scaffolds from common starting material. Majority of oxidative annulations have been achieved using Rh or Pd catalysts, whereas the relatively inexpensive Ru-catalysts have been recently introduced as a suitable alternative.[4] Synthesis of polycyclic π-conjugated aromatics and heteroaromatics have received considerable attention in recent times due to their potential utility as organic electronic materials.[5] Their synthesis using C−H annulations is an obvious and attractive alternative to multistep routes.

Inspired by nature's approach in site selective C−H bond functionalizations, efforts have focused on designing catalysts, substrates or manipulation of ligands to provide switchable site-selective C−H bond functionalizations.[2f,6] The development of strategies capable of divergent functionalizations at distinct C−H sites through catalyst control is limited (Scheme 1).[7] However, substrate-controlled selectivity in C−H bond functionalizations through the cleavage of similar C−H bonds in analogous directing arenes is unfamiliar so far. In multidirecting systems, generally the stronger directing group controls the C−H bond functionalization. However, after the seminal work by Yu et al. where a weak directing group overrides the stronger one and controls the C−H activation,[8] there is no other report of this kind. Herein, we report first oxygen-directed C−H annulation in the presence of a strong nitrogen-directing group in 2-arylquinolinones and 2-arylbenzoxazinones (Scheme 1).

Scheme 1. Catalyst vs Substrate Controlled Annulations



Our initial investigation started with the evaluation of reaction conditions for oxidative annulation of 2-phenylquinolinone (**1**) with diphenyl acetylene (**a**). 2-Arylquinolinone was chosen as the model substrate as this core represents a

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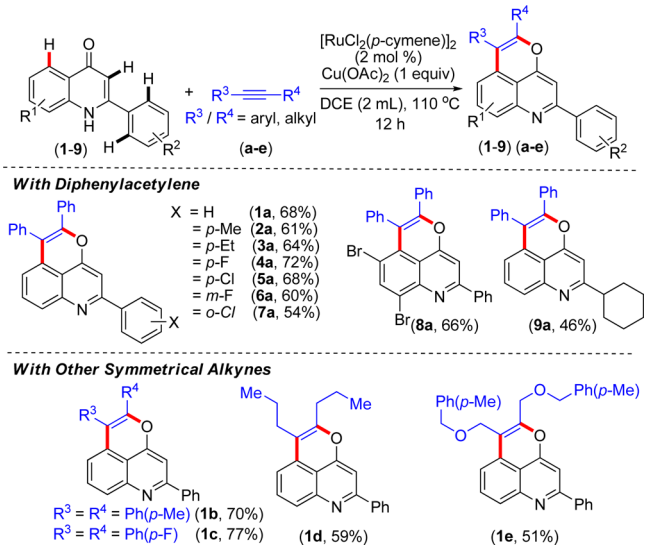
highly privileged, biologically important molecular scaffold[9] which has several possible C−H's (via C−H/N−H, C−H/C−H and C−H/O−H bonds) for oxidative annulations with an alkyne. In an initial reaction 2-phenylquinolinone (**1**) was treated with diphenylacetylene (**a**) in the presence of a well explored $[RuCl_2(p\text{-cymene})]_2$ (2 mol %) catalyst,[4] $Cu(OAc)_2$ (1.0 equiv) as the terminal oxidant and Cs_2CO_3 (1 equiv) as the base in toluene (2 mL). A new product was isolated by column chromatography, spectroscopic (^1H and ^{13}C NMR) analysis of the product (**1a**) revealed the presence of two extra phenyl moieties and the absence of singlets for C3−H and −NH protons. This confirms the aromatization of 2-arylquinolinone to 2-aryl-4-hydroxyquinoline along with the addition of a diphenyl acetylene moiety via C−H/O−H annulation. However, this unprecedented annulated product was obtained in a low yield of 37% (Table S1, entry 1, Supporting Information, SI). Since the tautomerization of quinone to its corresponding phenol is favorable, 2-arylquinolinone acts as a "masked" phenolic substrate to trigger the C−H/O−H annulation over other possible (viz. C−H/N−H and C−H/C−H) annulation paths (Scheme in Table S1, SI). Switching the solvent from toluene to chlorobenzene (PhCl) under identical reaction conditions provided the annulated product (**1a**) in an improved yield of 60% (Table S1, entry 2, SI). Among other solvents such as DMF, NMP, DMSO and DCE tested (Table S1, entries 3−6, SI), later provided the best yield (70%) (Table S1, entry 6, SI). Further, by varying the oxidant from $Cu(OAc)_2$ to $Cu(OAc)_2{\cdot}H_2O$, AgOAc, $AgCO_3$ and $AgSbF_6$ under identical conditions to that of entry 6, did not improve the yield of product (**1a**) (Table S1, entries 7−10, SI). Later, it was found that the use of Cs_2CO_3 was redundant as the yield remained unaltered (68%) (Table S1, entry 11, SI) even when the reaction was performed in its absence. Reaction when carried out without co-oxidant $[Cu(OAc)_2]$ under otherwise identical conditions (to that of entry 11) provided the annulated product (**1a**) in low yield (25%) (Table S1, entry 12, SI). No annulated product was formed in the absence of Ru(II) catalyst (Table S1, entry 13, SI).

After establishing the optimized reaction conditions for annulation (Table S1, entry 11, SI), we started to explore the coupling between various 2-arylquinolinone (**1**−**9**) with symmetrical internal alkynes (**a**−**e**). 2-Aryl ring of quinolinone bearing electron-donating as well as electron-withdrawing substituents were all compatible providing their desired annulated products in moderate yields (Scheme 2). 2-Arylquinolinone containing electron-donating substituents such as *p*-Me (**2**), *p*-Et (**3**) in the 2-aryl ring provided their expected annulated products (**2a**) and (**3a**) in moderate yields (Scheme 2). Electron-withdrawing substituents such as *p*-F (**4**), *p*-Cl (**5**), *m*-F (**6**) and *o*-Cl (**7**) present in the 2-aryl ring of 2-arylquinolinone also underwent annulations giving their corresponding products (**4a**), (**5a**), (**6a**) and (**7a**) respectively in decent yields (Scheme 2). The structure of the annulated product (**5a**) has been further confirmed by X-ray crystallographic analysis (Figure S1, SI). For directed C−H bond functionalization, C−H metalation generally occurs at the less sterically hindered C−H site of phenyl rings having the *meta*-substituent. However, in 6,8 dibromo substituted quinolinone (**8**) the annulation took place smoothly even at the sterically hindered site of quinolinone ring, giving 66% yield of (**8a**) along with retention of both the bromo functionality. This observation suggests the preferential C−H/O−H annulation

Scheme 2. Annulation of 2-Arylquinolinone with Internal Alkynes



over other C−H/N−H and C−H/C−H annulation paths. This protocol is equally compatible with 2-cyclohexyl substituted quinolinone (**9**) providing (**9a**) in a relatively low yield (46%).

To evaluate the scope and generality of this annulation strategy, other symmetrical alkynes (**b**−**e**) were investigated using 2-phenylquinoloinone (**1**) as the coupling partner (Scheme 2). Symmetrical 1,2-diarylacetylene possessing electron-donating *p*-Me substituent (**b**) when coupled with (**1**) provided the product (**1b**) in good yield (70%) (Scheme 2). Symmetrical 1,2-diarylacetylene having electron-withdrawing *p*-F substituents (**c**) when reacted with (**1**) provided an improved yield (77%) of the annulated product (**1c**). Aliphatic internal alkynes viz. 4-octyne (**d**) and 1,4-*bis*((4-methylbenzyl)oxy)but-2-yne (**e**) when treated with (**1**) afforded their annulated products (**1d**) and (**1e**) in 59% and 51% yields, respectively.

After the successful C−H/O−H annulation of 2-arylquinolinone (**1**) directed via its weaker carbonyl oxygen in the presence of stronger nitrogen (*N*) directing group, we looked for analogous systems. With this in mind, 2-phenylbenzoxazinone (**1′**) was selected as it is structurally analogous to 2-phenylquinolinone (**1**) except its C3 carbon is replaced with an oxygen atom. 2-Phenylbenzoxazinone (**1′**) having two different directing sites viz. nitrogen (N1) and carbonyl oxygen atoms both of which can potentially direct the oxidative annulations. The objective was to see whether the stronger nitrogen directs the anuulation or here as well, the weaker oxygen dictates the annulation as was observed in 2-phenylquinolinone (**1**). To verify this, coupling of 2-phenylbenzoxazinone (**1′**) and diphenylacetylene (**a**) was carried out under identical conditions to that of coupling between (**1**) and (**a**) (Table S2, entry 1, SI). A product was isolated by column chromatography, spectroscopic (^1H and ^{13}C NMR) analysis revealed its structure to be *N*-(1-oxo-3,4-diphenyl-1*H*-isochromen-8-yl)benzamide (**1′a**). The amidic group in (**1′a**) might have originated by the hydrolytic cleavage of one of the C−O bonds in 2-phenylbenzoxazinone (**1′**). Therefore, hydrated $Cu(OAc)_2{\cdot}H_2O$ was used in lieu of anhydrous $Cu(OAc)_2$ which gave a slight improvement in the yield (17%) (Table S2, entry 2, SI). Among various other solvents such as PhCl (38%), DMSO (00%), DMF (00%), NMP (00%), ^{t}BuOH (14%) and AcOH (50%) tested (Table S2, entries 3−8, SI), the

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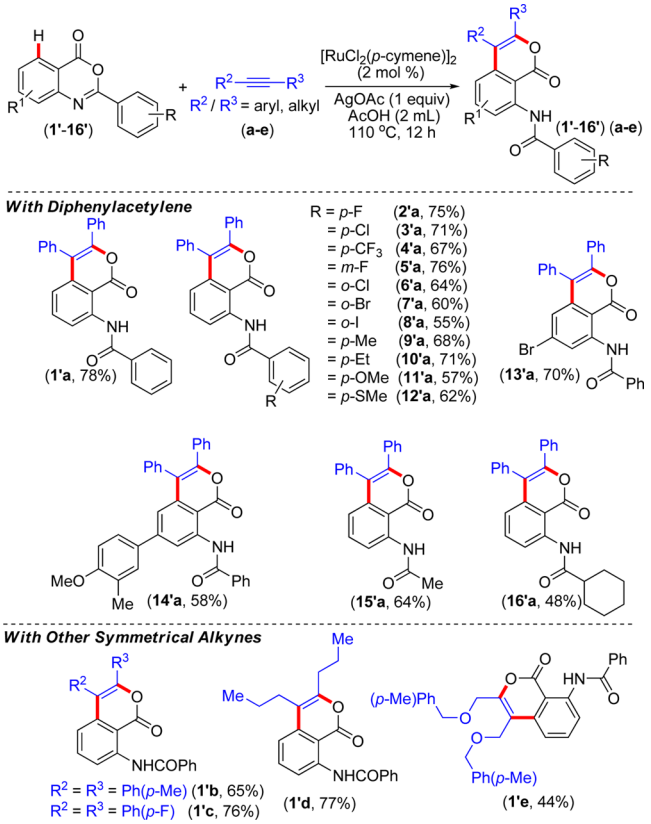
Org. Lett. XXXX, XXX, XXX−XXX

later was found to be superior (Table S2, entry 8). Co-oxidant AgOAc was found to be ideal giving 78% yield compared to other co-oxidants such as $Cu(OAc)_2$ (44%), $AgSbF_6$ (62%), $AgCO_3$ (56%) and Ag_2O (41%) screened (Table S2, entries 9−13, SI)

After establishing the optimized conditions for yet another C−H/O−H annulation directed by weaker carbonyl oxygen, we then implemented this strategy for various 2-arylbenzoxazinones (**1′**−**16′**) and symmetrical internal alkynes (**a**−**e**). 2-Arylbenzoxazinone containing electron-withdrawing as well as electron-donating substituents present in the 2-aryl ring all coupled efficiently with diphenylacetylene (**a**) providing their respective annulated products in moderate yields (Scheme 3).

Scheme 3. Annulation of 2-Arylbenzoxazinones with Alkynes

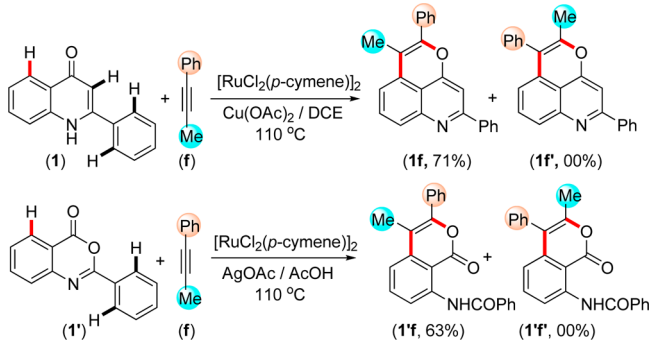


Irrespective of their positions, the presence of electron-withdrawing substituents in the 2-aryl ring of 2-arylbenzoxazinones such as *p*-F (**2′**), *p*-Cl (**3′**), *p*-CF_3 (**4′**), *m*-F (**5′**), *o*-Cl (**6′**), *o*-Br (**7′**) and *o*-I (**8′**) all provided their expected annulated products (**2′a**), (**3′a**), (**4′a**), (**5′a**), (**6′a**), (**7′a**) and (**8′a**) respectively in decent yields (Scheme 3). The presence of moderately electron-donating *p*-Me (**9′**), *p*-Et (**10′**) and strongly electron-donating *p*-OMe (**11′**), *p*-SMe (**12′**) substituents in the 2-aryl ring of benzoxazinone all afforded moderate yields of their annulated products (**9′a**), (**10′a**), (**11′a**) and (**12′a**) respectively (Scheme 3). Electron-withdrawing Br substituent presents at the C7 position of benzoxazinone provided the annulated product (**13′a**) in good yield (70%). Further, the presence of an extra aryl ring at C7 of benzoxazinone afforded the annulated product (**14′a**) in moderate yield (58%). The presence of methyl and cyclohexyl substituents at the C2 position of benzoxazinone yielded annulated products (**15′a**) and (**16′a**) in 64% and 48% yields, respectively.

The scopes of other symmetrical alkynes were then tested using 2-phenylbenzoxazinone (**1′**) as the coupling partner (Scheme 3). Symmetrical 1,2-diarylalkynes having electron-donating, Me (**b**), and electron-withdrawing, F (**c**), substituents present at their *para* position when reacted with (**1′**) provided their annulated products (**1′b**) and (**1′c**) in good yields (Scheme 3). Aliphatic internal alkynes such as 4-octyne (**d**) and 1,4-*bis*((4-methylbenzyl)oxy)but-2-yne (**e**) when treated with (**1′**) afforded their annulated products (**1′d**) and (**1′e**) respectively in 77% and 44% yields.

To check the regioselectivity in both of these annulations, an unsymmetrical alkyne 1-phenyl-1-propyne (**f**) was reacted separately with 2-phenylquinolinone (**1**) and 2-phenylbenzoxazinone (**1′**) under their respective optimized reaction conditions [(Table S1, entry 11, SI) and (Table S2, entry 10, SI)]. Both these directing substrates (**1**) and (**1′**) provided single regioisomer (**1f**) and (**1′f**) (Scheme 4). The structure of compound (**1′f**) was further confirmed by X-ray crystallographic analysis as shown in Figure S2 (SI).

Scheme 4. Regioselectivity Evaluation



To check whether the electron-deficient diphenylacetylene (**a**) or the electron-rich 4-octyne (**d**) undergoes preferential annulation, intermolecular competitive reactions were performed. Directing substrates 2-phenylquinolinone (**1**) and 2-phenylbenzoxazinone (**1′**) were reacted separately in the presence of an equimolar mixture (1:1) of (**a**) and (**d**) under their respective optimized conditions. In both these cases annulated products originating from the electron-deficient alkyne (**a**) were obtained in higher proportions [(**1a**, 44%), (**1′a**, 52%)] than products [(**1d**, 23%), (**1′d**, 27%)] derived from electron-rich (**d**) counterpart (Scheme S1, SI). Thus, in both these annulations electron deficient alkynes are better annulating partners. This has been reconfirmed in yet another set of competitive experiments where an equimolar mixture of electron-deficient 1,2-di(*p*-fluorophenyl)ethyne (**c**) and electron-rich 1,2-di-*p*-tolylethyne (**b**) were reacted separately with (**1**) and (**1′**). Here again, electron-deficient alkyne (**c**) annulated preferentially giving higher yields of products [(**1c**, 40%), (**1′c**, 46%)] than annulated products derived from electron-rich alkyne (**b**) [(**1b**, 27%), (**1′b**, 32%)] (Scheme S1, SI).

On the basis of experiments performed (Scheme 4 and S1, SI) and earlier reports, plausible mechanisms are depicted for these annulations (Scheme S2, SI). In both these cases the reactions are initiated via the displacement of a chloride ligand of $[RuCl_2(p\text{-cymene})]_2$ with an acetate anion either from

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Org. Lett. XXXX, XXX, XXX−XXX

AgOAc or $Cu(OAc)_2$. Under the reaction conditions 2-phenylquinolinone (**1**) aromatizes to 4-hydroxy-2-phenylquinoline (**A**). In the next step, a five-membered ruthenacycle intermediate (**B**) is generated from (**A**) (Scheme S2, SI). Migratory insertion of alkyne into the Ru-carbon bond of intermediate (**B**) afforded the intermediate (**C**). For unsymmetrical alkynes the Ru-carbon bond will be favorable at the alkyne carbon having higher electron density thus accounting for the regioselectivity in Scheme 4. Finally, a reductive elimination provided the expected annulated product (**1a**) along with the generation of catalyst Ru(0) (Scheme S2, SI). This Ru(0) is oxidized to an active Ru(II) catalyst in the presence of oxidant $Cu(OAc)_2$ or by an areal oxidation.[4j] Directing substrate 2-phenylbenzoxazinone (**1′**) undergoes initial hydrolytic cleavage under the reaction conditions to give *N*-benzoylanthranilic acid (**A′**). To confirm this when substrate (**1′**) was subjected to the reaction conditions but in the absence of diphenylaetylene (**a**), gave *N*-benzoylanthranilic acid (**A′**) as the exclusive product. Further, *N*-benzoylanthranilic acid (**A′**) when treated with diphenylaetylene (**a**) under the exact reaction condition (Table S2, entry 10, SI) provided product (**1′a**) but in a mere yield of 28%. Lower yield of product (**1′a**) obtained using (**A′**) may be due to the chelation of cat. Ru(II) with a large excess of (**A′**).[10] In the next step, the in situ generated (**A′**) forms a five-membered ruthenacycle intermediates (**B′**) via a weak oxygen directed selective metalation (Scheme S2, SI). Migratory insertion of alkyne into the Ru-carbon bond of intermediate (**B′**) generates the intermediate (**C′**). Reductive elimination in the next step provided annulated product (**1′a**) along with the generation of Ru(0) (Scheme S2, SI) which is oxidized further to Ru(II).

In conclusion, weaker oxygen-directed regiospecific annulations have been developed for directing arenes viz. 2-arylquinolinone and 2-arylbenzoxazinone in the presence of a stronger nitrogen-directing group. This is a unique demonstration of directing group controlled annulation in multi-directing systems.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b02967.

Experimental details, spectral, and analytical data. (PDF)

Crystal data. (CIF)

Crystal data. (CIF)

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Notes

The authors declare no competing financial interest.

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