Published in final edited form as:
Angew Chem Int Ed Engl. 2013 January 7; 52(2): 629–633. doi:10.1002/anie.201207995.

Rhodium(III)-Catalyzed Alkenyl C-H Bond Functionalization for the Convergent Synthesis of Furans and Pyrroles**

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Keywords

C-H activation; Rhodium; Heterocycles; Cyclization; Annulation

Furans and pyrroles are pervasive in natural products and pharmaceuticals.[1] For this reason, the synthesis of these five-membered ring heterocycles has been an intense topic for decades[2] with transition metal based C-H bond functionalization strategies recently providing powerful annulative approaches for their assembly.[3,4] Specifically, Glorius[3a] and Fagnou[3b] have reported on the synthesis of pyrroles by Rh(III)-catalyzed coupling of enamides with internal alkynes (eqs 1 and 2), and most recently, Lei has reported on the synthesis of furans by the silver acetate mediated oxidative coupling of terminal alkynes and 1,3-dicarbonyl compounds (eq 3).[3c] Herein, we report a new type of catalytic C-H bond functionalization-based annulation enabling the versatile and efficient synthesis of furans and pyrroles from simple electrophilic coupling partners that serve as very different inputs from those used previously (eq 4).[5] Additionally, in contrast to the other reported C-H functionalization-based annulations (eqs 1–3), no external oxidant is required.

[**]This work was supported by NIH Grant GM069559 (to J.A.E.). R.G.B. acknowledges funding from The Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, U.S. Department of Energy, under Contract DE-AC02-05CH11231. K.D.H. is grateful to the National Sciences and Engineering Research Council of Canada (NSERC) for a postdoctoral fellowship

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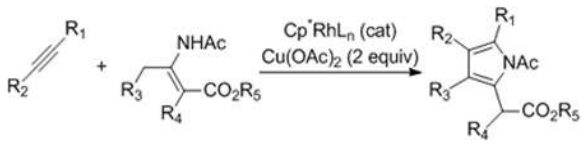

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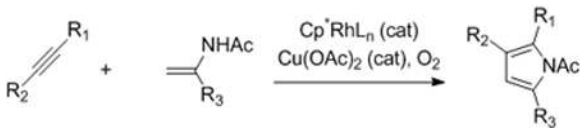

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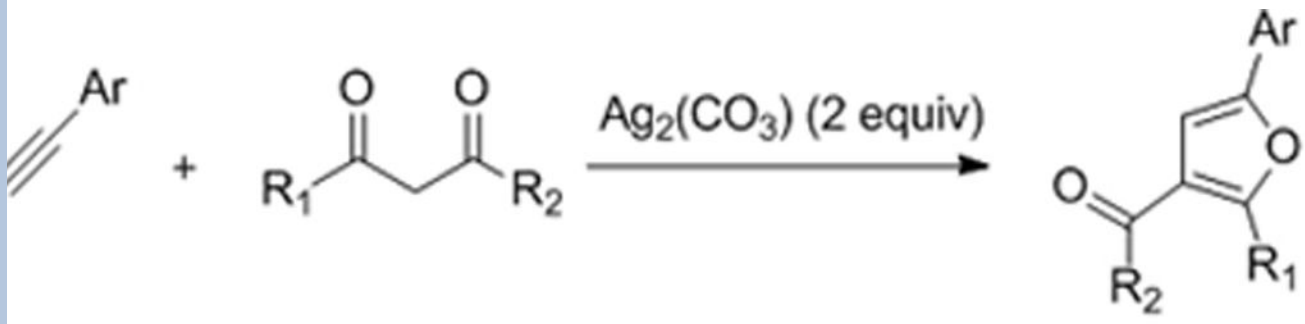

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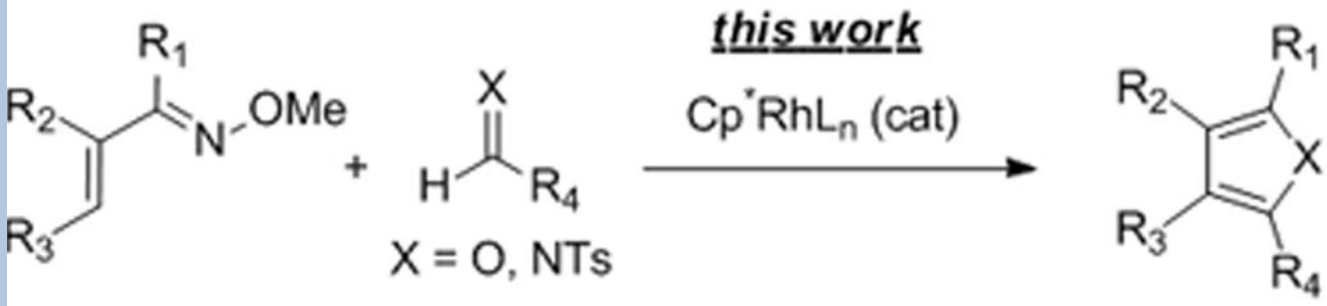

(4)

Over the past several years spectacular progress has been achieved on the Rh(III)-catalyzed addition of sp^2 C-H bonds across alkenes and alkynes.[6,7,8,9] Recently, we and others have also actively explored Rh(III)-catalyzed C-H bond additions across polarized C-N and C-O multiple bonds.[10] Our proposed annulation approach for the synthesis of furans and pyrroles in particular requires a Rh(III)-catalyzed alkenyl C-H bond addition to imines and aldehydes. However, few examples of the addition of alkenyl C-H bonds across C-N and C-O multiple bonds have been reported. We first described the addition of alkenyl C-H bonds

of enamides to isocyanates,[10m] and very recently, Shi reported alkenyl C-H bond addition to *N*-tosyl imines and activated aldehydes using the pyridyl directing group.[10f]

We initiated our investigation by exploring the Rh(III)-catalyzed addition of α,β-unsaturated oxime **1a** to ethyl glyoxylate **2a** (Table1).[11] Although the use of 5 mol % of $[Cp^*RhCl_2]_2$ and $AgSbF_6$ with commercially available **2a**, which is stored as a 50% toluene solution, afforded the desired product **3a** in good yield (entry 1),quantitative yield was observed when glyoxylate **2a** was used in pure form (entry 2). The reaction time could be shortened to 5 h without a reduction in yield (entry 3). Using 2.0 equiv of aldehyde **2a** is crucial because the yield dropped significantly when only 1.0 equiv was employed (entry 4). The use of the pre-formed cationic Rh(III) precursor $[Cp^*Rh(CH_3CN)_3(SbF_6)_2$ slightly reduced the yield (entry 5). Lower catalyst loading proved to be effective. At 2.5mol % of catalyst loading, complete conversion to product was maintained (entry 6), while at 1.25 mol % loading only a slight drop in yield was observed (entry 7). Conversion to product was not observed when either $[Cp^*RhCl_2]_2$ or $AgSbF_6$ alone were used(entries 8 and 9), which suggests that a cationic Rh(III) species is required for this C-H bond functionalization process. Although reaction of oxime **1a** with ethyl glyoxylate (**2a**) proceeds to complete conversion within 5 h at 50 °C (entry 6), a longer reaction time and a higher temperature (75 °C) did not result in any reduction in yield (entry 10). These more forcing conditions were found to be necessary for less reactive oxime substrates (vide infra).

Having defined an effective catalyst system and reaction conditions for the synthesis of furan **3a** in high yield, we next explored substrate scope with a range of α,β-unsaturated oximes **1**with different substitution patterns (Table 2). Annulation of cyclic and acyclic trisubstituted oximes resulted in fully substituted furan products in good yields (**3a–3g**), with cyclohexyl (**3a**, **3e** and **3g**) and cyclopentyl (**3b**) derivatives providing access to different bicyclic frameworks. The terminal substituent, R_3, is not essential for the success of the reaction thereby enabling the preparation of trisubstituted furans (**3h** and **i**). We also explored variation at R_1 and established that different alkyl groups work well in this transformation (**3e–g**). Varying the R_2 substituent demonstrated that alkyl, aryl (**3h**), and benzyl (**3i**) substituted oximes are effective substrates. However, a substituent at this position is crucial because no product was obtained when R_2 was hydrogen. To enhance the practicality of the method, we performed the reaction on the benchtop and found that the yield was comparable to that observed when the reaction was set up in a glovebox under inert atmosphere conditions (see **3a**).

Having demonstrated a broad scope for coupling oximes bearing different substitution patterns with glyoxylate **2a**, we next explored the possibility of extending this transformation to less activated aldehydes. To apply the transformation to aromatic aldehydes, or even to aliphatic aldehydes, the reversible nature of metal catalyzed C-H bond addition to aldehydes must be considered (Figure 1). In contrast to the reaction of the electron-deficient and destabilized glyoxylate **2a**, which likely favors formation of alcohol intermediates such as those illustrated in Figure 1, literature reports suggest that starting materials are generally more stable than the addition products when less electron deficient aldehydes are used.[12] For unactivated aldehydes we therefore envisioned that capture of the initial alcohol product by cyclization and aromatization might be necessary to drive the reaction to completion.[13]

We initially focused on the identification of suitable conditions for the efficient coupling of 4-trifluoromethylbenzaldehyde (**5a**) and oxime **1b** (Table 3). The use of DCE as a solvent, which we have previously found to be one of the most effective for Rh(III) catalyzed C-H additions to polarized C-N and C-O multiple bonds, provided the desired furan **7a** in poor yield (entry 1). A range of solvents with different polarities and hydrogen bonding

capabilities were therefore evaluated because different solvation properties might be expected to affect the equilibrium between the starting materials and the alcohol intermediate and could also impact the rate of cyclization and aromatization. A variety of alcohols with different steric properties and acidities were first explored, with CF_3CH_2OH increasing the yield to 50% (entries 2–4). Evaluation of aprotic solvents resulted in an interesting trend. Polar and strongly coordinating solvents, such as CH_3CN or DMF resulted in very low yields (entries 5 and 6). However, the use of moderately coordinating solvents significantly improved the yield (entries 7–10). Among the solvents screened, HOAc and THF were the most effective providing **7a** in excellent yield (78%).[14] THF was chosen for further experimentation because it is more easily removed than HOAc.

Having defined an effective solvent system for the synthesis of furans from aromatic aldehyde **5a**, we next explored a wider range of aldehydes. Good functional group compatibility was demonstrated, with aromatic aldehydes substituted with chloro, fluoro, trifluoromethyl, methoxy, nitro, and ester groups all proving to be effective coupling partners. Moreover, substitution at the o-,m-, and p-positions of the aromatic ring was found to be well tolerated (**7a–7h**). Electron poor aromatic aldehydes generally afford furan products in higher yields (**7a**, **7d**, and **7e**), but unactivated aromatic aldehydes are also effective substrates (**7b**, **7c**, and **7h**). Moreover, the annulation of aliphatic aldehydes proceeds in moderate yields (**7i** and **j**), which is notable because few prior examples of Rh(III)-catalyzed C-H bond additions to aliphatic aldehydes have been reported.[6l] The reaction is not limited to oxime **1b**, but is also effective for other oxime substitution patterns (**7k–m**).

With successful demonstration of this new type of annulation for the synthesis of diverse furan derivatives, we next investigated the possibility of extending this reaction to pyrrole synthesis. Reaction of oxime **1a** with the *N*-tosyl imine of ethyl glyoxylate **8** in DCE at 90 °C for 16 h afforded pyrrole **9a** in reasonable yield (Table 5). The reaction proved to be effective for □,□-unsaturated oximes **1** with different substituents and substitution patterns, but preliminary attempts to extend the reaction to *N*-Ts imines of aromatic aldehydes have not yet been successful.

In conclusion, a new type of annulation for the synthesis of substituted furans and pyrroles has been developed that proceeds via C-H bond activation. The annulation is initiated by the Rh(III)-catalyzed addition of an alkenyl C-H bond across an aldehyde C=O or imine C=N bond followed by cyclization and aromatization. This operationally simple process is amenable to a number of different substituents on the □,□-unsaturated oxime. Annulations with ethyl glyoxylate and the corresponding *N*-tosyl imine provide access to 2-carboxyethyl substituted furans and pyrroles, respectively. Moreover, a broad range of aromatic and also aliphatic aldehydes participate in the reaction to provide access to an extensive group of differently substituted furans. We are continuing to investigate this approach for the synthesis of other 5-membered ring heterocycles including azoles

Experimental Section

Representative procedure: In a N_2-filled glovebox, $[Cp^*RhCl_2]_2$ (3.1 mg, 0.0050 mmol, 0.025 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.10 equiv), the indicated *O*-methyl oxime (0.200 mmol, 1.0 equiv) and ethyl glyoxylate (40.8 mg, 0.400 mmol, 2.0 equiv) were added to a screw-capped conical vial with a stir bar followed by addition of DCE (0.66 mL, [*O*-methyl oxime] = 0.30 M). The vial was sealed with a cap containing a PTFE septum and was removed from the glovebox. The reaction vial was then placed in a temperature-controlled oil bath at 75 °C. After 16 h of stirring, the vial was removed from the oil bath and was cooled to ambient temperature. The mixture was filtered through a pad of celite and

the solvent was removed under reduced pressure. The crude residue was loaded onto a silica gel column for chromatographic purification.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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14. Reaction of oxime **1a** with **2a** in THF provided furan **3a** in 45% yield, and thus DCE remains the optimal solvent for reactions with ethyl glyoxylate.

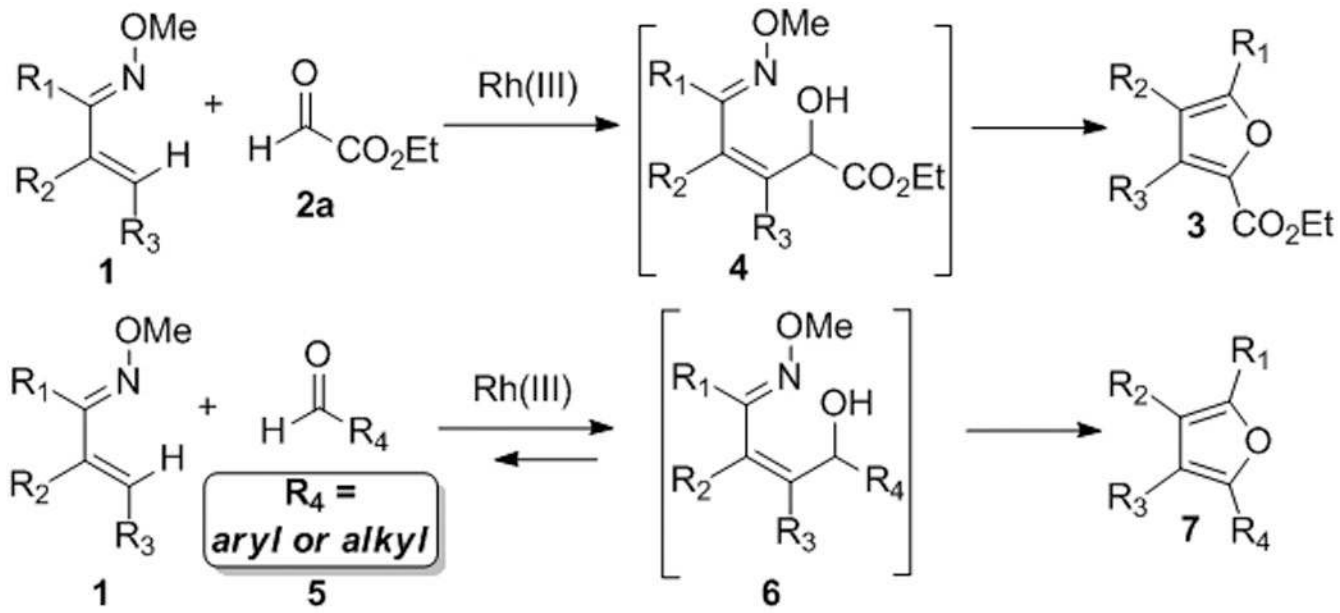
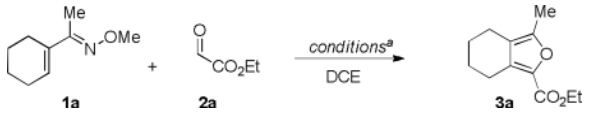


Figure 1.
Proposed reaction pathways.

Table 1

Screening of Reaction Conditions



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

entry	catalyst	catalyst loading (mol%)	temp [°C]	time [h]	yield[b] (%)
1[c]	$[RhCp^*Cl_2]_2$, $AgSbF_6$	5	75	20	84
2	$[RhCp^*Cl_2]_2$, $AgSbF_6$	5	75	20	>99
3	$[RhCp^*Cl_2]_2$, $AgSbF_6$	5	75	5	>99
4[d]	$[RhCp^*Cl_2]_2$, $AgSbF_6$	5	75	5	54
5	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$	5	75	5	87
6	$[RhCp^*Cl_2]_2$, $AgSbF_6$	2.5	50	5	>99
7	$[RhCp^*Cl_2]_2$, $AgSbF_6$	1.25	50	5	89
8	$[RhCp^*Cl_2]_2$	5	75	5	0
9	$AgSbF_6$	20	75	5	0
10	$[RhCp^*Cl_2]_2$, $AgSbF_6$	2.5	75	5	>99

[a] Conditions: **1a** (0.10 mmol), purified ethyl glyoxylate **2a** (0.20 mmol) in 0.33 mL of DCE.

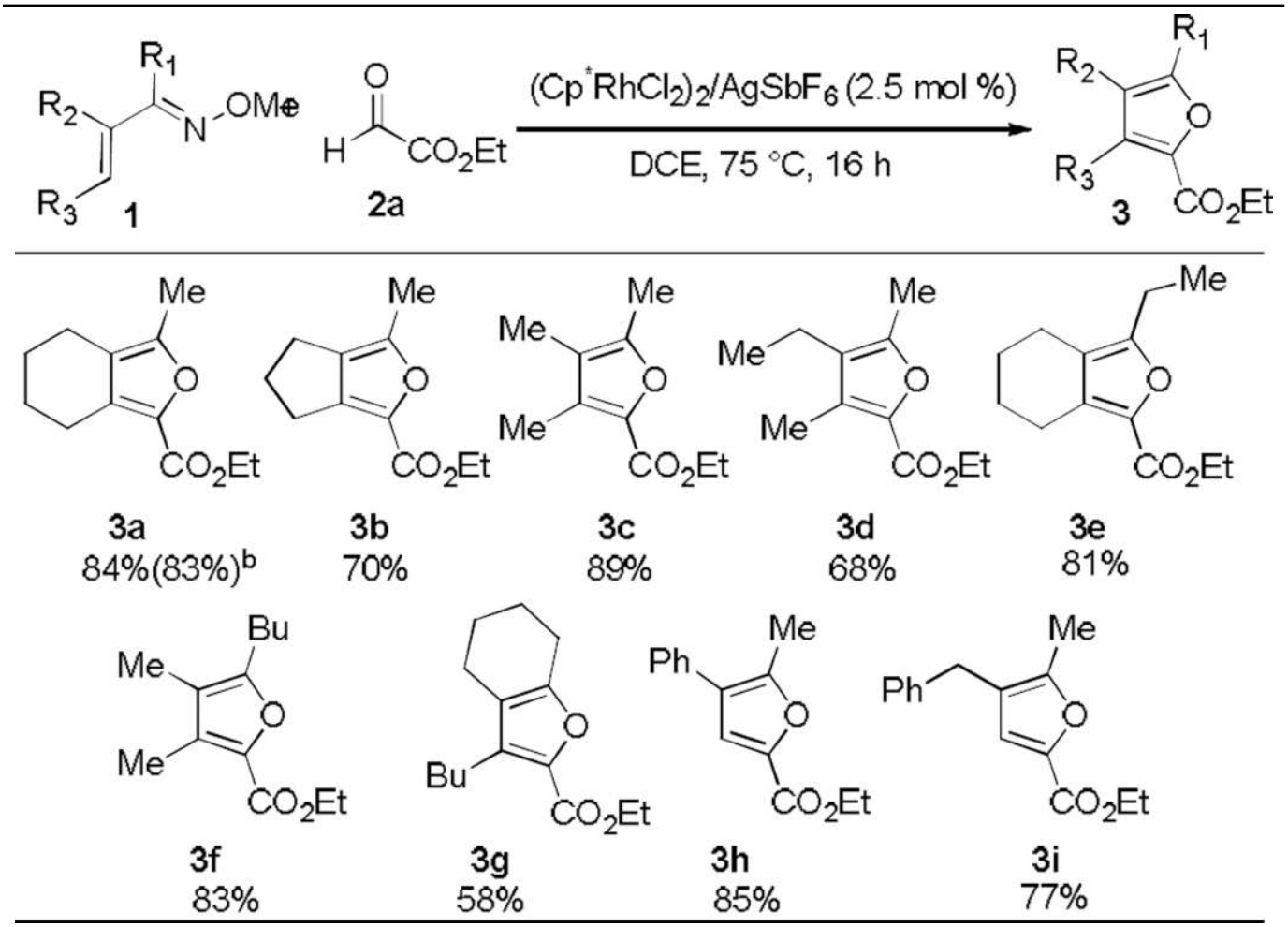
[b] Determined by ^1H NMR analysis relative to 1,3,5-trimethoxybenzene as an external standard.

[c] Commercially available 50% solution of ethyl glyoxylate in toluene used.

[d] 1.0 equiv of ethyl glyoxylate was used.

Table 2

Oxime Substrate Scope with Ethyl Glyoxylate[a]

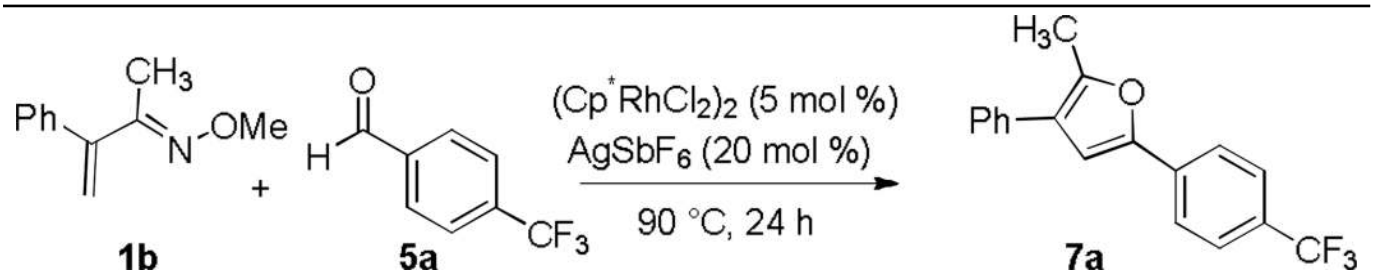


[a]Conditions: 1 (0.20 mmol), purified ethyl glyoxylate **2a** (0.40 mmol) in 0.67 mL of DCE. The isolated yield of purified material is reported for each product.

[b]Conducted in a Schlenk flask under N_2 on the benchtop.

Table 3

Reaction Optimization for Aromatic Aldehydes[a]



1b **5a** **7a**

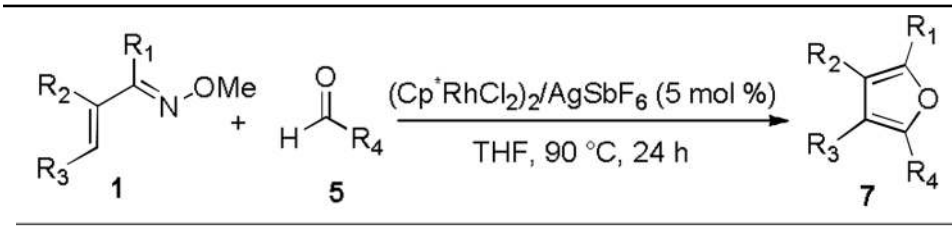
entry	solvent	yield[b] (%)
1	DCE	23
2	EtOH	trace
3	*i*-PrOH	20
4	CF_3CH_2OH	50
5	CH_3CN	trace
6	DMF	17
7	EtOAc	63
8	Dioxane	53
9	HOAc	78
10	THF	78

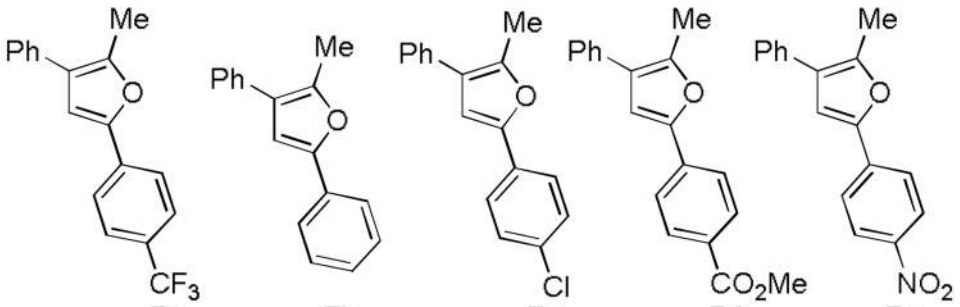
[a] Conditions: **1b** (0.10 mmol), aldehyde **5a** (0.20 mmol) in 0.33 mL of solvent

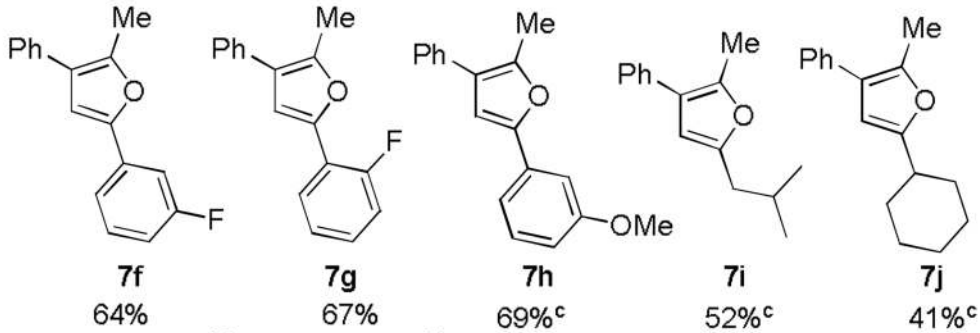
[b] Determined by ^{1}H NMR analysis relative to 1,3,5-trimethoxybenzene as an internal standard.

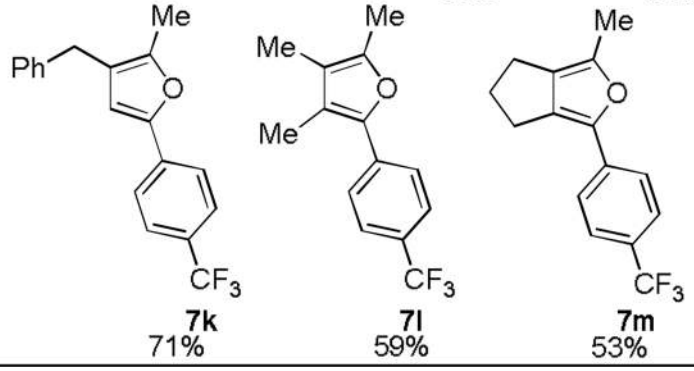
Table 4

Substrate Scope for Other Aldehydes[a]









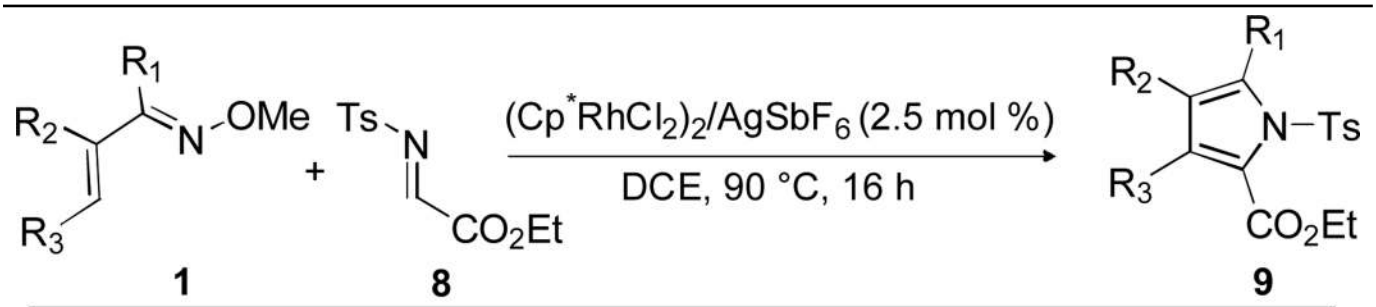
[a]Conditions: **1** (0.20 mmol), aldehyde **5** (0.40 mmol) in 0.67 mL of DCE. The isolated yield of purified material is reported for each product.

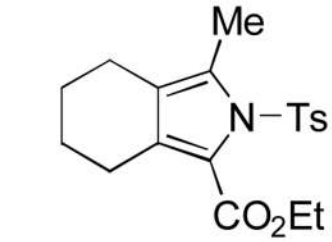
[b]Conducted in a Schlenk flask under N_2 on the benchtop.

[c] Using 10 mol % $[Cp^*RhCl_2]_2$.

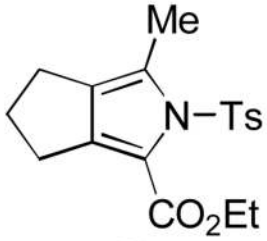
Table 5

Substrate Scope for Pyrrole Synthesis[a]

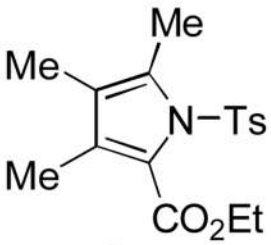




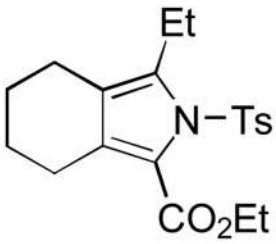
9a
62% yield



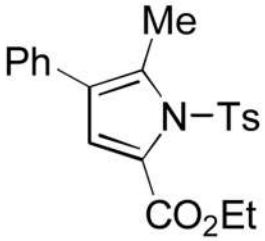
9b
60% yield



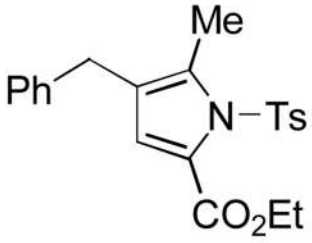
9c
62% yield



9d
66% yield



9e
78% yield



9f
65% yield

[a]Conditions: **1** (0.20 mmol), imine **8** (0.40 mmol) in 0.67 mL of DCE. The isolated yield of purified material is reported for each product.