



HAL
open science

Acylsilane Directed Rh-Catalyzed Arene C-H Alkylation with Maleimides and Visible-Light-Induced Siloxycarbene-Amide Cyclization: [3+2] Carbo-Annulation in Ru Catalysis

Raju Vaggu, Nagender Thadem, Manda Rajesh, René Grée, Saibal Das

► **To cite this version:**

Raju Vaggu, Nagender Thadem, Manda Rajesh, René Grée, Saibal Das. Acylsilane Directed Rh-Catalyzed Arene C-H Alkylation with Maleimides and Visible-Light-Induced Siloxycarbene-Amide Cyclization: [3+2] Carbo-Annulation in Ru Catalysis. *Organic Letters*, 2023, 25 (15), pp.2594-2599. 10.1021/acs.orglett.3c00487 . hal-04121005

HAL Id: hal-04121005

<https://hal.science/hal-04121005>

Submitted on 7 Jun 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

This document is confidential and is proprietary to the American Chemical Society and its authors. Do not copy or disclose without written permission. If you have received this item in error, notify the sender and delete all copies.

Acylsilane Directed Rh-Catalyzed Arene C-H Alkylation with Maleimides and Visible-Light-Induced Siloxycarbene-Amide Cyclization: [3+2] Carbo-Annulation in Ru Catalysis

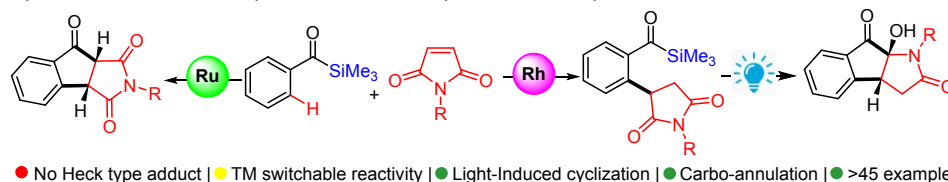
Journal:	<i>Organic Letters</i>
Manuscript ID	ol-2023-00487d.R2
Manuscript Type:	Communication
Date Submitted by the Author:	n/a
Complete List of Authors:	Vaggu, Raju; Indian Institute of Chemical Technology Thadem, Nagender; Indian Institute of Chemical Technology CSIR Rajesh, Manda; Purdue University, Department of Chemistry Gree, Rene; Universite de Rennes 1, Chimie et Photonique MoleculairesCNRS UMR 6226 Das, Saibal; Indian Institute of Chemical Technology

SCHOLARONE™
Manuscripts

Acylsilane Directed Rh-Catalyzed Arene C-H Alkylation with Maleimides and Visible-Light-Induced Siloxycarbene-Amide Cyclization: [3+2] Carbo-Annulation in Ru Catalysis

Raju Vaggu,^{a,b,†} Nagender Thadem,^{a,b,†} Manda Rajesh,^{a,‡} René Grée^c and Saibal Das^{a,b,*}

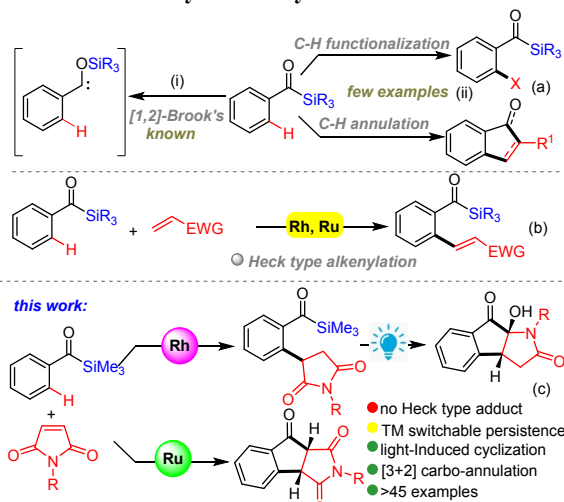
^aDepartment of Organic Synthesis & Process Chemistry, CSIR-Indian Institute of Chemical Technology (CSIR-IICT), Hyderabad 500007, India. E-mail saibal@iict.res.in. ^bAcademy of Scientific and Innovative Research (AcSIR), Ghaziabad, 201002, India. ^cInstitut des Sciences Chimiques de Rennes, Université de Rennes1, CNRS UMR 6226, 35042 Rennes, France.



ABSTRACT: We herein demonstrate the acylsilane directed Rh-catalyzed arene C-H bond alkylation with maleimides. The resulting derivatives were utilized in visible-light-induced intramolecular siloxycarbene-amide cyclization for the synthesis of new tricyclic γ -lactams. In Parallel, we also harnessed the same acylsilane and maleimide units through [3+2] carbo-annulation by using Ru-catalysis. A wide range of maleimides and aroylsilanes were used to establish the broadness of these transformations.

Acylsilanes are captivating chemical probes in organic chemistry¹⁻⁶ which are partaking in wide range of transformations, including cross couplings, aldol reactions, radical reactions, nucleophilic additions, C-H functionalizations, and annulation reactions. From a plethora of possible reactions of acylsilanes, the nucleophilic addition/1,2-Brook rearrangement is one of the most attractive transformations to construct C-C and C-X bonds through singlet nucleophilic siloxycarbene intermediates.³⁻⁵ This rearrangement offers chemists an expeditious path to probe in unearthed chemical space for various organic synthetic activities. Diverse elegant routes were established for such rearrangements, using visible-light, organo catalysts and transition-metal catalysts with a range of carbon and heteroatom trapping reagents (Scheme 1ai).

Scheme 1: Reactivity of benzoyl silanes



Conversely, directing group (DG) assisted transition-metal catalyzed site selective C-H functionalization is a swift strategy to construct verity of complex acyclic and cyclic motifs in a single operation.⁷ These strategies not only avoid the pre-

functionalization of the reactive centers but also fetch atom- and step-economy in the anticipated transformation with high functional group compatibility. Over the past few years, many splendid routes were established using a large spectrum of transition-metals (Pd, Rh, Ru, Ir, Cu, Co, Mn, Ni, etc.) and coupling partners. In this context, pendent chelating group assists the metal catalyst in activation of C-H bond through pre-coordination (concerted metalation-deprotonation). These chelating directing groups mainly nitrogen, oxygen, and carbon-based functional groups, which will also join in annulation reactions along with various π -congeners. In this paradigm, hefty series of DGs, including weakly coordinated carbonyls also illustrated in such C-H functionalization and annulation reactions.⁷

In stark contrast to the Brook rearrangement, the *ortho* C-H functionalization of arene acylsilanes is subtle,⁶ because, these chemprobs have aldehyde trait which can endure supplementary transformations in given condition. The unscathed acylsilane is a potential reactive handle for later transformations which offers novel potentialities to this arsenal, as the acylsilane itself is a uniquely reactive center (*vide supra*). Using this weakly coordinated functional group as C-H directing group, some elegant functionalizations (alkenylation, amidation, allylation) and annulation (indene) transformations were documented via Rh,^{6a,f} Ir,^{6b} Ru^{6c-e} and Co^{6g} catalysis (Scheme 1aii). The Rh/Ru catalyzed C-H alkenylation (Heck type)^{6a, c} was reported using unsaturated carbonyl derivatives through β -hydride elimination, where both metals shown identical reactivity (Scheme 1b). However, the availability of acylsilane C-H functionalization strategies remains scanty. In this letter, we demonstrate the acylsilane directed Rh-catalyzed C-H alkylation with maleimides and subsequent visible-light-induced siloxycarbene-amide cyclization affording tricyclic indeno- γ -lactams. Further, a stereoselective annulation was also achieved under Ru catalysis with the same reactive partners (Scheme 1c).

The easily available and flexible reactive maleimides have been recently dragged a great attention of synthetic organic

chemists, due to the omnipresent nature of these motifs in various fields of biology.⁸ Specially, the succinimide and its fused derivatives are frequently present in natural products and biologically intriguing molecules (Figure 1).⁸

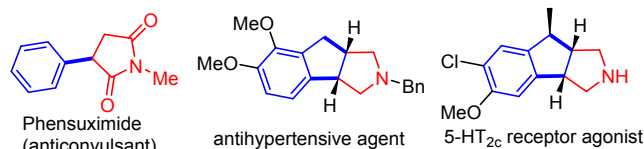
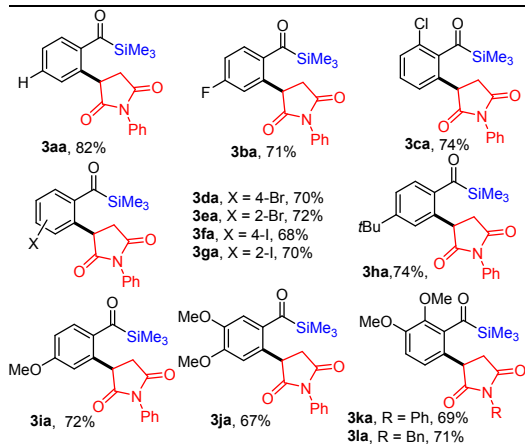
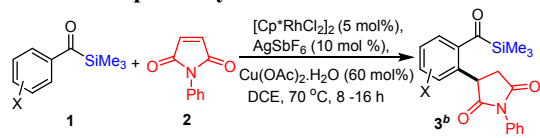


Figure 1. Some bioactive succinimide and indano-pyrrolidine derivatives

Maleimides are linchpin prototypes in DG assisted C-H activation reactions, which are most engaged one in three (*viz* alkenylating, alkylating and annulating reactions; depending on the kind of DG, metal catalyst and reaction conditions) coupling partners in C-H functionalization.⁹ Utilizing these maleimides, we herein report, the synthesis of acylsilylated phensuximide derivatives as well as indano- succinimide adducts in expeditious way.

Initially we conducted the reaction using benzoyl silane (**1a**) and *N*-phenyl maleimide (**2a**) as test substrates. After extensive optimization studies, we found that the reaction of **1a** with **2a** in presence of 5 mol% [Cp**Rh*Cl₂]₂, with 60 mol% of Cu(OAc)₂·H₂O as an additive and 10 mol % AgSbF₆ silver salt in DCE solvent at 70 °C afforded adduct **3aa** in 82% yield (for detailed optimization studies see Supporting Information). Having these optimized conditions in hand, we headed to examine the generality of the C-H alkylation path (Scheme 2).

Scheme 2. Scope of acylsilanes^a

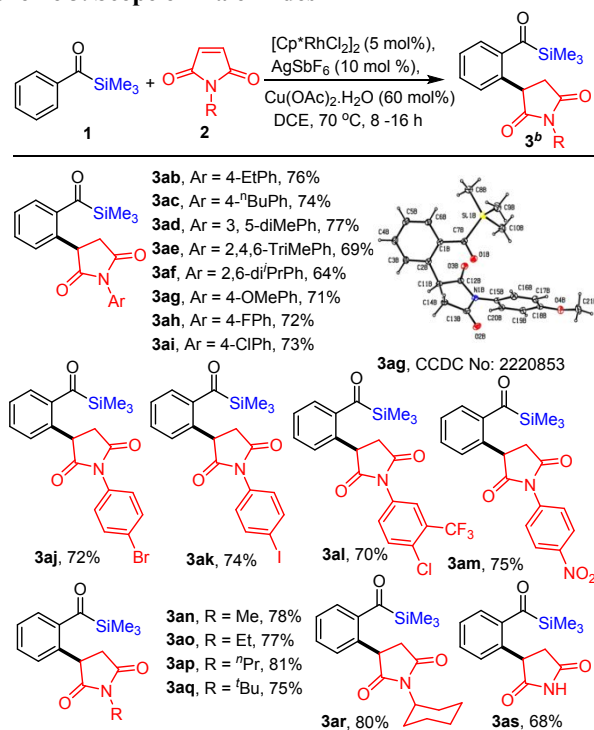


Reaction conditions: ^a **1** (0.25 mmol), **2** (0.375 mmol), [Cp**Rh*Cl₂]₂ (5 mol%), AgSbF₆ (10 mol %), Cu(OAc)₂·H₂O (60 mol%) in DCE (1.5 mL) ^bIsolated yield.

We first verified the substrate scope by using electronically distinct acylsilanes, thus the halogenated (F, Cl, Br and I) benzoyl silanes were well tolerated under the given conditions and afforded expected adducts **3ba-3ga** in 68-74% yields irrespective of their positions on core aryl group (*ortho* and *para*). The exquisite *iodo* functional group reactivity is particularly noteworthy, as it is one of the least often selected functional group in C-H activation. The resulting adducts could be used for further functionalization with various cross coupling conditions for succinimide handled products. To our astonishment, the *ortho* and *para* iodo substrates **1f-g** smoothly

transformed to C-H alkylated adducts **3fa-ga** in 68-70% yields. Subsequently, the electronically neutral *-tert*-Butyl and electronic rich alkoxy substitutions like methoxy, 3,4-dimethoxy and 2,3-dimethoxy benzoyl silanes (**1h-i**) could survive with equal ease in the formation of corresponding adducts **3ha-la** in 65-74% yields.

Scheme 3. Scope of Maleimides^a



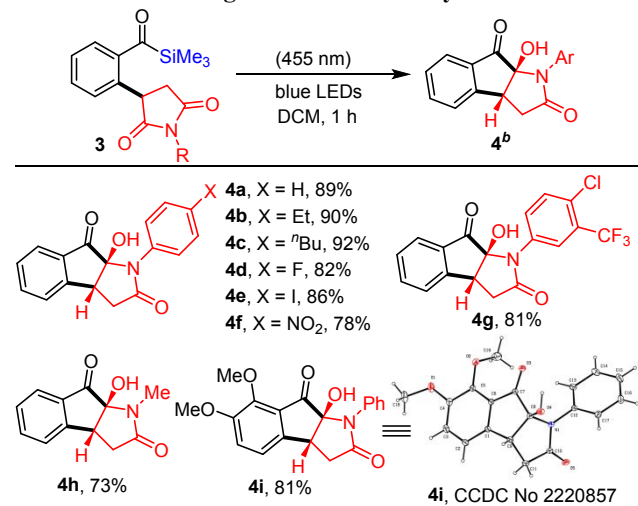
Reaction conditions: ^a **1** (0.25 mmol), **2** (0.375 mmol), [Cp**Rh*Cl₂]₂ (5 mol%), AgSbF₆ (10 mol %), Cu(OAc)₂·H₂O (60 mol%) in DCE (1.5 mL) ^bIsolated yield.

We subsequently investigated the reaction feasibility of various *N*-substituted maleimide coupling partners, as exemplified in Scheme 3. The alkyl groups (ethyl, dimethyl, trimethyl, diisopropyl and *n*-butyl) on *N*-aryl maleimides **2b-f** provided corresponding final products **3ab-af** in 64-77% yields. The *N*-*para*-methoxy phenyl maleimide delivered **3ag** in 71% yield and the structure was confirmed by X-ray crystallography. The halogenated *N*-aryl maleimides also showed equal reactivity in standard conditions. Thus, the F, Cl, Br and I substituted chemprobs **2h-k** afforded **3ah-ak** in good yields (72-74%). These functionalities could also be used in further extension reactions. The electron withdrawing CF₃, Cl and NO₂ aryl maleimides worked similarly to their halogenated cousins (**3al-am** in 70-75%). We further extended our focus to test the viability of *N*-alkylated maleimides under title conditions. The *N*-Methyl maleimide **2n** afforded the acylsilylated phensuximide **3an** in 78% yield. The other *N*-alkylated (Et, *n*-propyl, ^tBu and cyclohexyl) maleimides showed analogous reactivity to *N*-methyl maleimide (**3ao-ar**). To our delight, the *N*-unsubstituted maleimide **2s** also reacted with **1a** in equal manner. Setting a limitation, the other doubly activated alkenes (maleic anhydride, 1,4-benzoquinone) were found to be inapt in this transformation.

In continuation, the meticulous search on the aforementioned 1,2-Brook rearrangement brings to light the meagerness in the intramolecular trapping of such reactions.⁴ Thus the utility of unscathed acylsilane functionality in concomitant reaction with pendent reactive handle is limited to certain section of

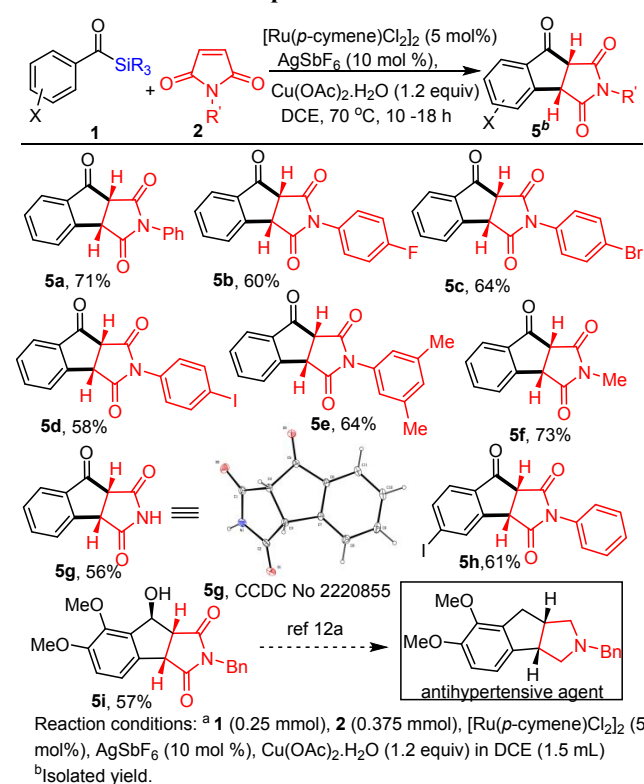
molecules.⁵ In order to exemplify such a possibility, we utilized the newly formed *o*-succinimide benzoyl silanes in siloxycarbene-amide cyclization through 1,2-silyl migration followed by a cyclization sequence towards pharmacologically significant tricyclic hydroxy γ -lactam derivatives **4** (Scheme 4).¹⁰

Scheme 4. Visible-light-induced amide cyclization



Owing to the occurrence of two stereogenic centers along with a quaternary carbon, the synthesis of these privileged tricyclic compounds are challenging.^{10a,b} To achieve this synthesis in easy and simple manner, we conducted a reaction with **3aa** under 455 nm visible-light (blue LEDs) (see SI for optimization studies) which provided the cyclization product **4a** in 89%.

Scheme 5. Substrate scope for carbo-annulation reaction^a



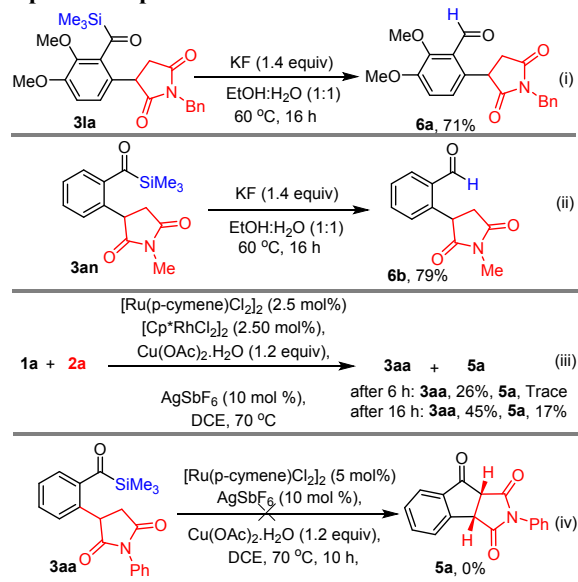
The other functionalized succinimide derivatives (aryl-alkyl, halo, NO₂ and alkyl) also participated well in this light-

mediated amide cyclization affording corresponding tricyclic products in good to excellent yields (**4b-4h** in 73-92%). The structure of the tricyclic γ -lactam **4i** was confirmed by X-ray crystal analysis. Moving further, the alteration in the reactivity (chemo-divergence and/or regio-divergence) of same substrates came from switching the metal catalysts, metal attached ligand.¹¹ An analogy to Rh(III)-catalyst, the other metal catalysts, for instance, less expensive Ru(II)-catalyst often provide complementary reaction patterns.^{11c} We then quested towards carbo-annulation using same substrates.

In this line, we harnessed aroylsilanes and maleimides in Ru(II)-catalyzed carbo-annulation approach for biologically intriguing indano-succinimide motifs.¹² Initially, we synthesized compound **5a** in 71% yield under Ru-catalysis (for optimization studies, see supporting information) as shown in Scheme 5. To ascertain the generality of this annulation, we screened electronically dissimilar substrates under established conditions. The *N*-aryl functionalized maleimides (with halogens and alkyls) proved to be good starting materials for this reaction with benzoyl silane (**5b-e** in 58-64% yields). Delightfully, the *N*-methylated and *N*-unsubstituted maleimides produce the corresponding **5f** and **5g** in fair to good yields (56-73%). The structure of **5g** was confirmed by X-ray crystallography. Subsequently, iodo-substituted indanone **5h** was also synthesized from aroylsilane and maleimide. Whereas, the *ortho*-methoxy substituted acylsilane afforded the indanol product^{12b} **5i** in 57% yield only, perhaps due to the *ortho*-methoxy coordination which might have promoted the 1,2-Brook and proto-demetalation sequence. It is noteworthy to mention that the reduced pyrido-indanol (**5i**) was found as antihypertensive agent.¹²

Lastly, we utilized the synthesized succinimide derivative for further transformation. First, we synthesized the aldehyde **6a** from **3la** in 71% yield. This aldehyde **6a** is an intermediate for antihypertensive agent^{12a} (Scheme 6, eq i). We further deacylated the compound **3an** for the synthesis of formylated phensuximide **6b** in 79% yield (Scheme 6, eq ii).

Scheme 6. Synthetic transformations and catalyst competitive experiments

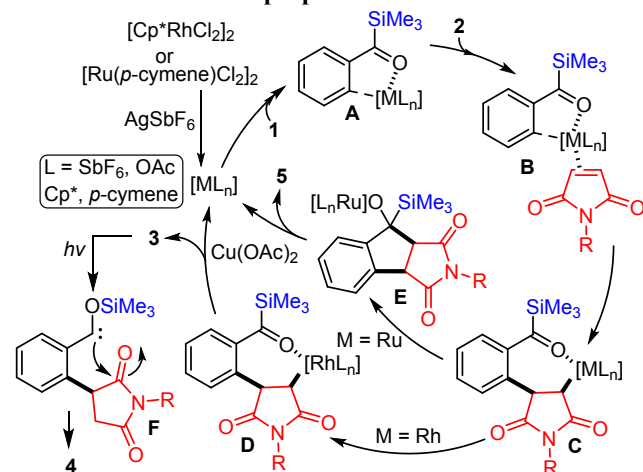


In continuation, to verify the competitive nature of rhodium and ruthenium catalysis, we performed a reaction using both catalysts in single pot (Scheme 6, eq iii). After 6 h of the

reaction we observed C-alkylation as the only product. In prolongation time we isolated **3aa** in 45% along with annulated adduct **5a** (17% yield). We further conducted the cyclization reaction using **3aa** under Ru-catalysis no expected product **5a** was observed (Scheme 6, eq iv). These results suggest that the C-metal interaction is crucial for annulation.

Based on these observations and literature precedence, we propose the tentative mechanism, as shown in Scheme 7. Initially the cationic metal catalyst activates the C-H bond through concerted-metalation-deprotonation process, which upon chelation, followed by insertion of maleimide affords the intermediate **C**. This intermediate deliver compound **3** through proto-derhodation of C-Rh bond. In the case of ruthenium, the less acidic C-Ru bond inserts into the acylsilane and provides the intermediate **E**, which upon desilyl-rutheniation gave carbo-annulated adduct **5**.

Scheme 7. Mechanistic proposal.



Further, the $\text{Cu}(\text{OAc})_2$ oxidizes the metal catalysts for the next cycle. The tricyclic hydroxy γ -lactams (**4**) were achieved through light-induced 1,2-rearrangement followed by the siloxycarbene insertion into amide bond and silyl migration sequence.

In conclusion, we have unveiled the acylsilane directed Rh-catalyzed C-H bond alkylation with maleimides for the synthesis of *ortho*-acylsilylated phensuximide derivatives. The weakly coordinated acylsilane group triggers the C-H bond functionalization and intervenes in the concurrent transformations. The synthesized *o*-succinimide aroylsilanes proved to be remarkable substrates in visible-light-induced intramolecular siloxycarbene-amide cyclization towards indano- γ -lactams. In contrast to the Rh-catalyzed alkylation, we further pursued the stereo-selective [3+2] annulation of aroylsilanes and maleimides using Ru-catalysis to indenol succinimide fused derivatives. Efforts to expand the aroylsilane reactivities are ongoing in our laboratory.

ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information Statement

“The Supporting Information is available free of charge at <https://pubs.acs.org>.”

This contains optimization studies, experimental procedures, characterization of related compounds and X-ray crystal structures (CCDC Nos 2220583 (**3ag**), 2220857 (**4i**) and 2220855 (**5g**)).

AUTHOR INFORMATION

Corresponding Author

Saibal Das -^aDepartment of Organic Synthesis & Process Chemistry, CSIR-Indian Institute of Chemical Technology (CSIR-IICT), Hyderabad 500007, India. E-mail saibal@iict.res.in.
^bAcademy of Scientific and Innovative Research (AcSIR), Ghaziabad, 201002, India.

Authors

Raju Vaggu -^aDepartment of Organic Synthesis & Process Chemistry, CSIR-Indian Institute of Chemical Technology (CSIR-IICT), Hyderabad 500007, India. ^bAcademy of Scientific and Innovative Research (AcSIR), Ghaziabad, 201002, India.

Nagender Thadem -^aDepartment of Organic Synthesis & Process Chemistry, CSIR-Indian Institute of Chemical Technology (CSIR-IICT), Hyderabad 500007, India. ^bAcademy of Scientific and Innovative Research (AcSIR), Ghaziabad, 201002, India.

Manda Rajesh -^aDepartment of Organic Synthesis & Process Chemistry, CSIR-Indian Institute of Chemical Technology, Hyderabad 500007, India. (Present address: Department of Chemistry, Purdue University, West Lafayette, Indiana, 47906 USA)

René Grée -^cUniv Rennes, Institute for Chemical Sciences in Rennes, CNRS UMR 6226, 35000 Rennes, France

Author Contributions

*These authors contributed equally.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

V. R. and N. T. thank CSIR for fellowship. M. R. thank CSIR-IICT for financial support. R. G. and S. D. thanks the Indo-French “Joint Laboratory for Natural Products and Synthesis toward Affordable Health” program between CSIR- Indian Institute of Chemical Technology and University of Rennes for the platform to carry out the finding jointly. We sincerely thank the Department of Analytical and Structural Chemistry at CSIR-IICT for all the analytical support and especially Dr. Sridhar Balasubramanian for X-ray crystal data. We gratefully acknowledge the overall support by CSIR-IICT to perform the research (IICT/Pubs./2023/011)

REFERENCES

1. *Reviews on acylsilanes* (a) Zhang, H.-J.; Priebbenow, D. L.; Bolm, C. Acylsilanes: Valuable Organosilicon Reagents in Organic Synthesis. *Chem. Soc. Rev.* **2013**, *42*, 8540-8571. (b) Priebbenow, D. L. Insights into the Stability of Siloxy Carbene Intermediates and Their Corresponding Oxocarbenium Ions. *J. Org. Chem.* **2019**, *84*, 11813-11822. (c) Priebbenow, D. L. Silicon-Derived Singlet Nucleophilic Carbene Reagents in Organic Synthesis. *Adv. Synth. Catal.* **2020**, *362*, 1927-1946. (d) Feng, J.-J.; Mao, W.; Zhang, L.; Oestreich, M. Activation of the Si-B interelement bond related to catalysis. *Chem. Soc. Rev.* **2021**, *50*, 2010-2073. (e) Hong, W. P.; Lim, H. N.; Shin, I. Recent progress and perspectives in photo-induced organic reactions of acylsilanes. *Org. Chem. Front.* **2023**, *10*, 819-836.
2. (a) Tatsumi, K.; Tanabe, S.; Tsuji, Y.; Fujihara, T. Zinc-Catalyzed Synthesis of Acylsilanes Using Carboxylic Acids and a Silylborane in the Presence of Pivalic Anhydride. *Org. Lett.* **2019**, *21*, 10130-10133. (b) Wang, X.; Liu, F.; Li, Y.; Yan, Z.; Qiang, Q.; Rong, Z.-Q. Recent Advances in the Synthesis of Acylsilanes. *ChemCatChem*

- 2020, 12, 5022-5033. (c) Cheng, L.-J.; Mankad, N. P. Cu-Catalyzed Carbonylative Silylation of Alkyl Halides: Efficient Access to Acylsilanes. *J. Am. Chem. Soc.* **2020**, *142*, 80-84. (d) Feng, J.-J.; Mao, W.; Zhang, L.; Oestreich, M. Activation of the Si-B interelement bond related to catalysis. *Chem. Soc. Rev.* **2021**, *50*, 2010-2073.
3. (a) Schmink, J. R.; Krska, S. W. Reversed-Polarity Synthesis of Diaryl Ketones via Palladium-Catalyzed Cross-Coupling of Acylsilanes. *J. Am. Chem. Soc.* **2011**, *133*, 19574-19577. (b) Labarre-Lainé, J.; Beniazza, R.; Desvergnés, V.; Landais, Y. Convergent Access to Bis-spiroacetals through a Sila-Stetter-Ketalization Cascade. *Org. Lett.* **2013**, *15*, 4706-4709. (c) Rong, J.; Oost, R.; Desmarchelier, A.; Minnaard, A. J.; Harutyunyan, S. R. Catalytic Asymmetric Alkylation of Acylsilanes. *Angew. Chem. Int. Ed.* **2015**, *54*, 3038-3042. (d) González, J.; Santamaría, J.; Ballesteros, A. Gold(I)-Catalyzed Addition of Silylacetylenes to Acylsilanes: Synthesis of Indanones by C-H Functionalization through a Gold(I) Carbenoid. *Angew. Chem. Int. Ed.* **2015**, *54*, 13678-13681. (e) Lu, P.; Feng, C.; Loh, T.-P. Divergent Functionalization of Indoles with Acryloyl Silanes via Rhodium-Catalyzed C-H Activation. *Org. Lett.* **2015**, *17*, 3210-3213. (f) Deng, Y.; Liu, Q.; Smith, A. B. III Oxidative [1,2]-Brook Rearrangements Exploiting Single-Electron Transfer: Photoredox-Catalyzed Alkylations and Arylations. *J. Am. Chem. Soc.* **2017**, *139*, 9487-9490. (g) Zhang, F.-G.; Marek, I. Brook Rearrangement as Trigger for Carbene Generation: Synthesis of Stereodefined and Fully Substituted Cyclobutenes. *J. Am. Chem. Soc.* **2017**, *139*, 8364-8370. (h) Takeda, M.; Mitsui, A.; Nagao, K.; Ohmiya, H. Reductive Coupling between Aromatic Aldehydes and Ketones or Imines by Copper Catalysis. *J. Am. Chem. Soc.* **2019**, *141*, 3664-3669. (i) He, X.; Zhao, Y.; Zhang, Z.; Shen, X. Tuning the Reactivity of Alkoxy Radicals from Cyclization to 1,2-Silyl Transfer: Stereoselective Synthesis of β -Substituted Cycloalcohols. *Org. Lett.* **2022**, *24*, 1991-1995.
4. (a) Shen, Z.; Dong, V. M. Benzofurans Prepared by C-H Bond Functionalization with Acylsilanes. *Angew. Chem. Int. Ed.* **2009**, *48*, 784-786. (b) Ito, K.; Tamashima, H.; Iwasawa, N.; Kusama, H. Photochemically Promoted Transition Metal-Free Cross-Coupling of Acylsilanes with Organoboronic Esters. *J. Am. Chem. Soc.* **2011**, *133*, 3716-3719. (c) Becker, P.; Priebbenow, D. L.; Zhang, H.-J.; Pirwerdjan, R.; Bolm, C. Photochemical Intermolecular Silylacetylations of Electron-Deficient Internal Alkynes. *J. Org. Chem.* **2014**, *79*, 814-817. (d) Capaldo, L.; Riccardi, R.; Ravelli, D.; Fagnoni, M. Acyl Radicals from Acylsilanes: Photoredox-Catalyzed Synthesis of Unsymmetrical Ketones. *ACS Catal.* **2018**, *8*, 304-309. (e) Ye, J.-H.; Quach, L.; Paulisch, T.; Glorius, F. Visible-Light-Induced, Metal-Free Carbene Insertion into B-H Bonds between Acylsilanes and Pinacolborane. *J. Am. Chem. Soc.* **2019**, *141*, 16227-16231. (f) Vale, J. R.; Valkonen, A.; Afonso, C. A. M.; Candeias, N. R. Synthesis of silacyclopent-2-en-4-ols via intramolecular [2 + 2] photocycloaddition of *be* zoyl(allyl)silanes. *Org. Chem. Front.* **2019**, *6*, 3793-3798. (g) Fan, Z.; Yi, Y.; Chen, S.; Xi, C. Visible-Light-Induced Catalyst-Free Carboxylation of Acylsilanes with Carbon Dioxide. *Org. Lett.* **2021**, *23*, 2303-2307. (h) Fan, Z.; Yi, Y.; Chen, S.; Xi, C. Visible-Light-Induced Catalyst-Free Carboxylation of Acylsilanes with Carbon Dioxide. *Org. Lett.* **2021**, *23*, 2303-2307. (i) Ma, L.; Yu, Y.; Xin, L.; Zhu, L.; Xia, J.; Ou, P.; Huang, X. Visible Light Enabled Formal Cross Silyl Benzoin Reaction as an Access to α -Hydroxyketones. *Adv. Synth. Catal.* **2021**, *363*, 2573-2577.
5. (a) Ye, J.-H.; Bellotti, P.; Paulisch, T. O.; Daniliuc, C. G.; Glorius, F. Visible-Light-Induced Cycloaddition of α -Ketoacylsilanes with Imines: Facile Access to β -Lactams. *Angew. Chem. Int. Ed.* **2021**, *60*, 13671-13676. (b) Yamaguchi, K.; Shimizu, T.; Miura, A.; Ishida, K.; Kusama, H. Photoinduced Intramolecular Cyclization of Acylsilanes Bearing a Boronate Moiety: Construction of a Highly Strained trans-Fused Bicyclo[3.3.0]octane Skeleton. *Org. Lett.* **2022**, *24*, 5807-5811. (c) Zhou, G.; Shen, X. Synthesis of Cyclopropenols Enabled by Visible-Light-Induced Organocatalyzed [2+1] Cyclization. *Angew. Chem. Int. Ed.* **2022**, *61*, No. e202115334. (d) Zhang, Y.; Zhou, G.; Gong, X.; Guo, Z.; Qi, X.; Shen, X. Diastereoselective Transfer of Tri(di)fluoroacetylsilanes-Derived Carbenes to Alkenes. *Angew. Chem. Int. Ed.* **2022**, *61*, No. e202202175.
6. *Acylsilane directed C-H activation*: (a) Becker, P.; Priebbenow, D. L.; Pirwerdjan, R.; Bolm, C. Acylsilanes in Rhodium (III)-Catalyzed Directed Aromatic C-H Alkenylations and Siloxycarbene Reactions with C-C Double Bonds. *Angew. Chem. Int. Ed.* **2014**, *53*, 269-271. (b) Becker, P.; Pirwerdjan, R.; Bolm, C. Acylsilanes in Iridium-Catalyzed Directed Amidation Reactions and Formation of Heterocycles via Siloxycarbenes. *Angew. Chem. Int. Ed.* **2015**, *54*, 15493-15496. (c) Lu, X.; Shen, C.; Meng, K.; Zhao, L.; Li, T.; Sun, Y.; Zhang, J.; Zhong, G. Acylsilane Directed Aromatic C-H Alkenylations by Ruthenium Catalysis. *Chem. Commun.* **2019**, *55*, 826-829. (d) Lu, X.; Zhang, J.; Xu, L.; Shen, W.; Yu, F.; Ding, L.; Zhong, G. Ruthenium-Catalyzed Brook Rearrangement Involved Domino Sequence Enabled by Acylsilane-Aldehyde Corporation. *Org. Lett.* **2020**, *22*, 5610-5616. (e) Yu, F.; Shen, W.; Sun, Y.; Liao, Y.; Jin, S.; Lu, X.; He, R.; Zhong, L.; Zhong, G.; Zhang, J. Ruthenium-catalyzed C-H amination of aroylsilanes. *Org. Biomol. Chem.* **2021**, *19*, 6313-6321.
7. (a) Engle, K. M.; Mei, T.-S.; Wasa, M.; Yu, J.-Q. Weak Coordination as a Powerful Means for Developing Broadly Useful C-H Functionalization Reactions. *Acc. Chem. Res.* **2012**, *45*, 788-802. (b) Sarkar, S. D.; Liu, W.; Kozhuskov, S.; Ackermann, L. Weakly Coordinating Directing Groups for Ruthenium(II)-Catalyzed C-H Activation. *Adv. Synth. Catal.* **2014**, *356*, 1461-1479. (c) Davies, H. M. L.; Morton, D.; Recent Advances in C-H Functionalization. *J. Org. Chem.* **2016**, *81*, 343-350. (d) Crabtree, R. W.; Lei, A. Introduction: CH Activation. *Chem. Rev.* **2017**, *117*, 8481-8482. (e) Gandeepan, P.; Müller, T.; Zell, D.; Cera, G.; Warratz, S.; Ackermann, L. 3d Transition Metals for C-H Activation. *Chem. Rev.* **2019**, *119*, 2192-2452. (f) Kumar, G.; Rajesh, M.; Lin, S.; Liu, S. Propargylic Alcohols as Coupling Partners in Transition-Metal-Catalyzed Arene C-H Activation. *Adv. Synth. Catal.* **2020**, *362*, 5238-5256. (g) Sinha, S. K.; Guin, S.; Maiti, S.; Biswas, J. P. Porey, S.; Maiti, D. Toolbox for Distal C-H Bond Functionalizations in Organic Molecules. *Chem. Rev.* **2022**, *122*, 5682-5841.
8. (a) Kinney, W.-A.; Luci, D.-K.; Maryanoff, B.-E. U.S. Patent Appl. 20050026917 A1 20050203, 2005. (b) Bennani, L.-Y.; Huck, B.; Robarge, M. J. U.S. Patent Appl. 20060025601 A1 20060202, 2006. (c) Sato, M.; Dander, J. E.; Sato, C.; Hung, Y.-S.; Gao, S.-S.; Tang, M.-C.; Hang, L.; Winter, J. M.; Garg, N. K.; Watanabe, K.; Tang, Y. Collaborative Biosynthesis of Maleimide- and Succinimide-Containing Natural Products by Fungal Polyketide Megasyntases. *J. Am. Chem. Soc.* **2017**, *139*, 5317-5320. (d) Wang, P.; Cui, Y.; Cai, C.; Chen, H.; Dai, Y.; Chen, P.; Kong, F.; Yuan, J.; Song, X.; Mei, W.; Dai, H. Two New Succinimide Derivatives *Cladosporins* A and B from the Mangrove-derived Fungus *Cladosporium* sp. HNSW-1. *Mar. Drugs* **2019**, *17*, 4-13. (e) Zhao, Z.; Yue, J.; Ji, X.; Nian, M.; Kang, K.; Qiao, H.; Zheng, X. Research progress in biological activities of succinimide derivatives. *Bioorg. Chem.* **2021**, *108*, 104557-104575. (f) Thadem, N.; Rajesh, M.; Das, S. Activator free diastereoselective 1,3-dipolar cycloaddition: a quick access to coumarin based spiro multi heterocyclic adducts. *RSC Adv.* **2021**, *11*, 29934-29938. (g) Thadem, N.; Rajesh, M.; Balaboina, H.; Das, S. Synthesis of bridgehead-azacycles via dual C-N/C-C annulation of α -amino acids, amins and maleimides. *Org. Biomol. Chem.* **2022**, *20*, 6368-6383.
9. *Maleimides in C-H activation*: (a) Manoharan, R.; Jeganmohan, M. Alkylation, Annulation and Alkenylation of Organic Molecules with Maleimides via Transition-Metal-Catalyzed C-H Bond Activation. *Asian J. Org. Chem.* **2019**, *8*, 1949-1969. (b) Gurram, R. K.; Rajesh, M.; Singam, M. K. R.; Nanubolu, J. B.; Reddy, M. S. A Sequential Activation of Alkyne and C-H Bonds for the Tandem Cyclization and Annulation of Alkynols and Maleimides through Cooperative Sc(III) and Cp*-Free Co(II) Catalysis. *Org. Lett.* **2020**, *22*, 5326-5330. (c) Liu, S.-L.; Shi, Y.; Xue, C.; Zhang, L.; Zhou, L.; Song, M.-P. Maleimides in Directing-Group-Controlled Transition-Metal-Catalyzed Selective C-H Alkylation. *Eur. J. Org. Chem.* **2021**, 5862-5879. (d) Liu, S.-L.; Ye, C.; Wang, X. Recent advances in transition-

- metal-catalyzed directed C–H alkenylation with maleimides. *Org. Biomol. Chem.* **2022**, *20*, 4837-4845.
10. (a) Wu, K.-J.; Li, G.-Q.; Li, Y.; Dai, L.-X.; You, S.-L. N-Heterocyclic carbene-catalyzed tandem aza-benzoin/Michael reactions: on site reversal of the reactivity of N-Boc imines. *Chem. Commun.* **2011**, *47*, 493-495. (b) Gesmundo, N. J.; Grandjean, J. M. M.; Nicewicz, D. A. Amide and Amine Nucleophiles in Polar Radical Crossover Cycloadditions: Synthesis of γ -Lactams and Pyrrolidines. *Org. Lett.* **2015**, *17*, 1316-1319.
11. (a) Lu, P.; Feng, C.; Loh, T.-P. Divergent Functionalization of Indoles with Acryloyl Silanes via Rhodium- Catalyzed C–H Activation. *Org. Lett.* **2015**, *17*, 3210-3213. (b) Song, S.; Lu, P.; Liu, H.; Cai, S.-H.; Feng, C.; Loh, T.-P. Switchable C–H Functionalization of *N*-Tosyl Acrylamides with Acryloylsilanes. *Org. Lett.* **2017**, *19*, 2869-2872. (c) Wang, M.; Kong, L.; Wu, Q.; Li, X. Ruthenium- and Rhodium-Catalyzed Chemodivergent Couplings of Ketene Dithioacetals and α -Diazo Ketones via C–H Activation/Functionalization. *Org. Lett.* **2018**, *20*, 4597-4600.
12. (a) Yang, H.; Liu, D.; Yu, Q.; Xia, S.; Yu, D.; Zhang, M.; Sun, B.; Zhang, F.-L. DBU-Promoted Intramolecular Crossed Aldol Reaction: A Facile Access to Indane-Fused Pyrrolidine. *Eur. J. Org. Chem.* **2019**, 852-856. (b) Li, X.-R.; Chen, S.-Q.; Fan, J.; Li, C.-J.; Wang, X.; Liu, Z.-W.; Shi, X.-Y. Controllable Tandem [3+2] Cyclization of Aromatic Aldehydes with Maleimides: Rhodium (III)-Catalyzed Divergent Synthesis of Indane-Fused Pyrrolidine-2,5-dione. *Org. Lett.* **2020**, *22*, 8808-881.