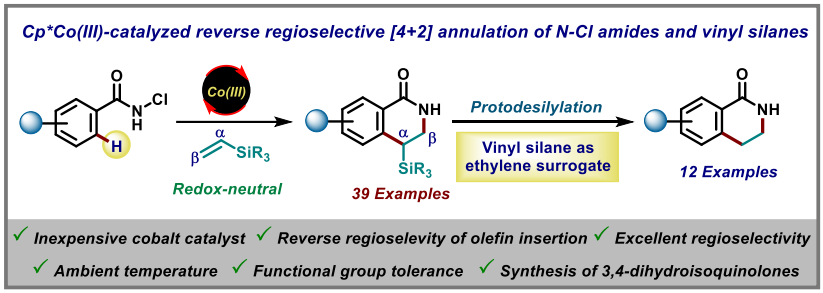
# Reverse Regioselective Cp*Co(III)-Catalyzed [4+2] C–H Annulation of *N*-Chloroamides with Vinyl Silanes: Synthesis of 4-Silylated Isoquinolones and its Application for the Synthesis of 3,4-Dihydroisoquinolones

Arijit Ghosh,[§] Tamanna Rana,[§] Nilanjan Bhaduri, and Amit B. Pawar*

School of Chemical Sciences, Indian Institute of Technology Mandi, Himachal Pradesh 175005, India

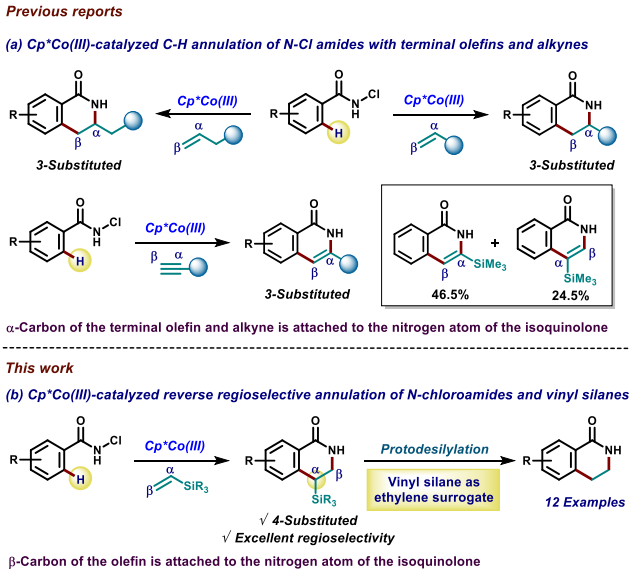
*Supporting Information Placeholder*

**ABSTRACT:** We have developed Cp*Co(III)-catalyzed reverse regioselective [4+2] annulation of *N*-chlorobenzamides/acrylamides with vinyl silanes for the synthesis of 4-silylated isoquinolones. The reaction was performed at ambient temperature under redox-neutral conditions. The reaction utilizes the N-Cl bond as an internal oxidant and furnished the required products with excellent regioselectivities and demonstrated high functional group tolerance. Moreover, 4-silylated isoquinolone derivatives were readily converted into 3,4-dihydroisoquinolones via protodesilylation thus making vinyl silane an ethylene surrogate.




Isoquinolone and its derivatives represents an important organic framework that is ubiquitous in many bio-active natural products, medicinally important compounds, pharmaceuticals, and agrochemicals.[1] Among the various methods known for the synthesis of isoquinolones,[2] transition metal-catalyzed redox-neutral [4+2] C–H activation/annulation strategy provides rapid access to these scaffolds.[3] This is attributed to the step-economy and atom efficiency of this strategy. Various transition metals like Pd, Rh, Ru, and Co were utilized for performing these transformations. Especially, due to the advent of first-row transition metals for C–H functionalizations,[4] Cp*Co(III)-catalysis has provided a viable alternative for expensive catalysts based on precious metals like Pd, Rh, and Ru to synthesize isoquinolone scaffolds via [4+2] C–H activation/annulation under redox-neutral conditions.[5] Initially, *N*-methoxybenzamide has been used as a choice of directing group for the synthesis of isoquinolone derivatives under redox-neutral conditions.[6] In 2017, Zhu et el. reported Cp*Co(III)-catalyzed [4+2] annulation using *N*-chlorobenzamide as a novel oxidizing directing group for the synthesis of isoquinolones using alkynes and olefins as coupling partners.[7] Following these reports, Jeganmohan's group reported various elegant protocols for [4+2] annulation of *N*-chlorobenzamides with different substituted olefins under Cp*Co(III)-catalysis.[8] However, in all these reports, the utilization of the terminal alkynes and olefins often led to the formation of 3-substituted isoquinolone derivatives, and α-C of the olefins/alkynes gets attached to the *N*-atom of the isoquinolnes (Scheme 1, eq. a). Moreover, Zhu et al. reported that the use of TMS acetylene furnished the mixture of 3- and 4-substituted isoquinolones, 3-substituted being the major one.[7a]

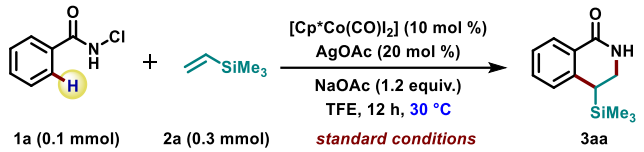
**Scheme 1. Cp*Co(III)-Catalyzed [4+2] Annulation of *N*-Chloroamides with Terminal Olefins and Alkynes**



Therefore, synthesis of 4-substituted isoquinolones using terminal olefins/alkynes under Cp*Co(III)-catalysis is rather challenging. In 2012, Cramer et al. reported an enantioselective chiral Cp*Rh(III)-catalyzed [4+2] annulation of various hydroxamic acid derivatives with olefins; with a sole example using vinyl silane to furnish 4-substituted isoquinolones.[9] In 2013, Molander et al. reported Cp*Rh(III)-catalyzed reverse regioselective [4+2] annulation of pivaloyloxyamides with potassium vinyltrifluoroborate to furnish 4-borylated isoquinolone derivatives.[10] Inspired by these reports, along with our continuous interest in Cp*Co(III)-catalysis[11] and due to the scarcity of any generalized methods to obtain 4-substituted isoquinolnes using Cp*Co(III)-catalysis, herein we report our studies for the synthesis of 4-silylated isoquinolones via reverse regioselective [4+2] annulation of *N*-chloroamides and vinyl silanes (Scheme 1, eq. b). The reaction was carried out at ambient temperature under redox-neutral conditions and furnished the 4-silylated isoquinolones with excellent regioselectivities. Moreover, to the best of our knowledge, Cp*Co(III)-catalyzed [4+2] annulation between hydroxamic acid derivatives and ethylene for the synthesis of 3,4-dihydroisoquinolones is not reported so far. In this context, we carried out base-catalyzed protodesilylation of 4-silylated isoquinolones to furnish 3,4-dihydroisoquinolones, hence making vinyl silane as an ethylene surrogate (Scheme 1, eq. b). We have also performed the consecutive annulation using pendant olefin for the synthesis of *bis*-isoquinolone with a silicon linker.

We have started our optimization studies using *N*-chlorobenzamide (**1a**) and vinyltrimethylsilane (**2a**) as model substrates. After performing several reactions, we found that the treatment of *N*-chlorobenzamide (**1a**, 0.1 mmol) with vinyltrimethylsilane (**2a**, 0.3 mmol) in the presence of [Cp*Co(CO)$I_2$] (10 mol %), AgOAc (20 mol %), and NaOAc (1.2 equiv.) at 30 °C for 12 h in 2,2,2-trifluoroethanol (TFE)

**Table 1. Optimization Study**[a]



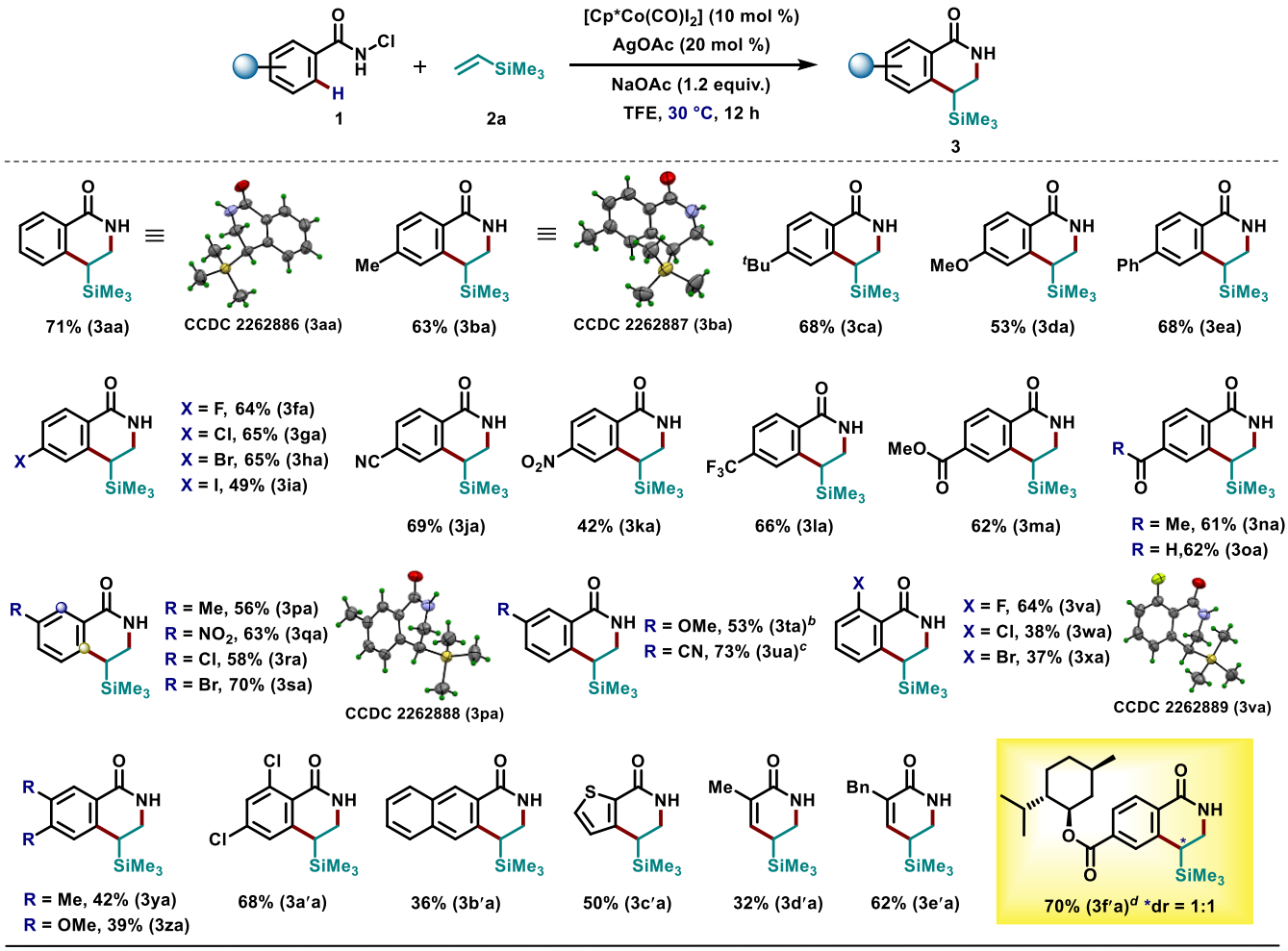

| Entry | Variation from standard conditions | Yield (%)[b] |
|---|---|---|
| 1 | none | 76 |
| 2 | Without AgOAc | 65 |
| 3 | KOAc instead of NaOAc | 64 |
| 4 | CsOAc instead of NaOAc | 48 |
| 5 | PivOH instead of NaOAc | trace |
| 6 | $AdCO_2H$ instead of NaOAc | trace |
| 7 | 1,2-DCE as a solvent instead of TFE | 56 |
| 8 | MeOH as a solvent instead of TFE | trace |
| 9 | 0.2 mmol of trimethylvinyl silane | 60 |
| 10 | without [Cp*Co(CO)$I_2$] | n.d. |
| 11 | without NaOAc | trace |

[a]Reaction conditions: **1a** (0.10 mmol), **2a** (0.30 mmol, 3.0 equiv.) in TFE (0.6 mL). [b]Yields are based on crude $^1$H NMR (internal standard: 1,1,2,2 tetrachloroethane). n.d. = not detected. TFE = 2,2,2-Trifluoroethanol. $AdCO_2H$ = 1-Adamantanecarboxylic acid.

furnished the desired 4-silylated isoquinolone derivative **3aa** in 75% yield (Table 1, entry 1) with excellent regioselectivity (< 20:1).[12] The regioselectivity of vinyl silane insertion was assigned based on the chemical shift values in $^1$H NMR. When the reaction was performed in the absence of AgOAc, it furnished the desired product **3aa** in 65% yield which indicates that the addition of NaOAc is promoting the reaction (Table 1, entry 2). Other acetate additives such as KOAc and CsOAc were found to be ineffective as compared to the NaOAc (Table 1, entries 3-4). The reaction furnished only a trace amount of the product when acid additives such as PivOH, and $AdCO_2H$ (1-Admantanecarboxylic acid) were used instead of NaOAc (Table 1, entries 5-6). The yield was dropped down when the reaction was carried out in a solvent other than TFE, Such as 1,2-DCE, and MeOH (Table 1, entries 7-8). When amount of vinyltrimethylsilane is decreased (2.0 equiv.), it resulted in the formation of the product in 45% yield (Table 1, entry 9). The reaction did not furnish any product of in the absence of a cobalt catalyst (Table 1, entry 10). Moreover, only a trace amount of the product was formed when the reaction was performed in the absence of NaOAc (Table 1, entry 11).

After successfully optimizing the reaction parameters for the current [4+2] annulation of *N*-chloroamides with vinyl silane, we initially investigated the scope of this reaction using various *N*-chlorobenzamides/acrylamides (Scheme 2). The *N*-chlorobenzamides having electron-donating groups like Me, OMe, $^t$Bu, and Ph at *para*-position furnished the required annulated products in good yields (**3aa**–**3ea**). Moreover, the reverse regioselectivity of the vinyl insertion was further confirmed from the X-ray crystal structures of **3aa** and **3ba**. The reaction tolerated all the halides (F, Cl, Br, and I) present at the *para*-position (**3fa**–**3ia**), thus providing a handle for further synthetic elaboration via cross-coupling reactions. The reaction was found to be compatible with electron-withdrawing groups such as CN, $NO_2$, and $CF_3$ furnishing the corresponding 4-silylated isoquinolones in 69%, 42%, and 66% yields (**3ja**–**3la**). Moreover, *N*-chlorobenzamide having electrophilic functional groups like ester, ketone, and aldehyde reacted smoothly reaction to furnish the desired products in 62%, 61%, and 62% yields respectively (**3ma**–**3oa**). The reaction was highly regioselective in the case of *N*-chlorobenzamides having *meta*-substituents like Me, $NO_2$, Cl, and Br, in which the C–H activation occurred at the less hindered position furnishing a single regioisomer of the product (**3pa**–**3sa**). The regioselectivity of the C–H activation was confirmed further by X-ray crystallographic analysis of **3ea**. However, in the case of 3-OMe and 3-CN substituted *N*-chlorobenzamides, the reaction furnished a mixture of the regioisomers (**3ta**–**3ua**). The reaction proceeded with good yields for the *N*-chlorobenazmides having *ortho*-substituents (**3va**–**3xa**). The scope of the reaction was further extended using di-substituted *N*-chlorobenzamides, in which the corresponding products were obtained in good yields (**3ya**–**3a′a**). In the case of 2-naphthyl derived *N*-chloroamide, the regioselective C–H activation at a less-hindered position was observed furnishing the desired product in 36% yield (**3b′a**). The reaction was found to be compatible with *N*-chloroamide having a thiophene ring (**3c′a**). Apart from arene C–H functionalization, the reaction is also applicable to the vinylic C–H functionalization. The *N*-chloroacrylamide derivatives furnished the corresponding cyclized products with low to moderate yields (**3d′a**–**3e′a**).

**Scheme 2. Scope of *N*-Chlorobenzamides/acrylamides[a]**

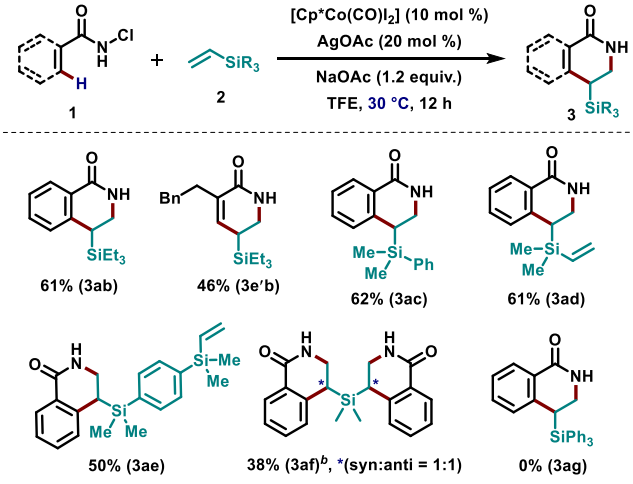



[a]Reaction conditions: **1** (0.40 mmol), **2a** (3.0 equiv.), [Cp*Co(CO)I$_2$] (10 mol %), AgOAc (20 mol %), and NaOAc (1.2 equiv.) in TFE (2.4 mL) at 30 °C for 12 h. Isolated yields are given. [b]Inseparable regioisomers in 1.0:0.11 ratio. [c]Inseparable regioisomers in 1.0:0.05 ratio. [d]Reaction was performed at 0.20 mmol scale.

Finally, the reaction was tested on the *N*-chlorobenzamide derivative possessing a menthol moiety, which resulted in the formation of the desired products in 68% yield as a 1:1 mixture of inseparable diastereomers (**3f′a**).

Next, we tested the scope of this reaction with various vinyl silanes (Scheme 3). The reaction proceeded smoothly with triethylvinylsilane (**2b**) and dimethylphenylvinylsilane (**2c**) furnishing the annulated products with 56% and 58% yields respectively (Scheme 2) (**3ab**–**3ac**). The triehtylvinylsilane was also successfully coupled with an acrylamide derivative also. The vinyl silanes having two alkene units such as dimethyldivinylsilane (**2d**) and 1,4-bis(dimethyl(vinyl)silyl)benzene (**2e**) furnished the corresponding mono-annulated isoquinolones in good yields (**3ad**–**3ae**). The compound **3ad** has a pendant vinyl silane moiety which was further utilized for the synthesis of bis-isoquinolone derivative (**3af**), which is obtained as an inseparable mixture of syn-anti diastereomers. Amongst them, the syn compound is a "meso" isomer, whereas the anti-compound is $C_2$ symmetric. However, the reaction failed to produce any desired product with triphenylvinylsilane (**2g**).

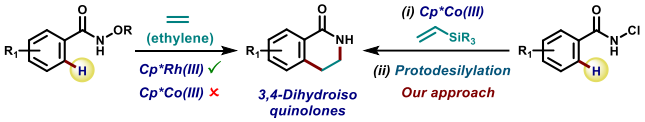
**Scheme 3. Scope of Vinyl Silanes[a]**




[a]Reaction conditions: **1a** (0.30 mmol), **2** (3.0 equiv), [Cp*Co(CO)I$_2$] (10 mol %), AgOAc (20 mol %), and NaOAc (1.2 equiv.) in TFE (2.4 mL) at 30 °C for 12 h. Isolated yields are given. [b]See ESI for details.

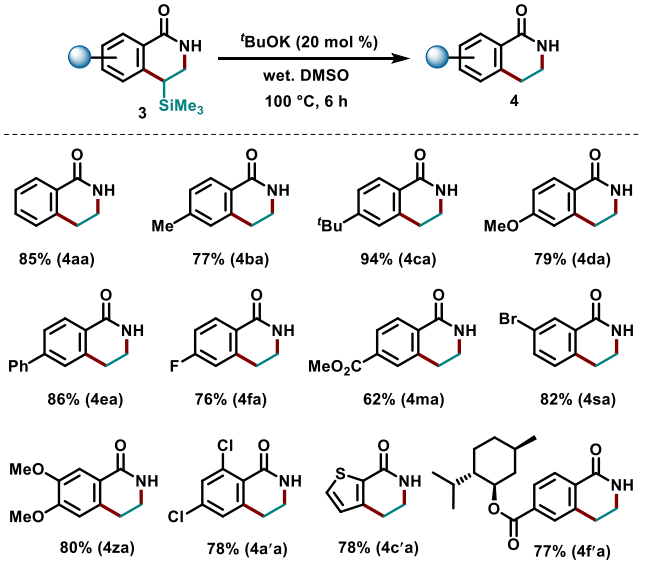
After synthesizing various 4-silylated isoquinolone derivatives, next, we were interested in utilizing 4-silylated isoquinolones for the synthesis of 3,4-dihydroisoquinolones. In 2011, Fagnou and Glorius groups reported a single example of [4+2] annulation of *O*-pivaloylhydroxamic acid with ethylene for the synthesis of 3,4-dihydroisoquinolones using Cp*Rh(III)-catalyst.[13-14] In 2021, Patman et al. reported [4+2] annulation of *O*-pivaloylhydroxamic acid with feedstock gases such as ethylene and propyne.[15] However, to the best of our knowledge such a reaction for the synthesis of 3,4-dihydroisoquinolones is not reported yet using Cp*Co(III)-catalysis. Therefore, we envisioned that the protodesilylation of the 4-silylated isoquinolones would furnish the required 3,4-dihydroisoquinolones. Hence, this 2 steps protocol can be visualized as [4+2] annulation of *N*-chlorobenzamides with ethylene utilizing vinyl silane as an ethylene surrogate.

**Scheme 4. [4+2] Annulation of Pivaloyloxyamides with Ethylene and Our Approach for the Synthesis of 3,4-Dihydroisoquinolones**




To perform protodesilylation we have used a reported protocol developed by Han et al.[16] The treatment of 4-silylated isoquinolnes with $^t$BuOK (20 mol %) in wet DMSO at 60 °C furnished the required 3,4-dihydroisoquinolnes in good to excellent yields. The reaction tolerated various functional groups such as chloro, bromo, fluoro, and ester (**3ba**–**3da**).

**Scheme 5. Protodesilylation of 4-Silylated Isoquinolones**[a]

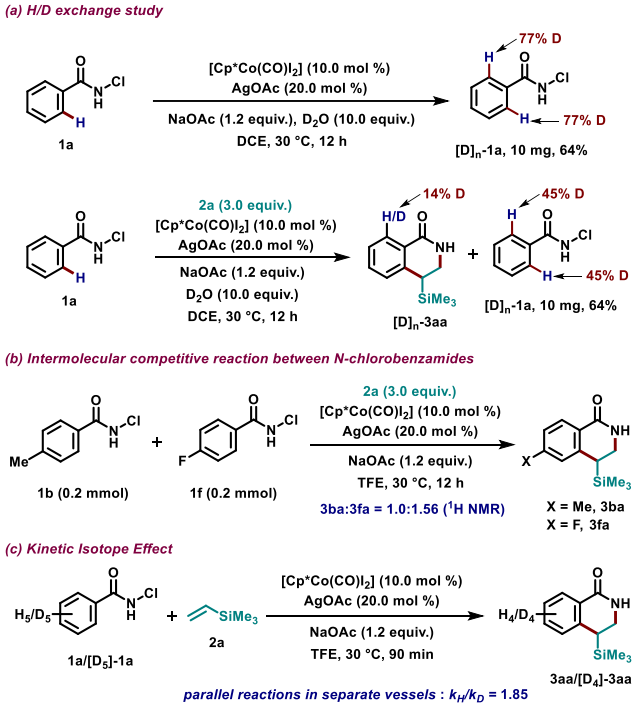



[a]Reaction conditions: **3** (0.20 mmol), $^t$BuOK (20 mol %), in Wet DMSO (2.4 mL) at 110 °C for 6 h. Isolated yields are given.

Using this protocol, we synthesized naturally occurring alkaloid corydaldine (**4za**) with a good yield. The substrate having a thiophene ring was also compatible with the reaction conditions, furnishing the required product in a good yield. Gratifyingly, protodesilylation worked efficiently on the isoquinolone having a menthol ester moiety furnishing the corresponding product in 77% yield.

After testing the scope of this reaction and synthesizing various 3,4-dihydroisoquinolones, we performed preliminary mechanistic studies to elucidate the mechanism of this [4+2] annulation reaction. The H/D exchange experiments were carried out with and without the coupling partner i.e., vinyl silane. The result from these experiments reveals that the C−H activation is reversible (Scheme 6, a). Later, the competitive reaction between 4-Me and 4-F substituted *N*-chlorobenzamides was performed, and it was observed that the substrate having the 4-F group reacts preferentially over the substrate having the 4-Me substituent (Scheme 6, b). This reactivity preference can be rationalized for carboxylate-assisted C−H activation. Finally, the KIE values has been determined for the parallel reactions and which come out to be 1.85. This indicates that the C−H bond breaking may not be the rate-determining step.

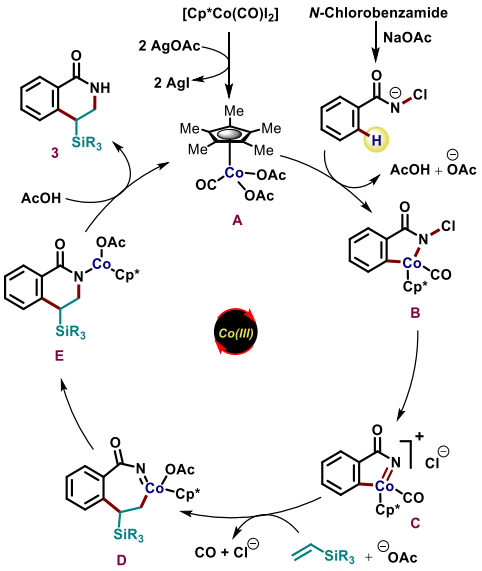
**Scheme 6. Mechanistic Findings**




Based on preceding literature[7-8] and preliminary mechanistic studies, a plausible mechanism for the current redox-neutral C-H annulation of N-chloroamides and vinyl silanes is depicted in Scheme 7. At first, [Cp*Co(CO)I$_2$] reacts with AgOAc to form catalytically active Co(III)-species **A**. The catalytically active species A reacts with the deprotonated *N*-chloroamide to generate a five-membered cobaltacyclic intermediate **B**. Then, cobaltacyclic intermediate undergoes the oxidation of the cobalt from +3 to +5 oxidation state forming an intermediate species **C**. Later, migratory insertion of the vinyl silane into the C-Co bond leads to the formation of 7-membered cobaltacyclic species **D**, in which cobalt is present in +5 oxidation state. The intermediate **D** upon reductive elimination generates an intermediate **E** in which cobalt is converted back into a +3-oxidation state. Finally, protodemetalation of intermediate **E** results in the formation of the 4-silylated isoquinolone

derivative (**3**) and regeneration of catalytically active species **A**, i.e., [Cp*Co(CO)(OAc)$_2$].

**Scheme 7. Plausible Mechanism**




In conclusion, Cp*Co(III)-catalyzed reverse regioselective [4+2] C–H annulation between *N*-chloroamides and vinyl silanes has been developed for the synthesis of 4-silylated isoquinolones. The reserve regioselectivity was unambiguously confirmed for the X-ray crystal structure analysis. The reaction was carried out at an ambient temperature and displayed an excellent functional group tolerance. Moreover, 4-silylated isoquinolnes were further utilized for the synthesis of 3,4-dihydroisoquinolones via protodesilylation and hence making vinyl silane an ethylene surrogate.

## ASSOCIATED CONTENT

### Supporting Information

Experimental procedure, mechanistic studies, characterization of new compounds ($^1$H, $^{13}$C NMR spectra) and X-ray structures of **3aa**, **3ba**, **3pa**, and **3va** (PDF).

### Accession Codes

CCDC 2262886, 2262887, 2262888, and 2262889 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

## AUTHOR INFORMATION


### Corresponding Authors

**Amit B. Pawar** – School of Chemical Sciences, Indian Institute of Technology Mandi, Himachal Pradesh, 175005, India; orcid.org/0000-0002-6472-8119; E-mail: amitpawar@iitmandi.ac.in

### Other Authors

**Arijit Ghosh** – School of Chemical Sciences, Indian Institute of Technology Mandi, Himachal Pradesh, 175005, India

**Tamanna Rana** – School of Chemical Sciences, Indian Institute of Technology Mandi, Himachal Pradesh, 175005, India

**Nilanjan Bhaduri** – School of Chemical Sciences, Indian Institute of Technology Mandi, Himachal Pradesh, 175005, India

### Author Contributions

§ A.G and T.R contributed equally.


### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENT


A.B.P thanks Science and Engineering Research Board (SERB), New Delhi, India for financial support in the form of Start-up Research Grant (File No:SRG/2020/000288; IITM/SERB/ABP/306). A.G and T.R. thanks the Ministry of Human Resources Development (MHRD), India, for the research fellowship.


## REFERENCES


(1) (a) Lewis, J. R. Amaryllidaceae and Sceletium Alkaloids. *Nat. Prod. Rep.* **1993**, *10*, 291. (b) Pettit, G. R.; Meng, Y.; Herald, D. L.; Graham, K. A. N.; Pettit, R. K.; Doubek, D. L. Isolation and Structure of Ruprechstyril from Ruprechtia Tangarana. *J. Nat. Prod.* **2003**, *66*, 1065–1069. (c) Ruchelman, A. L.; Houghton, P. J.; Zhou, N.; Liu, A.; Liu, L. F.; LaVoie, E. J. 5-(2-Aminoethyl)Dibenzo [*c*,*h*][1,6]Naphthyridin-6-Ones: Variation of *N*-Alkyl Substituents Modulates Sensitivity to Efflux Transporters Associated with Multidrug Resistance. *J. Med. Chem.* **2005**, *48*, 792–804. (d) Asano, Y.; Kitamura, S.; Ohra, T.; Itoh, F.; Kajino, M.; Tamura, T.; Kaneko, M.; Ikeda, S.; Igata, H.; Kawamoto, T.; Sogabe, S.; Matsumoto, S.; Tanaka, T.; Yamaguchi, M.; Kimura, H.; Fukumoto, S. Discovery, Synthesis and Biological Evaluation of Isoquinolones as Novel and Highly Selective JNK Inhibitors (2). *Bioorg. Med. Chem.* **2008**, *16*, 4699–4714. (e) Bosanac, T.; Hickey, E. R.; Ginn, J.; Kashem, M.; Kerr, S.; Kugler, S.; Li, X.; Olague, A.; Schlyer, S.; Young, E. R. R. Substituted 2*H*-Isoquinolin-1-Ones as Potent Rho-Kinase Inhibitors: Part 3, Aryl Substituted Pyrrolidines. *Bioorganic Med. Chem. Lett.* **2010**, *20*, 3746–3749. (f) Sunderland, P. T.; Woon, E. C. Y.; Dhami, A.; Bergin, A. B.; Mahon, M. F.; Wood, P. J.; Jones, L. A.; Tully, S. R.; Lloyd, M. D.; Thompson, A. S.; Javaid, H.; Martin, N. M. B.; Threadgill, M. D. 5-Benzamidoisoquinolin-1-Ones and 5-(ω-Carboxyalkyl)Isoquinolin-1-Ones as Isoform-Selective Inhibitors of Poly(ADP-Ribose) Polymerase 2 (PARP-2). *J. Med. Chem.* **2011**, *54*, 2049–2059. (g) Sunderland, P. T.; Woon, E. C. Y.; Dhami, A.; Bergin, A. B.; Mahon, M. F.; Wood, P. J.; Jones, L. A.; Tully, S. R.; Lloyd, M. D.; Thompson, A. S.; Javaid, H.; Martin, N. M. B.; Threadgill, M. D. 1-Ones as Isoform-Selective Inhibitors of Poly (ADP-Ribose) Polymerase. **2011**, *2*, 2049–2059. (h) Kiselev, E.; Sooryakumar, D.; Agama, K.; Cushman, M.; Pommier, Y. Optimization of the Lactam Side Chain of 7-Azaindenoisoquinoline Topoisomerase I Inhibitors and Mechanism of Action Studies in Cancer Cells. *J. Med. Chem.* **2014**, *57*, 1289–1298. (i) Gui, B.; Gui, F.; Takai, T.; Feng, C.; Bai, X.; Fazli, L.; Dong, X.; Liu, S.; Zhang, X.; Zhang, W.; Kibel, A. S.; Jia, L. Selective Targeting of PARP-2 Inhibits Androgen Receptor Signaling and Prostate Cancer Growth through Disruption of FOXA1 Function. *Proc. Natl. Acad. Sci. U. S. A.* **2019**, *116*, 14573–14582. (j) Francis, S.; Croft, D.; Schüttelkopf, A. W.; Parry, C.; Pugliese, A.; Cameron, K.; Claydon, S.; Drysdale, M.; Gardner, C.; Gohlke, A.; Goodwin, G.; Gray, C. H.; Konczal, J.; McDonald, L.; Mezna, M.; Pannifer, A.; Paul, N. R.; Machesky, L.; McKinnon, H.; Bower, J. Structure-Based Design, Synthesis and Biological Evaluation of a Novel Series of

Isoquinolone and Pyrazolo[4,3-*c*]Pyridine Inhibitors of Fascin 1 as Potential Anti-Metastatic Agents. *Bioorganic Med. Chem. Lett.* **2019**, *29*, 1023–1029. (k) Lee, H.; Ahn, S.; Ann, J.; Ha, H.; Yoo, Y. D.; Kim, Y. H.; Hwang, J. Y.; Hur, K. H.; Jang, C. G.; Pearce, L. V.; Esch, T. E.; Lewin, N. E.; Blumberg, P. M.; Lee, J. Discovery of Dual-Acting Opioid Ligand and TRPV1 Antagonists as Novel Therapeutic Agents for Pain. *Eur. J. Med. Chem.* **2019**, *182*, 111634.

(2) (a) Glushkov, V. A.; Shklyaev, Y. Synthesis of 1(2H) isoquinolones. *Chem. Heterocycl. Compd.* **2001**, *37*, 663−687. (b) Kulkarni, M. R.; Gaikwad, N. D. Recent Advances in Synthesis of 3,4-Dihydroisoquinolin-1(2*H*)-one. *ChemistrySelect* **2020**, *5*, 8157–8184.

(3) Hua, R. Isoquinolone Syntheses by Annulation Protocols. *Catalysts* **2021**, *11*, 620.

(4) For recent reviews on 3d-transition metals catalyzed C−H functionalizations, see: (a) Tzouras, N. V.; Stamatopoulos, I. K.; Papastavrou, A. T.; Liori, A. A.; Vougioukalakis, G. C. Sustainable Metal Catalysis in C−H Activation. *Coord. Chem. Rev.* **2017**, *343*, 25–138. (b) Loup, J.; Dhawa, U.; Pesciaioli, F.; Wencel-Delord, J.; Ackermann, L. Enantioselective C−H Activation with Earth-Abundant 3d Transition Metals. *Angew. Chem. Int. Ed.* **2019**, *58*, 12803–12818. (c) 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. (d) Singh, R.; Sathish, E.; Gupta, A. K.; Goyal, S. 3d-Transition Metal Catalyzed C–H to C–N Bond Formation: An Update. *Tetrahedron* **2021**, *100*, 132474. (e) Ilies, L. CH Activation Catalyzed by Earth-Abundant Metals. *Bull. Chem. Soc. Jpn.* **2021**, *94*, 404–417. (f) Mandal, R.; Garai, B.; Sundararaju, B. Weak-Coordination in C–H Bond Functionalizations Catalyzed by 3d Metals. *ACS Catal.* **2022**, *12*, 3452–3506.

(5) Bhaduri, N.; Pawar, A. B. *Org. Biomol. Chem.* **2023**, DOI: 10.1039/d3ob00133d. *14*, 3275.

(6) (a) Sivakumar, G.; Vijeta, A.; Jeganmohan, M. Cobalt-Catalyzed Cyclization of *N*-Methoxy Benzamides with Alkynes Using an Internal Oxidant through C−H/N−O Bond Activation. *Chem. - A Eur. J.* **2016**, *22*, 5899–5903. (b) Chavan, L. N.; Gollapelli, K. K.; Chegondi, R.; Pawar, A. B. Cp*Co(III)-Catalyzed C–H Functionalization Cascade of *N*-Methoxyamides with Alkynedione for the Synthesis of Indolizidines. *Org. Lett.* **2017**, *19*, 2186–2189. (c) Sen, M.; Mandal, R.; Das, A.; Kalsi, D.; Sundararaju, B. Cp*CoIII-Catalyzed Bis-Isoquinolone Synthesis by C−H Annulation of Arylamide with 1,3-Diyne. *Chem. - A Eur. J.* **2017**, *23*, 17454–17457. (d) Lerchen, A.; Knecht, T.; Koy, M.; Daniliuc, C. G.; Glorius, F. A General $Cp^*Co^{III}$ - Catalyzed Intramolecular C−H Activation Approach for the Efficient Total Syntheses of Aromathecin, Protoberberine, and Tylophora Alkaloids. *Chem. - A Eur. J.* **2017**, *23*, 12149–12152. (e) Dey, A.; Rathi, A.; Volla, C. M. R. Cobalt(III)-Catalyzed [4+2] Annulation of Heterobicyclic Alkenes by $sp^2$ C−H Activation. *Asian J. Org. Chem.* **2018**, *7*, 1362–1367.

(7) (a) Yu, X.; Chen, K.; Guo, S.; Shi, P.; Song, C.; Zhu, J. Direct Access to Cobaltacycles via C–H Activation: *N*-Chloroamide-Enabled Room-Temperature Synthesis of Heterocycles. *Org. Lett.* **2017**, *19*, 5348–5351. (b) Yu, X.; Chen, K.; Wang, Q.; Zhang, W.; Zhu, J. Co(III)-Catalyzed *N*-Chloroamide-Directed C–H Activation for 3,4-Dihydroisoquinolone Synthesis. *Org. Chem. Front.* **2018**, *5*, 994–997.

(8) (a) Ramesh, B.; Jeganmohan, M. Cobalt(III)-Catalyzed Redox-Neutral [4+2]-Annulation of *N* -Chlorobenzamides/Acrylamides with Alkylidenecyclopropanes at Room Temperature. *Chem. Commun.* **2021**, *57* (30), 3692–3695. (b) Yadav, S. K.; Jeganmohan, M. Cobalt(III)-Catalyzed Regioselective [4 + 2]-Annulation of *N*-Chlorobenzamides with Substituted Alkenes. *J. Org. Chem.* **2022**, *87*, 13073–13088. (c) Ramesh, B.; Jeganmohan, M. Cobalt(III)-Catalyzed Regio- and Chemoselective [4+2]-Annulation of *N*-Chlorobenzamides/Acrylamides with 1,3-Dienes at Room Temperature. *J. Org. Chem.* **2022**, *87*, 5713–5729. (d) Jothi Murugan, S.; Jeganmohan, M. Cp*Co(III)-Catalyzed Regioselective [4+2]-Annulation of N-Chlorobenzamides with Vinyl Acetate/Vinyl Ketones. *J. Org. Chem.* **2023**, *88*, 1578–1589.

(9) Ye, B.; Cramer, N. Chiral Cyclopentadienyl Ligands as Stereocontrolling Element in Asymmetric C−H Functionalization. *Science* **2012**, *338*, 504–506.

(10) Presset, M.; Oehlrich, D.; Rombouts, F.; Molander, G. A. Complementary Regioselectivity in Rh(III)-Catalyzed Insertions of Potassium Vinyltrifluoroborate via C−H Activation: Preparation and Use of 4-Trifluoroboratotetrahydroisoquinolones. *Org. Lett.* **2013**, *15*, 1528–1531.

(11) (a) Pawar, A. B.; Lade, D. M. *Org. Biomol. Chem.* **2016**, *14*, 3275. (b) Lade, D. M.; Pawar, A. B. *Org. Chem. Front.* **2016**, *3*, 836. (c) Pawar, A. B.; Agarwal, D.; Lade, D. M. *J. Org. Chem.* **2016**, *81*, 11409. (d) Aher, Y. N.; Pawar, A. B. Cp*Co(III)-Catalyzed C−H Amination/Annulation Cascade of Sulfoxonium Ylides with Anthranils for the Synthesis of Indoloindolones. *Chem. Commun.* **2021**, *57*, 7164–7167.

(12) The regioselectivity was determined by $^1$H NMR analysis.

(13) Guimond, N.; Gorelsky, S. I.; Fagnou, K. Rhodium(III)-Catalyzed Heterocycle Synthesis Using an Internal Oxidant: Improved Reactivity and Mechanistic Studies. *J. Am. Chem. Soc.* **2011**, *133*, 6449–6457.

(14) Rakshit, S.; Grohmann, C.; Besset, T.; Glorius, F. Rh(III)-Catalyzed Directed C-H Olefination Using an Oxidizing Directing Group: Mild, Efficient, and Versatile. *J. Am. Chem. Soc.* **2011**, *133*, 2350–2353.

(15) Barber, J. S.; Kong, D.; Li, W.; McAlpine, I. J.; Nair, S. K.; Sakata, S. K.; Sun, N.; Patman, R. L. Rhodium(III)-Catalyzed C-H Activation: Annulation of Petrochemical Feedstocks for the Construction of Isoquinolone Scaffolds. *Synlett* **2021**, *32*, 202–206.

(16) Yao, W.; Li, R.; Jiang, H.; Han, D. An Additive-Free, Base-Catalyzed Protodesilylation of Organosilanes. *J. Org. Chem.* **2018**, *83*, 2250–2255.