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Note

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Palladium-Catalyzed Oxidative Cross-Coupling of Conjugated Enynones with Allylarenes: Synthesis of Furyl-Substituted 1,3-Dienes

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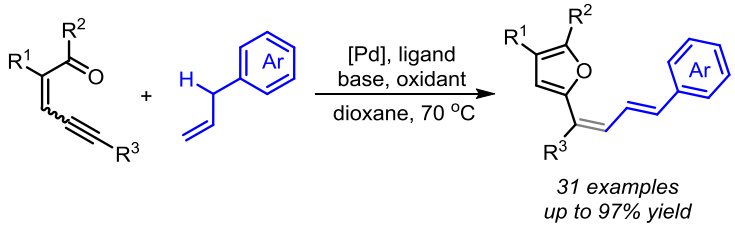


ABSTRACT. A new method for the synthesis of furyl-substituted 1,3-dienes *via* palladium-catalyzed oxidative cross-coupling of conjugated enynones with allylarenes is developed. This reaction shows broad substrate scope and good functional group tolerance. Palladium carbene migratory insertion is proposed as the key step for this transformation with conjugated enynones serving as the carbene precursors.

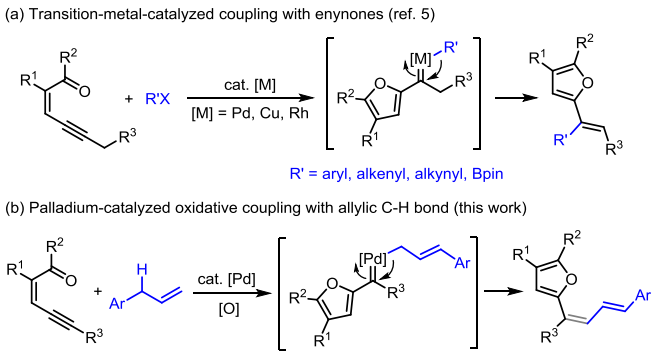
Transition-metal-catalyzed carbene-based cross-coupling reactions have emerged as powerful synthetic methods for the construction of C−C and C−X bonds.[1] In these transformations, diazo compounds or *N*-tosylhydrazones are the most common carbene precursors and carbene migratory insertion is the key step in C−C and C−X bond formation.[2] Recently, non-diazo carbene precursors have also been applied to this type of coupling reactions.[3] For example, Wang *et al.* have previously explored the carbene

coupling with conjugated enynones, which serves as furyl carbene precursors in the classic carbene transformations.[4] The transition-metal-catalyzed coupling of conjugated enynones with a series of coupling partners, such organohalides, boronic acids, terminal alkynes and diboron compounds, have been achieved (Scheme 1a).[5] These reactions provide efficient methods for the synthesis of furan derivatives. Besides, the organometallic intermediates generated *via* C−H activation can also participate in the carbene coupling.[6] For example, in 2017 Chang *et al.* reported the use of conjugated enynones as the carbene precursors in the Rh(III)-catalyzed aromatic C−H functionalization *via* carbene migratory insertion.[7]

On the other hand, palladium-catalyzed allylic C−H activation has become an efficient and atom-economical strategy in organic synthesis.[8] Because of the high reactivity of the allylpalladium intermediate, a series of methodologies have been disclosed for allylic C−H oxygenation,[9] amination,[10] alkylation,[11] borylation,[12] silylation[13] and fluorination.[14] Since the allylpalladium intermediate can also undergo carbene migratory insertion,[15] Gong *et al.* have explored the palladium-catalyzed oxidative cross-coupling of allylic C−H bonds with α-diazo esters.[16] More recently, Jiang *et al.* reported the allylic C−H bond coupling by using sulfoxonium ylides as the carbene precursors.[17]

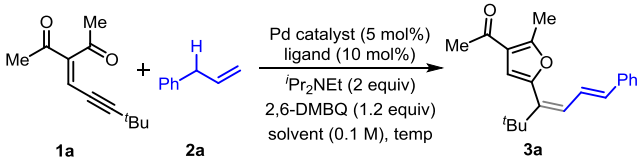
As the continuation of our interest in carbene-based coupling reactions, we envisioned that the allylpalladium intermediate generated *via* allylic C−H activation may also participate in the carbene coupling with conjugated enynones (Scheme 1b). Herein, we report the palladium-catalyzed oxidative cross-coupling of conjugated enynones with allylarenes. This reaction affords a series of furyl-substituted 1,3-dienes with high efficiency under mild conditions.

Scheme 1. Transition-Metal-Catalyzed Carbene Coupling Reaction Using Conjugated Enynones as the Carbene Precursor



At the outset of this investigation, we employed conjugated enynone **1a** and allylbenzene **2a** as the model substrates. The reaction was carried out in dioxane at 50 ^{o}C with $Pd(OAc)_2$ as the catalyst, PPh_3 as the ligand, $^{i}Pr_2NEt$ as the base and 2,6-DMBQ as the oxidant. Gratifyingly, the desired product **3a** could be obtained in 33% yield (Table 1, entry 1). We examined other solvents, however, in these cases the yields were slightly diminished (entries 2−4). Other palladium catalysts were tested (entries 5-8), but we didn't observe any product with these, indicating that the acetate anion and phosphine ligand are crucial for this reaction. Furthermore, we found that the temperature had a large influence on this transformation (entries 9-11), with 70 ^{o}C being the suitable temperature (entry 10). By increasing the amount of **2a** and oxidant, the yield could be further improved to 72% (entry 12). Finally, we added a catalytic amount of diphenylphosphate as additive, which may promote the allylic C−H activation,[18] and the reaction gave the desired product in 80% yield (entry 13).

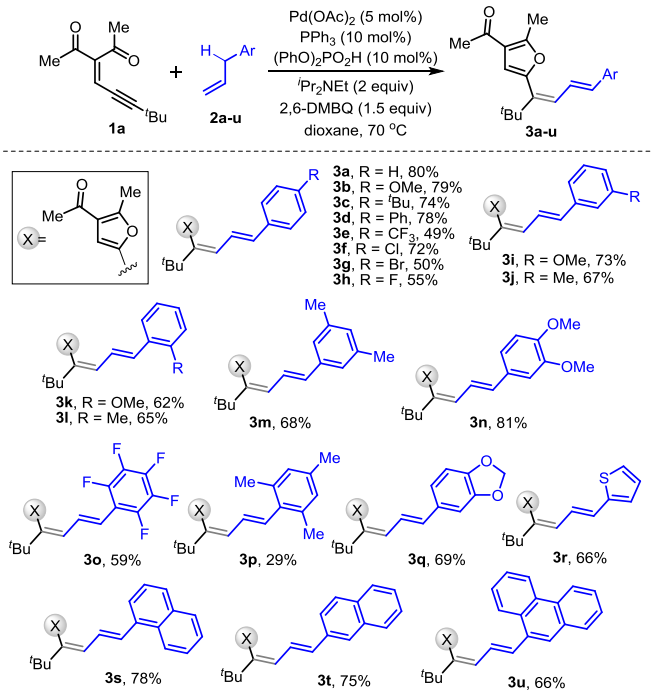
Table 1. Optimization of the Reaction Conditions[a]



entry	Pd catalyst	ligand	solvent	temp (^{o}C)	yield (%)[b]
1	$Pd(OAc)_2$	PPh_3	dioxane	50	33
2	$Pd(OAc)_2$	PPh_3	toluene	50	30
3	$Pd(OAc)_2$	PPh_3	THF	50	16
4	$Pd(OAc)_2$	PPh_3	DCE	50	26
5	$Pd(PPh_3)_4$	--	dioxane	50	0
6	$Pd_2(dba)_3$	PPh_3	dioxane	50	0
7	$Pd(PPh_3)_2Cl_2$	--	dioxane	50	0
8	no catalyst	--	dioxane	50	0
9	$Pd(OAc)_2$	PPh_3	dioxane	60	52
10	$Pd(OAc)_2$	PPh_3	dioxane	70	62
11	$Pd(OAc)_2$	PPh_3	dioxane	80	38
12[c]	$Pd(OAc)_2$	PPh_3	dioxane	70	72
13[c,d]	$Pd(OAc)_2$	PPh_3	dioxane	70	80

[a]Reaction conditions are the following if not otherwise noted: **1a** (0.1 mmol), **2a** (0.1 mmol), Pd catalyst (5 mol%), ligand (10 mol%), $^{i}Pr_2NEt$ (2 equiv), 2,6-DMBQ (1.2 equiv) in 1.0 mL of solvent at the indicated temperature for 16 h. [b]Determined by ^{1}H NMR using dibromomethane as the internal standard. [c]**2a** (1.5 equiv), 2,6-DMBQ (1.5 equiv). [d]$(PhO)_2PO_2H$ (10 mol%) is added.

Scheme 2. Scope of Allylarenes[a]

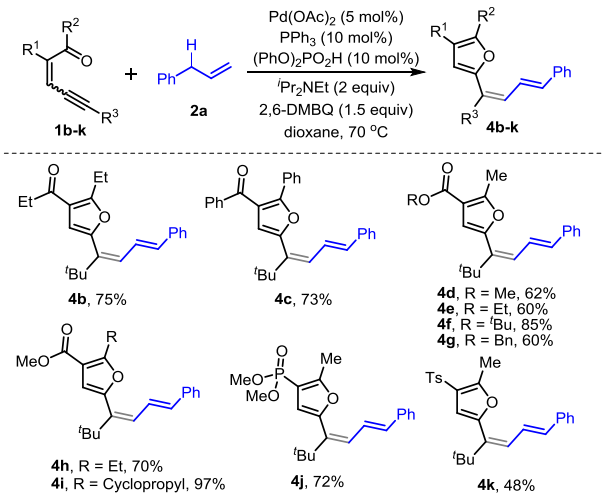


[a]Reaction conditions: **1a** (0.2 mmol), **2a-u** (0.3 mmol), $Pd(OAc)_2$ (5 mol%), PPh_3 (10 mol%), $(PhO)_2PO_2H$ (10 mol%), $^{i}Pr_2NEt$ (0.4 mmol), 2,6-DMBQ (0.3 mmol) in dioxane (2 mL) at 70 ^{o}C for 16 h. All the yields refer to the isolated yields after column chromatography.

With the optimized reaction conditions in hand, we then examined the scope of the reaction. A series of allylarenes **2a-u** with varied electronic properties were first explored (Scheme 2). Electron-rich substituents in the *para*-position of the aromatic ring were tolerated well, affording the products **3b-d** in good yields. The reaction of allylarenes bearing electron-withdrawing groups also proceeded, but the products **3e-h** were formed in slightly diminished yields. It is noteworthy that halide substituents are compatible with this palladium-catalyzed transformation (**3f-h**). The position of the substituents had a marginal influence on this reaction, both *meta*- and *ortho*-substituted allylarenes gave the corresponding products in good yields (**3i-l**). Poly-substituted allylarenes could also participate in this transformation, with most of them delivering the corresponding products **3m-q** in good yields. However, the tri-substituted product **3q** was obtained in low yield due to the large steric congestion. In addition, the

reaction is also applicable to heteroaromatic and polyaromatic substrates, affording the corresponding products **3r-u** in moderate to excellent yields.

Scheme 3. Scope of Conjugated Enynones[a]

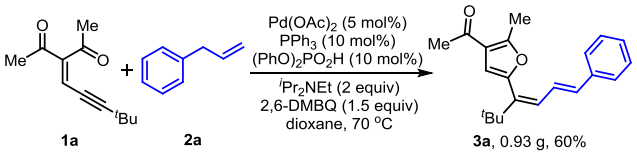


[a]Reaction conditions: **1b-k** (0.2 mmol), **2a** (0.3 mmol), $Pd(OAc)_2$ (5 mol%), PPh_3 (10 mol%), $(PhO)_2PO_2H$ (10 mol%), $^{i}Pr_2NEt$ (0.4 mmol), 2,6-DMBQ (0.3 mmol) in dioxane (2 mL) at 70 °C for 16 h. All the yields refer to the isolated yields after column chromatography

Next, a variety of conjugated enynones **1b-k** were investigated to react with allylbenzene **2a** under the same reaction conditions (Scheme 3). The coupling reaction worked smoothly in all cases, affording the products **4b-k** in moderate to good yields. Some functional groups, such as ester (**4d-i**), phosphate (**4j**) and tosyl (**4k**), were well tolerated. It is notable that conjugated enynones **1d-k** were synthesized as mixtures of *Z*/*E* isomers, but interestingly, these reactions afforded single products through cyclization of the ketone carbonyl oxygen. This indicates that the isomerization of the double bond occurred easily under the reaction conditions.

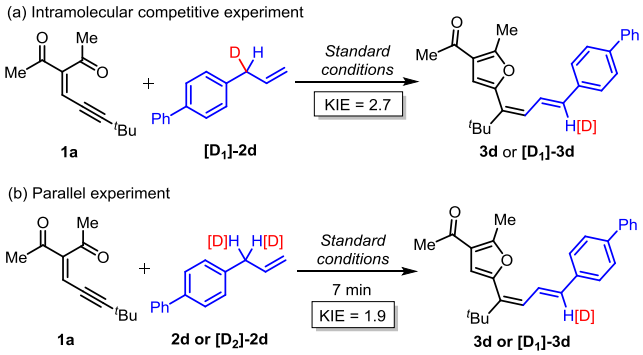
To demonstrate the synthetic utility of this methodology, a gram-scale experiment was performed (Scheme 4). Under the same condition, the furyl-substituted 1,3-diene **3a** was successfully obtained in slightly diminished yield.

Scheme 4. Gram-Scale Synthesis

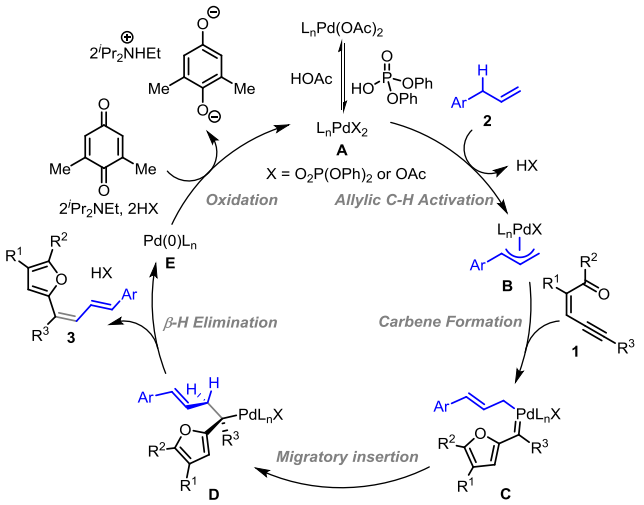


To gain insights into the reaction mechanism, kinetic isotope effect studies were carried out (Scheme 5). The coupling reaction between conjugated enynone **1a** and allylarene **[D_1]-2d** was first carried out and an intramolecular KIE (k_H/k_D = 2.7) was observed (Scheme 5a). Next, two separate reactions of **2d** or **[D_2]-2d** with **1a** were conducted in parallel. The rate constants were measured for these two substrates at low conversion and a moderate KIE valve (k_H/k_D = 1.9) was observed (Scheme 5b). These results indicated that the cleavage of C−H bond is likely involved in the rate-determining step.[19]

Scheme 5. Kinetic Isotope Effect Studies



Scheme 6. Proposed Reaction Mechanism



On the basis of our previous studies[5] and KIE experiments, a plausible mechanism is proposed in Scheme 6. $Pd(OAc)_2$ first undergoes a ligand exchange equilibrium with diphenylphosphate to form catalytically reactive intermediate **A**,[18] which activates an allylic C−H bond of allylarene **2** to generate π-allylpalladium species **B**. Then, the alkyne moiety of conjugated enynone **1** is activated by π-allylpalladium species **B** to form furyl palladium-carbene **C**. Afterwards, carbene migratory insertion occurs to form intermediate **D**, followed by β–H elimination to produce the final product **3** and Pd(0) **E**. Finally, the catalytic active Pd(II) intermediate **A** is regenerated through oxidation to complete the catalytic cycle. The exclusive *Z*-selectivity of the trisubstituted double bond is attributed to distinct steric hindrances of the furyl and *tert*-butyl groups in *cis* β–H elimination step (**D** to **E**).

In summary, we have developed an oxidative cross-coupling reaction of conjugated enynones with allylarenes under palladium catalysis. This approach shows good compatibility of Pd-catalyzed allylic C−H activation with carbene cross-coupling processes. A wide range of substrates were tolerated, and various furyl-substituted 1,3-dienes were obtained in good yields under mild conditions.

EXPERIMENTAL SECTION

General Methods. All the palladium-catalyzed reactions were performed under nitrogen atmosphere in a flame-dried reaction tube. All the solvents were distilled under nitrogen atmosphere prior to use. Toluene, dioxane and THF were dried over Na with benzophenone-ketyl intermediate as indicator. MeCN, MeOH were dried over CaH_2. For chromatography, 200–300 mesh silica gel (Qingdao, China) was employed. ^{1}H NMR spectra were recorded on Bruker ARX 400 (400 MHz); ^{13}C NMR spectra were recorded on Bruker ARX 400 (101 MHz). The data for NMR spectra were reported as follows: chemical shifts (δ) were reported in ppm using tetramethylsilane as internal standard when using $CDCl_3$ as solvent, and coupling constants (J) were in Hertz (Hz). IR spectra were recorded on Nicolet 5MX–S infrared spectrometer and were reported in terms of frequency of absorption (cm^{-1}). HRMS were obtained on Bruker APEX IV FTMS.

Preparation of Conjugated Enynones and Allylarenes. The conjugated enynones were prepared according to our previous reports, and the conjugated enynones **1a**, **1c**, **1e** and **1h** are known.[5] Allylarenes were synthesized according to the literature procedures.[9j]

*4-(4,4-Dimethylpent-2-yn-1-ylidene)heptane-3,5-dione (**1b**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.67 (s, 1H), 2.79 (q, J = 7.2 Hz, 2H), 2.62 (q, J = 7.2 Hz, 2H), 1.26 (s, 9H), 1.15 (t, J = 7.2 Hz, 3H), 1.09 (t, J = 7.2 Hz, 3H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 205.2, 198.3, 149.6, 121.3, 116.1, 75.4, 36.6, 32.5, 30.3, 28.7, 7.9, 7.4; HRMS (ESI, *m*/*z*): calcd for $C_{14}H_{21}O_2$ $[M+H]^+$ 221.1536, found 221.1534; IR (film): 2977, 2938, 2205, 1715, 1698, 1669, 1579, 1460, 1377, 807 cm^{-1}.

*Methyl 2-acetyl-6,6-dimethylhept-2-en-4-ynoate (**1d**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (s, 1H), 6.80 (s, 1H), 3.86 (s, 3H), 3.79 (s, 3H), 2.46 (s, 3H), 2.35 (s, 3H), 1.27 (s, 18H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 199.0, 193.9, 166.0, 164.4, 141.6, 141.3, 125.8, 124.1, 117.4, 116.1, 75.6, 75.2, 52.4, 52.0, 30.4, 30.3, 30.2, 28.8, 28.7, 27.2; HRMS (ESI, *m*/*z*): calcd for $C_{12}H_{17}O_3$ $[M+H]^+$ 209.1172, found 209.1174; IR (film): 2975, 2229, 2200, 1725, 1365, 1248 cm^{-1}.

*tert-Butyl 2-acetyl-6,6-dimethylhept-2-en-4-ynoate (**1f**)*. ^{1}H NMR (400 MHz, $CDCl_3$) Major isomer: δ 6.69 (s, overlapping, 1H), 2.31 (s, 3H), 1.57 (s, 9H), 1.28 (s, 9H); Minor isomer: δ 6.69 (s, overlapping, 1H), 2.42 (s, 3H), 1.49 (s, 9H), 1.26 (s, 9H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 199.4, 193.8, 165.0, 162.9, 143.7, 142.4, 123.2, 122.4, 115.5, 114.6, 82.4, 82.2, 75.3, 75.1, 30.3, 30.20, 30.16, 28.6, 28.5, 28.0, 27.9, 27.0; HRMS (ESI, *m*/*z*): calcd for $C_{15}H_{23}O_3$ $[M+H]^+$ 251.1642, found 251.1640; IR (film): 2977, 2224, 1718, 1586, 1372, 1250, 1162, 846 cm^{-1}.

*Benzyl 2-acetyl-6,6-dimethylhept-2-en-4-ynoate (**1g**)*. ^{1}H NMR (400 MHz, $CDCl_3$) Major isomer: δ 7.45–7.27 (m, overlapping, 5H), 6.80 (s, 1H), 5.30 (s, 2H), 2.30 (s, 3H), 1.18 (s, 9H); Minor isomer: δ 7.45–7.27 (m, overlapping, 5H), 6.84 (s, 1H), 5.21 (s, 2H), 2.44 (s, 3H), 1.25 (s, 9H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.5, 193.7, 165.2, 163.6, 141.5, 141.0, 135.1, 128.41, 128.38, 128.2, 128.10, 128.07, 127.9, 125.5, 124.2, 117.3, 116.1, 75.4, 75.2, 66.88, 66.85, 30.2, 30.0, 28.54, 28.52, 27.0; HRMS (ESI, *m*/*z*): calcd for $C_{18}H_{21}O_3$ $[M+H]^+$ 285.1485, found 285.1487; IR (film): 2970, 2224, 1723, 1598, 1250, 1196, 753, 702 cm^{-1}.

*Methyl 2-(cyclopropanecarbonyl)-6,6-dimethylhept-2-en-4-ynoate (**1i**)*. ^{1}H NMR (400 MHz, $CDCl_3$) Major isomer: δ 6.86 (s, 1H), 3.79 (s, 3H), 2.33–2.22 (m, overlapping, 1H), 1.26 (s, 9H), 1.25–1.21 (m, 2H), 1.06–1.00 (m, 2H); Minor isomer: δ 6.83 (s, 1H), 3.87 (s, 3H), 2.33–2.22 (m, overlapping, 1H), 1.28 (s, 9H), 1.17–1.12 (m, 2H), 1.00–0.95 (m, 2H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 201.8, 196.3, 166.1, 164.4, 142.0, 141.6, 124.7, 123.9, 116.5, 115.2, 75.6, 75.2, 52.3, 52.0, 30.3, 30.2, 28.9, 28.6, 21.9, 18.2, 12.5, 12.2; HRMS (ESI, *m*/*z*): calcd for $C_{14}H_{19}O_3$ $[M+H]^+$ 235.1329, found 235.1328; IR (film): 2977, 2222, 1725, 1598, 1389, 1248, 1004 cm^{-1}.

*Dimethyl (7,7-dimethyl-2-oxooct-3-en-5-yn-3-yl)phosphonate (**1j**)*. ^{1}H NMR (400 MHz, $CDCl_3$) Major isomer: δ 6.97 (d, J = 22.0 Hz, 1H), 3.78 (d, J = 11.6 Hz, 6H), 2.53 (s, 3H), 1.29 (s, 9H); Minor isomer: δ 7.14 (d, J = 42.0 Hz, 1H), 3.83 (d, J = 11.6 Hz, 6H), 2.45 (s, 3H), 1.31 (s, 9H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.1 (d, J = 7.9 Hz), 196.3 (d, J = 14.0 Hz), 139.1 (d, J = 177.6 Hz), 137.4 (d, J = 178.2 Hz), 134.3 (d, J = 2.1 Hz), 131.0 (d, J = 11.2 Hz), 119.7, 117.3, 76.2 (d, J = 10.1 Hz), 75.9 (d, J =

30.2 Hz), 52.9 (d, J = 5.9 Hz), 52.6 (d, J = 6.0 Hz), 30.5 (d, J = 4.1 Hz), 30.0, 29.9, 28.8, 28.6, 28.4; HRMS (ESI, *m*/*z*): calcd for $C_{12}H_{20}O_4P$ $[M+H]^+$ 259.1094, found 259.1098; IR (film): 2972, 2219, 1703, 1574, 1365, 1265, 1060, 1033, 831, 780 cm^{-1}.

*(E)-7,7-Dimethyl-3-tosyloct-3-en-5-yn-2-one (**1k**).* ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.0 Hz, 2H), 7.41 (s, 1H), 7.32 (d, J = 8.0 Hz, 2H), 2.52 (s, 3H), 2.42 (s, 3H), 1.29 (s, 9H); ^{13}C $\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 194.0, 148.6, 144.7, 137.0, 129.6, 128.7, 127.6, 121.7, 74.9, 31.2, 30.0, 29.1, 21.6; HRMS (ESI, *m*/*z*): calcd for $C_{17}H_{21}O_3S$ $[M+H]^+$ 305.1206, found 305.1212; IR (film): 2975, 2224, 2188, 1681, 1586, 1321, 1158, 1089, 712, 680 cm^{-1}.

General Procedure for Palladium-Catalyzed Oxidative Cross-Coupling of Conjugated Enynones with Allylarenes. $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 5 mol%), PPh_3 (5.3 mg, 0.02 mmol, 10 mol%), $(PhO)_2PO_2H$ (5.0 mg, 0.02 mmol, 10 mol%) and 2,6-dimethyl-1,4-benzoquinone (40.8 mg, 0.3 mmol, 1.5 equiv) were added to a flame-dried 10 mL Schlenk reaction tube. The reaction tube was degassed three times with nitrogen, then dry dioxane (2 mL, 0.1 M) was added using a syringe. $^iPr_2NEt$ (51.6 mg, 0.4 mmol, 2 equiv), allylarene **2** (0.3 mmol, 1.5 equiv) and conjugated enynone **1** (0.2 mmol) were added by syringe successively. The reaction tube was stirred at 70 ^oC in the oil bath for 16 h, then cooled to room temperature. The mixture was filtered through a short plug of silica gel and washed with Et_2O as the eluent. Solvent was then removed in vacuo to leave a crude mixture, which was purified by silica gel column chromatography to afford pure product **3**.

*1-(5-((3Z,5E)-2,2-Dimethyl-6-phenylhexa-3,5-dien-3-yl)-2-methylfuran-3-yl)ethan-1-one (**3a**).* Yield: 80% (48.2 mg); yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35–7.25 (m, 4H), 7.23–7.17 (m, 1H), 6.79 (dd, J = 15.6, 10.6 Hz, 1H), 6.65 (d, J = 15.6 Hz, 1H), 6.50 (d, J = 10.4 Hz, 1H), 6.44 (s, 1H), 2.64 (s, 3H), 2.44 (s, 3H), 1.18 (s, 9H); ^{13}C $\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 194.3, 157.6, 150.2, 141.2, 137.3, 133.6, 129.4, 128.6, 127.6, 126.6, 126.4, 122.0, 110.8, 36.3, 29.7, 29.2, 14.6; HRMS (ESI, *m*/*z*): calcd for $C_{21}H_{25}O_2$ $[M+H]^+$ 309.1849, found 309.1850; IR (film): 2975, 1679, 1589, 1559, 1367, 1228, 972, 948, 751, 695 cm^{-1}.

*1-(5-((3Z,5E)-6-(4-Methoxyphenyl)-2,2-dimethylhexa-3,5-dien-3-yl)-2-methylfuran-3-yl)ethan-1-one (**3b**)*. Yield: 79% (54.0 mg); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27–7.23 (m, 2H), 6.86–6.80 (m, 2H), 6.65 (dd, J = 15.4 Hz, 9.4 Hz, 1H), 6.59 (d, J = 15.2 Hz, 1H), 6.48 (d, J = 9.2 Hz, 1H), 6.43 (s, 1H), 3.79 (s, 3H), 2.64 (s, 3H), 2.44 (s, 3H), 1.17 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.4, 159.3, 157.5, 150.4, 140.1, 133.3, 130.1, 129.6, 127.7, 124.6, 122.0, 114.1, 110.6, 55.3, 36.2, 29.8, 29.2, 14.6; HRMS (ESI, *m*/*z*): calcd for $C_{22}H_{27}O_3$ $[M+H]^+$ 339.1955, found 339.1961; IR (film): 2961, 1674, 1606, 1507, 1251, 1173, 1037, 972, 824 cm^{-1}.

*1-(5-((3Z,5E)-6-(4-(tert-Butyl)phenyl)-2,2-dimethylhexa-3,5-dien-3-yl)-2-methylfuran-3-yl)ethan-1-one (**3c**)*. Yield: 74% (53.7 mg); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H), 6.75 (dd, J = 15.6, 10.4 Hz, 1H), 6.63 (d, J = 15.6 Hz, 1H), 6.49 (d, J = 10.4 Hz, 1H), 6.43 (s, 1H), 2.64 (s, 3H), 2.44 (s, 3H), 1.30 (s, 9H), 1.18 (s, 9H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 194.3, 157.5, 150.7, 150.4, 140.6, 134.6, 133.5, 129.5, 126.2, 126.0, 125.5, 122.0, 110.8, 36.2, 34.6, 31.2, 29.7, 29.2, 14.5; HRMS (ESI, *m*/*z*): calcd for $C_{25}H_{33}O_2$ $[M+H]^+$ 365.2475, found 365.2483; IR (film): 2958, 1677, 1581, 1365, 1229, 969, 944, 818, 734 cm^{-1}.

*1-(5-((3Z,5E)-6-([1,1'-Biphenyl]-4-yl)-2,2-dimethylhexa-3,5-dien-3-yl)-2-methylfuran-3-yl)ethan-1-one (**3d**)*. Yield: 78% (60.2 mg); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 7.2 Hz, 2H), 7.53 (d, J = 8.0 Hz, 2H), 7.45–7.36 (m, 4H), 7.35–7.30 (m, 1H), 6.84 (dd, J = 15.6, 10.8 Hz, 1H), 6.68 (d, J = 15.6 Hz, 1H), 6.52 (d, J = 10.8 Hz, 1H), 6.46 (s, 1H), 2.65 (s, 3H), 2.45 (s, 3H), 1.19 (s, 9H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 194.3, 157.6, 150.3, 141.3, 140.6, 140.3, 136.4, 133.2, 129.4, 128.8, 127.31, 127.26, 126.9, 126.8, 126.7, 122.1, 110.9, 36.3, 29.7, 29.2, 14.6; HRMS (ESI, *m*/*z*): calcd for $C_{27}H_{29}O_2$ $[M+H]^+$ 385.2162, found 385.2163; IR (film): 2955, 1677, 1585, 1486, 1229, 972, 765, 734, 700 cm^{-1}.

*1-(5-((3Z,5E)-2,2-Dimethyl-6-(4-(trifluoromethyl)phenyl)hexa-3,5-dien-3-yl)-2-methylfuran-3-yl)ethan-1-one (**3e**)*. Yield: 49% (36.6 mg); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 6.88 (dd, J = 15.6, 10.8 Hz, 1H), 6.66 (d, J = 15.6 Hz, 1H), 6.51 (d, J

= 10.8 Hz, 1H), 6.46 (s, 1H), 2.65 (s, 3H), 2.45 (s, 3H), 1.20 (s, 9H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 194.2, 157.8, 149.9, 143.1, 140.8, 131.9, 129.1 (q, J = 32.3 Hz), 129.0, 128.8, 126.5, 125.5 (q, J = 4.0 Hz), 124.1 (q, J = 272.7 Hz), 122.1, 111.1, 36.4, 29.6, 29.2, 14.6; HRMS (ESI, *m*/*z*): calcd for $C_{22}H_{24}F_3O_2$ $[M+H]^+$ 377.1723, found 377.1720; IR (film): 2962, 1684, 1328, 1170, 1126, 1067, 970, 953, 819 cm^{-1}.

1-(5-((3Z,5E)-6-(4-Chlorophenyl)-2,2-dimethylhexa-3,5-dien-3-yl)-2-methylfuran-3-yl)ethan-1-one ***(3f)***. Yield: 72% (49.3 mg); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.20 (m, 4H), 6.75 (dd, J = 15.6 Hz, 10.4 Hz, 1H), 6.59 (d, J = 15.6 Hz, 1H), 6.48 (d, J = 10.8 Hz, 1H), 6.44 (s, 1H), 2.64 (s, 3H), 2.44 (s, 3H), 1.18 (s, 9H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 194.2, 157.6, 150.1, 141.9, 135.8, 133.1, 132.2, 129.1, 128.8, 127.6, 127.1, 122.1, 110.9, 36.3, 29.7, 29.2, 14.6; HRMS (ESI, *m*/*z*): calcd for $C_{21}H_{24}ClO_2$ $[M+H]^+$ 343.1459, found 343.1458; IR (film): 2952, 1677, 1581, 1489, 1405, 1229, 1090, 969, 808 cm^{-1}.

1-(5-((3Z,5E)-6-(4-Bromophenyl)-2,2-dimethylhexa-3,5-dien-3-yl)-2-methylfuran-3-yl)ethan-1-one ***(3g)***. Yield: 50% (38.9 mg); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 8.8 Hz, 2H), 6.76 (dd, J = 15.4, 10.6 Hz, 1H), 6.57 (d, J = 15.6 Hz, 1H), 6.48 (d, J = 10.4 Hz, 1H), 6.44 (s, 1H), 2.64 (s, 3H), 2.44 (s, 3H), 1.18 (s, 9H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 194.3, 157.7, 150.1, 142.0, 136.3, 132.3, 131.7, 129.1, 127.9, 127.3, 122.1, 121.3, 110.9, 36.4, 29.7, 29.2, 14.6; HRMS (ESI, *m*/*z*): calcd for $C_{21}H_{24}BrO_2$ $[M+H]^+$ 387.0954, found 387.0957; IR (film): 2955, 1677, 1588, 1486, 1229, 1071, 969, 805, 651 cm^{-1}.

1-(5-((3Z,5E)-6-(4-Fluorophenyl)-2,2-dimethylhexa-3,5-dien-3-yl)-2-methylfuran-3-yl)ethan-1-one ***(3h)***. Yield: 55% (36.1 mg); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.24 (m, 2H), 6.97 (t, J = 8.6 Hz, 2H), 6.69 (dd, J = 15.4, 10.2 Hz, 1H), 6.60 (d, J = 15.6 Hz, 1H), 6.48 (d, J = 10.4 Hz, 1H), 6.44 (s, 1H), 2.64 (s, 3H), 2.44 (s, 3H), 1.18 (s, 9H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 194.3, 162.3 (d, J = 248.4 Hz), 157.6, 150.2, 141.3, 133.5 (d, J = 3.6 Hz), 132.4, 129.2, 127.9 (d, J = 8.0 Hz), 126.3 (d, J =

2.4 Hz), 122.1, 115.6 (d, J = 21.6 Hz), 110.8, 36.3, 29.7, 29.2, 14.6; HRMS (ESI, m/z): calcd for $C_{21}H_{24}FO_2$ $[M+H]^+$ 327.1755, found 327.1756; IR (film): 2961, 1680, 1507, 1229, 1155, 969, 814 cm^{-1}.

1-(5-((3Z,5E)-6-(3-Methoxyphenyl)-2,2-dimethylhexa-3,5-dien-3-yl)-2-methylfuran-3-yl)ethan-1-one ***(3i)***. Yield: 73% (49.2 mg); yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, J = 8.0 Hz, 1H), 6.92 (d, J = 7.6 Hz, 1H), 6.84 (t, J = 1.8 Hz, 1H), 6.80–6.73 (m, 2H), 6.62 (d, J = 15.2 Hz, 1H), 6.49 (d, J = 10.4 Hz, 1H), 6.44 (s, 1H), 3.79 (s, 3H), 2.64 (s, 3H), 2.44 (s, 3H), 1.18 (s, 9H); ^{13}C {^1H} NMR (101 MHz, $CDCl_3$) δ 194.3, 159.8, 157.6, 150.2, 141.5, 138.8, 133.5, 129.6, 129.3, 127.0, 122.0, 119.1, 112.9, 112.2, 110.9, 55.2, 36.3, 29.7, 29.2, 14.6; HRMS (ESI, m/z): calcd for $C_{22}H_{27}O_3$ $[M+H]^+$ 339.1955, found 339.1953; IR (film): 2964, 2918, 1674, 1585, 1232, 1155, 910, 734, 651 cm^{-1}.

1-(5-((3Z,5E)-2,2-Dimethyl-6-(m-tolyl)hexa-3,5-dien-3-yl)-2-methylfuran-3-yl)ethan-1-one ***(3j)***. Yield: 67% (43.7 mg); yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.18 (t, J = 7.4 Hz, 1H), 7.14−7.10 (m, 2H), 7.02 (d, J = 7.2 Hz, 1H), 6.77 (dd, J = 15.4, 10.6 Hz, 1H), 6.61 (d, J = 15.6 Hz, 1H), 6.49 (d, J = 10.4 Hz, 1H), 6.44 (s, 1H), 2.64 (s, 3H), 2.44 (s, 3H), 2.32 (s, 3H), 1.18 (s, 9H); ^{13}C {^1H} NMR (101 MHz, $CDCl_3$) δ 194.4, 157.6, 150.3, 141.0, 138.1, 137.3, 133.8, 129.4, 128.5, 128.4, 127.3, 126.4, 123.5, 122.0, 110.8, 36.3, 29.7, 29.2, 21.4, 14.6; HRMS (ESI, m/z): calcd for $C_{22}H_{27}O_2$ $[M+H]^+$ 323.2006, found 323.1998; IR (film): 2961, 1677, 1581, 1393, 1229, 969, 951, 777 cm^{-1}.

1-(5-((3Z,5E)-6-(2-Methoxyphenyl)-2,2-dimethylhexa-3,5-dien-3-yl)-2-methylfuran-3-yl)ethan-1-one ***(3k)***. Yield: 62% (42.2 mg); yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36–7.30 (m, 1H), 7.22-7.16 (m, 1H), 6.99 (d, J = 15.6 Hz, 1H), 6.92–6.77 (m, 3H), 6.54 (d, J = 10.8 Hz, 1H), 6.44 (s, 1H), 3.84 (s, 3H), 2.63 (s, 3H), 2.43 (s, 3H), 1.18 (s, 9H); ^{13}C {^1H} NMR (101 MHz, $CDCl_3$) δ 194.4, 157.5, 156.7, 150.5, 140.5, 130.2, 128.6, 128.4, 127.4, 126.6, 126.4, 122.0, 120.7, 110.8, 110.7, 55.4, 36.2, 29.8, 29.2, 14.6; HRMS (ESI, m/z): calcd for $C_{22}H_{27}O_3$ $[M+H]^+$ 339.1955, found 339.1952; IR (film): 2952, 1677, 1581, 1486, 1241, 1031, 947, 749, 654 cm^{-1}.

1-(5-((3Z,5E)-2,2-Dimethyl-6-(o-tolyl)hexa-3,5-dien-3-yl)-2-methylfuran-3-yl)ethan-1-one ***(3l)***. Yield: 65% (41.9 mg); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.31 (m, 1H), 7.14-7.10 (m, 3H), 6.87 (d, J = 15.6 Hz, 1H), 6.69 (dd, J = 15.2 Hz, 10.4 Hz, 1H), 6.54 (d, J = 10.8 Hz, 1H), 6.44 (s, 1H), 2.63 (s, 3H), 2.43 (s, 3H), 2.36 (s, 3H), 1.19 (s, 9H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 194.3, 157.6, 150.2, 141.1, 136.2, 135.6, 131.3, 130.4, 129.7, 127.8, 127.5, 126.1, 125.3, 122.0, 110.8, 36.3, 29.7, 29.2, 19.8, 14.6; HRMS (ESI, *m*/*z*): calcd for $C_{22}H_{27}O_2$ $[M+H]^+$ 323.2006, found 323.2002; IR (film): 2958, 1677, 1585, 1232, 969, 753, 654 cm^{-1}.

*1-(5-((3Z,5E)-6-(3,5-Dimethylphenyl)-2,2-dimethylhexa-3,5-dien-3-yl)-2-methylfuran-3-yl)ethan-1-one (****3m****)*. Yield: 68% (46.3 mg); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 (s, 2H), 6.86 (s, 1H), 6.75 (dd, J = 15.6 Hz, 10.4 Hz, 1H), 6.58 (d, J = 15.6 Hz, 1H), 6.48 (d, J = 10.8 Hz, 1H), 6.44 (s, 1H), 2.64 (s, 3H), 2.44 (s, 3H), 1.18 (s, 9H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 194.5, 157.6, 150.3, 140.7, 138.0, 137.2, 134.0, 129.5, 129.4, 126.2, 124.3, 122.0, 110.8, 36.3, 29.7, 29.2, 21.2, 14.6; HRMS (ESI, *m*/*z*): calcd for $C_{23}H_{29}O_2$ $[M+H]^+$ 337.2162, found 337.2161; IR (film): 2952, 1680, 1585, 1390, 1229, 969, 827, 651 cm^{-1}.

*1-(5-((3Z,5E)-6-(3,4-Dimethoxyphenyl)-2,2-dimethylhexa-3,5-dien-3-yl)-2-methylfuran-3-yl)ethan-1-one (****3n****)*. Yield: 81% (59.5 mg); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92–6.88 (m, 1H), 6.85-6.78 (m, 2H), 6.68 (dd, J = 15.4, 10.2 Hz, 1H), 6.60 (d, J = 15.2 Hz, 1H), 6.48 (d, J = 10.0 Hz, 1H), 6.45 (s, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 2.64 (s, 3H), 2.44 (s, 3H), 1.18 (s, 9H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 194.3, 157.5, 150.4, 149.0, 148.9, 140.2, 133.9, 130.5, 129.4, 125.0, 122.0, 119.5, 111.2, 110.8, 109.2, 55.9, 55.8, 36.2, 29.8, 29.2, 14.6; HRMS (ESI, *m*/*z*): calcd for $C_{23}H_{29}O_4$ $[M+H]^+$ 369.2060, found 369.2061; IR (film): 2967, 1677, 1510, 1266, 1139, 1025, 966 cm^{-1}.

*1-(5-((3Z,5E)-2,2-Dimethyl-6-(perfluorophenyl)hexa-3,5-dien-3-yl)-2-methylfuran-3-yl)ethan-1-one (****3o****)*. Yield: 59% (47.2 mg); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (dd, J = 16.0 Hz, 10.8 Hz, 1H), 6.57–6.41 (m, 3H), 2.64 (s, 3H), 2.45 (s, 3H), 1.21 (s, 9H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 194.1, 157.2, 149.6, 144.8, 144.5 (d, J = 249.6 Hz), 138.9 (m), 136.4 (m), 135.4, 128.7, 122.0, 116.7 (d,

J = 3.5 Hz), 112.6 (m), 111.6, 36.5, 29.6, 29.2, 14.5; HRMS (ESI, *m*/*z*): calcd for $C_{21}H_{20}F_5O_2$ $[M+H]^+$ 399.1378, found 399.1373; IR (film): 2965, 1681, 1523, 1496, 1232, 1002, 960 cm^{-1}.

*1-(5-((3Z,5E)-6-Mesityl-2,2-dimethylhexa-3,5-dien-3-yl)-2-methylfuran-3-yl)ethan-1-one (**3p**)*. Yield: 29% (20.3 mg); yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 6.84 (m, 2H), 6.65 (d, *J* = 16.0 Hz, 1H), 6.50 (d, *J* = 10.4 Hz, 1H), 6.39 (s, 1H), 6.26 (dd, *J* = 15.8 Hz, 10.6 Hz, 1H), 2.58 (s, 3H), 2.40 (s, 3H), 2.26 (s, 6H), 2.25 (s, 3H), 1.19 (s, 9H); ^{13}C {^1H} NMR (101 MHz, $CDCl_3$) δ 194.2, 157.4, 150.4, 140.4, 136.4, 135.9, 133.7, 132.0, 131.4, 129.7, 128.9, 121.8, 110.4, 36.1, 29.7, 29.1, 21.1, 20.9, 14.5; HRMS (ESI, *m*/*z*): calcd for $C_{24}H_{31}O_2$ $[M+H]^+$ 351.2319, found 351.2319; IR (film): 2970, 1686, 1586, 1233, 980, 953, 858, 663 cm^{-1}.

*1-(5-((3Z,5E)-6-(Benzo[d][1,3]dioxol-5-yl)-2,2-dimethylhexa-3,5-dien-3-yl)-2-methylfuran-3-yl)ethan-1-one (**3q**)*. Yield: 69% (48.5 mg); yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 6.83 (s, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 6.60 (dd, *J* = 15.4 Hz, 9.4 Hz, 1H), 6.55 (d, *J* = 15.2 Hz, 1H), 6.46 (d, *J* = 9.6 Hz, 1H), 6.43 (s, 1H), 5.94 (s, 2H), 2.64 (s, 3H), 2.45 (s, 3H), 1.17 (s, 9H); ^{13}C {^1H} NMR (101 MHz, $CDCl_3$) δ 194.3, 157.5, 150.3, 148.0, 147.3, 140.5, 133.3, 131.8, 129.4, 125.0, 122.0, 121.4, 110.7, 108.4, 105.5, 101.1, 36.2, 29.7, 29.2, 14.6; HRMS (ESI, *m*/*z*): calcd for $C_{22}H_{25}O_4$ $[M+H]^+$ 353.1747, found 353.1745; IR (film): 2965, 1679, 1506, 1491, 1447, 1260, 1231, 1041, 972, 953, 804, 731 cm^{-1}.

*1-(5-((3Z,5E)-2,2-Dimethyl-6-(thiophen-2-yl)hexa-3,5-dien-3-yl)-2-methylfuran-3-yl)ethan-1-one (**3r**)*. Yield: 66% (41.6 mg); yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.17–7.10 (m, 1H), 6.97-6.91 (m, 2H), 6.78 (d, *J* = 15.2 Hz, 1H), 6.63 (dd, *J* = 15.4 Hz, 10.6 Hz, 1H), 6.46 – 6.39 (m, 2H), 2.64 (s, 3H), 2.44 (s, 3H), 1.18 (s, 9H); ^{13}C {^1H} NMR (101 MHz, $CDCl_3$) δ 194.3, 157.6, 150.1, 142.9, 141.0, 128.6, 127.6, 126.6, 126.3, 125.8, 124.5, 122.0, 111.1, 36.3, 29.8, 29.2, 14.5; HRMS (ESI, *m*/*z*): calcd for $C_{19}H_{23}O_2S$ $[M+H]^+$ 315.1413, found 315.1413; IR (film): 2961, 1680, 1581, 1396, 1232, 963, 829, 703 cm^{-1}.

1-(5-((3Z,5E)-2,2-Dimethyl-6-(naphthalen-1-yl)hexa-3,5-dien-3-yl)-2-methylfuran-3-yl)ethan-1-one ***(3s)***. Yield: 78% (55.6 mg); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 8.0 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.53–7.39 (m, 5H), 6.85 (dd, J = 14.8 Hz, 10.8 Hz, 1H), 6.66 (d, J = 10.8 Hz, 1H), 6.47 (s, 1H), 2.64 (s, 3H), 2.42 (s, 3H), 1.22 (s, 9H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 194.3, 157.6, 150.2, 141.6, 134.7, 133.7, 131.1, 130.4, 129.7, 129.4, 128.6, 128,0, 126.0, 125.8, 125.6, 123.6, 123.5, 122.1, 110.9, 36.3, 29.7, 29.2, 14.6; HRMS (ESI, *m*/*z*): calcd for $C_{25}H_{27}O_2$ $[M+H]^+$ 359.2006, found 359.2009; IR (film): 2961, 1677, 1585, 1390, 1226, 951, 780 cm^{-1}.

1-(5-((3Z,5E)-2,2-Dimethyl-6-(naphthalen-2-yl)hexa-3,5-dien-3-yl)-2-methylfuran-3-yl)ethan-1-one ***(3t)***. Yield: 75% (54.1 mg); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79–7.66 (m, 4H), 7.53–7.37 (m, 3H), 6.92 (dd, J = 15.6 Hz, 10.4 Hz, 1H), 6.81 (d, J = 15.6 Hz, 1H), 6.56 (d, J = 10.4 Hz, 1H), 6.48 (s, 1H), 2.66 (s, 3H), 2.46 (s, 3H), 1.20 (s, 9H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 194.4, 157.7, 150.3, 141.4, 134.9, 133.8, 133.6, 133.0, 129.4, 128.2, 127.9, 127.7, 127.0, 126.5, 126.3, 125.9, 123.4, 122.1, 110.9, 36.3, 29.8, 29.2, 14.6; HRMS (ESI, *m*/*z*): calcd for $C_{25}H_{27}O_2$ $[M+H]^+$ 359.2006, found 359.2007; IR (film): 2961, 1677, 1581, 1387, 1229, 972, 811, 743, 651 cm^{-1}.

1-(5-((3Z,5E)-2,2-Dimethyl-6-(phenanthren-9-yl)hexa-3,5-dien-3-yl)-2-methylfuran-3-yl)ethan-1-one ***(3u)***. Yield: 66% (54.0 mg); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, J = 7.6 Hz, 1H), 8.63 (d, J = 8.4 Hz, 1H), 8.20 (d, J = 7.6 Hz, 1H), 7.84 (d, J = 7.6 Hz, 1H), 7.74 (s, 1H), 7.69–7.54 (m, 4H), 7.43 (d, J = 15.2 Hz, 1H), 6.92 (dd, J = 15.2 Hz, 10.8 Hz, 1H) 6.69 (d, J = 10.8 Hz, 1H), 6.50 (s, 1H), 2.65 (s, 3H), 2.43 (s, 3H), 1.24 (s, 9H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 194.3, 157.7, 150.2, 141.7, 133.6, 131.6, 131.0, 130.5, 130.4, 130.1, 129.9, 129.5, 128.7, 126.8, 126.60, 126.57, 126.5, 124.51, 124.48, 123.1, 122.5, 122.1, 111.0, 36.4, 29.8, 29.2, 14.6; HRMS (ESI, *m*/*z*): calcd for $C_{29}H_{29}O_2$ $[M+H]^+$ 409.2162, found 409.2160; IR (film): 2958, 1684, 1584, 1399, 1231, 972, 948, 751, 731 cm^{-1}.

1-(5-((3Z,5E)-2,2-Dimethyl-6-phenylhexa-3,5-dien-3-yl)-2-ethylfuran-3-yl)propan-1-one ***(4b)***. Yield: 75% (50.3 mg); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.25 (m, 4H), 7.23–7.17 (m, 1H), 6.84 (dd, J = 15.6 Hz, 10.4 Hz, 1H), 6.65 (d, J = 15.6 Hz, 1H), 6.50 (d, J = 10.8 Hz, 1H), 6.45 (s, 1H), 3.08

(q, *J* = 7.6 Hz, 2H), 2.78 (q, *J* = 7.2 Hz, 2H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.23–1.13 (m, 12H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 197.3, 162.4, 150.2, 141.4, 137.4, 133.5, 128.9, 128.6, 127.5, 126.7, 126.4, 120.4, 110.5, 36.3, 34.5, 29.7, 21.7, 12.0, 7.9; HRMS (ESI, *m*/*z*): calcd for $C_{23}H_{29}O_2$ $[M+H]^+$ 337.2162, found 337.2162; IR (film): 2975, 1681, 1589, 1557, 1467, 1211, 970, 929, 751, 695, 663 cm^{-1}.

(5-((3Z,5E)-2,2-Dimethyl-6-phenylhexa-3,5-dien-3-yl)-2-phenylfuran-3-yl)(phenyl)methanone ***(4c)***. Yield: 73% (63.1 mg); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.6 Hz, 2H), 7.82 (d, *J* = 6.8 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.43–7.28 (m, 9H), 7.24–7.19 (m, 1H), 7.07 (dd, *J* = 15.4, 10.6 Hz, 1H), 6.69 (d, *J* = 15.2 Hz, 1H), 6.59–6.51 (m, 2H), 1.29 (s, 9H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 191.9, 154.8, 151.3, 140.7, 138.3, 137.3, 134.0, 132.9, 129.8, 129.7, 129.3, 128.9, 128.6, 128.39, 128.35, 127.6, 127.2, 126.6, 126.5, 121.4, 114.9, 36.5, 29.9; HRMS (ESI, m/z): calcd for $C_{31}H_{29}O_2$ $[M+H]^+$ 433.2162, found 433.2160; IR (film): 2967, 1664, 1598, 1486, 1450, 1243, 975, 894, 731, 692 cm^{-1}.

Methyl 5-((3Z,5E)-2,2-dimethyl-6-phenylhexa-3,5-dien-3-yl)-2-methylfuran-3-carboxylate ***(4d)***. Yield: 62% (40.4 mg); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.24 (m, 4H), 7.22–7.17 (m, 1H), 6.79 (dd, *J* = 15.6, 10.8 Hz, 1H), 6.63 (d, *J* = 15.6 Hz, 1H), 6.52-6.44 (m, 2H), 3.84 (s, 3H), 2.63 (s, 3H), 1.17 (s, 9H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.7, 158.4, 150.3, 141.3, 137.4, 133.6, 129.3, 128.5, 127.5, 126.7, 126.5, 113.8, 111.0, 51.3, 36.3, 29.7, 13.9; HRMS (ESI, *m*/*z*): calcd for $C_{21}H_{25}O_3$ $[M+H]^+$ 325.1798, found 325.1800; IR (film): 2953, 1720, 1611, 1445, 1228, 1089, 975, 780, 753, 656 cm^{-1}.

Ethyl 5-((3Z,5E)-2,2-dimethyl-6-phenylhexa-3,5-dien-3-yl)-2-methylfuran-3-carboxylate ***(4e)***. Yield: 60% (40.6 mg); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.23 (m, 4H), 7.22-7.16 (m, 1H), 6.80 (dd, *J* = 15.6 Hz, 10.4 Hz, 1H), 6.63 (d, *J* = 15.6 Hz, 1H), 6.52–6.43 (m, 2H), 4.31 (q, *J* = 7.2 Hz, 2H), 2.63 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H), 1.18 (s, 9H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.3, 158.2, 150.2, 141.4, 137.4, 133.5 129.3, 128.5, 127.5, 126.8, 126.5, 114.1, 111.0, 60.1, 36.3, 29.7, 14.4, 13.4; HRMS (ESI, *m*/*z*): calcd for $C_{22}H_{27}O_3$ $[M+H]^+$ 339.1955, found 339.1959; IR (film): 2962, 1720, 1603, 1231, 1084, 970, 782, 753, 692 cm^{-1}.

tert-Butyl 5-((3Z,5E)-2,2-dimethyl-6-phenylhexa-3,5-dien-3-yl)-2-methylfuran-3-carboxylate (***4f***). Yield: 85% (62.6 mg); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.24 (m, 4H), 7.22–7.16 (m, 1H), 6.80 (dd, J = 15.4 Hz, 10.6 Hz, 1H), 6.63 (d, J = 15.6 Hz, 1H), 6.47 (d, J = 10.4 Hz, 1H), 6.43 (s, 1H), 2.59 (s, 3H), 1.58 (s, 9H), 1.17 (s, 9H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 163.7, 157.5, 149.9, 141.5, 137.4, 133.4, 129.1, 128.5, 127.5, 126.9, 126.5, 115.6, 111.3, 80.5, 36.3, 29.7, 28.3, 13.4; HRMS (ESI, *m*/*z*): calcd for $C_{24}H_{31}O_3$ $[M+H]^+$ 367.2268, found 367.2269; IR (film): 2965, 1713, 1367, 1233, 1167, 1087, 972, 780, 751, 692 cm^{-1}.

Benzyl 5-((3Z,5E)-2,2-dimethyl-6-phenylhexa-3,5-dien-3-yl)-2-methylfuran-3-carboxylate (***4g***). Yield: 60% (47.5 mg); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.12 (m, 10H), 6.79 (dd, J = 15.4 Hz, 10.6 Hz, 1H), 6.63 (d, J = 15.6 Hz, 1H), 6.51 (s, 1H), 6.48 (d, J = 10.8 Hz, 1H), 5.31 (s, 2H), 2.62 (s, 3H), 1.17 (s, 9H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.0, 158.6, 150.4, 141.2, 137.4, 136.2, 133.6, 129.3, 128.6, 128.5, 128.2, 128.1, 127.5, 126.7, 126.5, 113.8, 111.0, 65.9, 36.3, 29.7, 14.1; HRMS (ESI, *m*/*z*): calcd for $C_{27}H_{29}O_3$ $[M+H]^+$ 401.2111, found 401.2108; IR (film): 2967, 1720, 1231, 1080, 975, 787, 753, 695 cm^{-1}.

Methyl 5-((3Z,5E)-2,2-dimethyl-6-phenylhexa-3,5-dien-3-yl)-2-ethylfuran-3-carboxylate (***4h***). Yield: 70% (46.9 mg); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.24 (m, 4H), 7.23–7.17 (m, 1H), 6.83 (dd, J = 15.6 Hz, 10.8 Hz, 1H), 6.64 (d, J = 15.6 Hz, 1H), 6.52–6.43 (m, 2H), 3.84 (s, 3H), 3.07 (q, J = 7.6 Hz, 2H), 1.29 (t, J = 7.6 Hz, 3H), 1.18 (s, 9H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.6, 163.3, 150.3, 141.3, 137.4, 133.5, 129.0, 128.5, 127.5, 126.8, 126.4, 112.8, 111.0, 51.3, 36.3, 29.7, 21.2, 12.3; HRMS (ESI, *m*/*z*): calcd for $C_{22}H_{27}O_3$ $[M+H]^+$ 339.1955, found 339.1947; IR (film): 2953, 1720, 1603, 1442, 1243, 1092, 1043, 970, 751, 692 cm^{-1}.

Methyl 2-cyclopropyl-5-((3Z,5E)-2,2-dimethyl-6-phenylhexa-3,5-dien-3-yl)furan-3-carboxylate (***4i***). Yield: 97% (68.0 mg); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.26 (m, 4H), 7.23–7.16 (m, 1H), 6.85 (dd, J = 15.6 Hz, 10.8 Hz, 1H), 6.62 (d, J = 15.6 Hz, 1H), 6.47 (s, 1H), 6.44 (d, J = 10.8 Hz, 1H), 3.85 (s, 3H), 2.88–2.78 (m, 1H), 1.14 (s, 9H), 1.09–1.03 (m, 4H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ

164.9, 162.6, 149.1, 140.9, 137.4, 133.5, 128.8, 128.6, 127.5, 126.7, 126.4, 113.3, 111.5, 51.3, 36.3, 29.7, 9.2, 8.9; HRMS (ESI, *m*/*z*): calcd for $C_{23}H_{27}O_3$ $[M+H]^+$ 351.1955, found 351.1956; IR (film): 2958, 1720, 1601, 1447, 1233, 1072, 968, 814, 751, 692 cm^{-1}.

*Dimethyl (5-((3Z,5E)-2,2-dimethyl-6-phenylhexa-3,5-dien-3-yl)-2-methylfuran-3-yl)phosphonate (**4j**)*. Yield: 72% (54.1 mg); yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35–7.23 (m, 4H), 7.22-7.15 (m, 1H), 6.78 (dd, *J* = 15.4 Hz, 10.6 Hz, 1H), 6.63 (d, *J* = 15.6 Hz, 1H), 6.49 (d, *J* = 10.8 Hz, 1H), 6.28 (d, *J* = 2.8 Hz, 1H), 3.78 (d, *J* = 11.2 Hz, 6H), 2.58 (s, 3H), 1.18 (s, 9H); ^{13}C {^1H} NMR (101 MHz, $CDCl_3$) δ 159.7 (d, *J* = 26.9 Hz), 151.4 (d, *J* = 16.2 Hz), 141.0, 137.3, 133.6, 129.3, 128.5, 127.5, 126.6, 126.3, 112.4 (d, *J* = 11.7 Hz), 106.0 (d, *J* = 216.8 Hz), 52.3 (d, *J* = 5.7 Hz), 36.2, 29.7, 13.6; HRMS (ESI, *m*/*z*): calcd for $C_{21}H_{28}O_4P$ $[M+H]^+$ 375.1720, found 375.1724; IR (film): 2960, 1257, 1028, 829, 780, 751, 663 cm^{-1}.

*5-((3Z,5E)-2,2-Dimethyl-6-phenylhexa-3,5-dien-3-yl)-2-methyl-3-tosylfuran (**4k**)*. Yield: 48% (39.6 mg); yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.29-7.18 (m, 5H), 6.70–6.57 (m, 2H), 6.47 (d, *J* = 8.4 Hz, 1H), 6.40 (s, 1H), 2.62 (s, 3H), 2.45 (s, 3H), 1.14 (s, 9H); ^{13}C {^1H} NMR (101 MHz, $CDCl_3$) δ 155.3, 151.3, 143.9, 140.4, 139.9, 137.1, 134.0, 129.9, 129.8, 128.5, 127.7, 126.8, 126.4, 126.1, 123.3, 110.0, 36.2, 29.7, 21.6, 13.1; HRMS (ESI, *m*/*z*): calcd for $C_{26}H_{29}O_3S$ $[M+H]^+$ 421.1832, found 421.1830; IR (film): 2955, 1321, 1160, 970, 753, 680 cm^{-1}.

ASSOCIATED CONTENT

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Notes

The authors declare no competing financial interest.

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Supporting Information

Copies of ^{1}H and ^{13}C spectra for all products. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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