Hydroarylation Hot Paper

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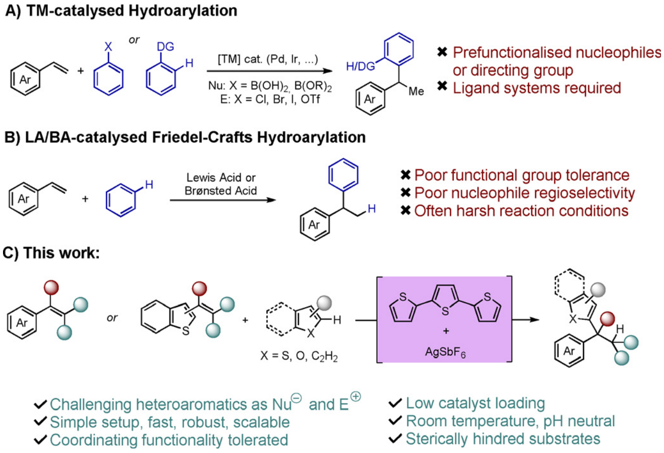
Silver-Catalysed Hydroarylation of Highly Substituted Styrenes

Toryn Dalton[+], *Steffen Greßies*[+], *Mowpriya Das*, *Maximilian Niehues*[++], *Malte L. Schrader*[++], *Christian Gutheil*[++], *Bart Jan Ravoo*, and *Frank Glorius**

In memory of Dr. Steven Cooper

Abstract: *Hydroarylation is an effective strategy to rapidly increase the complexity of organic structures by transforming flat alkene moieties into three-dimensional frameworks. Many strategies have already been developed to achieve the hydroarylation of styrenes, however most of these reports examine the hydroarylation of unpolar, β-mono- or β-unsubstituted styrenes, while exploring mainly electron-rich benzene nucleophiles. Herein, we report a mild and general catalytic system for the selective hydroheteroarylation of multiply substituted styrenes and heteroaromatic styrenes. Mechanistic analysis of the reaction led to the discovery of commercially available 2,2′:5′,2′′-terthiophene as a key reagent.*



Scheme 1. Hydroarylation of styrenes.

Styrenes are important feedstock chemicals for a variety of transformations. Many derivatives are cheap and commercially available compounds, while more complex substitution patterns are synthetically available by established chemistry. The styrene C–C double bond is a versatile functional handle and has been used extensively as an electrophile in directed, transition-metal catalysed C–H activation chemistry to give both branched and linear products.[1,2] Other transformations using prefunctionalised aryl halides or aryl nucleophiles, such as aryl boronic acids, have been developed in parallel (Scheme 1 A).[3] Alternatively, functionalisation via Friedel-Crafts-type hydroarylation or hydroheteroarylation of styrenes form new C–C bonds with complete atom economy. Frequently encountered challenges are the regioselectivity of the arene nucleophile, the poor reactivity of sterically hindered styrenes, and the stability of heteroaromatic compounds in the presence of transition metals, acidic conditions, or elevated temperatures. Furthermore, substrates bearing coordinating functional groups are usually incompatible with this chemistry. Many researchers have developed useful catalytic systems to achieve the Friedel-Crafts-type hydroarylation of styrenes. Metal catalysts based on Au,[4] Ca,[5] Fe,[6] Bi,[7] and others,[8] as well as non-metallic catalysts such as I_2,[9] Brønsted acids,[10] or heterogeneous systems[11] have been shown to facilitate the C–C bond formation in the presence of the appropriate nucleophile and electrophile (Scheme 1 B). While electron-rich benzene derivatives have been well-explored as suitable nucleophiles, there are only isolated scope entries involving heteroaromatic nucleophiles in these reports, and in most such cases mixtures of C2 and C3 isomers are reported. To the best of our knowledge, there have been no reports on the hydroheteroarylation of heteroaromatic styrenes as electrophiles. Furthermore, a general method for the hydroheteroarylation of densely substituted and sterically hindered styrenes, which tolerates a variety of functional groups, has yet to be developed. Since aromatic compounds play a central role across diverse chemical disciplines and fields, new methods to introduce such moieties under mild conditions are of high general interest.

Herein, we report our efforts to address these challenges. We began our investigation using 1-(cyclohexylidenemethyl)-4-methoxybenzene (**2a**) as a model substrate for styrenes bearing a β,β-disubstituted moiety. 2-Chlorothiophene (**3a**) was selected as the nucleophile, in order to investigate the robustness of the halogen handle as well as the selectivity between the three nucleophilic positions C3, C4, and C5. The C3 position was judged to be less reactive owing to the steric hindrance of the C2 substituent. We discovered that the desired hydroheteroarylation product **4a** was formed in 75% yield of isolated product when 0.3 mmol **2a** was mixed with 1.5 equivalents of **3a** with 5 mol% $AgClO_4$ in dichloromethane (0.2 M) at 60 °C. No regioisomers of the product were detected by GC–MS or NMR analysis. We also observed that the reaction mixture became dark and opaque. When we

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[*] T. Dalton,[+] Dr. S. Greßies,[+] M. Das, M. Niehues,[++] M. L. Schrader,[++] C. Gutheil,[++] Prof. Dr. B. J. Ravoo, Prof. Dr. F. Glorius
Organisch-Chemisches Institut
Westfälische Wilhelms-Universität Münster
Corrensstrasse 40, 48149 Münster (Germany)
E-mail: glorius@uni-muenster.de

[+] These authors contributed equally to this work.

[++] These authors contributed equally to this work.

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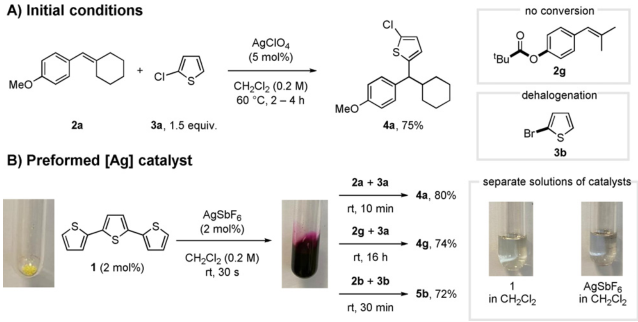
attempted to record the kinetic profile, it was observed that the reaction proceeded rapidly to completion at the time of colour change, which occurred stochastically following an induction period of between 2–4 h in repeat experiments.

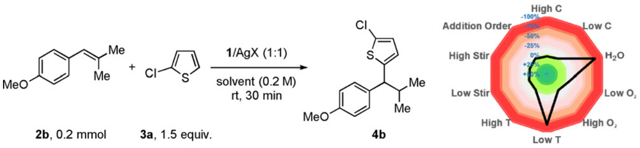
During a preliminary scope investigation, we encountered several limitations intrinsic to Friedel-Crafts-type hydroarylation. A majority of substrates explored, in particular those bearing polar functionality, required a high reaction temperature of 90 °C and up to 10 mol % loading of the more loosely coordinated $AgSbF_6$ salt to obtain sufficient conversion, or exhibited no reactivity at all. Poor chemoselectivities were frequently observed in the presence of labile functional groups: for example, debromination was observed when 2-bromo thiophene (**3b**) was used. When pivalate ester-bearing substrate **2g** was subjected to the reaction conditions, no product formation was observed even under the most forcing conditions and intriguingly, the aforementioned colour change was absent (Scheme 2 A).

We speculated that coordination of polar groups competes with substrate activation and therefore deactivates the catalyst. Control experiments showed that formation of the coloured solution did not require the presence of the styrene. When **2a** was subsequently added to a solution of **3a** and $AgClO_4$ (5 mol %) in CH_2Cl_2 that was preheated for several hours until the colour change was observed, the reaction proceeded to completion in 30 min at room temperature. The coloured solution could be formed by heating **3a** with $AgSbF_6$ in < 15 min. A preliminary TEM image revealed the presence of silver particles and higher-order organic material (for details, see Supporting Information). In keeping with these observations, at this point we speculated that thiophene dimers or oligomers might be formed in situ under the oxidative conditions and that they might be responsible for the stabilization of a coloured, catalytically active species. Commercially available 2,2′:5′,2′′-terthiophene (**1**) is an inexpensive yellow solid prepared on large scale as a common building block for the synthesis of organic semiconductors.[12] When **1** and $AgSbF_6$ were simply combined in a 1:1 ratio in dichloromethane at room temperature, a purple solution was formed instantly. Addition of **3a** and 1-methoxy-4-(2-methylprop-1-en-1-yl)benzene (**2b**) resulted in almost complete conversion to **4b** in 10 min (82 % GC–FID calibrated yield). Remarkably, when formerly inactive **2g** was added to a preactivated solution at room temperature, the reaction showed complete conversion and **4g** was successfully isolated in 74 % yield. In addition, the same mild conditions allowed the hydroarylation of **2b** by 2-bromo thiophene (**3b**) to furnish **5b** in 72 % yield of isolated product without dehalogenation (Scheme 2 B). Further experiments showed decreased yields when other chlorinated solvents were used, and no colour change or reactivity was seen in the presence of other solvents (Table 1 and for more details, see the Supporting Information).



Scheme 2. Development of the preformed catalyst strategy.

Table 1: Selected deviations from the optimised conditions.[a]



Entry	AgX	[Ag] [mol %]	Solvent	Yield [%]	Note
1	$AgSbF_6$	2	CH_2Cl_2	82	RT 10 min
2	$AgSbF_6$	1	CH_2Cl_2	76	RT 2 h
3	none	–	CH_2Cl_2	0	
4	none	–	CH_2Cl_2	0	+ 5 % $NaSbF_6$
6	$AgSbF_6$	2	CH_2Cl_2	1	without 1
7	$AgPF_6$	2	CH_2Cl_2	0	RT 16 h
8	$AgClO_4$	2	CH_2Cl_2	28	RT 16 h
9	$AgBF_4$	2	CH_2Cl_2	17	RT 16 h
10	$AgBF_4$	2	CH_2Cl_2	76	+ 5 % $NaSbF_6$
11	$AgSbF_6$	2	$CHCl_3$	76	
12	$AgSbF_6$	2	DCE	33	

[a] GC–FID yields. DCE = 1,2-Dichloroethane.

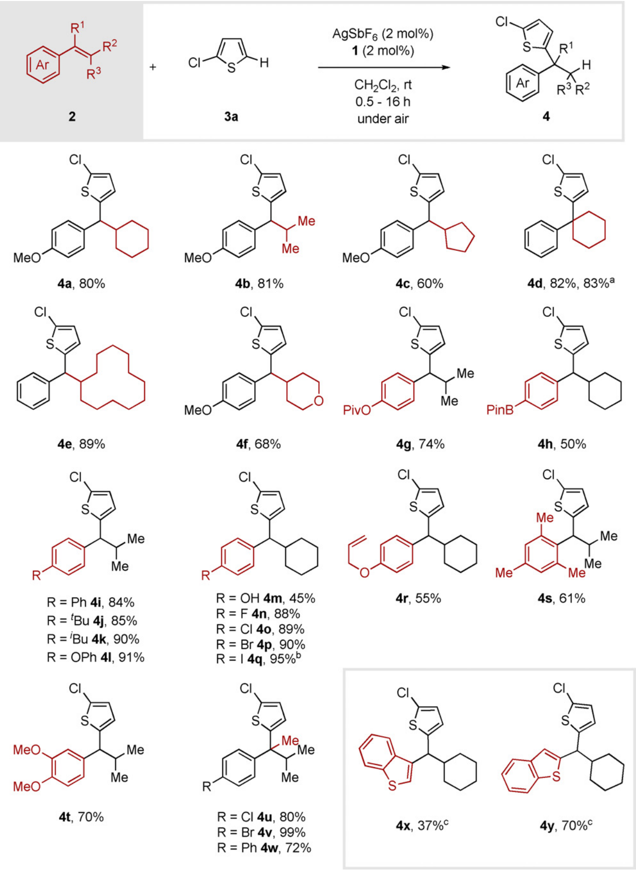
More coordinating silver salts, such as $AgBF_4$ or $AgClO_4$, enabled only low conversions to **4b** after extended reaction times, although some reactivity could be restored upon the addition of $NaSbF_6$ as a loosely coordinating counterion. A comparable yield was observed when organic-soluble reaction components were added as a stock solution to the silver salt, although in the latter case there was a delay of several minutes before the reaction became coloured. This modification was used to carry out the condition sensitivity screen published recently by our laboratory[13] (for details see the Supporting Information), which revealed that the transformation is insensitive to the factors of concentration, stir rate and the presence or absence of O_2, but the addition of 1 % H_2O by volume inhibited the formation of the coloured species and progress of the reaction. When the reaction was initiated at 0 °C neither colour nor conversion were observed until the reaction mixture was subsequently allowed to warm to room temperature.

Satisfied with the optimality of our conditions and the knowledge that we could conveniently run the reaction under air, we began to explore the scope of the hydroarylation. Although the system is also active for the hydroarylation of terminal and disubstituted styrenes, which have been investigated extensively elsewhere, we decided to focus on more challenging multisubstituted styrenes. The chemistry is selective for styrene double bonds, whereas aliphatic alkenes and stilbenes remain untouched. First, we investigated the generality of the styrene coupling partner (Scheme 3). Different cyclic alkyl chains as well as acyclic methyl substituents were well-tolerated at the β-position (**4a** to **4e**). Use of commercially available 1-phenyl cyclohexene (**2d**) delivered the congested quaternary carbon centre at **4d** and the good yield obtained was replicated on 20 mmol scale (4.60 g isolated). Notably, a pyran ring was also tolerated, which under the first set of conditions had inhibited the reaction, delivering the desired product **4f** in good yield. Several useful functional handles on the aromatic ring were likewise well-preserved; products bearing -BPin, halogens, a free -OH group, -OPh, the aforementioned ester, the potentially reactive -*O*-allyl group as well as aryl and alkyl derivatives were isolated in mostly excellent yields (**4g** to **4r**). A sterically hindered styrene **4s** bearing a mesitylene moiety also reacted smoothly. Tetrasubstituted styrenes are especially challenging substrates owing to the steric repulsion of the α-substituent. We were therefore especially pleased when tetrasubstituted styrenes were found to deliver the products **4u** to **4w** in good yields. Heteroaromatic styrenes have not yet been employed in the Friedel-Crafts-like hydroheteroarylation chemistry. These compounds are sensitive and unstable owing to their propensity towards dimerization and oxidative decomposition, especially under harsh reaction conditions. By simply increasing the loading of the thiophene coupling partner, we were able to isolate two examples of these multi-heteroaryl-substituted compounds (**4x** and **4y**).

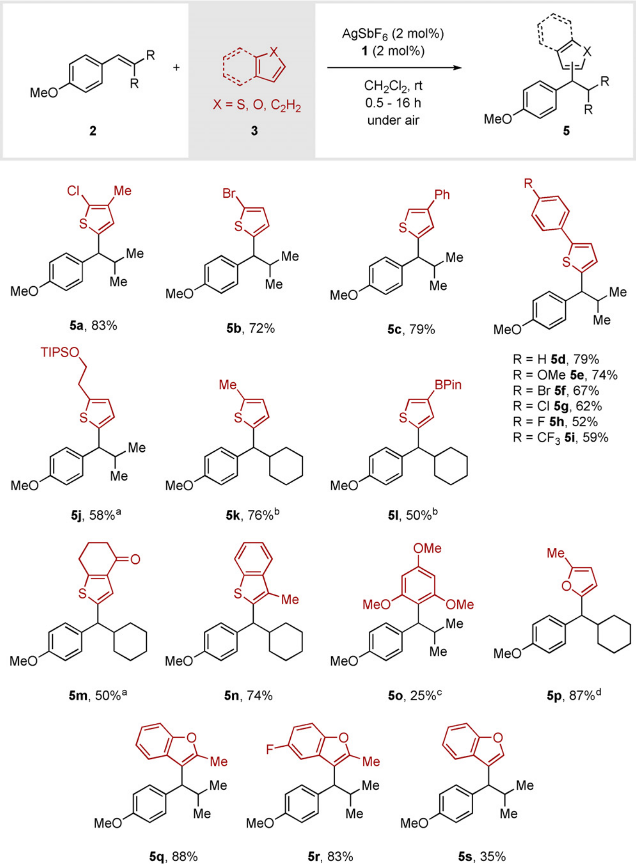
Next, we investigated the nucleophile scope of the transformation (Scheme 4). Thiophenes bearing alkyl or aryl substituents at the C2 or C3 position were suitable for this reaction (**5a** to **5k**). Notably, bromine and boron substituents, which permit later derivatisation, were tolerated (**5b**, **5f**, **5l**). A benzothiophene, benzofurans, and especially sensitive 2-Me furan were also convenient nucleophiles, delivering the expected products in good yields (**5p** to **5s**). An electron-rich benzene, represented by 1,3,5-trimethoxybenzene, was a competent nucleophile, although the yield was significantly lower (**5o**). We noted that the presence of basic nitrogen in any of our other substrates resulted in no conversion.

We were intrigued to understand the mode of action of our system. While there are numerous reports of Ag^I ions being exploited for their π-acidity towards triple bonds, they are generally considered to have a much weaker affinity for carbon−carbon double bonds.[14] We therefore set out to rationalise the unusually high activity of this system.

Terthiophenes are widely exploited for their fluorescent properties. The UV/Vis and fluorescence spectra of **1** and the catalytically active purple solution were measured and



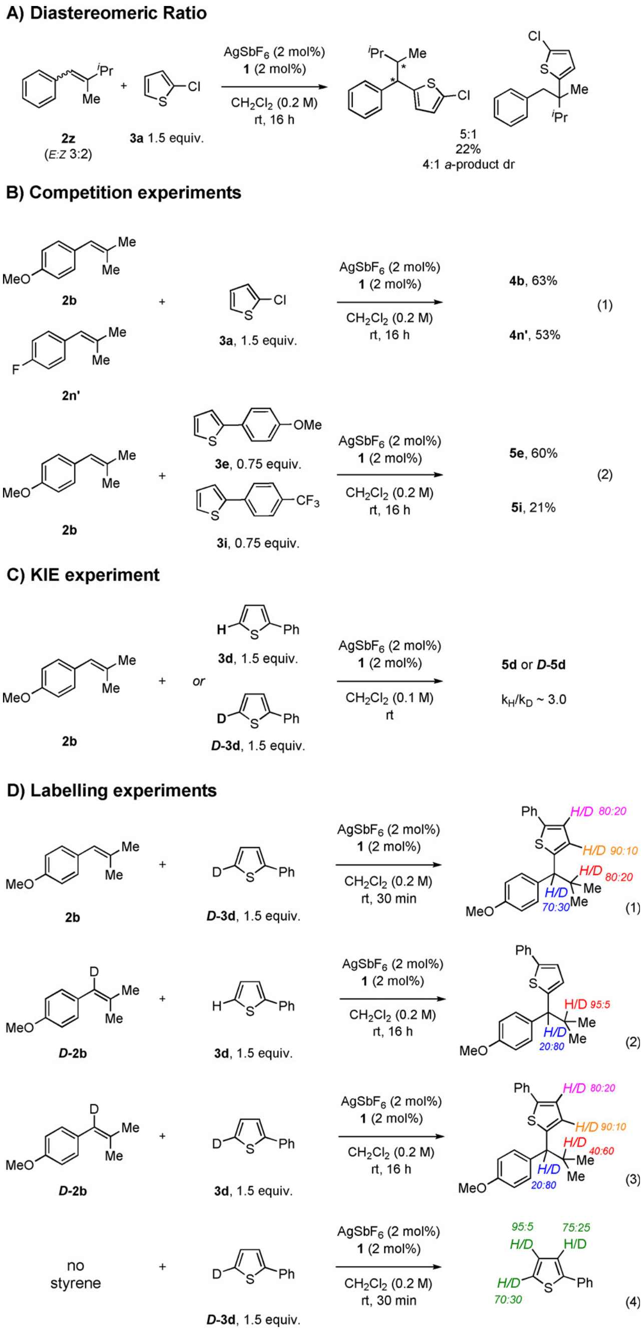
Scheme 3. Styrene scope of the hydroarylation. Yields of isolated product. Reaction conditions: **2** (0.3 mmol), **3a** (1.5 equiv); [a] 20 mmol scale; [b] 6:1 styrene α/β addition products; [c] 6 equiv of **3a.**



Scheme 4. Heteroaryl scope of the hydroarylation. Yields of isolated product. Reaction conditions: **2** (0.3 mmol), **3** (1.5 equiv); [a] Without **1**, $AgClO_4$ (5 mol%), 90 °C; [b] Without **1**, $AgClO_4$ (5 mol%), PhMe, 60 °C; [c] at 90 °C; [d] Without **1**, $AgClO_4$ (2.5 mol%), 60 °C.

fluorescence bands of 620–640 nm and 670–690 nm were observed, respectively. Since our class of styrene substrates are known to absorb in the region around 450 nm, we concluded that the fluorescence energy was too low to facilitate a photochemical excitation.[15] This result was confirmed by running the reaction with rigorous exclusion of light. When butylated hydroxy toluene was added as a radical trapping agent, full completion of the standard reaction was seen with no adducts detected, suggesting no radical species are present.

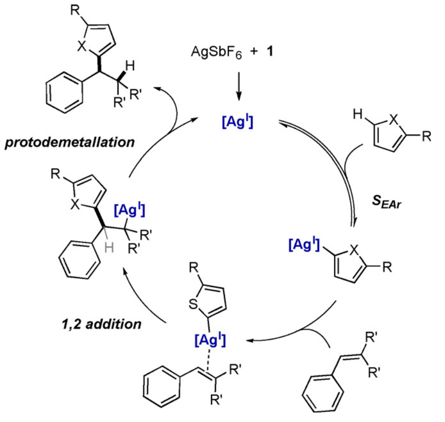
Next, we considered whether the catalyst might be heterogeneous.[16] Upon standing, settling of black solids from the active purple solution was visible. When $AgSbF_6$, **1**, and **2d** were combined in dichloromethane, TEM revealed Ag particles in the range of 20–100 nm and oligomers of **1** were detectable by MALDI–MS. During the scope investigation, traces of alkyl arenes were observed by GC–MS analysis. We initially hypothesised that silver nanoparticles, supported by terthiophene derivatives, were the catalytically active species. Literature-known heterogeneous Ag^I and Ag^0 catalysts were tested, along with a commercial Ag^0 nanopowder, and none gave any conversion. Addition of a mercury drop, a method used to agglomerate and deactivate heterogeneous species, did not prevent reaction completion. When the purple solution was centrifuged at 6000 rpm for 5 min, the supernatant was shown to retain its activity and no particles were observable by TEM. In contrast, the black pellet was inactive when resuspended in dichloromethane. Taken together, these results suggest that the formation of particles is a side reaction during oligomerisation of **1** and the active species is most likely homogeneous. An unsymmetrical 2,2-disubstituted styrene **2z** (3:2 *E*/*Z* ratio) subjected to the standard reaction conditions gave a dr of 4:1 (Scheme 5 A, see Supporting Information for further details). When the blocked, C5,C5″-dimethylated terthiophene **1*** was used instead of **1**, the previously seen particles were not observed by eye nor by TEM, and a GC–FID yield identical to the standard reaction was achieved. We propose that terthiophene-type ligands offer a loosely bound environment for the Ag^I ion in solution, with MLCT also responsible for the intense purple colour, rendering it highly suitable for catalysing the hydroarylation reaction.



Scheme 5. Mechanistic investigations.

Finally, we completed our present studies with mechanistic investigations. In a competition experiment, substrate **2b** was observed to react slightly faster than the analogous *para*-fluorinated **2n′** (Scheme 5B-1), however a clear preference for the more electron-rich thiophene was seen when **3e** and **3i** were together reacted with **2b** (Scheme 5B-2). The standard reaction was estimated to bear a primary kinetic isotope effect of 3.0 when C5-deuterated ***D*-3d** was used as nucleophile in the standard reaction with **2b** in parallel experiments (Scheme 5C). Positional scrambling of the deuterium label of ***D*-3d** was seen in the hydroarylation product (Scheme 5D-1,2,3), in the recovered starting material and also when no styrene (Scheme 5D-4) was added. Together, these observations suggest that a reversible electrophilic aromatic substitution (S_EAr) may be the rate-limiting step in a Friedel-Crafts-type catalytic cycle (Scheme 6). Counter-intuitively, we observed the deuterium label in both the α- and β-positions of the product, which could possibly result from a reversible β-hydride elimination/reinsertion process (for full details, see the Supporting Information).

In conclusion, we have discovered and developed a new system for the regioselective hydroheteroarylation of multiply substituted styrenes, providing complex, three-dimensional, multi-ring building blocks from flat precursors. Highlighted applications include the hydroheteroarylation of both quaternary and heterocyclic styrenes. The reaction is catalysed by a simple silver salt in combination with commercial



Scheme 6. Putative catalytic cycle.

and inexpensive terthiophene (**1**). The reaction setup is simple, practical, and amenable to larger-scale synthesis.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: catalysis · heteroarenes · hydroarylation · silver · styrenes

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