Rhodium-catalyzed coupling reactions with acyl- and vinylsilanes

Yue, Yanni

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2012

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Abstract

Organosilicon compounds have attracted synthetic organic chemists because they have a potential to be used as the organometallic reagents which are stable in the air and water. As the recent transition metal-catalyzed reactions developed, catalytic reactions with organosilicon compounds have been also studied. However, most of the reported transition metal-catalyzed reactions with organosilicon compounds require the addition of at least a stoichiometric amount of fluoride salt and/or the introduction of heteroatom such as halogen or alkoxy group on the silicon atom. These activation methods are not economical because fluoride sources are expensive. Introduction of a heteroatom on the silicon atom makes the reagents unstable against hydrolysis and self-condensation. Thus synthetic organic chemists have studied on the methods to activate C–Si bonds of tetraorganosilicon compounds without adding any additional reagents. In this thesis, the author describes a novel synthetic reaction of tetraorganosilicon compounds, triorgano(vinyl)- and triorgano(acyl)silanes, catalyzed by a rhodium complex.

The author's group reported the $[\text{RhCl}(\text{CO})_2]_2$ -catalyzed acylation of vinylsilanes in the reaction with acid anhydrides. Interestingly, this catalytic cross-coupling reaction proceeds with triorgano(vinyl)silane without adding any activating reagents such as fluoride salts. The author focused on this reaction and studied its scope. It was found that rhodium-catalyzed acylation of vinylsilanes proceeded even in the reaction with carboxylic acids as the acylation source (Scheme 1). The key is *in situ* generation of anhydrides in the reaction of carboxylic acids and dicarbonates. This reaction provides a simple method for the synthesis of α,β -unsaturated ketones.

Scheme 1. Rhodium-catalyzed acylation of vinylsilane with carboxylic acid as the acyl donor

Oxidative homocoupling reactions have been developed by using various organometallic reagents to form 1,3-dienes. However, none of these methods are applicable for the synthesis of 1,3-diene-2,3-diyl diesters because the corresponding (1-acyloxyvinyl)metals are not readily available. Among them, the triorgano(1-acyloxyvinyl)silane is the only main group organometallic compound that is stable enough to handle in the air. Thus oxidative homocoupling of (1-acyloxyvinyl)silane was developed to afford 1,3-diene-2,3-diyl diester which could be further converted to α,α -dialkoxy ketones and α -diketones (Scheme 2).

Scheme 2. Rhodium-catalyzed oxidative homocoupling of (1-acyloxyvinyl)silanes

We found that the activation of C–Si bond by the rhodium catalyst worked not only for triorgano(vinyl)silanes but also for triorgano(acyl)silanes. First, we tested the activation of C–Si bond of acylsilanes with 5-alkynoylsilanes. Desilylative cyclization of 5-

alkynoylsilanes proceeded in the presence of acid anhydride, to give α -alkylidenecyclopentanone derivatives (Scheme 3).

Scheme 3. Rh-catalyzed desilylative cyclization of alkynoylsilanes in the presence of acid anhydrides.

Further improvements were made by using various alkanoylsilane and acid anhydrides (Scheme 4). It is noteworthy that decarbonylative coupling reaction proceeded to give monoketones when aromatic anhydrides were used, alternatively, diketone derivatives were obtained by using aliphatic anhydrides.

Scheme 4. Rhodium-catalyzed cross-coupling reaction between an acylsilane and an acid anhydride.

During the course of study on cross-coupling reaction with acylsilanes, we found that the 3,4-dihydro-2H-naphthalen-1-one was obtained instead of coupling products when 4-phenylbutanoylsilane was treated with ethyl 2-iodoacetate in the presence of catalytic amount of rhodium catalyst (Scheme 5). The product was obtained as the result of C–H activation.

Scheme 5. C–H activation of acylsilane using ethyl 2-iodoacetate as an oxidant

Keywords: acylation, rhodium catalyst, transmetalation, organosilicon compounds, oxidative homocoupling, C–H activation

Index of Abbreviations

δ	chemical shift
Δ	heating
Ac	acetyl
Ac ₂ O	acetic anhydride
aq	aqueous
Con.	concentration
Cp*	η^5 -1,2,3,4,5-pentamethylcyclopentadienyl
<i>cat.</i>	catalytic
d	doublet
dt	doublet of triplets
dd	doublets of doublet
dppe	1,2-bis(diphenylphosphino)ethane
DMF	<i>N,N</i> -dimethylformamide
DMAP	4-(<i>N,N</i> -dimethylamino)pyridine
DMA	<i>N,N</i> -dimethylacetamide
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
dba	dibenzylideneacetone
DME	1,2-dimethoxyethane
DMSO	dimethyl sulfoxide
dppf	1, 1'-bis(diphenylphosphino)ferrocene
eq / equiv	equivalent
FT-IR	Fourier transform infrared spectroscopy
HMPA	hexamethylphosphoramide

hfacac	hexafluoroacetylacetonate
h	hour
$h\nu$	photoirradiation
HRMS	high resolution mass spectroscopy
IR	infrared
J	coupling constant
LiHMDS	lithium bis(trimethylsilyl)amide
LDA	lithium diisopropyl amide
M _w	microwave
M	concentration in mol dm ⁻³
M ⁺	parent ion peak (mass spectrometry)
m	multiplet
Min	minute
MS	mass spectrum
MW	molecular weight
n	normal chain
NMR	nuclear magnetic resonance
PTLC	preparative thin-layer chromatography
q	quartet
<i>rac</i> -BINAP	racemic-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl
rt	room temperature
rbf	round bottomed flask
<i>s</i> -Bu	secondary butyl
s	singlet
THF	tetrahydrofuran

^t Bu	<i>tert</i> -butyl
TASF	tris(dimethylamino)sulfonium difluorotrimethylsilicate
Temp	temperature
TEMPO	2,2,6,6-tetramethylpiperidine- <i>N</i> -oxyl
(<i>R</i>)-Tol-BINAP	(<i>R</i>)-(+)-2,2'-bis(di- <i>p</i> -tolylphosphino)-1,1'-binaphthyl
TMSCl	trimethylsilylchloride
t	triplet
TLC	thin layer chromatography
XPhos	2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl

Chapter I Introduction

1.1 Transition Metal-Catalyzed Coupling Reactions

Coupling reactions catalyzed by transition metal complexes are now regarded as one of the most useful methods for the formation of carbon–carbon bonds. In such coupling reactions, organic halides react with organometallic reagents in the presence of a catalytic amount of late transition metal complexes to give coupling products (Scheme 1–1).

Scheme 1–1. Late transition metal complexes-catalyzed coupling reactions

Early examples of transition metal-catalyzed cross-coupling reactions were reported by Kumada^[1] and Corriu^[2] using organomagnesium reagents with palladium or nickel catalysts (Scheme 1–2). Thereafter, various kinds of less nucleophilic organometallic reagents (Zn, Sn, B and so on) were found to be applicable for this reaction.

Scheme 1–2. Ni-catalyzed cross-coupling of organomagnesium reagents

Among the organometallic reagents, organotin and organoboron compounds have been widely used for construction of carbon–carbon bonds due to their relative stability in water and good functional group compatibility.^[3] The palladium-catalyzed cross-coupling reactions between organic halides and organotin or organoboron compounds are useful for $\text{sp}^2\text{C}\text{--}\text{sp}^2\text{C}$ bond formation, especially in natural product synthesis. Scheme 1–3 illustrates the application of Pd-catalyzed cross-coupling reaction in the synthesis of

Prostaglandin E1.^[4] This is one of the most promising ways for constructing the expanded conjugation system as the key step in natural product synthesis.^[4]

Scheme 1–3. Synthesis of Prostaglandin E1 by using organoboron compounds

Recently, an efficient methodology was developed to form the coupling product by using weakly reactive aryl halides. However, the organoboron compound is less nucleophilic and it requires addition of 2 equiv base to assist the transmetalation step (Scheme 1–4).^[5]

Scheme 1–4. Pd/C-catalyzed Suzuki coupling of aryl chlorides

In 1989, Suzuki *et al.* reported the coupling reaction with an iodobenzene and a B-octyl-9-BBN. The reaction proceeds smoothly by using a catalytic amount of [PdCl₂(dppf)] and a base to give the corresponding arene in excellent yield (Scheme 1–5).^[6]

Alkynylboranes are very useful synthetic intermediates. But they are easily hydrolyzed by bases. In 2002, Molander *et al.* have found a novel cross-coupling that occurred readily with potassium alkynyltrifluoroborates and 1-bromonaphthalenes (Scheme 1–7).^[7] The potassium alkynyltrifluoroborates are air- and moisture-stable and can be stored indefinitely.

Organotin reagents suffer from some obvious drawbacks with their toxicity. Their high molecular weight is also problematic in the view point of atom economy (Scheme 1–8).^[8]

Scheme 1–8. Stille coupling of aryl chlorides catalyzed by $\text{Pd}(\text{P}(\text{tBu})_3)_2$

Thus, since there are still drawbacks for the organometallic reagents which have been used in the catalytic cross-coupling reactions, synthetic chemists have studied on more practical organometallic reagents. Among the wide range of organometallic reagents, organosilicon compounds attracted the attention of the chemical society, due to their high stability in air and water. Furthermore, organosilicon compounds are easily prepared from cheap and readily available starting materials by various kinds of established procedures.^[9] During recent years, the coupling reactions of organosilicon compounds have been well developed.^[10] The pioneering work was demonstrated by Hiyama, whose discovery revealed the utility of chloro-, fluorosilanes^[10b] and alkoxy silanes^[11] as versatile cross-coupling partners with a variety of electrophiles. Till now, most coupling reactions are catalyzed by Pd complexes. Lautens demonstrated that transition metals such as palladium, nickel and platinum typically switch between the oxidation states (0) and (II) during the catalytic cycle (Scheme 1–9).^[12] Firstly, an appropriate electrophilic molecule must be oxidatively added to the $\text{Pd}(0)$ species to form $\text{Pd}(\text{II})$ species. Then the $\text{Pd}(\text{II})$ species can undergo transmetalation with an organometallic compound and subsequent reductive elimination would form the desired product and regenerate $\text{Pd}(0)$ catalyst.

Scheme 1–9. Generalized catalytic cycle for Ni, Pd, and Pt catalysis

However, the typical catalytic cycle for rhodium usually involves oxidation states between (I) and (III). As is well known, Rh(I) and Rh(III) species can give us two possible points at which transmetalation can take place, and thus two possible catalytic cycles are shown in Scheme 1–10. Transmetalation can take place between Rh(I) species and an organometallic compound, and then an electrophile oxidatively added to the Rh(I) intermediate to form a rhodium(III) species (Cycle 1). Alternatively, another catalytic cycle is similar to the group 10 metals. First, oxidative addition takes place on the rhodium(I) species, forming a rhodium(III) intermediate. Then transmetalation of the rhodium(III) species occurs (Cycle 2).

Scheme 1–10. Possible catalytic cycles for rhodium-catalyzed reactions

In summary, transition metal-catalyzed coupling reactions have become a versatile tool for the chemical bond formation. In this thesis, we will focus on coupling reactions of organosilanes because organosilanes are interesting building blocks in organic synthesis due to the large number of transformations that the C–Si bond can undergo and have the advantageous properties of being stable, non-toxic and readily available.

1.2 Transition Metal-Catalyzed Coupling Reactions with Organosilanes

Alkynylsilanes are widely used for Sonogashira coupling (Scheme 1–11). Lewis bases (such as: Cs_2CO_3 , NaOMe and NaOEt) can coordinate to a silyl group that can help to form a hypervalent silicate species which ultimately undergo mild and efficient reactions to nucleophiles. This is a giant step for Sonogashira coupling reaction using alkynylsilanes instead of terminal alkyne. Many chemists have made their contributions to develop the reactions of alkynylsilanes. Scheidt described the Lewis base-catalyzed additions of alkynyl nucleophiles to aldehydes, ketones, and imines,^[13] and Mukaiyama reported that Lewis base catalysts, especially phenoxide anion, were efficient for the activation of the silicon–carbon bond.^[14]

Scheme 1–11. Sonogashira coupling of aryl chlorides with trimethylsilyl acetylene

1.2.1 Coupling Reactions with Heteroatom Substituted Organosilanes

Up to now, the coupling of sp^2 organosilicon reagents catalyzed by transition metals prevails. Organosilicon reagents can be considered as good alternatives to the conventional organotin, organoboron, and other organometallic reagents in recent years.

However, the C–Si bond is less polar compared to other carbon–metal bond (C–B, C–Sn, C–Mg) because carbon and silicon are in the same group and have similar properties. Thus a fluoride source is normally used for activating the C–Si bond during silicon-based cross-coupling reactions. A fluoride ion was found to preferentially attack Si to generate anionic species which can enhance the polarity of the C–Si bonds, and that was critical for transmetalation of organosilicon reagents during the catalytic cycle of the cross-coupling reaction.^[15] Many chemists are interested in the research to form pentacoordinated silicates of metal-catalyzed cross-coupling of organosilicon reagents.

Hiyama and Hatanaka reported the pioneering work of silicon-based cross-coupling reactions.^[15a] They reported that cross-coupling reaction of organosilicon reagent with organic halide took place in the presence of an allylpalladium chloride dimer catalyst and TASF to afford the desired coupling product. This work was subsequently named for Hiyama. TASF is a good F[−] source which is critical to complete the cross-coupling reactions. Hiyama *et al.* found that no reaction took place without TASF and a slight excess of TASF is necessary to get a good yield (Scheme 1–12).

Scheme 1–12. TASf/Pd catalyst mediated cross-coupling of vinylsilanes with organic iodide

Thus Hiyama and Hatanaka thought the anionic nature of the organosilicon compound generated by F[−] source is essential for cross-coupling reactions because the anionic nature can enhance the polarity of C–Si bond. Furthermore, the anionic nature of the organic groups can facilitate the transmetalation of organosilicon reagents with palladium catalyst.

It has been noted that chloro-^[16] (Scheme 1–13) and fluorosilanes^[17] (Scheme 1–14) are more potent cross-coupling partners, although they are too hydrolytically sensitive to handle.

Scheme 1–13. Cross-coupling reactions of organic bromide with organochlorosilanes

Scheme 1–14. Cross-coupling reactions of organic halide with organofluorosilanes mediated by Pd catalyst and Bu_4NF

To solve these problems, more and more chemists focused on the cross-coupling reactions of organosilanes. The reactive oxygenated organosilicon compounds were then introduced to achieve broader utility since halogenated organosilicon compounds are generally known to be hydrolytically sensitive. They also introduced heteroatoms on the silicon moiety instead of fluoro and chloro group.^[18] Accordingly, heteroatom surrogates (siletanes, 2-pyridyl-, 2-thienyl, and benzylsilanes) with stability have been introduced which can be converted to more reactive heterofunctional silanes in the presence of fluoride sources.^[18-19] A representative work has been published by Denmark group, in which they successfully employed siletanes, organosilanol, organosiloxane and silyl ethers as the nucleophilic coupling partners in the presence of TBAF under very mild reaction conditions (Scheme 1–15).^[20] These findings accentuate the advantages of such organosilanes as suitable organometallic coupling reagents. Apart from being relatively

easily synthesized and atom economical, oxygenated organosilicon compounds have high functional group tolerance and undergo cross-coupling efficiently with high selectivities under mild reaction conditions. Moreover, the co-products and byproducts resulting from the cross-coupling reactions are usually non-toxic and easily removed.

Scheme 1-15. Cross-coupling of oxygenated organosilicon compounds under TBAF

Further studies showed that siletane **1** is the masked form of silanol and disiloxane. Many useful cross-coupling reactions have been developed on the basis of these findings. However, the requirement for excess amounts of fluoride is a significant drawback, which must be decreased so that the reaction would achieve the same breadth and utility as organoboranes.^[18]

In 2006, Nájera *et al.* revealed that cross-coupling reaction of vinylalkoxysilanes with aryl halides can take place in the absence of fluoride.^[21] Under the thermal or microwave conditions, aryl halides react with vinylalkoxysilanes in the presence of Pd catalyst and aq.

sodium hydroxide (Scheme 1–16). It should be noted that the reaction proceeded with retention of configuration of both components and no undesirable polymerization of the product was observed under this mild reaction conditions. This methodology is a better alternative to the Heck reaction by avoiding the use of gaseous ethylene.

Scheme 1–16. Cross-coupling reaction of vinylalkoxysilanes and aryl halides without fluoride source

Denmark and co-workers also reported a fluoride-free cross-coupling reaction of silanols to aryl iodides in the presence of KOSiMe_3 as a conjugate base of silanol (Scheme 1–17).^[18] They could use the conjugate base of silanol instead of fluoride to provide the desired product of the cross-coupling reaction. Therefore, Denmark mixed silanol with different kinds of aryl iodides in the presence of the potassium trimethylsilanolate in DME to get the desired product in high yield.

Scheme 1–17. Cross-coupling reaction of silanols and aryl iodides in the presence of KOSiMe_3

1.2.2 Coupling Reactions with Tetraorganosilanes

The cross-coupling of organosilanes having an electron-withdrawing heteroatom on silicon has met with significant progress. Considering the stability, the use of tetraorganosilanes is highly desirable. However, it is difficult for tetraorganosilanes to form active pentacoordinate silicates even with fluoride activation.^[22] Hence, different kinds of substituted organosilanes are designed to achieve transmetalation of silane-based cross-coupling.

Denmark and co-workers introduced masked silanols, such as alkenylsilacyclobutanes, 2-pyridyl (Scheme 1–18),^[19b, 23] 2-thienyl (Scheme 1–19),^[19c] and 3,5-bis(trifluoromethyl)phenyl,^[24] as well as benzyl,^[19a] and allyl groups.^[25] Because masked silanols behave as very stable tetraorganosilanes and thus tolerate various synthetic manipulations, they undergo the cross-coupling reaction upon treatment with fluoride under mild conditions. Furthermore, a phenyl group can also serve as a masking group, but the strong Si–Ph bond is supposed to be cleaved by a strong base to give silanols or siloxanes which undergo the cross-coupling reaction.

Scheme 1–18. Cross-coupling of 2-pyridyl silanes

Scheme 1–19. Cross-coupling of 2-thienyl silanes

Takeda *et al.* demonstrated efficient transmetalation of alkenyl(trimethyl)silanes with copper(I), in which transmetalation is effected *via* Brook rearrangement^[26] with the proximal hydroxyl group (Scheme 1–20).^[27] When **Z-3** is treated to *t*BuOCu, the silyl group at the vinyl position migrates to the oxygen at the allyl position via a 5-membered ring transition state. While the copper cation, in turn, takes the vinylic position. These vinyl copper species will then undergo cross-coupling reactions with allylic, vinylic and aryl halides. A similar phenomenon was observed in a fluoride-free palladium-catalyzed cross-coupling reaction of (*Z*)- β -(trialkylsilyl) acrylic acids reported by Shindo and co-workers (Scheme 1–21).^[28] It is proposed that the reaction mechanism involved an intramolecular pentacoordination of oxygen to silicon.

Scheme 1–20. Efficient trans-metalation of alkenyl(trimethyl)silanes with copper(I) complex

Scheme 1–21. Fluoride-free cross-coupling of compound **4**

In the view of the above reaction, transmetallation of silicon to a late transition-metal can be accelerated in a highly efficient manner *via* intramolecular coordination. However, these examples are limited to alkenylsilanes that have a transferable group containing the oxygen-based activating functionality. Accordingly, Hiyama *et al.* have focused on stable tetraorganosilicon reagents which have an active organofunctional group and independent transferable group to allow delivery of various organic groups (Scheme 1–22).^[29]

Scheme 1–22. Cross-coupling of **5** with aryl and alkenyl iodides.

Hiyama and coworkers ascertained the proposed involvement of the 5-membered ring in their research on Pd-catalyzed cross-coupling reaction of tetraorganosilicon to proximal hydroxyl group with aryl and alkenyl iodides. The 5-membered cyclic silyl ether was isolated and could be used to reform starting material **5** by a short series of reactions. Alternatively, Hiyama subjected the 5-membered cyclic silyl ether to a Grignard reagent to obtain tetraorganosilicon compound **5** (Scheme 1–23),^[30] in a later publication.

Scheme 1–23. Reaction of a cyclic silyl ether to reform **5**

It is known that cleavage of $\text{sp}^3\text{C-Si}$ bond normally requires extremely harsh conditions with the exception of allyl- and benzylsilanes. Recently, Chatani reported a Rh-catalyzed

benzosilole synthesis, which involves an unprecedented cleavage of a $\text{sp}^3\text{C-Si}$ bond (Scheme 1–24).^[31] In this reaction, Rh selectively undergoes transmetalation to the more reactive boron center, a subsequent alkyne insertion through an intermediate and finally a displacement of methyl group from Si center to furnish the desired benzosilole. This method shows that versatile trialkylsilyl group can be utilized as a synthetic intermediate for the formation of a new C–Si bond. Conventional C–Si bond formation reactions usually require active silicon reagents such as halo- and hydrosilanes, which often prevent their application in complex systems.

Scheme 1–24. Synthesis of benzosilole by cleavage of a $\text{sp}^3\text{C-Si}$ bond

Hiyama *et al.* also discovered that $\text{sp}^3\text{C-Si}$ bond can be cleaved without the use of highly unstable polyfluorinated alkylsilicon reagents nor fluoride activators. They demonstrated a Pd/copper-catalyzed transfer of both primary and secondary alkyl groups in the presence of K_3PO_4 as a mild activator (Scheme 1–25).^[32] It is noteworthy that $[\text{Cu}(\text{hfacac})_2]$ plays an important role as co-catalyst because its absence triggered *o*-arylation and Brook rearrangement of the starting material.

Scheme 1–25. Methylation of aryl halides with compound **6**

In 2008, Brown *et al.* revealed the discovery of a catalytic reaction for silyl-mediated methylation of electrophilic alkenes under oxidative coupling conditions.^[33] They realized that amide carbonyl can serve as an intramolecular activator to facilitate the cleavage of C–Si bond, allowing oxidative Heck type methylation with electron-deficient olefins to take place (Scheme 1–26).

Scheme 1–26. Silyl-mediated methylation of electrophilic alkenes

Xi *et al.* reported a novel process involving Pd-catalyzed selective cleavage of the sp^3C –Si bond in a trimethyl group and then intramolecular cyclization to form sp^2C –Si bond (Scheme 1–27). In this reaction, 4-nitrobenzaldehyde was proven to be able to promote the efficiency of the catalytic process.

Scheme 1–27. Pd-catalyzed intramolecular coupling of (2'-bromobiphen-2-yl)-trimethylsilane

1.3 Perspective of the Thesis

The cross-coupling reaction of organosilicon compounds is desirable due to their stability, non-toxicity, and the natural abundance of silicon. However, the organosilicon reagents are less reactive towards electrophiles, due to their less polarised C–Si bond. Thus, it is only in the recent years that cross-coupling reactions using silane-based reagents are explored more thoroughly and the developments in organosilicon chemistry are still in progress.

Cross-coupling reactions with oxygenated organosilicon reagents are efficient because the silicon center is Lewis acidic enough to facilitate the formation of pentacoordinate silicates, which is very important for the key transmetalation step. Tetraorganosilanes, on the other hand, are considered better organosilicon reagents for cross-coupling reactions where the formation of an active pentacoordinate silicate species is difficult even with fluoride activation and thus, impeding the transmetalation step.

In 2005, the acylation of alkenyldimethylphenylsilanes by acid anhydrides in the presence of a rhodium catalyst to give α,β -unsaturated ketones was reported by Yamane's group (Scheme 1–28).^[9f] This reaction was the first example in which simple 1-alkenyl organosilicon compounds having trimethylsilyl, dimethylphenylsilyl and methyldiphenylsilyl groups were successfully employed without any activation by fluoride ions or bases.

Scheme 1–28. Acylation of a vinylsilane with an acetic anhydride.

Furthermore, the key transmetalation was investigated *via* NMR studies. 1-Alkenylsilane **1a** and an acetic anhydride were allowed to react independently with a stoichiometric amount of $[\text{RhCl}(\text{CO})_2]_2$ in toluene at 80 °C and each of these reactions was monitored by ^1H NMR with the vinylsilane (Scheme 1–29). In the reaction of 1-alkenylsilane and $[\text{RhCl}(\text{CO})_2]_2$, chloro(dimethyl)phenylsilane **7**, dimethyl(phenyl)silanol **8**, and disiloxane **9** were detected in 38%, 9% and 33% yields respectively. However, no reaction was observed with acetic anhydride even after 5 hours. The detected products give an evidence for the formation of vinylrhodium intermediate **A** *via* transmetallation.

Scheme 1–29. Reaction of vinylsilane with Rh(I) in the absence of acetic anhydride

Scheme 1-30. Reaction of acetic anhydride with Rh(I) in the absence of vinylsilane

Following the NMR studies, a mechanistic cycle was proposed as shown in (Scheme 1–31). The vinylrhodium(I) intermediate **A** was obtained *via* first transmetalation of vinylsilane with the rhodium(I) catalyst, and oxidation of the vinylrhodium(I) intermediate **A** occurs by an anhydride to form intermediate **B** with a rhodium(III) center. The final reductive elimination gives the α,β -unsaturated ketone as well as regenerating active catalytic species **C**.

Scheme 1–31. Proposed mechanism for the rhodium(I)-catalyzed acylation of vinylsilane

This is a novel method because no fluoride ion, base or any other promoter is required. Notably, the acylation product of (1-acyloxyvinyl) silane could be easily converted into α -diketones *via* α,α -dialkoxyketones (Scheme 1–32).

Scheme 1–32. Acylation of (1-acyloxyvinyl)silanes and its applications

Alternatively, acylation of vinylsilanes with carboxylic acids as an acyl donor catalyzed by rhodium(I) catalyst would be investigated in the following reactions (Scheme 1–33).

Scheme 1–33. Acylation of vinylsilane with carboxylic acid

This methodology also provided us possibilities that could be applied to homocoupling reactions. Employing a similar transmetalation of rhodium to vinylsilane, the following work would focus on the $[RhCl(CO)_2]_2$ -catalyzed oxidative homocoupling reactions (Scheme 1–34).

Scheme 1–34. Proposed homocoupling reaction of vinylsilane

The rhodium(I)-catalyzed intramolecular acylation by the use of acylsilanes having an alkynyl moiety was reported in the author group (Scheme 1–35).^[34] The acylsilane can directly transmetalate with Rh(I), the alkynyl group can coordinate to Rh(I) catalyst to smooth the transmetalation of silane-based cross-coupling reactions.

Scheme 1–35. Rhodium-catalyzed acylation of alkynoylsilanes

On the basis of the above result, various reactions were developed by using acylsilanes with anhydrides, vinylhalides and so on. The problem is that this reaction is limited to the acylsilane with the alkynyl group. So we are curious whether the normal alkanoylsilane can transmetalate with Rh(I) catalyst or not (Scheme 1–36). If the transmetalation between Si and Rh can occur, acylsilanes would be widely used for a wide range of coupling reactions.

Scheme 1–36. Cross-coupling of alkanoylsilanes with acid anhydride

With the knowledge of $[\text{RhCl}(\text{CO})_2]_2$, a rhodium complex having an electron deficient rhodium centre, can successfully undergo transmetalation with tetraorganosilicon compounds. We hypothesize that it would also engage in the transmetalation of alkanoylsilanes.

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Chapter II Rhodium-Catalyzed Acylation of Vinylsilane

with Carboxylic Acid as the Acyl Donor

2.1 Introduction

Acylation of unsaturated compounds is an important process because unsaturated ketones, which are useful synthetic intermediates in organic synthesis, are prepared. One of the most promising ways for the regioselective acylation of unsaturated compounds is transition metal-catalyzed cross-coupling reactions between alkenyl- or arylmetal compounds and carboxylic acid chlorides or anhydrides.

Cross-coupling reactions using tetraorganosilicon compounds are still at an early stage. The acylation of triorgano(vinyl)silanes by acid anhydride was reported by the author's group. The reaction can be accomplished by using a catalytic amount of $[\text{RhCl}(\text{CO})_2]_2$ to afford the α,β -unsaturated ketone (Scheme 2–1).^[1]

Scheme 2–1. Acylation of vinylsilane with acetic anhydrides.

Recently, acylation of a variety of vinylmetal species with carboxylic acid derivatives as acyl donors were reported.^[2] In 2001, Yamamoto reported the cross-coupling reaction of carboxylic acids with organoboron compounds in the presence of dimethyl dicarbonate as an activator. The reaction was accomplished by palladium complexes to give ketones in excellent yields (Scheme 2–2).^[2d, e] The carboxylic acid is considered to react with

dimethyl dicarbonate to form a mixed anhydride which will undergo acylation with organoboron compounds.

Scheme 2–2. Palladium-catalyzed cross-coupling of carboxylic acids with boronic acids.

In 2001, Gooßen developed a methodology to prepare aryl ketones using boronic acids and carboxylic acids in the presence of a pivalic anhydride (Scheme 2–3).^[3] This is a convenient way for preparing ketones directly from carboxylic acids.

Scheme 2–3. Cross-coupling of boronic acids with carboxylic acids

Thus, acid anhydrides are generally prepared from carboxylic acids.^[4] Generation of the acid anhydride in situ from corresponding carboxylic acid would avoid the drawbacks of acid anhydrides which are unstable in the presence of water. Therefore, it would be an improvement to the reaction between vinylsilanes and anhydrides using corresponding carboxylic acids in place of acid anhydrides in acylation reaction of vinylsilanes (Scheme 2–4).

Scheme 2–4. Hypothesis of acylation of vinylsilanes with carboxylic acids as the acyl donors.

This is a more convenient methodology instead of preparing various mixed anhydrides or acid anhydrides which would lead to the development of a facile method for preparing α,β -unsaturated carbonyl compounds. Moreover, the reaction has a very low environmental impact and release water-soluble, volatile byproducts.

2.2 Results and Discussion

2.2.1 Optimization of the Reaction Conditions

As the first trial, the reaction of (*E*)-1-dimethyl(phenyl)silyl-4-phenylbut-1-ene (**1a**) with benzoic acid was performed in the presence of (*t*BuOCO)₂O in toluene. And the desired product (*2E*)-1,5-diphenylpent-2-en-1-one (**3aa**) was obtained in 20% yield (Table 2-1, Entry 1). It was reported that the Lewis acid MgCl₂·6H₂O enhanced the reaction pathway between carboxylic acid and (*t*BuOCO)₂O.^[4c] Thus, 10 mol% of MgCl₂·6H₂O was added into the reaction system, the yield increased to 32% (Entry 2). To explore the optimal reaction condition, a wide range of solvents were tested to increase the reaction yield. Ether-type solvent 1,4-dioxane gave a low yield (Entry 3). Aromatic-type solvents, toluene and benzene, were tested, and benzene gave the best yield at a temperature of 100 °C (Entry 5). The yield decreased to 50% at a lower temperature of 90 °C (Entry 4).

Table 2–1 Screening different solvents for Rh-catalyzed acylation of vinylsilane

Entry	Solvent	Additives	Temp./ °C	3aa / %
1	Toluene	-	100	20
2	Toluene	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	100	32
3	1,4-Dioxane	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	100	24
4	Benzene	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	90	50
5	Benzene	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	100	54

Next, a combination of reactants between various acids and di-*tert*-butyl dicarbonate was investigated (Table 2–2). Combining 6 equiv of benzoic acid and 6 equiv of $(^t\text{BuOCO})_2\text{O}$, the desired product (*E*)-1,5-diphenylpent-2-en-1-one (**3aa**) was obtained in 60% yield (Entry 1). The yield was improved to 68% by decreasing the amount of $(^t\text{BuOCO})_2\text{O}$ to 4 equiv (Entry 2). When 2 equiv of benzoic acid and 2 equiv of $(^t\text{BuOCO})_2\text{O}$ were added to the reaction system, the yield decreased to 61%. Finally, it was found that 4 equiv of benzoic acid and 3 equiv of $(^t\text{BuOCO})_2\text{O}$ gave the best yield of 77%.

Table 2–2. Optimization of reaction condition of vinylsilanes with carboxylic acids

Entry	x equiv	y equiv	Additives	3aa yield/ %
1	6	6	MgCl ₂ · 6H ₂ O	60
2	4	6	MgCl ₂ · 6H ₂ O	68
3	2	2	MgCl ₂ · 6H ₂ O	61
4	4	4	MgCl ₂ · 6H ₂ O	68
5	3	4	MgCl₂ · 6H₂O	77
6	3	4	ZnCl ₂	67
7	3	4	ZnBr ₂	16
8	3	4	AlCl ₃	63
9	3	4	FeCl ₃	70

Lewis acids are reported to enhance the rate of formation of acid anhydrides,^[4c] because they will coordinate to the oxygen of the carbonyl carbon to make it more electrophilic to undergo nucleophilic substitution of the acid. Thus, a variety of Lewis acids with different acidic strengths were investigated. After screening various Lewis acids, it was found that MgCl₂·6H₂O still gave the best yield although it is a weak Lewis acid. The product **3aa** was obtained in 67% yield using ZnCl₂ (Entry 6). However, the yield of the product decreased to 16% with ZnBr₂ (Entry 7). AlCl₃ and FeCl₃ having the chloride counter anions were investigated in this reaction. Although AlCl₃ and FeCl₃ are strong Lewis

acids compared to $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ as they are more electronegative to accept the lone pair of electrons better, the yield of the product was still low.

Table 2–3 Rhodium-catalyzed acylation of a vinylsilane with carboxylic acids^a

Entry	RCOOH	Time / h	Product	Yield of 3 / %
1	2a	7	3aa	77
2	2b	12	3ab	72
3	2c	12	3ac	91
4	2d	18	3ad	65
5	2e	12	3ae	51
6	2f	12	3af	78
7	2g	12	3ag	79

Continued

8		12		79
9		14		19
10		14		78
11		12		17
12		12		65
13		12		61
14		13		26

^a Reaction condition: 4 eq. carboxylic acid and 3 eq. (*t*BuOCO)₂O were mixed with 1 eq. (*E*)-1-dimethyl(phenyl)silyl-4-phenylbut-1-ene in the presence of 5 mol% [RhCl(CO)₂]₂ and 10 mol% MgCl₂·6H₂O at a temperature of 100 °C.

Under the optimal reaction conditions, several acids were employed in the rhodium catalyzed acylation of vinylsilane. A few representative results are shown in Table 2–3. Aromatic carboxylic acids gave good yields (Entries 1, 2, 4). Both electron-donating and electron-withdrawing groups were tolerated in this reaction although the electron deficient substrate gave a slightly lower yield. 2-Naphthoic acid gave an excellent yield of 91% (Entry 3). The extended π -system of the naphthoic acid may facilitate the oxidative addition to the vinylrhodium(I) intermediate. The acrylic acid gave the divinyl ketone in 51% yield which can undergo Nazarov cyclization to form cyclopentenone (Entry 5).^[5]

Next, the simple aliphatic acids like acetic acid, propanoic acid and butanoic acid were tested and they all gave good yields (Entries 6–8). Secondary and tertiary acids such as isobutyric acid and pivalic acid gave 19% and 78% yield respectively (Entries 9, 10). It was concluded that the bulkiness of pivalic acid did not affect the reaction yield as pivalic acid is more bulky than isobutyric acid but gave comparable yield to a primary alkanolic acid. With cyclopropanecarboxylic acid, (2*E*)-1-cyclopropyl-5-phenylpent-2-en-1-one (**3al**) was obtained in 65% yield (Entry 12). However, when cyclopentanecarboxylic acid and diphenylacetic acid were used, the corresponding products were obtained in 17% and 26% respectively (Entries 11, 14). We suspect that the low yield obtained from the isobutyric acid, cyclopentanecarboxylic acid and diphenyl acetic acid is due to the deprotonation of the acidic proton at the α -carbon of the corresponding anhydride formed, thus forming the unstable ketene byproduct. On the other hand, the formation of ketene from cyclopropanecarboxylic acid is difficult due to the highly strained ring. For 2-(4-methoxyphenyl)acetic acid, (3*E*)-1-(4-methoxyphenyl)-6-phenylhex-3-en-2-one (**3am**) was obtained in 61% yield (Entry 13).

Next, a wide variety of vinylsilanes were used to explore the substrate scope of the acylation (Table 2–4). Naphthoic acid is chosen as the acyl donor because it gave the best yield compared to other acyl donor.

Table 2–4. Testing various vinylsilanes to obtain various α,β -unsaturated ketones ^a

Entry	Vinylsilane	Time / h	Product Yield
1	1a	7	91% 3ac
2	1b	12	60% 3bc
3	1c	16	55% 3cc
4	1d	14	34% 3dc
5	1e	17	14% 3ec

^a Reaction condition: 4 equiv of naphthoic acid and 3 equiv of $(^t\text{BuOCO})_2\text{O}$ were used with 1 equiv of vinylsilane in the presence of 5 mol% $[\text{RhCl}(\text{CO})_2]_2$ and 10 mol% $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, heated at 100 $^\circ\text{C}$.

(*E*)-1-Dimethyl(phenyl)silyl-4-phenylbut-1-ene (**1a**) gave the best yield of 91% (Table 2–4, Entry 1). However, cyclopentenyl dimethyl(phenyl)silane (**1d**) and *tert*-butyl 2-(trimethylsilyl)-1*H*-indole-1-carboxylate (**1e**) only gave the corresponding acylation product in 34% yield and 14% yield, respectively (Entries 4, 5), which suggested

disubstituted vinylsilanes would decrease the yield due to the steric effect. Activated disubstituted vinylsilanes (*E*)-1-dimethyl(phenyl)silyl-4-phenyl-but-1-enyl benzoate (**1b**) and dimethylphenylsilylfuran (**1c**) gave acylation product in 60%, 55% yields respectively (Entries 2, 3). This may be due to strong coordination of oxygen to the rhodium center to facilitate the transmetalation.

2.2.2 Proposed Mechanism

Mixed anhydride was reported to be formed in the acylation reaction of dialkylcarbonate and carboxylic acid. An NMR experiment was carried out to investigate whether acid anhydrides or mixed anhydrides were formed. In order to confirm, investigations were made by using 4 eq. of carboxylic acid and 4eq. of (*t*BuOCO)₂ (assuming vinylsilane as 1 eq.) in the presence of 10 mol% of MgCl₂·6H₂O and monitored for 2 h by NMR spectroscopy. 0.5 Eq. of mesitylene is used as an internal standard and the results are summarized in **Figure 2–1**. It was found that an acid anhydride is formed from the carboxylic acid and (*t*BuOCO)₂O after 1 h, releasing carbon dioxide and *t*BuOH in the process.

Figure 2–1. NMR monitoring with benzoic acid in the presence of excess amount of (*t*BuOCO)₂O

The reaction mechanism between triorgano(vinyl)silanes and carboxylic acids is proposed in Scheme 2–5. Firstly, transmetalation of the vinylsilane occurs to form rhodium(I) complex **2II**, then oxidative addition of acid anhydride generated *in situ* to form rhodium(III) complex **2III**, reductive elimination of rhodium(III) complex **2III** gives the α,β -unsaturated ketone.

Scheme 2–5. Proposed mechanism of the rhodium (I)-catalyzed acylation of vinylsilane.

2.3 Conclusion

In conclusion, acylation of vinylsilanes using carboxylic acids as acyl donor has been described. The corresponding α,β -unsaturated ketones were obtained in good yields. Acid anhydrides were generated *in situ* by using carboxylic acids and di-*tert*-butyl dicarbonates, which facilitate the oxidative addition of acid anhydride to vinylrhodium(I) intermediate, forming vinylrhodium(III) intermediate.

The rhodium-catalyzed cross-coupling reaction disclosed herein represents a one-step, synthesis of α,β -unsaturated ketones. The reaction is easily performed with many functionalized derivatives. It is thus a valuable alternative to the standard procedures.

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Chapter III Rhodium-Catalyzed Oxidative

Homocoupling of (1-Acyloxyvinyl)silanes: Synthesis of

1,3-Diene-2,3-Diyl Diesters and Their Derivatives

3.1 Introduction

1,3-Dienes are fundamental structural units of numerous natural products such as Nafuredin-g and its analogues,^[1] Bafilomycin A₁,^[2] (+)-Phoslactomycin B,^[3] and Neooxazolomycin.^[4] In addition, 1,3-diene was usually used as a monomer for the synthesis of polymers with different properties.^[5] Moreover, 1,3-dienes also serve as important ligands in transition metal-catalyzed reactions,^[6] for example which exhibits remarkable regio-controlled effect on nickel-promoted cyclization.^[6d] Thus, various methods have been developed to synthesize 1,3-dienes,^[7] such as: 1) enyne metathesis, 2) olefination with a variety of aldehydes, 3) aryl-substituted cyclopropyl carbinol derivatives undergo a facile stereoselective rearrangement, 4) transition metal-catalyzed coupling reactions. Among these, transition metal-catalyzed coupling reactions have attracted more and more interest from chemists for high efficiency and selectivity. Recently, oxidative homocoupling reaction between two organometallic reagents has been developed to form 1,3-dienes.

In 2002, Lei *et al.* first reported oxidative homocoupling reactions of aryl boronic acids by using methyl 2-bromo-2-phenylacetate to realize double transmetallation (Scheme 3–1). They speculated that the mechanism of oxidative homocoupling reactions was shown as below (Scheme 3–2).^[8] Firstly, oxidative addition of Pd(0) to methyl 2-bromo-2-phenylacetate generates Pd(II) complex **3I**, then double transmetallation of 3,5-

dimethylphenyl boronic acid to **3I** affords Pd(II) intermediate **3II**. Finally reductive elimination occurs to give the homocoupling product and regenerates Pd(0).

Scheme 3–1. Palladium-catalyzed homocoupling of aryl boronic acids

Scheme 3–2. Proposed mechanism for oxidative homocoupling

In 2005, Hayashi *et al.* successfully developed the iron-catalyzed oxidative homocoupling of aryl Grignard reagents, in which organic oxidant 1,2-dihaloethane was used in the reaction system (Scheme 3–3).^[9] Various aryl magnesium reagents were homocoupled in high yields. Functional groups such as methoxy and halide were well tolerated.

Scheme 3–3. Iron-catalyzed oxidative homocoupling of Grignard reagents.

Recently, Studer *et al.* reported rhodium-catalyzed oxidative homocoupling of boronic acids by using Wilkinson's catalyst.^[10] In this reaction, they employed TEMPO as a stoichiometric oxidant (Scheme 3–4). This is the first Rh-catalyzed oxidative homocoupling reaction with various aryl- and alkenylboronic acids. O₂ is also considered as an oxidant for this reaction, however, it needs a longer reaction time and gives a lower yield.

Scheme 3–4. Rhodium-catalyzed oxidative homocoupling reaction of boronic acids

In 2009, Stefani *et al.* reported an Pd-catalyzed oxidative homocoupling reaction of potassium alkynyl-trifluoroborates using Ag₂O as oxidant (Scheme 3–5).^[11] As such, potassium organotrifluoroborate salts are more nucleophilic than their predecessors. This is a very powerful method to synthesize symmetrical 1,3-dienes. More recently, Shi *et al.* developed another oxidative coupling of organoboron compounds via C–H activation with the oxidant Ag₂O.^[12]

Scheme 3–5. Oxidative homocoupling of potassium alkynyl-trifluoroborates

Although various oxidative homocoupling reactions have been reported by using different oxidants,^[10, 12-13] the development of oxidative homocoupling reaction by using various nucleophiles is still in progress. Moreover, there is no report on oxidative homocoupling

by using organosilanes. Thus, there is still a room for the development of oxidative homocoupling reaction of organosilanes.

Among various 1,3-dienes, acyloxy- or alkoxy-substituted dienes are attractive tools especially for the synthesis of cyclic compounds via Diels–Alder reactions.^[14] Therefore, 1,3-diene-2,3-diyl diester, which possesses two acyloxy groups, is expected to be a useful synthetic intermediate. However, there is no report for the practical synthesis of 1,3-diene-2,3-diyl diesters.^[15] Similar oxidative homocoupling of organoboron compounds were reported to afford dienes and biaryls. Nevertheless, none of these methods are applicable for the synthesis of 1,3-diene-2,3-diyl diesters because the corresponding (1-acyloxyvinyl) metals are not readily available. Among (1-acyloxyvinyl)metals, triorgano(1-acyloxyvinyl)silane is the only main-group organometallic compound that is stable enough to handle in the air and can be prepared easily. Herein, we present a simple method to prepare 1,3-diene-2,3-diyl diesters *via* rhodium-catalyzed homocoupling of vinylsilane. The author's group found that the transmetalation between $[\text{RhCl}(\text{CO})_2]_2$ and tetraorganosilicon compounds can be achieved under certain reaction conditions. Then the similar transmetalation is supposed to be applied to the oxidative homocoupling of triorgano(1-acyloxyvinyl)silanes (Scheme 3–6).

Scheme 3–6. Proposed oxidative homocoupling reaction

This will be the first example of oxidative homocoupling of organosilicon compounds with $[\text{RhCl}(\text{CO})_2]_2$. The study of this methodology would contain the synthesis of suitable starting materials, finding the optimal reaction condition, as well as an investigation of its

functional groups tolerance and application. This would lead to the development of a facile method for preparing 1,3-diene-2,3-diyl diesters. If the reaction proceeds, the desired product 1,3-diene-2,3-diyl diesters will be further transformed to α -diketone.

3.2 Results and Discussion

The starting material for our standard reaction was chosen to be (*E*)-4-phenyl-1-(trimethylsilyl)but-1-en-1-yl benzoate (**5a**) which is easily prepared from the corresponding acylsilane. The acylsilane was prepared according to the Katritzky's reported method with modification.^[16] We successfully employed (bromomethyl)benzene, 1-bromohexane, 1-bromobutane, 1-bromo-6-chlorohexane and (5-bromopent-1-yn-1-yl)benzene to prepare the corresponding acylsilane in moderate to good yields (Scheme 3–7).

Scheme 3–7. Synthesis of acylsilanes by using benzotriazole

The reaction between the acylsilanes and various acid anhydrides afforded the different vinylsilanes in 75–89% yields according to the following procedure (Scheme 3–8).^[17] It is

known that *O*-acylation of acylsilanes proceeds in *E*-selective manner when we use HMPA as the co-solvent.^[18] When ethyl carbonochloridate or diphenyl dicarbonate was used, 1-carbonate vinylsilane was also obtained in good yields.

$R^1 =$	5a $R^2 = Ph$	88%
$R^1 =$	5b $R^2 = Ph$	80%
$R^1 =$	5c $R^2 = Ph$	86%
$R^1 =$	5d $R^2 = Ph$	81%
$R^1 =$	5e $R^2 = Ph$	87%
$R^1 =$	5f $R^2 = Ph$	87%
$R^1 =$	5h $R^2 = CH_3$	87%
$R^1 =$	5i $R^2 = Ph$	87%
$R^1 =$	5j $R^2 = CH_3$	60%
$R^1 =$	5k $R^2 = CH_3$	72%
$R^1 =$	5l $R^2 = EtO$	82%
$R^1 =$	5n $R^2 = PhO$	78%

Scheme 3–8. Synthesis of vinylsilanes with acylsilanes and organobromide

(1-Trimethylsilyl)ethenyl benzoate (**5g**) was easily obtained in 75% yield by treatment of ethenyl benzoate and trimethylsilylchloride in the presence of LDA (Scheme 3–9).^[19]

Scheme 3–9. Synthesis of vinylsilanes with ethenyl benzoate and trimethylsilylchloride

A two-step synthesis produced (*E*)-1-dimethyl(phenyl)silyl-4-phenylbut-1-ene (**5o**) in overall yield of 37% (Scheme 3–10).^{[20] [21]}

Scheme 3–10. Synthesis of (*E*)-1-dimethyl(phenyl)silyl-4-phenylbut-1-ene

Catalyst CuI was used for the reaction between benzyl bromide and ethynyltrimethylsilane, which gave 1-benzyl-4-(trimethylsilyl)-1H-1, 2, 3-triazole amine (**5q**) in 75% yield (Scheme 3–11).^[22]

Scheme 3–11. Synthesis of 1-benzyl-4-(trimethylsilyl)-1H-1, 2, 3-triazole amine

1-Benzofuran-2-yl-trimethylsilane (**5p**) was prepared from 1-benzofuran in 92% yield by adding *s*-BuLi and TMSCl in THF solution at -78 °C (Scheme 3–12).^[23]

Scheme 3–12. Synthesis of 1-benzofuran-2-yl-trimethylsilane

After the synthesis of various vinylsilanes, a wide range of additives were investigated as shown in Table 3–1. Halocarbonyl compounds could give (3*Z*, 5*Z*)-5-(benzoyloxy)-1,8-diphenylocta-3,5-dien-4-yl benzoate (**6a**) (Entries 1–4), but yields were not satisfactory. Only α -bromoacetophenone gave a moderate yield of the homocoupling product (Entry 1). Even though 2-chloro-1,2-diphenyl ethanone was known as a very efficient oxidant for Pd-catalyzed oxidative homocoupling reactions, it is not suitable for the Rh-catalyzed oxidative homocoupling reaction, giving the homocoupling product in 28% yield (Entry 3). As mentioned in the introduction, 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO) is an efficient oxidant for the homocoupling reaction of boronic acids but is not suitable for homocoupling reaction of organosilicon reagents (Entry 5). 2,3,5,6-Tetrachloro-1,4-benzoquinone(chloranil) would give the 1,3-diene in 48% yield (Entry 6). When copper diacetate, inorganic additive, was used, the reaction did not take place. At last, we found hexachloropropan-2-one could give the **6a** in 92% yield (Entry 9).

Table 3–1. Additives effect on oxidative homocoupling reactions^a

Entry	Additives ^a	Time (h)	Products % ^b	
			6a	7
1 ^c	(3)	1.5	50	9
2 ^c	(3)	10	21	22
3	(3)	5	28	26
4	(3)	12	trace	50
5	TEMPO ^d (3)	5	5	-

6	chloranil ^e (3)	5	48	4
7	Cu(OAc) ₂ (3)	5	-	-
8	(3)	1.5	43	24
9	(3)	1.5	92	<8
10	(2)	7.5	67	11
11	(1.1)	7.5	64	12

^a refers to the molar amount of the additives

^b Isolated yield using PTLC

^c Benzophenone was obtained as coproduct

^d 2,2,6,6-tetramethylpiperidine-N-oxyl

^e 2,3,5,6-tetrachloro-1,4-benzoquinone

It was shown that 3 equiv of hexachloropropan-2-one gave the best yield for oxidative homocoupling reactions. When the amount of the hexachloropropan-2-one was reduced to 2 equiv or 1.1 equiv, the yield was reduced to 67%, 64% respectively (Entries 10, 11). Herein, 3 equiv hexachloropropan-2-one is necessary to fulfill double transmetalations.

Next, the influence of various solvents on the reaction was studied (Table 3–2). The use of hydrocarbon made the reaction slower and gave an inferior yield (Entry 1). Aromatic solvents, such as benzene, toluene, and chlorobenzene, gave the homocoupling product in high yield (Entries 2, 4, and 6). When ether-type solvents such as THF and 1,4-dioxane were used, the yield decreased significantly due to some undetermined side reactions or deactivation of the catalyst while only dibutyl ether gave a modest yield (63%) (Entries 8–10). Among the different solvents, toluene gave the best yield at 80 °C (Entries 3–5). With a lower temperature (60 °C), longer reaction time for cross-coupling to consume

vinylsilane was required, while higher temperature (100 °C) might cause deactivation of the catalyst.

Table 3–2. Solvent effect on oxidative homocoupling of vinylsilanes

Entry	Solvent	Temp. / °C ^b	Time / h	6a / % ^c	7 / % ^c	5a / % ^d
1	Heptane	80	5	9	-	21
2	Benzene	80	1.5	95	<5	-
3	Toluene	60	8	34	5	22
4	Toluene	80	1.5	92	<8	-
5	Toluene	100	19	26	-	25
6	Chlorobenzene	80	5	56	-	11
7	1,2-Dichloroethane	80	30	16	39	-
8	THF	80	5	trace	36	-
9	1,4-Dioxane	80	17	-	-	90
10	Dibutyl ether	80	10	63	10	-

^a Molar ration: Vinylsilane **5a**: [RhCl(CO)₂]₂: Cl₃CCOCCl₃ = 1 : 0.05 : 3.

^b Oil bath temperature. ^c Isolated yield. ^d Recovery of **5a**.

The structure of (3*Z*, 5*Z*)-5-(benzoyloxy)-1,8-diphenylocta-3,5-dien-4-yl benzoate (**6a**) was confirmed by X-ray chromatography (Figure 3–1).

Figure 3–1. ORTEP structure of 1,3-diene-2,3-diyl diester **6a**

The proposed mechanism is shown in Scheme 3–13, transmetalation between rhodium(I) complex and vinylsilane **5** would form vinylrhodium(I) complex **3I**, followed by oxidative addition of hexachloropropan-2-one to afford vinylrhodium(III) complex **3II**. Subsequently, a second transmetalation between the vinylrhodium(III) intermediate **3II** and vinylsilane **5** would occur to generate divinylrhodium(III) complex **3III**. To complete the catalytic cycle, reductive elimination of divinylrhodium(III) complex would give the desired homocoupling product.

Scheme 3-13. Speculative mechanism for oxidative homocoupling of vinylsilanes

Under the optimal reaction conditions, the generality and scope of oxidative homocoupling reaction were examined (Table 3-3). The current catalytic system tolerates many functional groups, such as chloride, alkene and acetyl groups (Entries 6, 10, 11). All of the functionalized vinylsilanes gave the homocoupling product in good yields. However when (*E*)-5-phenyl-1-(trimethylsilyl)pent-1-en-4-ynyl benzoate (**5f**) was subjected to this reaction, **6f** was obtained in only 22% yield because of polymerization during heating. Both the small sized trimethylsilyl vinylsilane and large sized dimethyl(phenyl)vinylsilane provided the homocoupling product **6a** in 90%, 72% yield (Entries 1, 2). Meanwhile, the reaction of 2-unsubstituted vinylsilane **5g** was not compatible with this methodology due to the poor thermal instability of the product under the reaction conditions (Entry 8).

The substrates containing benzoyloxy group on 1 position give a moderate to excellent yield. And the structure of acyloxy group on 1-position of vinyl group did not show remarkable influence (Entries 9-12). Vinylsilanes **5l** and **5n** which have a carbonate

group are applied to synthesize 1,3-diene-2,3-diyl dicarbonate **6l** and **6n** in moderate yields (Entries 13, 15). Both alkyl and aryl groups on the 2-position of the vinylsilane did not affect the yield of homocoupling product (Entries 1, 3). (2-Phenylvinyl)silane gave the corresponding desired products (1Z, 3Z)-3-(benzoyloxy)-1, 4-diphenylbuta-1, 3-dien-2-yl benzoate (**6b**) in good yield (Entry 3). Unfortunately, simple (2-alkylvinyl)silane **5o** did not give homocoupling product at all (Entry 16). Thus, the acyloxy functionality is essential for this reaction. It may be suggested that the ester and carbonate moieties can coordinate to the rhodium center which can facilitate the second transmetalation. Heterocyclic vinylsilanes **5p** and **5q** were also subjected to the reaction and yielded 2,2'-bibenzofuran (**6p**) and 4,4'-bitriazole (**6q**) although the yields were not satisfactory (Entries 17, 18). But both 2,2'-bibenzofuran (**6p**) and 4,4'-bitriazole (**6q**) have interesting structures which may be used for ligands in catalytic reactions. In summary, 1,3-diene-2,3-diyl diesters can be synthesized through the oxidative homocoupling of (1-acyloxyvinyl)silanes which is difficult to be done by conventional methods.

Table 3–3. Rh-catalyzed homocoupling of vinylsilanes

$ \begin{array}{ccc} \begin{array}{c} \text{R}^2 \\ \\ \text{R}^1\text{---CH=CH---SiMe}_3 \\ \mathbf{5} \end{array} & \xrightarrow[\text{Toluene, 80 }^\circ\text{C, Time}]{\begin{array}{c} 5 \text{ mol\% } [\text{RhCl}(\text{CO})_2]_2 \\ \text{CCl}_3\text{COCCl}_3 (3 \text{ eq}) \end{array}} & \begin{array}{c} \text{R}^2 \\ \\ \text{R}^1\text{---CH=CH---CH=CH---R}^1 \\ \\ \text{R}^2 \\ \mathbf{6} \end{array} \end{array} $				
Entry	Vinylsilane	Time / h	Diene	Yield / % ^b
1	$ \begin{array}{c} \text{OCOPh} \\ \\ \text{Ph(CH}_2)_2\text{---CH=CH---SiMe}_3 \\ \mathbf{5a} \end{array} $	1.5	$ \begin{array}{c} \text{OCOPh} \\ \\ (\text{Ph(CH}_2)_2\text{---CH=CH})_2 \\ \mathbf{6a} \end{array} $	92

Continued

2	1a	5	6a	72
3	5b	9	6b	90
4	5c	7	6c	76
5	5d	7	6d	74
6	5e	5	6e	70
7	5f	7	6f	22
8	5g	24	6g	0
9	5h	5	6h	74
10	5i	5	6i	78
11	5j	10	6j	72
12	5k	20	6k	45

Continued

13		5		55
	5l		6l	
14		8		67
	5m		6m	
15		16		51
	5n		6n	
16		5		0
	5o		6o	
17		24		18
	5p		6p	
18		24		21
	5q		6q	

The structure of [(*IZ*,3*Z*)-2,3-bis[(ethoxycarbonyl)oxy]-4-phenylbuta-1,3-dien-1-yl]benzene (**6m**) was confirmed by X-ray chromatography (Figure 3–2).

Figure 3–2 ORTEP structure of 1,3-diene-2,3-diyl diethyl dicarbonate

3.3 Conversion of 1,3-Diene-2,3-Diyl Diesters to α -Diketone and its Mono-Protected Forms

Since vinyl esters are a masked form of carbonyl compounds, the homocoupling product, 1,3-diene-2,3-diyl diesters, are considered as a doubly masked form of α -diketones, which is a useful synthetic intermediate to prepare heterocyclic compounds. So we tried the conversion of the product, 1,3-diene-2,3-diyl diesters to α -diketones.^[24] The substrates **6a**, **6h** and **6k** were readily converted to 5,5-dimethoxy-1,8-diphenyloctan-4-one (**8a**), 3, 3-dimethoxy-1,4-diphenylbutan-2-one (**8b**) as shown in Table 3–4. These α,α -dimethoxy ketones were readily transformed to 1,8-diphenyloctane-4,5-dione (**9a**), 1,4-diphenylbutane-2,3-dione (**9b**) in a 1:10 mixture of trifluoroacetic acid–dichloromethane solution. This conversion method is also applicable to 1,3-diene-2,3-diyl dicarbonates as can be seen from substrate **6l**, α,α -dimethoxy ketone **8a** was obtained in moderate yield. The α,α -dimethoxy ketone **8a** can be further converted to α -diketone **9a** in 70% yield. Thus, using the rhodium-catalyzed homocoupling, the synthetic method to obtain symmetrical α,α -diketone and its mono- as well as doubly masked forms is available.

Table 3–4. Conversion 1,3-dienes to α,α -dimethoxy ketones and α -diketones

Entry	Diene (R, R')	α,α -Dialkoxy ketone	α -Diketone
	 6a	 8a 87%	 9a 70%
	 6h	 8a 72%	 9a 70%
	 6l	 8a 70%	 9a 70%
	 6k	 8b 67%	 9b 90%

The mechanism for forming α,α -dimethoxy ketones is described in Scheme 3–14: First, nucleophilic addition elimination occurs to give **3IV**, followed by protonation, then nucleophilic addition occurs again to the carbonyl group to give **3VI**. After this, neighbouring group assisted intramolecular nucleophilic addition of **3VII** furnishes **3VIII**. The dioxolane ring opening with protonation gives α -methoxyl- α -benzoyloxy ketone **3IX**, followed by substitution of the benzoyloxy group by methoxy group to give the α,α -dimethoxy ketone.

Scheme 3–14. Proposed mechanism for conversion 1,3-dienes to α,α -dimethoxy ketones

3.4 Conclusion

In conclusion, the Rh-catalyzed oxidative homocoupling reaction of (1-acyloxyvinyl)silane using hexachloropropan-2-one as an oxidant has been developed. Many functional groups were tolerated in such reactions. The homocoupling product 1,3-diene-2,3-diyl diester was obtained, which would be difficult to achieve by other methods. These acyloxy- or alkoxy-substituted dienes are attractive tools especially for the synthesis of cyclic compounds *via* the Diels-Alder reaction.

Furthermore, the 1,3-diene-2,3-diyl diesters can be converted to α -diketones and α,α -dimethoxy ketones. The α,α -dimethoxy ketones can be regarded as regioselectively-masked α -diketones at each of the carbonyl groups.

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Chapter IV Rhodium-Catalyzed Cross-Coupling

Reaction with Acylsilanes and Acid Anhydrides

1. Introduction

Transition metal-catalyzed cross-coupling reaction is one of the most powerful tools to prepare a variety of ketones. Numerous publications reported the synthesis of ketones from carboxylic acid derivatives or carbon monoxide as the carbonyl source in a catalytic manner. Majority of the reports involve the acylation of organometal with organo halides (Scheme 4–1, A) ^[1] or acyl donors (Scheme 4–1, B).^[2] Till now, there are only a few of reports on the cross-coupling of acyl anion equivalents with electrophiles to generate ketones (Scheme 4–1, C). ^[3]

Scheme 4–1. Cross-coupling approaches to ketone synthesis

In 1999, Korolev reported the phosphine-free palladium-catalyzed acylation of arylboronic acids with acyl chlorides under mild reaction conditions (Scheme 4–2).^[4]

Scheme 4-2. Cross-coupling of arylboronic acids with acyl chlorides

Recently, Liebeskind *et al.* described the copper-catalyzed coupling of a thiol ester and a boronic acid (Scheme 4-3) to form a ketone.^[5] In this reaction, the key is the requirement for a functional group positioned *ortho* but not *para* to the *s*-pendant linkage.

Scheme 4-3. Aerobic coupling of thiol esters and boronic acids

In 1992, Hiyama *et al.* reported palladium-catalyzed carbonylative cross-coupling reaction of organofluorosilanes in the presence of an atmospheric pressure of carbon monoxide (Scheme 4-4).^[6] Reaction conditions could be found that suppress side reactions such as competitive direct coupling and simple carboxylation of organic halides. Various functionalized groups are tolerated in this reaction system.

Scheme 4-4. Pd-catalyzed carbonylative coupling of arylsilanes in the presence of CO

In 2011, Jafarpour reported a versatile method for the synthesis diaryl ketones using iodoarenes and boronic acids in the presence of Mo(CO)_6 (Scheme 4-5).^[7] The method provides an efficient route for the synthesis of ketones without use of high pressure carbon monoxide.

Scheme 4-5. Carbonylative coupling of iodobenzenes and phenylboronic acids.

A general reaction by using organometallic acyl compound to form ketones has attracted the attention of chemists. In 1998, Taguchi *et al.* described the Pd-catalyzed reaction of nonanoylzirconocene chloride with organic halides (Scheme 4-6).^[3b] However, this reaction gave acylation products as a mixture of regioisomers and the yield was low. Furthermore, acylzirconocenes are difficult to handle in the air.

Scheme 4-6. Pd-catalyzed reaction of nonanoylzirconocene chloride with aryl iodide.

In 2002, Tsuji *et al.* reported the palladium-catalyzed acylation of acylstannanes with allyltrifluoroacetates (Scheme 4-7).^[3a] Although the reaction can afford unsaturated ketone without the isomerization, acylstannanes are very toxic reagents.

Scheme 4-7. Acylation of allylic trifluoroacetates with acylstannanes

Among organometallic acyl anion equivalents, acylsilanes are stable in air and are isolable compounds with a high functional group tolerance. More recently, Schmink *et al.* synthesized diaryl ketones via palladium-catalyzed cross-coupling of acylsilanes (Scheme 4-8).^[8] This reaction is a novel method to prepare ketones by using acylsilane and aryl halide. However, the acylation is limited to arylacylsilanes.

Scheme 4-8. Palladium-catalyzed cross-coupling reaction of acylsilane with aryl bromide

Thus, more attention is needed to expand the generality of the application of acylsilanes in catalytic acylation reactions. Herein, the acylation of acylsilanes with acid anhydrides is discussed.

Previously, the author's group reported that rhodium(I)-catalyzed desilylative cyclization of 5-alkynoylsilanes (Scheme 4-9). In the presence of acetic acid and a catalytic amount of $[\text{RhCl}(\text{CO}_2)]_2$, 5-alkynoylsilanes were converted into α -alkylidenecyclopentanone

derivatives. The reaction proceeds with a simple acylsilane having a dimethylphenylsilyl group, even without any functionalization on the silicon atom nor addition of expensive activation reagents such as fluoride salts, which play a crucial significant role in conventional palladium-catalyzed coupling reaction of organosilicon compounds.

Scheme 4-9. Rhodium-catalyzed acylation of alkyne with acylsilanes **4f**

This simple methodology is attributed to the unique catalytic activity of $[\text{RhCl}(\text{CO}_2)]_2$ as discussed in Chapter I. The initial finding promoted us to further investigate Rh(I)-catalyzed reaction of alkynoylsilanes. The focus of this chapter will be the use of various anhydrides as the coupling partner. Our initial interest was on the double acylation on the alkyne part of alkynoylsilane **4f** which is possible if intermediate **4III** could react with an acid anhydride (Scheme 4-10).

Scheme 4-10. Rh-catalyzed carboacylation of internal alkyne with 5-alkynyl-acylsilane and carboxylic acid anhydride

4.2 Results and Discussion

First, alkynoylsilane **4f** was treated with various acid anhydrides in the presence of 5 mol% $[\text{RhCl}(\text{CO})_2]_2$, and the results are summarized in Table 4–1. When the reaction was performed in the presence of acetic anhydride, three cyclopentanes were obtained; double acylation product **11a** (5%), decarbonylative acylmethylation product **12a** (66%), and acylhydrogenation product **10a** (6%) (Entry 1). The reaction with alkyl acid anhydride bearing a β -hydrogen revealed that the yields of acylalkylation products decreased while that of acylhydrogenation product increased (Entries 2–4). When the reactions were performed with benzoic anhydride or cinnamic anhydride (Entries 5 and 6), decarbonylative acylcarbonylation products **12e** or **12f** were obtained in good yields.

Table 4–1 Rh-Catalyzed Carboacylation of Alkynoylsilane **4f** with Acid anhydride.^a

Entry	$(\text{RCO})_2\text{O}$	Time / h	Product		Yield / %
			11	12	10
1	$(\text{CH}_3\text{CO})_2\text{O}$ 13a	12	5 11a	66 12a	6 10a

2	(C ₂ H ₅ CO) ₂ O 13b	32	4 11b	48 12b	30 10b
3	(ⁱ C ₃ H ₇ CO) ₂ O 13c	15	8 11c	-	66 10c
4	(^t C ₄ H ₉ CO) ₂ O 13d	32	-	-	47 10d
5	(PhCO) ₂ O 13e	24	-	76 12e	15 10e
6	(Ph-CH=CH-CO) ₂ O 13f	17	-	71 12f	-

^a The reaction was conducted by using the reagents in the molar ratio,

4f : [RhCl(CO)₂]₂ : (RCO)₂O = 1 : 0.05 : 3

The formation of three kinds of cyclopentones **11b**, **12b**, **10b** is described as follow (Scheme 4–11): the (2-acylvinyl)rhodium(I) complex **4III** was considered as an intermediate, oxidative addition of propionic acid to **4III** gives the acylvinylrhodium(III) complex **4III**¹, which provides double acylation product **11b** *via* reductive elimination. Decarbonylation of **4III**¹ gives the alkyl(vinyl)rhodium(III) complex **4III**², leading to acylcarbonation product **12b**. From the acylrhodium(III) hydride **4III**³ which is generated by β -elimination from **4III**², acylhydrogenation product **10b** is formed via reductive elimination.

Scheme 4–11. Proposed mechanism for double acylation of alkynoylsilanes and anhydrides.

In this reaction, the alkynyl group of **4f** is believed to be crucial for the coupling reaction because it can coordinate to the rhodium center to facilitate the transmetalation of the silyl group with the rhodium(I) complexes. It remains a challenge to activate simple acylsilane without any pre-coordination. For exploratory studies, 4-phenyl-1-(trimethylsilyl)-butan-1-one (**4a**) and benzoic anhydride were chosen and the reaction was carried out in toluene solution at a temperature of 100 °C. 1,4-Diphenylbutan-1-one (**14ae**) was obtained in 10% yield (Entry 1). Table 4–2 shows that when the concentration of the reaction system was increased to 1 M, the yield was improved dramatically to 82% after 36 hours (Entry 3). The yield decreased to 45% at a lower temperature of 100 °C (Entry 2). While the ketone **14ae** was obtained in 54% yield if the reaction time was shortened to 19 h (Entry 4).

Table 4–2. Optimization of cross-coupling of acylsilanes with benzoic anhydrides

$ \begin{array}{ccc} \text{Ph}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{C}(=\text{O})\text{SiMe}_3 & \xrightarrow[\text{Toluene, Temp., Time}]{\begin{array}{c} 5 \text{ mol\% } [\text{RhCl}(\text{CO})_2]_2 \\ (\text{PhCO})_2\text{O (3 eq.)} \end{array}} & \text{Ph}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{C}(=\text{O})\text{Ph} \\ \mathbf{4a} & & \mathbf{14ae} \end{array} $					
Entry	Temp.(°C)	Time(h)	Con. (M/L)	Yield of 14ae %	Recovery of 4a %
1	100	36	0.1	10	78
2	100	36	1	45	43
3	110	36	1	82	-
4	110	19	1	54	32

With the optimized reaction conditions at hand, the scope and generality of the cross-coupling reaction were investigated by screening various acid anhydrides with 4-phenyl-1-(trimethylsilyl)butan-1-one **4a** (Table 4–3). Non-substituted benzoic anhydride yielded 1,4-diphenylbutan-1-one (**14ae**) in 82% yield and (2*Z*)-1-oxo-1,5-diphenylpent-2-en-2-yl benzoate (**15ae**) in 15% yield (Entry 1). The carboxylic acid anhydride with an electro-donating methyl group at the para-position gave the product in totally 83% yield (Entry 2). The yield decreased dramatically when an electro-withdrawing group chloro or nitro group was introduced at the para-position which gave ketone in 45% and 30% yield respectively (Entries 3, 4). The substituents introduced at the meta-position on the arene appeared to have a similar trend as the substituents at the para-position (Entries 5–9). A cyano-substituent at the meta-position of benzoic anhydride gave a very low yield. This may due to strong coordination of the cyano group to rhodium center (Entry 9). Alkenyl acid anhydrides generally gave low yields, which are exemplified by cinnamic anhydride and (*E*)-but-2-enoic anhydride, providing the acylation products in 35% and 31% respectively (Entries 10, 11).

Table 4–3. Scope and limitation of 4-phenyl-1-(trimethylsilyl)butan-1-one with aromatic acid anhydrides

Entry	(RCO) ₂ O	Yield of 14 / %	Yield of 15 / %
1	<p>13e</p>	82% 14ae	15% 15ae
2	<p>13f</p>	72% 14af	11% 15af
3 ^a	<p>13g</p>	45% 14ag	-
4 ^b	<p>13h</p>	30% 14ah	-
5	<p>13i</p>	64% 14ai	14% 15ai

Continued

6		71% 14aj	8% 15aj
7		64% 14ak	-
8		52% 14al	-
9 ^c		4% 14am	-
10		35% 14an	-
11		32% 14ao	-

^a recovery of SM (17%), ^b recovery of SM (40%), ^c recovery of SM (72%).

To explore the scope of acylsilanes, cross-coupling reactions of various acylsilanes **4a–4e** with benzoic anhydrides were examined (Table 4–4). 1-(Trimethylsilyl)-heptan-1-one (**4c**) as well as 1-(trimethylsilyl)pentan-1-one (**4d**) reacted smoothly with benzoic anhydride to afford **14ce**, **14de** in excellent yields (Entries 3, 4). Chlorinated acylsilane **4e** worked well in the reaction system, giving 7-chloro-1-phenylheptan-1-one (**14ee**) in 84% yield (Entry 5). 2-Phenyl-1-(trimethylsilyl)-ethanone (**4b**) with benzoic anhydride gave ketone **14be** in a lower yield (Entry 2).

Table 4–4. Rhodium(I)-catalyzed cross-coupling of acylsilane

Entry	R	Yield of 14 %	Yield of 15 %
1		82% 14ae	15 15ae
2		76% 14be	4
3		87% 14ce	-
4		83% 14de	-
5		84% 14ee	-

This methodology can also be applied to primary alkyl carboxylic acid anhydrides. However, an α,β -unsaturated ketone was obtained in place of monoketone. Cross-Coupling of acylsilanes with various carboxylic acid anhydrides are screened as summarized in Table 4–5. Acetic anhydride gave the product in excellent yield (Entry 1). Propionic anhydride gave a slightly lower yield of 60% (Entry 2). Whereas isovaleric and isobutyric anhydrides yielded 32% and 29% of the products **15ap**, **15ac** respectively due to the bulkiness (Entries 3, 4).

Table 4–5. Rh-catalyzed reaction of acylsilane with saturated anhydrides

$ \begin{array}{ccc} \text{R}^1\text{CH}_2\text{C}(=\text{O})\text{SiMe}_3 & \xrightarrow[\text{toluene, 110 } ^\circ\text{C, 36 h}]{5 \text{ mol\%}[\text{RhCl}(\text{CO})_2]_2, (\text{R}^2\text{CO})_2\text{O (3 eq)}} & \text{R}^1\text{CH}=\text{C}(\text{COCH}_2\text{R}^2)\text{OCOR}^2 \\ \mathbf{4} & & \mathbf{15} \end{array} $			
Entry	acylsilane	anhydride	product
1		$(\text{CH}_3\text{CO})_2\text{O}$ 13a	80% 15aa
2	4a	$(\text{CH}_3\text{CH}_2\text{CO})_2\text{O}$ 13b	60% 15ab
3	4a	$[(\text{CH}_3)_2\text{CHCH}_2\text{CO}]_2\text{O}$ 13p	32% 15ap
4	4a^a	$[(\text{CH}_3)_2\text{CHCO}]_2\text{O}$ 13c	29% 15ac
5		$(\text{CH}_3\text{CO})_2\text{O}$ 13a	67% 15ga
6		13a	68% 15ha
7		13a	74% 15ca

^a recovery of **4a**, 35%.

Next, three representative acylsilanes were investigated for the cross-coupling reactions (Entries 5–7). The results of three acylsilanes were similar. Each acylsilane afforded the corresponding product in good yield, and the alkene group is also tolerated in this reaction system, giving the α,β -unsaturated ketone in 68% yield.

Scheme 4–12. Proposed mechanism **I** for rhodium-catalyzed cross-coupling of acylsilanes with acid anhydrides

Scheme 4–13. Proposed mechanism **II** for rhodium-catalyzed cross-coupling of acylsilanes with acid anhydrides

Proposed mechanism **I** (Scheme 4–12) involves transmetalation of the acylsilane to Rh(I) center, then oxidative addition of benzoic anhydride to Rh(I) complex, forming Rh(III) intermediate **4V**. The Rh(III) complex **4V** may undergo two paths: one path is decarbonylation to release another Rh(III) intermediate **4VI**. Subsequent reductive elimination of Rh(III) intermediate **4VI** would furnish the mono-ketone (**Path a**). The other path is reductive elimination to form a diketone, which reacts with benzoic anhydride to give a vinylketone (**Path b**); for the mechanism **II** (Scheme 4–13)

consideration: transmetalation of a vinylsilane **4VII** and a Rh(I) complex occurs to form the vinylrhodium(I) **4VIII** complex, followed by oxidative addition to give the acylvinylRh(III) complex **4IX**, then two paths go through: **path c** goes through decarbonylation and reductive elimination to furnish a monoketone, **path d** goes through reductive elimination to give an α,β -unsaturated ketones.

To gain insight on the mechanism, the reaction was monitored by ^1H NMR by using toluene- d^8 as the solvent. We checked if ether α -diketone (mechanism **I**) or α -acyloxyvinylsilane (mechanism **II**) was observed, however, none of them was detected and only compounds detected were acylsilane **4a** and the product **15aa**. Thus, we could not get the clear evidence to elucidate the mechanism, however, we could confirm that α -diketone could converted to α -acyloxyvinylketone in the same reaction conditions. That is, when the 6-phenylhexane-2,3-dikone was treated with an acetic anhydride in the presence of rhodium catalyst, acyloxyketones was obtained in 62% yield (Scheme 4–14). We also confirmed that this conversion did not occur in the absence of the rhodium catalyst. The result consists with the mechanism **I**.

Scheme 4–14. The reaction of diketone with acetic anhydride under $[\text{RhCl}(\text{CO})_2]_2$

4.3 Conclusion

In summary, double acylation on the alkyne part of alkynoylsilane with acid anhydrides was achieved. Not only alkynoylsilanes, but also alkanoylsilanes could react with different anhydrides *via* transmetalation of rhodium(I) to alkanoylsilane. Monoketones

were obtained upon the treatment of acylsilanes with aromatic acid anhydrides, while, vinylketones were obtained using acylsilanes with aliphatic acid anhydrides. This finding provides an alternative methodology for metal exchange between organosilicon compounds and transition metal catalyst.

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Chapter V Rhodium-Catalyzed Cyclization of 4-Phenylbutanoylsilane via C–H activation

5.1. Introduction

The transition metal-catalyzed activation of C–H bonds is a powerful tool for generating carbon–carbon bonds. Rhodium catalysts seem to play a prominent role in C–H bond activation.^[1] However, the development of methods for the activation of C–H bonds is still a challenge in synthetic chemistry.

5.1.1. Intermolecular C–H Activation by Rhodium Catalyst

Since the pioneering work of Kim on the Rh-catalyzed chelation assisted C–H alkylation employing pyridine groups to direct functionalization.^[2] In 2004, Jun *et al.* demonstrated that the imine of aromatic ketones and its derivatives with functionalized alkenes could be efficiently ortho-alkylated under Rh-catalyzed conditions (Scheme 5–1). In addition, the reaction proceeds smoothly under mild conditions when $(\text{C}_6\text{H}_5)_4\text{BNa}$ was used as an additive.^[3] A new recyclable supported catalyst system for ortho-alkylation was reported by the same group in 2005. The reaction is performed in the presence of 2,4,6-triaminopyrimidine to serve as a H-bond donor to the barbiturate.^[4]

Scheme 5–1. Aromatic ketones and their derivatives with functionalized alkenes

In 2008, Yu and co-workers developed an efficient Rh-catalyzed chelation assisted C–H alkylation using acid chlorides as the coupling partners under phosphine-free condition (Scheme 5–2).^[5] Furthermore, PPh₃ was found to retard the reaction.

Scheme 5–2. C–H functionalization *via* decarbonylation

Recently, Bergman and Ellman applied the Rh(III)-catalyzed oxidative olefination strategy to oxime derivatives (Scheme 5–3).^[6] Interestingly, the system can be extended unactivated aliphatic alkenes.

Scheme 5–3. Rh(III)-catalyzed oxidative olefination strategy to oxime derivatives

Almost at the same time, an efficient oxidative dehydrogenative coupling reaction of N-methoxybenzamides was reported by Glorius *et al* (Scheme 5–4).^[7] Interestingly, the N–O bond as the internal oxidant converts Rh(I) into Rh(III) to complete the catalytic cycle.

Scheme 5–4. Rhodium-catalyzed olefination

Cheng *et al.* successfully reported that acetophenone will undergo ortho-alkenylation with diphenylacetylene using $[(\text{RhCp}^*\text{Cl}_2)_2]$ as catalyst (Scheme 5–5).^[8] The key to success was the use of AgSbF_6 as an additive. The role of AgSbF_6 is probably to remove the chloride ligands from the $[(\text{RhCp}^*\text{Cl}_2)_2]$ complex to generate a more active rhodium complex.

Scheme 5–5. Rhodium-catalyzed C–H activation and carbocyclization of aryl ketones with alkynes

Very recently, Glorius *et al.* reported the synthesis of indenols and fulvenes from aryl ketones derivatives and internal alkynes through rhodium-catalyzed C–H activation/carbocyclization (Scheme 5–6).^[9] Additionally, it was found that α or γ dehydration step will occur depending on the substrate disposition to give the different functionalized fulvene products.

Scheme 5–6. Endo-cyclic C–H activation strategies

5.1.2. Intramolecular C–H Activation by Rhodium Catalyst

In 2001, Bergman and Ellman developed an intramolecular annulations of alkenylsubstituted aromatic derivatives using Wilkinson's catalyst $[(\text{PPh}_3)_3\text{RhCl}]$

(Scheme 5–7).^[10] This reaction is successful with a wide range of substrates, tolerating different tether lengths, the incorporation of heteroatoms into the tether, and a number of alkene substitution patterns.

Scheme 5–7. Cyclization of aromatic imines using Wilkinson's catalyst

In 2007, Fu and co-workers reported the rhodium-catalyzed intramolecular hydroacylation of 4-alkynals which represents a versatile new catalytic method for the synthesis of cyclopentenones.^[11] Later, Fu *et al.* advanced the reaction when they found that Rh(I)/(Tol-BINAP)-catalyzed cyclization of 4-alkynals furnishes enantioenriched cyclobutanones and cyclopentenones (Scheme 5–8).^[12]

Scheme 5–8. Rhodium-catalyzed formation of cyclobutanones and cyclopentenones

In 2010, Takai and co-workers developed an interesting example of C–Si bond forming reaction via both Si–H and C–H bond activation using Wilkinson's catalyst [(PPh₃)₃RhCl] (Scheme 5–9). The reaction was proposed to proceed *via* an organorhodium(II) species as the key intermediate. In addition, the dehydrogenation reaction does not require oxidants, such as molecular oxygen.^[13]

Scheme 5–9. Rhodium-catalyzed synthesis of silafluorenes from biphenyl-hydrosilanes

5.2. Results and Discussion

Reaction of 4-phenyl-1-(trimethylsilyl)butan-1-one with 2-iodoacetic anhydride was carried out in the presence of $[\text{RhCl(CO)}_2]_2$ heated at $110\text{ }^\circ\text{C}$ in toluene solution for 24 h. Neither ketone nor α,β -unsaturated ketone was obtained. Only a small amount C–H activation product, 1, 2, 3, 4-tetrahydronaphthalen-1-one (**16**), was obtained in 21% yield (Scheme 5–10). C–H activation by Rh(I) complexes to aromatic C–H bonds is very interesting, meaningful, and environmental benign. Thus, C–H activation by using Rh(I) complexes is discussed.

Scheme 5–10. C–H activation of acylsilane using iodoacetic anhydride as an oxidant

To the best of our knowledge, there is no report on cross-coupling of acylsilanes with non-functionalized arenes. Thus, we decided to focus our attention on this C–H activation of acylsilane.

At the beginning, different oxidants were screened at $110\text{ }^\circ\text{C}$ in toluene solution (Table 5–1). The reaction proceeded well by using ethyl iodo-acetate as an oxidant and afforded the desired product in 41% yield (Entry 5). All the α -halo ketones were found to be effective

additives although the desired 3,4-dihydro-2H-naphthalen-1-one (**16**) was obtained in low yield (Entries 1, 2, 4). The reaction did not take place when an inorganic oxidant, silver carbonate, was employed as an additive, suggesting inorganic salts were not suitable for the C–H activation of acylsilane. Next, different solvents were tested. 1,4-Dioxane and heptane give trace amounts of products which were not obtained in DMF or CH₃CN. The temperature was tested in toluene. 150 °C was found to be the ideal temperature for the reaction system as it gave the best yield of 64%, compared to 110 °C and 120 °C (Entries 5,10,11).

Table 5–1. Optimization of the reaction conditions for C–H activation ^a

<div style="display: flex; align-items: center; justify-content: center;"> <div style="text-align: center;"> 1M/L 4a </div> <div style="text-align: center; margin: 0 20px;"> $\xrightarrow[\text{Solvent, Temp., 36 h}]{\begin{matrix} 5 \text{ mol\% } [\text{RhCl}(\text{CO})_2]_2 \\ \text{Oxidant (3 eq)} \end{matrix}}$ </div> <div style="text-align: center;"> 16 </div> </div>				
Entry	Oxidant	Temp. ^d / °C	Solvent	Product/ %
1	Cl ₃ CCOCCl ₃	110	Toluene	15
2	N-iodosuccinimide	110	Toluene	7
3 ^b	Ag ₂ CO ₃	110	Toluene	-
4	desyl chloride	110	Toluene	19%
5		110	Toluene	41
6		110	1,4-Dioxane	trace
7		110	Heptane	trace
8		110	DMF	-

Continued

9 ^c		110	CH ₃ CN	-
10		120	Toluene	55
11		150	Toluene	64

^a the reaction was performed in a sealed tube, ^b Recovery acylsilane **4a** in 85% yield, ^c recovery acylsilane **4a** in 80% yield, ^d oil bath temperature.

A possible mechanism is proposed as shown in Scheme 5–11. The first reasonable step is transmetalation of the acylsilane to the Rh(I) center, furnishing acylrhodium(I) complex **5I**, a subsequent intramolecular C–H bond insertion would provide intermediate **5II**, then reductive elimination would furnish the desired 3,4-dihydro-2H-naphthalen-1-one (**16**) and regenerate Rh(I) which is oxidized by ethyl 2-iodoacetate to form the Rh(III) complex **5III**. Since we have no solid evidence to support this mechanism, further mechanistic investigation will lead to a clear understanding of the C–H activation of acylsilane.

Scheme 5–11. Putative mechanism for intramolecular C–H activation

Next, the scope of acylsilane substrates was explored. In an initial study, treatment of 2-(2-methylphenyl)-1-(trimethylsilyl)ethan-1-one (**4g**) with 3 equiv ethyl iodoacetate at 150 °C did not give the desired 2-methyl-bicyclo[4.2.0]-octa-1,3,5-trien-7-one (Scheme 5–12). Studies of additional substrates and mechanistic studies are underway.

Scheme 5–12. C–H activation of acylsilanes

5.3. Conclusion

In summary, the rhodium-catalyzed cross-coupling of acylsilane and non-functionalized arene was developed. Ethyl 2-iodoacetate was found to be a suitable oxidant for this transformation. C–H activation of the acylsilane is only at an early stage, and further effort is required to complete this work. It is still a promising and powerful method to prepare the cyclic compound. Furthermore, it indicates a wide field for the application of acylsilanes.

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Chapter VI Summary

Transition metal-catalyzed coupling reactions of organometallic reagents are one of the most useful methods for the formation of carbon–carbon bond. Among various organometallic reagents, organotin and organoboron compounds have been widely used for the formation of carbon–carbon bonds due to their relative stability in water and good functional group compatibility. However, coupling reactions of organoboron compounds require addition of a stoichiometric amount of base to facilitate the transmetalation step. Organotin compounds suffer some drawbacks with their toxicity and high molecular weight.

Thus, synthetic chemists still need to study more practical organometallic reagents. Organosilicon compounds have attracted the attention of chemists due to their high stability in air and water. Recently, the coupling reactions of organosilicon compounds have been developed. However, a fluoride source is normally used for activating the C–Si bond during silicon-based coupling reaction.

As previous studies in the author's group on the cross-coupling reaction between vinylsilanes and anhydrides, it was discovered that transmetalation between vinylsilane and $[\text{RhCl}(\text{CO})_2]_2$ can proceed smoothly in the absence of a fluoride source (Scheme 6–1).

Scheme 6–1. Acylation of acetic anhydride to vinylsilane

In chapter II, the rhodium-catalyzed acylation of a vinylsilane with a carboxylic acid as an acyl donor was developed. This is because acid anhydride is generally prepared from corresponding carboxylic acid. Thus, it would be an improvement to the acylation by using *in situ* generated anhydride (Scheme 6–2). In this reaction, di-*tert*-butyl dicarbonate was used as an activator for generating anhydride which is considered to be the key step in this acylation.

Scheme 6–2. Acylation of vinylsilanes and carboxylic acids

In chapter III, the rhodium-catalyzed oxidative homocoupling was successfully developed by using (1-acyloxyvinyl)silanes (Scheme 6–3). It is an interesting method for the synthesis of 1,3-diene-2,3-diyl diesters which are difficult to be synthesized using other organometallic compounds because the corresponding (1-acyloxyvinyl)metals are not readily available.

Scheme 6–3. Oxidative homocoupling of (1-acyloxyvinyl)silane

For an application, 1,3-diene-2,3-diyl diesters were converted to α -diketones and α,α -dimethoxy ketones (Scheme 6–4). The α,α -dimethoxy ketone is regarded as regioselectively-masked α,α -diketone at each of the carbonyl groups.

Scheme 6–4. Conversion of a 1,3-diene to an α -diketone and an α,α -dimethoxy ketone

In chapter IV, The cross-coupling between alkynoylsilanes and various anhydrides was developed by using $[\text{RhCl}(\text{CO})_2]_2$ (Scheme 6–5). Acid anhydrides provided a double acylation to the alkyne part of the alkynoylsilane to give three cyclopentanes. The alkynyl group is considered to coordinate to rhodium center to facilitate transmetalation of alkynoylsilane to Rh(I) complex.

Scheme 6–5. Rh-catalyzed acylation between alkynoylsilane and acid anhydride

Furthermore, the cross-coupling reaction of alkynoylsilane was expanded to alkanoylsilanes by using a similar transmetalation. It is noteworthy that the monoketone was obtained when an aromatic anhydride was used, alternatively, diketone derivatives were obtained by using aliphatic anhydrides (Scheme 6–6).

Scheme 6–6. Rh-catalyzed acylation between alkylacylsilane and acid anhydride.

C–H activation of acylsilane was detected when the reaction of acylsilane and iodoacetic anhydride was prepared (Scheme 6–7). The product of C–H activation was obtained in high yield by employing ethyl 2-iodoacetate as an oxidant.

Scheme 6–7. C–H activation of acylsilane using ethyl 2-iodoacetate as an oxidant

The C–H activation of acylsilane is at an early stage. The further optimization is still underway to form 6-membered ring and further application is expected to form 5- or 7-membered rings.

On the whole, the author studied coupling reaction of vinyl- and acylsilanes. Transmetalation of silyl group to rhodium center is thought to be the key step in the

coupling reaction. This is a giant step in organic chemistry by employing tetraorganosilicon compound as coupling partner without fluoride source.

Experimental Section

7.1 General

^1H NMR (500, 400 and 300 MHz) spectra were recorded on Bruker AVANCE 500, 400 and 300 instruments in CDCl_3 . Spectra were calibrated using the residual ^1H chemical shift in CDCl_3 (7.26 ppm), which was used as internal reference standards. ^{13}C NMR (125, 100 and 75 MHz) spectra were recorded on Bruker AVANCE 500, 400 and 300 instruments in CDCl_3 . Spectra were calibrated using CDCl_3 (77.0 ppm) for ^{13}C NMR spectra. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = double of doublets, dt = double triplet, m = multiplet. Melting points were uncorrected. IR spectra were recorded on a Shimadzu IR Prestige-21 FT-IR Spectrometer. High-resolution mass spectra were obtained with a JEOL MS-700P mass spectrometer and a Finnigan MAT 95 XP mass spectrometer (Thermo Electron Corporation) and Q-ToF Premier. Flash column chromatography was performed using Merck silica gel 60 with distilled solvents, and preparative thin-layer chromatography (PTLC) was carried out using Wakogel B-5F. Dry tetrahydrofuran (THF) and toluene were taken from a solvent purification system (PS-400-5, Innovative Technology Inc.).

Tetracarbonyldichlorodirhodium $[\text{RhCl}(\text{CO})_2]_2$ was prepared according to a literature procedure¹ and purified *via* sublimation.

7.2 Rhodium-Catalyzed Acylation of vinylsilane with Carboxylic acid as an Acyl

Donor

(*E*)-1-dimethyl(phenyl)silyl-4-phenylbut-1-ene (**1a**)^[1]

To a round-bottom flask containing 200 mL of diethyl ether at -78 °C, was added 30 mL (39.0 mmol, 1.31 M in hexane) of *n*-BuLi. (*E*)-1-iodo-4-phenylbut-1-ene (10.0 g, 39.0 mmol) was rapidly added to the flask via cannula as a solution in 120 mL of diethyl ether. The solution was allowed to stir for 1 h before the addition of 6.5 mL of ClSiMe₂Ph (6.6 g, 39.0 mmol). After 1 h, the mixture was slowly warmed up to room temperature while stirring over 12 h. The reaction mixture was quenched with 200 mL of saturated NH₄Cl and extracted with diethyl ether (3 x 100 mL). The organic layer was washed with brine, dried with MgSO₄ and evaporated. The crude mixture was purified by column chromatography on silica gel (100% hexane) to give the product (6.3g, 61%) as a colorless oil.

Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 0.33 (6H, s), 2.48 (2H, dt, *J* = 7.6, 6.8 Hz), 2.76 (2H, t, *J* = 7.6 Hz), 5.81 (1H, d, *J* = 18.4 Hz), 6.18 (1H, dt, *J* = 18.4, 6.0 Hz), 7.23–7.17 (3H, m), 7.32–7.27 (2H, m), 7.38–7.35 (3H, m), 7.51–7.48 (2H, m); ¹³C NMR (100 MHz, CDCl₃) δ -2.5, 35.1, 38.5, 125.8, 127.7, 128.2, 128.3, 128.5, 128.8, 133.8, 139.1, 141.8, 148.1.

1-dimethyl(phenyl)silyl-4-phenyl-butan-1-one (0b)^[1-2]

To a solution of 1-(phenoxymethyl)benzotriazole (3.0 g, 13.3 mmol) in THF (100 mL) at -78 °C was added *n*-BuLi (1.6 M in hexane, 8.3 mL, 13.3 mmol) and the solution was stirred for 5 min at this temperature. Chlorodimethylphenylsilane (2.2 mL, 13.3 mmol) was added, and the mixture was stirred at this temperature for 5 min, adding a second portion of *n*-BuLi (1.6 M in hexane, 8.3 mL, 13.3 mmol) and the solution was stirred for 5 min. After addition of 3-phenylpropyl bromide (2.0 mL, 13.3 mmol), the solution was

kept at -78 °C for 5 min and allowed to warm to room temperature over 1 h. Then the solution was quenched with water and the organic layer was extracted with diethyl ether. The combined organic extracts were dried over magnesium sulphate, concentrated under reduced pressure, and the residue was dissolved in 40 mL of acetic acid and 10 mL of H₂O. The solution was heated at 80 °C for 0.5 h. After cooling, the solution was quenched with water and the organic layer extracted with diethyl ether, and the combined extracts were washed with brine and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica (Hexane: EtOAc = 50: 1) to afford the compound in 56% yield (2 steps).

Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 0.47 (6H, s), 1.78 (2H, tt, *J* = 7.8, 7.2 Hz), 2.49 (2H, t, *J* = 7.8 Hz), 2.59 (2H, t, *J* = 7.2 Hz), 7.05 (2H, d, *J* = 7.6 Hz), 7.15 (1H, t, *J* = 6.4 Hz), 7.23 (2H, t, *J* = 7.6 Hz), 7.42–7.36 (3H, m), 7.54–7.52 (2H, m); ¹³C NMR (100 MHz, CDCl₃) δ -4.8, 23.7, 35.0, 47.9, 125.8, 128.2, 128.3, 128.4, 129.9, 134.0, 134.4, 141.8, 246.1.

Preparation of (*E*)-1-dimethyl(phenyl)silyl-4-phenyl-but-1-enyl benzoate^[1] (**1b**)

To a solution of LiHMDS (1.0 M in THF, 8.2 mL, 8.2 mmol) in 30 mL of THF was added hexamethyl-phosphoric triamide (12.9 mL, 74.3 mmol) at -78 °C, and the solution was stirred for 5 min at this temperature. A solution of 1-dimethyl(phenyl)silyl-4-phenyl-butan-1-one (2.1 g, 7.4 mmol) in 8 mL of THF was added, and the mixture was stirred at this temperature for 2 h. After addition of benzoic anhydride (2.52 g, 11.1 mmol), the solution was kept at -78 °C for 5 min and warmed up to room temperature for an additional 1 h. Then the solution was quenched with saturated NH₄Cl solution and the organic layer was extracted with diethyl ether. The combined organic extracts were dried

over magnesium sulphate concentrated under reduced pressure, and the residue was purified by column chromatography on silica (Hexane: EtOAc = 50: 1) to furnish the product in 91% yield.

Yellowish oil; IR (neat): 3067, 3024, 2955, 2924, 1721, 1450, 1265 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.45 (6H, s), 2.44 (2H, q, $J = 7.2$ Hz), 2.70 (2H, t, $J = 7.2$ Hz), 5.62 (1H, t, $J = 7.2$ Hz), 7.28–7.12 (5H, m), 7.37–7.33 (3H, m), 7.44 (2H, t, $J = 7.8$ Hz), 7.59–7.55 (3H, m), 8.01 (2H, dd, $J = 8.1$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ -2.6, 27.9, 35.0, 125.9, 127.7, 128.3, 128.4, 128.5, 129.2, 129.8, 129.9, 132.9, 133.0, 134.1, 137.1, 141.5, 153.8, 164.7; HRMS ESI (m/z): found, 387.1789, calcd for $\text{C}_{25}\text{H}_{27}\text{O}_2\text{Si}$: $[\text{M}+\text{H}]^+$, 387.1780.

Synthesis of dimethylphenylsilylfuran (**1c**)^[3]

To a solution of furan (1.0 g, 14.7 mmol) in anhydrous diethyl ether (25 ml) was added *n*-BuLi (9.2 mL, 1.6 M in hexanes, 14.7 mmol) at 25 °C and the mixture was heated at reflux for 3 h. After cooling to 0 °C, trimethylsilyl chloride (0.9 mL, 14.0 mmol) was added dropwise and the resulting mixture stirred for 1 h at 25 °C before being quenched with water (20 mL). The layers were separated and the organic layer was washed with brine (30 mL) and dried (MgSO_4). Dimethylphenylsilylfuran (3.47 g, 24 %) was collected by careful distillation of the organic solution.

Colorless oil; IR (neat): 3068, 2958, 1427, 1249, 1203, 1114, 1004, 898, 812, 779 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.53 (6H, s), 6.38–6.39 (1H, m), 6.66 (1H, d, $J = 3.3$ Hz), 7.31–7.39 (3H, m), 7.53–7.57 (2H, m), 7.67 (1H, d, $J = 1.5$ Hz); ^{13}C NMR (75 MHz,

CDCl₃) δ -2.8, 109.4, 121.0, 127.8, 129.4, 133.9, 137.0, 147.1, 158.2; HRMS ESI (m/z): found, 203.2158, calcd for C₁₂H₁₅OSi: [M+H]⁺, 203.2155.

Preparation of cyclopentenyl dimethyl(phenyl)silane (**1d**)^[4]

To a stirred solution of sodium (0.72 g, 31.2 mmol) in 8.0 mL of ether, was treated with chlorodimethylphenylsilane (2.1 mL, 12.7 mmol). After stirring for 0.5 h, 1-chlorocyclopent-1-ene (1.0 g, 9.8 mmol) was added over a period of 15 min. The reaction mixture was stirred at 60 °C for 6 h, then cooled and filtered through celite. The combined filtrates were combined and washed with saturated NaHCO₃, water and brine, dried over MgSO₄, and concentrated in *vacuo*. The crude mixture was purified by flash column chromatography on silica gel (hexane: EtOAc = 5: 95) to afford the product in the 55% yield.

Colorless oil; ¹H NMR (300 MHz, CDCl₃) δ 0.36 (6H, s), 1.83 (2H, qn, J = 7.8 Hz), 2.43–2.37 (4H, m), 6.08 (1H, t, J = 1.8 Hz), 7.36–7.34 (3H, m), 7.53–7.50 (2H, m); ¹³C NMR (75 MHz, CDCl₃) δ -3.0, 24.1, 35.0, 36.0, 127.7, 128.8, 133.8, 138.8, 142.4, 142.6.

Preparation of *tert*-butyl 1*H*-indole-1-carboxylate (**0e**)^[5]

To a solution of indole (3.00 g; 25.6 mmol) and DMAP (0.32 g; 2.6 mmol) in 20 mL of CH₂Cl₂, was added a solution of Boc anhydride (6.15 g; 28.2 mmol) in 5 mL of CH₂Cl₂. After stirring at room temperature for 4 h, the reaction was quenched with 1.0 M HCl (25 mL). The organic layer was separated, dried over MgSO₄, filtered and concentrated. The

crude mixture was purified by flash column chromatography on silica gel (hexane: EtOAc = 2: 98) to afford the product in the quantitative yield.

Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 1.68 (9H, s), 6.57 (1H, dd, $J = 3.6, 0.8$ Hz), 7.23 (1H, td, $J = 7.6, 0.8$ Hz), 7.31 (1H, td, $J = 7.2, 1.2$ Hz), 7.56 (1H, d, $J = 7.2$ Hz), 7.60 (1H, d, $J = 3.6$ Hz), 8.15 (1H, d, $J = 8.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 28.2, 83.6, 107.2, 115.1, 120.9, 122.6, 124.1, 125.9, 130.5, 135.1, 149.8.

Preparation of *tert*-butyl 2-(trimethylsilyl)-1*H*-indole-1-carboxylate (**1e**)^[5]

To a solution of *tert*-butyl 1*H*-indole-1-carboxylate (3.0 g, 13.8 mmol) in 17 mL of THF, was added chlorotrimethylsilane (2.3 g, 20.7 mmol). The solution was cooled to 0 °C; freshly prepared LDA (2.0 M in THF, 10 mmol) was added over 0.5 h. After stirring for 1 h, the reaction mixture was quenched with 25 mL of water. The organic layer was separated, dried over MgSO_4 , filtered and concentrated. Flash chromatography on silica gel (hexane: EtOAc = 19: 1) affords the product in quantitative yield.

White solid; IR (neat): 3017, 1732, 1366, 1335 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.35 (9H, s), 1.72 (9H, s), 6.84 (1H, s), 7.19 (1H, t, $J = 7.6$ Hz), 7.27 (1H, t, $J = 8.0$ Hz), 7.54 (1H, d, $J = 7.6$ Hz), 7.99 (1H, d, $J = 8.4$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 0.001, 28.2, 83.8, 115.5, 119.2, 120.7, 122.3, 124.3, 131.0, 137.6, 142.2, 151.2; HRMS ESI (m/z): found, 290.1565, calcd for $\text{C}_{16}\text{H}_{24}\text{O}_2\text{NSi}$: $[\text{M}+\text{H}]^+$, 290.1576.

General procedure for rhodium-catalyzed one-pot synthesis of α,β -unsaturated ketone

To a flame dried round bottom flask, $[\text{RhCl}(\text{CO})_2]_2$ (5 mol%), vinylsilane (1 eq.), carboxylic acid (4 eq.) and di-tert-butyl-dicarbonate (3 eq.) were added in a solution of benzene (0.1 M). The reaction was stirred at 100 °C (oil bath temperature) ranging from 7 to 18 h. The crude was concentrated in *vacuo* and purified by plate thin-layer chromatography to afford the corresponding α,β -unsaturated ketone.

(2E)-1,5-diphenylpent-2-en-1-one (3aa)^[6]

Colorless oil, ^1H NMR (300 MHz, CDCl_3) δ 2.60–2.67 (2H, m), 2.82–2.87 (2H, m), 6.82 (1H, dd, $J = 1.2, 18$ Hz), 7.02–7.10 (1H, m), 7.19–7.24 (3H, m), 7.28–7.32 (2H, m), 7.42–7.44 (2H, m), 7.51–7.54 (1H, m), 7.87 (2H, d, $J = 6.9$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 34.5, 34.5, 126.2, 126.6, 128.4, 128.4, 128.5, 128.5, 132.6, 137.9, 140.8, 148.4, 190.9.

(2E)-1-(4-methoxyphenyl)-5-phenylpent-2-en-1-one (3ab)

Colorless oil; ^1H NMR (300 MHz, CDCl_3) δ 2.59–2.66 (2H, m), 2.82–2.87 (2H, m), 3.86 (3H, s), 6.86 (1H, d, $J = 1.2, 15$ Hz), 6.91–6.94 (2H, m), 7.03–7.08 (1H, m), 7.19–7.22 (3H, m), 7.25–7.30 (2H, m), 7.89 (2H, dd, $J = 1.8, 6$ Hz) ^{13}C NMR (75 MHz, CDCl_3) δ

34.5, 34.6, 55.5, 113.7, 126.1, 126.2, 128.4, 128.5, 130.7, 130.8, 140.9, 147.3, 163.3, 189.0. HRMS ESI (m/z): found, 267.1377, calcd for C₁₈H₁₉O₂: [M+H]⁺, 267.1385.

(2E)-1-(naphthalen-2-yl)-5-phenylpent-2-en-1-one (3ac)

Yellow oil; IR (neat) 3059, 3024, 2926, 1666, 1616, 1494, 1467, 1454, 1188 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 2.65–2.73 (2H, m), 2.86–2.91 (2H, m), 7.01 (1H, d, *J* = 15.6 Hz), 7.09–7.16 (1H, m), 7.22–7.25 (4H, m), 7.30–7.35 (2H, m), 7.54–7.60 (2H, m) 7.86–7.93 (2H, m), 7.97–8.00 (2H, m), 8.35 (1H, s); ¹³C NMR (75 MHz, CDCl₃) δ 34.5, 34.5, 124.5, 126.2, 126.6, 126.7, 127.8, 128.3, 128.5, 128.5, 129.4, 129.5, 130.0, 132.5, 135.2, 135.4, 140.8, 148.3, 190.6; HRMS ESI (m/z): found, 287.1437, calcd for C₂₁H₁₉O: [M+H]⁺, 257.0974.

6-[(2E)-5-phenylpent-2-enoyl]-2,3-dihydro-1H-inden-1-one (3ad)

Colorless oil; IR (neat) 3059, 3026, 2924, 1712, 1668, 1614, 1496, 1454, 1437, 1330, 1292, 1213, 1188 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 2.61–2.68 (2H, m), 2.74–2.78 (2H, m), 2.82–2.87 (2H, m), 2.96–2.98 (2H, m), 3.18–3.22 (2H, m), 6.91 (1H, d, *J* = 18 Hz), 7.06–7.16 (1H, m) 7.20–7.22 (3H, m), 7.26–7.33 (2H, m), 7.55–7.58 (1H, d, *J* = 9 Hz), 8.17 (1H, d, *J* = 6 Hz), 8.21 (1H, s); ¹³C NMR (75 MHz, CDCl₃) δ 25.9, 34.3, 34.5, 36.4, 123.7, 125.9, 126.2, 127.1, 128.3, 128.4, 134.4, 137.1, 137.2, 140.6, 149.1, 159.3, 189.4, 206.0; HRMS ESI (m/z): found, 291.1389, calcd for C₂₀H₂₀O₂: [M+H]⁺, 291.1385.

(4E)-7-phenylhepta-1,4-dien-3-one (3ae)^[7]

Colorless oil; ¹H NMR (300 MHz, CDCl₃) δ 2.54–2.61 (2H, m), 2.78–2.83 (2H, t, *J* = 9 Hz), 5.80 (1H, dd, *J* = 1.2, 12 Hz), 6.24 (1H, dd, *J* = 1.5, 15 Hz), 6.36 (1H, d, *J* = 15 Hz), 6.53–6.62 (1H, m), 6.91–7.01 (1H, dt, *J* = 6.6, 15.6 Hz), 7.17–7.22 (3H, m), 7.25–7.29 (2H, m); ¹³C NMR (75 MHz, CDCl₃) δ 34.3, 34.4, 126.2, 128.3, 128.4, 128.5, 128.6, 134.9, 140.6, 147.5, 189.7.

(3E)-6-phenylhex-3-en-2-one (3af)^[8]

Colorless oil; ¹H NMR (300 MHz, CDCl₃) δ 2.22 (3H, s), 2.51–2.59 (2H, m), 2.77–2.82 (2H, m), 6.09 (1H, dt, *J* = 1.2, 18 Hz), 6.81 (1H, dt, *J* = 6, 15 Hz), 7.17–7.23 (3H, m), 7.27–7.33 (1H, m); ¹³C NMR (75 MHz, CDCl₃) δ 26.9, 34.1, 34.4, 126.2, 128.3, 128.5, 131.7, 140.6, 147.5, 198.6.

(4E)-7-phenylhept-4-en-3-one (3ag)^[1]

Colorless oil; ¹H NMR (300 MHz, CDCl₃) δ 1.08 (3H, t, *J* = 6 Hz), 2.50–2.57 (4H, m), 2.75–2.80 (2H, m), 6.10 (1H, dt, *J* = 3, 17.1 Hz), 6.84 (1H, dt, *J* = 6, 15 Hz), 7.16–7.22 (3H, m), 7.25–7.31 (2H, m); ¹³C NMR (75 MHz, CDCl₃) δ 8.0, 33.2, 34.0, 34.4, 126.1, 128.2, 128.4, 130.4, 140.6, 145.5, 200.9.

(5E)-8-phenyloct-5-en-4-one (3ah)^[9]

Colorless oil; ¹H NMR (300 MHz, CDCl₃) δ 0.92 (3H, t, *J* = 9 Hz), 1.56–1.68 (2H, m), 2.46–2.57 (4H, m), 2.76–2.81 (2H, t, *J* = 3, 9 Hz), 6.10 (1H, dt, *J* = 1.5, 18 Hz), 6.79–6.89 (1H, dt, *J* = 9, 15 Hz), 7.16–7.27 (3H, m), 7.29–7.32 (2H, m); ¹³C NMR (75 MHz, CDCl₃) δ 13.7, 17.7, 34.1, 34.4, 42.0, 126.1, 128.3, 128.4, 130.8, 140.7, 145.7, 200.6.

(4E)-2-methyl-7-phenylhept-4-en-3-one (3ai)^[1]

Colorless oil; ¹H NMR (300 MHz, CDCl₃) δ 1.08 (6H, d, *J* = 6.9 Hz), 2.50–2.57 (2H, m), 2.74–2.83 (3H, m), 6.16 (1H, d, *J* = 18 Hz), 6.90 (1H, dt, *J* = 6.9, 18 Hz), 7.16–7.22 (3H, m), 7.26–7.31 (2H, m); ¹³C NMR (75 MHz, CDCl₃) δ 18.3, 34.1, 34.4, 38.4, 126.1, 128.3, 128.4, 128.8, 140.7, 145.7, 203.8.

(4E)-2,2-dimethyl-7-phenylhept-4-en-3-one (3aj)^[10]

Colorless oil; ¹H NMR (300 MHz, CDCl₃) δ 1.11 (9H, s), 2.48–2.56 (2H, m), 2.75–2.80 (2H, t, *J* = 9 Hz), 6.45 (1H, dt, *J* = 1.2, 15 Hz), 6.95 (1H, dt, *J* = 6, 15 Hz), 7.15–7.20 (3H, m), 7.25–7.30 (2H, m); ¹³C NMR (75 MHz, CDCl₃) δ 26.1, 34.2, 34.5, 42.8, 124.8, 126.1, 128.4, 128.4, 140.9, 146.0, 204.2.

(2E)-1-cyclopentyl-5-phenylpent-2-en-1-one (3ak)

Colorless oil; IR (neat) 3026, 2951, 2866, 1691, 1664, 1625, 1454 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.54–1.70 (5H, m), 1.73–1.80 (3H, m), 2.49–2.57 (2H, m), 2.76–2.81 (2H, t, $J = 9$ Hz), 3.02–3.07 (1H, m), 6.14 (1H, dt, $J = 1.5, 15.9$ Hz), 6.81–6.91 (1H, dt, $J = 6.9, 15.9$ Hz), 7.16–7.22 (3H, m), 7.26–7.32 (2H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 26.1, 26.1, 29.2, 29.2, 34.1, 34.5, 48.9, 126.1 (CH), 128.3, 128.4, 130.0, 140.8, 145.6, 202.6; HRMS ESI (m/z): found, 229.3413, calcd for $\text{C}_{16}\text{H}_{21}\text{O}$: $[\text{M}+\text{H}]^+$, 229.3409.

(2E)-1-cyclopropyl-5-phenylpent-2-en-1-one (3al)^[11]

Colorless oil; ^1H NMR (300 MHz, CDCl_3) δ 0.86–0.92 (2H, m), 1.04–1.09 (2H, m), 2.04–2.14 (1H, m), 2.52–2.59 (2H, m), 2.77–2.83 (2H, m), 6.24 (1H, dt, $J = 1.5, 18$ Hz), 6.92 (1H, $J = 6, 15$ Hz), 7.18–7.23 (3H, m), 7.25–7.32 (2H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 10.9, 18.6, 34.1, 34.4, 126.1, 128.3, 128.4, 130.7, 140.7, 145.4, 200.1.

(3E)-1-(4-methoxyphenyl)-6-phenylhex-3-en-2-one (3am)

Colorless oil; IR (neat) 3016, 2933, 2835, 1687, 1666, 1624, 1512, 1454, 1247, 1217, 1178 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 2.47–2.54 (2H, m), 2.72–2.77 (2H, m), 3.72

(2H, s), 3.78 (3H, s), 6.12 (1H, d, $J = 15$ Hz), 6.83–6.96 (3H, m), 7.08–7.16 (4H, m), 7.19–7.29 (3H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 34.1, 34.3, 46.7, 55.2, 114.1, 126.2, 126.4, 128.3, 128.5, 129.7, 130.4, 140.6, 146.9, 158.5, 197.7; HRMS ESI (m/z): found, 281.3738, calcd for $\text{C}_{19}\text{H}_{21}\text{O}_2$: $[\text{M}+\text{H}]^+$, 281.3729.

(3E)-1,1,6-triphenylhex-3-en-2-one (3an)

Colorless oil; IR (neat) 3068, 2958, 1635, 1427, 1253, 1118 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 2.44–2.51 (2H, m), 2.69–2.74 (2H, m), 5.26 (1H, s), 6.19 (1H, d, $J = 12$ Hz), 6.92–7.03 (1H, m), 7.08 (2H, d, $J = 6$ Hz), 7.18–7.27 (14H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 34.1, 34.3, 62.3, 126.1, 127.0, 128.3, 128.4, 128.6, 129.1, 129.7, 138.5, 140.6, 147.1, 197.3; HRMS ESI (m/z): found, 327.4452, calcd for $\text{C}_{24}\text{H}_{23}\text{O}$: $[\text{M}+\text{H}]^+$, 327.4447.

(2Z)-1-(naphthalen-2-yl)-1-oxo-5-phenylpent-2-en-2-yl benzoate (3bc)

Yellow oil; IR (neat) 3068, 2958, 1732, 1658, 1259, 1114, 1062, 1024 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 2.68–2.76 (2H, m), 2.82–2.87 (2H, m), 6.28 (1H, t, $J = 9$ Hz), 7.19–7.30 (6H, m), 7.46–7.54 (2H, m), 7.5–7.62 (3H, m), 7.84–7.91 (4H, m), 8.12–8.15 (2H, m), 8.29 (1H, s); ^{13}C NMR (75 MHz, CDCl_3) δ 27.9, 34.4, 125.3, 126.3, 126.7, 127.7, 128.2, 128.3, 128.5, 128.6, 129.3, 130.2, 130.8, 132.1, 132.9, 133.7, 134.0, 135.2, 140.5,

146.2, 164.3, 189.6; HRMS ESI (m/z): found, 407.2070, calcd for C₂₈H₂₃O₃: [M+H]⁺, 407.2067.

2-[(naphthalen-2-yl)carbonyl]furan (3cc)

Yellow oil; IR (neat) 3068, 2958, 1643, 1463, 1390, 1300 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 6.62–6.64 (1H, m), 7.30 (1H, d, *J* = 3 Hz), 7.56–7.63 (2H, m), 7.75 (1H, s), 7.89–8.05 (4H, m), 8.54 (1H, s); ¹³C NMR (75 MHz, CDCl₃) δ 112.2, 120.5, 125.2, 126.8, 127.8, 128.3, 129.4, 130.8, 132.4, 134.5, 135.3, 147.0, 152.5, 182.4; HRMS ESI (m/z): found, 223.0763, calcd for C₁₅H₁₁O₂: [M+H]⁺, 223.0759.

(cyclopent-1-en-1-yl)(naphthalen-2-yl)methanone (3dc)

Yellow oil; IR (neat) 3057, 2953, 1635, 1463, 1355, 1298, 1186, 1134, 1103 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.99–2.09 (2H, m), 2.62–2.69 (2H, m), 2.77–2.83 (2H, m), 6.58–6.61 (1H, m), 7.50–7.60 (2H, m), 7.81–7.94 (4H, m), 8.24 (1H, s); ¹³C NMR (75 MHz, CDCl₃) δ 22.9, 32.1, 34.4, 125.2, 126.6, 127.8, 127.8, 128.1, 129.2, 130.0., 132.4, 135.0, 136.2, 144.8, 146.7, 194.1; HRMS ESI (m/z): found, 223.1336, calcd for C₁₆H₁₅O: [M+H]⁺, 223.1335.

***tert*-butyl 2-[(naphthalen-2-yl)carbonyl]-1H-indole-1-carboxylate (3ec)**

Yellow oil; IR (neat) 3059, 3007, 1737, 1654, 1473, 1369, 1327, 1276, 1224, 1159 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.33 (9H, s), 6.97 (1H, s), 7.30–7.35 (1H, m), 7.45 (1H, t, $J = 1.20$ Hz), 7.50–7.60 (3H, m), 7.92 (3H, t, $J = 9$ Hz), 8.07 (1H, dd, $J = 1.5, 8.4$ Hz), 8.25 (1H, d, $J = 8.4$ Hz), 8.38 (1H, s); ^{13}C NMR (75 MHz, CDCl_3) δ 27.5, 84.9, 114.2, 115.2, 128.1, 123.5, 124.7, 126.6, 126.8, 127.8, 128.0, 128.5, 128.6, 129.6, 131.8, 132.4, 134.8, 135.7, 137.1, 137.5, 149.2, 187.7; HRMS ESI (m/z): found, 372.1609, calcd for $\text{C}_{24}\text{H}_{22}\text{NO}_3$: $[\text{M}+\text{H}]^+$, 372.1600.

7.3 Rhodium-Catalyzed Homocoupling of (1-Acyloxy-vinyl)silanes: Synthesis of 1,3-Diene-2,3-Diyl Diesters and Their Derivatives

4-phenyl-1-(trimethylsilyl) butan-1-one (4a) ^[1-2]

This compound was synthesized according to the same procedure as for **0b**.

Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 0.18 (9H, s), 1.86 (2H, tt, $J = 7.6, 7.6$ Hz), 2.58 (2H, t, $J = 7.6$ Hz), 2.62 (2H, t, $J = 7.2$ Hz), 7.15–7.20 (3H, m), 7.26–7.29 (2H, m); ^{13}C NMR (100 MHz, CDCl_3) δ -3.2, 23.7, 35.2, 47.5, 125.8, 128.3, 128.4, 141.8, 248.1.

2-phenyl-1-(trimethylsilyl)ethanone (4b) ^[1-2]

This compound was synthesized according to the same procedure as for **0b**.

Colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 0.09 (9H, s), 3.83 (2H, s), 7.10–7.12 (2H, m), 7.21–7.24 (1H, m); ^{13}C NMR (125 MHz, CDCl_3) δ -2.8, 55.5, 126.8, 128.6, 129.9, 133.1, 244.2.

1-(trimethylsilyl)heptan-1-one (4c)^[12]

This compound was synthesized according to the same procedure as for **0b**.

Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 0.19 (9H, s), 0.87 (3H, $J = 6.8$ Hz), 1.23–1.31 (6H, m), 1.49–1.52 (2H, m), 2.58 (2H, $J = 7.2$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ -3.14, 14.0, 22.1, 22.5, 29.0, 31.7, 48.6, 248.8.

1-(trimethylsilyl)pentan-1-one (4d)^[13]

This compound was synthesized according to the same procedure as for **0b**.

Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 0.19 (9H, s), 0.89 (3H, t, $J = 7.2$ Hz), 1.28 (2H, m), 1.49 (2H, tt, $J = 7.6, 7.6$ Hz), 2.59 (2H, t, $J = 7.6$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ -3.1, 13.9, 22.4, 24.3, 48.2, 248.8.

7-chloro-1-(trimethylsilyl)heptan-1-one(4e)

This compound was synthesized according to the same procedure as for **0b**.

Colorless oil; IR (neat): 2936, 2858, 1643, 1400, 1250, 845, 752, 648 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.19 (9H, s), 1.27 (2H, tt, $J = 7.6, 7.6$ Hz), 1.42 (2H, tt, $J = 7.6, 7.6$ Hz), 1.52 (2H, tt, $J = 7.2, 7.6$ Hz), 1.75 (2H, tt, $J = 6.8, 7.2$ Hz), 2.60 (2H, t, $J = 7.2$ Hz), 3.52 (2H, t, $J = 6.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ -3.2, 21.8, 26.7, 28.5, 32.4, 48.2, 248.4. HRMS ESI (m/z): found, 221.1134, calcd for: $[\text{M}+\text{H}]^+$, 221.1128.

6-phenyl-1-(trimethylsilyl)hex-5-yn-1-one (4f)

This compound was synthesized according to the same procedure as for **0b**.

Colorless oil; IR (neat); 2955, 2900, 1716, 1643, 1597, 1443, 1354, 1250, 1068, 845, 756, 690 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.22 (9H, s), 1.83 (2H, tt, $J = 7.2, 6.8$ Hz), 2.42 (2H, t, $J = 6.8$ Hz), 2.81 (2H, t, $J = 7.2$ Hz), 7.26–7.28 (3H, m), 7.37–7.40 (2H, m); ^{13}C NMR (100 MHz, CDCl_3) δ -3.2, 18.9, 21.1, 46.9, 81.3, 89.4, 123.8, 127.6, 128.2, 131.5, 247.8; HRMS ESI (m/z): found, 245.1370, calcd for: $[\text{M}+\text{H}]^+$, 245.1362.

2-(2-methylphenyl)-1-(trimethylsilyl)ethan-1-one (4g)

This compound was synthesized according to the same procedure as for **0b**.

Colorless oil; ^1H NMR (300 MHz, CDCl_3) δ 0.14 (9H, s), 2.17 (3H, s), 3.87 (2H, s), 7.03–7.06 (m, 1H), 7.13–7.18 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ -2.7, 20.0, 54.2, 126.2, 127.4, 130.6, 131.0, 132.6, 137.3, 244.3.

1-(trimethylsilyl)hept-6-en-1-one (4h)

This compound was synthesized according to the same procedure as for **0b**.

Colorless oil; IR (neat): 3078, 2936, 2858, 1717, 1643, 1439, 1404, 1250, 991, 910, 845, 752 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.19 (9H, s), 1.35 (2H, tt, $J = 7.6, 7.6$ Hz), 1.53 (2H, tt, $J = 7.6, 7.2$ Hz), 2.04 (2H, dt, $J = 7.2, 7.2$ Hz), 2.60 (2H, t, $J = 7.2$ Hz), 4.94 (1H, d, $J = 10$ Hz), 4.99 (1H, d, $J = 17.2$ Hz), 5.73–5.84 (1H, m); ^{13}C NMR (100 MHz, CDCl_3) δ -3.2, 21.6, 28.6, 33.6, 48.3, 114.5, 138.6, 248.2; HRMS ESI (m/z): found, 185.1336, calcd for: $[\text{M}+\text{H}]^+$, 185.1362.

6-hydroxy-1-(trimethylsilyl)hexan-1-one (4i)

This compound was synthesized according to the same procedure as for **0b**.

Colorless oil; IR (neat) 2945, 1730, 1714, 1215, 844, 756, 667 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.20 (9H, s), 1.29–1.36 (2H, m), 1.51–1.58 (4H, m), 1.61 (1H, s), 2.62 (2H, t, $J = 7.2$ Hz), 3.64 (2H, t, $J = 6.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ -3.2, 21.7, 25.4, 32.5, 48.3, 62.6, 248.6; HRMS ESI (m/z): found, 189.1312, calcd for $\text{C}_9\text{H}_{21}\text{O}_2\text{Si}$: $[\text{M}+\text{H}]^+$, 189.1311.

(E)-4-phenyl-1-(trimethylsilyl) but-1-en-1-yl benzoate (5a):^[1]

This compound was synthesized according to the same procedure as for **1b**.

Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 0.17 (9H, s), 2.42 (2H, dt, $J = 7.6, 8.0$ Hz), 2.71 (2H, t, $J = 7.2$ Hz), 5.62 (1H, t, $J = 6.8$ Hz), 7.15–7.25 (3H, m), 7.26–7.28 (2H, m), 7.44–7.48 (2H, m), 7.57–7.60 (1H, m), 8.05–8.06 (1H, m); ^{13}C NMR (100 MHz, CDCl_3) δ -1.3, 27.7, 35.1, 125.9, 128.3, 128.4, 128.4, 129.8, 129.9, 130.7, 133.0, 141.6, 155.6, 164.8.

(*E*)-2-phenyl-1-(trimethylsilyl) ethenyl benzoate (5b):^[1]

This compound was synthesized according to the same procedure as for **1b**

Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 0.30 (9H, s), 6.40 (1H, s), 7.22–7.24 (1H, m), 7.27–7.30 (2H, m), 7.49–7.53 (4H, m), 7.62–7.63 (2H, m), 8.15 (2H, d, $J = 7.2$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ -0.9, 127.6, 128.3, 128.4, 128.6, 129.1, 129.7, 130.0, 133.3, 134.3, 156.6, 164.9.

(*E*)-1-(trimethylsilyl)hept-1-enyl benzoate (5c)

This compound was synthesized according to the same procedure as for **1b**

Colorless oil; IR (neat) 2929, 2860, 2399, 2349, 1730, 1454, 1215, 1068, 1014, 928, 844, 756, 669 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.17 (9H, s), 0.86 (3H, t, $J = 6.8$ Hz), 1.25–1.31 (4H, m), 1.35–1.43 (2H, m), 2.10 (2H, dt, $J = 7.2, 7.6$ Hz), 5.58 (1H, t, $J = 7.2$ Hz), 7.47 (2H, dd, $J = 7.6, 7.6$ Hz), 7.59 (1H, dd, $J = 7.6, 7.2$ Hz), 8.10 (2H, d, $J = 7.2$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ -1.3, 14.0, 22.4, 25.8, 28.5, 31.5, 128.4, 129.8, 130.1, 132.1, 132.9, 154.9, 164.9; HRMS ESI (m/z): found, 291.1788, calcd for $\text{C}_{17}\text{H}_{27}\text{O}_2\text{Si}$: $[\text{M}+\text{H}]^+$, 291.1780.

(E)-1-(trimethylsilyl)pent-1-enyl benzoate (5d)

This compound was synthesized according to the same procedure as for **1b**

Colorless oil; IR (neat) 2958, 1963, 1722, 1645, 1583, 1485, 1454, 1408, 1373, 1271, 1246, 1180, 1107, 1068, 844, 842, 756, 707 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ -1.74 (9H, s), 0.90 (3H, t, $J = 7.6$ Hz), 1.41 (2H, tt, $J = 7.2, 7.6$ Hz), 2.09 (2H, dt, $J = 7.2, 7.2$ Hz), 5.58 (1H, t, $J = 7.2$ Hz), 7.45–7.49 (2H, m), 7.57–7.61 (1H, m), 8.09–8.11 (2H, m); ^{13}C NMR (100 MHz, CDCl_3) δ -1.3, 13.8, 22.0, 27.8, 128.4, 129.8, 130.1, 131.8, 132.9, 155.1, 164.8; HRMS ESI (m/z): found, 263.1777, calcd for $\text{C}_{15}\text{H}_{23}\text{O}_2\text{Si}$: $[\text{M}+\text{H}]^+$, 263.1780.

(E)-7-chloro-1-(trimethylsilyl)hept-1-enyl benzoate (5e)

This compound was synthesized according to the same procedure as for **1b**.

Colorless oil; IR (neat); 2935, 1717, 1600, 1315, 1265, 1246, 1177, 1107, 1069, 1026, 841, 756, 709 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.18 (9H, s), 1.42–1.43 (4H, m), 1.73–1.77 (2H, m), 2.11–2.17 (2H, m), 3.51 (2H, t, $J = 6.8$ Hz), 5.57 (1H, t, $J = 7.2$ Hz), 7.48 (2H, dd, $J = 7.6, 7.6$ Hz), 7.59 (1H, dd, $J = 7.2, 7.6$ Hz), 8.10 (2H, d, $J = 7.6$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ -1.3, 25.6, 26.4, 28.0, 32.3, 45.0, 128.5, 129.8, 130.0, 131.4, 133.0, 155.4, 164.8; HRMS ESI (m/z): found, 325.1393, calcd for: $[\text{M}+\text{H}]^+$, 325.1391.

(E)-6-phenyl-1-(trimethylsilyl)hex-1-en-5-ynyl benzoate (5f)

This compound was synthesized according to the same procedure as for **1b**

Colorless oil; IR (neat); 3016, 1716, 1489, 1265, 1215, 1107, 1068, 844, 756, 709, 667 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.15 (9H, s), 2.39 (2H, t, $J = 6.4$ Hz), 2.45 (2H, dt, $J = 6.4, 6.8$ Hz), 5.69 (1H, t, $J = 6.4$ Hz), 7.20–7.21 (3H, m), 7.32–7.34 (2H, m), 7.38–7.41 (2H, m), 7.50–7.53 (1H, m), 8.05 (2H, m); ^{13}C NMR (100 MHz, CDCl_3) δ -1.3, 19.0, 25.2, 81.1, 89.2, 123.8, 127.6, 128.1, 128.5, 129.7, 129.9, 129.9, 131.5, 133.1, 156.1, 164.8; HRMS ESI (m/z): found, 349.1632, calcd for: $[\text{M}+\text{H}]^+$, 349.1624.

(*E*)-4-phenyl-1-(trimethylsilyl) but-1-en-1-yl acetate (5h)^[1]

This compound was synthesized according to the same procedure as for **1b**

Colorless oil; ^1H NMR (300 MHz, CDCl_3) δ 0.12 (9H, s), 2.12 (3H, s), 2.34 (2H, tt, $J = 7.2, 8.4$ Hz), 2.67 (2H, t, $J = 7.5$ Hz), 5.51 (1H, t, $J = 6.9$ Hz) 7.16–7.21 (3H, m), 7.26–7.31 (2H, m); ^{13}C NMR (100 MHz, CDCl_3) δ -1.5, 20.6, 27.6, 35.0, 125.9, 128.3, 128.4, 130.5, 141.6, 155.3, 169.2.

(*E*)-1-(trimethylsilyl)hepta-1,6-dienyl acetate (5i)

This compound was synthesized according to the same procedure as for **1b**

Colorless oil; IR(neat): 3017, 2928, 1717, 1601, 1450, 1315, 1250, 1215, 1103, 1026, 845, 752, 710, 667 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.12 (9H, s), 1.46 (2H, tt, $J = 7.2, 7.6$ Hz), 2.04 (2H, dt, $J = 7.2, 7.2$ Hz), 2.04 (2H, dt, $J = 7.2, 7.2$ Hz), 2.14 (3H, s), 4.95 (1H, d, $J = 10.4$ Hz), 5.00 (1H, d, $J = 17.6$ Hz), 5.46 (1H, t, $J = 7.2$ Hz), 5.74–5.84 (1H, m); ^{13}C

NMR (100 MHz, CDCl₃) δ -1.5, 20.6, 25.2, 27.9, 33.3, 114.7, 131.3, 128.5, 155.1, 169.3;
HRMS ESI (m/z): found, 227.1456, calcd for: [M+H]⁺, 227.1467.

(E)-6-(acetyloxy)-1-(trimethylsilyl)hex-a-en-1-yl acetate (5j)

This compound was synthesized according to the same procedure as for **1b**

Colorless oil; IR (neat); 3020, 2959, 2399, 1724, 1369, 1215, 1041, 844, 748, 667 cm⁻¹;
¹H NMR (400 MHz, CDCl₃) δ 0.113 (9H, s), 1.38–1.46 (2H, m); 1.57–1.67 (2H, m),
2.02–2.08 (2H, m), 2.03 (3H, s), 2.14 (3H, s), 4.04 (2H, t, J = 6.8 Hz), 5.44 (2H, t, J = 7.2
Hz); ¹³C NMR (100 MHz, CDCl₃) δ -1.5, 20.6, 21.0, 25.1, 25.2, 28.2, 64.2, 130.9, 155.4,
169.2, 171.2; HRMS ESI (m/z): found, 273.1532, calcd for: [M+H]⁺, 273.1522.

(E)-2-phenyl-1-(trimethylsilyl) ethenyl acetate(5k)

This compound was synthesized according to the same procedure as for **1b**

Colorless oil; IR (neat) 1730, 1632, 1493, 1446, 1368, 1223, 1057, 841, 758, 692 cm⁻¹; ¹H
NMR (400 MHz, CDCl₃) δ 0.23(9H, s), 2.20 (3H, s), 6.26 (1H, s), 7.23–7.25 (1H, m),
7.30–7.33 (2H, m) 7.47 (2H, d) ; ¹³C NMR (100 MHz, CDCl₃) δ -0.1, 20.9, 127.7, 1281,
128.4, 129.1, 134.5, 156.6, 169.1; HRMS ESI (m/z): found, 257.0969, calcd for
C₁₃H₁₈O₂SiNa: (M+Na)⁺, 257.0974.

Ethyl (*E*)-4-phenyl-1-(trimethylsilyl) but-1-en-1-yl carbonate (5l)

This compound was synthesized according to the same procedure as for **1b**

Colorless oil; IR (neat) 1741, 1603, 1522, 1422, 1371, 1250, 1218, 928, 844, 759, 669 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.14 (9H, s), 1.32 (3H, t, $J = 7.2$ Hz), 2.41 (2H, tt, $J = 7.6, 8.0$ Hz); 2.68 (2H, t, $J = 7.6$ Hz); 4.21 (2H, q, $J = 7.2$ Hz), 5.49 (1H, t, $J = 6.8$ Hz), 7.17–7.20 (3H, m), 7.26–7.30 (2H, m); ^{13}C NMR (100 MHz, CDCl_3) δ -1.5, 14.3, 27.2, 35.0, 64.2, 125.9, 128.3, 128.4, 130.8, 141.5, 153.5, 155.5; HRMS ESI (m/z): found, 293.1572, calcd for $\text{C}_{16}\text{H}_{25}\text{O}_3\text{Si}$: $[\text{M}+\text{H}]^+$, 293.1573.

Ethyl (*E*)-2-phenyl-1-(trimethylsilyl) ethenyl carbonate (5m)

This compound was synthesized according to the same procedure as for **1b**

White solid; IR (neat) 1742, 1634, 1243, 1215, 1026, 928, 847, 768, 667 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.26 (9H, s), 1.32 (3H, t, $J = 7.2$ Hz), 4.22 (2H, q, $J = 6.8$ Hz), 6.23 (1H, s), 7.22–7.26 (1H, m), 7.30–7.34 (2H, m), 7.50–7.52 (2H, m); ^{13}C NMR (100 MHz, CDCl_3) δ -1.1, 14.3, 64.4, 127.8, 128.2, 128.4, 129.2, 134.1, 153.2, 156.4; HRMS ESI (m/z): found, 265.1258, calcd for $\text{C}_{14}\text{H}_{21}\text{O}_3\text{Si}$: $[\text{M}+\text{H}]^+$, 265.1260.

Phenyl(*E*)-4-phenyl-1-(trimethylsilyl)but-1-en-1-yl carbonate (5n)

This compound was synthesized according to the same procedure as for **1b**

Colorless oil; IR (neat) 1756, 1623, 1494, 1251, 1215, 1091, 928, 842, 756, 668; ^1H NMR (400 MHz, CDCl_3) δ 0.18 (9H, s), 2.49 (2H, dt, $J = 7.6, 7.8$ Hz), 2.72 (2H, t, $J = 7.2$ Hz), 5.55 (1H, t, $J = 7.2$ Hz), 7.16–7.22 (5H, m), 7.24–7.31 (3H, m), 7.36–7.40 (2H, m); ^{13}C NMR (100 MHz, CDCl_3) δ -1.4, 27.3, 34.9, 120.9, 125.9, 126.0, 128.3, 128.4, 129.5, 131.1, 141.3, 151.1, 151.9, 155.7; HRMS ESI (m/z): found, 341.1573, calcd for $\text{C}_{20}\text{H}_{25}\text{O}_3\text{Si}$: $[\text{M}+\text{H}]^+$ 341.1573.

Preparation of (*E*)-1-trimethylsilyl-4-phenylbut-1-ene ((*E*)-1a') (5o)^[1]

This compound was synthesized using chlorotrimethylsilane according to the same procedure of synthesis of **1a**. Yield: 95%.

Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 0.05 (6H, s), 2.41 (2H, dt, $J = 7.6, 6.0$ Hz), 2.72 (2H, t, $J = 7.6$ Hz), 5.67 (1H, d, $J = 19.2$ Hz), 6.08 (1H, dt, $J = 18.4, 6.0$ Hz), 7.19–7.17 (3H, m), 7.28 (2H, t, $J = 7.6$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ -1.2, 35.2, 38.5, 125.7, 128.2, 128.5, 130.4, 142.0, 146.1.

Preparation of 2-trimethylsilylbenzofuran (5p)^[3]

To a stirred solution of benzofuran (3.0 g, 25.4 mmol) in 50 mL of dry THF at $-78\text{ }^\circ\text{C}$ under nitrogen atmosphere, was added *sec*-butyllithium (1.4 M in cyclohexane, 18.1 mL, 25.4 mmol) dropwise. After stirring for 5 min, chlorotrimethylsilane (3.53 mL, 27.9 mmol) was added and the reaction mixture was allowed to warm up to room temperature for another 1 h. Then the reaction mixture was quenched with saturated water and the organic layer was extracted with diethyl ether. The combined organic extracts were dried

over magnesium sulfate concentrated under reduced pressure. The crude was purified by distillation in *vacuo* to furnish the product in 90% yield.

Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 0.36 (9H, s), 6.97 (1H, s), 7.20 (1H, t, $J = 7.6$ Hz), 7.28 (1H, t, $J = 8.0$ Hz), 7.51 (1H, d, $J = 8.4$ Hz), 7.57 (1H, d, $J = 7.6$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ -1.8, 111.2, 116.0, 120.9, 122.3, 124.3, 128.0, 158.1, 163.5.

1-benzyl-4-(trimethylsilyl)-1H-1, 2, 3-triazole amine (5q)^[14]

To a stirred solution of ethynyltrimethylsilane (14.2 mL, 100 mmol) and CuI (3.17 g, 16.7 mmol) in 250 mL of H_2O at room temperature under nitrogen atmosphere, was added (azidomethyl)benzene (10.9 g, 83.4 mmol) in one portion. After stirring overnight at room temperature, then the reaction mixture was extracted with diethyl ether. The combined organic extracts were dried over magnesium sulfate and concentrated under reduced pressure. The crude was purified by hexane : ethyl acetate = 4 : 1 to furnish the product in 80% yield.

White solid; ^1H NMR (400 MHz, CDCl_3) δ 0.30 (9H, s), 5.56 (2H, s), 7.26–7.29 (2H, m), 7.35–7.38 (3H, m), 7.43 (1H, m); ^{13}C NMR (100 MHz, CDCl_3) δ -1.2, 53.4, 128.0, 128.5, 128.7, 128.7, 129.0, 134.9, 147.1.

General Procedure for Rh-catalyzed homocoupling of Homocoupling of (1-Acyloxy-vinyl)silanes

Tetracarbonyldichlorodirhodium ($[\text{RhCl}(\text{CO})_2]_2$) (0.01 mmol), (1-Acyloxy-vinyl)silanes (0.2 mmol) and hexachloropropan-2-one (0.6 mmol) were added one by one into toluene solution (2 mL), then heated for 5 h–24 h, 80 $^\circ\text{C}$, the solvent was removed under reduced

pressure, and the residue was purified by PTLC (hexane: EtOAc = 5:1) to get 1,3-diene-2,3-diyl diesters.

(3Z, 5Z)-5-(benzoyloxy)-1,8-diphenylocta-3,5-dien-4-yl benzoate (6a)

White solid; IR (neat) 1734, 1452, 1257, 1215, 1102, 1094, 1068, 1019, 754, 668 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 2.34 (4H, dt, $J = 8$ Hz, 7.6 Hz), 2.67 (4H, t, $J = 7.2$ Hz), 5.61 (2H, t, $J = 7.2$ Hz), 7.07–7.11 (5H, m), 7.13–7.19 (5H, m), 7.50–7.54 (4H, m), 7.64–7.68 (2H, m), 8.16–8.18 (4H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 27.9, 34.8, 117.3, 125.9, 128.3, 128.4, 128.6, 128.9, 130.3, 133.7, 141.0, 141.2, 163.8; HRMS ESI (m/z): found, 503.2220, calcd for $\text{C}_{34}\text{H}_{31}\text{O}_4$: $[\text{M}+\text{H}]^+$, 503.2222; m.p. 123–124 $^\circ\text{C}$ (EtOAc).

(Z)-4-phenylbut-1-en-1-yl benzoate (7)

Colorless oil; IR(neat) 1726, 1602, 1452, 1269, 1216, 1177, 1114, 1070, 1027, 763, 709, 667 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 2.62 (2H, dt, $J = 7.2$, 7.6 Hz), 2.78 (2H, t, $J = 7.2$ Hz), 5.05 (2H, dt, $J = 7.2$, 6.8 Hz), 7.17–7.03 (1H, m), 7.23–7.31 (5H, m), 7.45–7.49 (1H, m), 7.58–7.60 (2H, m), 8.05–8.07 (2H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 26.5, 35.4, 113.6, 126.0, 128.3, 128.4, 128.6, 129.3, 129.9, 133.5, 134.6, 141.5, 163.5; HRMS ESI (m/z): found, 253.1227, calcd for $\text{C}_{17}\text{H}_{17}\text{O}_2$: $[\text{M}+\text{H}]^+$, 253.1229.

(1Z, 3Z)-3-(benzoyloxy)-1, 4-diphenylbuta-1, 3-dien-2-yl benzoate (6b)

White solid; IR (neat) 1737, 1603, 1507, 1429, 1336, 1215, 928, 770, 669 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 6.64 (2H, s), 7.16–7.23 (6H, m), 7.44–7.46 (4H, m), 7.52–7.56 (4H, m), 7.66–7.70 (2H, m), 8.24–8.26 (4H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 117.7, 128.1, 128.6, 128.6, 128.8, 128.9, 130.4, 133.5, 134.0, 141.4, 163.6; HRMS ESI (m/z): found, 447.1591, calcd for $\text{C}_{30}\text{H}_{23}\text{O}_4$: $[\text{M}+\text{H}]^+$, 447.1596; m.p. 204–206 $^\circ\text{C}$ (EtOAc).

(Z)-oct-2-en-2-yl benzoate (6c)

White solid; IR (neat); 3020, 1732, 1601, 1450, 1242, 1215, 1176, 1087, 1068, 1026, 748, 713, 667 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.83–0.88 (2H, m), 1.20–1.22 (4H, m), 1.27–1.43 (2H, m), 1.99–2.04 (2H, m), 5.55 (1H, t, $J = 7.2$ Hz), 7.52 (2H, dd, $J = 7.6$, 7.6 Hz), 7.64 (1H, dd, $J = 7.2$, 7.6 Hz), 8.21 (2H, d, $J = 7.6$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 13.9, 22.3, 25.9, 28.3, 31.4, 118.2, 128.6, 129.0, 130.2, 133.6, 140.8, 163.8; HRMS ESI (m/z): found, 435.2527, calcd for: $[\text{M}+\text{H}]^+$, 435.2535; m.p. 59–62 $^\circ\text{C}$ (EtOAc).

(Z)-hex-2-en-2-yl benzoate (6d)

White solid; IR (neat); 3017, 1732, 1601, 1450, 1242, 1215, 1088, 1026, 768, 752, 667 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.84 (3H, t, $J = 7.2$ Hz), 1.33–1.43 (2H, m), 2.01 (2H,

dt, $J = 7.2$, 7.6 Hz), 5.56 (1H, t, $J = 7.6$ Hz), 7.52, (2H, dd, $J = 7.6$, 8 Hz), 7.64 (1H, dd, $J = 7.6$, 7.6 Hz), 8.21 (2H, d, $J = 8$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 13.8, 21.9, 27.9, 117.9, 128.6, 129.0, 130.2, 133.6, 140.9, 163.8; HRMS ESI (m/z): found, 379.1906, calcd for: $[\text{M}+\text{H}]^+$, 379.1909; m.p. 48–50 °C (EtOAc).

(Z)-8-chlorooct-2-en-2-yl benzoate (6e)

White solid; IR (neat); 3016, 2939, 2399, 1732, 1600, 1450, 1242, 1215, 1176, 1103, 1087, 1026, 744, 717, 667 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.38–1.39 (4H, m), 1.67–1.72 (2H, m), 2.03–2.05 (2H, m), 3.46 (2H, t, $J = 6.8$ Hz), 5.54 (1H, t, $J = 7.2$ Hz), 7.52 (2H, dd, $J = 7.6$, 7.6 Hz), 7.65 (1H, dd, $J = 7.6$, 7.6 Hz), 8.20 (2H, d, $J = 7.6$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 25.7, 26.4, 27.8, 32.2, 44.8, 117.8, 128.7, 128.9, 130.2, 133.8, 141.0, 163.9; HRMS ESI (m/z): found, 503.1758, calcd for: $[\text{M}+\text{H}]^+$, 503.1756; m.p. 88–90 °C (EtOAc).

(Z)-6-phenylhex-2-en-5-yn-2-yl benzoate (6f)

Yellow solid; IR (neat); 1739, 1489, 1242, 1064, 1026, 756, 663 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 2.35 (2H, dt, $J = 6.8$, 7.2 Hz), 2.47 (2H, t, $J = 6.8$ Hz), 5.83 (1H, t, $J = 7.2$ Hz), 7.16–7.24 (5H, m), 7.44–7.48 (2H, m), 7.60–7.64 (1H, m), 8.19–8.20 (1H, d, $J = 7.6$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 18.8, 25.4, 81.4, 88.7, 116.8, 123.6, 127.5, 128.1, 128.6, 128.7, 130.3, 131.5, 133.8, 141.3, 163.8; HRMS ESI (m/z): found, 431.2231, calcd for: $[\text{M}+\text{H}]^+$, 431.2222; m.p. 150–152 °C (EtOAc).

(3Z, 5Z)-5-(acetyloxy)-1,8-diphenylocta-3,5-dien-4-yl acetate (6h)

White solid; IR (neat) 1769, 1627, 1423, 1384, 1216, 928, 771, 667 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 2.22 (6H, s), 2.28 (4H, dt, $J = 7.6, 8$ Hz), 2.68 (4H, t, $J = 7.6$ Hz), 5.41 (2H, t, $J = 7.6$ Hz), 7.15–7.21 (4H, m), 7.26–7.30 (6H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 20.5, 27.7, 34.8, 117.0, 126.0, 128.4, 128.4, 140.9, 141.2, 168.0; HRMS ESI (m/z): found, 379.1907, calcd for $\text{C}_{24}\text{H}_{27}\text{O}_4$: $[\text{M}+\text{H}]^+$, 379.1909; m.p. 218–221 $^\circ\text{C}$ (EtOAc).

(5Z, 7Z)-dodeca-5, 7-diene-1, 6, 7, 12-tetrayl tetraacetate (6j)

Colorless oil; IR (neat) 3018, 2945, 2872, 2399, 2349, 1730, 1467, 1373, 1215, 927, 844, 756, 669, 491 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.40–1.48 (2H, m), 1.58–1.71 (2H, m), 1.98–2.01 (m, 2H), 2.04 (3H, s), 2.24 (3H, s), 4.04 (2H, t, $J = 7.2$ Hz), 5.36 (1H, t, $J = 7.2$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 20.5, 21.0, 25.0, 28.2, 64.1, 117.4, 141.0, 168.0, 171.1; HRMS ESI (m/z): found, 399.2018, calcd for $\text{C}_{20}\text{H}_{31}\text{O}_8$: $[\text{M}+\text{H}]^+$, 399.2019.

(1Z,3Z)-3-(acetyloxy)-1, 4-diphenylbuta-1,3-dien-2-yl acetate (6k)

White solid; IR (CDCl_3) 1764, 1634, 1431, 1215, 1046, 929, 765, 668 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 2.31 (6H, s), 6.48 (2H, s), 7.26–7.28 (2H, m), 7.32–7.36 (4H, m), 7.26 (4H, d, $J = 8$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 21.0, 117.4, 128.2, 128.6, 128.9,

133.6, 141.5, 167.8; HRMS ESI (m/z): found, 323.1285, calcd for C₂₀H₁₉O₄: [M+H]⁺, 323.1283; 165–167 °C (EtOAc).

[(3Z,5Z)-4,5-bis[(ethoxycarbonyl)oxy]-8-phenylocta-3,5-dien-1-yl] (6l)

White solid; IR (neat) 1601, 1476, 1422, 1217, 928, 849, 757, 668 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.33 (6H, t, *J* = 6.8 Hz), 2.38 (4H, tt, *J* = 8, 7.6 Hz), 2.70 (4H, t, *J* = 7.6 Hz), 4.25 (4H, q, *J* = 7.2 Hz); 5.51 (2H, t, 7.2 Hz); 7.16–7.20 (6H, m), 7.25–7.29 (4H, m); ¹³C NMR (100 MHz, CDCl₃) δ 14.2, 27.4, 34.7, 64.9, 117.5, 126.0, 128.4, 128.4, 141.1, 141.2, 152.3; HRMS ESI (m/z): found, 439.2112, calcd for C₂₆H₃₁O₆: [M+H]⁺ 439.2121; m.p. 84–87 °C (EtOAc).

[(1Z,3Z)-2,3-bis[(ethoxycarbonyl)oxy]-4-phenylbuta-1,3-dien-1-yl]benzene (6m)

White solid; IR (neat) 1765, 1616, 1423, 1338, 1215, 927, 759, 668 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.29 (6H, t, *J* = 7.2 Hz), 4.25 (4H, q, *J* = 7.2 Hz), 6.54 (2H, s), 7.26–7.29 (2H, m), 7.33–7.37 (4H, m), 7.52 (4H, d, *J* = 8 MHz); ¹³C NMR (100 MHz, CDCl₃) δ 14.2, 65.3, 117.3, 128.3, 128.7, 129.2, 133.3, 141.5, 151.7; HRMS ESI (m/z): found, 383.1492, calcd for C₂₂H₂₃O₆: [M+H]⁺, 383.1495; m.p. 125–130 °C (EtOAc).

[(3Z,5Z)-4,5-bis[(phenoxycarbonyl)oxy]-8-phenylocta-3,5-dien-1-yl]benzene (6n)

White solid; IR (neat) 1780, 1645, 1494, 1214, 1095, 928, 761, 669 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 2.51 (4H, dt, $J = 7.6$ Hz, 7.6 Hz), 2.77 (4H, t, $J = 7.6$ Hz), 5.68 (2H, t, $J = 7.2$ Hz), 7.16–7.22 (10H, m), 7.25–7.30 (6H, m), 7.37–7.41 (4H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 27.4, 34.7, 118.3, 120.8, 126.1, 126.3, 128.4, 128.5, 129.5, 140.9, 141.0, 150.7, 150.9; HRMS ESI (m/z): found, 535.2122, calcd for $\text{C}_{34}\text{H}_{31}\text{O}_6$: $[\text{M}+\text{H}]^+$, 535.2121; m.p. 124–127 $^\circ\text{C}$ (EtOAc).

2-(1-benzofuran-2-yl)-1-benzofuran (6p)

White Solid; IR (neat); 2399, 2349, 1467, 1454, 1238, 1215, 1180, 1049, 1014, 927, 756, 669 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.17 (2H, s), 7.26–7.29 (2H, m), 7.32–7.36 (2H, m), 7.54–7.56 (2H, m), 7.63–7.64 (2H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 103.7, 111.3, 121.4, 123.3, 125.1, 128.5, 147.7, 155.1; HRMS ESI (m/z): found, 235.0770, calcd for $\text{C}_{16}\text{H}_{11}\text{O}_2$: $[\text{M}+\text{H}]^+$ 235.0759; m.p. 196–198 $^\circ\text{C}$ (EtOAc).

1-benzyl-4-(1-benzyl-1H-1,2,3-triazol-4-yl)-1H-1,2,3-triazole amine (6q)

Colorless oil; IR (neat) 2399, 2349, 1485, 1467, 1454, 1215, 1068, 927, 754, 669 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.57 (4H, s), 7.26–7.27 (4H, m), 7.36–7.39 (4H, m), 7.48 (2H,

s), 7.72 (2H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 53.9, 123.3, 128.00, 128.7, 129.1, 134.2, 134.6; HRMS ESI (m/z): found, 317.1507, calcd for $\text{C}_{18}\text{H}_{17}\text{N}_6$: $[\text{M}+\text{H}]^+$, 317.1515.

General Procedure for α,α -Dimethoxyketone^[1]

To a methanol solution (3 mL) of potassium carbonate (494 mg, 3.57 mmol) was added (1Z, 3Z)-3-(benzoyloxy)-1, 4-diphenylbuta-1, 3-dien-2-yl benzoate (159 mg, 0.357 mmol) in methanol (1 mL) at room temperature and the solution was stirred at this temperature for 30 min. Then the solution was quenched with water and the organic layer was extracted three times with diethyl ether. The combined organic extracts were dried over magnesium sulfate. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on Florisil (hexane: EtOAc = 5:1) to afford 3, 3-dimethoxy-1,4-diphenylbutan-2-one (68.2 mg, 0.24 mmol) in 67% yield.

5,5-dimethoxy-1,8-diphenyloctan-4-one (8a)

Colorless oil; IR (neat) 3026, 2939, 2862, 2831, 2249, 1946, 1872, 1724, 1602, 1496, 1454, 1398, 1365, 1190, 1126, 1085, 1043, 948, 910, 734, 700, 648 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.39–1.47 (2H, m), 1.75–1.79 (2H, m), 1.84–1.91 (2H, m), 2.51–2.61 (6H, m), 3.13 (6H, s), 7.11–7.13 (2H, m), 7.15–7.19 (4H, m), 7.24–7.28 (4H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 24.6, 24.7, 32.3, 35.1, 35.6, 38.4, 49.3, 104.2, 125.9, 128.3, 128.4, 128.4, 128.6, 141.4, 141.7, 209.2. HRMS ESI (m/z): found, 341.2116, calcd for $\text{C}_{22}\text{H}_{29}\text{O}_3$: $[\text{M}+\text{H}]^+$, 341.2117.

3, 3-dimethoxy-1,4-diphenylbutan-2-one (8b)

Colorless oil; IR (neat) 2831, 2399, 1730, 1602, 1215, 1124, 1055, 1020, 979, 927, 756, 700, 669 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 3.12 (2H, s), 3.35 (6H, s), 3.40 (2H, s), 6.83–6.85 (2H, m), 7.15–7.16 (2H, m), 7.18–7.24 (3H, m), 7.25–7.30 (3H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 39.2, 47.1, 49.7, 105.2, 126.6, 127.0, 128.2, 128.5, 129.9, 130.3, 134.2, 206.9; HRMS ESI (m/z): found, 285.1481, calcd for $\text{C}_{18}\text{H}_{21}\text{O}_3$: $[\text{M}+\text{H}]^+$, 285.1491.

General Procedure for Preparation of α -Diketone^[1]

To a dichloromethane–trifluoroacetic acid 10:1 solution (3 mL) was added 3, 3-dimethoxy-1,4-diphenylbutan-2-one (68.2 mg, 0.24 mmol) at room temperature and the solution was stirred at this temperature for 2 h. Then the solution was quenched with saturated NaHCO_3 solution and the organic layer was extracted three times with dichloromethane. The combined organic extracts were dried over magnesium sulfate. The solvent was removed under reduced pressure, and the residue was purified by Florisil column chromatography (hexane: EtOAc = 5: 1) to afford 1,4-diphenylbutane-2,3-dione (52.4 mg, 0.22 mmol) in 90% yield.

1,8-diphenyloctane-4,5-dione (9a)^[15]

Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 1.91 (2H, tt, $J = 7.2, 7.6$ Hz), 2.63 (2H, t, $J = 7.6$ Hz), 2.72 (2H, t, $J = 7.2$ Hz), 7.12–7.20 (5H, m), 7.22–7.29 (5H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 24.6, 35.0, 35.3, 126.0, 128.4, 128.5, 141.2, 199.5.

1,4-diphenylbutane-2,3-dione (**9b**)^[16]

yellowish oil; ¹H NMR (400 MHz, CDCl₃) δ 4.00 (4H, s), 7.10–7.12 (3H, m), 7.23–7.28 (7H, m); ¹³C NMR (100 MHz, CDCl₃) δ 43.1, 127.2, 128.7, 129.7, 131.9, 196.3.

7.4 Activation of Inert Carbon-Silicon Bond of Acylsilane by Rhodium Catalyst

General Procedure for Rh-Catalyzed Reaction of Alkynoylsilane with Acid Anhydride

To a toluene solution (2.6 mL) of 6-phenyl-1-trimethylsilylhex-5-yn-1-one (**4f**) (62.9 mg, 0.257 mmol) was added [RhCl(CO)₂]₂ (5.0 mg, 0.013 mmol) and acid anhydride (1.29 mmol) and the mixture was heated at 100 °C for 12 h. After evaporation of the solvent, the crude products were purified by PTLC (hexane: EtOAc = 5: 1) to afford cyclopentanone.

(2*E*)-2-(phenylmethylidene)cyclopentan-1-one (**10**)^[17]

White solid; ¹H NMR (500 MHz, CDCl₃) δ 1.99 (2H, tt, *J* = 7.2, 7.9 Hz), 2.37 (2H, t, *J* = 7.9 Hz), 2.93 (2H, dt, *J* = 2.7, 7.2 Hz), 7.31–7.39 (4H, m), 7.49 (2H, d, *J* = 7.3 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 20.0, 29.1, 37.6, 128.5, 129.1, 130.3, 132.0, 135.3, 135.9, 207.9.

(2Z)-2-(2-oxo-1-phenylpropylidene)cyclopentan-1-one (11a)

Colorless oil; IR (neat) 1712, 1699, 1614, 1495, 1444, 1352, 1203, 1072, 845, 700 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 1.97 (2H, tt, $J = 7.1, 7.8$ Hz), 2.33 (3H, s), 2.38 (2H, t, $J = 7.8$ Hz), 2.76 (2H, t, $J = 7.1$ Hz), 7.35–7.42 (5H, m); ^{13}C NMR (125 MHz, CDCl_3) δ 20.8, 29.6, 29.9, 38.2, 128.3, 128.8, 129.5, 133.3, 133.6, 147.9, 206.2, 207.1; HRMS ESI (m/z): found, 215.1069, calcd for $\text{C}_{14}\text{H}_{15}\text{O}_2$: $[\text{M}+\text{H}]^+$, 215.1072.

(2Z)-2-(2-oxo-1-phenylbutylidene)cyclopentan-1-one (11b)

Colorless oil; IR (ZnSe) 1714, 1701, 1608, 1203, 698 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 1.12 (3H, t, $J = 7.2$ Hz), 1.98 (2H, tt, $J = 7.1, 7.8$ Hz), 2.37 (2H, t, $J = 7.8$ Hz), 2.55 (2H, q, $J = 7.2$ Hz), 2.77 (2H, t, $J = 7.1$ Hz), 7.34–7.41 (5H, m); ^{13}C NMR (125 MHz, CDCl_3) δ 7.5, 20.8, 30.9, 35.7, 38.2, 128.2, 128.7, 129.5, 133.6, 133.9, 141.8, 207.2, 209.2; HRMS ESI (m/z): found, 229.1201, calcd for $\text{C}_{15}\text{H}_{17}\text{O}_2$: $[\text{M}+\text{H}]^+$, 229.1229.

(2Z)-2-(3-methyl-2-oxo-1-phenylbutylidene)cyclopentan-1-one (11c)

Colorless oil; IR (neat) 1714, 1695, 1493, 1466, 1444, 1205, 1074, 847, 702 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 1.05 (6H, d, $J = 7.0$ Hz), 1.96 (2H, tt, $J = 7.1, 7.8$ Hz), 2.37 (2H, t, $J = 7.8$ Hz), 2.75 (1H, m), 2.76 (2H, t, $J = 7.1$ Hz), 7.34–7.38 (5H, m); ^{13}C NMR (125 MHz, CDCl_3) δ 18.2, 20.8, 29.7, 38.3, 41.2, 128.1, 128.6, 129.3, 134.3, 134.7, 148.0, 207.0, 212.4; HRMS ESI (m/z): found, 243.1394, calcd for $\text{C}_{16}\text{H}_{19}\text{O}_2$: $[\text{M}+\text{H}]^+$, 243.1385.

(2*E*)-2-(1-phenylethylidene)cyclopentan-1-one (12a)^[18]

Colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 1.77 (2H, tt, $J = 7.1, 7.8$ Hz), 2.36 (2H, t, $J = 7.8$ Hz), 2.51 (3H, t, $J = 2.0$ Hz), 2.56 (2H, tq, $J = 2.0, 7.1$ Hz), 7.22–7.24 (2H, m), 7.27–7.30 (1H, m), 7.34–7.37 (2H, m); ^{13}C NMR (125 MHz, CDCl_3) δ 19.9, 20.3, 31.7, 40.5, 127.2, 127.8, 128.1, 132.6, 143.5, 147.4, 208.9.

(2*E*)-2-(1-phenylpropylidene)cyclopentan-1-one (12b)

Colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 0.93 (3H, t, $J = 7.5$ Hz), 1.76 (2H, tt, $J = 7.1, 7.8$ Hz), 2.34 (2H, t, $J = 7.8$ Hz), 2.47 (2H, t, $J = 7.1$ Hz), 3.01 (2H, q, $J = 7.5$ Hz), 7.16–7.19 (2H, m), 7.26–7.30 (1H, m), 7.32–7.36 (2H, m); ^{13}C NMR (125 MHz, CDCl_3) δ 13.0, 20.3, 25.8, 31.5, 40.5, 127.4, 127.6, 128.1, 132.0, 142.0, 154.2, 208.4; IR (neat) 1703, 1614, 1597, 1441, 1198, 1174, 771, 702 cm^{-1} ; HRMS ESI (m/z): found, 201.2876, calcd for $\text{C}_{14}\text{H}_{17}\text{O}$: $[\text{M}+\text{H}]^+$, 201.2873.

2-(diphenylmethylidene)cyclopentan-1-one (12e)

Pale yellow solid; IR (ZnSe) 1699, 1587, 1568, 1171, 754, 700 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 1.92 (2H, tt, $J = 7.0, 7.8$ Hz), 2.36 (2H, t, $J = 7.8$ Hz), 2.81 (2H, t, $J = 7.0$ Hz), 7.10–7.12 (2H, m), 7.17–7.19 (2H, m), 7.28–7.34 (6H, m); ^{13}C NMR (125 MHz, CDCl_3) δ 20.5, 32.9, 39.8, 127.8, 127.9, 128.3, 129.4, 129.6, 134.3, 140.1, 141.8, 148.3, 206.6; m.p. 108–110 $^\circ\text{C}$ (EtOAc).

(2E)-2-[(2E)-1,3-diphenylprop-2-en-1-ylidene]cyclopentan-1-one (12f)

Pale yellow solid; IR (ZnSe) 1689, 1562, 1491, 1446, 1198, 1174, 754, 692 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 1.83 (2H, tt, $J = 7.1, 7.7$ Hz), 2.44 (2H, t, $J = 7.1$ Hz), 2.45 (2H, t, $J = 7.7$ Hz), 6.33 (1H, d, $J = 16.1$ Hz), 7.18–7.24 (3H, m), 7.27–7.30 (2H, m), 7.36–7.39 (1H, m), 7.41–7.44 (4H, m), 8.81 (1H, d, $J = 16.1$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 20.0, 32.0, 41.0, 126.5, 127.4, 127.7, 128.3, 128.4, 128.5, 128.6, 133.2, 136.9, 128.8, 147.6, 208.2. HRMS ESI (m/z): found, 275.1425, calcd for $\text{C}_{20}\text{H}_{19}\text{O}_2$: $[\text{M}+\text{H}]^+$, 275.1436; m.p. 132–136 $^\circ\text{C}$ (EtOAc).

General procedure for Rh-catalyzed reaction of alkylsilane with aromatic anhydride

To a toluene solution (0.2 ml) of acylsilane (0.2 mmol) was added $[\text{RhCl}(\text{CO})_2]_2$ (3.9 mg, 0.05 mmol) and acid anhydride (0.6 mmol) and the mixture was heated at 110 $^\circ\text{C}$ for 36 h

in sealed tube under N₂ atmosphere. After evaporation of the solvent, the crude products were purified by PTLC (hexane: EtOAc = 9: 1) to afford monoketone.

1,4-diphenylbutan-1-one (14ae)^[19]

White solid; ¹H NMR (400 MHz, CDCl₃) δ 2.05–2.12 (2H, m), 2.72 (2H, t, *J* = 7.6 Hz), 2.98 (2H, t, *J* = 7.2 Hz), 7.20–7.25 (3H, m), 7.27–7.31 (2H, m), 7.42–7.46 (2H, m), 7.52–7.56 (1H, m), 7.91–7.93 (2H, m); ¹³C NMR (100 MHz, CDCl₃) δ 25.7, 35.2, 37.7, 125.9, 128.0, 128.4, 128.50, 128.53, 132.9, 137.0, 141.7, 200.1; m.p. 55–56 °C (EtOAc).

1, 2-diphenylethan-1-one (14be)^[20]

White solid; ¹H NMR (400 MHz, CDCl₃) δ 4.29 (2H, s), 7.23–7.27 (3H, m), 7.28–7.35 (2H, m), 7.46 (2H, dd, *J* = 7.6 Hz), 7.56 (1H, dd, *J* = 7.2, 7.6 Hz), 8.02 (2H, d, *J* = 7.2 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 45.5, 126.9, 128.6, 128.6, 128.7, 129.4, 133.1, 134.5, 136.6, 197.6; m.p. 53–56 °C (EtOAc).

1-phenylheptan-1-one (14ce)^[21]

Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 0.89 (3H, t, *J* = 6.8 Hz), 1.26–1.40 (6H, m), 1.70–1.77 (2H, m), 2.96 (2H, t, *J* = 7.6 Hz), 7.46 (2H, dd, *J* = 7.2, 8 Hz), 7.55 (1H, dd, *J* =

7.2 Hz), 7.96 (2H, d, $J = 8$ Hz). ^{13}C NMR (100 MHz, CDCl_3) δ 14.0, 22.5, 24.3, 29.0, 31.7, 38.6, 128.1, 128.5, 132.8, 137.1, 200.6.

1-phenylpentan-1-one (14de)^[22]

Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 0.96 (3H, t, $J = 7.2$, 7.2 Hz), 1.37–1.46 (2H, m), 1.69–1.76 (2H, m), 2.97 (2H, t, $J = 7.2$ Hz), 7.46 (2H, dd, $J = 7.6$, 7.6 Hz), 7.55 (1H, dd, $J = 7.2$, 7.6 Hz), 7.96 (2H, d, $J = 7.6$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 13.9, 22.5, 26.5, 38.3, 128.1, 128.5, 132.8, 137.1, 200.6.

7-chloro-1-phenylheptan-1-one (14ee)^[23]

White solid; ^1H NMR (400 MHz, CDCl_3) δ 1.39–1.54 (4H, m), 1.73–1.83 (2H, m), 2.98 (2H, t, $J = 7.6$ Hz), 3.54 (2H, t, $J = 6.8$ Hz), 7.46 (2H, dd, $J = 7.6$, 7.6 Hz), 7.56 (1H, dd, $J = 7.2$, 7.2 Hz), 7.96 (2H, d, $J = 7.2$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 24.1, 26.7, 28.6, 32.4, 45.0, 128.0, 128.6, 132.9, 137.0, 200.3; m.p. 32–34 °C.

1-(4-methylphenyl)-4-phenylbutan-1-one (14af)^[24]

White solid; ^1H NMR (400 MHz, CDCl_3) δ 2.04–2.11 (2H, m), 2.40 (3H, s), 2.72 (2H, t, $J = 7.6$ Hz), 2.95 (2H, t, $J = 7.2$ Hz), 7.17–7.31 (7H, m), 7.82 (2H, d, $J = 8.0$ Hz). ^{13}C NMR

(100 MHz, CDCl₃) δ 21.6, 25.8, 35.2, 37.6, 125.9, 128.1, 128.4, 128.5, 129.2, 134.5, 141.7, 143.6, 199.8; m.p. 39–40 °C (EtOAc).

1-(4-chlorophenyl)-4-phenylbutan-1-one (14ag)^[25]

White solid; ¹H NMR (400 MHz, CDCl₃) δ 2.04–2.11 (2H, m), 2.72 (2H, t, J = 7.6 Hz), 2.94 (2H, t, J = 7.6 Hz), 7.19–7.22 (3H, m), 7.26–7.31 (2H, m), 7.41 (2H, d, J = 8.4 Hz), 7.85 (2H, d, J = 8.4 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 25.6, 35.1, 37.6, 126.0, 128.4, 128.5, 128.9, 129.4, 135.3, 139.4, 141.5, 198.8; m.p. 53–54 °C (EtOAc).

1-(4-nitrophenyl)-4-phenylbutan-1-one (14ah)

Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 2.08–2.15 (2H, m), 2.74 (2H, t, J = 7.2 Hz), 3.01 (2H, t, J = 7.2 Hz), 7.19–7.23 (3H, m), 7.26–7.32 (2H, m), 8.05 (2H, d, J = 8.8 Hz), 8.29 (2H, d, J = 8.8 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 25.3, 34.9, 38.1, 123.8, 126.1, 128.5, 128.5, 129.0, 141.2, 141.3, 150.3, 198.4; HRMS ESI (m/z): found, 270.3067, calcd for C₁₆H₁₆NO₃: [M+H]⁺, 270.3064.

1-(3-methoxyphenyl)-4-phenylbutan-1-one (14ai)

Colorless oil; IR (neat) 3018, 2939, 2860, 2399, 1681, 1583, 1485, 1454, 1429, 1365, 1257, 1217, 1166, 1045, 1014, 844, 756, 700 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 2.10–2.18 (2H, m), 2.78 (2H, t, $J = 7.6$ Hz), 3.02 (2H, t, $J = 7.2$ Hz), 3.90 (3H, s), 7.14–7.16 (1H, m), 7.24–7.28 (3H, m), 7.32–7.42 (3H, m), 7.52–7.56 (2H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 25.8, 35.2, 37.8, 55.4, 112.3, 119.4, 120.6, 125.9, 128.4, 128.5, 129.5, 138.4, 141.6, 159.8, 199.3; HRMS ESI (m/z): found, 255.1380, calcd for $\text{C}_{17}\text{H}_{19}\text{O}_2$: $[\text{M}+\text{H}]^+$, 255.1385.

1-(3-methylphenyl)-4-phenylbutan-1-one (14aj)^[26]

Yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 2.04–2.11 (2H, m), 2.40 (3H, s), 2.72 (2H, t, $J = 7.6$ Hz), 2.96 (2H, t, $J = 7.2$ Hz), 7.18–7.22 (3H, m), 7.25–7.37 (4H, m), 7.70 (1H, d, $J = 7.2$ Hz), 7.72 (1H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 21.3, 25.8, 35.2, 37.7, 125.2, 125.9, 128.4, 128.4, 128.5, 128.5, 133.7, 137.0, 138.3, 141.7, 200.4.

1-(3-chlorophenyl)-4-phenylbutan-1-one (14ak)

White solid; IR (neat) 3018, 2941, 2860, 2399, 1688, 1571, 1421, 1350, 1215, 1076, 999, 927, 906, 771, 700, 669 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.39–1.54 (4H, m), 1.73–1.83 (4H, m), 2.98 (2H, t, $J = 7.6$ Hz), 3.54 (2H, t, $J = 6.8$ Hz), 7.46 (2H, dd, $J = 7.6$ Hz), 7.56 (1H, dd, $J = 7.2$ Hz), 7.96 (2H, d, $J = 7.2$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 24.1,

26.7, 28.6, 32.4, 38.4, 45.0, 128.0, 128.6, 132.9, 137.0, 200.3; HRMS ESI (m/z): found, 259.0889, calcd for C₁₆H₁₆OCl: [M+H]⁺, 259.0890.

1-(3-nitrophenyl)-4-phenylbutan-1-one (14al)

White solid; IR (neat) 3018, 1693, 1612, 1533, 1350, 1217, 756, 700, 669 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.09–2.16 (2H, m), 2.75 (2H, t, *J* = 7.6 Hz), 3.03 (2H, t, *J* = 7.2 Hz), 7.20–7.22 (3H, m), 7.28–7.32 (2H, m), 7.66 (1H, dd, *J* = 8 Hz), 8.24 (1H, d, *J* = 7.6 Hz), 8.41 (1H, d, *J* = 8 Hz), 8.73 (1H, s); ¹³C NMR (100 MHz, CDCl₃) δ 25.3, 35.0, 37.8, 122.9, 126.1, 127.3, 128.5, 129.8, 133.5, 138.2, 141.2, 148.4, 197.7; HRMS ESI (m/z): found, 250.1225, calcd for C₁₇H₁₆NO: [M+H]⁺, 250.1232.

3-(4-phenylbutanoyl)benzonitrile (14am)

Colorless oil; IR (neat) 2947, 2831, 1655, 1449, 1398, 1124, 1020 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.05–2.14 (2H, m), 2.73 (2H, t, *J* = 7.6 Hz), 2.96 (2H, t, *J* = 7.2 Hz), 7.19–7.23 (3H, m), 7.28–7.32 (2H, m), 7.58 (1H, dd, *J* = 7.6, 8 Hz), 7.82 (1H, d, *J* = 7.6 Hz), 8.12 (1H, d, *J* = 7.6 Hz), 8.17 (1H, s); ¹³C NMR (100 MHz, CDCl₃) δ 25.3, 35.0, 37.7, 113.2, 118.0, 126.2, 128.5, 129.6, 131.7, 131.9, 135.8, 137.7, 141.2, 197.9; HRMS ESI (m/z): found, 250.1227, calcd for C₁₇H₁₆NO: [M+H]⁺, 250.1232.

(1E)-1, 6-diphenylhex-1-en-3-one (14an)^[27]

Colorless liquid; ¹H NMR (400 MHz, CDCl₃) δ 1.99–2.07 (2H, m), 2.66–2.72 (4H, m), 6.72 (1H, d, *J* = 16.4 Hz), 7.20–7.22 (3H, m), 7.28–7.32 (2H, m), 7.39 (1H, d, *J* = 3.2 Hz), 7.49 (1H, s), 7.53 (1H, s); ¹³C NMR (100 MHz, CDCl₃) δ 25.7, 35.2, 40.0, 126.0, 126.2, 128.2, 128.4, 128.5, 128.9, 130.4, 134.5, 141.6, 142.4, 200.2.

(2E)-7-phenylhept-2-en-4-one (14ao)^[28]

Colorless liquid; ¹H NMR (400 MHz, CDCl₃) δ 1.88 (3H, dd, *J* = 5.2, 1.6 Hz), 1.91–1.98 (2H, m), 2.53 (2H, *J* = 7.2 Hz), 2.64 (2H, *J* = 7.6 Hz), 6.08–6.13 (1H, m), 6.76–6.85 (1H, m), 7.17–7.20 (3H, m), 7.26–7.30 (2H, m); ¹³C NMR (100 MHz, CDCl₃) δ 18.2, 25.6, 35.2, 39.1, 125.9, 128.3, 128.5, 131.9, 141.7, 142.4, 200.2.

(2Z)-1-oxo-1,5-diphenylpent-2-en-2-yl benzoate (15ae)^[1]

Colorless oil; ¹H NMR (500 MHz, CDCl₃) δ 2.68 (2H, dt, *J* = 7.4, 7.4 Hz), 2.82 (2H, t, *J* = 7.4 Hz), 6.22 (1H, t, *J* = 7.4 Hz), 7.17–7.22 (3H, m), 7.27–7.30 (2H, m), 7.39–7.42 (2H, m), 7.46–7.54 (3H, m), 7.57–7.63 (1H, m), 7.75–7.77 (2H, m), 8.11–8.12 (2H, m); ¹³C

NMR (125 MHz, CDCl₃) δ 28.0, 34.4, 126.3, 128.2, 128.4, 128.5, 128.5, 128.6, 129.4, 130.2, 132.4, 133.1, 133.7, 136.8, 140.5, 146.1, 164.3, 189.7.

(2Z)-1-(4-methylphenyl)-1-oxo-5-phenylpent-2-en-2-yl 4-methylbenzoate (15af)

White solid; IR (neat) 3018, 2941, 2399, 1734, 1662, 1271, 1215, 1076, 927, 756, 669 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.40 (3H, s), 2.44 (3H, s), 2.66 (2H, dt, J = 6.8, 7.6 Hz), 2.82 (2H, t, J = 7.6 Hz), 6.18 (1H, t, J = 7.6 Hz), 7.18–7.23 (5H, m), 7.26–7.31 (4H, m), 7.68 (2H, d, J = 8.4 Hz), 8.00 (2H, d, J = 8.4 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 21.6, 21.8, 27.9, 34.5, 126.0, 126.3, 128.4, 128.5, 128.9, 129.3, 129.6, 130.3, 132.1, 134.1, 140.7, 143.2, 144.6, 146.2, 164.4, 189.5; HRMS ESI (m/z): found, 385.1804, calcd for C₂₆H₂₅O₃: [M+H]⁺, 385.1804.

(2Z)-1-(3-methoxyphenyl)-1-oxo-5-phenylpent-2-en-2-yl-3-methoxybenzoate (15ai)

White solid; IR (neat) 3018, 2941, 2860, 2399, 1734, 1662, 1610, 1489, 1450, 1271, 1215, 1125, 756, 669 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.68 (2H, dt, J = 7.2, 7.6 Hz), 2.82 (2H, t, J = 7.6 Hz), 3.82 (3H, s), 3.86 (3H, s), 6.26 (1H, t, J = 7.6 Hz), 7.08 (1H, d, J = 7.6 Hz), 7.16–7.20 (3H, m), 7.22–7.35 (6H, m), 7.38–7.42 (1H, m), 7.62 (1H, s), 7.73 (1H, d,

$J = 7.6$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 28.0, 34.4, 55.4, 55.5, 113.7, 114.5, 119.0, 120.4, 122.1, 122.7, 126.3, 128.4, 128.6, 129.2, 129.6, 129.9, 133.2, 138.1, 140.5, 146.1, 159.5, 159.7, 164.2, 189.4.

(2Z)-1-(3-methylphenyl)-1-oxo-5-phenylpent-2-en-2-yl 3-methylbenzoate (15aj)

White solid; IR (neat) 3018, 2941, 2829, 2399, 1662, 1271, 1215, 1026, 927, 769, 669 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 2.38 (3H, s), 2.43 (3H, s), 2.67 (2H, dt, $J = 7.6$ Hz, 7.6 Hz), 2.82 (2H, t, $J = 7.6$ Hz), 6.22 (1H, t, $J = 7.6$ Hz), 7.18-7.23 (3H, m), 7.27-7.35 (4H, m), 7.38 (1H, d, $J = 7.6$ Hz), 7.43 (1H, d, $J = 7.6$ Hz), 7.55 (2H, d, $J = 8$ Hz), 7.92 (2H, d, $J = 7.6$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 21.2, 21.3, 28.0, 34.4, 126.3, 126.7, 127.4, 128.1, 128.4, 128.4, 128.5, 128.6, 129.9, 130.8, 133.0, 133.2, 134.5, 136.9, 138.0, 138.4, 140.6, 146.2, 164.6, 189.9; HRMS ESI (m/z): found, 385.1806, calcd for $\text{C}_{26}\text{H}_{25}\text{O}_3$: $[\text{M}+\text{H}]^+$, 385.1804.

General Procedure for Rh-Catalyzed Cross-Coupling of Acylsilane with Alkylanhydride.

To a toluene solution (0.2 ml) of acylsilane (0.2 mmol) was added $[\text{RhCl}(\text{CO})_2]_2$ (3.9 mg, 0.05 mmol) and acid anhydride (0.8 mmol) and the mixture was heated at 110 $^\circ\text{C}$ for 36 h in a sealed tube under N_2 atmosphere. After evaporation of the solvent, the crude products were purified by PTLC (hexane: EtOAc = 4: 1) to afford product.

(3Z)-2-oxo-6-phenylhex-3-en-3-yl acetate (15aa)

Colorless oil; IR (neat) 3061, 3028, 2972, 1762, 1686, 1647, 1371, 1265, 1207, 1099, 1049, 1020, 750, 700, 630 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 2.24 (s, 3H), 2.27 (s, 3H), 2.51 (2H, dt, $J = 7.6, 7.6$ Hz), 2.77 (2H, t, $J = 7.6$ Hz), 6.45 (1H, t, $J = 7.6$ Hz), 7.18–7.25 (3H, m), 7.29–7.32 (2H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 20.2, 25.1, 27.8, 34.1, 126.3, 128.2, 128.5, 131.6, 140.4, 146.4, 168.5, 191.2; HRMS ESI (m/z): found, 233.1174, calcd for $\text{C}_{14}\text{H}_{17}\text{O}_3$: $[\text{M}+\text{H}]^+$, 233.1178.

(3Z)-5-oxo-1-phenylhept-3-en-4-yl propanoate (15ab)

Colorless oil; IR (neat) 3061, 3026, 2980, 2939, 1759, 1691, 1653, 1603, 1497, 1454, 1418, 1352, 1190, 1143, 1092, 1082, 1020, 951, 804, 750, 700 cm^{-1} ; Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 1.09 (3H, t, $J = 7.2$ Hz), 1.23 (3H, t, $J = 7.6$ Hz), 2.47–2.63 (6H, m), 2.77 (2H, t, $J = 8$ Hz), 6.44 (2H, t, $J = 7.2$ Hz), 7.18–7.24 (3H, m), 7.29–7.32 (2H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 7.9, 9.0, 27.1, 27.7, 30.4, 34.2, 126.3, 128.3, 128.5, 130.1, 140.5, 146.1, 172.2, 194.4; HRMS ESI (m/z): found, 261.1489, calcd for $\text{C}_{16}\text{H}_{21}\text{O}_3$: $[\text{M}+\text{H}]^+$, 261.1491.

(3Z)-7-methyl-5-oxo-1-phenyloct-3-en-4-yl-3-methylbutanoate (15ap)

Colorless oil; IR (neat) 2958, 2872, 1757, 1682, 1645, 1468, 1454, 1373, 1290, 1238, 1180, 1153, 1103, 1014, 754, 700 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.92 (6H, d, $J = 6.8$ Hz), 1.04 (6H, d, $J = 6.8$ Hz), 2.40 (2H, d, $J = 6.8$ Hz), 2.44 (2H, d, $J = 7.2$ Hz), 2.50 (2H, dt, $J = 7.6, 7.6$ Hz), 2.77 (2H, t, $J = 7.6$ Hz), 6.42 (1H, t, $J = 7.2$ Hz), 7.17–7.24 (3H, m), 7.29–7.32 (2H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 22.4, 22.6, 25.3, 25.7, 27.9, 34.3, 42.7, 46.1, 126.3, 128.3, 128.6, 130.6, 140.5, 146.7, 170.3, 193.6. HRMS ESI (m/z): found, 317.2115, calcd for $\text{C}_{20}\text{H}_{29}\text{O}_3$: $[\text{M}+\text{H}]^+$, 317.2117.

(3Z)-6-methyl-5-oxo-1-phenylhept-3-en-4-yl 2-methylpropanoate (15ac)

Colorless oil; IR (neat) 3061, 3022, 2974, 2927, 1759, 1686, 1492, 1480, 1460, 1447, 1230, 1143, 1132, 985, 752, 700 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.11 (6H, d, $J = 6.8$ Hz), 1.29 (6H, d, $J = 7.2$ Hz), 2.50 (2H, $J = 7.6, 7.6$ Hz), 2.73–2.82 (3H, m), 3.01–3.08 (1H, m), 6.44 (1H, t, $J = 7.2$ Hz), 7.17–7.24 (3H, m), 7.28–7.32 (2H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 18.9, 19.0, 27.8, 33.8, 34.3, 34.7, 126.3, 128.3, 128.6, 130.1, 140.6, 145.4, 174.8, 198.0; HRMS ESI (m/z): found, 289.1803, calcd for $\text{C}_{18}\text{H}_{25}\text{O}_3$: $[\text{M}+\text{H}]^+$, 289.1804.

(1Z)-1-(2-methylphenyl)-3-oxobut-1-en-2-yl acetate (15ga)

Colorless oil; IR (neat) 3061, 3022, 2974, 2927, 1764, 1681, 1637, 1598, 1483, 1462, 1431, 1371, 1298, 1286, 1244, 1201, 1076 1047, 1008, 968, 920, 881, 816, 754, 640 cm^{-1} ; Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 2.22 (3H, s), 2.39 (3H, s), 2.44 (3H, s), 7.19–7.29 (3H, m), 7.39 (s, 1H), 7.55 (1H, d, $J = 7.6$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 20.0, 20.6, 25.4, 126.1, 126.2, 128.8, 129.7, 130.5, 130.8, 137.6, 145.0, 168.7, 192.2; HRMS ESI (m/z): found, 219.1016, calcd for $\text{C}_{13}\text{H}_{15}\text{O}_3$: $[\text{M}+\text{H}]^+$, 219.1021.

(3Z)-2-oxonona-3,8-dien-3-yl acetate (15ha)

Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 1.53–1.60 (2H, m), 2.09 (2H, dt, $J = 7.2, 6.8$ Hz), 2.20 (2H, dt, $J = 7.6, 7.6$ Hz), 2.25 (3H, s), 2.30 (3H, s), 5.00 (2H, dd, $J = 18.4, 10.8$ Hz), 5.73–5.83 (1H, m), 6.45 (1H, t, $J = 7.6$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 20.3, 25.1, 25.6, 27.3, 33.2, 115.3, 132.6, 137.7, 146.4, 168.6, 191.3; HRMS ESI (m/z): found, 197.1180, calcd for $\text{C}_{11}\text{H}_{17}\text{O}_3$: $[\text{M}+\text{H}]^+$, 197.1178.

(3Z)-2-oxonon-3-en-3-yl acetate (15ca)

Colorless oil; IR (neat) 3018, 2945, 2929, 2860, 2399, 1759, 1685, 1645, 1373, 1215, 1068, 927, 756, 669 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.90 (3H, t, $J = 6.8$ Hz), 1.29–1.33 (4H, m), 1.43–1.50 (2H, m), 2.18 (2H, dt, $J = 7.6$ Hz, 7.6 Hz), 2.25 (3H, s), 2.30 (3H, s), 6.45 (1H, t, $J = 7.6$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 13.9, 20.3, 22.3, 25.1, 26.2, 27.8, 31.4, 133.2, 146.2, 168.6, 191.3; HRMS ESI (m/z): found, 199.1329, calcd for $\text{C}_{11}\text{H}_{19}\text{O}_3$: $[\text{M}+\text{H}]^+$, 199.1334.

7.5. C–H Activation By Rhodium(I) Complex

To a toluene solution (0.2 ml) of 4-phenyl-1-trimethylsilylbutan-1-one (44 mg, 0.2 mmol) was added $[\text{RhCl}(\text{CO})_2]_2$ (3.9 mg, 0.05 mmol) and ethyl 2-iodoacetate (128 mg, 0.6 mmol) and the mixture was heated at 150 $^\circ\text{C}$ for 36 h in a sealed tube under N_2 atmosphere. After evaporation of the solvent, the crude products were purified by PTLC (hexane: diethyl acetate = 4:1) to afford 1,2,3,4-tetrahydronaphthalen-1-one in 64% yield.

1,2,3,4-tetrahydronaphthalen-1-one (16)^[29]

Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 2.11–2.18 (2H, m), 2.66 (2H, t, $J = 6.4$ Hz), 2.97 (2H, t, $J = 6$ Hz), 7.24–7.33 (2H, m), 7.45–7.49 (1H, m), 8.04 (1H, d, $J = 8$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 23.3, 29.7, 39.2, 126.6, 127.2, 132.6, 133.4, 144.5, 198.4.

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Yanni Yue; Hiroki Yamamoto; Motoki Yamane, “Rhodium-Catalyzed Homocoupling of (1-Acyloxyvinyl)silanes: Synthesis of the 1,3-Diene-2,3-diyl Diesters and Their Derivatives” *Synlett* **2009**, 2831.

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Conferences

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