Domino Palladium-Catalyzed Double Norbornene Insertion/ Annulation Reaction: Expeditious Synthesis of Overcrowded Tetrasubstituted Olefins

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Supporting Information

ABSTRACT: A Pd-catalyzed domino process involving a double norbornene insertion/annulation reaction was developed for the expeditious synthesis of overcrowded olefins. In this one-pot reaction, four new C–C bond formations were achieved by three consecutive Heck carbopalladations and C–H activation across the C \equiv C triple bond of 2-alkynyl bromobenzenes with two norbornene rings via a reactive vinylic-Pd(II) species. This protocol provides a step-economical synthetic system to access the structurally identical molecular machine motifs of overcrowded olefins with high yields.

vercrowded tetrasubstituted olefin compounds have attracted much interest in the past decade due to their iterative application in the field of artificial molecular machines (AMMs) designing.¹ Recently, various sterically overcrowded olefin derivatives were synthesized and employed in the lightdriven molecular switches and molecular motors,² and further, these kinds of motifs were used as a fluorescent material in the organic light-emitting diodes (OLEDs) and fluorescent bioprobes designing.³ Typically, McMurry coupling or Barton-Kellogg reactions are applied for the synthesis of symmetrical and unsymmetrical tetrasubstituted olefins.⁴ In this context, Lautens et al. developed an attractive domino approach based on the Catellani reaction to access sterically crowded olefins via a Pd-catalyzed multiple C-H activation. Consecutively, Tietze et al. and Perumal et al. realized the synthesis of multisubstituted olefins through Pd-catalyzed domino reactions.⁶ Although these methods have made a significant contribution to the synthesis of sterically hindered tetrasubstituted olefins, the development of a simple and stepeconomical domino approach for their efficient preparation is still highly desirable.

The insertion of norbornene and its derivatives into the organic molecules is creating a great impact in the field of medicinal and pharmaceutical chemistry.⁷ These types of insertion reactions are established with particular functional groups in the literature.⁸ In our continuous research on Pd-catalyzed reactions, we recently disclosed a first Pd-catalyzed single norbornene insertion reaction across alkyne derivatives for the efficient synthesis of tetrasubstituted olefins.⁹ This

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method offers a straightforward way to achieve a wide range of norbornene-fused tetrasubstituted olefins in good yields. Though the norbornene insertion reactions with a $C \equiv C$ triple bond or a C-C single bond are scarce,¹⁰ most of the disclosed methods deal with the bond formation of a C=C double bond and a norbornene ring.¹¹ For example, Kosugi et al. developed the stereoselective double norbornene insertion reactions with 1-alkenyltin trichlorides (Scheme 1a).^{11e} In this contrast, we set out to explore double norbornene insertion reactions with alkyne to construct the synthetically robust bisfluorene scaffold. This unexplored double norbornene







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insertion reaction provides a synthesis of structurally similar molecular machine motifs of overcrowded olefins. Therefore, we desire to develop this unexplored reaction in a step economical manner using easily accessible starting materials such as 2-alkynylaryl bromobenzene and norbornene in onepot (Scheme 1b). To the best of our knowledge, this is the first reductive difunctionalization reaction of alkyne with norbornene to synthesize the multisubstituted olefin compounds.

To investigate this domino Pd-catalyzed double norbornene insertion/annulation reaction, 1-bromo-2-(p-tolylethynyl)benzene 1a and norbornene 2 were used as trial substrates under different reaction conditions (see Supporting Information for more details). An extensive survey of various reaction parameters revealed that 10 mol % of Pd(OAc)₂, 20 mol % of PPh₃, and 3.0 equiv of K₂CO₃ in DMF at 100 °C under N₂ atmosphere were considered as optimal reaction conditions to this title reaction. Single-crystal X-ray diffraction analysis confirmed the structure of tetrasubstituted olefin 3a (Scheme 2).¹² Further characterization by ¹H and ¹³C NMR spectroscopy of the diastereomeric mixture 3a/3'a was performed and identified 3a as a major diastereomer.

Scheme 2. Scope of 2-Alkynylaryl Bromobenzenes with Norbornene a



^{*a*}Reactions were carried out with **1a–t** (0.3 mmol), norbornene **2** (3.0 equiv), $Pd(OAc)_2$ (10 mol %), PPh_3 (20 mol %), and K_2CO_3 (3.0 equiv) in DMF (4 mL) at 100 °C under N₂ atmosphere. Isolated yield by flash column chromatography, and ratios of the diastereomers were determined by ¹H NMR. ^{*b*}20 mol % of $Pd(OAc)_2$ and 40 mol % of PPh_3 for 5 h. ^{*c*}3.68 mmol scale of **1a**. Major isomer only presented in this table.

Under optimized reaction conditions, the scope of the Pdcatalyzed double norbornene insertion/annulation reaction of various 2-alkynylaryl bromobenzenes (1a-t) was examined with norbornene 2 (Scheme 2). The experimental results indicated that the electronic effects of the starting materials played a significant role in reaction efficiency, regardless of the diastereomeric ratio of the products. Initially, we investigated the reaction of the different R² substitution, which possesses electron-donating (-OMe and $-NEt_2$) and electron-withdrawing ($-CO_2Me$, -COMe, $-NO_2$, -CN, and -Cl) groups at the para-position of the alkynylaryl moiety. All of these substitutions underwent smooth conversion to afford the desired product of multisubstituted olefins (3b,c and 3e-i) in 74-95% yields. Remarkably, the biphenyl substrate 1d exhibited good reactivity to produce the desired product 3d in 82% yield. Interestingly, when the bromobenzene ring bearing various substituents at the *meta*-position of the \mathbb{R}^1 (H, $-Me_{1}$ $-CO_{2}Me_{1}$ $-CN_{1}$ and $-Cl_{2}$ were treated with norbornene, it provided the corresponding products (3k-o)in 80-95% yields. Subsequently, different substitutions on both rings were also explored in our title reaction conditions with norbornene and were found to provide the resultant olefin products (3p-s) in 72-96% yields. Under the optimized conditions, 2,4-dichloroalkynylaryl bromobenzene 1j was successfully transformed to the expected product 3i in 70% yield. Furthermore, the substrate 1t has two possible C-H activation sites. The reaction proceeded preferentially at the least sterically crowded site to generate the major product 3t(a) and the minor product 3t(b) from the crowded site. Next, a gram-scale reaction of 1a (1.0 g) was performed to test the practicality of this protocol, which produced an isolated yield of 90% (1.26 g) of 3a (Scheme 2). Functional groups like ether, amine, ester, keto, nitro, nitrile, and chloro were highly compatible in our reaction conditions, providing opportunities for further elaboration of these multisubstituted olefins. In this protocol, 2-alkynylaryl bromobenzene, bearing electron-withdrawing groups, provided excellent yields compared with electron-rich 2-alkynylaryl bromobenzene. Further, the exact structure of the major isomer 3k was confirmed by singlecrystal X-ray analysis.¹²

To further explore the synthetic versatility of the double norbornene insertion/annulation reactions, the scope of 2alkynylheteroaryl bromobenzenes (1u-z) was subjected to optimized reaction conditions (Scheme 3). The Pd-catalyzed domino reaction of 2-alkynylthienyl 1u with norbornene afforded our desired product 3u in 72% yield. A slightly lower yield of product 3v was obtained for the 3-alkynylthienyl substrate. Gratifyingly, excellent yields of norbornene-incorporated overcrowded olefin products (3w,x) were isolated when electron-withdrawing groups $(-CO_2Me \text{ and } -CN)$ were





^aReactions were carried out with 1u-z (0.3 mmol), norbornene 2 (3.0 equiv), Pd(OAc)₂ (10 mol %), PPh₃ (20 mol %), and K₂CO₃ (3.0 equiv) in DMF (4 mL) at 100 °C under N₂ atmosphere. Isolated yield by flash column chromatography, and ratios of the diastereomers were determined by ¹H NMR. Major isomer is only presented in this table. introduced at the bromobenzene ring (R) of 3-alkynylthienyl substrates (1w,x). The double norbornene insertion reaction was not successful when we employed the 2-alkynylpyridyl and 3-alkynylindole bromobenzene (1y,z) substrates in our general reaction. In addition, the standard reaction conditions were favorable for norbornadiene 4 to undergo the desired domino reaction with 1a to provide the norbornadiene-fused over-crowded olefin 5a/5'a in 30% yield (Scheme 4).

Scheme 4. Pd-Catalyzed Domino Reaction of 1a with Norbornadiene



After establishing the scope of 2-alkynylaryl/heteroaryl bromobenzene derivatives, we examined the influence of the π -system containing 2-alkynylaryl bromobenzenes (**6a**,**b**) with norbornene (Scheme 5). Under optimal reaction conditions,

Scheme 5. Reaction of π -System Containing 2-Alkynylaryl Bromobenzenes



the 2-phenoxy **6a** substrate afforded a mixture of products with the desired double norbornene moiety 7a/7'a in 38% yield and another single norbornene insertion product $7b^{13}$ in 48% yield. The substrate **6b** did not undergo the desired reaction to provide product **8a**, instead it yielded a single norbornene inserted product **8b** with 40% yield by C–H_b activation.⁹ This is due to the stronger coordination of the aryl ring π -system (phenyl compare to phenoxy) with active vinylic-Pd(II) intermediate and thereby limits the reactivity of a second norbornene insertion reaction and did not produce a double norbornene insertion product. This result strongly suggests the regio- and stereoselective formation of a key vinylic-Pd(II) intermediate **C** via *syn*-carbopalladation of *cis-exo*-arylnorbornyl Pd(II) bromide complex **B** (Scheme 7).

Next, the mechanistic insight was obtained through intramolecular kinetic isotope effect (KIE) studies using the substrate 1a- D_1 and norbornene 2. Under standard conditions, the corresponding products 3a/3a- D_1 were obtained in 95% yield with an intramolecular KIE of 3.3 (Scheme 6a). This high KIE clearly indicates that the C–H activation step was involved in the C–H bond cleavage and is incompatible for an electrophilic aromatic substitution-type mechanism.¹⁴ To further deduce the mechanistic pathway, an intermolecular competition experiment between the electron-rich 1a and electron-deficient 1f of 2-alkynylaryl bromobenzenes with norbornene 2 was performed (Scheme 6b). A ratio of 1.1:1.0 Scheme 6. Competitive Experiments



was obtained between 3f/3a, which suggests that the electronic effects do not have a strong influence. Further, these results confirm an incompatibility for an electrophilic aromatic substitution mechanism in the C-H activation step. A competition experiment between substrate 1e with norbornene 2 and diphenylacetylene 9 was conducted (Scheme 6c). This study demonstrates the developed catalytic system was only applicable for selective norbornene insertion reactions across 2-alkynyl bromobenzenes, and norbornene was the key substrate in the success of this transformation.

Based on previous reports¹¹ and competition experimental studies, a plausible reaction mechanism for a double norbornene insertion/C-H activation annulation reaction was proposed (Scheme 7). First, the oxidative addition of 1k

Scheme 7. A Plausible Mechanism for Pd-Catalyzed Double Norbornene Insertion/Annulation Reaction



to Pd(0) would afford the active organo Pd(II) intermediate **A**, which undergoes intermolecular carbopalladation with norbornene **2** on the *exo* face exclusively to generate the *cis-exo*-arylnorbornyl Pd(II) bromide complex **B**. This intermediate undergoes intramolecular *syn*-carbopalladation on the tethered alkyne to generate an active key vinylic-Pd(II) species **C** with regio- and stereoselective manner. Subsequently, **C** would

undergo intermolecular carbopalladation via either the sterically favored *endo* face or sterically nonfavored *exo* face of another norbornene molecule, leading to intermediates **D** or **F**, respectively. Formation of **D** is favored over that of **F** due to less steric hindrance in the former. Further, these intermediates undergo C-H activation with the adjacent aryl ring to form the corresponding palladacycles **E** and **G**. Finally, reductive coupling of the intermediates **E** and **G** gives the final products **3k** and **3'k** with regeneration of the active Pd(0) catalyst in the presence of a base.

Notably, all of the synthesized overcrowded olefins displayed interesting photoluminescence (PL) properties.¹⁵ For instance, the PL spectrum of 3k/3'k in a thin-film state showed absorption and emission maxima at 357 and 466 nm, respectively (Figure 1a). This result indicates the aggrega-



Figure 1. (a) Normalized absorption (black line) and PL (blue line) spectra of 3k/3'k in a thin-film state. (b) PL spectra of 3k/3'k in THF and THF/H₂O mixtures. Concentration: 10 μ M and excitation wavelength: 310 nm. (c) Plot of PL peak intensity of 3k/3'k vs water fractions in THF/H₂O mixtures. Photos of 3k/3'k in THF/H₂O mixtures ($f_w = 99$, 90, 80, and 70%) taken under UV luminescence.

tion-induced emission (AIE) phenomenon of $3\mathbf{k}/3'\mathbf{k}$ attributed to the restriction of intramolecular motions.³ To investigate the AIE behavior of $3\mathbf{k}/3'\mathbf{k}$, its PL spectra were recorded in THF/H₂O mixtures (Figure 1b and 1c). In THF/H₂O mixtures with $f_w = 0-80\%$, $3\mathbf{k}/3'\mathbf{k}$ emitted a faint fluorescence. The fluorescence intensity of $3\mathbf{k}/3'\mathbf{k}$ was enhanced gradually with increasing water content from $f_w = 80$ to $f_w = 99\%$, and a maximum emission intensity was obtained at $f_w = 99\%$.

In conclusion, we have demonstrated a highly efficient Pdcatalyzed double norbornene insertion/annulation domino reaction for the proficient synthesis of overcrowded tetrasubstituted olefins from easily accessible starting materials of 2alkynylaryl/heteroaryl bromobenzenes and norbornene. Using this method, two norbornene moieties were sequentially incorporated to construct bis-fluorene frameworks in a onepot operation involving the formation of four new C-C bonds via three consecutive Heck carbopalladations and C-H activation. The success of the protocol relies on the insertion of the second norbornene moiety with the key vinylic-Pd(II) intermediate. The expediency of this reaction was highlighted by the broad substrate scope, good functional group tolerance, mild reaction conditions, and gram-scale synthesis. Furthermore, this predominant methodology provides a new platform for the synthesis of structurally identical molecular machine motifs. Additionally, this synthesized overcrowded olefin system exhibits interesting AIE fluorescent properties that might be useful for OLED and other applications. These studies will provide new opportunities to design other transformations related to norbornene insertion reactions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.or-glett.9b01543.

Experimental procedures, optimization details, characterization data, copies of NMR spectra of all compounds, and crystallographic data for **3a**, **3k** and **7b** (PDF)

Accession Codes

CCDC 1020303, 1483642, and 1872729 contain 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.

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Notes

The authors declare no competing financial interest.

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(12) See the Supporting Information for ORTEP diagram of 3a, 3k, and 7b.

(13) The structure of the overcrowded olefin 7b (CCDC 1872729) was confirmed by X-ray diffraction analysis of the single crystal; see the Supporting Information.

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(15) See the Supporting Information for PL spectra of all synthesized compounds in 99% of H_2O/THF .