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# Acylsilane directed aromatic C–H alkenylations by ruthenium catalysis<sup>†</sup>

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A ruthenium-catalyzed C–H alkenylation of aroylsilanes with electron-deficient alkenes was developed, using acylsilane as the directing group. The mild reaction conditions enable the tolerance of a wide scope of functionalities such as OMe, F, Cl, Br and CF<sub>3</sub>, providing a convenient and highly effective method for the synthesis of styrene derivatives bearing acylsilane. Steroid and heterocycles such as furan and thiophene were also well tolerated. Furthermore, acylsilane was efficiently converted to the corresponding aldehyde or carboxylic acid.

Acylsilanes have been known for long time and their spectral behavior and certain chemical properties have been extensively studied. The electron inherent in acylsilane leads to a reactivity profile that is distinct from other carbonyl compounds.<sup>1</sup> In the past decades, they have emerged as versatile synthetic intermediates for use in a variety of chemical transformations.<sup>2</sup> For example, acylsilanes are known to undergo thermally or photochemically induced 1,2-silicon-to-oxygen migrations (known as the Brook rearrangements) to form siloxycarbenes.<sup>3</sup> Furthermore, there are reports on cross-coupling reactions using acylsilanes *via* C–Si bond cleavage.<sup>4</sup> Moreover, acylsilane intermediates have been proven to be useful in complex molecule synthesis.<sup>5</sup>

Vinyl arenes are valuable intermediates, offering broad applications in synthetic and materials chemistry.<sup>6</sup> Thus, numerous aromatic C–H alkenylation reactions have been reported due to high atom- and step economy.<sup>7</sup> The site-selectivity of C–H activations is usually achieved using directing groups (DGs), which usually play dual roles.<sup>8</sup> First, the DG acts as a  $\sigma$ -donor ligand to the active catalyst and brings the metal in close proximity to the target C–H bond, thus ensuring site-selectivity. Second, DGs can increase the effective concentration of the catalyst at the site of interest to improve the reaction efficiency. Directed C–H activation typically proceeds *via* five- or six-membered cyclometalation processes, using various functionalities as directing groups, such as carboxylate, amide, alcohol, amine and imine.<sup>8,9</sup> There are also reports on *meta*-<sup>10</sup> and *para*-selective<sup>11</sup> aromatic C–H activation, using a nitrile embedded in the template that serves as a linear end-on directing group. Unfortunately, the use of DGs often limits broader applications of the developed reactions, since the DGs are usually not an integral part of the desired molecules. Recently, considerable research has hence focused on the development of easily removable and modified DGs for C–H functionalizations.<sup>12</sup>

Due to the great utility of an acylsilane moiety as well as its versatility in chemical conversions, it is intriguing to develop C-H functionalization using such a weakly coordinating acylsilane as a reactant.<sup>13</sup> In light of the recent work on acylsilane-directed aromatic C-H amidation by iridium catalysis<sup>14a</sup> and alkenylation catalyzed by rhodium,<sup>14b</sup> it is still highly desirable to extend the approach to ruthenium-catalyzed C-H activation processes for a number of reasons. First, both the substrate and reaction type can be complementary to that of the Rh- and Ir-catalyzed C-H functionalizations. Second, the conditions used for Rh(III), Ir(III) and Ru(II) are often different, which could offer new opportunities for developing ligand-controlled, enantioselective and remote C-H activation reactions. Third, ruthenium complexes are much cheaper, which facilitate their potential application in synthetic chemistry. Given the importance of acylsilane and our continuous interest in chelation-assisted C-H activation,15 herein, we focus on the Ru(II)-catalyzed aromatic C-H olefination to address these issues (Scheme 1). The generality of this approach is also demonstrated by accomplishing C-H olefination of heterocyclic substrates such as furan and thiophene.

The initial optimization experiments were performed with benzoylsilane (1a) derived from benzoyl chloride and butyl acrylate (2a), in the presence of robust and inexpensive  $[RuCl_2(p-cymene)]_2^{15,16}$  (2.5 mol%) and AgOTf (10 mol%) in DCE at 60 °C as the catalytic conditions, and the reaction afforded desired vinyl arene 3aa in 40% yield (Table 1, entry 1). Various silver salts, such as Ag<sub>2</sub>O, AgOTFA, Ag<sub>2</sub>CO<sub>3</sub>, AgOAc, AgSbF<sub>6</sub> and AgBF<sub>4</sub>, were tested,

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Scheme 1 Acylsilane directed aromatic C–H alkenylation by ruthenium catalysis.

 Table 1
 Optimization of catalytic conditions<sup>a</sup>

O H	`SiMe <sub>3</sub> + 🥢	[RuCl <sub>2</sub> ( <i>p</i> -cymer addtive ( OBu <u>oxidant (</u> solvent (1	ne)] <sub>2</sub> (2.5 mol%) 10 mol%) 1.2 equiv) mL), 60 °C	SiMe <sub>3</sub>
1a		2a		3aa 0
Entry	Additive	Oxidant	Solvent	Yield <sup>b</sup> (%
1	AgOTf	$Cu(OAc)_2$	DCE	40
2	$Ag_2O$	$Cu(OAc)_2$	DCE	NR
3	AgOTFA	$Cu(OAc)_2$	DCE	< 5
4	$Ag_2CO_3$	$Cu(OAc)_2$	DCE	NR
5	AgOAc	$Cu(OAc)_2$	DCE	NR
6	AgSbF <sub>6</sub>	$Cu(OAc)_2$	DCE	41
7	$AgBF_4$	$Cu(OAc)_2$	DCE	23
8	AgSbF <sub>6</sub>	$Cu(OAc)_2$	$CHCl_3$	15
9	AgSbF <sub>6</sub>	$Cu(OAc)_2$	DCM	39
10	AgSbF <sub>6</sub>	$Cu(OAc)_2$	DME	0
11	AgSbF <sub>6</sub>	$Cu(OAc)_2$	MeCN	0
12	AgSbF <sub>6</sub>	$Cu(OAc)_2$	THF	< 5
13	AgSbF <sub>6</sub>	$Cu(OAc)_2$	DMF	0
14	AgSbF <sub>6</sub>	$Cu(OAc)_2$	Toluene	0
15 <sup>c</sup>	AgSbF <sub>6</sub>	$Cu(OAc)_2$	DCE	79
16 <sup>c</sup>	AgSbF <sub>6</sub>	$Cu(OAc)_2 \cdot H_2O$	DCE	49
17 <sup>c</sup>	AgSbF <sub>6</sub>	$Cu(OTf)_2$	DCE	0
18	_	$Cu(OAc)_2$	DCE	0
$19^d$	AgSbF <sub>6</sub>	$Cu(OAc)_2$	DCE	0
20	AgSbF <sub>6</sub>	_ ` `	DCE	0
$21^e$	AgSbF <sub>6</sub>	$Cu(OAc)_2$	DCE	73
$22^e$	_	Cu(OAc)2	DCE	0
$23^{f}$	AgSbF <sub>6</sub>	$Cu(OAc)_2$	DCE	25

<sup>*a*</sup> Unless otherwise noted, the reactions were carried out using acylsilane (**1a**, 0.20 mmol), alkene (**2a**, 0.40 mmol),  $[\text{RuCl}_2(p\text{-cymene})]_2$  (2.5 mol%), additive (10 mol%), and oxidant (1.2 equiv.) in a solvent (0.2 M, 1.0 mL) at 60 °C for 24 h under an argon atmosphere (1 atm). <sup>*b*</sup> The yields indicated in the table are isolated yields. <sup>*c*</sup> 5 mol%  $[\text{RuCl}_2(p\text{-cymene})]_2$  was used. <sup>*d*</sup> Without  $[\text{RuCl}_2(p\text{-cymene})]_2$ . <sup>*e*</sup> 10 mol% Ru( $p\text{-cymene})(\text{OAc})_2$  was used instead of  $[\text{RuCl}_2(p\text{-cymene})]_2$ . <sup>*f*</sup> 5 mol%  $[\text{IrCp}^*\text{Cl}_2]_2$  was used instead of  $[\text{RuCl}_2(p\text{-cymene})]_2$ . *f* 5 mol%  $[\text{IrCp}^*\text{Cl}_2]_2$  was used instead of  $[\text{RuCl}_2(p\text{-cymene})]_2$ . *f* 5 mol%  $[\text{IrCp}^*\text{cl}_2]_2$  was used instead of  $[\text{RuCl}_2(p\text{-cymene})]_2$ .

and only  $AgSbF_6$  showed comparable results (entries 2–7). Replacing the DCE by DCM and chloroform even led to worse results (entries 8 and 9). Meanwhile, commonly used solvents such as DME, MeCN, THF, DMF and toluene greatly hindered the reaction (entries 10–14), showing the remarkable solvent effect in such a reaction. Much to our delight, increasing the amount of  $[RuCl_2(p-cymene)]_2$  to 5.0 mol% led to 79% product yield (entry 15). Furthermore, other copper salts such as Cu(OTf)<sub>2</sub> and Cu(OAc)<sub>2</sub>·H<sub>2</sub>O did not promote the reaction (entries 16 and 17). Control experiments carried out have validated the mandatory presence of a ruthenium catalyst, silver additive, and copper salt to provide the cross-coupling product (entries 18–20). Moreover, complex Ru(*p*-cymene)(OAc)<sub>2</sub> was also tested and led to comparable results in the mandatory presence of AgSbF<sub>6</sub> (entries 21 and 22). Interestingly, an iridium complex such as [IrCp\*Cl<sub>2</sub>]<sub>2</sub> also showed limited catalytic activity toward this reaction (entry 23).<sup>14a</sup>

With the optimized catalytic conditions in hand, we next examined the scope of this acylsilane directed aromatic C-H alkenvlation reaction. Various acrvlates such as methyl acrvlate. tert-butyl acrylate, benzyl acrylate, phenyl acrylate, methoxyethyl acrylate and tetrahydrofurfuryl acrylate were all efficiently reacted with benzoylsilane (1a) to produce the corresponding styrenes in good to excellent yields with excellent regio- and stereo-selectivities (Table 2, 3aa-3ag). Intriguingly, ethyl vinyl ketone 2h reacted well with 1a, affording the expected product 3ah in moderate yield. Styrene was also a suitable coupling partner, affording stilbene 3ai in 61% yield. Moreover, styrenes bearing a trifluoromethyl group led to better results (3aj and 3ak). Some other electron-deficient alkenes were also tested, and both phenyl vinyl sulfone and diethyl vinylphosphonate reacted smoothly (3al and 3am). The structurally complex steroid analogue 3an could also be obtained by such acylsilane directed C-H activation, exhibiting high chemoselectivity and good functionality tolerance. Although acrylic acid showed limited reactivity, 2-hydroxyethyl acrylate led to excellent yield (3ao and 3ap).17

The scope of the cross-coupling of differently substituted aroylsilanes **1** was also investigated (Table 3). Functional



<sup>*a*</sup> Unless otherwise noted, the reactions were carried out using acylsilane (1a, 0.20 mmol), alkene (2a, 0.40 mmol),  $[\text{RuCl}_2(p\text{-cymene})]_2$  (5.0 mol%), AgSbF<sub>6</sub> (10 mol%), and Cu(OAc)<sub>2</sub> (1.2 equiv.) in DCE (1.0 mL) at 60 °C for 24 h under an argon atmosphere (1 atm). The yields are isolated yields.

#### Table 3 Substrate scope of aroylsilanes<sup>a</sup>



<sup>*a*</sup> Unless otherwise noted, the reactions were carried out using acylsilane (1a, 0.20 mmol), alkene (2a, 0.40 mmol),  $[\text{RuCl}_2(p\text{-cymene})]_2$  (5.0 mol%), AgSbF<sub>6</sub> (10 mol%), and Cu(OAc)<sub>2</sub> (1.2 equiv.) in DCE (1.0 mL) at 60 °C for 24 h under an argon atmosphere (1 atm). The yields are isolated yields.

groups such as Me, OMe, COOMe and even  $CF_3$  attached to the *para*-position of the phenyl ring were all tolerated, regardless of their electron-withdrawing or electron-donating properties (Table 3, **3ba-3ea**). Sensitive and valuable functional groups such as F, Cl, or Br could also be well tolerated, without any decrease in product yields, indicating the great synthetic value of this protocol (**3fa-3ia**). Notably, though *meta*-substituted aroylsilanes reacted well with acrylate, *ortho*-substituted benzoylsilane showed very limited reactivity due to steric hindrance (**3ia-3ka**). However, aroylsilane bearing a nitrile group was totally inactive presumably due to the strong coordination to the metal center. Incorporation of a large aromatic ring such as naphthalene also led to good yield as well as excellent regio-selectivity (**3la**). Intriguingly, heterocycles such as furan and thiophene were also suitable, affording the corresponding products **3ma** and **3ma** in moderate yields.

We also conducted inter-molecular competition experiments using differently substituted aroylsilanes **1** and alkenes **2**. Alkenylation of aroylsilanes **1c** and **1e** with alkene **2a** in a one-pot fashion exhibited an electron-rich substrate to be preferentially converted, which is in good agreement with an electrophilic activation manifold, like in the Ru-catalyzed aromatic C–H alkenylation directed by the carbonyl group (Scheme 2a).<sup>9,16</sup> In contrast, the competition experiments of acrylate **2b** and ketone **2h** with aroylsilane **1a** under optimal conditions revealed that the acrylate coupling partner reacted preferentially (Scheme 2b). Considering the remarkable activity of the cationic ruthenium(n) catalyst, we became interested in probing its mode of action in the alkenylation reactions. When



Scheme 2 Competition/deuterium-labeled experiments.

aroylsilanes were subjected to standard conditions in the presence of  $D_2O$  or  $CD_3COOD$ , H/D scrambling was observed both in **1b** and product **3aa**, showing a reversible C-H cyclometalation event (Scheme 2c and d). Moreover, a considerable intermolecular kinetic isotope effect (KIE) of 2.4 and an intramolecular KIE of 1.1 were observed (Scheme 2e and f). These data indicated that the C-H metalation was unlikely the rate-determining step.<sup>18</sup>

When exposed to visible-light irradiation, the *ortho*-olefinated acylsilanes underwent an intramolecular cyclization to afford indanone derivatives.<sup>14b</sup> To demonstrate the further utility of our acylsilane directed C–H olefination, we attempted elaboration of the alkenylated product 3 (Scheme 3). Treatment of benzoyltrimethylsilane **3aa** with one equivalent of KF in a mixed solvent EtOH/H<sub>2</sub>O (v/v = 3/1) at 50 °C for 16 hours gives the corresponding benzaldehyde **4** in 65% isolated yield (Scheme 3a). Meanwhile, acylsilane **3aa** could also be smoothly converted to carboxylic acid 5 in 73% yield, promoted by a simple Fe(NO<sub>3</sub>)<sub>3</sub> salt (Scheme 3b). This result paves the way for the development of new transformations involving acylsilane intermediates.

Plausible mechanisms are illustrated in Scheme 4. First, reversible acetate-assisted C-H metalation of **1** takes place to give a five-membered ruthenacycle intermediate **I** accompanied



Scheme 3 Synthetic applications.



Scheme 4 Plausible mechanism.

by the loss of HOAc.<sup>9,16</sup> Then, alkene insertion into the resulting Ru–C bond takes place to form intermediate **II**. Next,  $\beta$ -hydride elimination of **II** furnishes the desired product **3**. Finally, catalytically active species was regenerated by reoxidation by Cu(II) salt.

In conclusion, we have developed an inexpensive rutheniumcatalyzed oxidative C–H alkenylation reaction between aroylsilanes and alkenes. With the assistance of the directing group acylsilane, this protocol provides a mild and straightforward method for the preparation of valuable vinyl arenes with excellent regio- and stereoselectivities. The operationally simple reaction is applicable to a broad range of aroylsilane substrates and displays wide functional group tolerance, demonstrating the practicality of this C–H alkenylation protocol.

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## Conflicts of interest

There are no conflicts to declare.

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