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# Ruthenium(II)-catalyzed selective monoarylation in water and sequential functionalisations of C–H bonds†

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**The ruthenium(II)-phosphine catalyst $RuCl_2(PPh_3)$(*p*-cymene) operating water selectively leads to *ortho* monoarylation, with arylchlorides and heteroarylhalides, of functional arenes. Further catalytic heteroarylation with $Ru(OAc)_2$(*p*-cymene) in water produces mixed bifunctional derivatives.**

## Introduction

The direct catalytic functionalisation of C–H bonds is attracting tremendous interest to develop at low cost C–C bond cross-coupling reactions without the use of a stoichiometric amount of organometallic reagents, thus *via* a better atom economy and greener process.[1] However many influencing factors need to be elucidated and improved such as catalyst efficiency and cost, compatible non-toxic solvents, and multiple controlled regioselectivities. Another rising objective consists in the consecutive regioselective functionalisations of several C–H bonds for both synthetic efficiency and green chemistry contribution. The diarylation with arylhalides and heteroarylhalides of *ortho* C–H bonds of functional arenes can now be achieved easily,[1] especially with cheap ruthenium(II) catalysts in the presence of catalytic amounts of carboxylate.[2–4] The sequential monoarylations with two different functional (hetero)arylhalides of two identical C–H bonds have not been achieved yet in spite of their potential to reach new mixed bifunctional polyaryl molecules of interest for molecular materials and as polymer precursors.

Selective monoarylations are easily achieved only when one *ortho* substituent is present or when only one C–H bond is protected by steric hindrance of a substituent at an arene *meta* position. However a few ruthenium(II)-phosphine catalysts operating in organic solvents have shown the ability to preferentially generate monoarylated arenes with rather good selectivity.[4] The first example of direct arylation with arylbromides using the ruthenium(II)-$PPh_3$ catalyst was shown by Oi and Inoue and led predominantly to the *ortho* monoarylation of 2-phenylpyridine and arylimines in NMP.[4a,b] Chanjuan Xi *et al.*[4c] demonstrated a selective monoarylation of 2-phenylpyridine in the presence of a $[RuCl_2(PPh_2(–C(Ph)=CHPh)(arene))]$ catalyst precursor. The $[RuCl_2(L)(p\text{-cymene})]_2$ complex containing a bulky monophosphine L ligand was efficient to monoarylate 2-phenylpyridine and *N*-phenylpyrazole with arylchlorides in NMP at 120 °C as reported by Doherty *et al.*[4d] In parallel the carboxylate-ruthenium(II) catalysts when operating in water were revealed to provide in a rare example a high ratio of mono(hetero)arylation of functional arene C–H bonds.[3c] Thus we have investigated the positive influence of these two factors: ruthenium(II)-phosphine catalyst and ruthenium catalysis in water in the search for selective monoarylation, thus in a non-toxic solvent and under greener chemistry conditions. Several industrial processes are already operating under aqueous phase organometallic-catalyzed reaction conditions and there are already some technical solutions such as membrane filtration or phase separation for water recovery.[5]

We now report that Ru(II)-$PPh_3$ catalyst $RuCl_2(PPh_3)$(*p*-cymene) operating in water, without a carboxylate promoter, constitutes a good catalytic system for selective monoarylation of functional arenes and that the sequential catalytic functionalisations in water of two *ortho* C–H bonds of functional arenes can be applied to reach unsymmetrical *ortho* diarylated arenes and one example of mixed *ortho* arylated and alkenylated arenes.

## Results and discussion

The activity of an arylation catalyst was often revealed by the ratio of the diarylation of (hetero)arenes as mono and diarylations had almost similar rates.[3] Thus conditions were searched to differentiate these two reaction rates. We first investigated the reaction of a slight excess of 2-phenylpyridine (0.6 mmol) with chlorobenzene (0.5 mmol) in the presence of various

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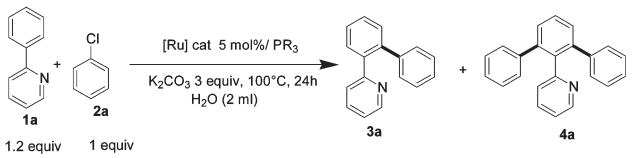
†Electronic supplementary information (ESI) available: Experimental procedures, spectroscopic and analytical data. See DOI: 10.1039/c2gc36222h

**Table 1** Catalytic monoarylation of 2-phenylpyridine in water[a]

| Entry | Catalyst | Time (h)/ Conv[b] (%) | 3a/4a[c] |
|---|---|---|---|
| 1 | $[RuCl_2(p\text{-cymene})]_2$ | 24 h – 97 | 78/22 |
| 2 | $Ru(OPiv)_2(p\text{-cymene})$ | 24 h – 98 | 78/22 |
| 3 | $Ru(OPiv)_2(p\text{-cymene})$ + 2 equiv. $PPh_3$ | 24 h – 100 | 82/12 |
| 4 | $Ru(OAc)_2(p\text{-cymene})$ | 24 h – 97 | 80/20 |
| 5 | $Ru(OAc)_2(p\text{-cymene})$ + 2 equiv. $PPh_3$ | 24 h – 89 | 94/6 |
| 6 | $RuCl_2(PPh_3)(p\text{-cymene})$ | 24 h – 100 | 89/11 |
| 7 | $RuCl_2(P(CH_2Ph)_3)(p\text{-cymene})$ | 24 h – 98 | 85/15 |
| 8 | $RuCl_2(PCy_3)(p\text{-cymene})$ | 24 h – 94 | 89/11 |
| 9 | $RuCl_2(Pi\text{-}Pr_3)(p\text{-cymene})$ | 24 h – 93 | 85/15 |
| 10 | $[RuCl_2(p\text{-cymene})]_2$ + $(P(o\text{-Me-}C_6H_4)_3)$ | 24 h – 96 | 80/20 |
| 11[d] | $RuCl_2(PPh_3)(p\text{-cymene})$ | 3 h – 81 | 96/4 |
| | | 5 h – 92 | 95/5 |
| | | 5 h – 45[e] | 98/2 |
| 12[f] | $RuCl_2(PPh_3)(p\text{-cymene})$ | 16 h – 70 | 98/2 |

[a] Reaction conditions: 0.6 mmol of 2-phenylpyridine, 5 mol% of [Ru], 3 equiv. of $K_2CO_3$, 10 μL of tetradecane (internal standard) for GC, 0.5 mmol of chlorobenzene in 2 mL of water, 24 h, 100 °C. [b] Conversion determined by gas chromatography based on arylhalide. [c] **3a**/**4a** ratio determined by gas chromatography. [d] Reaction at 80 °C. [e] Reaction performed in NMP as a solvent. [f] Reaction at 60 °C.

catalysts in water at 100 °C and in the presence of $K_2CO_3$ as a base, as




(1)

carbonate also contributes to the C–H bond activation/deprotonation[6] (eqn (1) and Table 1).

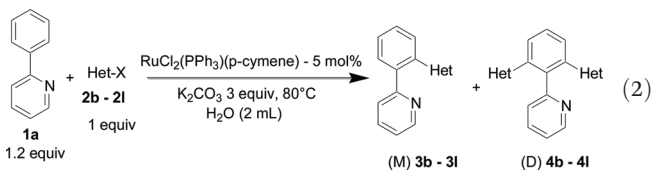
The reactions produced only **3a** and **4a** derivatives without side products such as homocoupling products. With $[RuCl_2(p\text{-cymene})]_2$ as the catalyst precursor in the absence of a carboxylate ligand a conversion of 97% was reached in 24 h with a **3a**/**4a** ratio of 78/22 (Table 1, entry 1). The reaction performed in the presence of $Ru(OPiv)_2(p\text{-cymene})$ and $Ru(OAc)_2(p\text{-cymene})$, which were previously shown to be efficient catalysts for diarylation in water,[3c,7] led to 97% conversion, with a moderate **3a**/**4a** ratio (Table 1, entries 2, 4). Addition of 2 equiv. of $PPh_3$ to the ruthenium carboxylate catalysts showed only a slight improvement in the selectivity towards **3a** (Table 1, entries 3, 5 *vs.* 2, 4).

Better conversion and selectivity towards the monoarylated product were obtained after 24 h with 5 mol% of $RuCl_2(PPh_3)(p\text{-cymene})$ (Table 1, entry 6). The replacement of $PPh_3$ by bulkier and more electron donating phosphines such as $P(CH_2Ph)_3$, $PCy_3$, $Pi\text{-}Pr_3$ or $P(o\text{-Me-}C_6H_4)_3$ did not improve the selectivity of the formation of **3a** (Table 1, entries 7–10). Neither steric nor electronic property of the phosphine ligand had a significant positive effect on the selective formation of **3a** with respect to $PPh_3$ in water. Noteworthily, the selective formation of **3a** could be achieved at 80 °C in 5 h, and even at 60 °C in 16 h (Table 1, entries 11–12). The reaction performed in NMP at 80 °C for 5 h provided only 45% of conversion (entry 11). This reveals that water is a more efficient solvent at lower temperature than NMP for monoarylation.

We performed a kinetic study, in order to better observe the variations of conversion and selectivity as a function of the reaction time with 5 mol% of the $RuCl_2(PPh_3)(p\text{-cymene})$ catalyst in water. After 1 h, the conversion was only 71% with 99% of selectivity towards the monoarylated product. When the reaction was carried out for 24 h, the selectivity of **3a** decreased from 99% to 89%, which showed that the diarylated product was formed during the course of the reaction at the expense of the monoarylated product. We observed that the best formation of monoarylated 2-phenylpyridine **3a** was obtained in 3 h (Table S1†). The reaction was performed with various catalysts in 3 h at 100 °C in order to evaluate the influence of various phosphorous and arene ligands coordinated to ruthenium (Tables S2 and S3†). Hence, after the screening of the reaction of 2-phenylpyridine with chlorobenzene it could be concluded that the best conditions to reach the monoarylated product **3a** were to use the $RuCl_2(PPh_3)(p\text{-cymene})$ catalyst: (i) at 80 °C, with 5 mol% of the catalyst with a reaction time of 5 h, or (ii) at 100 °C, with 5 mol% of the catalyst with a reaction time of 3 h.

### Selective monoarylation of 2-phenylpyridine with (hetero)aryl halides in water

The selective monoarylation with various (hetero)arylhalides was investigated using 5 mol% of the $RuCl_2(PPh_3)(p\text{-cymene})$ catalyst in water at 80 °C (eqn (2), Table 2).



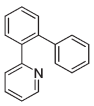
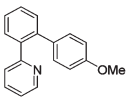
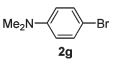
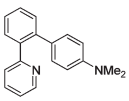
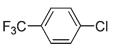
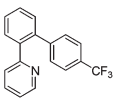
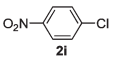
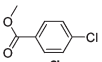
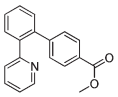
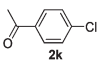
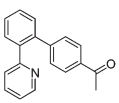
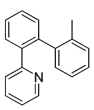
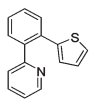
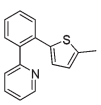
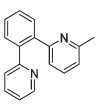

(2)

The reaction of 2-phenylpyridine with various electron donating and electron withdrawing heteroarenes was performed. The monophenylated 2-phenylpyridine **3a** was obtained by the reaction with phenylchloride in 5 h with 76% isolated yield (Table 2, entry 1). The reaction with arylhalides containing the *para* substituted electron donating groups, –OMe, $–NMe_2$, gave 69% and 72% yield, respectively in 8–13 h (Table 2, entries 2–3). With the electron withdrawing *para* $CF_3$-substituted phenylchloride 99% of conversion was obtained in 13 h leading to 80% of monoarylated product **3h** (Table 2, entry 4). With 4-methyl chlorobenzoate **2j** and 4-chloroacetophenone **2k** the reactions were completed in shorter reaction times (3–10 h), providing 83% and 77% of monoarylated products **3j** and **3k**, respectively (Table 2, entries 6–7). With *o*-methylchlorobenzene **2l** only 30% of product **3l** was isolated after 24 h (Table 2, entry 8).

The reaction with heterocyclic halides such as 2-chlorothiophene, 5-methyl-2-chlorothiophene, 6-bromo-2-methylpyridine was performed successfully with short reaction times (Table 2,

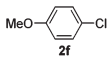
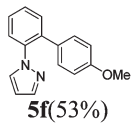
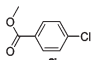
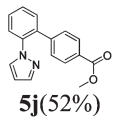
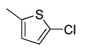
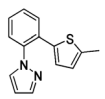
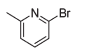
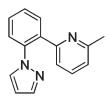
**Table 2** Selective monoarylation of 2-phenylpyridine with various aryl and heteroarylhalides[a]

| Entry | Het-X | *T* (h) | Conv[b] (%) | M/D[c] | Yield[d] (%) |
|---|---|---|---|---|---|
| 1 |  | 5 | 98 | 94/6 |  **3a**(76%) |
| 2 |  **2f** | 8<br>10 | 88<br>89 | 96/4<br>96/4 |  **3f**(69%) |
| 3 |  **2g** | 13<br>14 | 90<br>92 | 90/10<br>90/10 |  **3g**(72%) |
| 4 |  **2h** | 6<br>13 | 78<br>99 | 96/4<br>90/10 |  **3h**(80%) |
| 5 |  **2i** | 6 | 10 | | — |
| 6 |  **2j** | 3<br>4 | 96<br>97 | 96/4<br>95/5 |  **3j**(83%) |
| 7 |  **2k** | 6<br>10 | 90<br>96 | 90/10<br>88/12 |  **3k**(77%) |
| 8 |  **2l** | 8<br>24 | 50<br>60 | 88/12<br>80/20 |  **3l** (30%) |
| 9 |  **2b** | 3<br>4 | 100<br>100 | 86/14<br>85/15 |  **3b**(76%) |
| 10 |  **2c** | 3<br>4 | 100<br>100 | 89/11<br>87/13 |  **3c**(79%) |
| 11 |  **2d** | 3<br>4<br>6 | 81<br>83<br>100 | 81/19<br>80/20<br>73/22 |  **3d**(52%) |

[a] Reaction conditions: 0.6 mmol of 2-phenylpyridine, 5 mol% of $RuCl_2(PPh_3)(p\text{-cymene})$, 3 equiv. of $K_2CO_3$, 10 μL of tetradecane (internal standard) for GC, 0.5 mmol of Het-X in 2 mL of water, 80 °C. [b] Conversion determined by gas chromatography based on (hetero) arylhalide. [c] M/D ratio determined by gas chromatography. [d] Isolated yield.

entries 9–11). With **2b** and **2c**, the reaction went to completion within 3 h affording **3b** and **3c** in 76–79% isolated yields,

**Table 3** Selective monoarylation of *N*-phenylpyrazole with various aryl and heteroarylhalides[a]

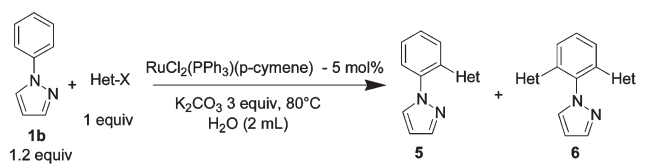
| Entry | Het-X | *T* (h) | Conv[b] (%) | M/D[c] | *Y*[d] (%) |
|---|---|---|---|---|---|
| 1a<br>1b |  **2f** | 7<br>14 (65 °C) | 97<br>62 | 90/10<br>93/7 |  **5f**(53%) |
| 2a<br>2b |  **2j** | 5<br>20 (65 °C) | 96<br>98 | 89/11<br>90/10 |  **5j**(52%) |
| 3a<br>3b |  **2c** | 5<br>7<br>20 (65 °C) | 80<br>84<br>98 | 78/22<br>75/25<br>74/26 |  **5c**(44%) |
| 4a<br>4b |  **2d** | 8<br>24 (65 °C) | 78<br>91 | 84/16<br>75/25 |  **5d**(44%) |

[a] Reaction conditions: 0.6 mmol of phenylpyrazole, 5 mol% of $RuCl_2(PPh_3)(p\text{-cymene})$, 3 equiv. of $K_2CO_3$, 10 μL of tetradecane (internal standard) for GC, 0.5 mmol of Het-X in 2 mL of water, 80 °C. [b] Conversion determined by gas chromatography. [c] M/D ratio determined by gas chromatography. [d] Isolated yield.

whereas with **2d**, only 81% conversion of 2-phenylpyridine was obtained in 3 h, but the complete conversion was obtained in 6 h leading only to 52% of isolated **3d** (Table 2, entry 11).

### Selective monoarylation of *N*-phenylpyrazole with (hetero)aryl halides

The reaction of *N*-phenylpyrazole **1b** with 4-chloromethoxybenzene and 4-methyl chlorobenzoate was performed in the presence of $RuCl_2(PPh_3)(p\text{-cymene})$ and 3 equiv. of $K_2CO_3$ in water at 80 °C, affording the monoarylated products **5f** and **5j** in a moderate yield of 52–53% (eqn (3), Table 3, entries 1a–2a). Bidentate ligands **5c** and **5d** were isolated in moderate yields from the reaction of *N*-phenylpyrazole with 5-methyl-2-chlorothiophene and 6-bromo-2-methylpyridine (Table 3, entries 3a–4a). It is noteworthy that the efficient catalytic system allowed us to carry out the reaction in water at 65 °C in reasonable reaction times (14–24 h), with good conversion and selectivity (Table 3, entries 1b–4b).




(3)

Similar conditions for selective catalytic monoarylation were used to produce new monoarylated products in water from functional arenes containing already one *ortho* substituent. As there is no risk to get parasite *ortho* diarylation the

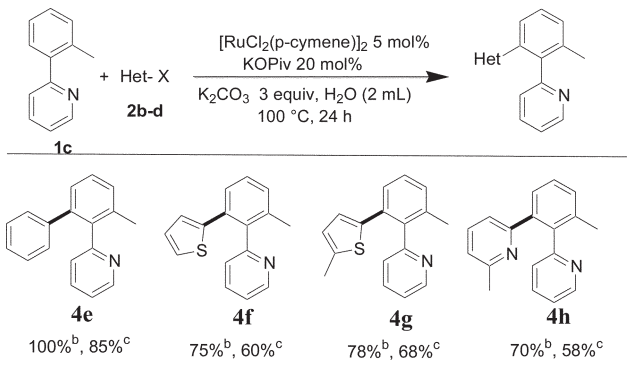
phosphine can be replaced by the carboxylate ligand. Thus the $[RuCl_2(p\text{-cymene})]_2$–4 KOPiv catalytic system was applied for the monoarylation of the *ortho* C–H bond of 2-*o*-tolylpyridine **1c**. Thus the *ortho* (hetero)arylated derivatives **4e** (71%), **4f** (60%), **4g** (63%), **4h** (58%) were obtained by direct arylation with chlorobenzene, and the heterocyclic halides **2b**, **2c** and **2d** (Scheme 1).

### Successive monoarylations in water

One major aim of the selective monoarylation reaction is to utilize the remaining available *ortho* C–H bond, as a functional group, for further functionalisation in order to prepare unsymmetrical bifunctional arenes.

The monoheteroarylated derivative **3j** was first obtained from the monoarylation of phenylpyridine with 4-chlorobenzoate in water in the presence of $RuCl_2(PPh_3)(p\text{-cymene})$ (Table 2). The reaction of **3j** with 2-chlorothiophene was then performed in the presence of $RuCl_2(PPh_3)(p\text{-cymene})$ in water for 20 h to give only 70% of conversion. Then the same reaction in the presence of $Ru(OAc)_2(p\text{-cymene})$ or $Ru(OPiv)_2(p\text{-cymene})$[7] was carried out at 120 °C and provided the mixed diarylated product with 99% conversion in 20 h and afforded 77% isolated yield of **7** (Scheme 2). For comparison, when the same reaction with **3j** was performed in NMP as a solvent, only 20% conversion was obtained after 20 h. The advantage of using water as a solvent medium was obvious as water not only acts as a solvent but also enhances the rate of the reaction for the formation of unsymmetrical or mixed diarylated products.

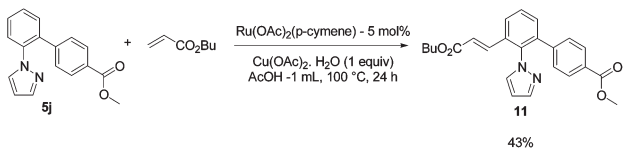
The transformation in water of **3j** with 4-chloroacetophenone provided the mixed ketone carboxylate product **8** isolated in 71% yield after 24 h. Similarly, the monoarylated pyrazole **5j** was reacted in water with 2-chlorothiophene and 4-chloroacetophenone. After 24 h the unsymmetrical diarylated products **9** and **10** were isolated in 72 and 83% yields.



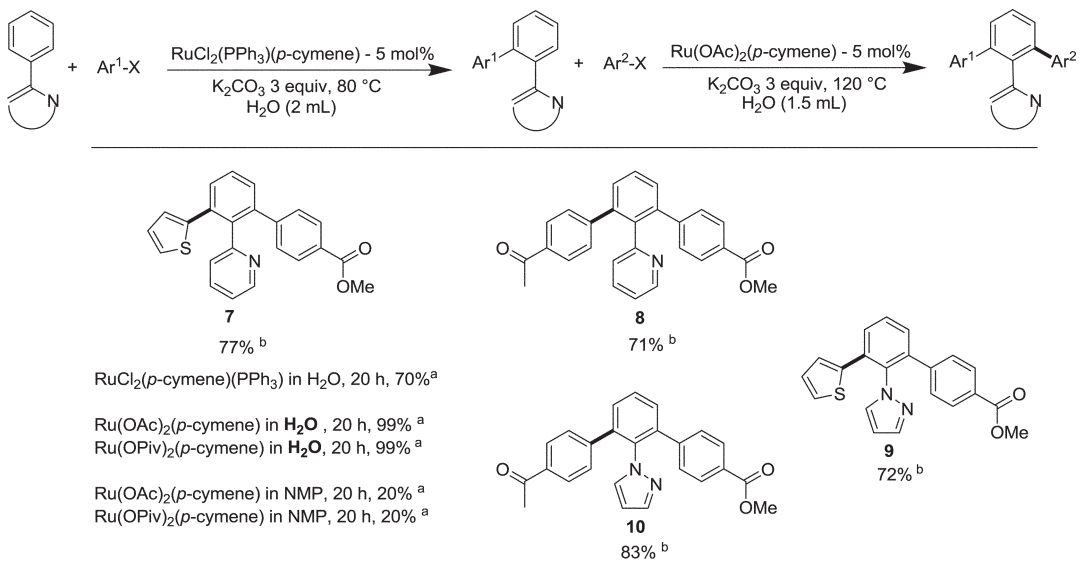

**Scheme 1** Selective monoarylation of 2-*o*-tolylpyridine with (hetero)arylhalides in water. (a) Reaction conditions: 0.5 mmol of 2-*o*-tolylpyridine, 5 mol% of $[RuCl_2(p\text{-cymene})]_2$, 20 mol% of KOPiv, 3 equiv. of $K_2CO_3$, 10 μL of tetradecane (internal standard) for GC, 1.25 mmol of aryl(hetero)halide in 2 mL of water. (b) Conversion determined by gas chromatography. (c) Isolated yield.

### Successive alkenylation of monoarylated heteroarene

The ruthenium(II)-catalyzed alkenylation of monoarylated heteroarenes was then investigated. The reaction of monoarylated 2-phenylpyridine and phenylpyrazole derivatives **3j** and **5j** with *n*-butyl acrylate was attempted in the presence of a $[RuCl_2(p\text{-cymene})]_2/AgSbF_6$ catalyst[8] with $Cu(OAc)_2{\cdot}H_2O$ as an oxidant which was shown to be an efficient catalytic system for the alkenylation of arenes containing weakly coordinating directing groups.[8] Unfortunately, this catalytic system did not provide any conversion of **3j** and **5j**.




(4)




**Scheme 2** Successive arylations in water and preparation of difunctional unsymmetrical diarylated arenes. Reaction conditions: 0.25 mmol of monoarylated heteroarenes, 5 mol% of $Ru(OAc)_2(p\text{-cymene})$, 3 equiv. of $K_2CO_3$, 10 μL of tetradecane (internal standard) for GC, 0.5 mmol of Het-X in 1.5 mL of water. (a) Conversion determined by gas chromatography. (b) Isolated yield.

However it was recently established that arenes containing a nitrogen directing group were successfully alkenylated with a carboxylate-ruthenium(II) catalyst but in acetic acid.[9] The alkenylation of monoarylated product **5j** with *n*-butyl acrylate was attempted using these conditions in the presence of $Ru(OAc)_2$(*p*-cymene) as a catalyst with $Cu(OAc)_2{\cdot}H_2O$ as an oxidant in AcOH at 100 °C during 24 h. The difunctional mixed aryl alkenylheteroarene **11** was thus successfully isolated in 43% yield (eqn (4)).

## Conclusion

The above results show the selective *ortho* monoarylation of functional arenes directed by N-containing heterocyclic directing groups. It is selectively obtained using the $RuCl_2(PPh_3)$(*p*-cymene) catalyst operating in water, for which both phosphine $PPh_3$ linked to ruthenium(II) and water medium are cooperative to the monoarylation catalyst activity. The profit of this selective mono(hetero)arylation is shown in the sequential preparations of bifunctional polyaryl derivatives. One example of synthesis of mixed *ortho* aryl alkenyl benzene is shown and mixed *ortho* diarylated arenes are produced using the $Ru(O_2CMe)_2$(*p*-cymene) catalyst in water for the second monoarylation step.

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