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Concise Report

2-(Quinolin-2-yl)oxazoles, Cyclization, Metal ions probes, *N*-Sulfonyl-1,2,3-triazoles

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Rh-catalyzed formal [3+2] cyclization for synthesis of 5-aryl-2-(quinolin-2-yl)oxazoles and its applications in metal ions probes

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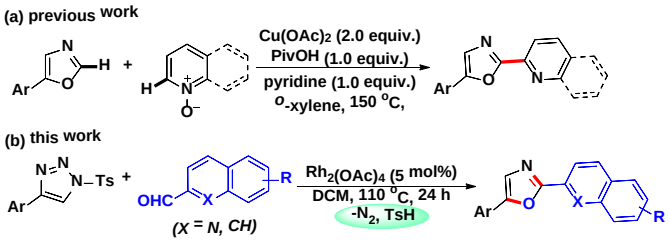
Summary of main observation and conclusion A facile and efficient strategy for the synthesis of 5-aryl-2-(quinolin-2-yl)oxazoles via rhodium-catalyzed formal [3+2] cyclization of 4-aryl-1-tosyl-1*H*-1,2,3-triazoles with quinoline-2-carbaldehydes has been described. The protocol employs mild conditons and offers good yields of diverse 2,5-aryloxazole derivatives with a broad reaction scope. It is amenable to gram-scale synthesis and easily transformation. Moreover, this 5-aryl-2-(quinolin-2-yl)oxazole skeleton is indeed a new fluorophore and its applications in metal ions probes are also investigated and showed fluorescent responses to mercury ion.

Background and Originality Content

In the last few decades, the design and synthesis of functional mole-cules that could sense specific ions has attracted intense interest in diverse research fields.[1] Oxazoles, quinolines and their derivatives are well recognized for their important role designing novel drug moieties for medicinal applications.[2,3] As a consequence, the combination of these two structural features within a single framework giving novel quinolone-oxazoles has potential for biological and pharmacological activities.[4] In addition, the extend π structure of these compound also has potential fluorescence properties to expedite their applications in material science as ligands and chemosensors. To date, only one method has been reported for the synthesis of 2-(quinolin-2-yl)oxazoles based on the cross-dehydrogenative coupling of quinoline *N*-oxides with 1,3-azoles (Scheme 1a).[5] However, this strategy still possesses some limitations, including excess metal catalyst, additive/base, and high temperature, and the substrate scope is also relatively limited. Therefore, the development of simple, efficient, and environmentally benign strategies for the formation of 2-(quinolin-2-yl)oxazoles is quite appealing.

N-Sulfonyl-1,2,3-triazoles have recently emerged as structural motifs that are studied for synthesizing a variety of biologically active heterocycles,[6] including pyrrole,[7] tetrahydropyridines,[8] imidazoles,[9] pyrroloindoline[10] and others.[11] In these transformations, the highly reactive rhodium azavinyl carbenes (Rh-AVC), derived from Rh(II)-catalyzed denitrogenation of *N*-sulfonyl-1,2,3-triazoles has been successfully employed as a [1C], [2C], or *aza*-[3C]-synthon in various [3+n] cycloaddition reactions.[12] In particularly, a wide range of unsaturated chemical bonds, including aldehyde, nitrile, have been well explored in the [3 + 2] cycloadditions. For instance, Fokin and co-workers exploited the reactivity of Rh-AVC to achieve imidazoles in good to excellent yields with *N*-sulfonyl 1,2,3-triazoles and nitriles.[13] Very recently, they reported that Rh-AVC reacted with aldehydes to give 3-sulfonyl-4-oxazolines through an intramolecular cyclization.[14] Inspired by our previous reports and in line with our long-standing interesting in diazo chemistry,[15] we herein report our new results on the synthesis of 5-aryl-2-(quinolin-2-yl)oxazoles in good yields *via* Rh-catalyzed formal [3+2] cyclization from 4-aryl-1-tosyl-1*H*-1,2,3-triazoles and quinoline-2-carbaldehydes under mild conditions (Scheme 1b).

Scheme 1 Synthetic strategies for 2-(quinolin-2-yl)oxazoles



Results and Discussion

We commenced our investigation using 4-phenyl-1-tosyl-1*H*-1,2,3-triazole (1a), quinoline-2-carbaldehyde (**2a**) as the model substrates to identify the reaction conditions for this formal [3+2] cyclization. Preliminary examination identified DCM (dichloromethane) as the solvent choice in the presence of

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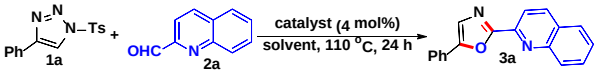
$Rh_2(oct)_4$ as catalyst, affording the target product **3a** in 39% yield (Table 1, entries 1-7). No reaction occurred in the absence of transition metal catalyst (Table 1, entry 8). To our delight, increasing the catalyst loading to 5 mol% resulted in a significantly higher yield (75%, Table 1, entry 9). However, the desired product **3a** was isolated in 28% yield in DCE as solvent with the same catalyst loading (Table 1, entry 3). Subsequently, changing the catalyst to other metal catalysts and rhodium catalysts did not improve the efficiency (Table 1, entries 11-16). In addition, the effects of the temperature and reaction time were also investigated. It was found that neither increasing nor decreasing the reaction temperature/time could improve the yield (Table 1, entries 17-20). Taken together, 5 mol% $Rh_2(oct)_4$ as catalyst, DCM as solvent at 110 °C for 24 h were selected as the optimized reaction conditions (Table 1, entry 9).

Table 1 Optimization of the reaction conditions.[a]



Entry	Catalyst	Solvent	Yield/%
1	$Rh_2(oct)_4$	DCM	39
2	$Rh_2(oct)_4$	toluene	24
3	$Rh_2(oct)_4$	DCE	14 (28[c])
4	$Rh_2(oct)_4$	PhCl	30
5	$Rh_2(oct)_4$	$MeNO_2$	trace
6	$Rh_2(oct)_4$	$CHCl_3$	trace
7	$Rh_2(oct)_4$	THF	trace
8	/	DCM	nr
9[c]	$Rh_2(oct)_4$	DCM	75
10[d]	$Rh_2(oct)_4$	DCM	54
11[c]	CuI	DCM	17
12[c]	$[Cp^*RhCl_2]_2$	DCM	nd
13[c]	$[(PPh)_3P]_3RhCl$	DCM	45
14[c]	$Co_2(CO)_8$	DCM	32
15[c]	$Ni(acac)_2$	DCM	50
16[c]	$Rh_2(OAc)_4$	DCM	27
17[c,e]	$Rh_2(oct)_4$	DCM	17
18[c,f]	$Rh_2(oct)_4$	DCM	29
19[c,g]	$Rh_2(oct)_4$	DCM	56
20[c,h]	$Rh_2(oct)_4$	DCM	75

[a] Reaction conditions: 4-phenyl-1-tosyl-1*H*-1,2,3-triazole **1a** (0.2 mmol), quinoline-2-carbaldehyde **2a** (0.2 mmol), catalyst (4 mol%), and solvent (2 mL) under argon atmosphere at 110 °C for 24 h. [c] The catalyst loading was 5 mol%. [d] The catalyst loading was 6 mol%. [e] 90 °C. [f] 120 °C. [g] For 12 h. [h] For 30 h.

With the optimized conditions established, the substrate scope of this formal [3+2] cyclization was evaluated as shown in Table 2. The yield of **3a** was relatively moderate (48%, 30%, and 28%, respectively) changing the *p*-tosyl group to (4-fluorophenyl)sulfonyl, (4-methoxyphenyl)sulfonyl, and (2,4,6-triisopropylphenyl)sulfonyl groups of the substrate 1,2,3-triazoles. Similarly, the substrates 1 with electron-donating group (e.g., Me, Et, OMe) on the *para*-position of aryl group were well suitable for this reaction, affording the corresponding products **3b**, **3c**, and **3d** in 65%, 62%, and 76% yields, respectively. While the same position was replaced by moderate electron-withdrawing groups (e.g., F, Br), the reactivity of the process was hampered and the yield was lightly reduced (**3e**, **3f**). These results indicated that electronic effect of the substituents on the phenyl ring had a certain effect on the Rh-carbene intermediate derived from 1,2,3-triazoles in the presence of Rh-catalyst. Though the electron-withdrawing group (e.g. F, Br) could improve the activity of Rh-carbene intermediate, which also was easily decomposed in the reaction conditions to decrease the yield of the desired product. To our surprise, trifluoromethyl as strong electron-withdrawing substituent afforded the desired product **3g** in 76% yield. Similarly, the yield of compound **3l** was decreased to 49% when the Rh-carbene intermediate bearing with two CF_3 groups for its higher reactivity and easily decomposed. The reaction also effectively for *meta*- and *ortho*-substituted 1,2,3-triazoles on the aryl group, generating the corresponding products **3h**-**3k** in 71%-82% yields. In addition, 1,2,3-triazoles bearing with ditrifluoromethyl group at the *meta*-position of phenyl ring was also compatible. Noteworthy was the ability to incorporate an extend π structure into the product (**3m**), providing potential applications in photochemical properties and chemosensors.

The optimized reaction conditions were then challenged with a diversity of substituted quinoline-2-carbaldehydes to probe its scope, by taking **1a** as the reaction partner. Satisfactorily, substituents including electron-rich (e.g., Me) groups and electron-deficient (e.g., F, Cl, and Br) groups at the 6-, 7-, and 8-positons of the quinolyl rings were well-tolerated. The corresponding products **3n**-**3r** were obtained in 66%-78% yields. In addition to quinoline-2-carbaldehydes, 2-naphthaldehydes and benzofuran-2-carbaldehyde were examined. The desired products **3s**, **3t**, and **3u** were successfully obtained in 71%, 64%, and 70% yields, respectively. Unfortunately, when other heteroaromatic aldehydes, such as benzo[*b*]thiophene-2-carbaldehyde, 1-methyl-1*H*-indole-2-carbaldehyde, benzo[*d*]thiazole-2-carbaldehyde, and quinoxaline-2-carbaldehyde were employed, the reaction system became sluggish and the corresponding products **3v**-**3y** were hardly observed, which trouble the [3+2] cyclization process.

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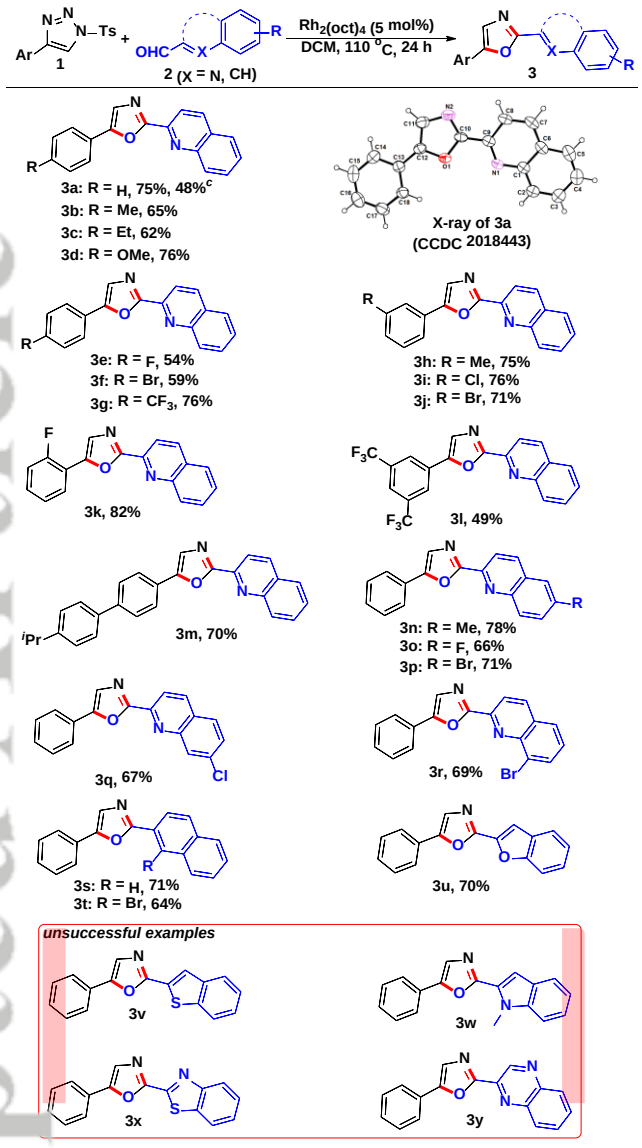
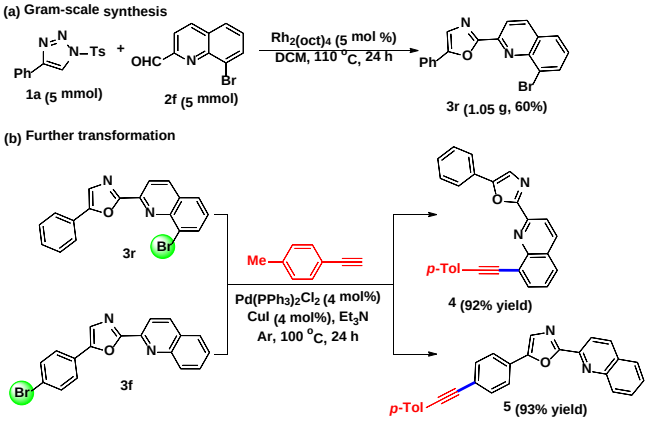
Table 2 Substrate scope.[a,b]



[a] Reaction conditions: 4-aryl-1-tosyl-1*H*-1,2,3-triazoles **1** (0.2 mmol), aromatic aldehydes **2** (0.2 mmol), and $Rh_2(OAc)_4$ (5 mol%) in DCM (2 mL) under argon atmosphere at 110 °C for 24 h. [b] Isolated yields. [c] (4-fluorophenyl)sulfonyl was used instead of *p*-tosyl group.

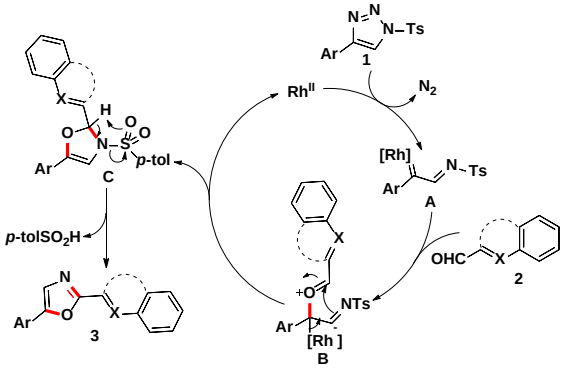
To demenstrate the efficiency and utility of this strategy, a gram-scale synthesis was performed by using 4-phenyl-1-tosyl-1*H*-1,2,3-triazole (**1a**, 5 mmol) and 8-bromoquinoline-2-carbaldehyde (**2f**, 5 mmol) as substrates under the standard conditions (Scheme 2a). Gratifyingly, the desired product 3r was afforded in 60% yield (1.05 g). In addition, the halo-substituted product **3r** and **3f** were used for late-stage transformation, affording the Sonogashira coupling products **4** and **5** in 92% and 93% yields, respectively (Scheme 2b). This fantastic outcome indicates that this method is a prospectively powerful tool for late-stage modification of π extend molecules, which has potential applications in material science as ligands and chemosensors.

Scheme 2 Further studies



On the basis of the previously described experimental finding and the literature precedence,[14,16] a proposed mechanism is illustrated in Scheme 3. Initially, 1,2,3-triazoles **1** reacted with Rh-catalyst extruding nitrogen and generated Rh(II)-azavinyl carbine species **A**. Subsequently, interaction of the carbene center with the carbonyl group of substrate **2** formed the intermediate ylide **B**, which underwent cyclization, leading to the intermediate C. Finally, removal of the *p*-toluenesulfonic acid (detected by GC-MS) followed by affording the desired 2,5-aryloxazoles **3**.

Scheme 3 Proposed mechanism



We previously reported a novel ferrocenyl-isoxazoles as a multiple signal probe for highly selective recognition of Cu^{2+} ions.[17] This class of compounds have rarely been reported in the field of molecular sensing and might have a potential significance for the application of the π extent isoxazole derivatives in molecular recognition. During the preparation of 5-aryl-2-(quinolin-2-yl)oxazoles, we found that these compound were strongly emissive under UV light and this skeleton was indeed a new fluorophore. Therefore, we selectively investigated the photophysical properties of compounds **3a**, **3d**, **3g**, **3m**, **3s**, **3u**, **4** and **5** (see the ESI). These

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compounds have good fluorescence properties in mixed methanol under 365 nm irradiation with a hand-held UV lamp (Figure 1).

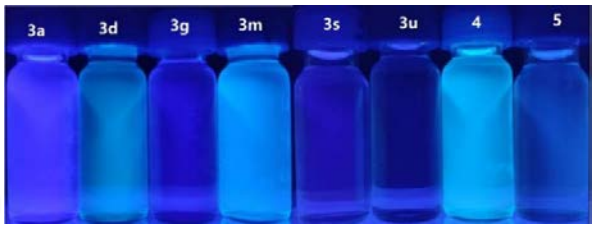

Figure 1 The fluorescence colours of 2-(quinolin-2-yl)oxazoles in MeOH (2.5×10^{-5} M) under UV irradiation (365 nm).

We next studied the impact of the different substituents on the absorbance and fluorescent properties of the selected 2,5-aryloxazoles (Table 3). 2-(quinolin-2-yl)oxazole **3a** absorbs light at 348 nm (ε = 2.08 × 10^4). When 2-quinolinyl changed to 2-naphthalenyl and 2-benzofuranyl, we found that the maximum absorption wavelength of compounds **3s** (λ_{max} = 323 nm, ε = 3.12 × 10^4) and **3u** (λ_{max} = 336 nm, ε = 2.27 × 10^4) had a light blue shift. On the other hand, the presence of electron-donating (**3d**) and π extend groups (**3m**) on the phenyl ring showed a light red shift of the maximum absorption wavelength. Also the emission spectra of these selective compounds were evaluated (see ESI, Figure S2). Similarly, the compounds **3d** and **3m** showed intense emission spectra (492 nm and 476 nm) with an excellent Stokes shifts (136 nm and 117 nm).

Table 3 Photophysical properties of the selected compounds in MeOH (2.5×10^{-5} M).

Compound	λabs[a]/nm	ε($M^{-1}cm^{-1}$)	λem[b]/nm	Stokes shift (nm)
3a	348	20840	435	87
3d	356	3520	492, 594	136, 211
3g	343	23640	415	72
3m	359	19560	476	117
3s	323	31200	399	76
3u	336	22760	392	56
4	290	29560	482	192
5	383	3360	459, 594	76, 211

[a] Absorption maxima. [b] Fluorescent emission maxima.

Subsequently, the metal-recognition properties of receptor **3a** as ligand (L) were evaluated by UV-Vis spectroscopy (Figure 2a). A very strong high-energy (HE) absorption peak at 348 nm (ε = 2.26 × 10^4) and a weak low-energy (LE) waveless peak at 287nm can be observed for compound **3a** in MeOH (c = 2.5 ×10^{-5} M). To our delight, we found that a red shift of the HE absorption wavelength to 353 nm and no LE absorption wavelength can be observed upon the addition of 2.5 ×10^{-5} M Hg^{2+} cations to the solution of compound **3a**, compared to other metal ions which increased either HE absorption peak or LE absorption peak at 294 nm and 349 nm to 362 nm. On the other hand, the fluorescence character of compound 3a and the response towards K^+, Na^+, Ni^{2+}, Mg^{2+}, Ca^{2+}, Pb^{2+} and Hg^{2+}metal ions were investigated (Figure 2b). To our delight, dramatic fluorescence quenching of compound **3a** was observed upon the addition of Hg^{2+} ion to the solution and a new emission peak appeared at 594 nm. By contrast, a gradually decreased fluorescent intensity was observed when gradually addition of other metal ions including Na^+, K^+, Mg^{2+}, Ca^{2+}, Pb^{2+}, and Ni^{2+}. These results indicated that compound **3a** showed highly selective sensing toward Hg^{2+} ion over the other metal ions investigated.

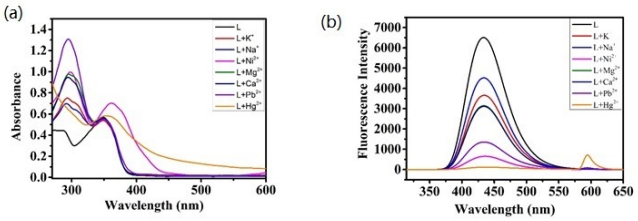

Figure 2 (a) absorption spectra of compound **3a** (c = 2.5 × 10^{-5} M) in MeOH-H_2O (v/v = 1:1) upon addition of several cations. (b) fluorescence emission spectra of **3a** (c = 2.5 × 10^{-5} M) in MeOH-H_2O (v/v = 1:1) upon addition of several cations.

Conclusions

In summary, the synthesis of novel 5-aryl-2-(quinolin-2-yl)oxazole derivatives as a new chemosensor in metal ion recognition has been achieved *via* Rh-catalyzed formal [3+2] cyclization of 4-aryl-1-tosyl-1*H*-1,2,3-triazoles with quinoline-2-carbaldehydes. This highly efficient protocol constructs two new carbon-heteroatom bonds and one new five-membered ring through sequential denitrogenation/1,3-dipolar cycloaddition/elimination process. This process does not require additive/base in the presence lower catalyst loadings under mild conditions, thus, this protocol is complementary to the inherent shortcomings of the existing cross-dehydrogenative coupling of quinoline *N*-oxides with 1,3-azoles. In addition, this work not only provided a simple and efficient one-pot reaction for the construction of multifunctional oxazole derivatives that are not easy accessible by other approaches but also demonstrated their application in metal ion probes.

Experimental

General procedure for the synthesis of 2,5-aryloxazoles 3. A mixture of 4-aryl-1-sulfonyl-1*H*-1,2,3-triazoles **1** (0.2 mmol), quinoline-2-carbaldehydes **2** (0.2 mmol) or 2-naphthaldehydes (0.2 mmol) or benzofuran-2-carbaldehyde (0.2 mmol), and $Rh_2(oct)_4$ (0.01 mmol) in DCM (2 mL) was heated to 110 °C in an oil bath for 24 h. After the reaction was complete (as determined using TLC), the reaction mixture was cooled to room temperature, extracted with CH_2Cl_2 (3 × 10 mL), and washed with brine. The organic layers were combined, dried over Na_2SO_4, filtered, and then evaporated under vacuum. The residue was purified using flash column chromatography with a silica gel (200-300 mesh), using ethyl acetate and petroleum ether (1:10, v/v) as the elution solvent to

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give desired products **3**.

General procedure for the synthesis of compounds 4 and 5. A mixture of 2-(8-bromoquinolin-2-yl)-5-phenyloxazole **3r** (0.2 mmol) or 5-(4-bromophenyl)-2-(quinolin-2-yl)oxazole **3f** (0.2 mmol), 1-ethynyl-4-methylbenzene (0.2 mmol), $Pd(PPh_3)_2Cl_2$ (4 mol%), and CuI (4 mol%) in triethylamine (2 mL) was stirred under argon atmosphere at 100 ºC in an oil bath for 24 h. After the reaction was complete (as determined using TLC), the reaction mixture was cooled to room temperature, extracted with CH_2Cl_2 (3 × 10 mL), and washed with brine. The organic layers were combined, dried over Na_2SO_4, filtered, and then evaporated under vacuum. The residue was purified using flash column chromatography with a silica gel (200-300 mesh), using ethyl acetate and petroleum ether (1:12, v/v) as the elution solvent to give the Sonogashira products **4** or **5**.

Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.2018xxxxx.

Acknowledgement

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Rh-catalyzed formal [3+2] cyclization for synthesis of 5-aryl-2-(quinolin-2-yl)oxazoles and its applications in metal ions probes

Tongtong Zhou, Xinwei He,* Youpeng Zuo, Yuhao Wu, Wangcheng Hu, Shiwen Zhang, Jiahui Duan and Yongjia Shang*

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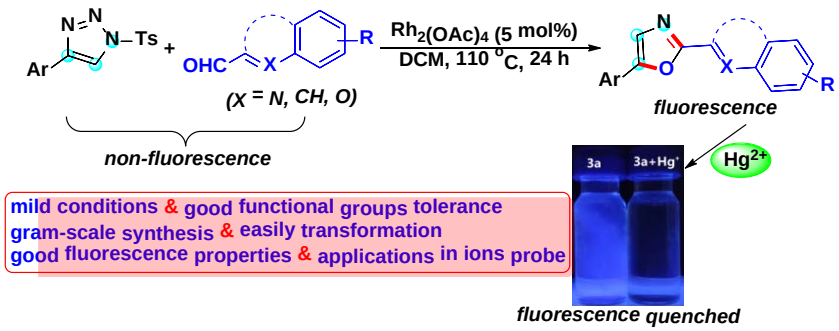

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