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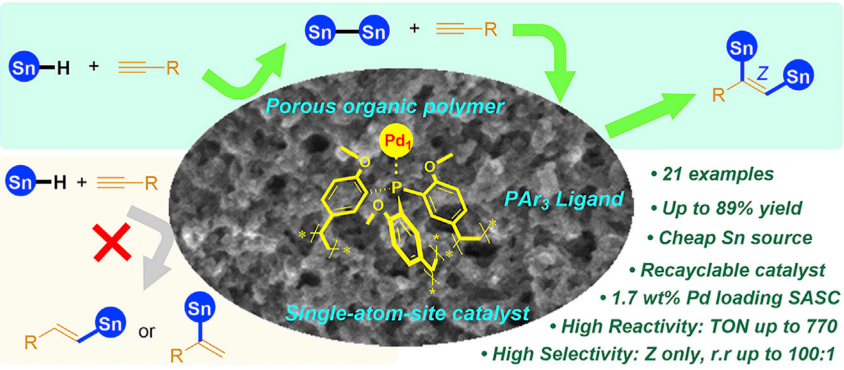

We proposed a unique research concept of "mechanism-oriented catalyst design": The structural elements of single-atom catalyst are designed according to the requirements of organic synthesis mechanism. This concept is totally different from the previous "electrocatalytic" single-atom-site research concept. This work suggests that single-atom-site catalysts not only afford an efficient platform for transforming homogeneous reactions into heterogeneous reactions, but also possess many interesting potentials in developing new synthetic reactions and solving homogeneous reaction problems.

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HIGHLIGHTS

Design single-atom-site catalyst based on organic synthesis mechanism

Utilizing pores, ligands, and SAS for synergistic controlling reaction paths

A highly selective distannylation of terminal alkynes was achieved

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Porous Ligand Creates New Reaction Route: Bifunctional Single-Atom Palladium Catalyst for Selective Distannylation of Terminal Alkynes

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SUMMARY

Single-atom-site (SAS) catalyst, as a highly reactive heterogeneous catalytic system, is one of the effective tools for complex organic synthesis. However, excessive attention on the catalysis and regulation of metal atoms has led to the neglect of the role of supports and ligands. Here, we employed a P-doped porous organic polymer as a support, as well as a ligand in the developed Pd SAS catalysts. The enrichment of the substrates by the pores, ligand action of the support, and high chemoselectivity and anti-agglomeration of SAS catalysts were the most striking features of this SAS catalyst. A highly selective distannylation of terminal alkynes with a new mechanism was achieved by using the multiple properties of SAS catalyst. This catalytic system offers an effective strategy to utilize the enrichment of the substrate by the pores to regulate the reaction mechanism, which opens a new frontier to use pores, ligands, and SASs for synergistic controlling reaction paths.

INTRODUCTION

Controllable synthesis of structurally specific compounds has become one of the research frontiers in contemporary synthetic chemistry.[1] To achieve this goal, a metal-ligand catalytic system is usually used to control reaction selectivity in homogeneous catalysis.[2] In some competitive reactions, ligand screening is complicated, because it often involves structurally complex and expensive homogeneous organic ligands that are challenging to separate and recycle.[3–6] Thus, converting homogeneous catalysts for value-added reaction into a heterogeneous counterpart is an increasingly popular strategy.[7] The conventional strategy is to synthesize novel heterogeneous catalysts via organic or inorganic reactions and to apply them in homogeneous organic reactions to achieve high catalytic performance.[8–10] This strategy has almost completely dominated the field of heterogeneous catalysis and has been successfully extended to the field of single-atom catalysis,[11–27] which considerably improved the reaction results, such as yield, catalytic efficiency, chemo-, and regioselectivity. However, to date, single-atom-sites (SASs) catalysts can only achieve some reactions that have been realized under homogeneous or heterogeneous catalysis, but their application in the development of more complex and selective new reactions has not been reported yet. Therefore, according to the characteristics of SASs, it is an attractive challenge to design and synthesize catalytic systems with universal prospect applications in the development of new reaction routes that cannot be accomplished by homogeneous catalysis.

The Bigger Picture

Single-atom-site catalysts have many applications in organic synthesis. However, most of the research models related to organic synthesis still stay in the mode of "pursuing higher catalytic performance," mainly based on electrocatalysis. This article provides a reasonable design of the catalyst in accordance with the characteristics and reaction requirements of organic synthesis and finally uses it for the development of a new reaction route.

The distannylation of alkynes is very useful in the construction of complex molecules. In the past, only a few terminal alkynes could be achieved by selective distannylation. Based on the mechanism of the reaction, the porous organic polymer catalyst with triarylphosphonate as the backbone was designed and prepared with advantages including pore enrichment, ligand regulation, and single-atom selective regulation. This catalyst solved all the problems in this reaction, such as narrow substrate scope, poor selectivity, and low catalytic efficiency.

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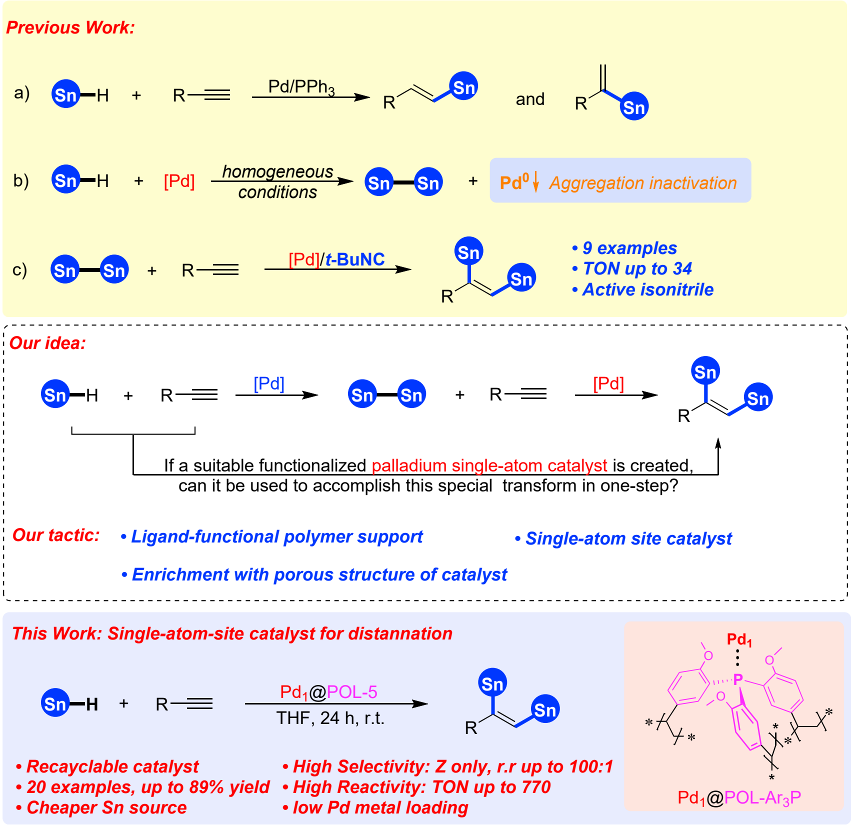

Scheme 1. Metal-Catalyzed Selective Distannylation of Terminal Alkynes

1.2-Ditin-substituted olefins can be easily converted into poly-functionally diverse olefins via the Migita-Kosugi-Stille cross-coupling reaction,[28] which are often used as important synthetic blocks in organic synthesis.[29] The distannylation of alkyne is the only route for this special compound. Most of the existing distannylation of alkynes uses alkylditin as substrates; these reactions suffer from inevitable short-coming, such as high metal loading, low yields, poor stereo- and chemoselectivity, narrow substrate scope, and requirement of stoichiometric amount of base (Scheme 1, path c).[30–33] The use of alkyl tin hydrides as a source of tin is ideal for achieving highly selective distannylation, due to their high reactivity and low cost (at only one-third price of alkylditin). Kazmaier group reported the only example of W-catalyzed highly regioselective distannylation of terminal alkynes by using alkyl tin hydride as a tin source with a narrow substrate scope (only six species have been successfully converted).[34] In general, direct synthesis of a 1.2-ditin-substituted olefin using alkyl tin hydride under palladium (Pd) catalysis is unfavored under homogeneous catalysis, because Sn-Pd-H and Sn-Pd-Sn intermediates are readily formed. Sn-Pd-H is favorable in the homogeneous catalytic system and is readily converted into a tin hydrogenation product (Scheme 1, path a).[35–37] The Sn-Pd-Sn is the ideal intermediate for 1.2-ditin-substituted olefins, but it rapidly agglomerates into large Pd nanoparticles after a catalytic cycle, which in turn leads to loss of catalytic activity (Scheme 1, path b).

On the other hand, SAS catalysts with silicon- or carbon-based materials as supports are also difficult to achieve this reaction because these materials do not play a role of ligands. Our group has been working on the development of atomically dispersed

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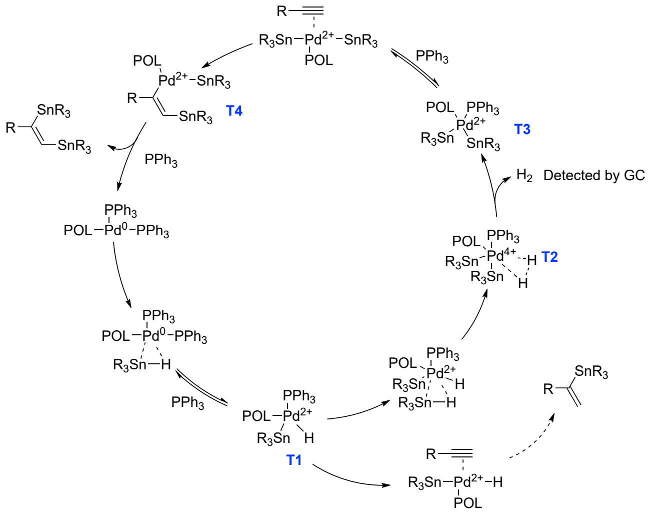

Scheme 2. The Mechanisms of Distannylation

metal catalysts that are supported on a porous organic ligand polymer (POLs).[38–40] These POL-supported atomically dispersed catalysts integrate the advantages of SAS (mononuclear) catalysts and homogeneous metal-ligand catalysts for known reactions. The high stability and dispersion of the single-atom metal active center ensure its catalytic activity and chemoselectivity. The special steric hindrance and electronic effects of the ligands, as well as the overall synergistic catalytic center, improve the chemo- and stereoselectivity.[41–49] However, different from the previous metal-POL-catalyzed known reactions, the development of a new reaction mechanism, which is controlled by the pore enrichment of the support and high dispersion and anti-agglomeration nature of the SAS has not been explored to date. It has been difficult to achieve so far, because it requires a complete and rational adjustment of various factors, such as finding suitable reaction templates, designing reaction mechanisms, controlling metal particle size, and selecting potential carriers.

RESULTS

Key Challenges and Their Origins

Challenge 1, for Ligand Support

As mentioned earlier, when isonitrile is used as a ligand, its instability leads to a lower yield and narrow substrate scope.[33] Triphenylphosphine (PPh_3) can improve the yield with a poor selectivity. On the other hand, as shown in Scheme 2, the key point to realize distannylation is to control the selective formation of Pd-Sn and Sn-Pd-Sn intermediates. For alkyl terminal alkynes with weak chelation and inductive effects, it is hard to achieve the high selectivity with a simple homogeneous ligand. Thus, a suitable heterogeneous ligand polymer is needed.

Challenge 2, for Metal

The heterogeneous catalyst needs to maintain dispersibility to restrain the competition of hydrostannylation. The SAS catalyst with single catalytic particle size and atomic orbital can effectively regulate the chemoselectivity of the reaction when the catalyst faces competitive reactions with different mechanisms.

Challenge 3, for the Catalytic System

The stability of Pd SASs is another important issue. Since the metal and the ligand are free under homogeneous conditions, the catalytically active Pd can readily form a

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stable structure of tetracoordinate with 18 electrons. During the reaction process, Pd dissociates from the ligand and forms a transient intermediate state. In this process, the homogeneous catalyst begins to slowly agglomerate. Therefore, if the support introduced into the heterogeneous catalyst is not properly coordinated to the metal, it is difficult to obtain atomically dispersed palladium, and the catalyst is usually agglomerated into nanoparticles during the loading preparation stage. In particular, when a catalytic cycle has been completed, the support should provide a corresponding force to prevent Pd(0) aggregation and inactivation.

Solutions

(1) Using a POL with a triarylphosphine-skeleton as support for the heterogeneous catalyst. The enrichment of the pores of the polymer can effectively enrich the Sn–H compounds, make the Sn–H concentration around the metal active center higher, and promote the formation of Sn-Pd-Sn intermediates. Compared with homogeneous isonitrile and PPh_3 ligands, the ligand polymer not only improves the yield and substrate scope, but it also improves the selectivity. This kind of vinyl polymer material has excellent swelling properties. This special property can make it quickly absorb a large amount of organic mixture during the reaction process, and then simulate the reaction conditions closer to homogeneous catalysis. A special "semi-homogeneous" catalytic environment can effectively enhance catalytic activity.

(2) Using air-stable tetra-coordinated bistriphenylphosphine palladium dichloride as the metal precursor, through the exchange of the ligand, the atomic level dispersion of the metal active sites in the polymer can be effectively realized. Please note that for metal active centers, a stable coordination environment of 18 electrons is the key to the formation of monoatomic discrete catalysts. The nature of the Pd metal-catalyzed reaction is the dissociation and re-coordination of the ligand. If $Pd(OAc)_2$ is used, after polymerization, the ligand polymer will often lead to the formation of a rigid structure with large steric hindrance. The distance between the coordination points becomes longer, so $Pd(PPh_3)_2(OAc)_2$, which can only form a lively 16-electron structure, often causes the catalyst to agglomerate during the preparation process.

(3) The preparation of the catalyst center as a discrete SAS catalyst cannot only effectively prevent side reactions caused by the difference in catalyst size, but also improve the utilization rate of the atoms in the catalyst, further promoting the chemoselectivity of the reaction.

With these basic ideas, we have achieved a Pd-catalyzed distannylation of terminal alkynes with high selectivity and broad substrate scope, through rational design and synergistic control of ligand polymer, porous, and SAS catalyst. It is noteworthy that the distannylation reaction we developed under SAS catalysis affords a completely different reaction result than that under the corresponding homogeneous conditions (see Table S1).

Synthesis of Pd_1@POL-PAr3 Samples

Vinyl functionalized PPh_3 derivative was prepared by employing the Witing reaction and substitution reaction. The Pd_1@POL-PAr_3 was prepared following the literature procedure via a simple polymerization-coordination method (Scheme 5). A series of PPh_3-derived ligand polymers containing different substituent groups were successfully synthesized (see Supplemental Information for experimental details).

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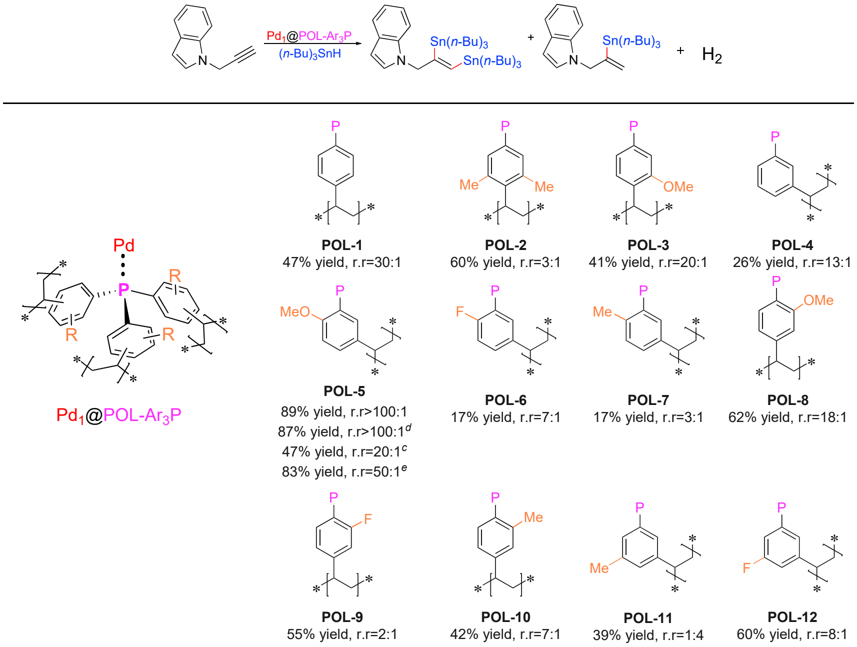

Scheme 3. Reaction Optimization

[a] Standard conditions: alkyne (0.5 mmol), $(n\text{-Bu})_3SnH$ (0.5 mmol), Pd_1@POL-Ar_3P (0.5 mol %), and THF (2 mL), 25 °C, 36 h. Isolated yield, the yields are based on a half amount of $HSnBu_3$.

[b] Ratio of distannylation product:other isomers as determined by ^1H NMR. [c] 0.25 mmol of $(n\text{-Bu})_3SnH$ was used. [d] 0.75 mmol of $(n\text{-Bu})_3SnH$ was used. [e] 1.0 mmol of $(n\text{-Bu})_3SnH$ was used.

Distannylation of Weak Electronically Terminal Alkynes

Weak electronically terminal alkynes are generally the most quintessential and challenging substrates for regio-, chemo-, and stereoselective transformations, due to the lack of inductive and chelation effects. Thus, 1-(prop-2-yn-1-yl)-1H-indole and tributyltin hydride were selected as substrates. Phosphine ligands can promote the dehydrogenation coupling of Pd-catalyzed tributyltin hydride under homogeneous conditions with poor selectivity (see Table S1). After trying a series of mono- or bi-dentate phosphine ligands, it was found that the typical mono- or bi-dentate phosphine ligands exhibited low reactivity or selectivity under the homogeneous reaction conditions. Based on the previous results, we synthesized a simple vinyl functionalized PPh_3 polymer POL-1 and investigated its catalytic performance. The results showed that the PPh_3 polymer exhibited better reactivity than the homogeneous ligand, but the chemoselectivity of the reaction was not satisfactory. Therefore, we synthesized a series of PPh_3 polymers with different substituents and substitution positions (Scheme 3, POL 2–12) and investigated their reactivity and selectivity in the reaction. It turned out that the ligand polymer POL-5 was the best ligand for the catalytic system, by which the Z-bis-tin-substituted olefin product could be efficiently obtained in a short time, with a yield of 89% and a total selectivity of 100:1. We think that this reaction has special requirements for the electronic properties of metal catalytic center. We propose that POL-5 has the most suitable electronic effect for a metal center. Surprisingly, under the catalysis of Pd_1@POL-5, the amount of $(n\text{-Bu})_3SnH$ did not affect the selectivity of the reaction, which is in stark contrast to the result of homogeneous Pd catalysis reported by the Lautens group. In order to understand this reaction more deeply, we also analyzed hydrogen and by-products by GC and LC (See Supplemental Information).

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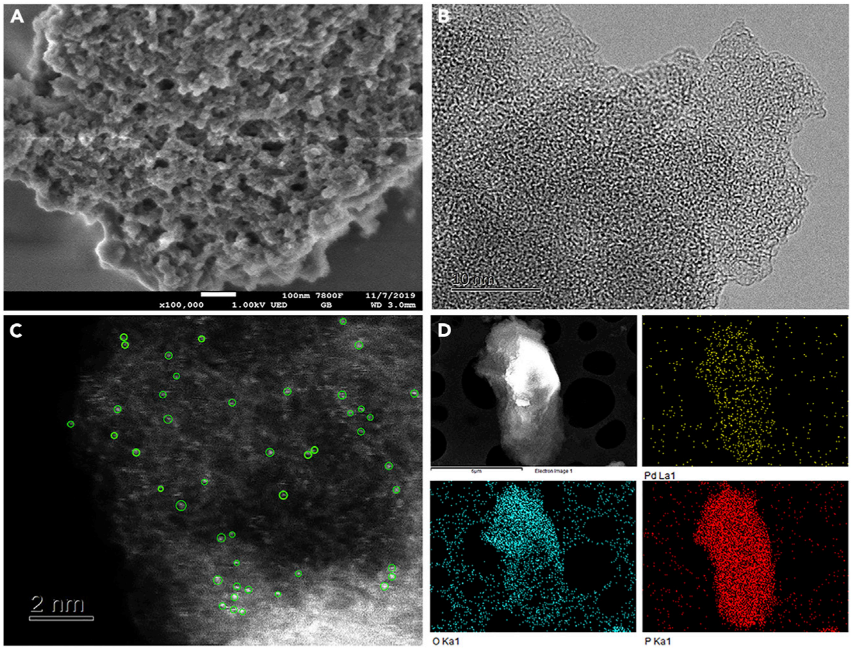

Figure 1. Characterization of the Pd$_1$@POL-5 Sample

(A) SEM image of Pd$_1$@POL-5. Scale bar, 100 nm.

(B) HR-TEM image of a Pd$_1$@POL-5. Scale bar, 10 nm.

(C) Representative AC HAADF-STEM image of the Pd$_1$@POL-5. The green circles were drawn around SAS Pd. Scale bar, 2 nm.

(D) EDX elemental mapping analysis of the Pd$_1$@POL-5. Scale bar, 6 μm.

DISCUSSION

Characterization of Pd$_1$@POL-5 Samples

To elucidate the structure-reactivity relationship and the synergistic effect of ligand and porous structure, the prepared POL-5 and Pd$_1$@POL-5 were characterized in detail. Scanning electron microscopy (SEM, Figure 1A), transmission electron microscopy (TEM, Figure 1B), energy-dispersive X-ray spectroscopy (EDS, Figure 1D), elemental mapping images, and line scan analyses revealed that O and P were distributed over the polymer sample, and Pd element was evenly distributed. High-angle annular dark-field scanning TEM (HAADF-STEM, Figure 1C) image further demonstrated that all of the Pd species in the polymer was uniformly dispersed in the sample as a single atom. The HAADF-STEM image of the used Pd$_1$@POL-5 (see Figure S9) showed that the catalyst retained a highly dispersed metal active site after use. This result confirmed that the highly stable and dispersed metal catalyst center in the polymer could effectively ensure the reactivity of catalyst after the completion of the Sn-H dehydrogenation coupling, which is different than the metal agglomeration after the reaction under homogeneous conditions. The support (POL-5) could effectively suppress the agglomeration tendency of metal sites in the polymer, which facilitates the subsequent distannylation of terminal alkynes. The X-ray diffraction (XRD) pattern of Pd$_1$@POL-5 (see Figure S16) showed that Pd$_1$@POL-5 was a highly polymerized and amorphous material. The Pd loadings of Pd$_1$@POL-5 was determined to be 1.7 wt % by inductively coupled plasma atomic emission Spectrometry (ICP-AES).

The thermogravimetric (TG) curves of POL-5 and Pd$_1$@POL-5 show that the catalyst remains intact at temperatures up to 430°C (see Figure S1). Nitrogen

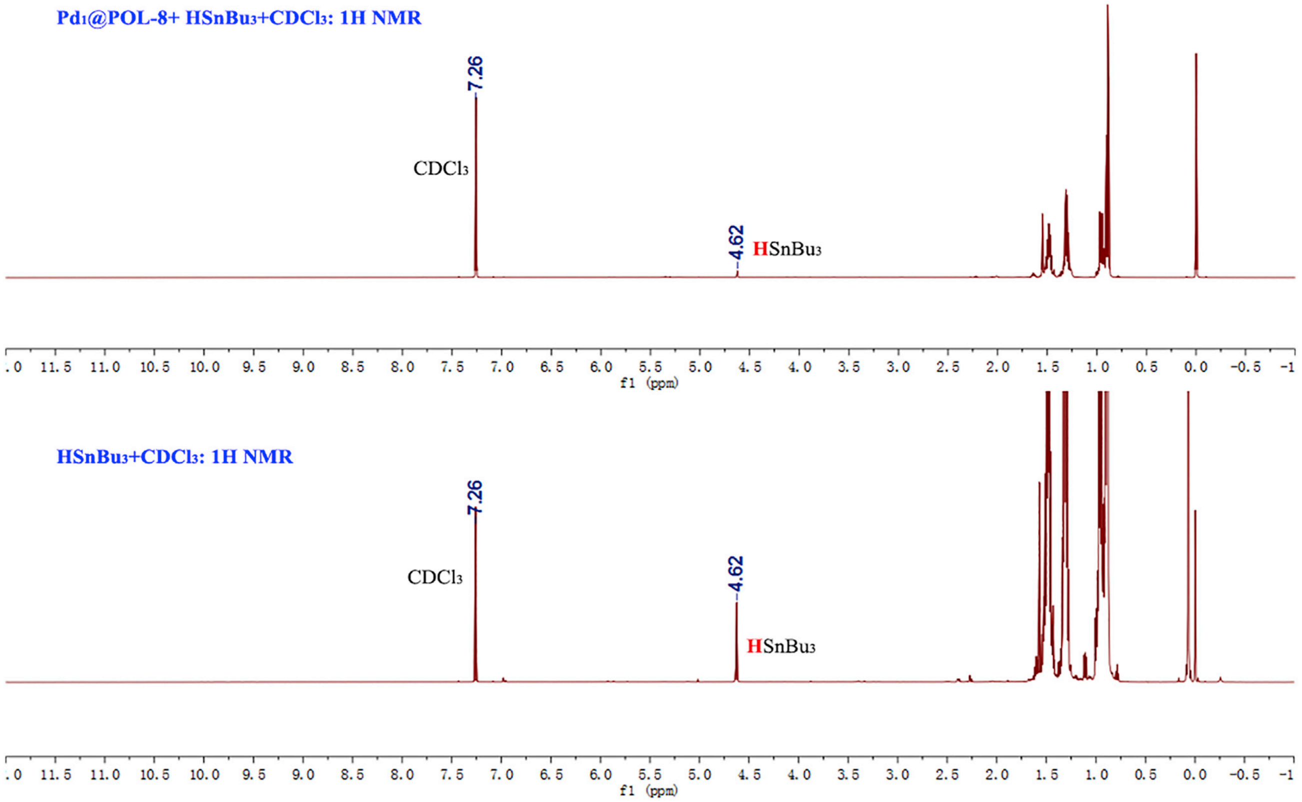

Figure 2. ^{1}H NMR Spectroscopy Experiment for Chemical Adsorption of HSn(*n*-Bu)$_3$

adsorption-desorption analysis (see Figure S2) of Pd_1@POL-5 demonstrates that the catalyst has large pore volume, high surface areas, and hierarchical porosity (BET surface area and pore volume of Pd_1@POL-5 were 810 m^2/g and 0.759 cm^3/g, respectively). Based on non-local density functional theory (NLDFT), the pore sizes of Pd_1@POL-5 were primarily distributed between 0.6 and 4 nm (see Figure S3). The NMR spectrum of the tributyltin hydride solution mixed with the catalyst confirmed that the catalyst exhibited a strong adsorption effect on the compound (Figures 2 and S24). Combined with the physical adsorption experiment on Pd_1@POL-5, it can be concluded that the porous structure of the catalyst could effectively adsorb and concentrate tri-*n*-butyltin hydride to boost the concentration of the reactants around the catalyst, thereby effectively promoting the formation of the Sn-Pd-Sn intermediate. On the other hand, *in situ* FT-IR spectra in an acetylene atmosphere were employed to investigate the formation and evolution of the active species on the surface of Pd_1@POL-5, which were recorded and are shown in Figure 3. After acetylene was introduced into the system at 0 min, the FT-IR spectrum of acetylene was scanned at about 3–5 min. The peak intensity at 2,070 cm^{-1} gradually increased from almost zero, which hardly decreased after purging with argon for at least half an hour. This result indicated that there was coordination between the alkyne and the active Pd metal center during the reaction, which further promoted the conversion of the reaction.

The X-ray photoelectron spectroscopy (XPS) spectrum of Pd_1@POL-5 (see Figure S20) demonstrated the binding energies of P2p at 132.1 eV (PAr_3 units). As shown in the P spectrum fitting results of XPS, a small peak area at 132.1 eV was 1/14.4 (6.9%) of the main peak area (131 eV). This result indicates that only 6.9%

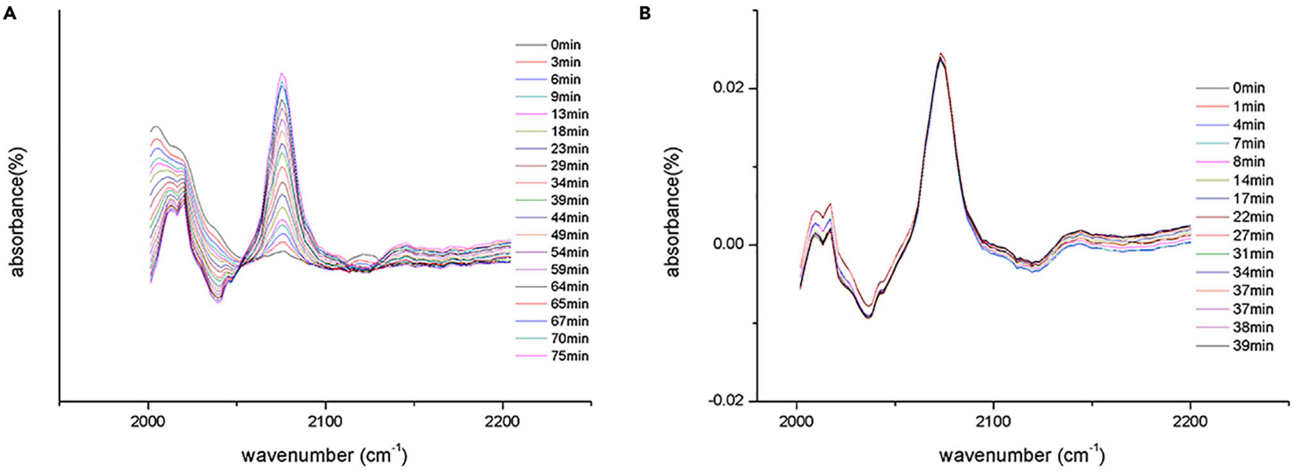

Figure 3. The *In Situ* FT-IR Spectrum of Pd_1@POL-5

(A) Under acetylene atmosphere

(B) Under an argon atmosphere.

of P atoms (0.161 mmol/g) coordinated with Pd metal, which corresponds to the calculated value (0.160 mmol/g) measured by the ICP-AES. Thus, from these results, we can conclude that the P atoms in the polymer do coordinate with the Pd metals. Solid-state ^{31}P NMR analysis also corroborated the formation of the coordination bonds (see Figure S13). Extended X-ray absorption fine structure (EXAFS) spectra were carried out to provide further insights into the coordination environment of the Pd atoms in the Pd_1@POL-5 catalyst. It can be seen that the Pd K-edge XANES of Pd_1@POL-5 was very different compared with the Pd foil (Figure 4), suggesting that Pd was completely separated into isolated single Pd sites. The quantitative coordination configuration of the Pd atom in the Pd_1@POL-5 catalyst can be obtained by EXAFS fitting (see Table S2). These characterizations (XPS, solid state nuclear magnetic resonance, and EXAFS) effectively demonstrated that the active ligand skeleton in the catalyst did not collapse and deteriorate during the polymerization.

Substrate Scope and Applications

We further investigated the substrate scope of the distannylation to study the applicability of the substrate and the influence of different substrates under the catalysis of Pd_1@POL-5. The Pd_1@POL-5 catalytic system facilitated the generation of the *Z*-dis-tin product and demonstrated to have broad application in synthesizing *Z*-dis-tin products with various functional groups. For example, alkynes with oxygen-containing functional groups (**3a–3i**), such as alcohol (**3a** and **3h**), ether (**3b**, **3d–3f**, and **3i**), ester (**3c**), even sensitive epoxyethane (**3g**), were all readily converted to the expected products in good to excellent yields. As shown in Scheme 4, the catenarain alkynes bearing nitrogen-containing groups (**3j–3o**) also form the *Z*-dis-tin product under the same conversion conditions in good yields. The aryl alkyne with the electron-withdrawing group could also produce the target compounds successfully. Interestingly, para-nitro (**3p**), meta-nitro (**3q**), or ortho-nitro (**3r**) substituted phenylacetylene completely converted into the target products without any reduction in the reaction rate, which indicated that substituent positions do not affect the catalytic performance of Pd_1@POL-5. When the substituents were aryl alkyne with electron-donating group, however, an opposite reaction selectivity occurred to afford completely different products. Under standard conditions, electron-deficient ethynylpyridines were also converted into the corresponding products (**3s**).

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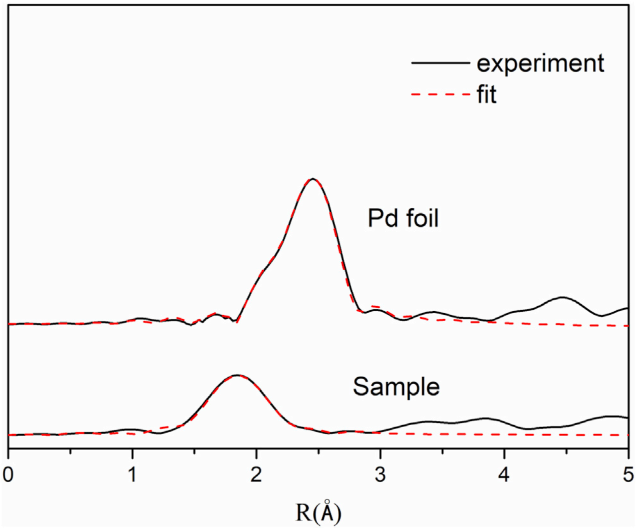

Figure 4. Pd K-Edge Fourier Transform EXAFS Spectra and Corresponding Fitting Analysis for Pd Foil

Encouragingly, the commercial herbicide, clodinafop-propargyl, afforded the corresponding product (**3t**) in a yield of up to 83% under the standard reaction conditions, which further demonstrated the application potential of this reaction in structural modification of medicinal molecular. Moreover, the catalytic performance of Pd_1@POL-5 catalyst was not compromised in the scale-up reactions.

To date, the distannylation reaction of the alkyne is an optimal solution to synthesize natural products containing a (*Z*,*Z*)-configured chloro-1,3-diene (Scheme 6, **3hb**) motif, which can tolerate a variety of sensitive functional groups. In this regard, the distannylation product is superior to the similar 1,2-disubstituted boronization olefins. Forstner group completed the first total synthesis of the natural product, putative chagosensine, with a (*Z*,*Z*)-configured chloro-1,3-diene motif, by employing this distannylation strategy. This work is an excellent example for demonstrating that the double tin reaction can tolerate sensitive enol structures. The demonstrated substrate scope in our work confirmed the broad applicability of this distannylation reaction. Unlike the boronation reaction, the developed distannylation reaction can generally tolerate sensitive functional groups, such as nitro, chlorine, cyano, and ethylene oxide under classical coupling conditions. Interestingly, 3,3-diethoxyprop-1-yne was used as the starting material for the first time to accomplish a one-step efficient and high chemo- and regioselective synthesis of dis-tin-substituted propynal (Scheme 6, **4b**) via a distannylation reaction. In addition, to explore the practicality of the distannylation process, the distannylation reaction of commercial herbicide, clodinafop-propargyl, was conducted with 0.2 mmol% Pd_1@POL-5 at 20 mmol scale, which readily afforded a good yield of **3t** (Scheme 6, 71%).

Conclusions

In summary, we report a series of POL-supported SAS Pd catalysts with remarkable catalytic performance in distannylation reactions. The POL-n with different electrical PPh_3 structure were synthesized for the first time and successfully loaded with SAS Pd via a simple solvothermal polymerization-coordination method. Different from common carbon-based material, the developed POL-n support is abundant in phosphate coordination sites with special electrical properties that play a key role in stabilizing the Pd atoms at single atomic sites. Using this catalyst, we have, for the first time, achieved a highly chemo- and

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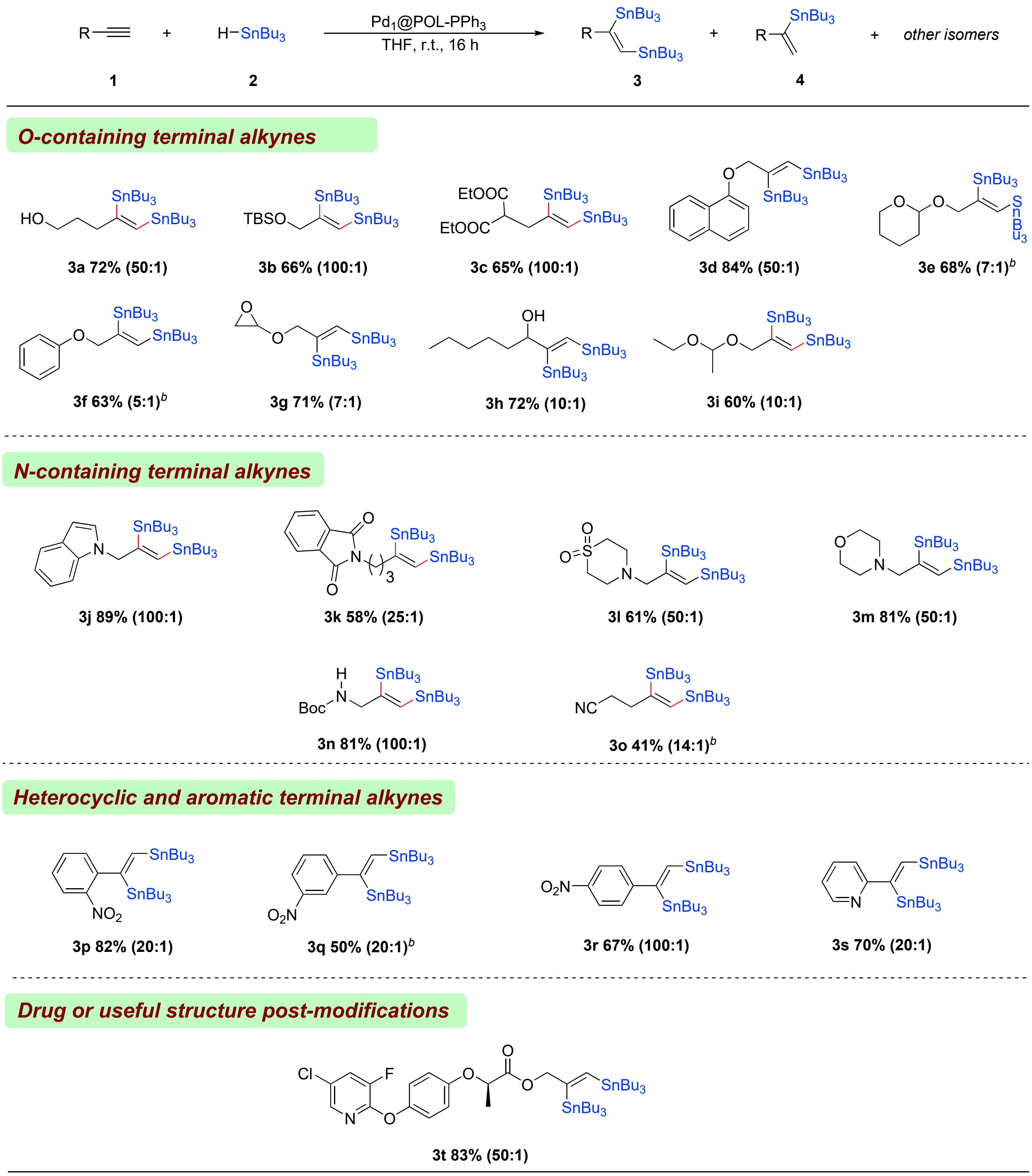

Scheme 4. Evaluation of Terminal Alkyne Scope

[a]Standard conditions: alkyne (0.5 mmol), (n-Bu)$_3$SnH (0.6 mmol), Pd$_1$@POL-Ar$_3$P (0.5 mol %), and THF (2 mL), 25°C, 36 h. Isolated yield, the yields are based on a half amount of HSnBu$_3$. The selectivity was determined by ^{1}H NMR. We also isolated the excess alkynes, see Supplemental Information for details. [b]Pd-catalyst (1 mol %), 45°C, 24 h.

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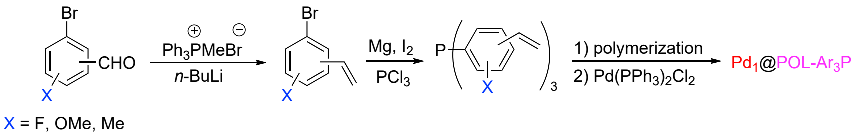


Scheme 5. Synthesis of Pd_1@POL-PAr_3

stereoselective distannylation of terminal alkyne with tri-*n*-butyltin hydride as a raw material. The as-fabricated Pd_1@POL-5 catalyst displayed a superior catalytic activity and selectivity in distannylation of various weak electronically terminal alkynes. The selectivity (*Z* only, *r.r.* up to 100:1) and catalytic performance were much higher than those of any other heterogeneous or homogenous protocols reported in the literature. More importantly, the catalytic results of this SAS Pd catalyst were opposite to those hydrostannylation products obtained by conventional homogeneous Pd catalysts for the same substrates. Finally, our work suggests that SAS catalysts not only afford an efficient platform for transforming homogeneous reactions into heterogeneous reactions but also possess many interesting potentials in developing new synthetic reactions and solving homogeneous reaction problems.

EXPERIMENTAL PROCEDURES

Full experimental procedures are provided in Supplemental Information.

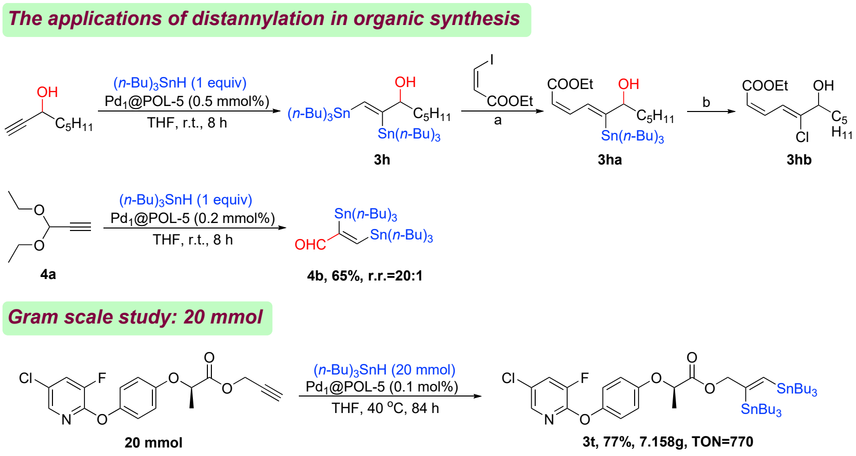
Resource Availability

Lead Contact

Further information and requests for resources and reagents should be directed to and will be fulfilled by the Lead Contact, Ying-Ming Pan (panym@mailbox.gxnu.edu.cn).

Materials Availability

Unique and stable reagents generated in this study will be made available on request, but we may require a payment and/or a completed materials transfer agreement if there is potential for commercial application.



Scheme 6. Gram Scale and the Applications of Pd_1@POL-5 in Organic Synthesis

[a] $Pd(PPh_3)_4$ (20 mol%), CuTC, $[Ph_2PO_2][NBu_4]$, DMF, Ar, 52% yield.

[b] $CuCl_2$, 2,6-lutidine, THF, 71% yield.

Data and Code Availability

This study did not generate or analyze datasets or code.

General Procedure for Distannylation of Terminal Alkynes

A flame-dried Schlenk tube was flushed under an atmosphere of nitrogen and charged with 15.5 mg of Pd_1@POL-5 (0.0025 mmol, 0.005 equiv-). The vial was sealed with a rubber septum and 2 mL of distilled THF was added followed by addition of the alkyne (0.5 mmol). Tributyltin hydride (0.5 mmol, 1 equiv) was added dropwise to the reaction vial. The reaction mixture was left to stir for 24–36 h at room temperature. When the reaction was completed (monitored by TLC), the solution was filtered and washed with EtOAc. The filtered solution was evaporated under vacuum. The crude product was purified directly by silica gel column chromatography eluting with petroleum ether, ethyl acetate, and 1% triethylamine to afford the corresponding product.

SUPPLEMENTAL INFORMATION

Supplemental Information can be found online at https://doi.org/10.1016/j.chempr.2020.06.020.

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AUTHOR CONTRIBUTIONS

W.-H.L. and W.-Y.H. conceived the idea. W.-H. L., G.-Q.W., and H.-T.T. analyzed the data and wrote the manuscript. W.-H.L., T.T.L., and S.-C.R. synthesized the catalysts. W.-Y.H. and W.-H.L. carried out the catalysis experiments. G.-Q.W., M.J., and G.-J.J. characterized the catalysts. L.Y. and Y.-J.D. designed the characterization schemes. Y.-M.P. directed the project. All the authors have read the manuscript and agree with its content.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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