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Stereoselective Construction of Trisubstituted 1,3-Enynes *via* Aryl to Vinyl 1,4-Palladium Migration

Jie Lin,[a, b] Juan Ma,[a, b] Liandi Wang,[a] Ping Wu,[a] Kaikai Wu,[a] Yong-Gui Zhou,[a,*] and Zhengkun Yu[a,*]

[a] Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian, Liaoning 116023, People's Republic of China
E-mail: zkyu@dicp.ac.cn; ygzhou@dicp.ac.cn
[b] University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China

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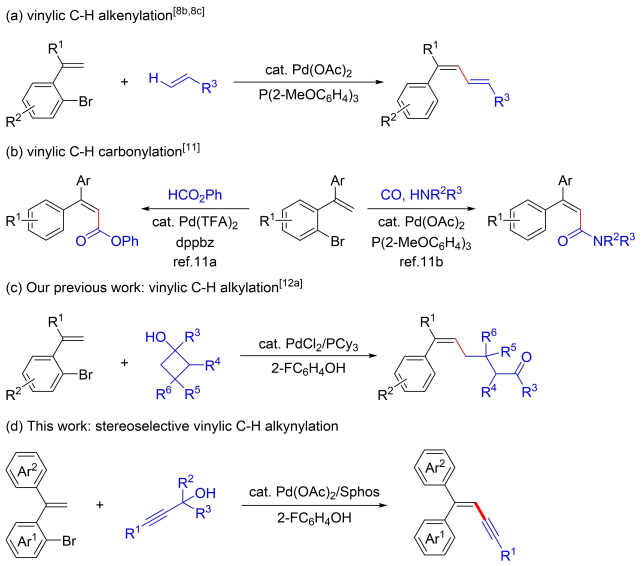
Abstract: Palladium-catalyzed stereoselective olefinic C–H alkynylation of *gem*-diarylsubstituted ethylenes with propargylic alcohols was achieved to access diverse unsymmetrical 1,3-enynes. The regio- and stereoselectivities were established through a 1,4-palladium migration from aryl to vinyl in the presence of 2-FC_6H_4OH as additive. Mechanistic investigations suggest that cleavage of the olefinic C–H bond might not be involved in the rate-determining step of the catalytic process.

Keywords: C–H activation; Propargylic alcohols; 1,3-Enynes; 1,4-Palladium migration

Introduction

Transition metal-catalyzed C–H activation has emerged as an increasingly powerful tool for C–C bond formation in organic synthesis.[1] Efficient 1,*n*-migration of a transition metal has been used as a prospective C–H activation approach for converting C–H bonds in intricate substrates into beneficial functional moieties.[2] In this regard, 1,4-palladium migration has provided a unique reaction mode adopted to selectively achieve remote C–H bond modification.[3] Various processes involving 1,4-palladium migration such as aryl to aryl,[4] vinyl to aryl,[5] alkyl to acyl,[6] and aryl to alkyl,[7] have been explored. Following the work by Lin and Feng, et al. on palladium-catalyzed vinylic C–H borylation of *ortho*-vinyl bromobenzenes,[8a] efforts have been focused on the functionalization of alkenes through aryl to vinyl 1,4-palladium migration,[8b–10] especially for the construction of C–C bonds. Olefinic C–H alkenylation[8b,c] (Scheme 1a) and arylation[8d] of *gem*-disubstituted ethylenes were established through a 1,4-palladium migration/Heck or Suzuki-Miyaura coupling sequence, respectively. Strategies for intercepting the vinylpalladium species generated *via* 1,4-palladium migration to enable vinylic C–H carbonylation have been separately described (Scheme 1b).[11] Recently, we documented highly regioselective C–H alkylation of *o*-vinyl bromobenzenes with cyclobutanols through a 1,4-palladium migration/C–C cleavage protocol



Scheme 1. C–C Bond formation *via* aryl to vinyl 1,4-palladium migration.

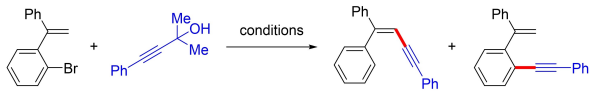
(Scheme 1c),[12a] C–H allenylation/alkenylation of styrenes with *N*-tosylhydrazones *via* such a palladium migration/carbene migratory insertion/*β*-hydride elimination sequence,[12b] and C–H polyfluoroarylation of *gem*-diaryl alkenes employing polyfluoroarenes.[12c]

Propargylic alcohols are widely used as reactive handles in organic synthesis.[13] For example, alkyne-functionalized dihydrobenzofurans and indolines were accessed with propargylic alcohols as coupling components through a vinyl to acyl 1,5-palladium migration.[14a] A Pd/Rh cooperatively catalyzed cascade reaction was developed to merge an alkynylidene moiety with benzosilacycle.[14b] Regarding C–C alkenylation of propargylic alcohols, the method for the regio- and stereoselective synthesis of 1,3-enynes has not yet been established. In line with the known work,[8–11] and considering our ongoing research on olefinic C–H functionalization,[12,15] it was reasonably envisioned that 1,4-palladium migration of *o*-vinyl bromobenzenes may be potent for the alkenylation of propargylic alcohols to execute highly regio- and stereoselective formation of 1,3-enynes, which are important building blocks in organic synthesis,[16,17] and also occur widely in natural products.[18] Herein, we report a concise protocol to access synthetically useful unsymmetrical 1,3-enynes *via* aryl to vinyl 1,4-palladium migration under mild conditions (Scheme 1d). During our submission process, Feng's group[19] disclosed such a metal migration using the terminal alkyne ethynyltriisopropylsilane (H–C≡C-TIPS) *via a* 1,4-palladium migration/Sonogashira sequence to access TIPS-substituted enynes.

Results and Discussion

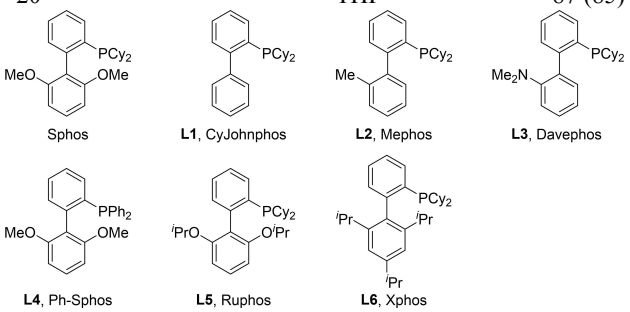
Initially, the reaction of 1-bromo-2-(1-phenylvinyl)benzene (**1 a**) with 2-methyl-4-phenylbut-3-yn-2-ol (**2 a**) was performed to optimize the reaction conditions (Table 1). Referring to the reaction of olefinic C–H alkylation previously reported by our

Table 1. Optimization of the reaction conditions.[a]



1a **2a** **3a** **3a'**

Entry	Ligand	2-FC_6H_4OH (mol%)	Solvent	Yield of **3 a**[b] (%)	rr[c] (**3 a**:**3 a′**)
1	PPh_3	10	toluene	14	1:1.8
2	Sphos	10	toluene	72	8.4:1
3	**L1**	10	toluene	19	1.3:1
4	**L2**	10	toluene	49	3.8:1
5	**L3**	10	toluene	39	1.8:1
6	**L4**	10	toluene	47	5.2:1
7	**L5**	10	toluene	68	6.8:1
8	**L6**	10	toluene	36	16:1
9	Sphos	10	THF	82	>20:1
10	Sphos	10	2-MeTHF	73	>20:1
11	Sphos	20	THF	87	>20:1
12	Sphos		THF	5	1:9
13[d]	Sphos	20	THF	87 (85)[e]	>20:1

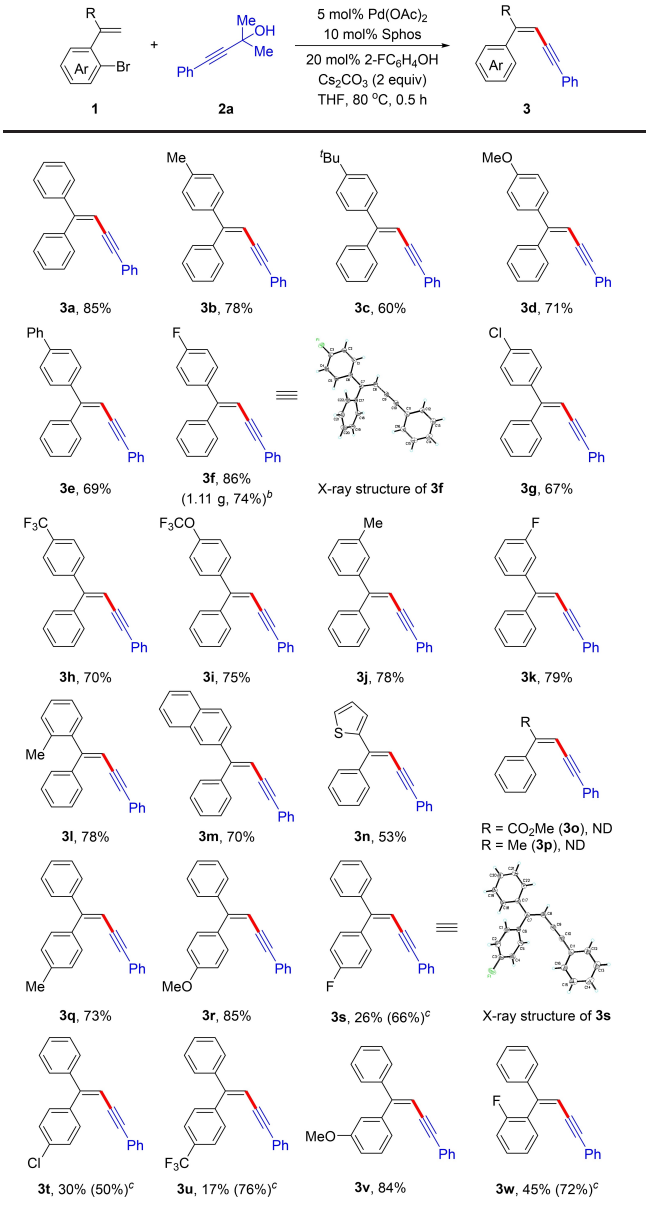


[a] Conditions: **1 a** (0.2 mmol), **2 a** (0.3 mmol), $Pd(OAc)_2$ (5 mol%), ligand (10 mol%), Cs_2CO_3 (2 equiv.), 2-FC_6H_4OH, solvent (2 mL), argon, 80 °C, 0.5 h.
[b] Determined by ^1H NMR analysis using 1,3,5-trimethoxylbenzene as the internal standard.
[c] The rr represents the ratio of the target product **3 a** to its regioisomer **3 a′**, determined by ^1H NMR analysis.
[d] **1 a** (0.3 mmol), **2 a** (0.45 mmol), THF (3 mL).
[e] Isolated yield given in parentheses.

lab,[12a] with PPh_3 as the ligand and Cs_2CO_3 as the base the reaction only gave the target migratory product **3 a** in 14% yield along with major generation of the direct coupling product **3 a′** (**3 a**/**3 a′** = 1:1.8) (Table 1, entry 1). Using Sphos as the ligand obviously enhanced both the yield and regioselectivity (72%) (8.4:1 rr) of the target product (Table 1, entry 2). Screening of phosphine ligands has shown that the desired 1,4-palladium migration process could be accelerated by the biphenyl-type phosphines, especially those (Sphos and **L5**) bearing both alkoxyl and dicyclohexyl groups (Table 1, entries 2 and 7). With THF (82%) or 2-MeTHF (73%) as the reaction medium, **3 a** was formed in a more efficient manner with high regioselectivity (> 20:1 rr), demonstrating that THF solvent was crucial to avoid formation of the side-product **3 a′** (Table 1, entries 9 and 10). Addition of 2-FC_6H_4OH significantly expedited the intended aryl-to-vinyl 1,4-palladium migration process and suppressed generation of the regioisomer **3 a′**, presumably due to a thermodynamically favourable process assisted by 2-FC_6H_4OH according to our previous DFT calculations.[12a] Increasing the loading of 2-FC_6H_4OH additive from 10 mol% to 20 mol% further optimized the reaction efficiency (Table 1, entries 2 and 11). However, in the absence of 2-FC_6H_4OH compound **3 a** (5%) could hardly be formed, and direct cross-coupling of **1 a** with **2 a** predominantly occurred to give the direct coupling product **3 a′** in 45% yield (Table 1, entry 12). The choice of bases exerted a decisive influence on this transformation, and Cs_2CO_3 was identified as the most suitable one (see the details in SI). Eventually, the reaction was conducted on a 0.3 mmol scale of **1 a**, yielding the migratory product **3 a** in 85% isolated yield with a > 20:1 rr (Table 1, entry 13).

Next, the scope of 1-bromo-2-vinylbenzenes (**1**) was explored under the optimal conditions (Table 2). In a manner akin to the preparation of **3 a** (Table 1, entry 13), 1-bromo-2-(1-(substituted)phenylvinyl)-benzenes (**1 b-1 l**) coupled with 2-methyl-4-phenylbut-3-yn-2-ol (**2 a**) gave the target unsymmetrical 1,1,4-triphenyl-substituted 1,3-enynes **3 b-3 l** in 60–86% yields with tolerance of electron-donating and withdrawing substituents such as methyl, *tert*-butyl, methoxy, phenyl, fluoro, chloro, trifluoromethyl, and trifluoromethoxy at the *para*-, *meta*-, or *ortho*-position of one phenyl of the 1,1-diphenyl moiety in **1**. In the cases of 4-^{t}Bu group an obvious negative substituent effect deteriorated the formation of **3 c** (60%), 4-chloro and 4-phenyl showed a moderate substituent effect to diminish the yields of **3 e** (69%) and **3 g** (67%), respectively, while both methyl and fluoro facilitated the reaction to afford the target products (**3 b**, **3 f**, **3 j**, **3 k**, and **3 l**) in 78–86% yields. Notably 2-methyl in 1-bromo-2-vinylbenzene **1 l** demonstrated no obvious steric effect on the formation of **3 l** (78%). Gram-scale synthesis of **3 f** was conducted to reach a 74% isolated yield. 1-(2-Naphthyl) and 1-(2-thienyl)-functionalized 1-bromo-2-vinylbenzenes **1 m** and **1 n** underwent the reaction with **2 a** to produce the corresponding target products **3 m** (70%) and **3 n** (53%), respectively, but no desired product was detected when one of the phenyl group in the 1,1-diphenyl moiety of **1** was replaced by CO_2Me (**3 o**) or methyl (**3 p**). Notably, neither 2-bromostyrene nor 1-bromo-2-(2,2-dimethyl-1-meth-

Table 2. Scope of 1-bromo-2-vinylbenzenes.[a]



[a] Conditions: **1** (0.3 mmol), **2 a** (0.45 mmol), $Pd(OAc)_2$ (5 mol%), Sphos (10 mol%), 2-FC_6H_4OH (20 mol%), Cs_2CO_3 (2 equiv.), THF (3 mL), 80 °C, argon, 0.5 h.

[b] **1 f** (5 mmol), **2 a** (7.5 mmol), $Pd(OAc)_2$ (5 mol%), Sphos (10 mol%), 2-FC_6H_4OH (20 mol%), Cs_2CO_3 (2 equiv.), THF (50 mL), 80 °C, argon, 0.5 h.

[c] $Pd(OAc)_2$ (10 mol%), Sphos (20 mol%).

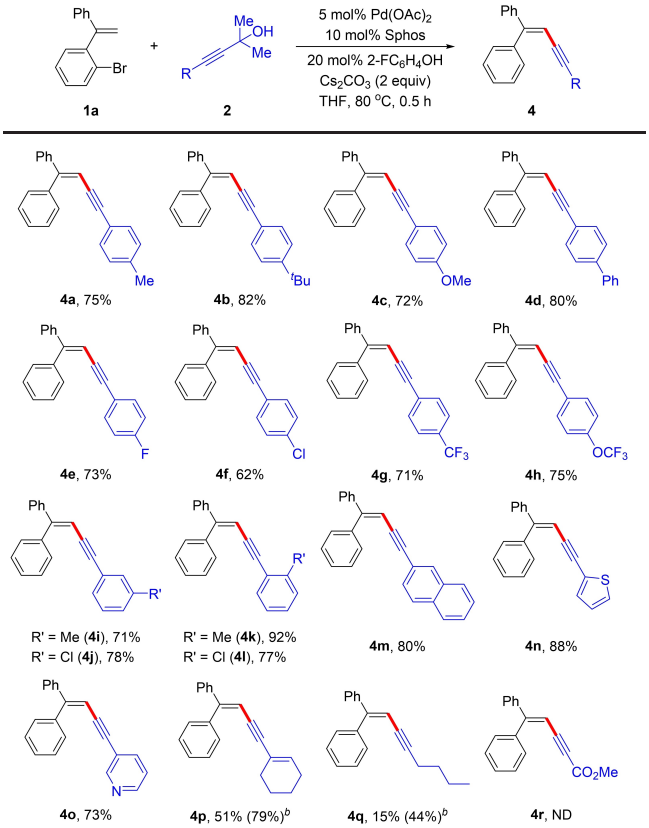
yleneprop yl)benzene could react with **2a** to afford the desired products. These outcomes have suggested that the reactivity of *gem*-diaryl alkenes is particularly sensitive to the electronic surrounding of their vinyl functionality. When the 1-bromophenyl was substituted by electron-donating 4-methyl or methoxy, the target products **3q** (73%) and **3r** (85%) were efficiently formed, whereas electron-withdrawing 4-fluoro, chloro and trifluoromethyl groups exhibited a remarkable negative electronic impact on the yields of **3s**–**3u** (17–30%) which could be enhanced to 50–76% by increasing the catalyst loading to 10 mol%. 3-Methoxy in the 1-bromophenyl moiety facilitated the reaction to form **3v** in 84% yield, and 5-fluoro exhibited an obvious steric/electronic effect on the formation of **3w**. It is noteworthy that all the products were regio- and stereoselectively obtained as the (*E*) or (*Z*)-isomer with >20:1 rr, and the molecular structures of compounds **3** were further confirmed by the X-ray single crystal structural determination of compounds **3f** and **3s**, respectively, which was also confirmed by the ^{1}H NMR analysis of the reaction mixture of **1f** with **2a** in which only the migratory product **3f**, instead of **3s** was detected (see the SI).

Under the optimal conditions, other alkyne sources, including phenylacetylene, 1-phenyl-2-trimethylsilylacetylene, 2,4-diphenylbut-3-yn-2-ol (**2a1**), 1,1,3-triphenylprop-2-yn-1-ol (**2a2**), 1-(phenylethynyl)cyclobutan-1-ol (**2a3**), 1-(phenylethynyl)cyclopentan-1-ol (**2a4**), 1-(phenylethynyl)cyclohexan-1-ol (**2a5**) and 3-isopropyl-4-methyl-1-phenylpent-1-yn-3-ol (**2a6**), were tested. It was found that phenylacetylene and 1-phenyl-2-trimethylsilylacetylene as the coupling reagents led to the migratory product **3a** in 30% (1:2.2 rr) and 9% (1:3.7 rr) yields, respectively, along with more efficient formation of regioisomer **3a′**. With propargylic alcohols **2a1**–**2a6** as the masked alkyne source, the migratory reaction efficiently proceeded with a high regioselectivity (≥15:1 rr). In the cases of using **2a1**, **2a2**, and **2a3**, the target product **3a** was formed in ≥81% yields with a >20:1 rr (see Table S2 in SI).

Then, the protocol generality was investigated by using various propargylic alcohols of type **2** as the masked alkyne source (Table 3). Substituted aryl propargylic alcohols **2b**–**2n** proved to be compatible in their reaction with **1a**, giving the target 1,3-enynes (**4a**–**4m**) in 62–92% yields with >20:1 rr. Electron-donating and withdrawing substituents such as methyl, *tert*-butyl, phenyl, methoxy, fluoro, chloro, trifluoromethyl, and trifluoromethoxy were tolerated. Only in the cases of 4-Cl group, product **4f** was obtained in 62% yield, exhibiting an obvious negative substituent effect. In other cases, the target products were accessed in 71–92% yields. In all the cases, the electronic effect seems to be much greater than the steric effect. For example, 2-methyl-4-(2-methylphenyl)but-3-yn-2-ol (**2l**) led to **4k** in 92% yield, while 2-methyl-4-(2-chlorophenyl)but-3-yn-2-ol (**2m**) resulted in **4l** in 77% yield under the same conditions. Bulky 2-methyl-4-(2-naphthyl)but-3-yn-2-ol (**2n**) also underwent the reaction with **1a**, efficiently giving **4m** (80%). Heteroaryl-functionalized propargylic alcohols, that is, 2-methyl-4-(2-thienyl)but-3-yn-2-ol (**2o**) and 2-methyl-4-(3-pyridyl)but-3-yn-2-ol (**2p**), also reacted well with **1a** to offer **4n** (88%) and **4o** (73%), respectively. However, 4-alkenyl or alkyl-based propargylic alcohols **2q** and **2r** only demonstrated a poor to moderate reactivity to **1a**, forming **4p** (79%) and **4q** (44%) by using 10 mol% catalyst. It should be noted that electron-deficient 4-methoxycarbonyl propargylic alcohol (**2s**) showed no reactivity to **1a**. These results have revealed that the reactivity of propargylic alcohols is susceptible to the electronic surrounding around the alkynyl moiety.

1,1,2-Trisubstituted olefin such as (1-phenyl-1-propen-1-yl)benzene (**5**) was also employed in the reaction. Alkene **5** (*E*/*Z*=2.1:1) reacted with **2a** under the standard conditions, only producing the direct

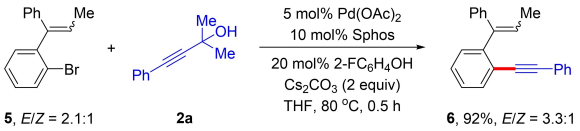
Table 3. Scope of propargylic alcohols.[a]



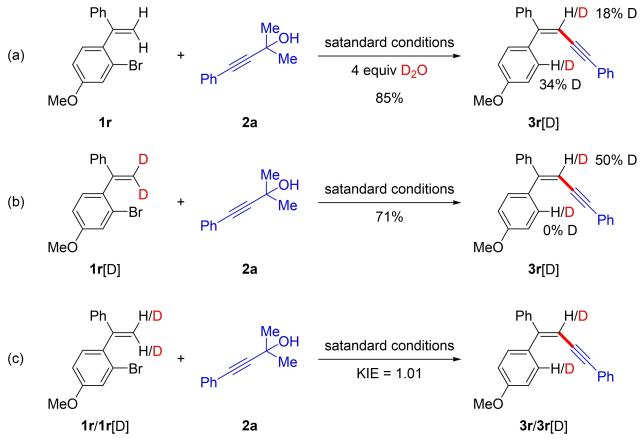
[a] Conditions: **1a** (0.3 mmol), **2** (0.45 mmol), $Pd(OAc)_2$ (5 mol%), Sphos (10 mol%), 2-FC_6H_4OH (20 mol%), Cs_2CO_3 (2 equiv.), THF (3 mL), 80 °C, argon, 0.5 h.
[b] $Pd(OAc)_2$ (10 mol%), Sphos (20 mol%).

coupling product **6** (*E*/*Z* = 3.3:1) in 92% yield, and no migratory product was detected (Scheme 2). This result suggests that compound **5** and product **6** may undergo *E*/*Z* isomerization under the standard conditions.

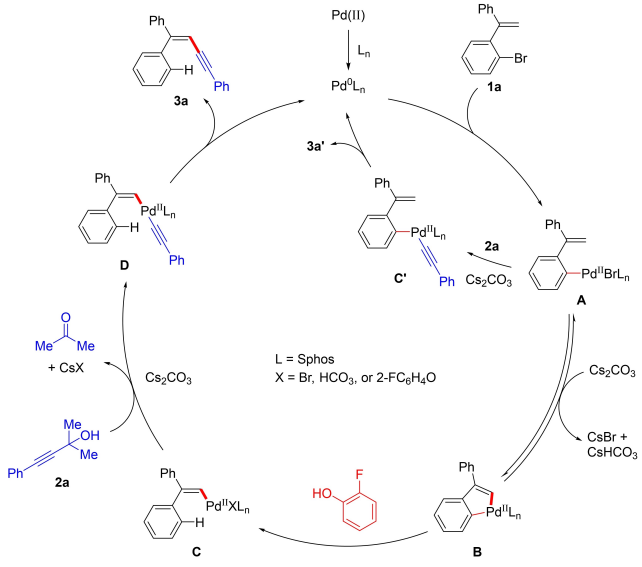
To probe into the reaction mechanism, control experiments were performed (Scheme 3). When alkene **1 r** reacted with **2 a** in the presence of 4 equiv. of D_2O under the standard conditions, 34% deuterium incorporation was observed at the *ortho*-position (Scheme 3a). Deuterated alkene **1 r**[D] reacted with **2 a** to result in **3 r**[D] without deuterium incorporation onto the *ortho*-position (Scheme 3b). These results suggest that the hydrogen atom at the *ortho*-position of the phenyl ring in **3 r**[D] partially came from the reaction medium, rather than from alkene **1 r**. In these cases, olefinic hydrogens in the 1,3-enyne products were partially deuterated. The kinetic isotope effect (KIE) was measured, and a secondary KIE of 1.01 from the parallel reactions of alkene **1 r** and its deuterated form **1 r**[D] with **2 a** (Scheme 3c) suggests that the olefinic C–H bond cleavage of **1** might not contribute to the rate-determining step throughout the catalytic process[20] (see the SI for details).



Scheme 2. Reaction with 1,1,2-trisubstituted olefin **5**.



Scheme 3. Control experiments.



Scheme 4. Proposed mechanism.

A plausible reaction mechanism is presented in Scheme 4. Initially, oxidative addition of **1 a** to the *in situ* generated Pd(0) species forms Pd(II) intermediate **A**, which undergoes cyclopalladation in the presence of Cs_2CO_3 base, producing palladacycle **B** *via* a CMD process. Protonation of species **B** with 2-FC_6H_4OH additive leads to Pd(II) intermediate **C** *via* a net aryl to vinyl 1,4-palladium migration, owing to a thermodynamically favourable process assisted by 2-FC_6H_4OH according to our previous DFT calculations.[12a] Subsequently, intermediate **C** reacts with the alkyne anion generated *in situ* from **2 a** forming Pd(II) intermediate **D** through a *retro*-alkynylation process *via* a *β*-carbon elimination in the presence of Cs_2CO_3.[13b] Eventually, species **D** undergoes reductive elimination to afford the target product 1,3-enyne **3 a**, and while regenerating the catalytically active Pd(0) species, closing the catalytic cycle. Without the assistance of 2-FC_6H_4OH, intermediate **A** directly reacts with **2 a** to generate Pd(II) intermediate **C′**, followed by reductive elimination to yield the regioisomer **3 a′**.

Conclusions

In summary, an 1,4-palladium migration cascade involving bromo-functionalized *gem*-diaryl ethylenes and propargylic alcohols has been established, offering a straightforward and rapid method to access diverse synthetically valuable 1,3-enynes. The utilization of 2-FC_6H_4OH additive improves the reaction efficiency by expediting the crucial 1,4-palladium migration process. Mechanistic studies have suggested that the olefinic C–H bond cleavage might not be involved in the rate-determining step.

Experimental Section

Typical Procedure for the Synthesis of 3 a

Under an argon atmosphere a mixture of alkene **1 a** (78 mg, 0.3 mmol), 2-methyl-4-phenyl-3-butyn-2-ol **2 a** (72 mg, 0.45 mmol), $Pd(OAc)_2$ (3.3 mg, 0.015 mmol), Sphos (12.3 mg, 0.03 mmol), 2-FC_6H_4OH (6.7 mg, 0.06 mmol), and Cs_2CO_3

(195 mg, 0.6 mmol) in 3 mL of THF was stirred at 80 °C for 30 min. After cooled to ambient temperature, the reaction mixture was diluted with CH_2Cl_2 (10 mL), filtered through a short pad of celite, and rinsed with 5 mL of CH_2Cl_2. The combined filtrate was concentrated under reduced pressure. The resultant residue was subjected to purification by column chromatography on silica gel (eluent: petroleum ether (60–90 °C) to afford **3 a** as a white solid (71 mg, 85%).

CCDC-2327561 (**3 f**), and 2327562 (**3 s**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/structures.

Acknowledgements

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