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Ruthenium-Catalyzed Synthesis of Pyrrolo[1,2-*a*]quinoxaline Derivatives from 1-(2-Aminophenyl)pyrroles and Sulfoxonium Ylides

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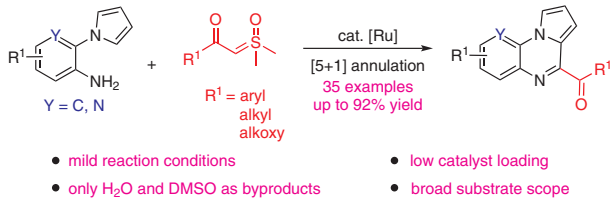

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Abstract A ruthenium-catalyzed [5+1] annulation of 1-(2-aminophenyl)pyrroles with α-carbonyl sulfoxonium ylides is reported. This reaction provides a one-step method for synthesizing pyrrolo[1,2-*a*]quinoxaline derivatives under ambient conditions. The system proceeds with a short reaction time and a high functional-group tolerance. Notably, this divergent protocol tolerates β-keto sulfoxonium ylides and can be applied to α-ester sulfoxonium ylides. A preliminary study was made of the mechanism of the reaction, and a reaction pathway is proposed.

Key words pyrroloquinoxalines, sulfoxonium ylides, aminophenylpyrroles, ruthenium catalysis, activation–cyclization, [5+1] annulation

Pyrrolo[1,2-*a*]quinoxalines are core structural scaffolds in many natural products, synthetic pharmaceuticals, and functional materials.[1] Because of their unique structure, pyrrolo[1,2-*a*]quinoxalines have garnered considerable attention over the past century. As versatile building blocks, functionalized pyrrolo[1,2-*a*]quinoxalines that possess antimalarial,[2] antileishmania,[3] or antitumor properties,[4] or which can behave as glucagon receptor antagonists[5] or human protein kinase CK2 inhibitors[6] have been synthesized (Figure 1).

In view of the importance described above, the synthesis of bioactive pyrrolo[1,2-*a*]quinoxaline derivatives has attracted considerable attention. Hence, numerous approaches toward functionalized quinoxaline have been developed during recent decades. In 1965, Cheeseman and Tuck[7] reported a metal-free catalytic coupling reaction of 2-(1*H*-pyrrol-1-yl)aniline with HCO_2H under reflux as a key contribution toward the synthesis of quinoxalines. Based on this pioneering work, many similar strategies for the preparation of pyrrolo[1,2-a]quinoxalines have been successively reported. It was found that the presence of a nitro or amino group at the C-2 position in the phenyl ring and a carbonyl group in the pyrrole are essential for successful cyclization and aromatization. Preetam and Nath reported a cyclization

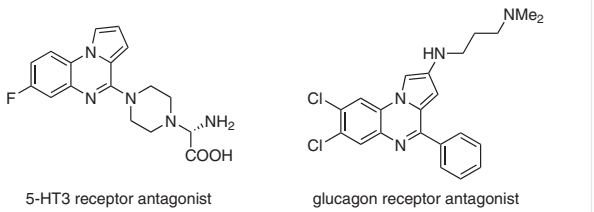
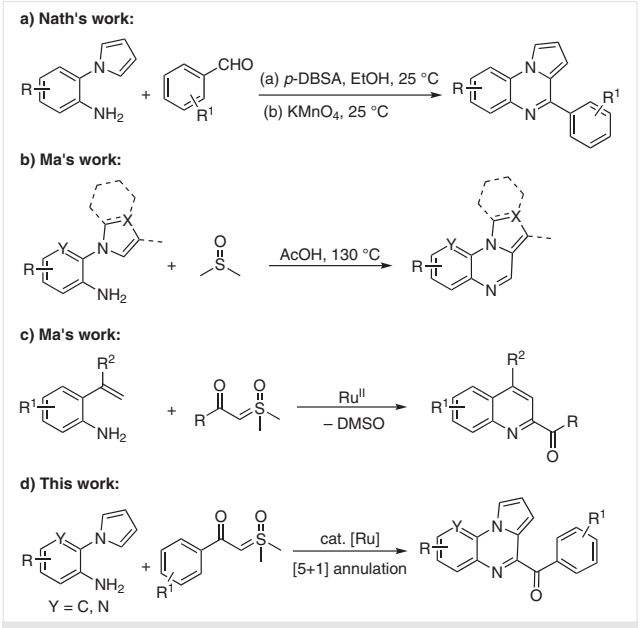


Figure 1 Examples of biologically active quinoxalines



Scheme 1 Previous work and our approach to the synthesis of pyrrolo[1,2-*a*]quinoxalines; *p*-DBSA = 4-dodecylbenzenesulfonic acid

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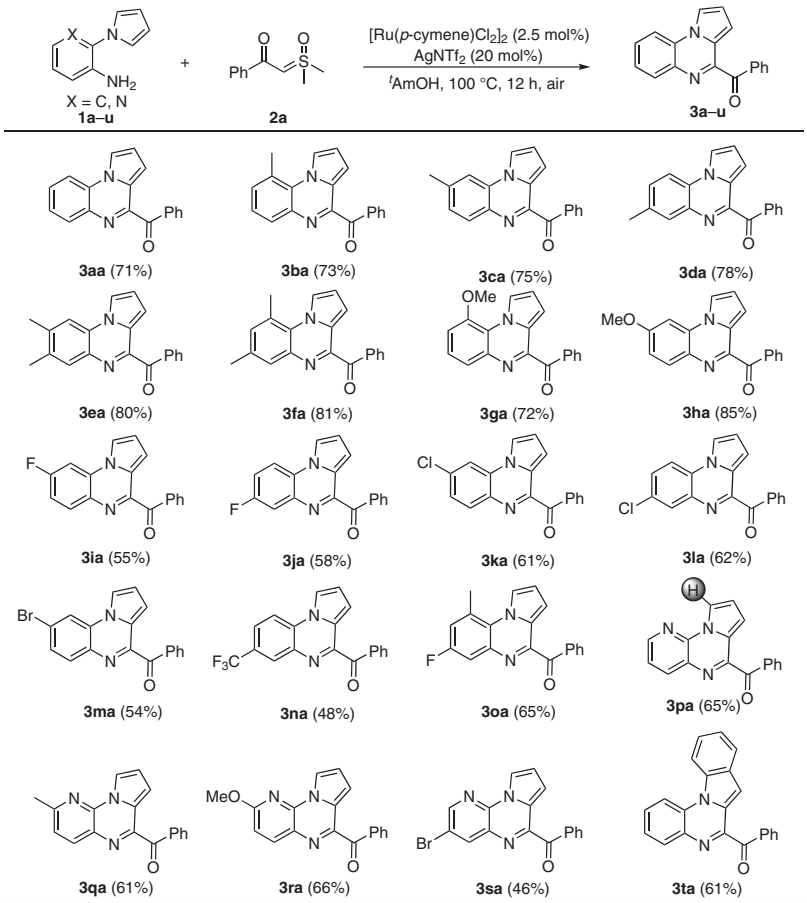
reaction that uses 2-(1*H*-pyrrol-1-yl)anilines and aldehydes as starting materials (Scheme 1a).[8] In 2017, Jiang and co-workers developed a novel and concise oxidative strategy for the synthesis of pyrrolo[1,2-*a*]quinoxaline derivatives from simple primary alcohols under a dioxygen atmosphere.[9] Ma and co-workers reported a simple, green, and efficient method for the construction of pyrrolo[1,2-*a*]quinoxalines from 2-(1*H*-pyrrol-1-yl)anilines and dimethyl sulfoxide under mild conditions (Scheme 1b).[10] Yan and co-workers have reported an $FeCl_3$-catalyzed reaction between 1-(2-aminophenyl)pyrroles and cyclic ethers for the synthesis of (hydroxyalkyl)pyrrolo[1,2-*a*]quinoxalines.[11a] More-powerful synthetic methods involving [5+1]-annulation reactions have been developed by the same group.[11] Kundu and co-workers reported a diversity-oriented synthesis of indoloquinoxalines from 1-(2-nitroaryl)-2-alkynylindoles and NaN_3 in hexamethylphosphoramide (HMPA) with CuI as a catalyst.[12] Although progress has been made in this field, further development of more efficient C1-synthons to access structurally diverse N-heterocycles is still desirable.

Sulfur ylides were first introduced by Jessop in 1930,[13] but it was only after the 1960s, with important contributions by Johnson and LaCount,[14] Franzen et al.,[15] and Corey and Chaykovsky,[16] that these compounds were widely used as surrogates of the corresponding C2 or C1 synthons in organic reactions. More recently, the groups of Aïssa and Li independently reported Cp*Rh(II)-catalyzed couplings of arenes with sulfoxonium ylides to synthesize the corresponding α-aryl ketones.[17] Chen and co-workers discovered an efficient copper-mediated formal [4+1] cycloaddition of *N*-sulfonylhydrazones with sulfoxonium ylides to give a variety of highly substituted 4,5-dihydropyrazoles.[18] The Ma group demonstrated a Ru-catalyzed [5+1] annulation through an NH_2-directed highly selective alkenyl C–H activation process with sulfoxonium ylides as coupling partners (Scheme 1c).[19] Our group recently reported a strategy for the synthesis of indoles by using easily accessible sulfur ylides and *N*-aryl-2-aminopyridines as functional surrogates.[20] Despite these developments, the use of sulfoxonium ylides for the synthesis of quinoxalines remains underdeveloped. In view of this, and as part of our ongoing research, we studied the reactions of 2-(1*H*-pyrrol-1-yl)anilines with



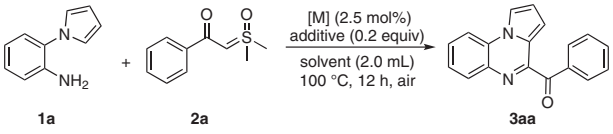
Scheme 2 *Reagents and conditions*: **1a–u** (0.2 mmol), **2a** (0.3 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (2.5 mol%), $AgNTf_2$ (0.2 equiv), ^{t}AmOH (2.0 mL), 100 °C, 12 h, under air.

carbonyl sulfoxonium ylides (as stable carbene precursors and bifunctional C1 synthons) with the aim of developing an alternative approach to the synthesis of pyrrolo[1,2-*a*]quinoxaline derivatives. The results of this study are reported below.

We commenced our study by identifying the optimal conditions for the reaction of 1-(2-aminophenyl)pyrrole (**1a**) with the sulfoxonium ylide **2a** (Table 1). The desired product **3aa** was obtained in 37% yield from the reaction at 100 °C for 12 hours in 1,2-dichloroethane (DCE) with [Ru(*p*-cymene)Cl_2]$_2$ as the catalyst and $AgSbF_6$ as an additive (Table 1, entry 1). Encouraged by this observation, we investigated the effects of the solvent and we found that *tert*-amyl alcohol (^{t}AmOH) gave the desired product **3aa** in 59% yield (entries 2–8). Other transition-metal catalysts, such as [Cp*$IrCl_2$]$_2$, [Cp*$RhCl_2$]$_2$, and Cp*Co(CO)I_2 were also tested and were found to be less effective than [Ru(*p*-cymene)Cl_2]$_2$ (entries 9–11). An exploration of various silver salts revealed that $AgNTf_2$ gave the best yield of 71% (entries 12–14), whereas an examination of various additives demonstrated that the yield decreased when silver salts were absent (entries 15–17). Temperature was also found to influence the reaction significantly, as indicated by the low reactivity of **1a** at 80 °C or 120 °C (entries 18 and 19). A reaction performed under an N_2 atmosphere gave only 19% of product **3aa** (entry 20). We therefore concluded that for optimal results, the reaction should be performed at 100 °C in ^{t}AmOH with [Ru(*p*-cymene)Cl_2]$_2$ (2.5 mol %) as catalyst in the presence of $AgNTf_2$ (0.2 equiv).

Having determined the optimal reaction conditions, we turned our attention to investigating the scope of the 1-(2-aminophenyl)pyrrole for the present transformation (Scheme 2). The position of the substituents did not significantly affect the yield of the reaction and, as expected, a wide variety of pyrrolo[1,2-*a*]quinoxaline derivatives, **3aa**–**ta**, were successfully obtained in moderate to good yields. Additionally, all methyl- or methoxy-substituted 1-(2-aminophenyl)pyrroles reacted readily to give the desired

Table 1 Optimization of the Reaction Conditions[a]



1a **2a** **3aa**

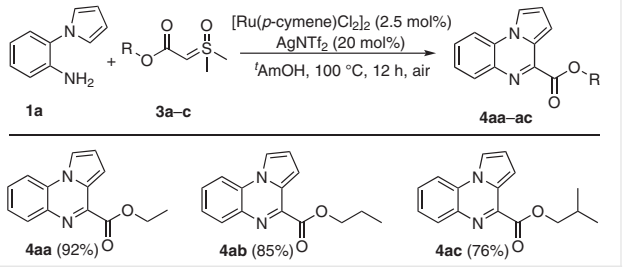
Entry	Catalyst	Additive	Solvent	Temp (℃)	Yield[b] (%)
1	[Ru(*p*-cymene)Cl_2]$_2$	$AgSbF_6$	DCE	100	37
2	[Ru(*p*-cymene)Cl_2]$_2$	$AgSbF_6$	^{t}AmOH	100	59
3	[Ru(*p*-cymene)Cl_2]$_2$	$AgSbF_6$	TFE	100	34
4	[Ru(*p*-cymene)Cl_2]$_2$	$AgSbF_6$	THF	100	37
5	[Ru(*p*-cymene)Cl_2]$_2$	$AgSbF_6$	1,4-dioxane	100	–
6	[Ru(*p*-cymene)Cl_2]$_2$	$AgSbF_6$	DME	100	32
7	[Ru(*p*-cymene)Cl_2]$_2$	$AgSbF_6$	^{i}PrOH	100	29
8	[Ru(*p*-cymene)Cl_2]$_2$	$AgSbF_6$	EtOAc	100	39
9	[Cp*$IrCl_2$]$_2$	$AgSbF_6$	^{t}AmOH	100	47
10	[Cp*$RhCl_2$]$_2$	$AgSbF_6$	^{t}AmOH	100	12
11	[Cp*Co(CO)I_2]$_2$	$AgSbF_6$	^{t}AmOH	100	–
12	[Ru(*p*-cymene)Cl_2]$_2$	$AgNTf_2$	^{t}AmOH	100	71
13	[Ru(*p*-cymene)Cl_2]$_2$	$AgBF_4$	^{t}AmOH	100	27
14	[Ru(*p*-cymene)Cl_2]$_2$	AgOTf	^{t}AmOH	100	29
15	[Ru(*p*-cymene)Cl_2]$_2$	$Zn(OAc)_2$	^{t}AmOH	100	62
16	[Ru(*p*-cymene)Cl_2]$_2$	PivOH	^{t}AmOH	100	64
17	[Ru(*p*-cymene)Cl_2]$_2$	K_2CO_3	^{t}AmOH	100	17
18	[Ru(*p*-cymene)Cl_2]$_2$	$AgNTf_2$	^{t}AmOH	80	56
19	[Ru(*p*-cymene)Cl_2]$_2$	$AgNTf_2$	^{t}AmOH	120	51
20[c]	[Ru(*p*-cymene)Cl_2]$_2$	$AgNTf_2$	^{t}AmOH	100	19

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), catalyst (2.5 mol %), additive (0.2 equiv), solvent (2.0 mL), 12 h, under air.
[b] Isolated yield.
[c] N_2 atmosphere.

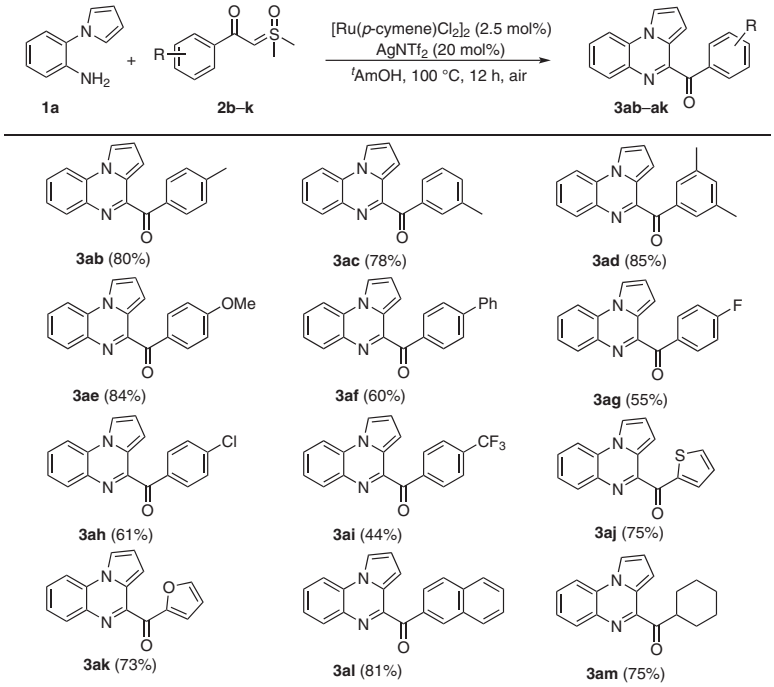
products **3aa–ha** in good yields. Halogenated 1-(2-aminophenyl)pyrroles also performed well, providing the desired products **3ia–ma** in moderate yields. These products could also significantly expand the utilization of the [5+1]-cyclization procedure. Substrate **1n** with strongly electron-deficient trifluoromethyl group afforded the desired product **3na** with excellent efficiency. When the disubstituted substrate **1o** was used, the corresponding product **3oa** was obtained in 65% yield. To our delight, heterocyclic group-substituted 2-(1*H*-pyrrol-1-yl)pyridin-3-amines **1p–s** reacted smoothly with **2a** to give products **3pa–sa** in yields of 46–66%. Note that substrate **1p**, which contains other possible C–H functionalization sites, reacted well at the terminal position to give the desired product **1pa**, but the reaction did not proceed to the acylmethylation stage.[17] The challenging substrate **1t**, which contains pyrrolyl group on the phenyl ring, was also found to be suitable for this transformation, affording product **3ta** in a moderate yield of 61%.

In an attempt to further expand the scope of the formal [5+1]-cycloaddition reaction, various β-ketosulfoxonium ylides were tested (Scheme 3). A variety of sulfoxonium ylides were subjected to the standard conditions, and moderate to good yields of the corresponding products were obtained. All benzoyl-substituted sulfoxonium ylides bearing electron-donating or -withdrawing groups on the phenyl ring reacted smoothly with 1-(2-aminophenyl)pyrrole (**1a**) to afford the corresponding products **3ab–ai** in moderate to excellent yields. Moreover, substrates substituted with a 2-thienyl (**2j**) or 2-furyl group (**2k**) gave the corresponding products **3aj** and **3ak**, in yields of 75 and 73%, respectively. In addition, a sulfoxonium ylides containing a 2-naphthyl group was also investigated and it provided the corresponding pyrrolo[1,2-*a*]quinoxaline **3al** in 81% yield. The scope of the reaction was further extended to a sulfoxonium ylide that contained a substituent other than an aryl or alkyl group, and the reaction gave product **3am** in 75% yield.

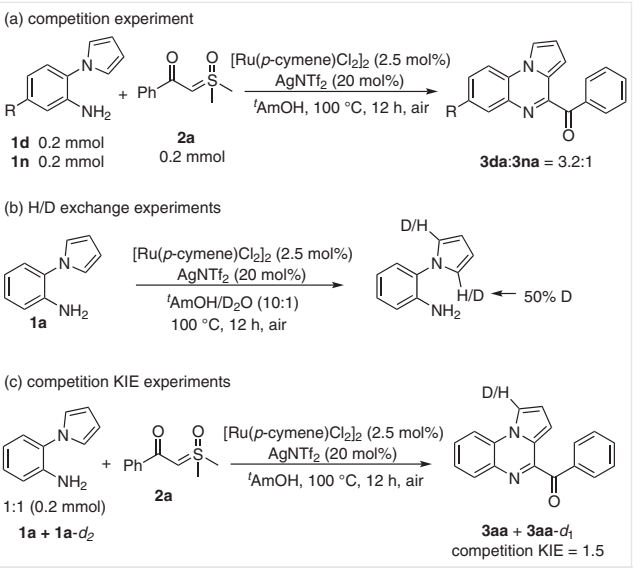
By using the optimal conditions, we examined whether the [5+1] cascade annulation reaction could be efficiently extended to α-ester sulfoxonium ylides **3a–c** (Scheme 4), which would be advantageous. To our delight, sulfoxonium ylides bearing an alkyl group gave the expected products **4aa–ac** in excellent yields, highlighting a potential application of our transformation.



Scheme 4 *Reagents and conditions*: **1a** (0.2 mmol), **3a–c** (0.3 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (2.5 mol%), $AgNTf_2$ (0.2 equiv), ^tAmOH (2.0 mL), 100 °C, 12 h, under air.



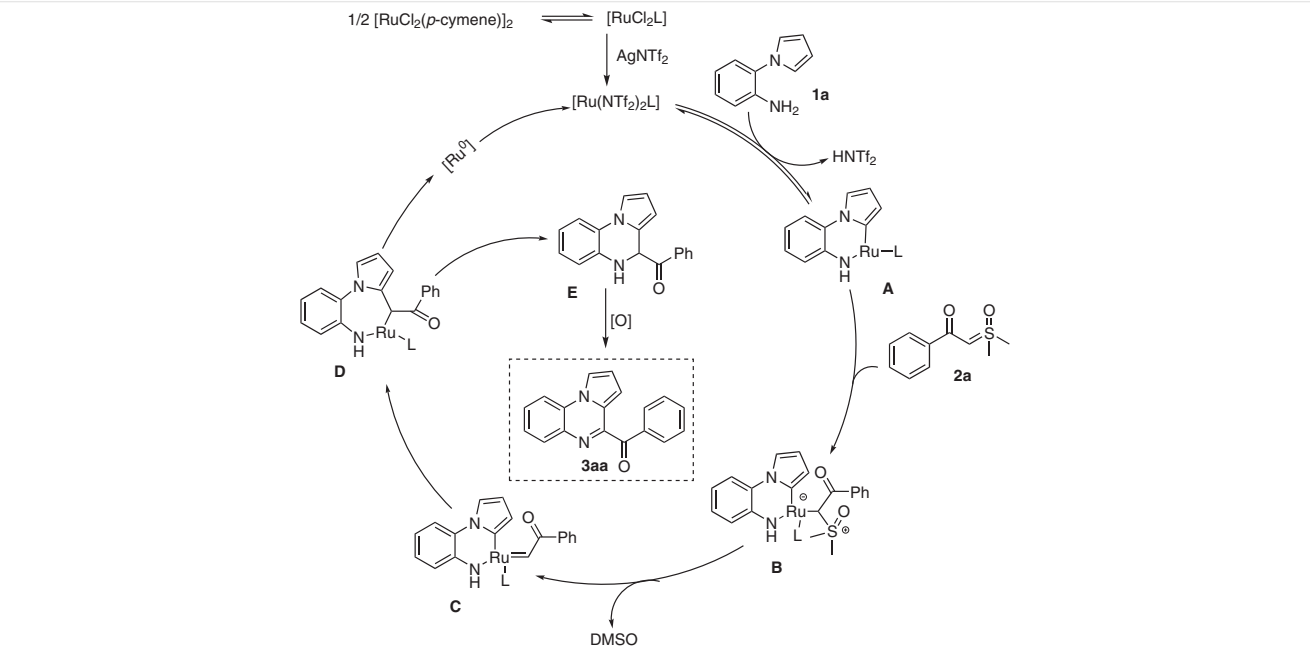
Scheme 3 *Reagents and conditions*: **1a** (0.2 mmol), **2b–k** (0.3 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (2.5 mol%), $AgNTf_2$ (0.2 equiv), ^tAmOH (2.0 mL), 100 °C, 12 h, under air.



Scheme 5 Mechanistic study experiments

To gain more insight into the mechanism of this transformation, several further experiments were conducted. Under Ru(II)-catalyzed conditions, a set of intermolecular competitive reactions between 5-methyl-2-(1*H*-pyrrol-1-yl)aniline (**1d**) and 2-(1*H*-pyrrol-1-yl)-5-(trifluoromethyl)aniline (**1n**) with **2a** were performed in a one-pot fashion. The NMR yield of **3da** was higher than that of **3na**, indicating that the electron-rich substrate had a higher reactivity (Scheme 5a). An H/D exchange experiment was subsequently performed in which 1-(2-aminophenyl)pyrrole (**1a**) was subjected to the optimized reaction conditions in the presence of D_2O. NMR analysis of the resulting 1-(2-aminophenyl)pyrrole (obtained in 85% yield) revealed that H/D exchange (50% D) had occurred at the *ortho*-position of the pyrrole (Scheme 5b). These results indicate the possible involvement of reversible C–H bond cleavage and metal protonation in the transformation. A kinetic-isotope-effect (KIE) experiment showed that competitive deuteriation between substrates **1a** and **1a**-d_2 occurred with a k_H/k_D ratio of 1.5 (Scheme 5c). This result indicates that the ruthenium-mediated C–H cleavage might not be involved in the turnover-determining step of the reaction.

Based on our previous work and results published in the literature,[19–21] a plausible catalytic cycle for the [5+1]-annulation reaction of **1a** with **2a** was proposed (Scheme 6). Initially, the dimeric precursor [Ru(*p*-cymene)Cl_2]$_2$ is converted into a cationic species. 1-(2-Aminophenyl)pyrrole (**1a**) is then coordinated with the Ru(II) catalyst and, following intermolecular attack on the pyrrole fragment, a five-membered ruthenacycle intermediate **A** is produced. Sulfoxonium ylide **2a** is then coordinated to generate the alkyl–Ru(II) species **B**. A reactive ruthenium α-oxo carbene species **C** is then formed from **B** through α-elimination of dimethyl sulfoxide (DMSO). Subsequent carbene migratory insertion of the Ru-aryl bond gives the seven-membered ruthenacycle **D**. The key intermediate **D** then undergoes reductive elimination to form the ring molecule **E** (rather than undergoing protonation as previously reported by others), releasing Ru(II) for the next catalytic cycle. Finally, the cyclic com-



Scheme 6 Proposed mechanism

pound **E** is oxidized by molecular oxygen to generate the target phenyl(pyrrolo[1,2-*a*]quinoxalin-4-yl)methanone (**3aa**).

In summary, we have successfully developed a ruthenium(II)-catalyzed coupling-cyclization of 1-(2-aminophenyl)pyrroles with sulfoxonium ylides.[22] This new annulation process uses a commercially available ruthenium catalyst together with a free amino group as a traceless directing group to permit alkenyl C–H functionalization and to provide an efficient access to pyrrolo[1,2-*a*]quinoxaline skeletons. The protocol not only is expeditious and operationally simple, but also permits the use of a wide range of substrates and has excellent tolerance to various functional groups.

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0040-1707119.

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(22) **Phenyl(pyrrolo[1,2-*a*]quinoxalin-4-yl)methanone (3aa); Typical Procedure**

A Schlenk tube (20 mL) equipped with a stirrer bar was charged with 1-(2-aminophenyl)pyrroles (**1a**; 0.2 mmol, 31.6 mg), sulfoxonium ylide **2a** (0.3 mmol, 58.8 mg), $[RuCl_2(p\text{-cymene})]_2$ (2.5 mol%, 3.1 mg), and $AgNTf_2$ (20 mol%, 15.5 mg) under an air atmosphere (1 atm). Anhyd ^{t}AmOH was added, and the mixture was stirred at 100 °C for 12 h, then cooled to r.t. The mixture was filtered through a short Celite pad, and the filtrate was concentrated. The residue was purified by column chromatography [silica gel, PE–EtOAc–$CHCl_3$ (8:1:1)] to give a yellow solid; yield: 71%.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.20–8.14 (m, 2 H), 8.04–7.99 (m, 2 H), 7.91 (d, *J* = 8.2 Hz, 1 H), 7.62 (m, 2 H), 7.49 (m, 3 H), 7.21 (d, *J* = 4.1 Hz, 1 H), 6.96 (m, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.36, 149.90, 135.79, 134.73, 133.55, 131.06, 131.00, 129.40, 128.30, 127.92, 125.43, 124.34, 114.87, 114.72, 113.85, 108.86. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{18}H_{13}N_2O$: 273.1023; found: 273.0939.

