

Complexes of the Cobalt Pincer Type that Exhibit Unusual Selectivity for the Hydroboration of Olefins Under Favourable Circumstances

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Abstract

A cost-effective and readily available cobalt pincer complex was utilized as a catalyst for the hydroboration of alkenes, based on a PN5P triazine backbone. This approach enables the efficient anti-Markovnikov functionalization of alkenes with diverse functional groups, including unsaturated amines, carbonates, ethers, vinylarenes, vinylsilanes, and natural products. The reaction can be conducted under mild conditions, resulting in high yields of the desired products. Remarkably, the technique exhibits exceptional selectivity, allowing for the selective separation of vinylsilyl groups from other alkenyl or alkyne groups. The versatility of this approach was demonstrated through various model adjustments, indicating its broad applicability. Furthermore, this methodology produces a captivating class of bifunctional compounds that hold potential for use in the synthesis of advanced materials. Overall, this study presents a valuable and practical strategy for the functionalization of alkenes using a cheap and accessible cobalt pincer complex, offering a low-stress environment and high yields of functionalized products.

Introduction

Organic synthesis has been transformed by transition metal catalysis, which provides effective and specialised pathways to complex compounds. Among the numerous transition metal catalysts, cobalt pincer-type complexes have shown outstanding reactivity and selectivity in a variety of organic transformations, making them interesting options. Their remarkable selectivity for olefin hydroboration under benign reaction conditions is particularly intriguing.

The production of functionalized organic molecules may be aided by hydroboration processes, which add a boron-hydrogen link to an unsaturated carbon-carbon bond. Rhodium and iridium complexes have historically been used as precious metal catalysts in hydroboration processes. Researchers are now looking at alternative catalysts built on more affordable and widely available transition metals due to the high cost and restricted availability of these metals.

Due to their exceptional catalytic abilities, cobalt pincer-type complexes, which are characterised by a tridentate ligand that closely binds the cobalt centre, have attracted a lot of interest lately. These

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compounds have special benefits such high stability, adjustable electrical characteristics, and ease of production. Cobalt is a plentiful and eco-friendly metal, making it a desirable substitute for precious metal catalysts.

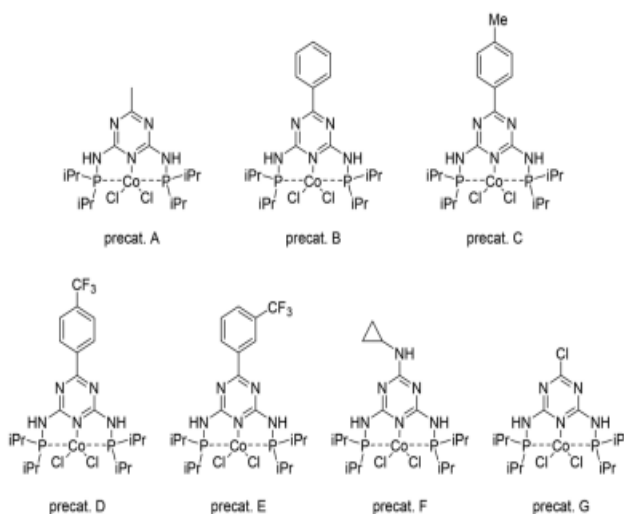
Notably, at mild reaction conditions, cobalt pincer-type complexes have shown a particular selectivity for the hydroboration of olefins. These complexes provide benefits in terms of functional group compatibility and control over regio- and stereoselectivity, as opposed to conventional catalysts, which may drive hydroboration processes at lower temperatures and with gentler reagents. The selective hydroboration of olefins is a highly desired transition in organic synthesis because it makes it possible to synthesise a wide variety of useful building blocks and exquisite compounds.

Results and discussion

A number of PNP ligands based on the triazine ring were created using commercially available substrates in a two-step synthesis. From the cobalt chloride precursor, they were used to synthesise the appropriate complexes (Scheme 1).

First, we evaluated the performance of the cobalt precatalyst F, the most promising one, in a simulated hydroboration process involving pinacolborane and dimethylphenylvinylsilane (Table 1).

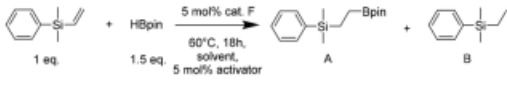
Pinacolborane served as the substrate and precatalyst activator in the first reaction, which was conducted in chlorobenzene, and the conversion of vinylsilane was 66% (entry 1).



Scheme 1: The obtained pincer cobalt complexes' structures

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Entry	Activator	Solvent	Conversion ^a	Selectivity ^b A : B
1	—	Chlorobenzene	66%	99 1
2	Cs ₂ CO ₃	Chlorobenzene	98%	99 1
3	Cs ₂ CO ₃	Chlorobenzene	80% ^c	99 1
4	Cs ₂ CO ₃	Chlorobenzene	26% ^d	84 16
5	—	Chlorobenzene	Trace ^e	— —
6	Cs ₂ CO ₃	Chlorobenzene	Trace ^e	— —
7	—	THF	95%	98 2
8	Cs ₂ CO ₃	THF	99%	90 10
9	—	Toluene	16%	94 6
10	Cs ₂ CO ₃	Toluene	98%	91 9
11	—	Solvent-free	97%	99 1
12	—	Solvent-free	Trace ^f	— —

Table 1 Preliminary experiments for the hydroboration of dimethyl phenylvinylsilane with cobalt (optimal reaction conditions are bolded)

Subsequently, we utilized cesium carbonate as an additional activator to help transformation, which empowered us to totally change the substrate (Section 2). Dimethylphenylvinylsilane was changed by diminishing the response temperature to 40 °C (section 3) or room temperature (passage 4), which came about at 80% and 26% of the transformation rate, respectively.

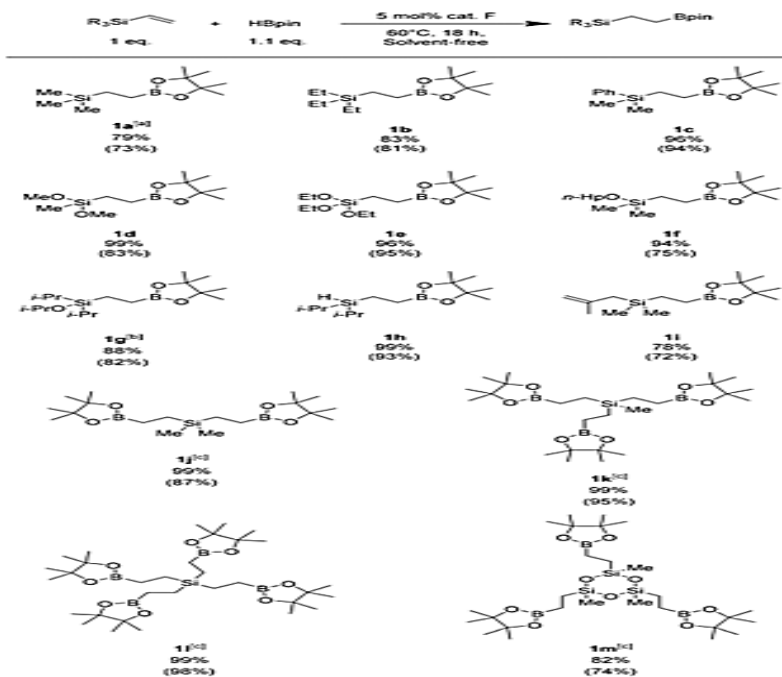
Other dissolvable analyses (passages 7–10) created results like the model response in chlorobenzene. Nonetheless, a response acted in a dissolvable-free climate (passage 11) showed that the strategy might be directed without the utilization of an activator, despite everything producing an item that is explicitly hostile to Markovnikov hydroboration. Just follow the amounts of the item that were created in a control experiment without an impetus or dissolvable (section 12). Thus, in the ensuing step, we decided to look at the reactant movement of extra combined cobalt precatalysts in a dissolvable-free climate (ESI Table S1). Among these, intricate F (ESI Table S2), for which we also enhanced the amount of pinacolborane utilized to 1.1 counterparts, created the best outcomes.

We decided to explore other vinylsilanes in the hydroboration cycle with pinacolborane subsequent to deciding the ideal response conditions (Scheme 2). The expected items with high changes and yields were delivered in tests utilizing vinylsilanes with both aliphatic (1a and 1b) and sweet-smelling (1c) substituents. Touchy alkoxysilanes (1d–1g), which are a class of critical polymer forerunners frequently utilized in materials science, may likewise be specifically functionalized utilizing the recently proposed approach. The proposed technique is totally viable with vinylsilanes that incorporate the Si-H bunch (1h) and can utilize the created items in ensuing hydrosilylation activities. It is fascinating to take note of the fact that the laid-out reactant framework just permitted

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the vinyl bunch (1i) to be functionalized on account of 2-methylallyldimethyl(vinyl)silane, showing that the proposed approach was insufficient for functionalizing 2-methylallyl subsidiaries. Furthermore, we had the option to make extended subsidiaries (1j–1m) using multi-vinyl subbed silanes, which are captivating structure blocks for the production of dendrimers.



Scheme 2 Vinylsilane hydroboration without solvent is catalysed by cobalt.

Tragically, humble transformations (7%) were obtained when allyltrimethylsilane or allyltriisopropylsilane were hydroborated.

Like how we tracked down just halfway transformations of the substrate on account of non-silylated alkenes (allylbenzene and decene), this shows a huge effect of the silicon impact on the did response.

Thus, we adjusted our strategy and incorporated an activator (NaHB_{Et}3). The objective item was completely changed over; as indicated by primer discoveries for the triisopropylallylsilane model hydroboration system (ESI Table S4).

To address this, we implemented a streamlining system; the particulars are itemized in the ESI (Tables S4–S8).

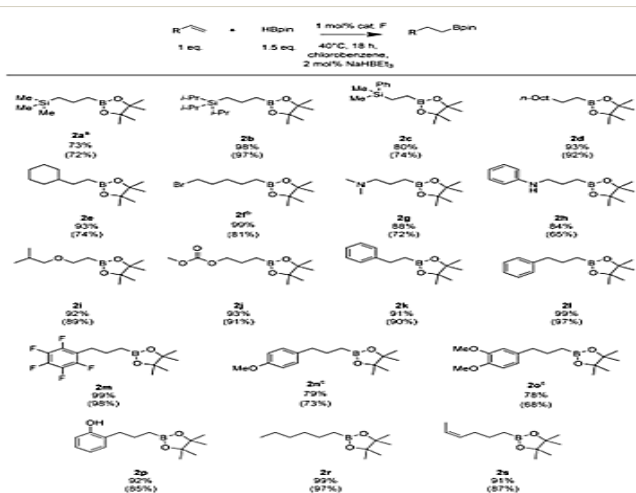
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Each of the tested activators allowed the complex to be effectively actuated. At long last, on the grounds of its far and wide business accessibility and direct taking care of, we decided to use sodium triethylboron hydride. Eventually, the responses were led at 40 °C with the precatalyst F utilized at 1 mol% and the activator utilized at 2 mol% to arrive at the best circumstances.

We analyzed different alkenes in the hydroboration cycle under these high-level circumstances (Scheme 3). With exceptional returns of allylsilanes (2a and 2b), vinylsilanes (2c), aliphatic alkenes (2d and 2e), haloalkenes (2f), unsaturated amines (2g and 2h), ethers (2i), carbonates (2j), or vinylarenes (2k), we functionalized as a result.

Moreover, we investigated extra-normally occurring allylbenzene subordinates such as estragole (2n) and methyl eugenol (2o) as an outcome of the remarkable consequences of the hydroboration of allylbenzene (2l) and pentafluoroallylbenzene (2m). These mixtures are in many cases a part of recently evolved drugs⁴⁷⁻⁵⁰ inferable from their natural action, and hence, the found items give charming biorelevant platforms to the combination of prescriptions. We specifically functionalized 2-allylphenol (2p) under the laid-out conditions, keeping the hydroxyl bunch free, in spite of logical reports of impetus-free dehydrocoupling of pinacol with nucleophiles (counting phenols).



Scheme 3: Sodium triethylboron hydride acts as an activator for the precatalyst in the cobalt-catalyzed hydroboration of alkenes.

We completed responses with four unsaturated hexane subordinates at the ideal conditions to survey as far as possible. The expected item was totally changed from the substrate by means of the 1-hexene (2r) response. In any case, no item creation was seen for trans-3-hexene or cis-3-hexene.

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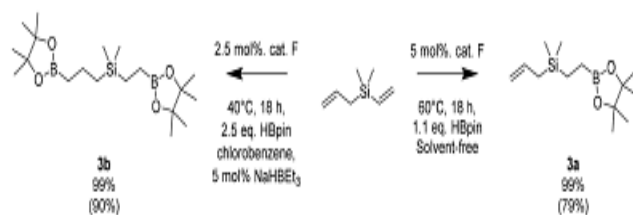
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Consequently, we had the option to specifically functionalize monohydroborate cis-1,4-hexadiene (2s) utilizing the proposed approach, which just allows the functionalization of terminal olefins.

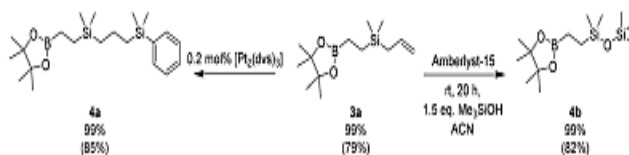
Inquisitively, the different elements of the reactant frameworks that have been given consider specific functionalization of the vinyl bunch in alkenyl(vinyl)silane subordinates. We played out the hydroboration of allyldimethyl (vinyl)silane under the two recommended conditions (Scheme 4) to test this hypothesis.

We specifically changed the vinyl bunch while keeping the allyl twofold bond unblemished when the response was led in a dissolvable and without activator climate (3a), but when an activator was utilized, a twofold hydroboration item was created (3b).

This particular selectivity offers various captivating conceivable outcomes that may be utilized in the union of extremely convoluted forerunners of state-of-the-art materials. Two model functionalization responses of the monohydroborated item, including an unblemished allylic gathering (Scheme 5), showed the appropriateness of this strategy. As far as we could possibly know, this is the principal occasion of a reactant hydroboration that isolates silanes' vinyl bunches from other alkenyl gatherings and licenses particular functionalization without extra isomerization or decrease of the subsequent particle.



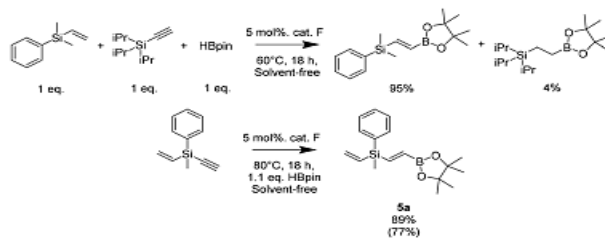
Scheme 4: Selectivity comparison between the two newly discovered hydroboration techniques.



Scheme 5: Hydrosilylation and O-silylation processes are used to functionalize the monohydroborated product.

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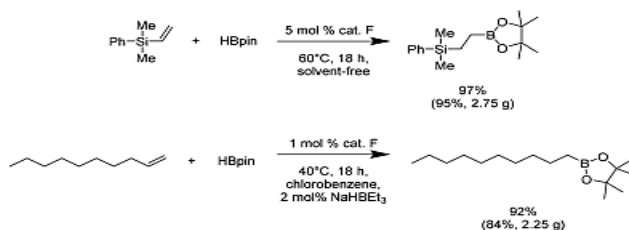


Scheme 6 Hydroboration competition between inter- and intramolecular competitors

Finally, we tested our system's selectivity in the competitive hydroboration process of vinylsilane when triisopropylsilylacetylene was present (Scheme 6). The findings indicated that acetylene converted virtually completely (95%) whereas vinylsilane only produced a little quantity (4%). Due to this, we altered the bifunctional (methylphenyl(vinyl)silyl)acetylene molecule, enabling the acetylene group to be selectively functionalized. This is consistent with our earlier publications in which we showed that silylacetylenes may hydroborate on the catalyst mentioned.⁴⁶

We evaluated the scalability of the devised approach in two gram-scale reactions for the solvent-free hydroboration of vinylsilanes and the reaction with an activator in order to demonstrate the synthetic potential of the procedure. We observed quantitative conversion in both situations, producing high isolation yields (Scheme 7).

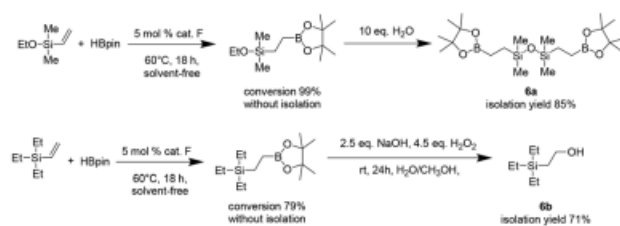
The building blocks of synthetic chemistry that have distinct reactivities in their moieties are bifunctional organometallic compounds. Therefore, we made the decision to carry out two one-pot functionalizations (Scheme 8) in order to illustrate the opportunities provided by the discovered approach. By hydrolyzing and condensing the organosilicon moiety in the first synthetic route, we altered the hydroboration product; in the second, we created a new functional group by transforming the organoboron moiety. The method's excellent compatibility with conventional reactions makes it unnecessary to separate the hydroboration products, which fits in nicely with the principles of contemporary chemistry and expands the method's possible applications.



Scheme 7: Hydroboration processes on a gram-scale.

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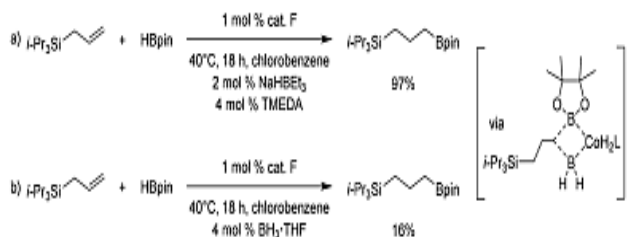


Scheme 8: Hydroboration product functionalization in a single pot.

We completed various examinations to check the response cycle. In the first place, BH₃ creation, which might act as a secretive impetus, is plausible if sodium triethylboron hydride is utilized as an activator. Tetramethylethylenediamine was added to our examination under regular conditions with the goal of potentially delivering borane, but the outcomes uncovered that TMEDA did not affect the transformation of the substrate (Scheme 9a). We possibly saw a halfway change in the substrate when BH₃THF was utilized instead of NaHBET₃ (Scheme 9b).

Considering this, we can't totally preclude an interaction in view of the breakdown of HBpin into BH₃, which then, at that point, goes through expansion to the twofold bond while at the same time going through transborylation with LCoH₂Bpin, despite the fact that it is without a doubt a negligible event.

We played out the hydroboration response under the created conditions by adding a drop of mercury to the response vessel to preclude the chance of a heterogeneous instrument driven by chemically dynamic cobalt nanoparticles, which might have been shaped because of the decrease of the complex with sodium triethylboron hydride (allude to the ESI for subtleties). Complete substrate change was checked by GC-MS examination of the trial, precluding the presence of a heterogeneous component in the response.



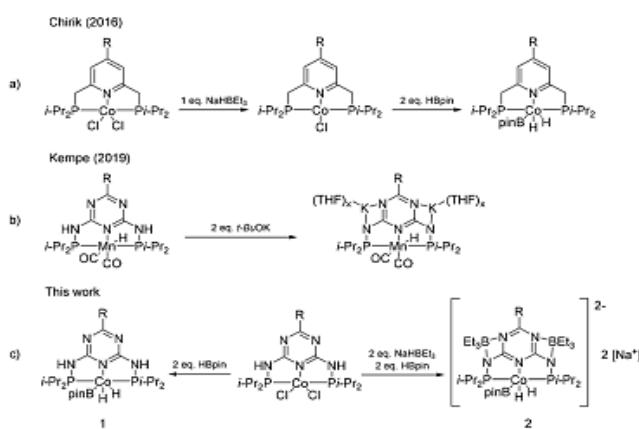
Scheme 9 Experiments that confirm the possibility for the emergence of borane as a covert catalyst for reaction.

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So, in an effort to identify the catalyst's active form, we ran NMR studies. The results of the NMR studies show unequivocally that cobalt's oxidation state changes during activation because our precatalysts are paramagnets.

The activation of pinacolborane complexes with NaHBET₃, in which cobalt is reduced from its second oxidation state to the first oxidation state, and then an oxidative addition by HBpin to the third oxidation state, was studied in previous investigations by Chirik et al. (Scheme 10a).⁵⁷ However, in the case of our precatalysts, a similar activation mechanism for both the reactions involving pinacolborane and the addition of NaHBET₃ results in the same active form of the complex, not accounting for the variations in the activity that we observed. Additionally, the acidic NH protons were absent from the structure of the ligand from the Chirik group. Accordingly, for our precatalysts, the addition of NaHBET₃ is likely responsible for the deprotonation of the complex's NH groups, in a manner similar to that suggested in the studies of the Kempe group (Scheme 10b), which contends that the catalyst's high activity is influenced by its anionic nature.⁵⁸ Accordingly, we believe that the complex's high catalytic activity in the olefin hydroboration reaction is entirely due to its deprotonated form. In our study, we did not observe any differences in the catalytic activity depending on the activator used or its counterion (see the ESI, Table S8). In accordance with findings in the literature by the Pawlu group, the ¹¹B NMR spectrum obtained for structure 2 (Scheme 10c) reveals the presence of a variety of boron nuclei (see the ESI), most likely originating from BEt₃ adducts with the anionic form of the complex.⁵⁹ The -silicon effect stabilises the alkyl complex in the non-anionic state, making up for its reduced catalytic activity and dramatically boosting the pace of reaction.

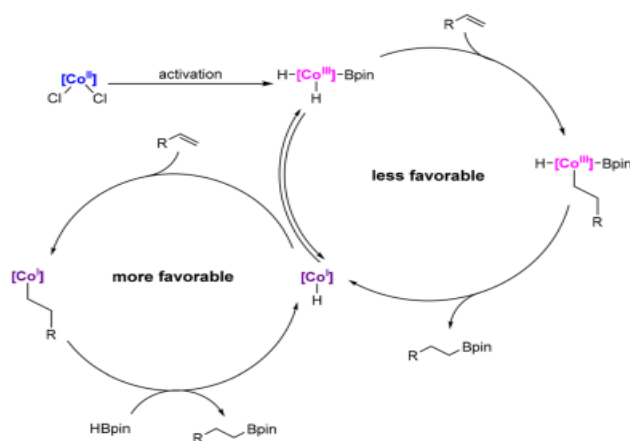


Scheme 10: Pincer complexes' activation mechanisms

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Based on these findings, our earlier research on pincer cobalt complexes, and reports in the literature,^{44–46,57,63–67} we hypothesise that the two forms of the cobalt complex (Co(I) and Co(III)) coexist in equilibrium in the reaction mixture as a result of activation with pinacolborane or sodium triethylboron hydride. Both of them have the ability to catalyse the reaction; however, in light of recent reports⁶⁶, we believe that Co(I) (LCo-H) is the more catalytically active form. The regeneration of the active form occurs as a consequence of the alkene first undergoing 1,2-insertion into a Co-H bond, followed by transmetalation with the pinacolborane moiety (Scheme 11). In the case of activation with the addition of NaHBt₃, we are unable to definitively determine the active form of the complex; however, we postulate analogous structures with a deprotonated ligand (Scheme 9c and see the ESI). In the case of activation with the addition of Pinacolborane alone, we assume that the active form of the complex is LCo-H being in equilibrium with structure 1 (Scheme 9c and see the ESI).



Scheme 11 Proposed catalytic cycle.

Conclusions

In conclusion, by utilizing a minimal expense impetus in light of earth-plentiful cobalt and working under harmless conditions, we have made novel, extremely viable reactant methods for hostile Markovnikov hydroboration of terminal alkenes. With the assistance of the proposed conventions, an assortment of alkene subordinantes, including silanes, amines, ethers, and regular items, can be functionalized. The subsequent mixtures are intriguing synthons for the blend of fine synthetic compounds, medications, and polymers. We likewise showed that, utilizing the newfound dissolvable and without activator strategy, it is feasible to specifically functionalize the vinyl bunch in alkenyl (vinyl) silanes or the alkynyl bunch in alkynyl (vinyl) silanes. Also, we exhibited the extraordinary

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versatility and similarity of the expressed strategy with different cycles, empowering further one-pot adjustment of the delivered items and showing the high application nature of the convention.

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