Strained Carbocycles

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Selective Alkynylallylation of the C–C σ Bond of Cyclopropenes

Zeqi Jiang, Sheng-Li Niu, Qiang Zeng, Qin Ouyang, Ying-Chun Chen und Qing Xiao**

Dedicated to Professor Youqi Tang, Peking University, on the occasion of his 100th birthday

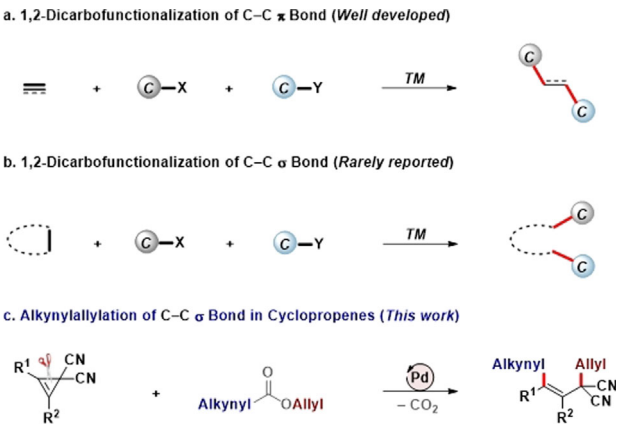
Abstract: *A Pd-catalyzed regio- and stereoselective alkynylallylation of a specific C–C σ bond in cyclopropenes, using allyl propiolates as both allylation and alkynylation reagents, has been achieved for the first time. By merging selective C-(sp^2)-C(sp^3) bond scission with conjunctive cross-couplings, this decarboxylative reorganization reaction features fascinating atom and step economy and provides an efficient approach to highly functionalized dienynes from readily available substrates. Without further optimization, gram-scale products can be easily obtained by such a simple, neutral, and low-cost catalytic system with high TONs. DFT calculations afford a rationale toward the formation of the products and indicate that the selective insertion of the double bond of cyclopropenes into the C-Pd bond of ambidentate Pd complex and the subsequent nonclassical β-C elimination promoted by 1,4-palladium migration are critical for the success of the reaction.*

Introduction

The transition-metal-catalyzed 1,2-dicarbofunctionalization of C–C π bonds has been attracting increasing interest of synthetic chemists recently for the efficient construction of acyclic complex molecular scaffolds from readily available unsaturated substrates such as alkenes and alkynes (Scheme 1 a).[1,2] In general terms, C–C π bonds are easy to coordinate and interact with transition-metal centers, which facilitates the carbometallation of unsaturated reactants. Then another carbon moiety can also be effortlessly introduced through various coupling reactions. In sharp contrast, the analogous transformation of C–C σ bonds, which predictably introduces two different carbon moieties towards the reactive carbon terminus generated by a specific σ-bond cleavage,[3] has been rarely reported so far (Scheme 1 b).[4] To the best of our knowledge, Lewis acid catalyzed bisarylation of σ-bond has been achieved until very recently by employing donor–acceptor cyclopropanes and cyclobutanes as the substrates.[4g] C–C σ bonds are ubiquitous and constitute fundamental frameworks in most organic molecules. Considering their thermodynamic stability and kinetically inertness, this selective manipulation of C–C σ bonds affords an unconventional and straight approach to edit or alter molecular textures and represents a more challenging and valuable goal in organic synthesis. The realization of this envision relies on merging C–C σ bond cleavage with conjunctive cross-coupling processes appropriately.

As highly strained but readily accessible substances, the three-membered carbocycles such as cyclopropanes[5] and cyclopropenes[6] possess unique structural and electronic properties. From the view of thermodynamics, the cleavage of C–C σ bond is an energy-costly process that can be greatly promoted by the high strain release in small cyclic compounds. From the view of kinetics, because the C–C σ bonds in three-membered carbocycles have certain π bond properties, they are relatively easier to coordinate with metal catalysts than ordinary C–C σ bonds. Therefore, cyclopropanes and cyclopropenes can serve as ideal candidates to preliminarily verify the feasibility of the selective 1,2-dicarbofunctionalization of C–C σ bonds. For the rapid production of carbon metal complexes that would react with σ bonds under neutral and mild conditions, allyl propiolates[7,8] that can generate ambidentate organometallic species via Pd-catalyzed decarboxylation[9] were chosen as both allylation and alkynylation reagents.

After trying a series of three-membered carbocycles with allyl propiolates under Pd catalysis, we found an alkynylallylation reaction of C–C σ bond in tetrasubstituted cyclopropenes to afford highly functionalized dienynes in excellent regio- and stereoselectivity (Scheme 1 c). In this reaction, one C–C σ bond is selectively cut off and the two in situ generated reactive carbon terminus are alkynylated and allylated, respectively. Astonishingly, the normally more active C–C π bonds in cyclopropenes are retained and the two C(sp^2)–C-



Scheme 1. Pd-catalyzed selective alkynylallylation of the C–C σ bond in tetrasubstituted cyclopropenes.

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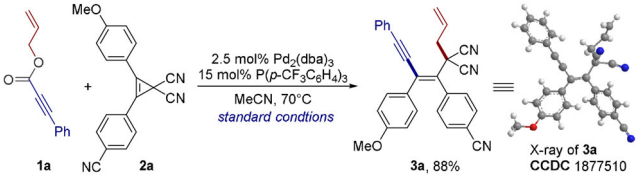
(sp^3) σ bonds with little difference can be well distinguished. Although stoichiometric byproduct CO_2 is released, the whole transformation still shows fascinating atom and step economy. Furthermore, allyl propiolates used in this method can be easily obtained through the esterification between propiolic acids and allyl alcohols. 1,1-Dicyano cyclopropenes can be expediently synthesized via a hypervalent iodine^{III}-mediated cyclopropenation of alkynes with malononitriles.[10]

Results and Discussion

Our initial attempts were aimed at investigating the model reaction of allyl phenylpropiolate **1a** and cyclopropene **2a** (Table 1). After a series of experiments, we found the optimal conditions for the reaction. An acetonitrile solution of the substrates in the presence of 2.5 mol% $Pd_2(dba)_3$ and 15 mol% P(*p*-$CF_3C_6H_4)_3$ at 70 °C furnished the desired product **3a** in 88% isolated yield (entry 1), and its structure was confirmed by single-crystal X-ray diffraction.[16] This model reaction exhibited outstanding chemo-, regio-, and stereoselectivity. None of the other isomers had been found by the rough NMR or LC-MS testing. Control experiments established the importance of P(*p*-$CF_3C_6H_4)_3$ (entries 2–4). Appropriate Pd to ligand ratio was critical for the efficient formation of the target molecule (entry 5). The reaction was more likely to occur in polar solvents (entry 6). When the temperature was lower than 45 °C, the reaction would not take place, and the two substrates can be recovered almost quantitatively. Too high temperature made the system slightly disordered and reduced the yield of the reaction (entry 7).

With the optimized conditions in hand, we first explored the scope of cyclopropenes (Figure 1). The reactions of symmetrical cyclopropenes with non-polarized double bonds also occurred smoothly (**3b**–**3d**), although it was necessary to raise the reaction temperature properly and change the solvent from acetonitrile to 1,4-dixoane. Similar to the model reaction, most transformations of unsymmetrical cyclopropenes showed excellent reactivity and selectivity (**3e**–**3v**). They always preferentially broke the σ-bond between C2 bearing relatively electron-donating groups and C1. Then, alkynylation occurred at C2 and allylation occurred at C1, affording *Z* type tetrasubstituted alkene scaffolds, with no exception. The selective ratio of bond breaking (C1–C2 or C1–C3) in each reaction was described in parentheses, unless the product was

Tabelle 1: Effect of reaction parameters.[a]



Entry	Variation of standard conditions	**3a** Yield [%]
1	None	88
2	PPh_3 instead of P(*p*-$CF_3C_6H_4)_3$	45
3	P(*p*-$MeOC_6H_4)_3$ instead of P(*p*-$CF_3C_6H_4)_3$	36
4	P(2-furyl)$_3$ instead of P(*p*-$CF_3C_6H_4)_3$	44
5	10 mol% or 20 mol% P(*p*-$CF_3C_6H_4)_3$	61/52
6	PhMe/THF/1,4-dioxane instead of MeCN	21/37/79
7	40 °C/90 °C instead of 70 °C	0/73

[a] All reactions were performed using 0.30 mmol **1a** and 0.20 mmol **2a** in 2 mL solvent for 16 hrs. Yield of isolated product.

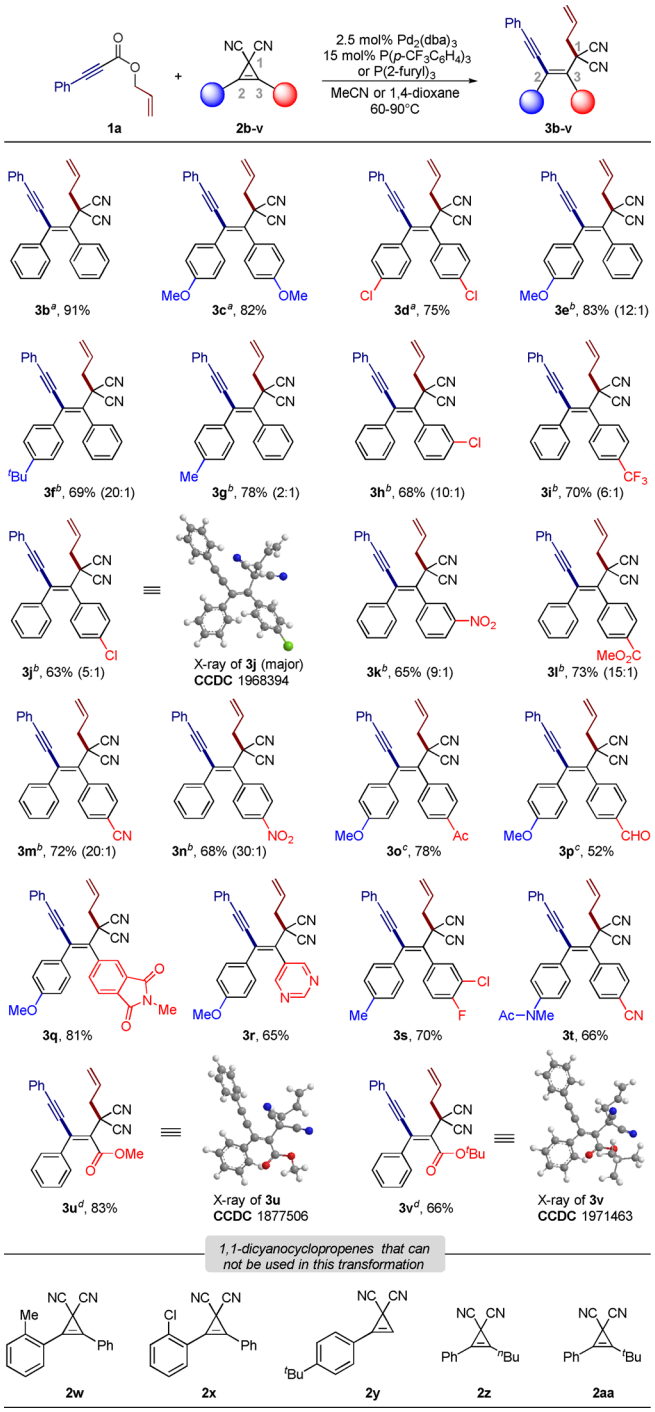


Figure 1. Scope of cyclopropenes. Unless otherwise noted, all reactions were carried out with 0.30 mmol **1a** and 0.20 mmol **2** in 2 mL MeCN under standard conditions for 16 h. Yield of isolated product. a) 1,4-dioxane, 90 °C, 12 h; b) 80 °C, 18 h; c) 50 °C, 36 h; d) P(2-furyl)$_3$, 60 °C, 12 h.[16]

unique. The ratio mainly depended on the combined effect of the electron pushing and pulling ability of the groups at C2 and C3. Even the weak polarity of the double bond can lead to significant σ-bond selectivity of the reaction. In these examples, **3g** had the worst ratio (2:1), but we have to point out that it is just caused by the electron pushing effect of a methyl group. As long as the electron pushing or pulling effect was properly enhanced, the reaction showed attractive selectivity (**3e, 3f, 3h–3n**). When electron-donating and electron-withdrawing groups were used cooperatively in cyclopropenes, the corresponding product become a unique isomer (**3o–3v**). For the efficient synthesis of **3u** and **3v** from cyclopropenes with electron-deficient double bond, the ligand P(p-$CF_3C_6H_4$)$_3$ needed to be replaced with a relatively more electron-donating ligand P(2-furyl)$_3$. To further confirm the structure of the products, we measured the single crystals of **3j**, **3u**, and **3v**, respectively.[16] These results demonstrated that the selectivity of representative product **3j** was consistent with our inference from the model reaction and the σ-bond selectivity of the reaction is not reversed by the enhance of steric effect (from **3u** to **3v**). It should be noted that some 1,1-dicyanocyclopropenes cannot be smoothly used in this transformation even if the conditions were further optimized (Figure 1). **2w**, **2x**, and **2aa** were nearly quantitively recovered using standard protocol, meanwhile, **1a** underwent its own decarboxylative allylation reaction.[7] It might be attributed to the effect of large steric hindrance. The reaction system containing **2y** or **2z** was messy, and we can only find a few product signals in LC-MS.

Then, we investigated the scope of alkynyl moieties in allyl propiolates (Figure 2a). Allyl phenylpropiolates with either an electron-donating or electron-withdrawing group on benzene ring, were able to react with **2a** to offer the corresponding products with the exclusive configuration in good to excellent yields (**3w–3ag**). The reaction conditions were compatible with alkyl, trifluoromethyl, fluoride, chloride, bromide, cyano, nitro, and acetal groups at *ortho*-, *meta*-, and *para*- position of the benzene ring. Furthermore, naphthyl and hetero aromatic propiolates also can be used for the construction of dienynes (**3ah–3ak**). Gratifyingly, allyl silylpropiolates can be used successfully in this transformation to afford products with silyl groups that are easy to be derived (**3al**, **3am**). The slight decline of σ-bond selectivity of these two reactions might be attributed to the stronger nucleophilicity of silyl ethynyl moieties. Moreover, the scope of allyl moieties in allyl propiolates was examined (Figure 2b). The representative α-, β-, or γ-substituted allyl propiolates also can participate effortlessly in the transformation to synthesize the corresponding alkynylallylation products in linear selectivity (**3an–3aq**). And a series of allyl propiolates derived from natural allyl alcohols, such as eraniol (**3ar**), nerol (**3as**), perrilly alcohol (**3at**), farnesol (**3au**), phytol (**3av**), and solanesol (**3aw**), were also successfully used in our method.

Besides, the reaction can be efficiently performed on a gram scale with high turnover numbers (TONs) of the catalyst (for details, see the Supporting Information, Tables S6, S7). On the basis of standard protocol, the scale-up reaction of 7.5 mmol of **1a** with 5 mmol of **2a** can be achieved only by increasing concentration and prolonging time. With the decrease of the amount of catalyst, the yield of the reaction decreased slightly, but the TONs of the catalyst increased greatly. Using 0.1 mol% catalyst, the reaction produced 1.52 g of **3a**, with the yield of 69% and the TONs being 345. Furthermore, 0.1 mol% catalyst loading afforded 1.49 g of **3b**, with the isolated yield of 78% and the TONs being 390.

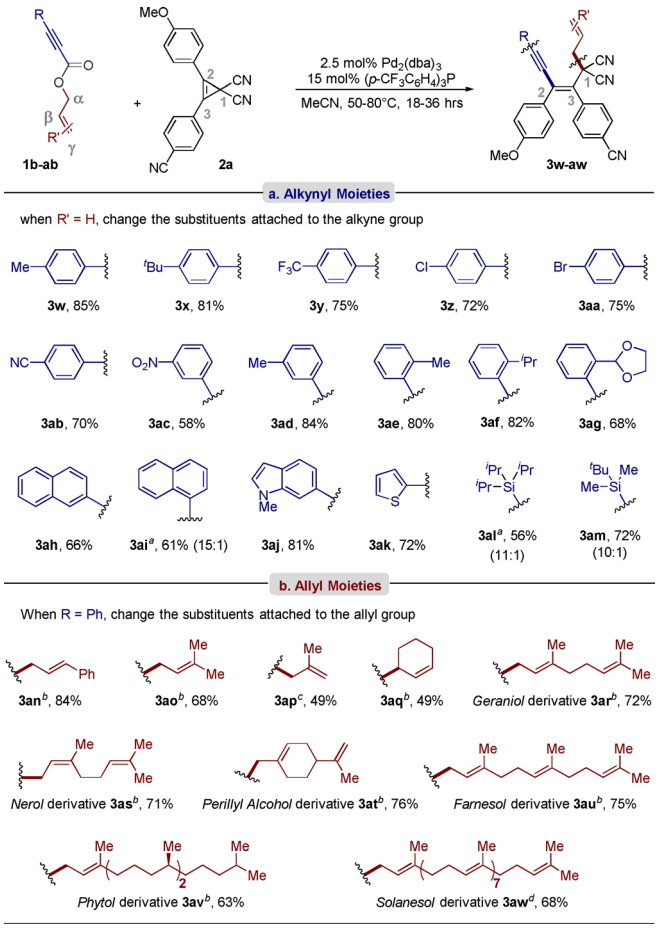


Figure 2. Scope of allyl propiolates. Unless otherwise noted, all reactions were performed using 0.30 mmol **1** and 0.20 mmol **2a** in 1 mL MeCN at 60°C for 18 h. Yield of isolated product. a) 80°C, 36 h; b) 80°C, 24 h; c) 50°C, 36 h; d) 5 mol% $Pd_2(dba)_3$, 30 mol% P(p-$CF_3C_6H_4)_3$, 80°C, 18 h.

Next, the highly functionalized dienynes **3** provided by this method can be further transformed with no trouble (Figure 3). In order to take full advantage of the structural characteristics of most products, that is, having two controllable aryls on the same side of the tetrasubstituted alkenes, we made use of the air-driven oxidative photocyclization developed by Watanabe's group[11] for efficiently constructing specific position functionalized phenanthrenes, which are not easy to be obtained through other ways. With or without substituents on its benzene rings, the compound **3** was able to successfully participate in the oxidative cyclization (**4a–4f**) to offer a single product in good to excellent yield. It is worth mentioning that the configuration of representative product **4a** was determined by X-ray diffraction[16] and the reaction of **3q** also exhibited satisfactory regioselectivity that was regulated by steric effect. Moreover, the *tert*-butyl carboxylate

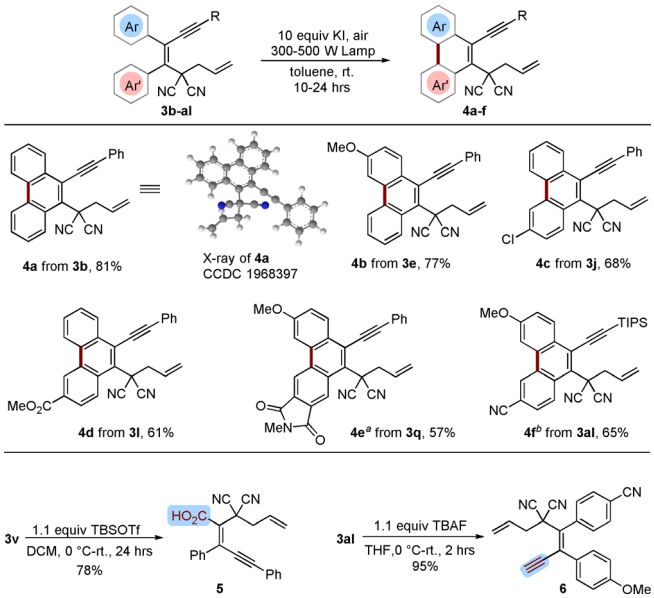
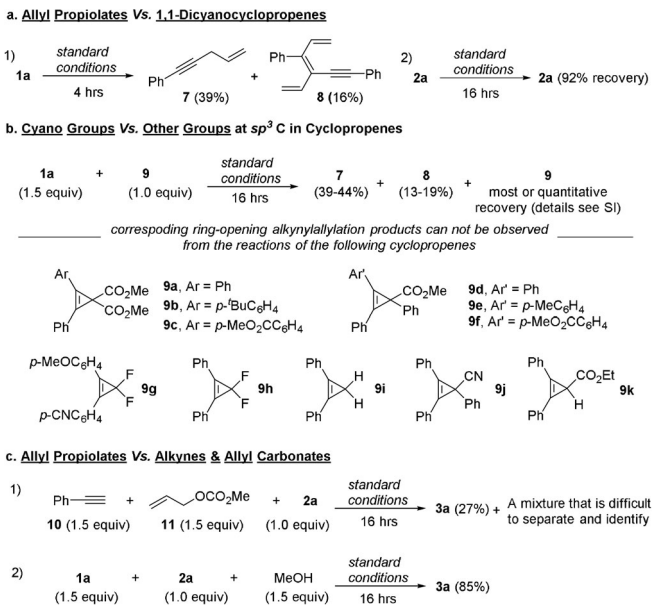


Figure 3. Downstream transformations of products. Unless otherwise noted, all reactions of **3** (0.2 mmol) using KI (2 mmol) as additives and toluene (20 mL) as solvent in an open-flask was irradiated with a 450 W high-pressure mercury lamp at room temperature for 12 h. Yield of isolated product. a) 500 W, 24 h; b) 300 W, 12 h.



Scheme 2. Control experiments for mechanism research.

moiety in **3v** can be hydrolyzed smoothly under mild conditions to produce corresponding carboxylic acid **5** in 78% isolated yield. The silyl group on the product **3al** can be easily removed, and the compound 6 which is convenient for further derivatization can be generated in 95% isolated yield. Furthermore, the 1,5-diene-7-ynes can be considered as a special class of 1,7-enynes with complex linkers, so it is no doubt that they can serve as potential substrates in the transition-metal-catalyzed cycloisomerization reactions[12] and radical cascade transformations[13] for the rapid assembly of complex carbo- and heterocycles.

Insights into Mechanisms

To understand the mechanism of our reaction in-depth, a series of control experiments were carried out. Firstly, the two substrates **1a** and **2a** were separately placed under standard conditions to investigate their reaction activity and preliminarily determine what triggered the reaction (Scheme 2a). We found that most **1a** was quickly converted to the mixture of **7** and **8** through decarboxylative allylation and dimerization processes, respectively.[8] Nevertheless, **2a** appeared very inert and can be recovered in 92% yield after 16 hours. From this, we can infer that the reaction was initiated by the decarboxylation of **1a**, rather than the generation of vinyl metal carbenoid from **2a** or oxidative addition of Pd^0 species into $C(sp^2)$–$C(sp^3)$ bond of **2a**.

The successful implementation of the reaction depends on the design of the substrates. To verify the indispensability of the cyano groups at sp^3 C in cyclopropene scaffold, we prepared a variety of cyclopropene compounds **9a**–**9k** for further examination (Scheme 2b). Without exception, the corresponding ring-opening alkynylallylation products cannot be observed and the standard protocol just generated the decarboxylative allylation product **7** and dimerization product **8** from **1a**. Impressively, the other reactant **9** can be most or quantitatively recovered after 16 hours (for details, see the Supporting Information, pages S79, S80). Based on the results, we speculated that the realization of expected transformation is attributed to the small steric resistance and strong electron-withdrawing ability of cyano group.

Furthermore, the three-component reaction of alkyne **10**, allyl carbonate **11** and cyclopropene **2a** was investigated (Scheme 2c-1), because it might be more convenient to access the ambidentate alkynyl-Pd-allyl intermediates through the reaction between **10** and **11**, rather than through the decarboxylation of allyl propiolates. However, the alternative strategy only offered the expected product in a low yield and the reaction system was messy, even after a series of optimizations of the reaction conditions. Another control reaction of **1a** and **2a** with methanol as additives was performed and the yield of **3a** had hardly decreased (Scheme 2c-2). It indicated that the in situ generated methanol was not the cause of the failure of the three-component reaction. The decarboxylation of **1a** direct produced the alkynyl-Pd-allyl species, in sharp contrast, the reaction between **10** and **11** had to firstly generate allyl-Pd species and alkynyl-Pd species, which might react with **2a** to manufacture large amounts of undesired products. These facts also disclosed that the Pd species with two carbon ligands coordination played a vital role in the transformation merging C–C bond cleavage and two sequential cross-coupling reactions.

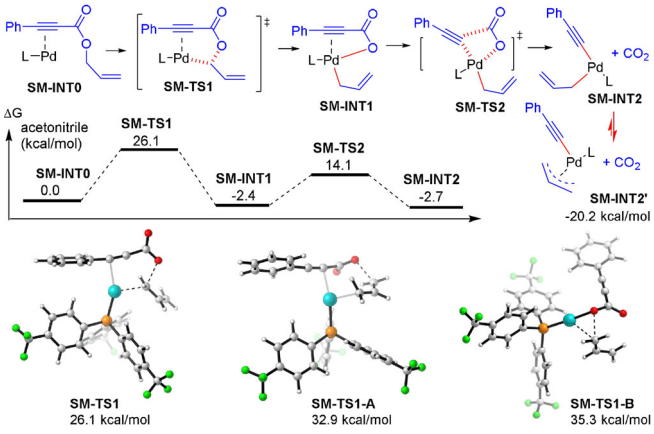
To elucidate the excellent selectivity of the reaction and further understand the mechanism, comprehensive computational DFT calculations were conducted. The geometries of all intermediates were optimized using B3LYP functional together with LANL2DZ basis set for Pd atom and the standard 6-31G(*d*) basis set for the others, and the energies

were calculated using M06L at LANL2DZ for Pd atom and 6-31++G(*d*,*p*) level for the others (acetonitrile as solvent).

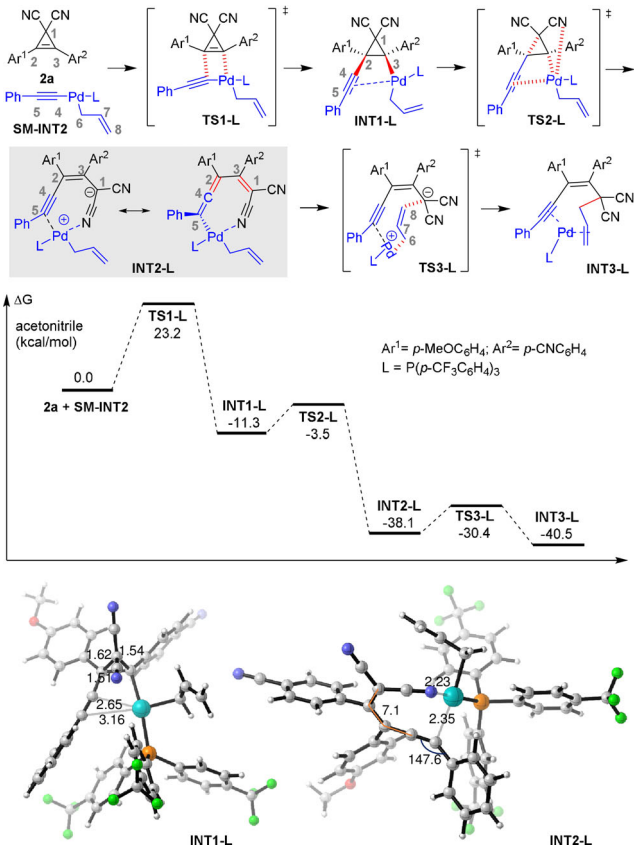
According to the calculations, phenylethynyl η^1-allyl palladium complex **SM-INT2**, the important intermediate formed via the Pd-catalyzed process of removing CO_2 moiety from allyl propiolate **1a**, would react with cyclopropene **2a** to produce dienyne **3a**.

Considering the possibility of η^1- and η^3-allyl coordination, the formation of **SM-INT2** was proposed and calculated to Figure out its initial coordination type (Scheme 3). First, the allyl C–O bond in **SM-INT0** would be broken under Pd catalyst to form **SM-INT1** via **SM-TS1**. Three possible transition states were proposed according to different models. The C–O bond breaking was accompanied with the formation of C-Pd bond via S_N2 process in **SM-TS1** with the energy barrier of 26.1 kcal mol^{-1}, while S_N2' mechanism was involved in **SM-TS1-A** forming C–Pd bond at the other terminated carbon of ally (32.9 kcal mol^{-1}). Moreover, **SM-TS1-B**, involving a three-membered ring structure, employed the highest energy barrier with the value of 35.3 kcal mol^{-1}. Because the energy barrier of **SM-TS1** was the lowest, the S_N2 process was proposed as the favorable mechanism for this step and η^1-allyl coordinated **SM-INT1** was reasonable. Next, the removal of CO_2 moiety from **SM-INT1** leaded to **SM-INT2** via a four-membered ring transition state **SM-TS2** with the energy barrier of 14.1 kcal mol^{-1}. Reactive η^1-allyl coordinated **SM-INT2** was the intermediate to react with **2a** directly, although it also would be transferred into η^3-allyl coordinated **SM-INT2′**, whose energy was 17.5 kcal mol^{-1} lower than that of **SM-INT2**. However, the transition state started from the interaction of **2a** and **SM-INT2′** cannot be generated after a lot of attempts. It might be attributed to lack of enough coordination sites at the palladium of **SM-INT2′**.

Then, the plausible reaction process of **SM-INT2** and **2a** was rationalized by calculations (Scheme 4). Initially, **SM-INT2** *syn*-added to the double bond of **2a** via a four-membered ring transition state (**TS1-L**) to form **INT1-L,** in which, the bond length of C1–C2 (1.62 Å) was much longer than those of C2–C3 (1.51 Å) and C1–C3 (1.54 Å), and the distance between C4 and Pd atom was only 2.65 Å. It meant that the bond of C1–C2 was more likely to break and coordination existed between the alkynyl and palladium atom attached to adjacent carbons. Ring-opening process of **INT1-L** played a key role in our transformation. We have tried many possibilities for the ring opening process, such as the classical *syn* coplanar β-C elimination but failed to obtain any conventional TSs. Eventually, only **TS2-L** was generated to form **INT2-L**. This step can be described as a nonclassical β-C elimination promoted by 1,4-palladium migration.[14] The interaction between alkynyl and palladium as well as the migration of palladium from C3 to C5 elevated the relative electron-donating ability of alkynyl at C2. The C1–C2 bond breaking can be regarded as the ring-opening process of the Pd-containing donor–acceptor cyclopropane. In **INT2-L,** the distance between the Pd and C5 was 2.35 Å and the distance between the Pd and the nitrogen atom of the cyan attached to C1 was 2.23 Å. C2, C4, and C5 lay on a straight line. The angle between the line and the phenyl was 147.6° that was far from 180°. The dihedral angle of C1-C3-C2-C4 was 7.1°, which meant that they were approximately in the same plane. The negative charge produced by the bond breaking can be spread out or delocalized in the large conjugated system. This chelating coordination mode prevented the C2–C3 bond from rotating freely. And the nucleophilic C1 would attack the allyl to generate the final product via a nine-membered transition state (**TS3-L**). Although we cannot exclude other possibilities, the proposed process in Scheme 4 is possible because the



Scheme 3. Computed potential energy surface of the formation of phenylethynyl η^1-allyl palladium complex.



Scheme 4. Computed potential energy surface of the reaction and structures of **INT1-L** and **INT2-L**. Energies are given in kcal mol^{-1} relative to reactants.

energy barriers are reasonable and the mechanism is consistent with our experiments.

The energy barrier of **TS1-L** was the highest among these TSs in the reaction process of **SM-INT2** and **2a**, and the selective insertion of the double bond of **2a** into the C(sp)–Pd bond of **SM-INT2** primarily determined the regio- and stereoselectivity as well as the σ-bond selectivity of the reaction. Firstly, the insertion of C(sp)–Pd bond might be the reason for the regioselectivity. Generally, alkene is inclined to insert into the C(sp)–M bond than C(sp^3)–M bond.[15] In terms of our reaction, if C(sp^3)–Pd bond had been selectively inserted, C2 or C3 would be allylated directly rather than alkynlated, which did not agree with the experimental results. In addition, the *syn* insertion and the structure characteristics of **INT2-L** should be the reason for the stereoselectivity (*Z* type). More importantly, the σ-bond selectivity of this reaction can also be rationalized by calculations. The insertions in different directions were also proposed and calculated (Figure 4). The energy of **2a-TS1-L** (**TS1-L**) with value of 23.2 kcal mol^{-1} was much lower than that of **2a-TS1A-L** (26.1 kcal mol^{-1}) in which the insertion direction was opposite, which should be the reason for the σ-bond selectivity. By the Gibbs free energy difference of 2.9 kcal mol^{-1}, the selective ratio of σ-bond can be calculated as high as 70.4. Similarly, the calculated Gibbs free energy difference between **2u-TS1-L′** and **2u-TS1-L′** (L′ = P(2-fruyl)$_3$) is 4.6 kcal mol^{-1} and the selective ratio is 853. To further analyze the σ-bond selectivity, the natural population analysis (NPA) charge evaluation towards the cycloproenes **2** was also conducted (Supporting Information, Figures S81–S83). The results indicated that the σ-bond selectivity might be positively correlated with the difference of the NPA charges at C2 and C3.

Conclusion

We have described a Pd-catalyzed selective alkynylallylation of the C–C σ bond of tetrasubstituted cyclopropenes. While the substrate scope of the reaction still has room for further improvement, the transformation that two different carbon moieties, respectively couple with the reactive carbon terminus generated by a specific C–C σ bond cleavage is promising and encouraging. This atom- and step-economic reaction provides an efficient route to highly functionalized dienynes in an excellent regio- and stereoselective manner. Without further optimization, gram-scale products can be obtained effortlessly by such a simple, neutral, and low-cost catalytic system with high TONs. The selective insertion of cyclopropenes into the C–Pd bond of the ambidentate Pd complex and the subsequent nonclassical β-Carbon elimination promoted by 1,4-palladium migration are critical for the success of the reaction. These domino processes also supply a novel strategy to selectively open and fully exploit cyclopropenes.

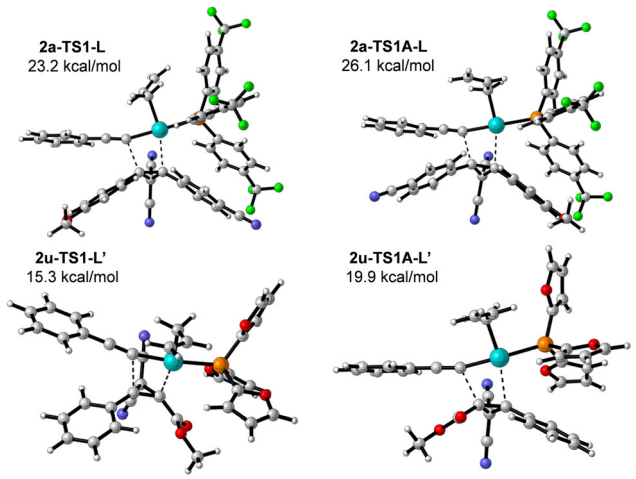


Figure 4. Structures and energy barriers for TS1. Energies are given in kcal mol^{-1} relative to reactants.

Acknowledgements

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Conflict of interest

The authors declare no conflict of interest.

Stichwörter: C–C bond cleavage · cyclopropene · dicarbofunctionalization · palladium

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Forschungsartikel

Strained Carbocycles

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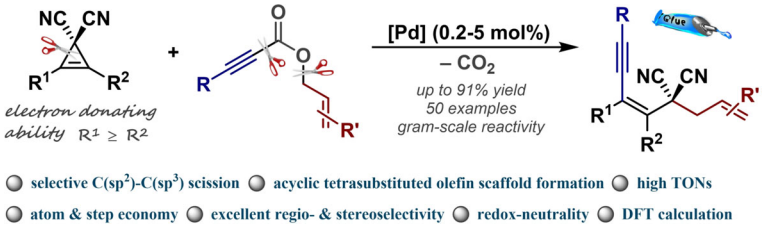
Selective Alkynylallylation of the C–C σ Bond of Cyclopropenes



1,2-Alkynylallylation of a specific C–C σ bond in cyclopropenes was realized by a simple, neutral, low-cost palladium catalytic system with high TONs. This decarboxylative reorganization reaction is an efficient way to construct highly functionalized dienynes in excellent regio- and stereoselectivity. A nonclassical β-C elimination promoted by 1,4-palladium migration was described herein for the first time.