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Ruthenium-Catalyzed Brook Rearrangement Involved Domino Sequence Enabled by Acylsilane–Aldehyde Corporation

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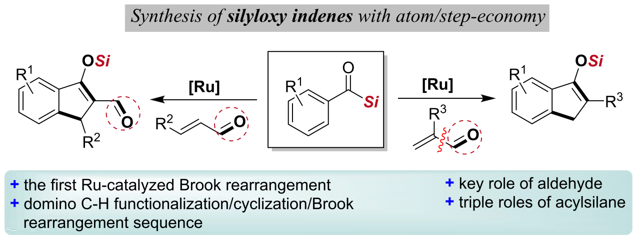
ABSTRACT: A ruthenium-catalyzed [1,2]-Brook rearrangement involved domino sequence is presented to prepare highly functionalized silyloxy indenes with atomic- and step-economy. This domino reaction is triggered by acylsilane-directed C–H activation, and the aldehyde controlled the subsequent enol cyclization/Brook Rearrangement other than β–H elimination. The protocol tolerates a broad substitution pattern, and the further synthetic elaboration of silyloxy indenes allows access to a diverse range of interesting indene and indanone derivatives.



Acylsilane represents a fascinating class of organosilicon compounds, exhibiting a wide variety of synthetic applications, including nucleophilic addition, cross-coupling, radical cyclization, and aldol reaction.[1] Notably, acylsilanes are intriguing for potential [1,2]-anion transposition, defined as the Brook rearrangement, and there are many reports on nucleophilic addition/Brook rearrangement reactions using a quantitative amount of organometallic reagents (Scheme 1a).[1a,2] Acylsilane also undergoes a photochemical or thermal [1,2]-Brook rearrangement to provide the siloxycarbene intermediate for further insertion of C–H, B–H, C–B, and unsaturated C–C bonds (Scheme 1b).[3] Furthermore, there have been several exciting organo-catalytic sequences,[4] including thiazolium-catalyzed acylsilane addition to unsaturated esters/ketone (Scheme 1c),[4a] cyanide-catalyzed silyl benzoin reaction (Scheme 1d),[4b] phosphine-promoted sequential Brook/Wittig reactions (Scheme 1e),[4c] and enantioselective bisguanidinium-catalyzed anionotropic rearrangement (Scheme 1f).[4d] To the best of our knowledge, transition-metal-catalyzed Brook rearrangement of acylsilanes still remains elusive,[5] although there are several Cu- or Pd-catalyzed examples using other different carbonyl or organosilicon substrates.[6]

Indenes are widely utilized as building blocks for the synthesis of natural products and pharmaceutical molecules as well as ligands in various transition-metal-catalyzed reactions.[7] Consequently, many efforts have been devoted to the preparation of indene frameworks, but these conventional approaches usually require multiple steps and/or suffer from limited substrate scopes.[8] In recent years, tremendous advances have been made in transition-metal-catalyzed C–H activations[9] as well as the C–H activation/carbocyclization sequence to construct indenes, indenones, and heterocycles.[10−12] Silyl enol ethers are recognized as versatile functionalities that have been utilized in numerous synthetic transformations, so the synthesis of silyloxy indenes seems particularly attractive. Recently, rhodium(III)-catalyzed *ortho*-olefination of aroylsilanes followed by light-induced intramolecular cyclization via siloxycarbenes represents an efficient two-step access to silyloxy indenes (Scheme 1g).[3e]

Domino-type reactions by careful design of a multistep reaction in one-pot sequence provide efficient and step-economical approaches using much simpler raw chemicals. Despite the wide application of acylsilanes in synthetic organic chemistry, there is still no report on tandem bond formation integrating directed C–H activation[9] and Brook rearrangement to produce valuable organosilicon compounds. With our ongoing interest in directed C–H activation,[9f−h,13j] herein, we report the first ruthenium-catalyzed C–H functionalization/cyclization/[1,2[-Brook rearrangement sequence, and such a one-pot/cascade transformation provides one atom/step-economic access toward silyloxy indenes from readily available aroylsilanes and acroleins. Cooperation of the acylsilane and aldehyde controls the selectivity and sequence of the domino reaction efficiently (Scheme 1h).

Control of chemoselectivity is highly sought after in organic synthesis. In the realm of directed C–H functionalization, chemoselectivity can be controlled by change of catalyst, directing group, electron-withdrawing group, or additive.[13] We postulated that the C–H functionalization of aroylsilanes using acroleins or vinyl ketones could facilitate the carbocyclization-involved cascade sequence due to a key metallo–enol

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Scheme 1. Brook Rearrangements of Acylsilanes in Organic Synthesis

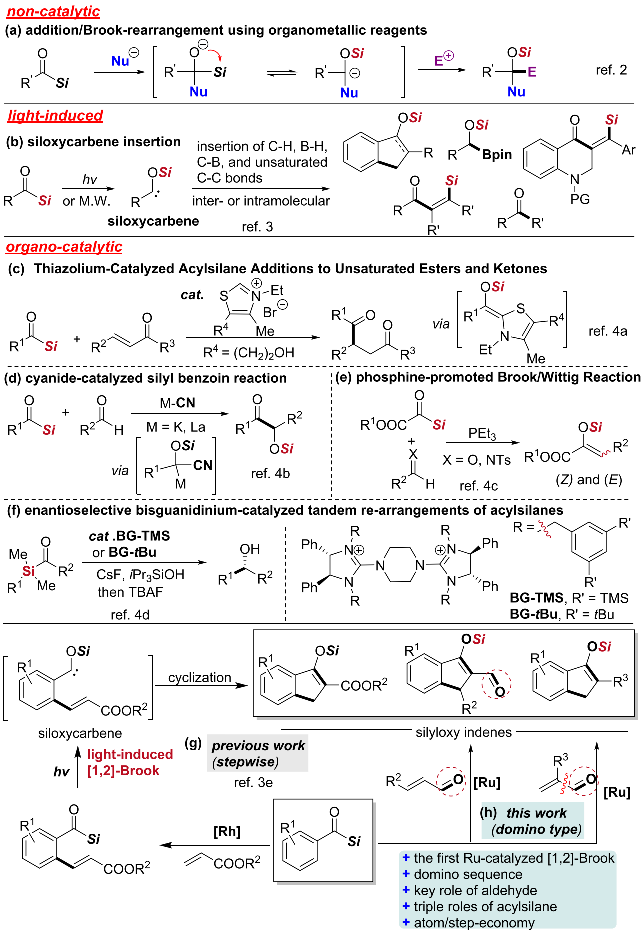
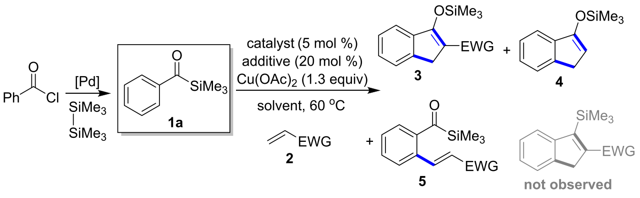


Table 1. Optimization of Catalytic Conditions[a]



entry	catalyst	EWG group	additive	solvent	yield[b] (%) of 3, 4, 5
1	[**Ru**]-1	CHO		DCE	
2	[**Ru**]-1	CHO	AgSbF$_6$	DCE	62, <5, 18
3	[**Ru**]-1	CHO	Ag$_2$O	DCE	
4	[**Ru**]-1	CHO	AgBF$_4$	DCE	<5, <5, 5
5	[**Ru**]-1	CHO	AgOAc	DCE	
6	[**Ru**]-1	CHO	Ag$_2$CO$_3$	DCE	
7	[**Ru**]-1	CHO	AgSbF$_6$	toluene	
8	[**Ru**]-1	CHO	AgSbF$_6$	MeOH	
9	[**Ru**]-1	CHO	AgSbF$_6$	THF	<5, –, –
10	[**Ru**]-1	CHO	AgSbF$_6$	DMF	
11	[**Ru**]-1	CHO	AgSbF$_6$	HCCl$_3$	39, –, –
12	[**Ru**]-**1**	**CHO**	**AgSbF$_6$**	**DCM**	**73, <5, 5**
13	[**Ru**]-2	CHO	AgSbF$_6$	DCM	61, 6, 5
14	[**Rh**]	CHO	AgSbF$_6$	DCM	52, 0, 5
15	[Ir]	CHO	AgSbF$_6$	DCM	<5, <5, –
16	[**Ru**]-1	COEt	AgSbF$_6$	DCM	–, –, 19
17	[**Ru**]-1	COOMe	AgSbF$_6$	DCM	–, –, 31
18	[**Ru**]-1	PO(OEt)$_2$	AgSbF$_6$	DCM	–, –, 69
19	[**Ru**]-1	SO$_2$Ph	AgSbF$_6$	DCM	–, –, 79
20	[**Ru**]-1	4-CF$_3$C$_6$H$_4$	AgSbF$_6$	DCM	–, –, 53

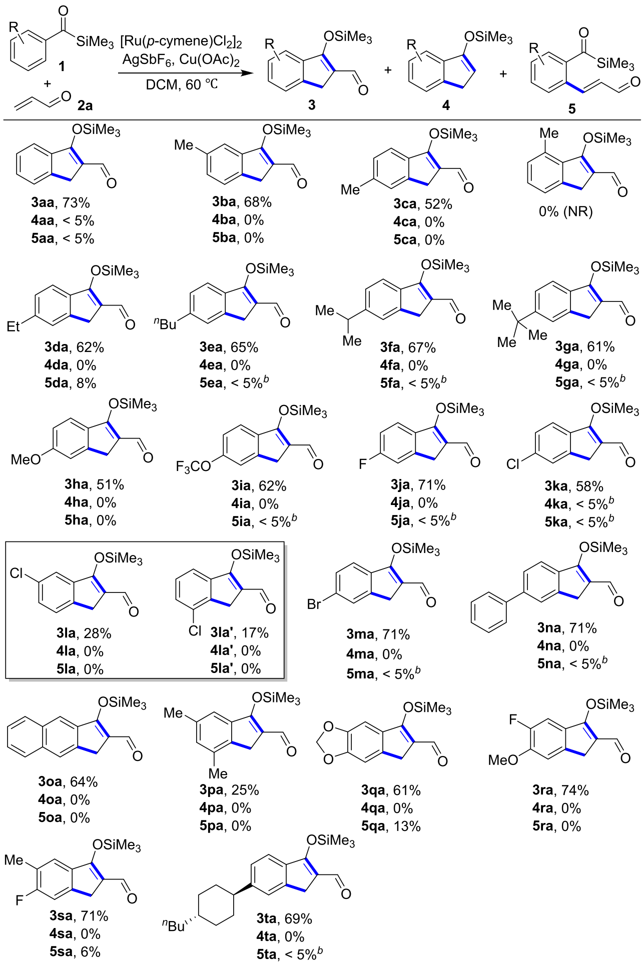
[a]Reaction conditions: **1** (0.2 mmol, 1.0 equiv), **2** (0.6 mmol, 3.0 equiv), catalyst (5 mol %), additive (20 mol %), Cu(OAc)$_2$ (1.3 equiv), in solvent at 60 °C for 16 h. [b]Isolated yields. [**Ru**]-**1** = [Ru(*p*-cymene)Cl$_2$]$_2$; [**Ru**]-**2** = Ru(*p*-cymene)(OAc)$_2$; [**Rh**] = [RhCp*Cl$_2$]$_2$; [Ir] = [IrCp*Cl$_2$]$_2$.

isomerization. Our study commenced with the model reaction between acrolein **2a** and acylsilane **1a** obtained from aroyl chloride (Table 1).[1,2] Although robust complex [Ru(*p*-cymene)Cl$_2$]$_2$ alone did not catalyze the reaction in DCE, addition of AgSbF$_6$ greatly promoted the cascade reaction, leading to silyloxy indene **3** in 62% yield, albeit with the formation of alkenylation product **5** in 18% yield (Table 1, entries 1 and 2). However, other silver salts such as Ag$_2$O, AgBF$_4$, AgOAc, and Ag$_2$CO$_3$ were inefficient (entries 3–6). Next, a series of representative solvents, including toluene, MeOH, THF, and DMF, were examined, but none of them led to the desired products, exhibiting a significant solvent effect (entries 7–10). Although chloroform only produced indene in moderate yield, DCM further improved the reaction, and the desired product was obtained in 73% yield (entries 11 and 12). Notably, silyl indene product was not observed in all of the conditions, although there have been catalytic nucleophilic additions without Brook rearrangement.[1b,c] Another complex [Ru(*p*-cymene)(OAc)$_2$] was also tested, albeit with slightly decreased efficacy (entry 13). Notably, while [RhCp*Cl$_2$]$_2$ was also effective in such cascade reactions, [IrCp*Cl$_2$]$_2$ exhibited no catalytic activity (entries 14 and 15). Finally, a wide variety of alkenes were investigated, but all of them only produced styrene derivatives due to the preference of β-H elimination over cyclization, exhibiting the key role of the aldehyde in such cascade transformation (entries 16–20).

We next examined the scope of acylsilane substrates **1** by varying the substituents (Scheme 2). Although both of the *p*- and *m*-methyl-substituted aroylsilanes were effective (**3ba** and **3ca**), *o*-Methyl-substituted substrates were totally inert due to great steric repulsion. A number of aroylsilane substrates bearing *p*-Et, *n*-Bu, *i*-Pr, *t*-Bu, OMe, OCF$_3$, F, Cl, Br, and Ph on the aromatic ring were investigated, and all of them underwent tandem C–H functionalization/cyclization/[1,2]-Brook rearrangement to provide the corresponding silyloxy indenes **3** in good to excellent yields (**3da**–**3na**). Notably, *meta*-Cl substituted aroylsilane led to mixed products generated from *o*- and *p*-C–H activation (**3la** and **3la′**), but *m*-Me-substituted aroylsilane **1b** led to the only product **3ba**, presumably due to the bulkier of methyl group retarding the *o*-C–H activation. Interestingly, incorporation of a large aromatic ring such as naphthalene also led to good yield as well as excellent regioselectivity (**3oa**). The optimized reaction conditions were also smoothly applied to various multisubstituted aroylsilanes, providing moderate to good yields for the formation of a range of silyloxy indenes **3** with excellent chemo- and site-selectivities (**3pa**–**3sa**). A chiral substrate from 4-(*trans*-4-propylcyclohexyl)benzoic acid still converted well to afford good yield (**3ta**).

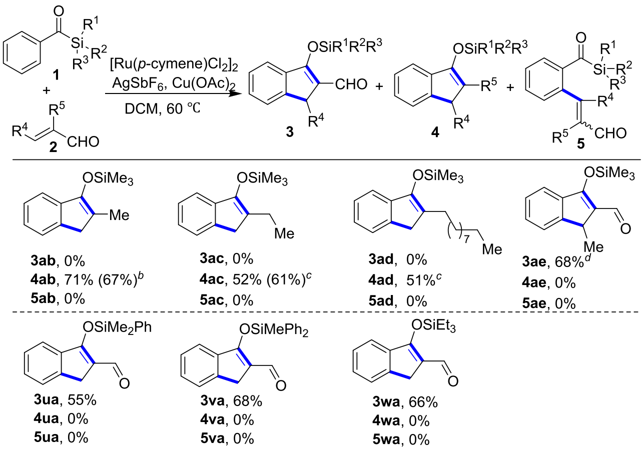
The scope of other representative α,β-unsaturated aldehydes as substrates was investigated (Scheme 3). The reaction of benzoylsilane **1a** with methacrolein **2b** converted well, giving decarbonyl indene product **4ab** in 71% yield, albeit using 10

Scheme 2. Reaction Scope of Acylsilanes[a]



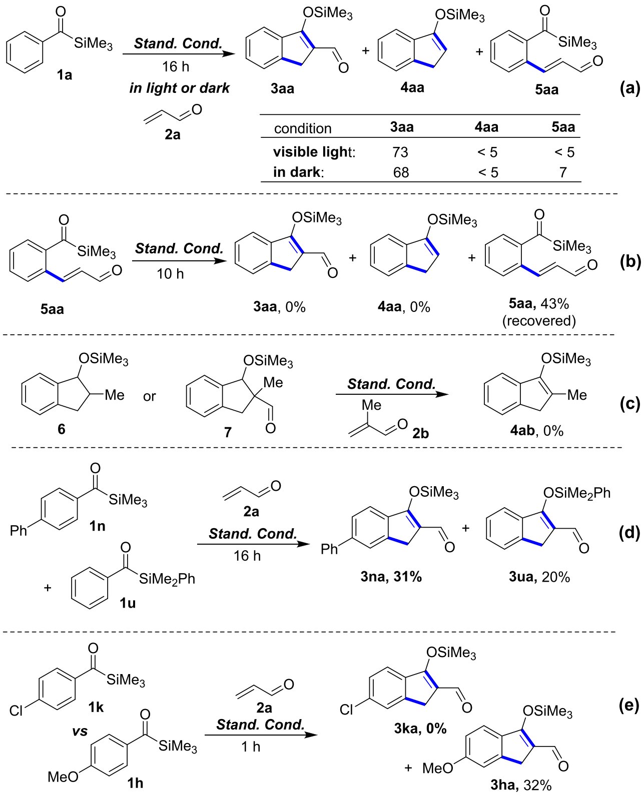
[a] Reaction conditions: **1** (0.2 mmol, 1.0 equiv), **2a** (0.6 mmol, 3.0 equiv), [Ru(p-cymene)Cl$_2$]$_2$ (5 mol %), AgSbF$_6$ (20 mol %), Cu(OAc)$_2$ (1.3 equiv) in DCM (0.6 mL) at 60 °C for 16 h. Isolated yields are shown. [b] These compounds were not cleanly isolated; however, they are believed to be the coproducts **4** or **5** as drawn.

Scheme 3. Reaction Scope of Aldehydes and Acylsilanes[a]



[a] Reaction conditions: **1** (0.2 mmol, 1.0 equiv), **2** (2.0 mmol, 10 equiv), [Ru(p-cymene)Cl$_2$]$_2$ (10 mol %), AgSbF$_6$ (40 mol %), Cu(OAc)$_2$ (1.3 equiv) in DCM (1 mL) at 40 °C for 36−48 h. [b] 7 equiv of **2** used, 48 h. [c] 15 equiv of **2** used, 24 h. [d] Acrolein **2** (0.6 mmol, 3 equiv), [Ru(p-cymene)Cl$_2$]$_2$ (5 mol %), AgSbF$_6$ (20 mol %), at 60 °C for 16 h.

Scheme 4. Controlled Experiments



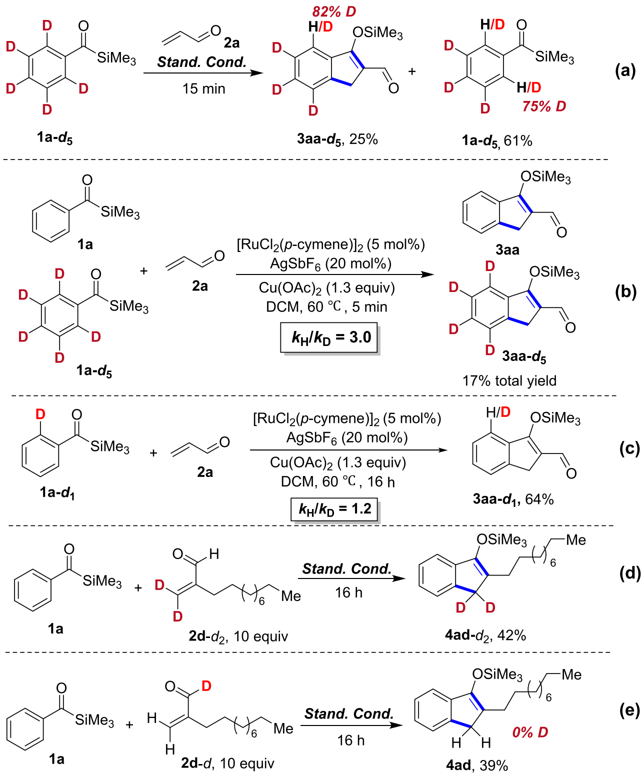
condition	3aa	4aa	5aa
visible light:	73	< 5	< 5
in dark:	68	< 5	7

equiv of aldehyde to promote the conversion. Notably, acrolein bearing ethyl or even longer aliphatic chains still converted, producing the corresponding products in moderate yields (**4ac** and **4ad**). Moreover, the reaction of a β-substituted acrolein such as crotonaldehyde **2e** proceeded well to give indene aldehyde **3ae** in 68% yield, showing the robustness of this protocol. Finally, we turned to examine some other representative silyl groups such as −SiMe$_2$Ph, −SiMePh$_2$, and −SiEt$_3$, and good yields were achieved in all cases (**3ua**, **3va**, and **3wa**; 55%, 68%. and 66% yields respectively).

In order to elucidate the working mode of the protocol, we conducted experimental mechanistic studies. The cascade reaction still proceeded in the dark, excluding the possible light-induced 6-π electrocyclizations and 1,5-hydride shift mechanism by siloxycarbene intermediate (Scheme 4a).[3e] If alkenylation product **5aa** was exposed to the optimal conditions, no cyclization was observed with 43% recovery, exhibiting that **5aa** is not an intermediate in the cascade reaction (Scheme 4b). Compounds **6** and **7** were synthesized and subjected to the optimal conditions, respectively, but no product **4ab** was obtained, excluding the formation of both **6** and **7** (Scheme 4c). Moreover, crossover experiments using **1n** and **1u** led to only products **3na** and **3ua** in 31% and 20% yields, respectively, not only exhibiting the comparable reactivity of **1n** and **1u**, but also supporting an intramolecular [1,2]-silyl group migration event (Scheme 4d). To this end, we performed intermolecular competition experiments using aroylsilanes **1k** and **1h**, showing the electron-rich substrate to be converted preferentially (Scheme 4e).

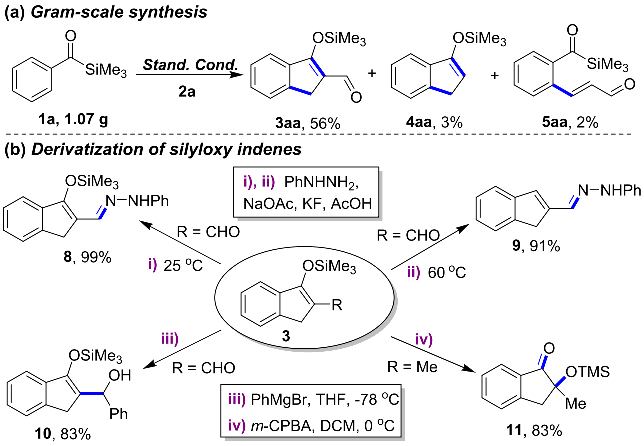
Deuterium-labeling experiments were performed to gain mechanistic insights. Treatment of **1a**-d_5 with acrolein under the optimal conditions led to an extensive H/D exchange on both indene and recovered aroylsilane within 15 min, indicating a rapid and reversible *ortho*-C−H bond activation (Scheme 5a). While a KIE value of 3.0 was obtained from the intermolecular competition of **1a**-d_5 versus **1a**, intramolecular competition in **1a**-d_1 led to a KIE value of 1.2 (Scheme 5b,c). These results indicated the C−H bond cleavage was not the rate-determining step.[14] Olefinic deuterium acrolein **2d**-d_2 was also prepared and reacted with aroylsilane **1a**, leading to the complete deuterium incorporation to the benzylic position of product **4ad**-d_2, exhibiting a directed hydroarylation of olefin (Scheme 5d). However, deuterium aldehyde **2d−d** produced **4ad** with complete loss of deuterium (Scheme 5e).

Scheme 5. Deuterium-Labeled Experiments

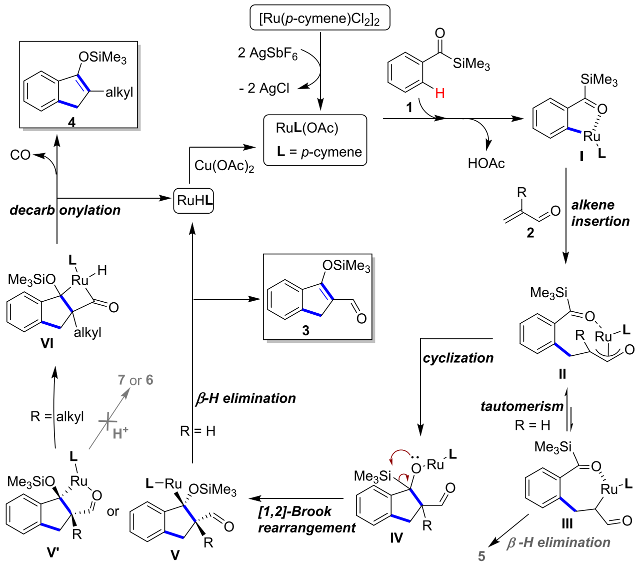


To establish scalability, the conversion of **1a** was also run at a gram scale to give **3aa** in 56% yield, exhibiting the robustness of the protocol (Scheme 6a). Several synthetic elaborations were attempted to reveal the synthetic potential of thus obtained indene derivatives. As outlined in Scheme 6b, while **3aa** was treated with phenyl hydrazine, phenyl hydrazones **8** and **9**, with or without a silyloxy group, can be smoothly obtained. Moreover, **3aa** reacted well with a Grignard reagent such as phenylmagnesium bromide to provide alcohol **10** in 83% yield, with the silyloxy group intact. Interestingly, if **3ab** was treated with 3-chloroperbenzoic acid (*m*-CPBA), 2-silyloxy-1-indanone derivative **11** was obtained in 83% yield.

Scheme 6. Synthetic Applications



Scheme 7. Proposed Mechanism



On the basis of previous reports,[3,10−13] a possible mechanism is proposed (Scheme 7). The reaction starts with the removal of the chloride ligands from the $[RuCl_2(p\text{-cymene})]_2$ complex with the aid of the $AgSbF_6$ salt. Next, coordination of the carbonyl oxygen of **1** to the active ruthenium cationic species followed by *ortho*-C−H metalation provides intermediate **I**. Coordinative insertion of acrolein **2** into the Ru−C bond of **I** affords enolate intermediate **II**. Notably, the sterically less bulk and enolate tautomerism of the aldehyde group drives the following nucleophilic cyclization of enolate **II**,[13] and a disfavored acyl intermediate **III** led to alkenylation product **5** by *β*-hydride elimination. For other electron-withdrawing groups such as ester, phosphonate and sulfone, the formation of ruthenium enolate species is impossible, thus driving the reaction toward the C−H olefination *via* *β*-H elimination (Table 1, entries 17−20).[15] After the five-membered intermediate **IV** was generated by cyclization, the following [1,2]-Brook rearrangement occurred to afford **V** in which the [Ru] and H-atom adopt the *syn*-configuration due to favored steric effects and the subsequent *β*-hydride elimination produces **3**.[16] If *α*-substituted acrolein was employed (R = alkyl), intermediate **V′** was afforded presumably due to decreased steric repulsion and the Ru−O chelation between metal and aldehyde group. As both compounds **6** and **7** led to no product **4ab** under optimal conditions (Scheme 4c), an intramolecular oxidative addition of aldehyde likely to occur and generate the Ru(IV) complex **VI**,[17] and the subsequent decarbonylation by *β*-carbon elimination could produce **4**.[18]

In summary, we have reported a novel ruthenium-catalyzed alkylation/carbocyclization/Brook rearrangement sequence using readily available aroylsilanes and acroleins. Such cascade reaction features operational simplicity, high efficacy, broad functionality tolerance, and good selectivity, providing a step- and atom-economic route to valuable silyloxy indenes. The decreasing steric bulk and enolate tautomerism of the aldehyde group drives the nucleophilic cyclization other than β−H elimination, and this transformation also provides a good example of the intriguing multiple roles of acylsilane in domino reactions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c01983.

Experimental procedures and spectral data for all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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(15) Although ruthenium enolate intermediate is also favorable using vinyl ketone according to previous reports (ref 13), the increased steric repulsion between alkyl and silyl group likely retard the cyclization significantly (Table 1, entry 16).

(16) Although the details of the stereoselectivity mechanism are not clear, it is supposed that steric repulsion and/or the Ru−O chelation effect lead to the stereoselective formation of **V** or **V′**.

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(18) Both compounds **6** and **7** led to no product **4ab** under optimal conditions (Scheme 1c), excluding the possible proto-demetalation of **V** to afford **7** and the oxidative addition/decarbonylation process to provide **6**. Moreover, if **3ka** was subjected to the optimal conditions, no **4ka** was detected, also supporting the formation of intermediate **VI**.