

Tunable Construction of Multisubstituted 1,3-Dienes and Allenes via a 1,4-Palladium Migration/Carbene Insertion Cascade

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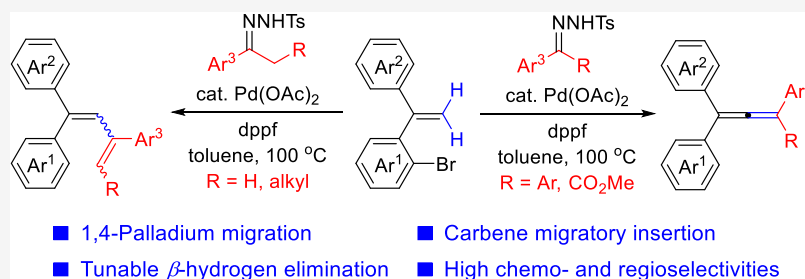
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ABSTRACT: Efficient palladium-catalyzed vinylic C–H alkenylation and allenylation of *gem*-disubstituted ethylenes with *N*-tosylhydrazones of aryl alkyl and diaryl ketones were achieved to access trisubstituted 1,3-dienes and tetrasubstituted allenes, respectively. An aryl to vinyl 1,4-palladium migration/carbene insertion/ β -hydride elimination sequence proceeded to switch the chemo- and regioselectivities to give structurally diverse products. Use of 2-FC₆H₄OH additive enables enhancement of the reaction efficiency through accelerating the key 1,4-palladium migration process.

INTRODUCTION

Transition-metal-catalyzed C–H activation has become a promising strategy for C–C bond formation in organic synthesis.¹ However, a C–H activation process usually requires elaborate substrates and reaction conditions although direct C–H bond functionalization can avoid prefunctionalization and does not result in hazardous byproducts.² As a matter of fact, it is still challenging to develop efficient processes to transform the C–H bonds of complex substrates into useful functional groups under controllable conditions. 1,*n*-Migration of transition metals in a catalytic cycle is considered as an alternative strategy to realize a desired transformation by initiating an indirect C–H activation process.³ In this regard, 1,4-palladium migration can introduce a palladium moiety to a remote site, where direct introduction of the metal is often inaccessible by means of the conventional methods.⁴ Diverse 1,4-palladium migration processes have been explored including those from aryl to aryl,⁵ aryl to alkyl,⁶ aryl to benzyl,^{7a} aryl to imino,^{7b} aryl to acyl,^{7c} alkyl to aryl,⁸ alkyl to acyl,⁹ imino to acyl,¹⁰ and vinyl to aryl.¹¹ A cascade reaction of *o*-iodobiphenyls or (*Z*)- β -halostyrenes with *o*-bromobenzyl alcohols catalyzed by a palladium complex afforded triphenylenes and phenanthrenes, respectively.^{5b} A 1,4-palladium migration at the methyl group, followed by intramolecular trapping by C(sp²)-H or C(sp³)-H activation led to isoindolines and β -lactams,^{6a} or cyclopropanes.^{6c} Dibenzosilolepin derivatives^{11a} and benzophenanthrosilines^{11b} were also accessed by C–H/C–H coupling through 1,*n*-palladium migration/carbopalladation of alkyne separately. In addition,

consecutive 1,4-palladium migrations were realized in a biphenyl system,^{5a,11d} or a three-component reaction between aryl halide and internal alkyne,^{5f} which usually involve intramolecular arylation or inter-/intramolecular Heck coupling. Lin, Feng, and co-workers have documented aryl to vinyl 1,4-palladium migration processes of *gem*-diaryl alkenes for vinylic C–H borylation,^{12a} alkenylation (Scheme 1a),^{12b} arylation and alkenylation,^{12c} and annulation with alkynes.^{12d} A 1,4-palladium migration/C(sp³)-H activation sequence provided arylidene γ -lactams,¹³ and 2,2-diaryl 2*H*-chromenes were accessed through palladium-catalyzed annulation of *ortho*-vinyl bromobenzenes with *N*-tosylhydrazones of *ortho*-hydroxybenzaldehydes.¹⁴ Vinylic C–H alkylation of *gem*-disubstituted ethylenes with cyclobutanols was also achieved via an aryl to vinyl 1,4-palladium migration/ring-opening C–C cleavage cascade.^{15a}

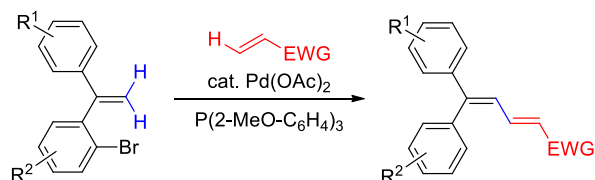
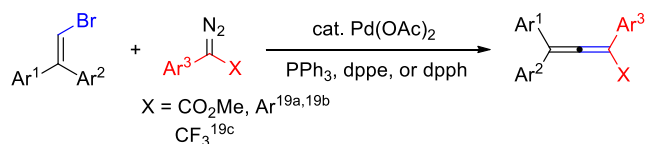
N-Tosylhydrazones¹⁶ have been successfully applied as alkenyl coupling partners¹⁷ and carbonyl olefination reagents¹⁸ in transition-metal-catalyzed cross-coupling transformations, which usually undergo the reaction via an *in situ* generated diazo intermediate, followed by metal carbene formation/

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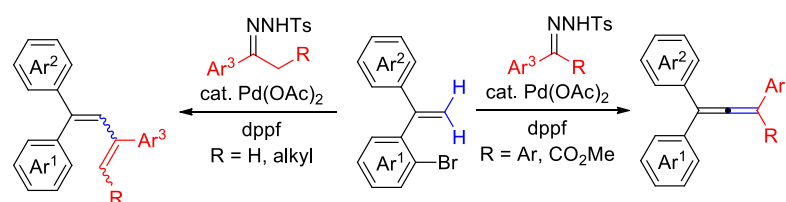
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Scheme 1. Aryl to Vinyl 1,4-Palladium Migrations and Related Allene Synthesis

(a) vinylic C-H alkenylation^{12b}(b) allene synthesis from vinyl bromides and diazo compounds¹⁹

(c) This work: C-H alkenylation/allenylation

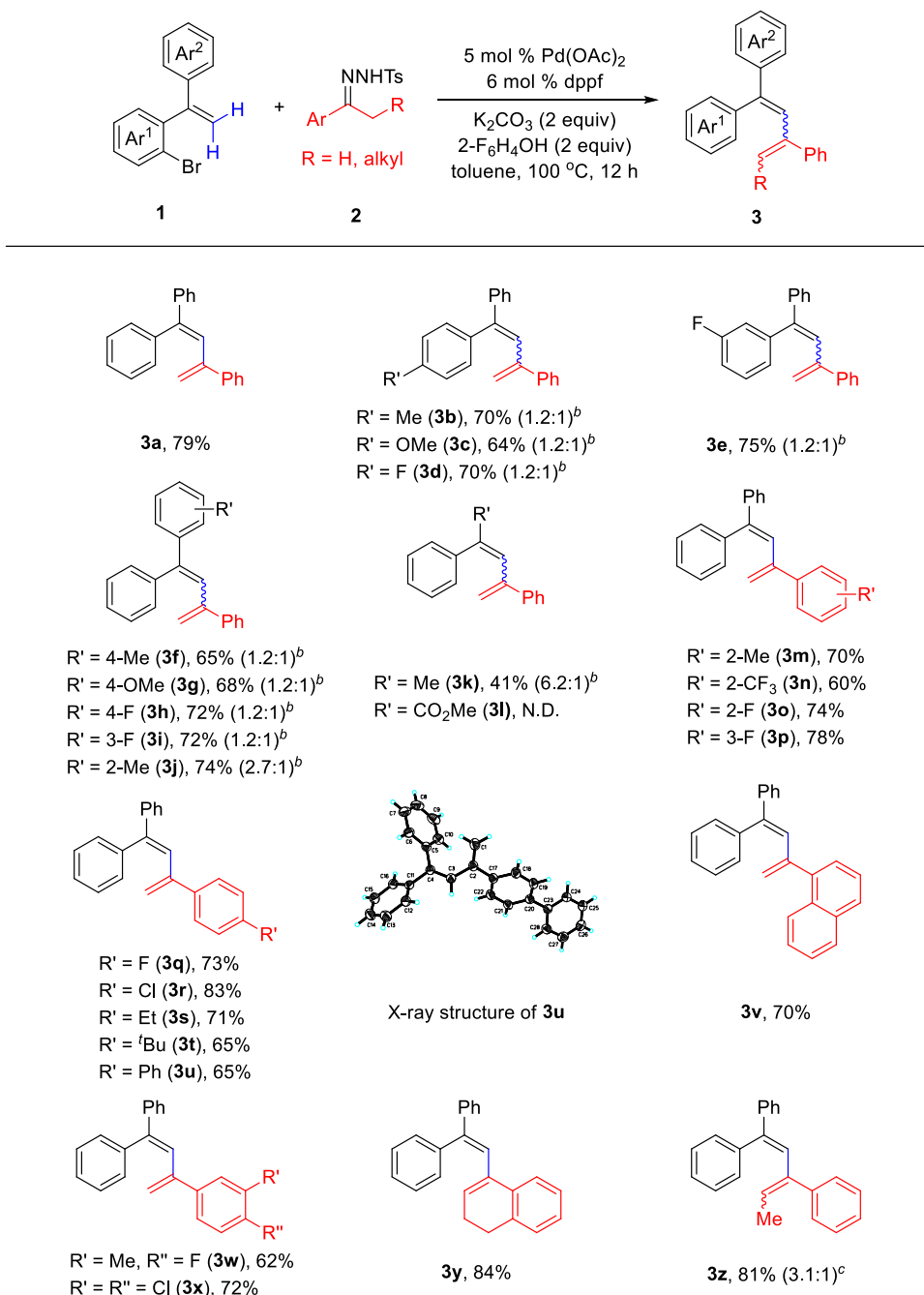
Table 1. Optimization of the Reaction Conditions^a

entry	1a:2a ^b	ligand (mol %)	2-FC ₆ H ₄ OH (equiv)	yield of 3a (%) ^c	3a:4a ^d
1	1:1.5	PCy ₃ (20)	2	10	1:7
2	1:1.5	DPEphos (10)	2	57	5.2:1
3	1:1.5	dppf (10)	2	66	>20:1
4 ^e	1:1.5	DPEphos (10)		—/80 ^f	<1:20
5	1:1.5	dppf (10)		32	1:1.7
6	1:1.5	dppf (10)	2	26	12.7:1
7	1:1.5	Xantphos (10)	2	35	9.5:1
8	1:1.5	PPh ₃ (20)	2	39	1.2:1
9	1:1.5	Xphos (20)	2	21	2:1
10	1:1	dppf (10)	2	64	>20:1
11 ^g	1.2:1	dppf (10)	2	76	>20:1
12 ^g	1.2:1	dppf (6)	2	81 (78)^h	>20:1
13 ^g	1.2:1	dppf (6)	1.5	74	18.5:1
14 ^g	1.2:1	dppf (6)	0.5	63	2.8:1
15 ⁱ	1.2:1	dppf (6)	2	81 (79)^h	>20:1

^aConditions: **1a** (0.2 mmol), Pd(OAc)₂ (5 mol %), K₂CO₃ (0.4 mmol), 3 mL of toluene, 100 °C, argon, 12 h. ^bMolar ratio of **1a** and **2a**.^cDetermined by ¹H NMR analysis using 1,3,5-trimethoxybenzene as the internal standard. ^dDetermined by ¹H NMR analysis. ^eUsing LiO^tBu instead of K₂CO₃. ^fIsolated yield of **4a**. ^g**2a** (0.3 mmol), 4.5 mL of toluene. PCy₃ = tricyclohexylphosphine; DPEphos = (oxydi-2,1-phenylene)bis(diphenylphosphine); dppf = 1,1'-bis(diphenylphosphino)ferrocene; dtbpf = 1,1'-bis(di-*tert*-butylphosphino)ferrocene; Xantphos = 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene; PPh₃ = triphenylphosphine; Xphos = 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl.

migratory insertion, and subsequently a β -hydride elimination process. Lin and Feng,^{19a,b} and Koenigs et al.^{19c} recently reported palladium-catalyzed carbene transfer/ β -hydride elimination sequences for the synthesis of tetrasubstituted allenes from vinyl bromides and donor/acceptor or donor/donor diazo compounds (Scheme 1b), respectively. During the

ongoing investigation of carbene insertions²⁰ and vinylic C–H functionalization,^{15a,21} we reasonably envisioned that *gem*-diaryl alkenes might undergo C–H alkenylation and allenylation with *N*-tosylhydrazones as the coupling partners through an aryl to vinyl 1,4-palladium migration, followed by electronic effect-directing β -hydride elimination. Herein, we

Scheme 2. Cross-Coupling of 1-Bromo-2-vinylbenzenes (**1**) with *N*-Tosylhydrazones of Aryl Alkyl Ketones (**2**)^{a,b,c}

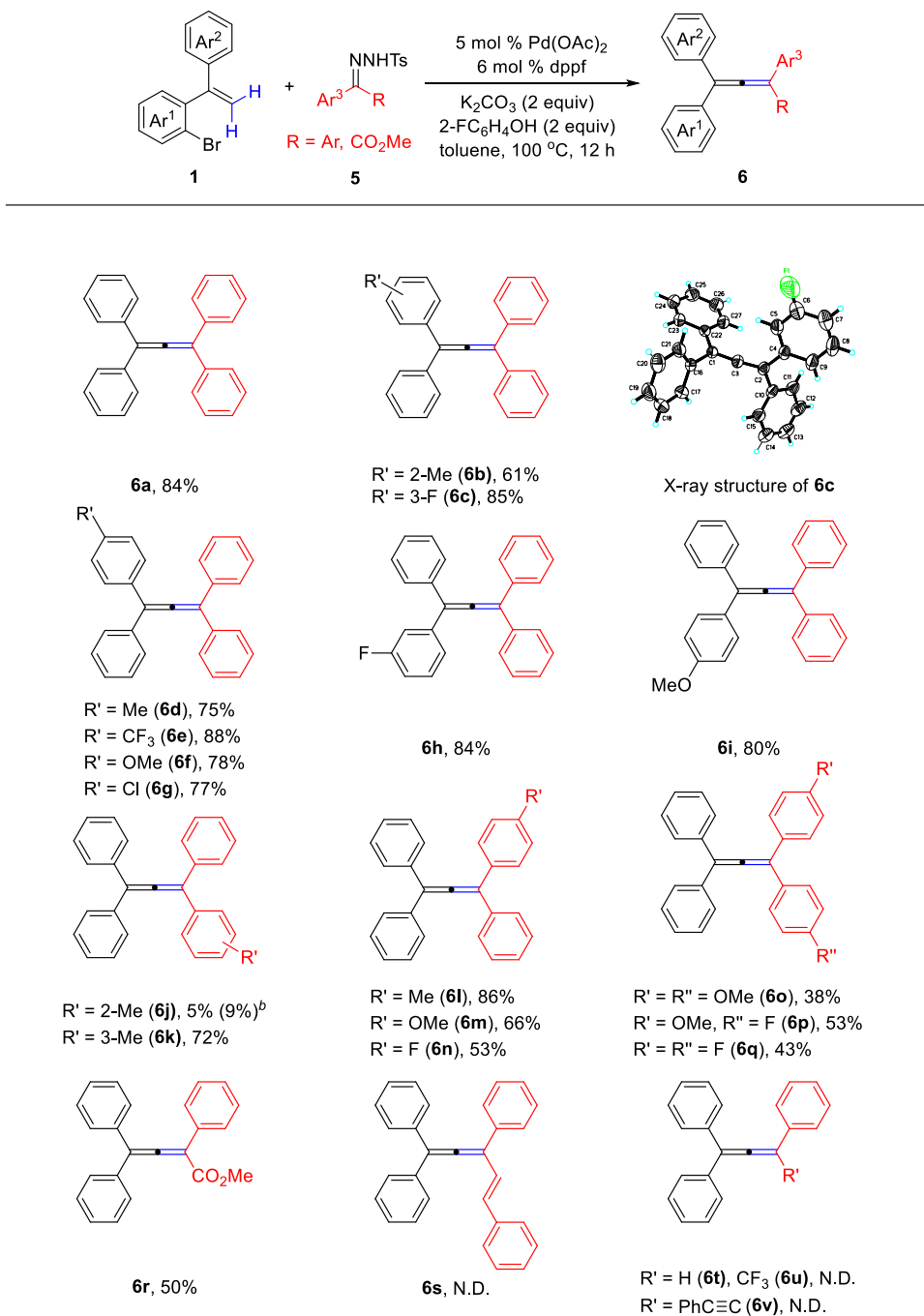
^aConditions: **1a** (0.36 mmol), **2** (0.3 mmol), Pd(OAc)₂ (5 mol %), dppf (6 mol %), K₂CO₃ (2 equiv), 2-FC₆H₄OH (2 equiv), 4.5 mL of toluene, 100 °C, argon, 12 h. ^bMolar ratio of (*E*)/(*Z*)-isomers determined by ¹H NMR analysis. ^cMolar ratio of (*Z*)/(*E*)-isomers determined by ¹H NMR analysis.

disclose palladium-catalyzed vinylic C–H functionalization of *gem*-diaryl alkenes with *N*-tosylhydrazones for highly chemo- and regioselective construction of trisubstituted 1,3-butadienes and tetrasubstituted allenes (Scheme 1c).

RESULTS AND DISCUSSION

Initially, the reaction of 1-bromo-2-(1-phenylvinyl)benzene (**1a**) with *N*-tosylhydrazone of acetophenone (a donor/donor carbene precursor) (**2a**) was conducted to screen the reaction conditions (Table 1). Under the conditions similar to those for vinylic C–H alkylation of **1a** with cyclobutanols previously

reported by our lab,^{15a} the reaction only gave the target aryl to vinyl 1,4-palladium migration product **3a** in a low yield (10%) with major formation of the cross-coupling olefination product **4a** (**3a**:**4a** = 1:7) (Table 1, entry 1). Use of DPEphos as the ligand led to **3a** in a much higher yield (57%) (**3a**:**4a** = 5.2:1) (Table 1, entry 2). With dppf as the ligand, **3a** was formed in a more efficient manner (66%) (**3a**:**4a** => 20:1) (Table 1, entry 3). In the absence of 2-FC₆H₄OH, compound **3a** was only formed in 32% yield (**3a**:**4a** = 1:7) (Table 1, entry 5). As the loading of 2-FC₆H₄OH was increased, both the yield and chemoselectivity of **3a** could be obviously enhanced (entries

Scheme 3. Cross-Coupling of 1-Bromo-2-Vinylbenzenes (**1**) with *N*-Tosylhydrazones of Diaryl Ketones (**5**)^{a,b}

^aConditions: **1** (0.36 mmol), **5** (0.3 mmol), Pd(OAc)₂ (5 mol %), dppf (6 mol %), K₂CO₃ (2 equiv), 2-FC₆H₄OH (2 equiv), 4.5 mL of toluene, 100 °C, argon, 12 h. ^bPd(OAc)₂ (10 mol %), dppf (12 mol %).

6–15, Table 1 and SI). Addition of 2-FC₆H₄OH remarkably accelerated the desired aryl to vinyl 1,4-palladium migration process and inhibited formation of the unexpected cross-coupling olefination product **4a**, which is presumably attributed to a thermodynamically favorable process assisted by 2-FC₆H₄OH according to our previous DFT calculations.^{15a} It is noteworthy that compound **4a** was isolated in 80% yield by means of LiO^tBu as the base and in the absence of 2-FC₆H₄OH (Table 1, entry 4). Ligands dtbpf, Xantphos, PPh₃, and Xphos were also tested in the reaction, but they effected the reaction much less efficiently than dppf (Table 1, entries 6–9, and see the Supporting Information for details). A 1:1

molar ratio reaction of **1a** and **2a** resulted in **3a** in a decreased yield (64%), while use of excessive amount of substrate **1a** obviously enhanced the yield of **3a** to 76% (Table 1, entries 10 and 11). Lowering the ligand loading from 10 to 6 mol % gave a better yield for **3a** (78% isolated yield) (Table 1, entry 12). The best loading of 2-FC₆H₄OH additive was found to be two equivalents (Table 1, entries 11–14). Eventually, the reaction was performed on a 0.3 mmol scale of **2a** to afford the aryl to vinyl 1,4-palladium migration product **3a** in 79% isolated yield (Table 1, entry 15).

Under the optimal conditions, the scopes of 1-bromo-2-vinylbenzenes (**1**) and *N*-tosylhydrazones of aryl alkyl ketones

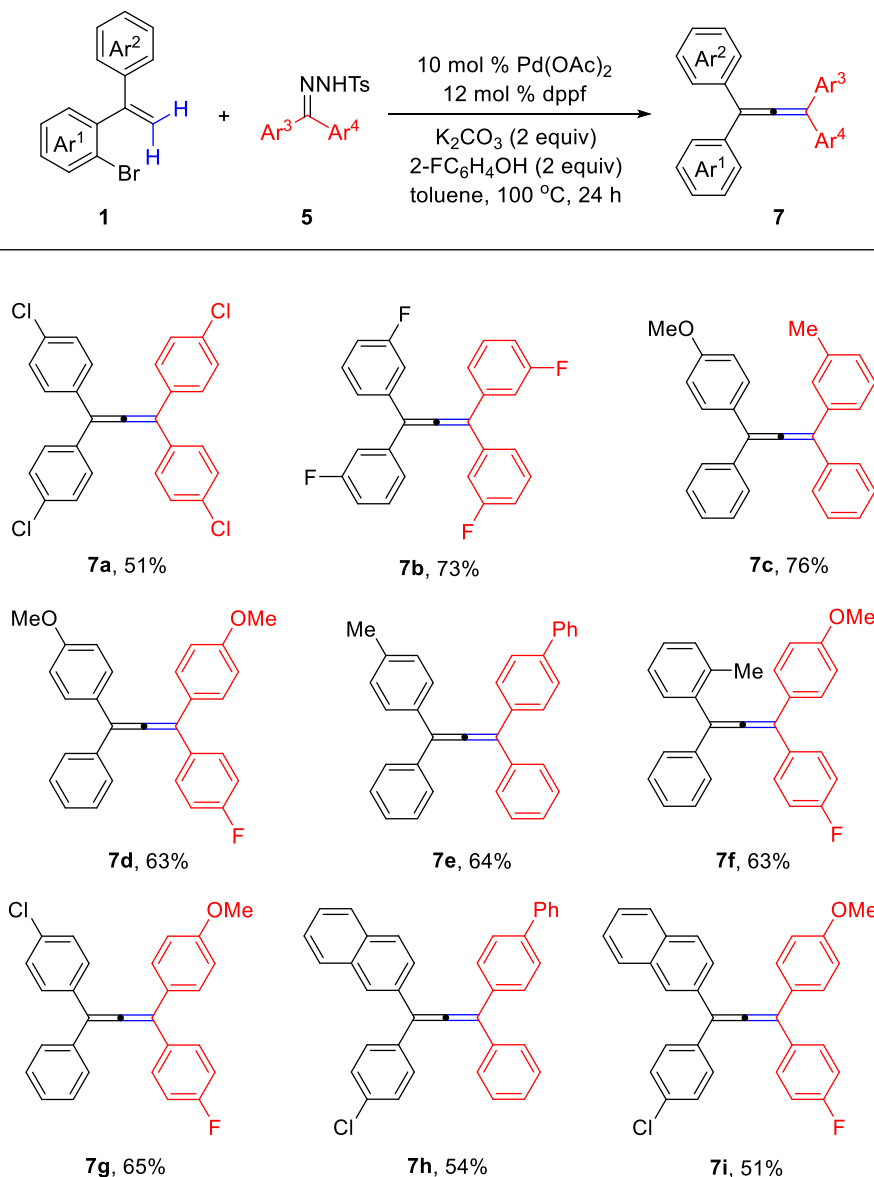
(2) were explored (Scheme 2). In a manner similar to the synthesis of **3a** (Table 1, entry 15), 1-bromo-2-(1-phenylvinyl)benzenes (**1b–1e**) reacted with *N*-tosylhydrazone **2a** to give the target triaryl-substituted 1,3-butadiene products **3b–3e** in 64–75% yields with tolerance of the electron-donating and -withdrawing substituents such as methyl, methoxy, and fluoro at the *para* and *meta*-positions of the bromo-functionalized phenyl ring. Notably, the products were obtained as inseparable (*E*)/(*Z*)-isomers of type **3**, suggesting that the reaction may proceed *via* an aryl to vinyl 1,4-palladium pathway to *in situ* generate an isomeric mixture of (*E*)/(*Z*)-vinylpalladium intermediates in the catalytic cycle.^{11b,22} In the cases of using 1-bromo-2-(1-(substituted)phenylvinyl)benzenes (**1f–1j**), the target products **3f–3j** were obtained in 65–74% yields. *para*-, *meta*-, and *ortho*-Substituents such as methyl, methoxy, and fluoro were also tolerated, exhibiting no obvious substituent effect. When the 2-(1-substituted)phenyl was replaced by a methyl group, compound **3k** was only formed in a decreased yield (41%) with a distinctly augmented regioselectivity (*E/Z* = 6.2:1), and replacement of such a methyl with an electron-withdrawing ester group (CO₂Me) completely inhibited the desired reaction. NO₂-substituted *gem*-diaryl ethylene was not successfully synthesized, and the reaction of CN-substituted *gem*-diaryl ethylene with **2a** afforded no desirable product, presumably due to the strong electron-withdrawing effect. These results suggest that the reactivity of *gem*-diarylated alkene substrates is very susceptible to the electronic environment around the vinylic C=C moiety.

The *N*-tosylhydrazones of substituted acetophenones (**2b–2j**) could also be applied in the reaction with **1a**, giving **3m–3u** in 60–83% yields. In these cases, only 2-CF₃ group exhibited an obvious negative electronic effect on the formation of **3n** (60%), 4-*tert*-butyl and 4-phenyl showed a moderate substituent effect to diminish the yields of **3t** and **3u** to 65%, respectively, while fluoro and chloro facilitated the reaction to afford the target products **3o–3r** in 73–83% yields. The *N*-tosylhydrazones of 1-(naphthalen-1-yl)ethanone and multisubstituted acetophenones also efficiently underwent the reaction with **1a** to give products **3v–3x** (62–72%). As discussed in the case of **3l**, introduction of an electron-withdrawing ester group onto the vinylic C=C backbone lessens the electron density on the alkenyl moiety, which diminishes its reactivity to undergo the key 1,4-palladium migration process for the desired reaction.^{15a} The analogues of **2a**, that is, *N*-tosylhydrazones of alkyl chain-extended α -tetralone and propiophenone, reacted with **1a** very efficiently to give the desired products **3y** (84%) and **3z** (81%), respectively, revealing that the increased electron-donating capability of the alkyl groups in the *N*-tosylhydrazones of aryl alkyl ketones enhances the reaction efficiency. However, *N*-tosylhydrazones derived from isobutyrophenone, phenyl cyclohexyl ketone, and 2,2-diethoxyacetophenone could not react with **1a** to afford the corresponding outcomes due to the intrinsic steric hindrance from the alkyl groups. *N*-Tosylhydrazones of benzaldehydes, acetone and cyclohexanone did not react with **1**, which is presumably attributed to the *in situ* generated donor metal carbene intermediate that are not able to undergo migratory carbene transfer in the catalytic cycle. In addition, *N*-tosylhydrazones of NO₂ and CN-substituted acetophenones did not react with **1a** to give the corresponding products, either. It is noteworthy that the structures of compounds **3** were further confirmed by the X-ray single-

crystal structural determination of compound **3u** (see the SI for details).

The protocol generality was then investigated by means of other types of donor/donor carbene precursors, that is, *N*-tosylhydrazones of diaryl, arylvinyl, and aryl alkynyl ketones, and those of donor/acceptor and acceptor carbene precursors (**5**), as the coupling partners (Scheme 3). Unexpectedly, tetrasubstituted allene **6a** instead of a 1,3-diene product of type **3** was obtained in 84% yield from the reaction of **1a** and *N*-tosylhydrazone of benzophenone (**5a**) under the standard conditions. Formation of **6a** has unambiguously demonstrated another type of β -hydride (vinylic C–H) elimination occurring in the catalytic cycle,¹⁹ which is different from the β -hydride (aliphatic C–H) elimination present in the reaction of **1** and **2** (Scheme 2). Such an allene molecule has been shown unique properties in materials science, catalysis, and molecular recognition.²³ Introduction of *ortho*-, *meta*-, and *para*-substituents onto the 2-(1-aryl) moiety in 1-bromo-2-(1-arylvinyl)benzenes (**1**) was tolerant, and their reaction with **5a** resulted in the target products **6b** (61%) and **6c–6g** (75–88%), respectively. Only in the case of *ortho*-methyl was observed an obvious negative steric effect, leading to **6b** in a lower yield. In other cases the reaction proceeded efficiently. Placement of an electron-withdrawing (3-F) or electron-donating (4-OMe) substituent onto the bromo-functionalized phenyl ring of **1** did not affect the efficient formation of the target products **6h** (84%) and **6i** (80%). It was found that the substituents on the diaryl moieties of the *N*-tosylhydrazones of diaryl ketones could exhibit various substituent effects. *ortho*-Methyl showed a remarkable negative steric impact on the reaction efficiency to generate **6j** (5%), and increasing the catalyst loading to 10 mol % could not obviously improved the product yield (9%). *meta*-Methyl-functionalized *N*-tosylhydrazone reacted well with **1a** to afford **6k** (72%), and a single *para*-methyl enhanced the yield of compound **6l** to 86%. However, *para*-methoxy and fluoro groups deteriorated the reaction, leading to **6m** (66%) and **6n** (53%), respectively. Unexpectedly, *N*-tosylhydrazones of di(substituted)aryl ketones did not react well with **1a** under the stated conditions, and thus concurrent *para*-methoxy and fluoro groups on both the aryl moieties further diminished the reaction efficiency, reducing the yields of **6o–6q** to 38–53%. Using a donor/acceptor carbene precursor, that is, *N*-tosylhydrazone of methyl 2-oxo-2-phenylacetate, an equivalent of phenyl diazoacetate, to react with **1a** under the same conditions resulted in the target product **6r** in a moderate yield (50%). Notably, the *N*-tosylhydrazones of aryl vinyl/aryl trifluoromethyl/aryl alkynyl ketones and benzaldehyde did not undergo the desired reaction to form the target allene products **6s–6v** presumably owing to the negative electronic effect from these functional groups (vinyl, CF₃, ethynyl, and formyl H) although they were partially or completely consumed under the stated conditions. It is noteworthy that the molecular structures of compounds **6** were further confirmed by the X-ray single-crystal structural determination of compound **6c** (see the SI for details).

Diverse methods to access allenes have been developed. They can start from alkenes by 1,2-elimination, from alkynes by isomerization/substitution, or from conjugated enynes and their derivatives.²⁴ Although radical intermediates have been well explored for allene synthesis,^{24a} most of the related existing strategies have relied too much on elaborate alkynes, and alternative approaches for allene synthesis, especially for

Scheme 4. Synthesis of Diverse Tetraaryl-Substituted Allenes (7)^a

^aConditions: **1** (0.36 mmol), **5** (0.3 mmol), Pd(OAc)₂ (10 mol %), dppf (12 mol %), K₂CO₃ (2 equiv), 2-FC₆H₄OH (2 equiv), 4.5 mL of toluene, 100 °C, argon, 24 h.

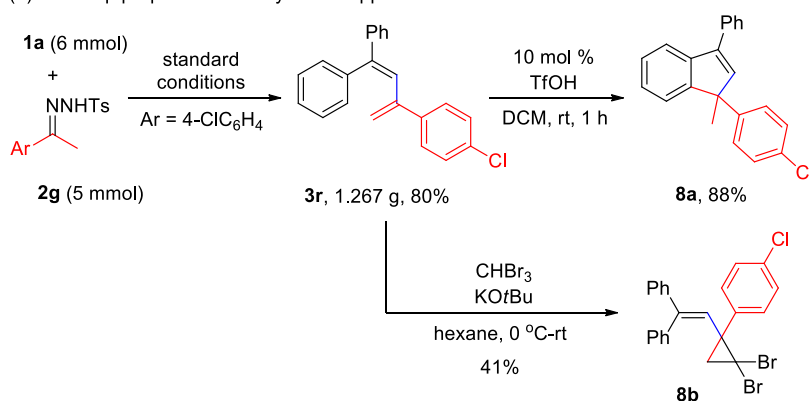
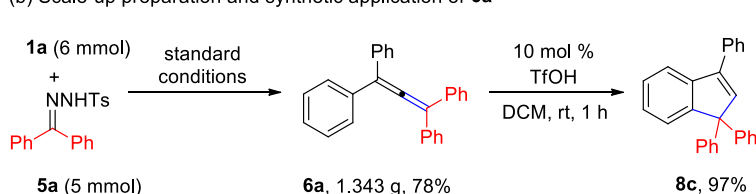
the synthesis of diverse tetraaryl-substituted ones, are still desirable. In the present cascade reaction, *gem*-diaryl alkenes **1** were coupled with *N*-tosylhydrazones (**5**) via 1,4-palladium migration/carbene insertion, followed by β -(vinyl)hydride elimination to generate diverse tetraaryl-substituted allene products. To further extend the synthetic protocol as shown in Scheme 3, multiply functionalized tetraaryllallenes were synthesized (Scheme 4). Symmetrical tetra(4-chlorophenyl)-allene (**7a**) and tetra(3-fluorophenyl)allene (**7b**) were thus obtained in 51% and 73% yields using 10 mol % Pd(OAc)₂/12 mol % dppf as the catalyst system, respectively. In a similar manner, allenes **7c–7i** were accessed in 51–76% yields. These allene derivatives are potentially transformable due to installation of diverse functional groups such as chloro, fluoro, and methoxy on the aryl moieties.

To demonstrate the applicability of the synthetic protocol, gram-scale preparation of compounds **3r** and **6a** was performed under the standard conditions, achieving 80% and

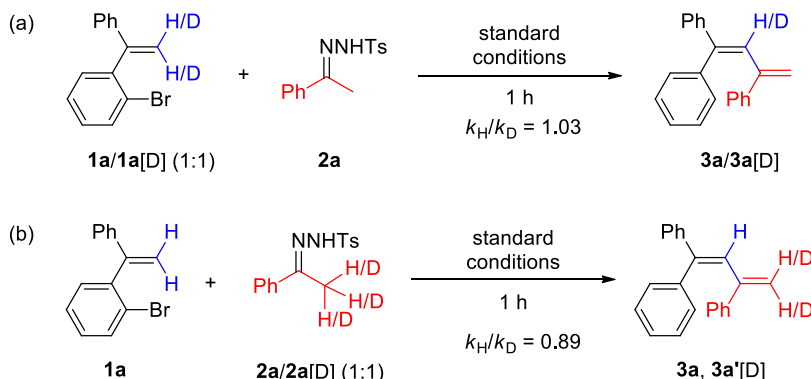
78% yields, respectively (Scheme 5). Treatment of **3r** and **6a** in the presence of a catalytic amount of triflic acid (10 mol %) efficiently gave indene derivatives **8a** (Schemes 5a) and **8c** (Scheme 5b) in 88% and 97% yields, respectively, through an acid-promoted intramolecular Friedel–Crafts cyclization sequence. Because multiple functional groups are installed in compounds **3**, **6**, and **7**, they are potentially synthetically useful in organic synthesis. The reaction of **3r** with bromoform was conducted under basic conditions, leading to regioselective formation of *gem*-dibromocyclopropane **8b** in 41% yield through an intermolecular [2 + 1] annulation, a building block that may allow for further derivatization (Scheme 5a).

The kinetic isotope effect (KIE) was measured as shown in Scheme 6 (see the SI for details). Under the standard conditions, the reaction of a 1:1 molar ratio mixture of **1a**/**1a**[D] with **2a** gave rise to a *k*_H/*k*_D value of 1.03, suggesting that the vinylic C–H bond activation/cleavage is not involved in the rate-determining step in the overall catalytic cycle^{15a,25}

Scheme 5. Scale-up Preparation and Applications

(a) Scale-up preparation and synthetic application of **3r**(b) Scale-up preparation and synthetic application of **6a**

Scheme 6. Kinetic Isotope Effect



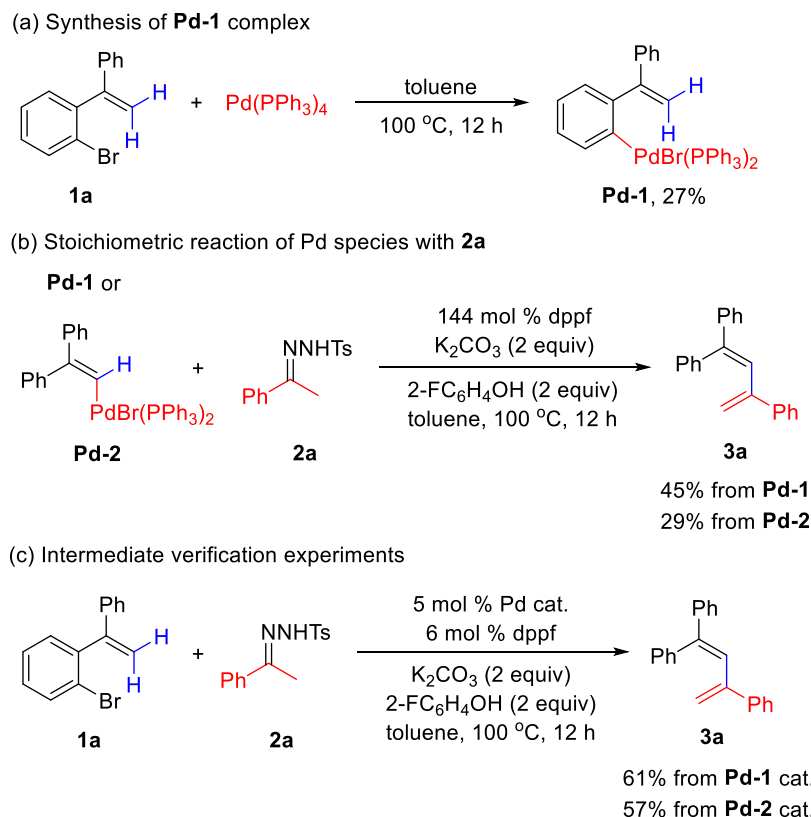
(Scheme 6a). A value of $k_{\text{H}}/k_{\text{D}} = 0.89$ from the two parallel reactions²⁶ of **1a/2a** and **1a/2a[D]** reveals a small, perhaps secondary, isotope effect, which indicates that aliphatic C–H bond cleavage (by β -hydride elimination) occurs during the cascade reaction, but it is not a turnover-limiting step²⁵ (Scheme 6b; see the SI for details).

The control reactions were then performed to verify the possible reaction intermediates in the catalytic cycle (Scheme 7). Arylpalladium(II) complex **Pd-1** was successfully prepared in 27% yield from the 1:1 molar ratio oxidative addition of **1a** to Pd(0) complex Pd(PPh₃)₄ (Scheme 7a). The stoichiometric reactions of **Pd-1** and vinylpalladium(II) complex **Pd-2**^{19b} with *N*-tosylhydrazone **2a** formed **3a** in 45% and 29% yields, respectively (Scheme 7b). It should be noted that **Pd-1** could not effectively react with **2a** in the presence of a catalytic amount of dppf ligand, and use of 6 mol % dppf only led to 10% yield for **3a**, suggesting that the ligand plays a crucial role in stabilizing the metal intermediate during the reaction. In the absence of 2-FC₆H₄OH additive complex **Pd-2** also reacted with **2a** to form **3a** (58%), implicating that 2-FC₆H₄OH may not be involved in the β -hydride elimination step, but facilitates the aryl to vinyl 1,4-palladium migration step in

the overall catalytic cycle. Furthermore, palladium complexes **Pd-1** and **Pd-2** were applied as the catalysts for the reaction of **1a** with **2a** under the standard conditions, giving the target product **3a** in comparative 57–61% yields (Scheme 7c), demonstrating that both aryl-Pd and vinyl-Pd species **Pd-1** and **Pd-2** are the possible reactive intermediates and/or catalytically active species for the desired reaction (see the SI for details).

A plausible reaction mechanism is proposed in Scheme 8. Initially, *in situ* oxidative addition of *ortho*-bromo-substituted vinylbenzene **1** to Pd(0) species generates Pd(II) intermediate **A** (**Pd-1**), followed by cyclopalladation in the presence of K₂CO₃ base to form C(vinyl), C(aryl)-palladacycle (**B**) through a concerted metalation-deprotonation (CMD) process, instead of a second oxidative addition to form palladium-(IV) species,¹² which is energetically favored by theoretical studies.²⁷ Interaction of species **B** and 2-FC₆H₄OH additive results in Pd(II) complex intermediate **C** (X = Br; **Pd-2**) via a net 1,4-palladium migration from aryl to vinyl,^{12a} which is presumably attributed to a thermodynamically favorable process assisted by 2-FC₆H₄OH according to our previous DFT calculations.^{15a} Protonation of vinylpalladium species **C**

Scheme 7. Mechanistic Studies



by an external proton donor may give cationic alkylpalladium complex **C'**, which undergoes deprotonation to generate vinylpalladium species **C''**, in a dynamic equilibrium involving metallated alkene stereoisomerization.^{11b} Subsequently, the *in situ* generated diazo species from *N*-tosylhydrazones **2** or **5** reacts with **C** or **C''** to initiate the carbene migratory insertion^{16a} to Pd–C bond process *via* Pd(II) carbene complex intermediate **D**, resulting in allylpalladium(II) species **E**. Eventually, electronic effect-driven β -(aliphatic or vinylic)-hydride elimination^{19,26} occurs to afford 1,3-butadienes **3** or allenes **6** or **7**, and regenerates the catalytically active Pd(0) species to furnish a catalytic cycle. It should be noted that generation of the *E/Z* isomers in the synthesis of dienes **3** may be attributed to the aryl to vinyl 1,4-palladium process, which *in situ* generates an isomeric mixture of (*E*)/(*Z*)-vinyl and/or allylpalladium intermediates (**C** to **E**) in the catalytic cycle.^{11b}

In conclusion, a sequential 1,4-palladium migration/carbene insertion/ β -hydride elimination cascade of bromo-functionalized *gem*-diarylsubstituted ethylenes and *N*-tosylhydrazones of aryl alkyl and diaryl ketones has been successfully established, providing a direct and modular approach to access diverse synthetically useful 1,3-dienes and tetrasubstituted allenes. The present synthetic protocol features tunable high chemo- and regioselectivities, broad substrate scopes, and good functional group tolerance.

EXPERIMENTAL SECTION

General Considerations. The solvents were dried and distilled prior to use by the literature methods. ¹H and ¹³C{¹H} NMR spectra were recorded on a Bruker DRX-400 spectrometer, and all chemical shift values refer to $\delta_{\text{TMS}} = 0.00$ ppm or CDCl₃ ($\delta(^1\text{H})$, 7.26 ppm and $\delta(^{13}\text{C})$, 77.16 ppm). ¹⁹F{¹H} and ³¹P{¹H} NMR spectra are not calibrated by an internal reference. For reactions that require heating,

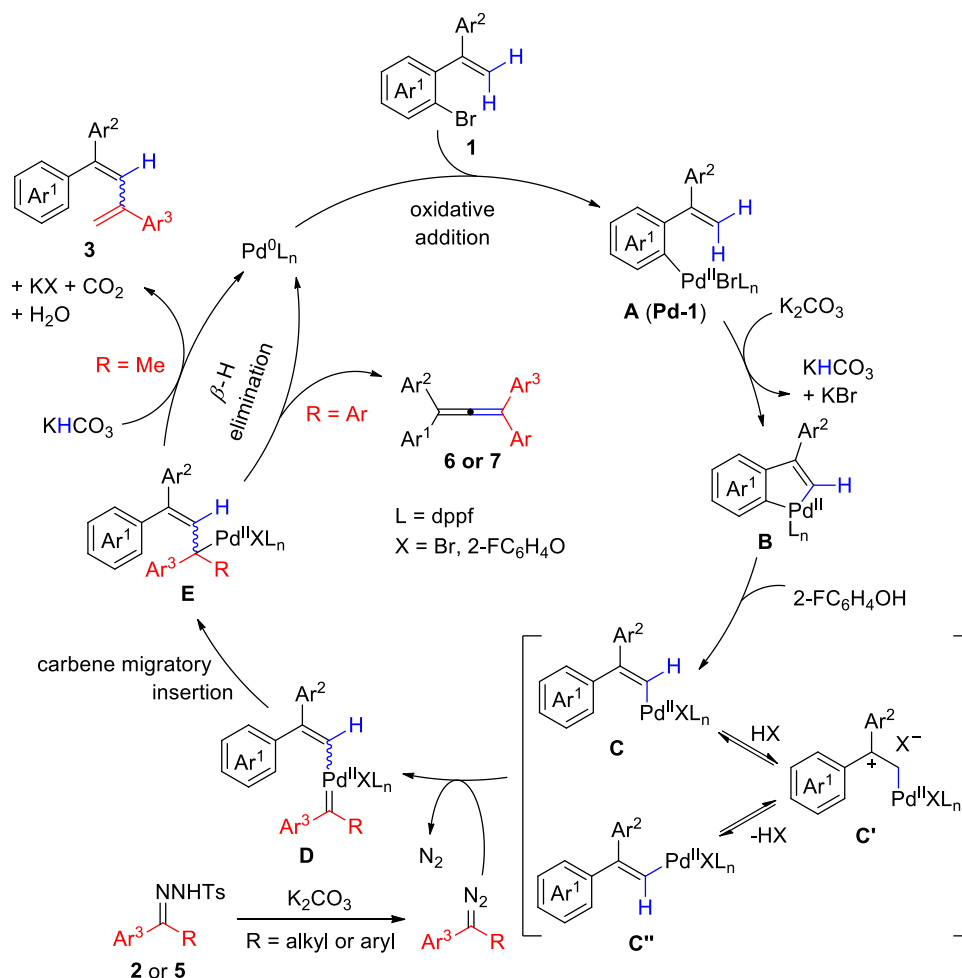
the heat source was an oil bath. The HRMS analysis was obtained on a Waters GC-TOF CA156 mass spectrometer. All of the melting points were measured and uncorrected. X-ray crystallographic analysis was achieved by the Analysis Center, Dalian Institute of Chemical Physics, Chinese Academy of Sciences. Analytical TLC plates were viewed by UV light (254 nm). Column chromatographic purifications were performed on SDZF silica gel 160. All of the chemical reagents were purchased from commercial sources and used as received unless otherwise indicated. The *gem*-disubstituted ethylenes **1**¹⁵ and *N*-tosylhydrazones^{20c} were prepared by the reported methods.

2-Bromo-4-chloro-1-(1-(4-chlorophenyl)vinyl)benzene (1o). Following the reported methods,¹⁵ compound **1o** was obtained by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)). 1.31 g, 80%; colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 2.0 Hz, 1 H), 7.74–7.68 (m, 1 H), 7.68–7.61 (m, 3 H), 7.54 (d, *J* = 8.6 Hz, 2 H), 6.19 (s, 1 H), 5.64 (s, 1 H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 147.0, 140.7, 137.7, 134.3, 133.9, 132.8, 132.3, 129.6, 128.7, 128.6, 127.9, 127.8, 123.7, and 117.1. HRMS (ESI) *m/z*: [*M* + NH₄]⁺ calcd for C₁₄H₁₃BrCl₂N: 343.9603; found: 343.9604.

1-Bromo-4-fluoro-2-(1-(3-fluorophenyl)vinyl)benzene (1p). Following the reported methods,¹⁵ compound **1p** was obtained by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)). 0.93 g, 62%; colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.58 (dd, *J* = 8.8, 5.3 Hz, 1 H), 7.34–7.27 (m, 1 H), 7.11–6.96 (m, 5 H), 5.89 (s, 1 H), 5.36 (s, 1 H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 163.0 (d, *J* = 243.9 Hz), 161.9 (d, *J* = 246.7 Hz), 147.2 (d, *J* = 1.5 Hz), 143.8 (d, *J* = 7.8 Hz), 141.3 (d, *J* = 7.7 Hz), 134.4 (d, *J* = 8.0 Hz), 129.9 (d, *J* = 8.2 Hz), 122.3 (d, *J* = 2.8 Hz), 118.7 (d, *J* = 22.5 Hz), 117.8, 117.6 (d, *J* = 3.1 Hz), 116.5 (d, *J* = 22.2 Hz), 114.9 (d, *J* = 21.1 Hz), and 113.5 (d, *J* = 22.3 Hz). ¹⁹F{¹H} NMR (376 MHz, CDCl₃) δ –113.16, –114.95. HRMS (ESI) *m/z*: [*M* + Na]⁺ calcd for C₁₄H₉BrF₂Na: 316.9748; found: 316.9739.

2-(1-(2-Bromo-4-chlorophenyl)vinyl)naphthalene (1q). Following the reported methods,¹⁵ compound **1q** was obtained by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)). 2.18 g, 69%; pale yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.83

Scheme 8. Proposed Mechanism



(d, $J = 8.3$ Hz, 2 H), 7.78–7.72 (m, 1 H), 7.68 (d, $J = 2.0$ Hz, 1 H), 7.57 (dd, $J = 8.6, 1.8$ Hz, 1 H), 7.52 (s, 1 H), 7.50–7.44 (m, 2 H), 7.39 (m, 1 H), 7.33 (m, 1 H), 6.00 (s, 1 H), 5.37 (s, 1 H). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3) δ 148.0, 141.3, 136.5, 134.1, 133.3, 133.0, 132.7, 132.4, 128.4, 128.2, 127.7, 127.7, 126.4, 126.3, 126.0, 124.3, 123.9, and 117.1. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{13}\text{BrCl}$: 342.9884; found: 342.9889.

N-(1-(4-Fluoro-3-methylphenyl)ethylidene)-4-methylbenzenesulfonohydrazide (**2l**). Following the reported method,^{20c} compound **2l** was obtained by recrystallization with MeOH. 1.73 g, 82%; white solid, m.p.: 145–146 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.42 (s, 1 H), 7.95 (d, *J* = 8.2 Hz, 2 H), 7.50–7.37 (m, 2 H), 7.32 (d, *J* = 8.2 Hz, 2 H), 6.93 (t, *J* = 8.9 Hz, 1 H), 2.40 (s, 3 H), 2.25 (s, 3 H), 2.15 (s, 3 H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 163.2 (d, *J* = 246.9 Hz), 152.3, 144.2, 135.3, 133.2 (d, *J* = 3.5 Hz), 129.7, 129.6, 128.1, 125.6 (d, *J* = 8.3 Hz), 124.7 (d, *J* = 17.5 Hz), 114.8 (d, *J* = 22.6 Hz), 21.6, 14.7 (d, *J* = 3.4 Hz), and 13.7. ¹⁹F{¹H} NMR (376 MHz, CDCl₃) δ –115.70 Hz. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₁₆H₁₅FN₂O₃S: 321.1068; found: 321.1072.

N-(4-Fluorophenyl)(4-methoxyphenyl)methylene)-4-methylbenzenesulfonohydrazide (**5h**). Following the reported method,^{20c} compound **5h** was obtained by recrystallization with MeOH. 3.23 g, 81%; white solid, m.p.: 195–196 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, *J* = 8.2 Hz, 2 H), 7.43–7.29 (m, 5 H), 7.21 (t, *J* = 8.5 Hz, 2 H), 7.17–7.08 (m, 2 H), 6.80 (d, *J* = 8.8 Hz, 2 H), 3.80 (s, 3 H), 2.43 (s, 3 H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 163.4 (d, *J* = 249.3 Hz), 161.2, 153.3, 144.3, 135.4, 130.6 (d, *J* = 8.4 Hz), 129.7, 129.2, 129.1, 128.0, 127.3 (d, *J* = 3.5 Hz), 117.1 (d, *J* = 21.6 Hz), 113.7, 55.4, 21.7. ¹⁹F{¹H} NMR (376 MHz, CDCl₃) δ -109.50. HRMS

(ESI) m/z : $[M + H]^+$ calcd for $C_{21}H_{20}FN_2O_3S$: 399.1173; found: 399.1177.

Typical Procedure for the C–H Alkenylation of Alkenes 1—Synthesis of Buta-1,3-diene-1,1,3-triyltribenzene (3a).⁴² Under an argon atmosphere, a mixture of alkene 1a (93 mg, 0.36 mmol), N-tosylhydrazone 2a (86 mg, 0.3 mmol), Pd(OAc)₂ (3.3 mg, 0.015 mmol), dppe (10 mg, 0.018 mmol), 2-FC₆H₄OH (67 mg, 0.6 mmol), and K₂CO₃ (83 mg, 0.6 mmol) in 4.5 mL of toluene was stirred at 100 °C for 12 h. After being cooled to ambient temperature, the reaction mixture was diluted with CH₂Cl₂ (10 mL), filtered through a short pad of celite, and rinsed with 5 mL of CH₂Cl₂. 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)/CH₂Cl₂ = 30:1, v/v) to afford 3a as a colorless liquid (67 mg, 79%). ¹H NMR (400 MHz, CDCl₃) δ 7.47–7.42 (m, 2 H), 7.41–7.32 (m, 5 H), 7.31–7.18 (m, 8 H), 6.80 (s, 1 H), 5.45 (s, 1 H), 5.09 (s, 1 H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 145.4, 144.8, 143.2, 140.8, 140.1, 130.2, 128.4, 128.3, 128.2, 128.0, 128.0, 127.7, 127.5, 127.1, 126.8, and 117.4.

Following the general procedure, compound **3b** or **3f** was obtained by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)/CH₂Cl₂ = 30:1, v/v). 62 mg, 70% yield (*E/Z* = 1.2:1) or 58 mg, 65% yield (*E/Z* = 1.2:1); colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.49–7.42 (m, 2 H), 7.41–7.17 (m, 10 H), 7.08 (m, 2 H), 6.77 (d, *J* = 0.8 Hz, 0.54 H), 6.75 (d, *J* = 0.9 Hz, 0.46 H), 5.45 (d, *J* = 1.2 Hz, 0.46 H), 5.43 (d, *J* = 1.2 Hz, 0.54 H), 5.09 (t, *J* = 1.2 Hz, 0.46 H), 5.07 (d, *J* = 1.2 Hz, 0.54 H), 2.41 (s, 1.62 H), 2.35 (s, 1.38 H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 145.4, 145.4, 144.8, 144.7, 143.4, 141.0, 140.9, 140.4, 140.3, 137.6, 137.2, 136.8, 130.2,

130.1, 129.0, 128.7, 128.2, 128.2, 128.2, 128.1, 128.1, 128.0, 127.9, 127.6, 127.4, 127.0, 126.8, 126.7, 117.2, 117.1, 21.3, and 21.2.

(1-(4-Methoxyphenyl)buta-1,3-diene-1,3-diyl)dibenzene (3c and 3g). Following the general procedure, compound **3c** or **3g** was obtained by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)/CH₂Cl₂ = 5:1, v/v). 60 mg, 64% yield (*E/Z* = 1.2:1) or 64 mg, 68% yield (*E/Z* = 1.2:1); colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.41–7.36 (m, 2 H), 7.35–7.13 (m, 9 H), 7.09–7.02 (m, 1 H), 6.86–6.82 (m, 1 H), 6.76–6.62 (m, 2 H), 5.40 (d, *J* = 1.2 Hz, 0.46 H), 5.35 (d, *J* = 1.2 Hz, 0.54 H), 5.07 (t, *J* = 1.2 Hz, 0.46 H), 5.00 (t, *J* = 1.2 Hz, 0.54 H), 3.80 (s, 1.62 H), 3.75 (s, 1.38 H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 159.4, 158.8, 145.6, 145.5, 144.4, 144.3, 143.6, 141.1, 140.9, 140.4, 135.8, 132.5, 131.4, 130.2, 129.2, 128.2, 128.1, 128.0, 127.9, 127.6, 127.4, 127.4, 127.1, 126.8, 117.2, 117.1, 113.6, 113.4, 55.4, and 55.2. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₂₃H₂₁O: 313.1587; found: 313.1585.

(1-(4-Fluorophenyl)buta-1,3-diene-1,3-diyl)dibenzene (3d and 3h). Following the general procedure, compound **3d** or **3h** was obtained by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)/CH₂Cl₂ = 20:1, v/v). 63 mg, 70% yield (*E/Z* = 1.2:1) or 65 mg, 72% yield (*E/Z* = 1.2:1); colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.49–7.32 (m, 6 H), 7.32–7.24 (m, 4 H), 7.24–7.19 (m, 1 H), 7.19–7.14 (m, 1 H), 7.07 (t, *J* = 8.7 Hz, 1 H), 6.92 (t, *J* = 8.7 Hz, 1 H), 6.85 (s, 0.55 H), 6.77 (s, 0.45 H), 5.50 (s, 0.55 H), 5.48 (s, 0.45 H), 5.17 (s, 0.55 H), 5.12 (s, 0.45 H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 162.5 (d, *J* = 245.7 Hz), 162.0 (d, *J* = 244.7 Hz), 145.5, 145.3, 143.7, 143.7, 143.0, 140.7, 140.6, 140.0, 139.3 (d, *J* = 3.2 Hz), 136.0 (d, *J* = 3.4 Hz), 131.8 (d, *J* = 7.9 Hz), 130.1, 129.6 (d, *J* = 7.9 Hz), 128.8, 128.3, 128.2, 128.2, 128.2, 128.2, 128.1, 128.0, 127.8, 127.5, 127.3, 126.8, 126.7, 117.8, 117.6, 115.1 (d, *J* = 22.7 Hz), and 114.9 (d, *J* = 22.4 Hz). ¹⁹F{¹H} NMR (376 MHz, CDCl₃) δ –114.73, –115.08. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₂₂H₁₈F: 301.1387; found: 301.1392.

(1-(3-Fluorophenyl)buta-1,3-diene-1,3-diyl)dibenzene (3e and 3i). Following the general procedure, compound **3e** or **3i** was obtained by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)/CH₂Cl₂ = 20:1, v/v). 67 mg, 75% yield (*E/Z* = 1.2:1) or 65 mg, 72% yield (*E/Z* = 1.2:1); colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.46–7.40 (m, 2 H), 7.49–7.36 (m, 2 H), 7.34–7.23 (m, 5 H), 7.23–6.87 (m, 5 H), 6.85 (s, 0.46 H), 6.83 (s, 0.54 H), 5.49 (d, *J* = 0.9 Hz, 0.46 H), 5.47 (d, *J* = 1.0 Hz, 0.54 H), 5.17 (s, 0.46 H), 5.12 (s, 0.54 H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 162.9 (d, *J* = 243.8 Hz), 162.6 (d, *J* = 243.9 Hz), 145.5 (d, *J* = 7.3 Hz), 145.3, 145.1, 143.7 (d, *J* = 2.2 Hz), 143.5 (d, *J* = 1.9 Hz), 142.6, 142.3 (d, *J* = 7.5 Hz), 140.6, 140.5, 139.5, 130.1, 129.6 (d, *J* = 8.4 Hz), 129.4 (d, *J* = 8.5 Hz), 129.3, 129.2, 128.4, 128.2, 128.2, 128.1, 128.0, 127.9, 127.6, 127.4, 126.8, 126.7, 126.0 (d, *J* = 2.8 Hz), 123.6 (d, *J* = 2.5 Hz), 118.0, 117.9, 117.2 (d, *J* = 21.4 Hz), 114.9 (d, *J* = 21.9 Hz), 114.5 (d, *J* = 21.1 Hz), and 114.0 (d, *J* = 21.0 Hz). ¹⁹F{¹H} NMR (376 MHz, CDCl₃) δ –113.48, –113.98. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₂₂H₁₈F: 301.1387; found: 301.1390.

(1-(*o*-Tolyl)buta-1,3-diene-1,3-diyl)dibenzene (3j). Following the general procedure, compound **3j** was obtained by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)/CH₂Cl₂ = 20:1, v/v). 66 mg, 74% yield (*E/Z* = 2.7:1); colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.56 (d, *J* = 7.1 Hz, 0.54 H), 7.49–7.43 (m, 1.46 H), 7.43–7.24 (m, 8 H), 7.24–7.13 (m, 4 H), 6.97 (s, 0.73 H), 6.52 (s, 0.27 H), 5.57 (s, 0.27 H), 5.40 (s, 0.73 H), 5.25 (s, 0.27 H), 5.01 (s, 0.73 H), 2.23 (s, 0.81 H), 2.17 (s, 2.19 H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 145.1, 144.9, 143.8, 143.8, 142.1, 141.4, 140.2, 140.0, 139.5, 136.5, 136.3, 130.5, 130.3, 130.3, 130.2, 130.1, 130.0, 129.5, 129.4, 128.8, 128.5, 128.4, 128.3, 128.1, 127.8, 127.6, 127.4, 127.4, 126.9, 126.9, 126.7, 125.8, 125.7, 117.1, 116.7, 20.6, and 20.1. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₂₃H₂₁: 297.1638; found: 297.1636.

Penta-1,3-diene-2,4-diyl)dibenzene (3k). Following the general procedure, compound **3k** was obtained by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)). 27 mg, 41% yield (*E/Z* = 6.2:1); colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.59–7.54 (m, 12.44 H), 7.53–7.48 (m, 12.44 H), 7.46–7.27 (m, 44.32 H),

7.23–7.20 (m, 3 H), 6.61 (s, 6.22 H), 6.30 (s, 1 H), 5.73 (d, *J* = 0.8 Hz, 6.22 H), 5.34 (d, *J* = 1.2 Hz, 1 H), 5.29 (s, 6.22 H), 4.93 (s, 1 H), 2.25 (d, *J* = 1.2 Hz, 3 H), 2.18 (d, *J* = 0.8 Hz, 18.66 H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 145.4, 145.1, 143.5, 141.7, 141.0, 140.9, 140.3, 138.9, 128.4, 128.4, 128.2, 127.9, 127.7, 127.5, 127.4, 127.3, 126.9, 126.7, 126.6, 126.0, 116.3, 115.5, 26.2, and 17.7. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₁₇H₁₇: 221.1325; found: 221.1326.

(3-(*o*-Tolyl)buta-1,3-diene-1,1-diyl)dibenzene (3m). Following the general procedure, compound **3m** was obtained by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)). 62 mg, 70% yield; colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.44–7.35 (m, 5 H), 7.22–7.16 (m, 3 H), 7.13 (m, 3 H), 7.09–7.03 (m, 2 H), 7.02–6.94 (m, 2 H), 5.55 (dd, *J* = 1.9, 1.1 Hz, 1 H), 5.27 (d, *J* = 2.0 Hz, 1 H), 2.37 (s, 3 H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 146.9, 143.4, 143.0, 141.4, 139.3, 134.7, 130.0, 129.7, 129.6, 129.1, 128.2, 127.8, 127.5, 127.5, 126.9, 126.7, 125.2, 121.4, and 20.6. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₂₃H₂₁: 297.1638; found: 297.1636.

(3-(2-Trifluoromethylphenyl)buta-1,3-diene-1,1-diyl)dibenzene (3n). Following the general procedure, compound **3n** was obtained by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)/CH₂Cl₂ = 20:1, v/v). 63 mg, 60% yield; colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.54–7.48 (m, 1 H), 7.38–7.29 (m, 5 H), 7.25–7.01 (m, 8 H), 6.96 (s, 1 H), 5.54 (s, 1 H), 5.23 (d, *J* = 1.2 Hz, 1 H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 144.6, 143.3, 143.1, 140.5 (1.8 Hz), 131.7, 130.8, 130.2, 128.9, 128.9, 128.2, 127.8, 127.6, 127.6, 127.6 (29.6 Hz), 126.9, 126.8, 125.8 (5.1 Hz), 124.4 (27.3 Hz), and 122.1. ¹⁹F{¹H} NMR (376 MHz, CDCl₃) δ –57.52. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₂₃H₁₈F₃: 351.1355; found: 351.1351.

(3-(2-Fluorophenyl)buta-1,3-diene-1,1-diyl)dibenzene (3o). Following the general procedure, compound **3o** was obtained by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)/EtOAc = 100:1, v/v). 66 mg, 74% yield; colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.42–7.31 (m, 5 H), 7.25–7.05 (m, 7 H), 7.00–6.91 (m, 2 H), 6.88–6.79 (m, 1 H), 5.52 (s, 1 H), 5.45 (s, 1 H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 159.5 (d, *J* = 246.2 Hz), 143.8, 143.3, 141.3, 139.6, 130.5 (d, *J* = 3.7 Hz), 130.3, 129.0 (d, *J* = 12.7 Hz), 128.7 (d, *J* = 8.3 Hz), 128.4, 128.2, 128.0, 127.6, 127.6, 127.0, 123.5 (d, *J* = 3.5 Hz), 122.2 (d, *J* = 2.4 Hz), and 115.3 (d, *J* = 22.4 Hz). ¹⁹F{¹H} NMR (376 MHz, CDCl₃) δ –113.97. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₂₂H₁₈F: 301.1387; found: 301.1392.

(3-(3-Fluorophenyl)buta-1,3-diene-1,1-diyl)dibenzene (3p). Following the general procedure, compound **3p** was obtained by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)). 70 mg, 78% yield; colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.47–7.37 (m, 5 H), 7.32–7.20 (m, 7 H), 7.17–7.12 (m, 1 H), 7.00–6.91 (m, 1 H), 6.84 (d, *J* = 0.6 Hz, 1 H), 5.51 (d, *J* = 0.6 Hz, 1 H), 5.23 (s, 1 H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 162.7 (d, *J* = 243.4 Hz), 145.2, 144.6 (d, *J* = 2.1 Hz), 143.1 (d, *J* = 7.3 Hz), 143.0, 139.9, 130.2, 129.5 (d, *J* = 8.4 Hz), 128.3, 128.1, 128.0, 127.8, 127.7, 127.3, 122.5 (d, *J* = 2.6 Hz), 118.6, 114.1 (d, *J* = 21.1 Hz), and 113.8 (d, *J* = 21.8 Hz). ¹⁹F{¹H} NMR (376 MHz, CDCl₃) δ –114.06. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₂₂H₁₈F: 301.1387; found: 301.1395.

(3-(4-Fluorophenyl)buta-1,3-diene-1,1-diyl)dibenzene (3q). Following the general procedure, compound **3q** was obtained by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)). 66 mg, 73% yield; colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.48–7.38 (m, 7 H), 7.31–7.21 (m, 5 H), 6.99 (t, *J* = 8.7 Hz, 2 H), 6.87 (s, 1 H), 5.46 (s, 1 H), 5.21 (s, 1 H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 162.2 (d, *J* = 244.7 Hz), 144.9, 144.6, 143.1, 140.0, 136.8 (d, *J* = 3.1 Hz), 130.2, 128.4 (d, *J* = 8.0 Hz), 128.3, 128.2, 128.1, 128.0, 127.8, 127.2, 117.6, and 114.8 (d, *J* = 21.2 Hz). ¹⁹F{¹H} NMR (376 MHz, CDCl₃) δ –115.22. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₂₂H₁₈F: 301.1387; found: 301.1388.

(3-(4-Chlorophenyl)buta-1,3-diene-1,1-diyl)dibenzene (3r).²⁸ Following the general procedure, compound **3r** was obtained by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)). 79 mg, 83% yield; white solid, m.p.: 109–110 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.42–7.29 (m, 7 H), 7.26–7.10 (m, 7 H), 6.79

(s, 1 H), 5.43 (s, 1 H), 5.17 (s, 1 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 145.1, 144.6, 143.0, 139.9, 139.2, 133.1, 130.2, 128.3, 128.2, 128.1, 128.0, 127.8, 127.8, 127.8, 127.2, and 118.1.

(3-(4-Ethylphenyl)buta-1,3-diene-1,1-diyl)dibenzene (3s). 66 mg, 71% yield; colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.46–7.36 (m, 7 H), 7.31–7.25 (m, 5 H), 7.18 (d, J = 8.4 Hz, 2 H), 6.83 (d, J = 1.1 Hz, 1 H), 5.47 (d, J = 1.4 Hz, 1 H), 5.07 (t, J = 1.4 Hz, 1 H), 2.71 (q, J = 7.6 Hz, 2 H), 1.32 (t, J = 7.6 Hz, 3 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 145.1, 144.6, 143.7, 143.2, 140.2, 138.2, 130.2, 128.6, 128.2, 128.0, 127.7, 127.6, 127.1, 126.7, 116.5, 28.6, and 15.7. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{23}$: 311.1794; found: 311.1793.

(3-(4-(Tert-butyl)phenyl)buta-1,3-diene-1,1-diyl)dibenzene (3t). Following the general procedure, compound **3t** was obtained by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)). 66 mg, 65% yield; colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.48–7.37 (m, 9 H), 7.31–7.26 (m, 5 H), 6.86 (d, J = 0.7 Hz, 1 H), 5.50 (d, J = 1.3 Hz, 1 H), 5.11 (s, 1 H), 1.42 (s, 9 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 150.4, 145.0, 144.5, 143.3, 140.2, 137.9, 130.2, 128.6, 128.2, 128.0, 127.6, 127.0, 126.5, 125.1, 116.8, 34.6, and 31.4. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{27}$: 339.2107; found: 339.2108.

4-(4,4-Diphenylbuta-1,3-dien-2-yl)-1,1'-biphenyl (3u). Following the general procedure, compound **3u** was obtained by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)/ CH_2Cl_2 = 20:1, v/v). 70 mg, 65% yield; white solid, m.p.: 108–109 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.69–7.60 (m, 2 H), 7.59–7.47 (m, 6 H), 7.47–7.35 (m, 6 H), 7.26 (d, J = 5.9 Hz, 5 H), 6.87 (d, J = 5.9 Hz, 1 H), 5.54 (d, J = 5.4 Hz, 1 H), 5.16 (d, J = 6.6 Hz, 1 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 145.0, 144.9, 143.2, 140.9, 140.3, 140.1, 139.7, 130.2, 128.8, 128.4, 128.3, 128.1, 128.0, 127.7, 127.3, 127.2, 127.1, 127.1, 126.9, and 117.5. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{28}\text{H}_{23}$: 359.1794; found: 359.1796.

1-(4,4-Diphenylbuta-1,3-dien-2-yl)naphthalene (3v). Following the general procedure, compound **3v** was obtained by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)/ CH_2Cl_2 = 20:1, v/v). 70 mg, 70% yield; colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 8.10 (d, J = 8.0 Hz, 1 H), 7.77–7.65 (m, 1 H), 7.62–7.53 (m, 1 H), 7.51–7.40 (m, 2 H), 7.37–7.20 (m, 7 H), 7.11 (s, 1 H), 6.97–6.67 (m, 5 H), 5.68 (s, 1 H), 5.40 (d, J = 1.4 Hz, 1 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 145.8, 143.4, 143.3, 139.6, 139.1, 133.4, 131.3, 129.7, 129.6, 128.2, 128.0, 127.7, 127.5, 127.3, 126.9, 126.6, 126.5, 126.1, 125.5, 125.3, 125.0, and 122.6. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{21}$: 333.1638; found: 333.1641.

(3-(4-Fluoro-3-methylphenyl)buta-1,3-diene-1,1-diyl)dibenzene (3w). Following the general procedure, compound **3w** was obtained by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)). 58 mg, 62% yield; colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.42–7.33 (m, 5 H), 7.26–7.16 (m, 7 H), 6.90 (t, J = 9.0 Hz, 1 H), 6.80 (s, 1 H), 5.40 (s, 1 H), 5.12 (s, 1 H), 2.26 (s, 3 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 160.8 (d, J = 243.5 Hz), 144.7, 143.1, 140.1, 136.4 (d, J = 3.6 Hz), 130.1, 130.0 (d, J = 5.1 Hz), 128.4, 128.3, 128.1, 127.9, 127.7, 127.1, 125.7 (d, J = 7.9 Hz), 124.2, 124.1, 117.3, 114.6 (d, J = 22.3 Hz), and 14.5 (d, J = 3.3 Hz). $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ –119.46. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{20}\text{F}$ $[\text{M} + \text{H}]^+$: 315.1544; found: 315.1545.

(3-(3,4-Dichlorophenyl)buta-1,3-diene-1,1-diyl)dibenzene (3x). Following the general procedure, compound **3x** was obtained by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)/ EtOAc = 50:1, v/v). 75 mg, 72% yield; colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.35–7.29 (m, 6 H), 7.23–7.11 (m, 5 H), 7.08–7.03 (m, 2 H), 6.73 (s, 1 H), 5.39 (s, 1 H), 5.20 (s, 1 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 145.6, 144.0, 142.8, 140.8, 139.7, 132.0, 131.0, 130.2, 129.9, 129.0, 128.3, 128.1, 128.0, 127.4, 127.2, 126.3, and 119.4. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{17}\text{Cl}_2$: 351.0702; found: 351.0697.

4-(2,2-Diphenylvinyl)-1,2-dihydronaphthalene (3y). Following the general procedure, compound **3y** was obtained by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)).

77 mg, 84% yield; colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.54–7.39 (m, 6 H), 7.39–7.23 (m, 8 H), 6.86 (d, J = 1.6 Hz, 1 H), 5.93–5.79 (m, 1 H), 2.83 (t, J = 7.9 Hz, 2 H), 2.30–2.16 (m, 2 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 144.3, 143.3, 140.7, 136.2, 135.3, 135.1, 130.1, 129.7, 128.2, 128.0, 128.0, 127.5, 127.4, 127.1, 127.0, 127.0, 126.5, 124.1, 27.9, and 23.4. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{21}$: 309.1638; found: 309.1635.

Penta-1,3-diene-1,1,3-triyltribenzene (3z). Following the general procedure, compound **3z** was obtained by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)). 72 mg, 81% yield (Z/E = 3.1:1); colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.56–7.50 (m, 12.45 H), 7.49–7.34 (m, 20.75 H), 7.32–7.18 (m, 20.05 H), 6.88 (d, J = 0.8 Hz, 1 H), 6.81 (d, J = 0.8 Hz, 3.15 H), 6.02–5.91 (m, 4.15 H), 1.75 (d, J = 7.2 Hz, 3 H), 1.70 (d, J = 7.1 Hz, 9.45 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 145.6, 143.8, 143.3, 141.8, 141.6, 140.5, 140.4, 139.6, 139.2, 138.3, 131.4, 130.5, 129.9, 129.8, 129.4, 128.3, 128.2, 128.1, 127.8, 127.7, 127.7, 127.6, 127.2, 127.1, 126.7, 126.5, 126.3, 126.1, 125.4, 15.8, and 15.3. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{21}$: 297.1638; found: 297.1635.

Typical Procedure for the Synthesis of 1,2-Bis(1-phenylvinyl)-benzene (4a).²⁹ Under an argon atmosphere, a mixture of alkene **1a** (93 mg, 0.36 mmol), *N*-tosylhydrazide **2a** (86 mg, 0.3 mmol), $\text{Pd}(\text{OAc})_2$ (3.3 mg, 0.015 mmol), DPEphos (16 mg, 0.03 mmol), and LiO^tBu (80 mg, 0.6 mmol) in 4.5 mL of toluene was stirred at 100 °C for 12 h. After being 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)/ CH_2Cl_2 = 30:1, v/v) to afford **4a** as a colorless liquid (67 mg, 80%). ^1H NMR (400 MHz, CDCl_3) δ 7.42–7.37 (m, 2 H), 7.33 (m, 2 H), 7.22–7.15 (m, 6 H), 7.09 (m, 4 H), 5.44 (d, J = 1.4 Hz, 2 H), 5.14 (d, J = 1.4 Hz, 2 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 149.3, 141.2, 141.1, 130.9, 127.8, 127.5, 127.4, 127.3, and 116.2.

Typical Procedure for the C–H Alkenylation of Alkenes 1—Synthesis of 1,1,3,3-Tetraphenylpropa-1,2-diene (6a).^{19b} Under an argon atmosphere, a mixture of alkene **1a** (93 mg, 0.36 mmol), *N*-tosylhydrazide **5a** (105 mg, 0.3 mmol), $\text{Pd}(\text{OAc})_2$ (3.3 mg, 0.015 mmol), dppf (10 mg, 0.018 mmol), 2- $\text{FC}_6\text{H}_4\text{OH}$ (67 mg, 0.6 mmol), and K_2CO_3 (83 mg, 0.6 mmol) in 4.5 mL of toluene was stirred at 100 °C for 12 h. After being 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)/ CH_2Cl_2 = 10:1, v/v) to afford **6a** as a white solid (87 mg, 84%). m.p.: 156–157 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.54–7.46 (m, 8 H), 7.44–7.32 (m, 12 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 208.6, 136.4, 128.6, 128.5, 127.6, and 112.7.

(3-(*o*-Tolyl)propa-1,2-diene-1,1,3-triyl)tribenzene (6b and 6j).^{19b} Following the general procedure, compound **6b** or **6j** was obtained by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)/ CH_2Cl_2 = 10:1, v/v), respectively. 66 mg, 61% yield or 6 mg, 5% yield (or 10 mg, 9% yield); white solid, m.p.: 115–116 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.52–7.46 (m, 4 H), 7.45–7.24 (m, 15 H), 2.22 (s, 3 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 207.0, 137.2, 136.5, 136.2, 135.7, 130.4, 130.3, 128.7, 128.6, 128.5, 127.9, 127.6, 127.3, 126.8, 126.2, 112.6, 110.7, and 20.4.

(3-(3-Fluorophenyl)propa-1,2-diene-1,1,3-triyl)tribenzene (6c and 6h). Following the general procedure, compound **6c** or **6h** was obtained by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)/ CH_2Cl_2 = 10:1, v/v), respectively. 92 mg, 85% yield or 91 mg, 84% yield; white solid, m.p.: 105–106 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.54 (d, J = 7.4 Hz, 6 H), 7.50–7.30 (m, 11 H), 7.29–7.23 (m, 1 H), 7.11–7.05 (m, 1 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 208.6, 163.0 (d, J = 244.5 Hz), 138.8 (d, J = 7.4 Hz), 136.1, 135.9, 130.0 (d, J = 8.4 Hz), 128.7, 128.7, 128.5, 127.8, 127.8, 124.1 (d, J = 2.7 Hz), 115.2 (d, J = 22.0 Hz), 114.5 (d, J = 21.2 Hz), 113.2,

and 112.0 (d, $J = 2.2$ Hz). $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ –113.52. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{20}\text{F}$: 363.1544; found: 363.1546.

(3-(*p*-Tolyl)propa-1,2-diene-1,1,3-triyl)tribenzene (6d and 6l).^{19b} Following the general procedure, compound **6d** or **6l** was obtained by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)/ $\text{CH}_2\text{Cl}_2 = 10:1$, v/v), respectively. 80 mg, 75% yield or 92 mg, 86% yield; white solid, m.p.: 79–80 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.50–7.43 (m, 6 H), 7.41–7.30 (m, 11 H), 7.20 (d, $J = 8.0$ Hz, 2 H), 2.40 (s, 3 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 208.5, 137.4, 136.6, 136.5, 133.4, 129.3, 128.6, 128.5, 128.4, 127.5, 112.6, 112.6, and 21.3.

(3-(4-(Trifluoromethyl)phenyl)propa-1,2-diene-1,1,3-triyl)tribenzene (6e).^{19b} Following the general procedure, compound **6e** was obtained by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)/ $\text{CH}_2\text{Cl}_2 = 15:1$, v/v). 109 mg, 88% yield; colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.61 (dd, $J = 26.7, 8.3$ Hz, 4 H), 7.51–7.29 (m, 15 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 208.9, 140.4, 135.9, 135.7, 129.6 (32.2 Hz), 128.8, 128.8, 128.7, 128.5, 128.0, 127.9, 125.6 (3.6 Hz), 122.9 (270.3 Hz), 113.5, and 111.9. $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ –62.41.

(3-(4-Methoxyphenyl)propa-1,2-diene-1,1,3-triyl)tribenzene (6f, 6i and 6m).^{19b} Following the general procedure, compound **6f** or **6i** or **6m** was obtained by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)/ $\text{CH}_2\text{Cl}_2 = 5:1$, v/v), respectively. 87 mg, 78% yield or 89 mg, 80% yield or 74 mg, 66% yield; colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.49–7.44 (m, 6 H), 7.42–7.35 (m, 8 H), 7.32–7.30 (m, 3 H), 6.95–6.91 (m, 2 H), 3.85 (s, 3 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 208.4, 159.2, 136.7, 136.6, 129.7, 128.6, 128.6, 128.5, 127.5, 127.5, 114.1, 112.5, 112.3, 77.4, 77.1, 76.8, and 55.4.

(3-(4-Chlorophenyl)propa-1,2-diene-1,1,3-triyl)tribenzene (6g).^{19b} Following the general procedure, compound **6g** was obtained by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)/ $\text{CH}_2\text{Cl}_2 = 15:1$, v/v). 87 mg, 77% yield; white solid, m.p.: 69–70 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.50–7.45 (m, 6 H), 7.45–7.33 (m, 13 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 208.5, 136.1, 136.0, 135.0, 133.4, 129.8, 128.8, 128.7, 128.7, 128.5, 128.4, 127.8, 127.8, 113.1, and 111.9.

(3-(*m*-Tolyl)propa-1,2-diene-1,1,3-triyl)tribenzene (6k).^{19b} Following the general procedure, compound **6k** was obtained by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)/ $\text{CH}_2\text{Cl}_2 = 10:1$, v/v). 78 mg, 72% yield; white solid, m.p.: 78–79 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.55–7.48 (m, 6 H), 7.47–7.39 (m, 6 H), 7.39–7.29 (m, 6 H), 7.22–7.15 (m, 1 H), 2.41 (s, 3 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 208.5, 138.2, 136.6, 136.5, 136.3, 129.1, 128.6, 128.5, 128.4, 127.6, 127.5, 125.7, 112.7, 112.6, and 21.6.

(3-(4-Fluorophenyl)propa-1,2-diene-1,1,3-triyl)tribenzene (6n).^{19b} Following the general procedure, compound **6n** was obtained by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)/ $\text{CH}_2\text{Cl}_2 = 10:1$, v/v). 57 mg, 53% yield; white solid, m.p.: 104–105 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.53–7.29 (m, 17 H), 7.13–7.05 (m, 2 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 208.4, 162.4 (d, $J = 245.5$ Hz), 136.3, 132.4 (d, $J = 3.2$ Hz), 130.1 (d, $J = 8.3$ Hz), 128.7, 128.7, 128.5, 128.4, 127.7, 127.7, 115.6 (d, $J = 21.5$ Hz), 112.9, and 111.9. $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ –114.49.

4,4'-(3,3-Diphenylpropa-1,2-diene-1,1-diyl)bis(methoxybenzene) (6o).³⁰ Following the general procedure, compound **6o** was obtained by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)/ $\text{CH}_2\text{Cl}_2 = 3:1$, v/v). 46 mg, 38% yield; yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.32 (m, 4 H), 7.29–7.21 (m, 8 H), 7.18 (m, 2 H), 6.83–6.74 (m, 4 H), 3.71 (s, 6 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 208.2, 159.2, 136.8, 129.6, 128.9, 128.6, 128.5, 127.4, 114.0, 112.2, 111.9, and 55.4.

(3-(4-Fluorophenyl)-3-(4-methoxyphenyl)propa-1,2-diene-1,1-diyl)dibenzene (6p). Following the general procedure, compound **6p** was obtained by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)/ $\text{CH}_2\text{Cl}_2 = 10:1$, v/v). 62 mg, 53% yield; yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.52–7.30 (m, 14 H), 7.09 (t, $J = 8.7$ Hz, 2 H), 6.95 (d, $J = 8.8$ Hz, 2 H), 3.86 (s, 3 H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 208.2, 162.3 (d, $J = 245.0$ Hz), 159.3, 136.5, 132.6 (d, $J = 3.3$ Hz), 130.1 (d, $J = 8.0$ Hz), 129.5, 128.6, 128.5, 128.4, 127.6, 115.5 (d, $J = 21.2$ Hz), 114.1, 112.6, 111.5, and 55.4. $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ –114.59. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{28}\text{H}_{22}\text{FO}$: 393.1649; found: 393.1648.

4,4'-(3,3-Diphenylpropa-1,2-diene-1,1-diyl)bis(fluorobenzene) (6q).^{19b} Following the general procedure, compound **6q** was obtained by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)/ $\text{CH}_2\text{Cl}_2 = 20:1$, v/v). 49 mg, 43% yield; colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.47–7.31 (m, 14 H), 7.08 (t, $J = 8.6$ Hz, 4 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 208.2, 162.5 (d, $J = 245.6$ Hz), 136.1, 132.3 (d, $J = 3.3$ Hz), 130.1 (d, $J = 8.0$ Hz), 128.7, 128.5, 127.8, 115.7 (d, $J = 21.6$ Hz), 113.0, and 111.0. $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ –114.25.

Methyl 2,4,4-triphenylbuta-2,3-dienoate (6r).^{19c} Following the general procedure, compound **6r** was obtained by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)/ $\text{CH}_2\text{Cl}_2 = 2:1$, v/v). 49 mg, 50% yield; white solid, m.p.: 95–96 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.68–7.62 (m, 2 H), 7.51–7.44 (m, 4 H), 7.44–7.29 (m, 9 H), 3.88 (s, 3 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 214.6, 166.4, 134.7, 132.4, 128.8, 128.8, 128.6, 128.4, 128.3, 128.0, 114.8, 105.3, and 52.6.

Typical Procedure for the C–H Alkenylation of Alkenes 1—Synthesis of 1,1,3,3-Tetrakis(4-chlorophenyl)propa-1,2-diene (7a). Under an argon atmosphere, a mixture of alkene **1o** (117 mg, 0.36 mmol), *N*-tosylhydrazide **5o** (125 mg, 0.3 mmol), $\text{Pd}(\text{OAc})_2$ (6.6 mg, 0.03 mmol), dppf (20 mg, 0.036 mmol), 2- $\text{FC}_6\text{H}_4\text{OH}$ (67 mg, 0.6 mmol), and K_2CO_3 (83 mg, 0.6 mmol) in 4.5 mL of toluene was stirred at 100 °C for 24 h. After being 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 **7a** as a white solid (74 mg, 51%). m.p.: 204–205 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.37–7.32 (m, 8 H), 7.32–7.26 (m, 8 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 208.3, 134.0, 134.0, 129.6, 129.1, and 111.8. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{17}\text{Cl}_4$: 481.0079; found: 481.0083.

1,1,3,3-Tetrakis(3-fluorophenyl)propa-1,2-diene (7b). Following the general procedure, compound **7b** was obtained by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)/ $\text{CH}_2\text{Cl}_2 = 20:1$, v/v). 91 mg, 73% yield; colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.40–7.33 (m, 4 H), 7.19 (d, $J = 7.8$ Hz, 4 H), 7.14–7.01 (m, 8 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 208.4, 163.1 (d, $J = 245.3$ Hz), 137.6 (d, $J = 7.4$ Hz), 130.4 (d, $J = 8.5$ Hz), 124.2 (d, $J = 2.8$ Hz), 115.7 (d, $J = 22.2$ Hz), 115.2 (d, $J = 21.2$ Hz), and 112.1 (t, $J = 2.3$ Hz). $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ –112.25. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{17}\text{F}_4$: 417.1261; found: 417.1258.

(1-(4-Methoxyphenyl)-3-(*m*-tolyl)propa-1,2-diene-1,3-diyl)dibenzene (7c). Following the general procedure, compound **7c** was obtained by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)/ $\text{CH}_2\text{Cl}_2 = 5:1$, v/v). 88 mg, 76% yield; colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.57–7.49 (m, 4 H), 7.48–7.39 (m, 6 H), 7.39–7.31 (m, 5 H), 7.22–7.15 (m, 1 H), 7.00–6.96 (m, 2 H), 3.88 (s, 3 H), 2.42 (s, 3 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 208.3, 159.2, 138.2, 136.7, 136.5, 129.7, 129.1, 128.6, 128.5, 128.3, 127.5, 127.4, 125.7, 114.0, 112.5, 112.2, 55.3, and 21.6. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{29}\text{H}_{25}\text{O}$: 389.1900; found: 389.1904.

4,4'-(1-(4-Fluorophenyl)-3-phenylpropa-1,2-diene-1,3-diyl)bis(methoxybenzene) (7d). Following the general procedure, compound **7d** was obtained by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)/ $\text{CH}_2\text{Cl}_2 = 2:1$, v/v). 80 mg, 63% yield; colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.51–7.30 (m, 11 H), 7.12–7.04 (m, 2 H), 6.94 (dd, $J = 8.7, 1.2$ Hz, 4 H), 3.85 (s, 6 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 208.0, 162.3 (d, $J = 245.0$ Hz), 159.2, 159.2, 136.8, 132.8 (d, $J = 3.2$ Hz), 130.0 (d, $J = 7.9$ Hz),

129.6, 129.5, 128.6, 128.6, 128.4, 127.5, 115.5 (d, $J = 21.2$ Hz), 114.1, 114.1, 112.2, and 55.4. $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ -114.76. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{29}\text{H}_{24}\text{FO}_2$: 423.1755; found: 423.1753.

4-(1,3-Diphenyl-3-(*p*-tolyl)propa-1,2-dien-1-yl)-1,1'-biphenyl (7e). Following the general procedure, compound **7e** was obtained by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)/ $\text{CH}_2\text{Cl}_2 = 10:1$, v/v). 84 mg, 64% yield; colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.77–7.69 (m, 4 H), 7.69–7.58 (m, 6 H), 7.58–7.39 (m, 11 H), 7.31 (d, $J = 8.0$ Hz, 2 H), 2.50 (s, 3 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 208.7, 140.8, 140.3, 137.4, 136.5, 136.5, 135.5, 133.3, 129.4, 128.9, 128.8, 128.6, 128.6, 128.5, 128.4, 127.6, 127.4, 127.3, 127.1, 112.7, 112.3, and 21.3. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{34}\text{H}_{27}$: 435.2107; found: 435.2110.

1-(3-(4-Fluorophenyl)-3-(4-methoxyphenyl)-1-phenylpropa-1,2-dien-1-yl)-2-methylbenzene (7f). Following the general procedure, compound **7f** was obtained by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)/ $\text{CH}_2\text{Cl}_2 = 4:1$, v/v). 77 mg, 63% yield; colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.55–7.44 (m, 5 H), 7.43–7.27 (m, 8 H), 7.19–7.10 (m, 2 H), 7.06–6.95 (m, 2 H), 3.90 (s, 3 H), 2.28 (s, 3 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 206.6, 162.3 (d, $J = 245.1$ Hz), 159.3, 137.1, 136.3, 135.8, 132.7 (d, $J = 3.1$ Hz), 130.4, 130.2, 130.1 (d, $J = 8.0$ Hz), 129.6, 128.7, 128.5, 127.9, 127.3, 126.7, 126.2, 115.4 (d, $J = 21.3$ Hz), 114.1, 111.3, 110.6, 55.3, and 20.4. $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ -114.40. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{29}\text{H}_{24}\text{FO}$ $[\text{M} + \text{H}]^+$: 407.1806; found: 407.1801.

1-Chloro-4-(3-(4-fluorophenyl)-3-(4-methoxyphenyl)-1-phenylpropa-1,2-dien-1-yl)benzene (7g). Following the general procedure, compound **7g** was obtained by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)/ $\text{CH}_2\text{Cl}_2 = 4:1$, v/v). 83 mg, 65% yield; colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.51–7.30 (m, 13 H), 7.16–7.05 (m, 2 H), 7.00–6.92 (m, 2 H), 3.86 (s, 3 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 208.2, 162.4 (d, $J = 245.6$ Hz), 159.4, 136.1, 135.1, 133.4, 132.4 (d, $J = 3.1$ Hz), 130.1 (d, $J = 8.1$ Hz), 129.7, 129.5, 128.8, 128.7, 128.4, 128.1, 127.8, 115.6 (d, $J = 21.3$ Hz), 114.2, 111.9, 111.8, and 55.4. $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ -114.22. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{28}\text{H}_{21}\text{ClFO}$: 427.1259; found: 427.1265.

2-(3-([1,1'-Biphenyl]-4-yl)-1-(4-chlorophenyl)-3-phenylpropa-1,2-dien-1-yl)naphthalene (7h). Following the general procedure, compound **7h** was obtained by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)/ $\text{CH}_2\text{Cl}_2 = 20:1$, v/v). 82 mg, 54% yield; yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.89–7.76 (m, 4 H), 7.67–7.58 (m, 5 H), 7.57–7.31 (m, 16 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 209.2, 140.7, 140.6, 136.1, 135.0, 135.0, 133.5, 133.4, 133.0, 130.0, 128.9, 128.9, 128.8, 128.6, 128.5, 128.2, 127.9, 127.8, 127.5, 127.4, 127.1, 126.5, 126.4, 126.3, 113.0, and 112.2. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{37}\text{H}_{26}\text{Cl}$: 505.1718; found: 505.1714.

2-(1-(4-Chlorophenyl)-3-(4-fluorophenyl)-3-(4-methoxyphenyl)propa-1,2-dien-1-yl)naphthalene (7i). Following the general procedure, compound **7i** was obtained by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)/ $\text{CH}_2\text{Cl}_2 = 4:1$, v/v). 73 mg, 51% yield; colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.92–7.78 (m, 4 H), 7.67–7.60 (m, 1 H), 7.56–7.36 (m, 10 H), 7.16–7.08 (m, 2 H), 7.01–6.94 (m, 2 H), 3.87 (s, 3 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 208.7, 162.4 (d, $J = 245.6$ Hz), 161.2, 159.5, 135.1, 133.5, 133.5, 132.9, 132.4 (d, $J = 3.4$ Hz), 130.1 (d, $J = 8.0$ Hz), 129.9, 129.6, 128.9, 128.4, 128.1, 128.1, 127.7, 127.1, 126.4, 126.4, 126.3, 115.6 (d, $J = 21.3$ Hz), 114.2, 112.1, 111.9, and 55.41. $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ -114.10. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{32}\text{H}_{23}\text{ClFO}$ $[\text{M} + \text{H}]^+$: 477.1416; found: 477.1412.

Gram-Scale Preparation and Cyclization. Gram-Scale Preparation of Compound 3r. Under an argon atmosphere, a mixture of alkene **1a** (1555 mg, 6 mmol), *N*-tosylhydrazone **2g** (1614 mg, 5 mmol), $\text{Pd}(\text{OAc})_2$ (55 mg, 0.25 mmol), dppf (166 mg, 0.30 mmol), 2- $\text{FC}_6\text{H}_4\text{OH}$ (1117 mg, 10 mmol), and K_2CO_3 (1383 mg, 10 mmol) in 75 mL of toluene was stirred at 100 °C for 12 h. After being cooled

to ambient temperature, the reaction mixture was diluted with CH_2Cl_2 (30 mL), filtered through a short pad of celite, and rinsed with 30 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)/ $\text{CH}_2\text{Cl}_2 = 30:1$, v/v) to afford **3r** as a white solid (1.267 g, 80%).

Bronsted Acid-Promoted Cyclization of Compound 3r—Synthesis of 8a. A mixture of 1,3-diene **3r** (63.4 mg, 0.2 mmol) and TfOH (3.0 mg, 0.02 mmol) in CH_2Cl_2 (2 mL) was stirred at ambient temperature in air for 1 h. After the solvent was removed under reduced pressure, the resultant residue was subjected to purification by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)/ $\text{CH}_2\text{Cl}_2 = 15:1$, v/v) to afford **8a** as a pale yellow liquid (56 mg, 88%).

1-(4-Chlorophenyl)-1-methyl-3-phenyl-1H-indene (8a). 56 mg, 88% yield, pale yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.57–7.50 (m, 2 H), 7.46 (d, $J = 7.5$ Hz, 1H), 7.40–7.33 (m, 2 H), 7.31–7.24 (m, 1 H), 7.20–7.15 (m, 1H), 7.14–7.08 (m, 6 H), 6.42 (s, 1 H), 1.67 (s, 3 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 154.1, 143.0, 142.3, 142.0, 141.6, 135.4, 132.3, 128.7, 128.6, 128.0, 127.8, 127.7, 126.9, 126.1, 123.2, 121.1, 55.2, and 22.9. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{18}\text{Cl}$: 317.1092; found: 317.1089.

[2+1] Annulation of 3r with Bromoform—Synthesis of 8b. Under an argon atmosphere, 31 μL of bromoform (89.2 mg, 0.35 mmol) was added to a stirred mixture of 1,3-diene **3r** (63.4 mg, 0.2 mmol) and potassium *tert*-butoxide (40.4 mg, 0.35 mmol) in 2 mL of dry hexane at 0 °C. After the mixture was stirred at ambient temperature for 15 h, the reaction was quenched by H_2O (20 mL) and extracted with CH_2Cl_2 (3 $\times$ 30 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (eluent: petroleum ether (60–90 °C)) to afford **8b** as a white solid (40 mg, 41%).

(2-(2,2-Dibromo-1-(4-chlorophenyl)cyclopropyl)ethene-1,1-diyl)-dibenzene (8b). 40 mg, 41% yield, white solid, m.p.: 152–153 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.37–7.32 (m, 5 H), 7.29 (s, 5 H), 7.25–7.20 (m, 2 H), 7.05–6.98 (m, 2 H), 6.64 (s, 1 H), 2.07 (dd, $J = 8.5$, 1.2 Hz, 1 H), 1.54 (d, $J = 8.5$ Hz, 1 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 145.6, 142.3, 140.2, 139.2, 133.1, 130.2, 130.1, 129.3, 128.8, 128.3, 128.2, 128.09, 127.9, 127.9, 38.5, 38.0, and 34.0. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{18}\text{Br}_2\text{Cl}$: 486.9458; found: 486.9456.

Gram-Scale Preparation of Compound 6a. Under an argon atmosphere, a mixture of alkene **1a** (1555 mg, 6 mmol), *N*-tosylhydrazone **5a** (1750 mg, 5 mmol), $\text{Pd}(\text{OAc})_2$ (55 mg, 0.25 mmol), dppf (166 mg, 0.30 mmol), 2- $\text{FC}_6\text{H}_4\text{OH}$ (1117 mg, 10 mmol), and K_2CO_3 (1383 mg, 10 mmol) in 75 mL of toluene was stirred at 100 °C for 12 h. After being cooled to ambient temperature, the reaction mixture was diluted with CH_2Cl_2 (30 mL), filtered through a short pad of celite, and rinsed with 30 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)/ $\text{CH}_2\text{Cl}_2 = 10:1$, v/v) to afford **6a** as a white solid (1.343 g, 78%).

Bronsted Acid-Promoted Cyclization of Compound 6a—Synthesis of 8c. A mixture of allene **6a** (68.8 mg, 0.2 mmol) and TfOH (3.0 mg, 0.02 mmol) in DCM (2 mL) was stirred at ambient temperature in air for 1 h. After the solvent was removed under reduced pressure, the resultant residue was subjected to purification by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)/ $\text{CH}_2\text{Cl}_2 = 8:1$, v/v) to afford **8b** as a white solid (67 mg, 97%).

1,1,3-Triphenyl-1H-indene (8c). 67 mg, 97% yield, white solid, m.p.: 132–133 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.77–7.71 (m, 2 H), 7.67 (d, $J = 7.4$ Hz, 1 H), 7.56–7.49 (m, 3 H), 7.48–7.43 (m, 1 H), 7.43–7.37 (m, 5 H), 7.36–7.27 (m, 7 H), 6.93 (s, 1 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 151.2, 143.8, 142.6, 142.5, 141.7, 135.3, 128.7, 128.4, 128.0, 128.0, 127.8, 127.1, 126.8, 126.0, 125.8, 121.5, and 65.7.

Kinetic Isotope Effect (KIE) Experiments. *Intermolecular Competition.* The reaction of a mixture of **1a** and its deuterated form **1a**[D]¹⁵ was carried out in an intermolecular competition manner for 1 h under the optimized conditions. The NMR yields from the reaction were carefully checked by the signal integration of the target products **3a** and **3a**[D] with 1,3,5-trimethoxybenzene as the internal standard. The k_H/k_D value was calculated according to the molar ratio of **3a** and **3a**[D] generated from the reaction.

Parallel Reaction. The reaction of **2a** or its deuterated form **2a**[D]³² was carried out with **1a** for 1 h under the optimized conditions. The NMR yields from the reaction were carefully checked by the signal integration of the target products **3a** and **3a**'[D] with 1,3,5-trimethoxybenzene as the internal standard, respectively. The k_H/k_D value was calculated according to the yields of **3a** and **3a**'[D] from the separate reactions.

Mechanistic Studies. Synthesis of Complex Pd-1. Under an argon atmosphere, a mixture of alkene **1a** (259 mg, 1 mmol) and Pd(PPh₃)₄ (1156 mg, 1 mmol) in 5 mL of toluene was stirred at 100 °C for 12 h. After being cooled to ambient temperature, the reaction mixture was diluted with CH₂Cl₂ (30 mL), filtered through a short pad of celite, and rinsed with 30 mL of CH₂Cl₂. 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)/EtOAc = 2:1, v/v) to afford **Pd-1** as a yellow solid (244 mg, 27%), m.p.: 204–205 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.36–7.29 (m, 12 H), 7.28–7.20 (m, 6 H), 7.08–7.01 (m, 14 H), 7.05 (t, J = 7.3 Hz, 1 H), 6.94 (t, J = 7.5 Hz, 2 H), 6.42 (t, J = 7.3 Hz, 1 H), 6.33–6.22 (m, 2 H), 6.19 (d, J = 7.2 Hz, 2 H), 5.32 (s, 1 H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 155.1, 152.1, 143.5, 143.4, 138.0, 134.9, 132.47, 131.6, 129.8, 128.9, 127.9, 127.5, 126.7, 125.8, 122.2, and 114.1. ³¹P{¹H} NMR (162 MHz, CDCl₃) δ 20.99. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₅₀H₄₂BrP₂Pd: 889.0974; found: 889.0946.

Stoichiometric Reaction of Complex Pd-1 with 2a in the Presence of dppe Ligand (1.44 equiv). Under an argon atmosphere, a mixture of *N*-tosylhydrazide **2a** (57.6 mg, 0.2 mmol), **Pd-1** (213.6 mg, 0.24 mmol), dppe (159.6 mg, 0.288 mmol), 2-FC₆H₄OH (44.8 mg, 0.4 mmol), and K₂CO₃ (55.3 mg, 0.4 mmol) in 3 mL of toluene was stirred at 100 °C for 12 h. After cooling to ambient temperature, all of the volatiles were evaporated under reduced pressure. The yield of **3a** (45%) was determined by ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard.

Stoichiometric Reaction of Complex Pd-2^{19b} with 2a. Under an argon atmosphere, a mixture of *N*-tosylhydrazide **2a** (57.6 mg, 0.2 mmol), **Pd-2** (213.6 mg, 0.24 mmol), dppe (159.6 mg, 0.288 mmol), 2-FC₆H₄OH (44.8 mg, 0.4 mmol), and K₂CO₃ (55.3 mg, 0.4 mmol) in 3 mL of toluene was stirred at 100 °C for 12 h. After cooling to ambient temperature, all of the volatiles were evaporated under reduced pressure. The yield of **3a** (29%) was determined by ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard.

Synthesis of Complex Pd-2. Following the reported method, complex **Pd-2** was obtained by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)/EtOAc = 2:1, v/v). 583 mg, 79% yield; yellow solid, m.p.: 170–171 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.64–7.47 (m, 12 H), 7.38–7.15 (m, 23 H), 7.08–6.94 (m, 3 H), 6.57 (m, 2 H), 6.39 (t, J = 9.8 Hz, 1 H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 151.8, 144.6, 141.6, 135.0, 130.9, 130.0, 129.6, 128.0, 127.3, 126.9, 126.8, 126.2, 124.9, and 77.3. ³¹P{¹H} NMR (162 MHz, CDCl₃) δ 22.75.

Intermediate Verification Experiments. Under an argon atmosphere, a mixture of alkene **1a** (62.2 mg, 0.24 mmol), *N*-tosylhydrazide **2a** (57.6 mg, 0.2 mmol), **Pd-1** or **Pd-2** (8.9 mg, 0.01 mmol), dppe (6.6 mg, 0.012 mmol), 2-FC₆H₄OH (44.8 mg, 0.4 mmol), and K₂CO₃ (55.3 mg, 0.4 mmol) in 3 mL of toluene was stirred at 100 °C for 12 h. After cooling to ambient temperature, all of the volatiles were evaporated under reduced pressure. The yields of **3a** (61% from **Pd-1** cat. and 57% from **Pd-2** cat.) were determined by ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.joc.2c01019>.

Experimental materials and procedures, NMR spectra of compounds, and X-ray crystallographic analysis for compounds **3u** and **6c** (PDF)

Accession Codes

CCDC 2082643 and 2082669 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

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