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Copper-Catalyzed Intramolecular Annulation of Conjugated Enynones to Substituted 1*H*-Indenes and Mechanistic Studies

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KEYWORDS: enynone, metal carbene, 1H-indene, vinylic C(sp^2)-H bond insertion, DFT calculations

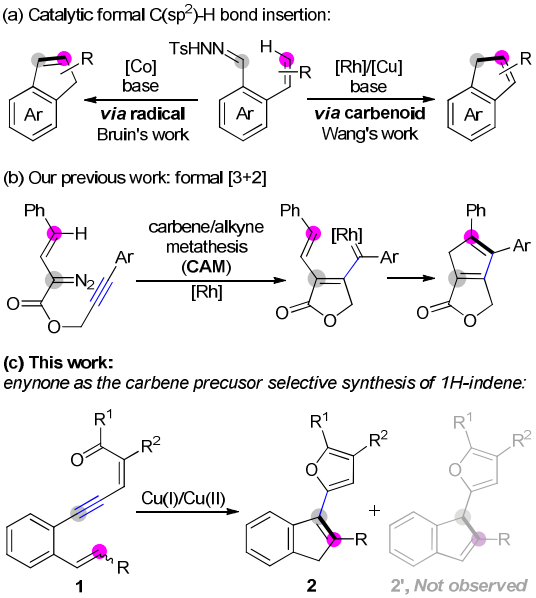
ABSTRACT: Herein, a copper-catalyzed intramolecular cascade reaction of conjugated enynones to deliver substituted 1*H*-indenes is reported. The inexpensive and lower toxic copper salt served as the only catalyst in the transformation, affording the 3-(2-furyl)-substituted 1*H*-indenes in good to excellent yields under mild reaction conditions with broad functional group tolerations and making it highly appealing for synthetic organic chemistry. Notably, detailed DFT calculations have been carried out to elucidate that the reaction undergoes a copper-mediated *5-exo-dig* cyclization of enynones to afford copper-(2-furyl)-carbene intermediate, followed by dienecarbene cyclization (one step but involving 6π cyclization of Cu-carbene and reductive elimination) and 1,5-hydrogen shift to provide the 1*H*-indenes.

INTRODUCTION

Metal carbene, which is commonly generated from the diazo compound, is one of the versatile intermediates in organic synthesis, and plays a critical role in the construction of complex molecules due to its versatile reactivity.[1] Particularly, metal carbene reactions show advantages in the direct C-C bond formation through various types of transformations, such as C-H insertion,[2] cross-coupling reaction,[3] cyclization reaction,[4] and others.[5] Among these advances, the vinylic C(sp^2)-H bond insertion to form C(sp^2)-C(sp^3) bonds remains much less developed, possibly because of the competing cyclopropanation reaction with electron-rich alkenes.[6] Recently, two formal vinylic C(sp^2)-H insertion reactions to form substituted 1*H*-indenes with *N*-tosylhydrazones were reported by Bas de Bruin's group and Wang's group *via* Co(III)-carbene radical and Rh(II)-carbene intermediates, respectively (Scheme 1a).[7] Meanwhile, our group have also disclosed a carbene/alkyne metathesis cascade reaction terminating in analogous vinyl carbene transfer procedure, which commonly considered as [3 + 2] cycloaddition (Scheme 1b).[8]

On the other hand, transition-metal-catalyzed cyclization reactions of conjugated enynals or enynones through *5-exo-dig* nucleophilic attack have become an efficient way to generate the furyl metal-carbene intermediate.[9] Many efforts have been endeavored to the development of effective catalytic transformations with this novel carbene precursor, including Cr,[10] Cu,[11] Au,[12] Rh,[13] Zn,[14] Pd,[15] and organo-catalysis.[16] Recently, aromatic C(sp^2)-H bond insertion and C(sp^3)-H bond insertion reactions with *in situ* generated Zn(II) (2-furyl) carbene were reported by Vicent, López and coworkers.[14a] Moreover, the enantioselective intramolecular C(sp^3)-H bond insertion

Scheme 1. Catalytic Carbon-Carbon Bond Formation of Metal Carbene



reaction to form new C-C bond catalyzed by chiral Rh(II) complexes has been reported by Zhu and coworkers.[13e] In addition,these conjugated enynones could also serve as safe and effective alternatives in Pd-catalyzed carbene coupling reactions according to Wang's work, providing a practical synthetic method for C-C and C=C bond formation.[15a,b] Encouraged by these works and as a continuation of our interest in the

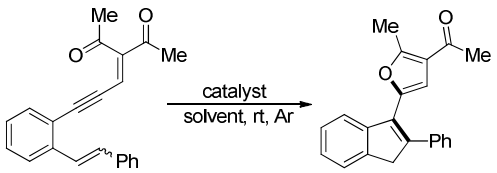
carbene cascade transformations,[15c,17] we were intrigued by the possibility that the conjugated enynone can act as carbene precursor for the formal vinylic C(sp^2)-H bond insertion reaction, thus realizing new C-C bond formation.

Considering that indenes are one of the most important structures pervasively existing in many natural products,[18] bioactive compounds[19] and metallocene complexes,[20] we decided to conduct the above envision for the synthesis of indenes by using **1** (Scheme 1c). During our experimental investigation, Wang group reported similar vinylic C(sp^2)-H bond insertion reaction with hydrazone as carbene precursor.[7b] We found that **1** gave a formal coupling product **2** instead of C(sp^2)-H insertion product **2'**, which was the expected product based on Wang's work. We hypothesized that **2'** was first generated and then converted to **2** *via* 1,5-hydrogen shift (this hypothesis will be studied in the present work). Here we disclose our results of converting **1** to **2** with inexpensive and low toxic copper salt as catalyst under mild conditions, which serves as an efficient method to access 1*H*-indenes. Meanwhile, we carried out DFT study of the mechanism of our present reaction. These computational studies will not only help to understand the reaction mechanisms of the present reaction, but also provide some insights and guidances for future design of vinylic C-H bond insertion reactions.

RESULTS AND DISCUSSION

We began our study by using the styrene tethered enynone **1a** as the model substrate ($Z : E \approx 1 : 1$). The 1*H*-indene **2a** was obtained in 95% isolated yield with $Rh_2(OAc)_4$ as the catalyst in 1,2-dichloroethane (DCE) at room temperature (Table 1, entry 1). In addition to $Rh_2(OAc)_4$, other catalysts, such as $Cu(OTf)_2$, $AuCl_3$, $(\eta^3\text{-}C_3H_5)_2Pd_2Cl_2$, CuI, CuCl, $CuCl_2$, and $CuSO_4{\cdot}5H_2O$, could also promote this annulation (entries 2-8). However, $ZnCl_2$, as the effective catalyst in other transformations with conjugated enynones, failed to catalyze this reaction (entry 9).[14] Notably, CuI or $CuSO_4{\cdot}5H_2O$ as a cheap and low toxic catalyst had an obvious advance (entries 5 and 8). To our delight, carrying out the reaction at higher temperature led to 100% conversion with 88%-95% isolated yields in the presence of corresponding copper salt (entries 10-12). Further investigation of solvents showed that > 90% yields were obtained when the reaction was carried out in DCE, chloroform, or ethyl acetate (entries 12-14), thus demonstrating extraordinary robustness of this process. The molecular structure of **2a** was inferred from NMR spectra analysis of its analogue **2b** (see the Supporting Information).[13b]

Table 1. Condition Optimization[a]



1a, ($Z : E$ = 1 : 1) **2a**

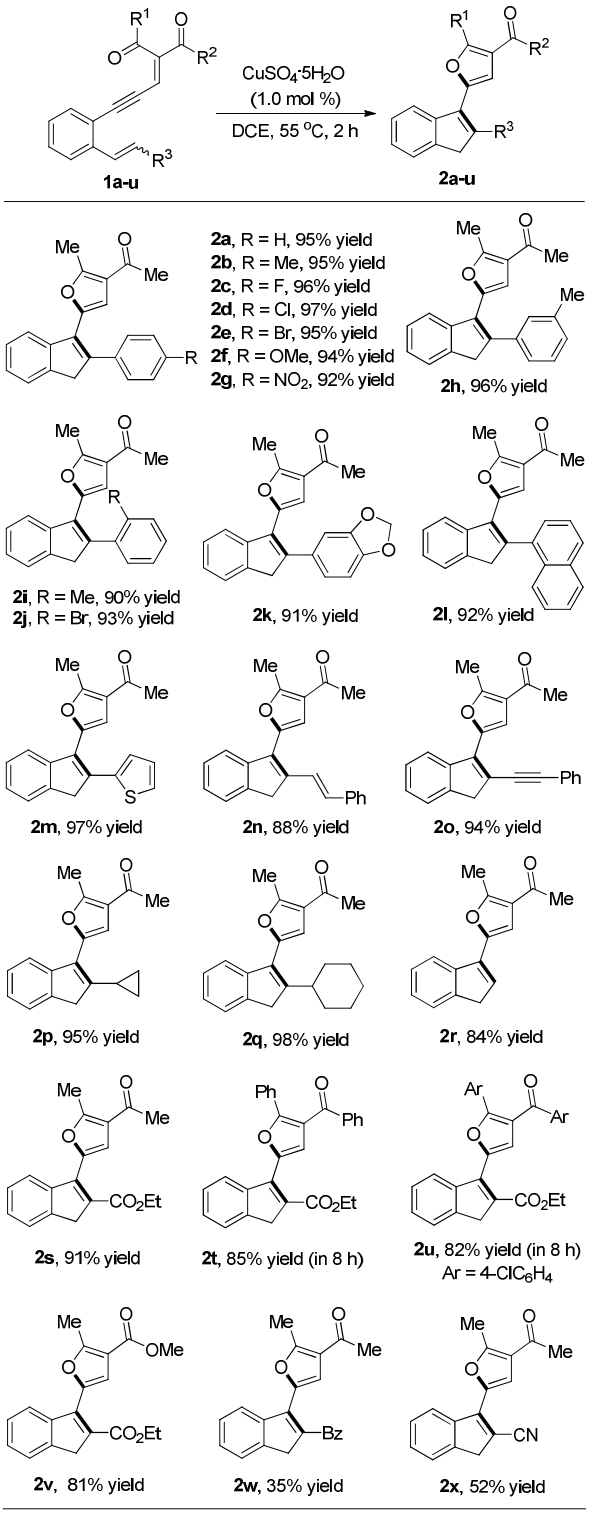
entry	solvent	catalyst	time	% yield (% conv.)[b]
1	DCE	$Rh_2(OAc)_4$	20 min	95 (100)
2	DCE	$Cu(OTf)_2$	20 min	90 (100)
3	DCE	$AuCl_3$	20 min	75 (100)
4	DCE	$(\eta^3\text{-}C_3H_5)_2Pd_2Cl_2$	20 min	65 (100)
5	DCE	CuI	8 h	92 (100)
6	DCE	CuCl	16 h	56 (60)
7	DCE	$CuCl_2$	16 h	42 (50)
8	DCE	$CuSO_4{\cdot}5H_2O$	16 h	32 (35)
9	DCE	$ZnCl_2$	16 h	<5 (100)
10[c]	DCE	CuCl	2 h	90 (100)
11[c]	DCE	$CuCl_2$	2 h	88 (100)
12[c]	DCE	$CuSO_4{\cdot}5H_2O$	2 h	95 (100)
13[c]	$CHCl_3$	$CuSO_4{\cdot}5H_2O$	2 h	92 (100)
14[c]	EA	$CuSO_4{\cdot}5H_2O$	2 h	92 (100)
15[c]	PhMe	$CuSO_4{\cdot}5H_2O$	2 h	50 (55)
16[c]	EtOH	$CuSO_4{\cdot}5H_2O$	2 h	85 (100)

[a]Reaction conditions: the reaction was carried out on a 0.2 mmol scale, **1a** (62.8 mg, 0.2 mmol), and catalyst (1.0 mol %) at room temperature in corresponding solvent (2.0 mL) under argon atmosphere. [b]Isolated yields. [c]Reaction was performed at 55 °C. EA = ethyl acetate.

SCOPE OF THE REACTION

With the optimized reaction conditions in hand, various enynones **1** were prepared to test the generality of this cyclization (Scheme 2). Firstly, we investigated the influence of the aromatic substituent attached the vinylic double bond (R^3 = Ar). The substrates with electron-withdrawing or electron-donating groups in the *para*-position on the aromatic ring all gave the corresponding products in excellent yields (92-97%, Scheme 2, **2b**-**2g**). Pleasingly, the sterically encumbered substrates had only a slight effect on this transformation, and comparably high yields were obtained for *ortho*, *meta*-substituted and disubstituted enynones (Scheme 2, **2h**-**2k**). It was noted that the substrates bearing 1-naphthyl and 2-thienyl substituent produced the corresponding products **2l** and **2m** in 92% and 97% yields, respectively. In addition to the aryl group, R^3 could also be alkenyl (**1n**), alkynyl (**1o**), and alkyl (**1p** and **1q**) groups, and the corresponding products were isolated in 88-98% yields. In all these above cases (**1a**-**1q**), mixed material with both *Z*- and *E*-isomers was used, and both of these isomers were converted to the same 1*H*-indene product **2**. Notably, the terminal alkene tethered enynone **1r** also smoothly transformed to the product **2r** in 84% yield. Next, when changing the R^3 to electron-withdrawing ester group, the cinnamate-tethered enynone **1s**, which was prepared and isolated as a single *E*-configuration, performed well to offer the target product **2s** in 91% yield under these conditions. Two other benzoyl and *para*-chlorobenzoyl derivatives were also suitable for this transformation, although longer reaction time was needed (**2t** and **2u**). It was worth mentioning that the enynone **1v**, which was prepared and isolated as a mixture of *Z*- and *E*-isomers, only the *E*-isomer worked in this reaction and delivered the corresponding product in 81% yield based

Scheme 2. Substrate Scope[a]

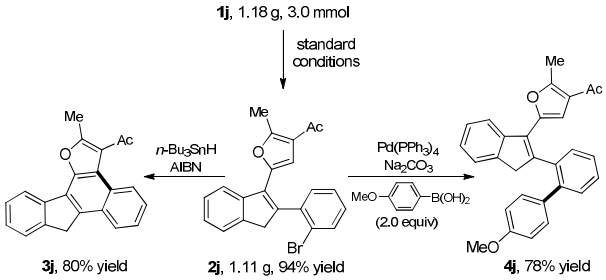


[a]Reaction conditions: **1** (0.20 mmol) and $CuSO_4·5H_2O$ (0.5 mg, 1.0 mol%) in DCE (2.0 mL) at 55 °C under argon atmosphere for 2 h, and the yields are given in isolated yields.

on the used amount of the *E*- isomer, and with *Z*-**1v** recovered in 98% yield.[11d] Moreover, the α,β-unsaturated ketone and nitrile substrates **1w** and **1x** worked less effective, producing the corresponding 1*H*-indenes in moderate yields (**2w** and **2x**), which may due to the lower nucleophilicity of these substrates.

Furthermore, this cascade cyclization reaction could be easily scaled up to gram scale, which afforded 1.11 g of product **2j** in 94 % yield in the presence of 1.0 mol % copper catalyst (Scheme 3). Further transformations were carried out to demonstrate the utility of these products, including radical annulation and Suzuki coupling reaction of the bromo-derivative **2j** to give **3j** and **4j** in 80% and 78% yields, respectively.

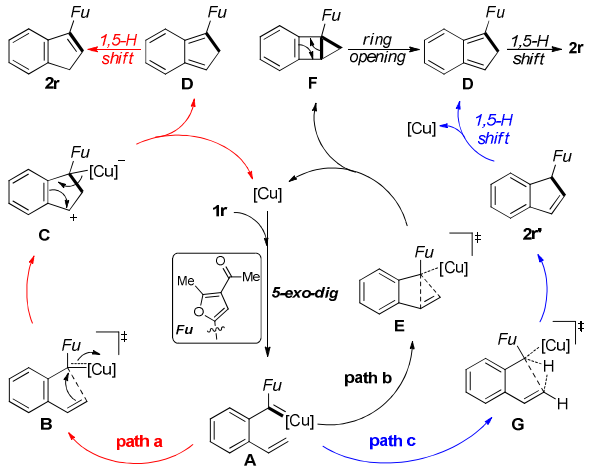
Scheme 3. Scale Up and Derivatinzations



MECHANISTIC STUDY

Scheme 4 depicts the proposed pathways of the present reaction. Firstly, in the presence of copper catalyst, enynone **1r** undergoes a *5-exo-dig* cyclization to form Cu-carbene intermediate **A** *via* nucleophilic attack of carbonyl oxygen to internal carbon of alkyne. From Cu-carbene **A**, three possible pathways are possible for the formation of product **2r**. In *path a*, intramolecular nucleophile attack of the vinylic double bond to the electron deficient carbene-carbon center of Cu-carbene **A** generates intermediate **C**. Then intermediate **C** releases copper catalyst to give isoindene intermediate **D**, which then gives product **2r** through a 1,5-hydrogen shift process.[7b] In *path b*, Cu-carbene **A** undergoes a cyclopropanation reaction

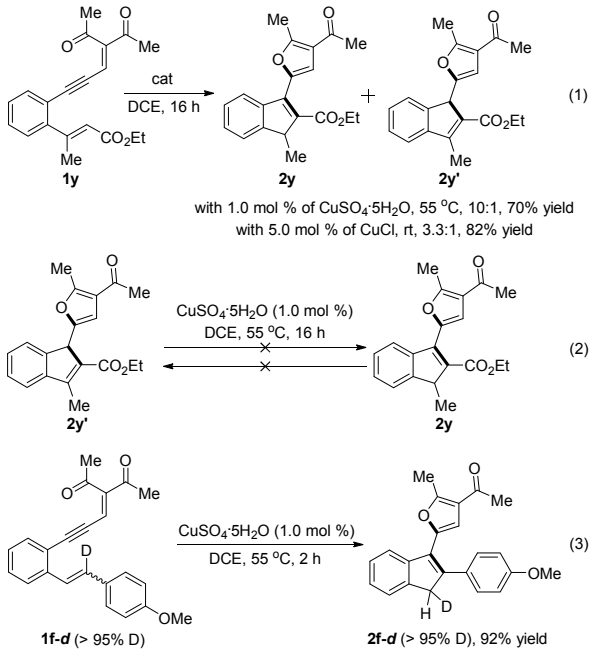
Scheme 4. Proposed Reaction Pathways



to give cyclopropane intermediate **F**, which produces isoindene intermediate **D** *via* ring expansion. Intermediate **D** then undergoes a 1,5-hydrogen shift to afford product **2r**. In *path c*, a direct intramolecular C(sp^2)-H bond insertion of Cu carbene **A** occurs *via* transition state **G**. The corresponding insertion product **2r'** is then converted to the target molecular **2r** through two successive 1,5-hydrogen shifts.

To get more mechanistic information, several control experiments were carried out (Scheme 5). Firstly, the reaction of trisubstituted olefin **1y** generated a mixture of **2y** and **2y'**, which were separated by column chromatography (eq 1). Further study showed that no interconversion of **2y'** and **2y** takes place under the standard reaction conditions (eq 2). These results ruled out the possibility of the proposed concerted C(sp^2)-H bond insertion path way (*path c*). In addition, we have also performed deuterium labelling experiments, finding that this reaction has an intramolecular hydrogen transfer process instead of adopting the deprotonation/protonation process mentioned in previous report (eq 3).[7b]

Scheme 5. Mechanistic Experiments



We then performed DFT calculations at the B3LYP/6-311+G(d,p)(SDD)//B3LYP/6-31G(d)(SDD) level to differentiate the above mentioned three pathways (same conclusions were found by using other DFT functionals such as B3LYP-D3,[21] see the Supporting Information). Experimentally both Cu(I) and Cu(II) salts, such as CuI, CuCl, $CuCl_2$ and $CuSO_4{\cdot}5H_2O$, can catalyze the target reaction with high efficiency. However, we found that calculations using $CuSO_4{\cdot}5H_2O$ were difficult to converge. Therefore, we concentrated our calculations using both $CuCl_2$ and CuCl. We present the potential energy surface for CuCl in the main text of this paper, while the potential energy surface for $CuCl_2$ is given in the Supporting Information. For simplification of the calculations, the terminal alkene substituted enynone **1r** was chosen as the model substrate. We discuss here all these pathways using the computed Gibbs free energy in solution, and the computed data in the gas phase were also given for reference in the potential energy surfaces.

As shown in Figure 1, our calculations indicate that the initial step of the coordination of CuCl with **1r** to form chelation complex **INT1** is a facile process and is exergonic by 7.0. kcal/mol. From copper complex **INT1**, the intramolecular ligand exchange to isomer **INT2** is endergonic by 4.0 kcal/mol. Then intermediate **INT2** undergoes another facile process, the *5-exo-dig* cyclization *via* **TS2-3** with an activation free energy of 10.1 kcal/mol, which prefers a *trans*-addition of the carbonyl group and copper to the alkyne, giving the Cu-carbene intermediate **INT3**.[22] In Cu-carbene intermediate **INT3**, the copper-carbon bond has a length of 1.89 Å, which is slightly longer than the value obtained from experimental data for other Cu-carbene complexes (1.87-1.89 Å).[23]

For the followed transformation, firstly, we considered the intramolecular nucleophile attack of the vinylic double bond from Cu carbene intermediate **INT3** in *path a*. The required free energy *via* transition state **TS3-4** in converting **INT3** to **INT4** is 9.9 kcal/mol, and this step is exergonic by 14.6 kcal/mol. This step can be understood by analogy to diene-carbene cyclization, which involves 6π cyclization and reductive elimination process (Figure 2). We computed a simple model system of dienyl carbene **INT6**, finding that it undergoes a facile 6-π cyclization to give intermediate **INT7** *via* **TS6-7** with the activation free energy of 10.3 kcal/mol. Then the $\Delta G^{\ddagger}$ for reductive elimination to give the cyclopentadiene-CuCl complex **INT8** needs only 0.7 kcal/mol. However, in the present system for **INT3**, which is similar to **INT6** and more stable due to the additional aromatic ring, the IRC calculations showed that it does not go through cyclization process but directly gives the isoindene **INT4** through reductive elimination transition state (see the Supporting Information). Actually in **INT3**, the distance between vinyl carbon and copper is 2.84 Å and in the **TS3-4**, this distance is reduced to 2.42 Å and the forming C-C bond is 2.06 Å. We reasoned that, for **INT3**, the 6-π cyclization transition state, its intermediate, and the followed reductive elimination transition state, all are close in energy and only the reductive elimination transition state **TS3-4** can be located computationally**.**

Formation of isoindene intermediate **INT4** is irreversible because the followed step of 1,5-*H* shift is easier (see later discussion) than the backward reaction from **INT4** to **INT3**. Isoindene intermediate **INT4** can be converted to the more favorable intermediate **INT5** through an intramolecular ligand exchange, which is exergonic by 7.3 kcal/mol.[24] Then an intramolecular 1,5-hydrogen shift converts intermediate **INT5** to the indene-coordinated copper intermediate **2r-CuCl** irreversibly *via* a three-membered ring transition state **TS5-2r** with an energy barrier of 16.9 kcal/mol. An alternative pathway of 1,5-hydrogen shift *via* transition state **TS5-2r'** has also been considered. This step giving the isomer **2r'-CuCl** has an activation free energy of 20.4 kcal/mol, which is 3.5 kcal/mol higher than its competing process *via* **TS5-2r**. Therefore, 3-(2-furyl)-1*H*-indenes will be dominantly generated, with a predicted ratio of **2r** : **2r'** by 180 : 1 at 55 ℃. This agrees with

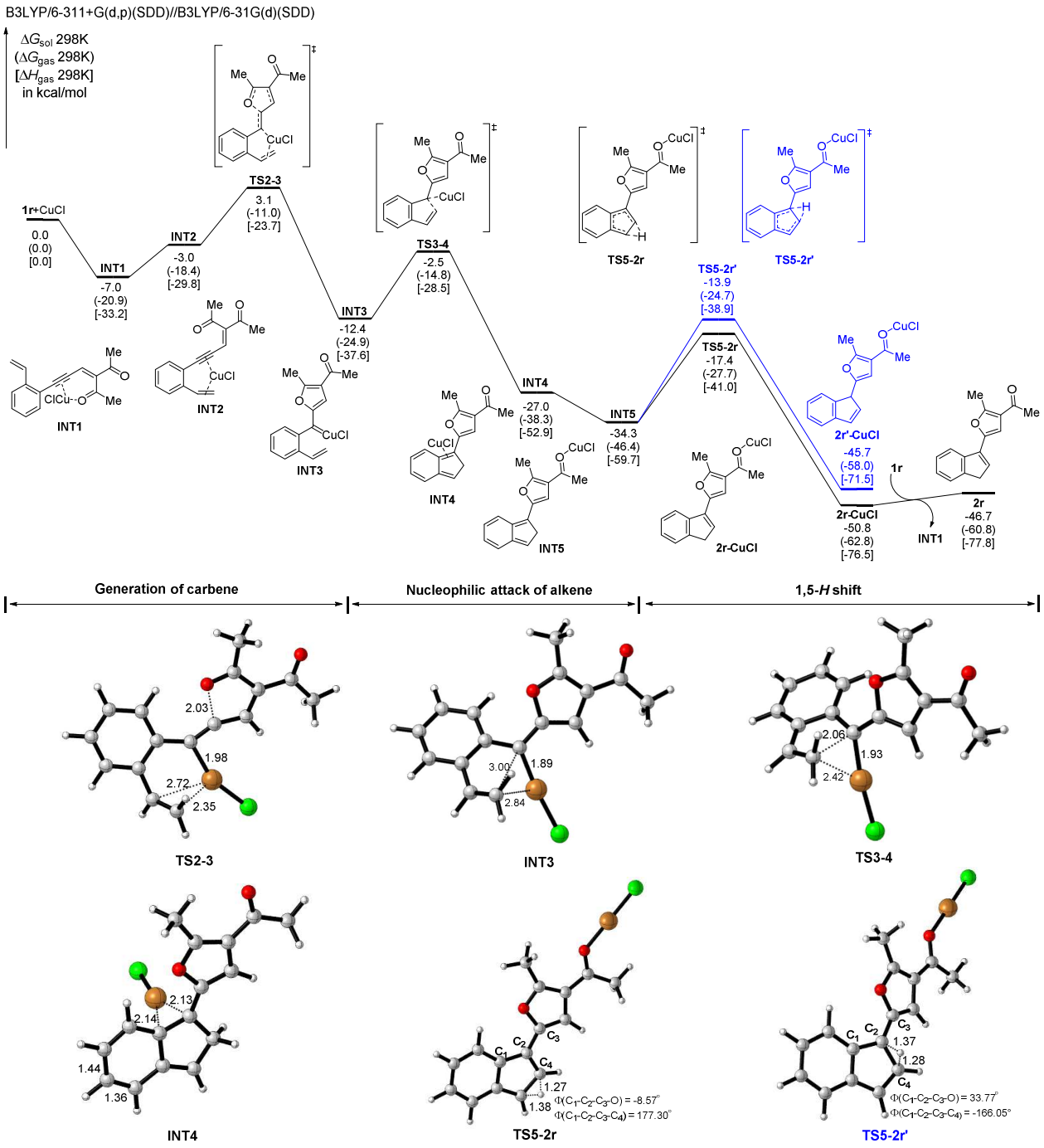


Figure 1. Potential energy surface and 3D structures of key species of CuCl-catalyzed cascade annulation of **1r**. The bond lengths in the structures at the bottom are given in Å.

experimental results (this ratio was greater than 20 : 1, as determined by NMR experiments). The preference of 1,5-*H* shifts can be understood because the formation of **2r'** *via* **TS5-2r'** has to disrupt the conjugation between indene and furan, which is kept in **TS5-2r**. This can be appreciated by the structures of 1,5-*H* migration transition states **TS5-2r** and **TS5-2r'**, in which the coplanar structure was kept in transition state **TS5-2r** with dihedral angles of C_1-C_2-C_3-O -8.57° and C_1-C_2-C_3-C_4 177.30°. While the coplanarity was broken in the transition state **TS5-2r'** for the increase of dihedral angles of C_1-C_2-C_3-O (33.77°) and C_1-C_2-C_3-C_4 (-166.05°), confirming the disruption of conjugation in the formation of **2r'** from **INT5** *via* **TS5-2r'**.

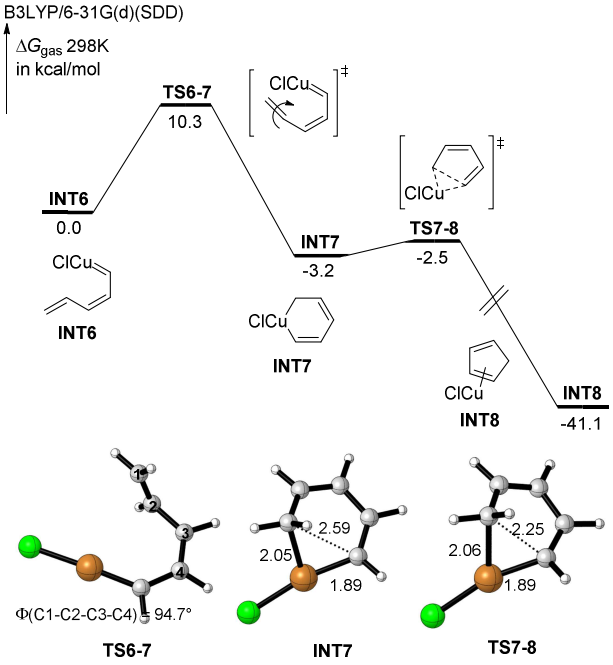


Figure 2. Potential energy surface and 3D structures of key species for the annulation of dienyl-carbene. The bond lengths in the structures at the bottom are given in Å.

In the final step of the catalytic cycle, product **2r** is released *via* catalyst transfer between complex **2r-CuCl** and substrate **1r**, together with liberation of CuCl for the next catalytic cycle. Calculations indicated that this ligand exchange process is slightly endergonic by 4.1 kcal/mol.

The pathway for intramolecular cyclopropanation in *path b* is shown in Figure 3. The corresponding activation free energy of this cyclopropanation *via* transition state **TS3-9** is 30.4 kcal/mol, which is higher than the cyclization transition state **TS3-4** in pathway a by 20.5 kcal/mol. Generation of cyclopropanation intermediate **INT9** from **INT3** is endergonic by 24.8 kcal/mol. Therefore, pathway b is not favored compared to pathway a.

Furthermore, we tried to locate a concerted C(sp^2)-H bond insertion transition state from intermediate **INT3**, which was described in *path c*. However, all attempts in locating such a transition state led to the nucleophilic attack transition state in *path a*. Therefore, this pathway would not exist at this computational level. Overall, the experimental and calculation results unveil that the nucleophilic attack of the vinylic double bond, and then 1,5-hydrgon shift in *path a* is the most favorable pathway to account for this transformation.

CONCLUSIONS

In summary, we have developed a novel Cu-catalyzed cascade cyclization reaction of enynones with a tethered alkene for the straightforward synthesis of 1*H*-indenes. The reaction was proposed to go through a copper-catalyzed *5-exo-dig* cyclization of enynones to afford the key intermediate, copper (2-furyl) carbene, which then undergoes formal C(sp^2)-H insertion to provide the furyl-substituted 1*H*-indenes. In addition,

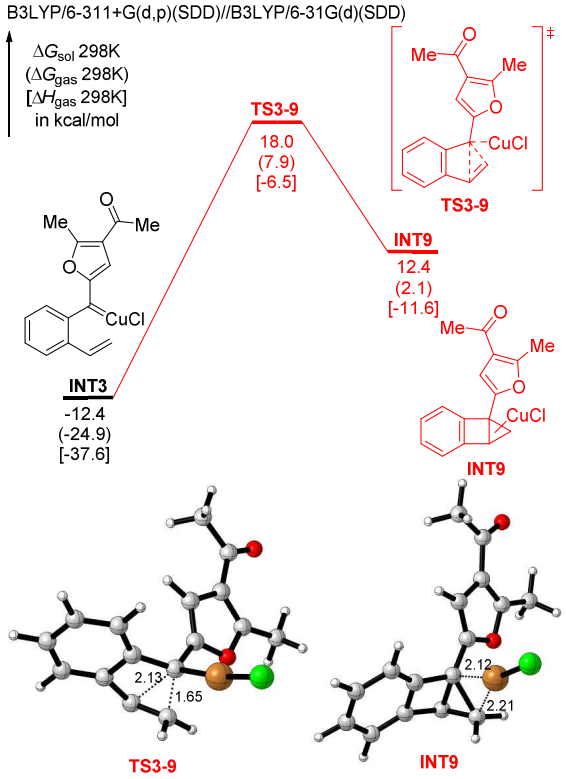


Figure 3. Potential energy surface and 3D structures of key species of intramolecular cyclopropanation. The bond lengths in the structures at the bottom are given in Å.

the DFT calculations indicate that the proposed formal C(sp^2)-H insertion is a stepwise process, involving diene-carbene cyclization (one step but involving 6π cyclization of Cu-carbene and reductive elimination), followed by 1,5-hydrogen shift. The use of inexpensive and low toxic catalysts, mild and neutral reaction conditions, good functional-group tolerance and high atom economy make this protocol appealing for synthetic applications.

EXPERIMENTAL SECTION

General. All reactions were carried out in oven-dried glassware under an atmosphere of dry argon. Metal catalysts used in this reaction were purchased from commercial sources and used without further purification. Solvents were dried and degassed by the standard methods. Flash column chromatography was performed using silica gel (300-400 mesh). Analytical thin-layer chromatography was performed using glass plates pre-coated with 200-300 mesh silica gel impregnated with a fluorescent indicator (254 nm). ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a 400 MHz spectrometer; chemical shifts are reported in ppm with the solvent signals as reference, and coupling constants (*J*) are given in Hertz. The peak information is described as: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, comp = composite. High-resolution mass spectra (HRMS) were recorded on a commercial apparatus (CI Source). Enynones **1** were prepared according to the reported method.[13e]

*3-(3-(2-Styrylphenyl)prop-2-yn-1-ylidene)pentane-2,4-dione (**1a**)*. *trans/cis* = 48/52, 590.5 mg, 63% yield. Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 7.4 Hz, 2H), 7.54 (d, *J* = 16.3 Hz, 1H), 7.51-7.47 (comp, 2.1H), 7.45-7.38 (comp, 3H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.28-7.13 (comp, 11.3H), 7.00 (s, 1H), 6.94 (s, 1.1H), 6.78-6.70 (comp, 2.2H), 2.54 (s, 3.2H), 2.52 (s, 3H), 2.39 (s, 3H), 2.36 (s, 3.2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.2, 201.0, 195.8, 195.7, 149.29, 149.28, 140.7, 140.1, 137.0, 136.7, 133.6, 133.1, 132.5, 131.9, 130.6, 129.9, 129.5, 129.1, 128.9, 128.40, 128.36, 128.1, 127.6, 127.5, 127.4, 127.2, 125.8, 125.0, 122.5, 122.4, 121.2, 120.6, 106.1, 105.9, 90.0, 89.4, 31.3, 31.1, 27.5, 27.4; HRMS (TOF MS CI$^+$) calculated for $C_{22}H_{19}O_2$ $[M+H]^+$: 315.1385, found 315.1379.

*3-(3-(2-(4-Methylstyryl)phenyl)prop-2-yn-1-ylidene)pentane-2,4-dione (**1b**)*. *trans/cis* = 75/25; 608.3 mg, 62% yield. Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 1H), 7.49 (comp, 4.4H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.23 (comp, 4.2H), 7.14 (d, *J* = 16.3 Hz, 1H), 7.07-7.03 (m, 0.7H), 6.97 (comp, 2H), 6.69 (s, 0.7H), 2.53 (s, 1H), 2.52 (s, 3H), 2.38 (s, 3H), 2.37 (s, 3H), 2.35 (s, 1H), 2.28 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.2, 201.0, 195.8, 195.7, 149.21, 149.17, 140.9, 140.2, 138.4, 137.4, 134.1, 133.7, 133.6, 133.0, 132.3, 131.8, 130.5, 129.9, 129.5, 129.4, 129.0, 128.9, 127.23, 127.20, 127.18, 127.1, 124.8, 124.7, 122.5, 122.3, 121.1, 120.4, 106.1, 106.0, 89.9, 89.4, 31.2, 31.1, 27.4, 27.3, 21.4, 21.3; HRMS (TOF MS CI$^+$) calculated for $C_{23}H_{21}O_2$ $[M+H]^+$: 329.1542, found 329.1544.

*3-(3-(2-(4-Fluorostyryl)phenyl)prop-2-yn-1-ylidene)pentane-2,4-dione (**1c**)*. *trans/cis* = 78/22; 320.1 mg, 32% yield. Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 1H), 7.65-7.58 (m, 2H), 7.52-7.43 (comp, 2.5H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.37-7.32 (comp, 0.3H), 7.28-7.19 (comp, 2.2H), 7.16-7.01 (comp, 3.9H), 6.97 (s, 1H), 6.94-6.84 (comp, 0.8H), 6.73 (d, *J* = 12.2 Hz, 0.3H), 6.67 (d, *J* = 13.5 Hz, 0.3H), 2.53 (s, 0.8H), 2.49 (s, 3H), 2.39 (s, 3H), 2.36 (s, 0.8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.2, 201.0, 195.8, 195.7, 162.8 (d, *J* = 248.2 Hz), 149.4, 140.4, 139.9, 133.6, 133.2, 133.1, 131.2, 130.7 (d, *J* = 8.0 Hz), 130.6, 130.0, 129.3, 128.9 (d, *J* = 8.1 Hz), 128.0 (d, *J* = 1.2 Hz), 127.5, 125.5 (d, *J* = 2.4 Hz), 124.8, 122.5, 122.2, 121.2, 120.5, 115.8 (d, *J* = 21.7 Hz), 115.3 (d, *J* = 21.4 Hz), 105.8, 105.7, 89.9, 89.4, 31.2, 31.1, 27.4, 27.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.13, -113.73; HRMS (TOF MS CI$^+$) calculated for $C_{22}H_{18}FO_2$ $[M+H]^+$: 333.1291, found 333.1289.

*3-(3-(2-(4-Chlorostyryl)phenyl)prop-2-yn-1-ylidene)pentane-2,4-dione (**1d**)*. *trans/cis* = 90:10; 586.0 mg, 56% yield. Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 16.5 Hz, 1H), 7.50-7.47 (m, 1H), 7.43-7.38 (m, 1H), 7.38-7.34 (m, 2H), 7.28-7.24 (m, 1H), 7.11 (d, *J* = 16.4 Hz, 1H), 6.96 (s, 1H), 2.49 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.0, 195.8, 149.4, 139.7, 135.5, 134.0, 133.7, 130.6, 130.5, 129.0, 128.4, 127.7, 126.4, 124.9, 122.4, 120.7, 105.6, 90.0, 31.1, 27.2; HRMS (TOF MS CI$^+$) calculated for $C_{22}H_{18}ClO_2$ $[M+H]^+$: 349.0995, found 349.0991.

*3-(3-(2-(4-Bromostyryl)phenyl)prop-2-yn-1-ylidene)pentane-2,4-dione (**1e**)*. *trans/cis* = 65/35; 355.4 mg, 30% yield. Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 1H), 7.58-7.45 (comp, 6.7H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 7.28-7.24 (comp, 1.6H), 7.24-7.18 (m, 1.7H), 7.09 (d, *J* = 16.3 Hz, 1H), 7.01 (d, *J* = 8.5 Hz, 1H), 6.96 (s, 1H), 6.91 (s, 0.5H), 6.78 (d, *J* = 12.2 Hz, 0.5H), 6.64 (d, *J* = 12.2 Hz, 0.5H), 2.52 (s, 1.6H), 2.49 (s, 3H), 2.39 (s, 3H), 2.36 (s, 1.6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.1, 201.0, 195.8, 195.6, 149.5, 149.4, 140.2, 139.7, 135.9, 135.5, 133.7, 133.2, 132.0, 131.5, 131.1, 130.64, 130.59, 130.5, 130.0, 129.3, 128.9, 128.7, 127.7, 127.6, 126.5, 124.9, 122.4, 122.2, 122.1, 121.5, 121.2, 120.7, 105.7, 105.6, 90.0, 89.5, 31.2, 31.1, 27.4, 27.2; HRMS (TOF MS CI$^+$) calculated for $C_{22}H_{18}BrO_2$ $[M+H]^+$: 393.0490, found 393.0486.

*3-(3-(2-(4-Methoxystyryl)phenyl)prop-2-yn-1-ylidene)pentane-2,4-dione (**1f**)*. *trans/cis* = 75/25; 590.2 mg, 57% yield. Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.7 Hz, 1H), 7.57 (d, *J* = 8.7 Hz, 2H), 7.51-7.41 (comp, 2H), 7.41-7.35 (comp, 1.6H), 7.32-7.28 (m, 0.5H), 7.24-7.18 (comp, 1.8H), 7.16-7.07 (comp, 1.8H), 7.01-6.97 (m, 1H), 6.96-6.90 (comp, 2.4H), 6.72 (d, *J* = 8.8 Hz, 0.7H), 6.67-6.60 (comp, 0.7H), 3.83 (s, 3H), 3.76 (s, 1H), 2.53 (s, 1H), 2.52 (s, 3H), 2.38 (s, 3H), 2.35 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.2, 201.1, 195.8, 195.7, 159.9, 159.0, 149.18, 149.15, 141.1, 140.4, 133.6, 133.1, 131.9, 131.4, 130.5, 130.4, 129.9, 129.7, 129.4, 129.1, 128.5, 127.2, 127.0, 126.3, 124.6, 123.5, 122.6, 122.4, 121.1, 120.2, 114.3, 113.7, 106.2, 106.1, 89.9, 89.3, 55.4, 55.3, 31.3, 31.1, 27.4, 27.3; HRMS (TOF MS CI$^+$) calculated for $C_{23}H_{21}O_3$ $[M+H]^+$: 345.1491, found 345.1497.

*3-(3-(2-(4-Nitrostyryl)phenyl)prop-2-yn-1-ylidene)pentane-2,4-dione (**1g**)*. *trans/cis* = 50/50; 482.0 mg, 45% yield. Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31-8.21 (m, 2H), 8.09-8.02 (m, 2H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.81-7.73 (comp, 2H), 7.53 (d, *J* = 7.6 Hz, 2H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.36-7.27 (m, 4H), 7.26-7.19 (m, 2H), 7.16 (d, *J* = 7.7 Hz, 1H), 7.01-6.91 (comp, 3H), 6.79 (d, *J* = 12.2 Hz, 1H), 2.53 (s, 3H), 2.50 (s, 3H), 2.42 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.1, 200.9, 195.8, 195.6, 149.8, 149.7, 147.2, 146.8, 143.5, 143.4, 139.4, 138.9, 133.8, 133.4, 131.9, 130.7, 130.3, 130.17, 130.15, 129.8, 129.2, 128.5, 128.2, 127.8, 125.2, 124.2, 123.7, 122.3, 121.8, 121.33, 121.30, 105.0, 104.9, 90.3, 89.7, 31.2, 31.1, 27.3, 27.1; HRMS (TOF MS CI$^+$) calculated for $C_{22}H_{18}NO_4$ $[M+H]^+$: 360.1236, found 360.1245.

*3-(3-(2-(3-Methylstyryl)phenyl)prop-2-yn-1-ylidene)pentane-2,4-dione (**1h**)*. *trans/cis* = 61/39; 611.2 mg, 62% yield. Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.56-7.46 (comp, 7.1H), 7.44-7.38 (comp, 4.3H), 7.32-7.27 (comp, 2.6H), 7.27-7.19 (comp, 4.2H), 7.19-7.10 (comp, 4.9H), 7.10-7.05 (m, 0.8H), 7.01-6.93 (comp, 4.6H), 6.74 (d, *J* = 12.3 Hz, 0.7H), 6.70 (d, *J* = 12.3 Hz, 0.7H), 2.54 (s, 1.9H), 2.52 (s, 3H), 2.42 (s, 6.3H), 2.39 (s, 6.2H), 2.36 (s, 1.9H), 2.24 (s, 1.9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.2, 201.0, 195.8, 195.7, 149.2, 140.8, 140.2, 138.5, 137.9, 136.9, 136.6, 133.7, 133.1, 132.6, 132.0, 130.6, 129.9, 129.8, 129.5, 129.3, 128.7, 128.3, 128.2, 127.82, 127.76, 127.4, 127.3, 126.0, 125.5, 124.9, 124.5, 122.5, 122.4, 121.2, 120.5, 106.1, 105.9, 89.9, 89.4, 31.3, 31.1, 27.4, 27.3, 21.5, 21.4; HRMS (TOF MS CI$^+$) calculated for $C_{23}H_{21}O_2$ $[M+H]^+$: 329.1542, found 329.1548.

*3-(3-(2-(2-Methylstyryl)phenyl)prop-2-yn-1-ylidene)pentane-2,4-dione (**1i**).* *trans/cis* = 58/42; 551.2 mg, 56% yield. Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.52-7.48 (m, 1H), 7.47-7.39 (comp, 3.8H), 7.31-7.11 (comp, 6.9H), 7.07 (m, 0.7H), 7.04-6.96 (comp, 3.8H), 6.90 (d, *J* = 12.2 Hz, 0.7H), 6.83 (d, *J* = 12.2 Hz, 0.7H), 2.57 (s, 2.1H), 2.50 (s, 3H), 2.44 (s, 3H), 2.38 (s, 2.1H), 2.38 (s, 3H), 2.28 (s, 2.1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.2, 200.9, 195.8, 195.7, 149.4, 149.3, 140.3, 140.2, 136.3, 136.1, 135.9, 133.5, 133.0, 131.8, 130.5, 130.2, 129.7, 129.5, 129.2, 129.1, 128.28, 128.25, 127.6, 127.4, 127.1, 127.0, 126.5, 126.0, 125.7, 125.1, 122.4, 122.3, 121.2, 120.6, 106.0, 105.8, 89.9, 89.6, 31.2, 31.1, 27.4, 27.3, 20.00, 19.97; HRMS (TOF MS CI$^+$) calculated for $C_{23}H_{21}O_2$ $[M+H]^+$: 329.1542, found 329.1543.

*3-(3-(2-(2-Bromostyryl)phenyl)prop-2-yn-1-ylidene)pentane-2,4-dione (**1j**).* *trans/cis* = 8/92; 525.2 mg, 45% yield. Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.54 (m, 1H), 7.47-7.42 (m, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.09-6.98 (m, 4H), 6.97 (s, 1H), 6.90 (d, *J* = 12.1 Hz, 1H), 6.80 (d, *J* = 12.1 Hz, 1H), 2.54 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.0, 195.7, 149.4, 139.5, 137.3, 133.1, 132.8, 131.8, 130.9, 129.8, 129.4, 129.3, 129.0, 127.4, 127.1, 124.0, 122.3, 121.3, 105.7, 89.5, 31.2, 27.4; HRMS (TOF MS CI$^+$) calculated for $C_{22}H_{18}BrO_2$ $[M+H]^+$: 393.0490, found 393.0501.

*3-(3-(2-(2-(Benzo[d][1,3]dioxol-5-yl)vinyl)phenyl)prop-2-yn-1-ylidene)pentane-2,4-dione (**1k**).* *trans/cis* = 84/16; 336.0 mg, 31% yield. Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.0 Hz, 1H), 7.49-7.42 (comp, 1.3H), 7.41-7.32 (comp, 2.1H), 7.30-7.24 (comp, 1.4H), 7.24-7.15 (comp, 1.5H), 7.07 (d, *J* = 16.2 Hz, 1H), 7.02-6.90 (comp, 2.3H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.68-6.57 (comp, 0.9H), 5.97 (s, 2H), 5.88 (s, 0.4H), 2.51 (s, 3.6H), 2.37 (s, 3H), 2.34 (s, 0.6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.2, 200.9, 195.8, 195.7, 149.22, 149.15, 148.3, 147.9, 147.5, 147.0, 140.7, 140.1, 133.6, 133.1, 131.9, 131.5, 131.4, 130.6, 130.5, 130.0, 129.4, 127.3, 127.1, 126.8, 124.6, 123.9, 123.4, 122.6, 122.5, 122.3, 121.1, 120.3, 108.8, 108.5, 108.3, 106.1, 105.9, 101.3, 101.1, 90.0, 89.3, 31.2, 31.1, 27.4, 27.2; HRMS (TOF MS CI$^+$) calculated for $C_{23}H_{19}O_4$ $[M+H]^+$: 359.1283, found 359.1289.

*3-(3-(2-(2-(Naphthalen-1-yl)vinyl)phenyl)prop-2-yn-1-ylidene)pentane-2,4-dione (**1l**).* *trans/cis* = 77/23; 439.8 mg, 40% yield. Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 7.9 Hz, 1H), 8.12-8.07 (m, 0.3H), 7.99 (d, *J* = 16.0 Hz, 1H), 7.93-7.83 (comp, 4.5H), 7.75 (d, *J* = 8.0 Hz, 0.3H), 7.61-7.40 (comp, 7.5H), 7.33-7.24 (comp, 2.3H), 7.21 (d, *J* = 7.1 Hz, 0.3H), 7.14-7.07 (comp, 0.6H), 7.02-6.94 (comp, 1.7H), 6.78 (s, 0.3H), 2.54 (s, 0.9H), 2.46 (s, 3H), 2.36 (s, 3H), 2.35 (s, 0.9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.2, 201.0, 195.8, 195.7, 149.34, 149.25, 140.2, 140.0, 134.5, 134.4, 133.82, 133.76, 133.6, 133.0, 131.6, 131.5, 131.0, 130.6, 129.8, 129.7, 129.4, 128.84, 128.77, 128.74, 128.65, 127.9, 127.6, 127.2, 126.9, 126.4, 126.3, 126.1, 126.0, 125.9, 125.6, 125.3, 124.7, 124.4, 123.6, 122.3, 121.2, 120.7, 106.1, 105.8, 89.9, 89.5, 31.2, 31.1, 27.4, 27.3; HRMS (TOF MS CI$^+$) calculated for $C_{26}H_{21}O_2$ $[M+H]^+$: 365.1542, found 365.1541.

*3-(3-(2-(2-(Thiophen-2-yl)vinyl)phenyl)prop-2-yn-1-ylidene)pentane-2,4-dione (**1m**).* *trans/cis* = 88/12; 330.8 mg, 34% yield. Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 1H), 7.61-7.57 (m, 0.15H), 7.55-7.50 (m, 1.15H), 7.46-7.38 (m, 1.37H), 7.36 (s, 2H), 7.33-7.23 (m, 3.5H), 7.13 (d, *J* = 5.0 Hz, 0.15H), 7.11-7.07 (m, 1H), 7.06 (s, 1H), 7.00 (d, *J* = 3.5 Hz, 0.14H), 6.96-6.91 (m, 0.29H), 6.87 (d, *J* = 12.0 Hz, 0.14H), 6.64 (d, *J* = 12.0 Hz, 0.13H), 2.62 (s, 3H), 2.52 (s, 0.4H), 2.44 (s, 3H), 2.38 (s, 0.4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.9, 195.8, 149.1, 142.4, 139.5, 133.7, 130.5, 127.9, 127.4, 127.2, 125.6, 125.2, 124.8, 124.6, 122.5, 120.3, 105.8, 90.1, 31.2, 27.5; HRMS (TOF MS CI$^+$) calculated for $C_{20}H_{17}O_2S$ $[M+H]^+$: 321.0949, found 321.0957.

*3-(3-(2-(4-Phenylbuta-1,3-dien-1-yl)phenyl)prop-2-yn-1-ylidene)pentane-2,4-dione (**1n**).* *trans/cis* = 77/23; 422.7 mg, 41% yield. Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 1H), 7.59-7.47 (comp, 4H), 7.45-7.37 (comp, 4H), 7.37-7.21 (comp, 4H), 7.20-7.13 (comp, 2H), 7.11-6.97 (comp, 3H), 6.85-6.72 (comp, 1.7H), 6.65-6.56 (comp, 0.6H), 2.61 (s, 3H), 2.60 (s, 0.9H), 2.44 (s, 3H), 2.40 (s, 0.9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.24, 201.16, 195.8, 195.7, 149.5, 149.4, 140.4, 140.1, 137.2, 137.1, 136.0, 134.5, 133.3, 133.2, 132.2, 132.1, 130.5, 130.1, 129.8, 129.3, 128.81, 128.75, 128.10, 128.07, 128.0, 127.3, 126.8, 126.7, 124.8, 124.7, 122.3, 122.2, 121.2, 120.2, 105.9, 105.8, 90.0, 89.7, 31.23, 31.21, 27.3, 27.2; HRMS (TOF MS CI$^+$) calculated for $C_{24}H_{21}O_2$ $[M+H]^+$: 341.1542, found 341.1536.

*(E)-3-(3-(2-(4-Phenylbut-1-en-3-yn-1-yl)phenyl)prop-2-yn-1-ylidene)pentane-2,4-dione (**1o**).* 246.6 mg, 24% yield. Yellow solid; mp: 83-85 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.9 Hz, 1H), 7.54-7.50 (m, 2H), 7.47 (d, *J* = 7.4 Hz, 1H), 7.45-7.32 (m, 5H), 7.31-7.25 (m, 1H), 6.99 (s, 1H), 6.47 (d, *J* = 16.2 Hz, 1H), 2.60 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.1, 195.7, 149.7, 138.7, 138.3, 133.5, 131.8, 130.5, 128.6, 128.54, 128.45, 124.7, 123.3, 122.0, 120.5, 111.2, 104.9, 93.5, 90.1, 88.9, 31.2, 27.4; HRMS (TOF MS CI$^+$) calculated for $C_{24}H_{19}O_2$ $[M+H]^+$: 339.1385, found 339.1389.

*3-(3-(2-(2-Cyclopropylvinyl)phenyl)prop-2-yn-1-ylidene)-pentane-2,4-dione (**1p**).* *trans/cis* = 93/7; 530.3 mg, 64% yield. Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 7.7 Hz, 1H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 6.97 (s, 1H), 6.87 (d, *J* = 15.7 Hz, 1H), 5.78 (dd, *J* = 15.7, 9.2 Hz, 1H), 2.56 (s, 3H), 2.37 (s, 3H), 1.74-1.65 (m, 1H), 0.92-0.85 (m, 2H), 0.58-0.52 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.2, 195.7, 149.2, 140.5, 138.8, 133.2, 130.4, 126.5, 124.8, 124.5, 122.5, 119.2, 106.3, 89.5, 31.2, 27.3, 15.1, 7.8; HRMS (TOF MS CI$^+$) calculated for $C_{19}H_{19}O_2$ $[M+H]^+$: 279.1385, found 279.1388.

*3-(3-(2-(2-Cyclohexylvinyl)phenyl)prop-2-yn-1-ylidene)-pentane-2,4-dione (**1q**).* *trans/cis* = 89/11; 390.4 mg, 41% yield. Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 7.7 Hz, 1H), 7.31 (t, *J* = 7.7 Hz, 1H), 7.16 (t, *J* = 7.5 Hz, 1H), 6.98 (s, 1H), 6.73 (d, *J* = 15.9 Hz, 1H), 6.24 (dd, *J* = 15.9, 7.2 Hz, 1H), 2.55 (s, 3H), 2.36 (s, 3H), 2.28-2.15 (m, 1H), 1.87-1.73 (m, 4H), 1.72-1.64 (m, 1H), 1.39-1.27 (m, 2H), 1.27-1.07 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.9, 195.7, 149.0, 140.7, 140.3, 133.2, 130.4, 126.7, 124.9, 124.8, 122.5, 119.7, 106.3, 89.4, 41.6, 32.9, 31.2,

27.4, 26.2, 26.0; HRMS (TOF MS CI$^+$) calculated for $C_{22}H_{25}O_2$ [M+H]$^+$: 321.1855, found 321.1859.

*3-(3-(2-Vinylphenyl)prop-2-yn-1-ylidene)pentane-2,4-dione (**1r**)*. 328.0 mg, 46% yield. Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 7.7 Hz, 1H), 7.41-7.34 (m, 1H), 7.27-7.21 (m, 1H), 7.10 (dd, *J* = 17.5, 11.0 Hz, 1H), 6.98-6.91 (m, 1H), 5.88-5.76 (m, 1H), 5.45-5.34 (m, 1H), 2.53 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.1, 195.7, 149.4, 140.1, 134.3, 133.2, 130.5, 127.8, 125.0, 122.2, 120.3, 117.0, 105.5, 89.5, 31.2, 27.3; HRMS (TOF MS CI$^+$) calculated for $C_{16}H_{15}O_2$ [M+H]$^+$: 239.1072, found 239.1068.

*Ethyl (E)-3-(2-(4-acetyl-5-oxohex-3-en-1-yn-1-yl)phenyl) acrylate (**1s**)*. 538.8 mg, 58% yield. Yellow solid; mp: 66-68 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 16.0 Hz, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.56-7.47 (m, 1H), 7.45-7.33 (m, 2H), 6.97 (s, 1H), 6.50 (d, *J* = 16.0 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 2.57 (s, 3H), 2.38 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.9, 195.7, 166.6, 149.9, 141.4, 136.7, 133.8, 130.5, 130.0, 126.4, 122.3, 121.8, 121.1, 104.0, 90.4, 60.9, 31.1, 27.4, 14.5; HRMS (TOF MS CI$^+$) calculated for $C_{19}H_{19}O_4$ [M+H]$^+$: 311.1283, found 311.1280.

*Ethyl (E)-3-(2-(4-benzoyl-5-oxo-5-phenylpent-3-en-1-yn-1-yl)phenyl)acrylate (**1t**)*. 764.3 mg, 59% yield. Yellow solid; mp: 116-118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05-7.99 (m, 2H), 7.93 (d, *J* = 16.0 Hz, 1H), 7.86-7.80 (m, 2H), 7.59-7.52 (comp, 3H), 7.49-7.42 (comp, 4H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.02 (s, 1H), 6.95 (d, *J* = 7.5 Hz, 1H), 6.43 (d, *J* = 16.0 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.9, 193.0, 166.6, 148.5, 141.5, 136.7, 136.36, 136.35, 133.9, 133.7, 133.2, 130.1, 129.7, 129.6, 129.4, 128.9, 128.8, 126.2, 123.9, 122.3, 120.8, 103.4, 90.6, 60.8, 14.4; HRMS (TOF MS CI$^+$) calculated for $C_{29}H_{23}O_4$ [M+H]$^+$: 435.1596, found 435.1602.

*Ethyl 3-(2-(4-(4-chlorobenzoyl)-5-(4-chlorophenyl)-5-oxopent-3-en-1-yn-1-yl)phe nyl)acrylate (**1u**)*. *trans/cis* = 98/2; 772.1 mg, 51% yield. Yellow solid; mp: 126-127 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.5 Hz, 2H), 7.89 (d, *J* = 16.0 Hz, 1H), 7.81-7.72 (m, 2H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.47-7.40 (comp, 4H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.06-6.93 (m, 2H), 6.44 (d, *J* = 16.0 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.5, 191.5, 166.6, 147.6, 141.3, 140.6, 139.9, 136.5, 134.9, 134.6, 133.6, 131.1, 130.8, 130.3, 129.7, 129.3, 129.2, 126.2, 124.2, 122.0, 120.9, 104.0, 90.2, 60.8, 14.4; HRMS (TOF MS CI$^+$) calculated for $C_{29}H_{21}Cl_2O_4$ [M+H]$^+$: 503.0817, found 503.0833.

*Methyl 2-acetyl-5-(2-((E)-3-ethoxy-3-oxoprop-1-en-1-yl)phenyl)pent-2-en-4-yno ate (**1v**)*. *Z/E* = 50/50; 533.6 mg, 55% yield. Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 16.0 Hz, 1H), 8.05 (d, *J* = 16.0 Hz, 1H), 7.64 (t, *J* = 7.3 Hz, 2H), 7.54-7.48 (m, 2H), 7.44-7.32 (comp, 4H), 7.10 (s, 1H), 7.09 (s, 1H), 6.51 (d, *J* = 16.0 Hz, 1H), 6.49 (d, *J* = 16.0 Hz, 1H), 4.32-4.23 (m, 4H), 3.93 (s, 3H), 3.83 (s, 3H), 2.53 (s, 3H), 2.42 (s, 3H), 1.37-1.29 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 193.9, 166.4, 165.5, 164.2, 142.2, 141.3, 141.1, 136.51, 136.45, 133.8, 133.7, 130.3, 130.2, 129.8, 129.7, 126.2, 124.6, 123.0, 122.4, 122.2, 120.9, 103.6, 102.4, 90.7, 90.3, 60.6, 52.6, 52.5, 30.4, 27.8, 14.3; HRMS (TOF MS CI$^+$) calculated for $C_{19}H_{19}O_5$ [M+H]$^+$: 327.1232, found 327.1240.

*(E)-3-(3-(2-(3-Oxo-3-phenylprop-1-en-1-yl)phenyl)prop-2-yn-1-ylidene)pentane-2,4-dione (**1w**)*. 520.8 mg, 51% yield. Yellow solid; mp: 101-102 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 15.7 Hz, 1H), 8.04-7.98 (m, 2H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.61-7.55 (comp, 2H), 7.54-7.47 (comp, 3H), 7.46-7.41 (m, 1H), 7.40-7.35 (m, 1H), 6.95 (s, 1H), 2.54 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.8, 195.7, 190.1, 150.0, 141.4, 138.0, 137.0, 133.8, 133.1, 130.4, 130.1, 128.8, 128.6, 126.5, 124.5, 122.8, 121.6, 104.0, 90.6, 31.1, 27.3; HRMS (TOF MS CI$^+$) calculated for $C_{23}H_{19}O_3$ [M+H]$^+$: 343.1334, found 343.1331.

*3-(2-(4-Acetyl-5-oxohex-3-en-1-yn-1-yl)phenyl)acrylonitrile (**1x**)*. *trans/cis* = 99/1; 197.0 mg, 25% yield. Yellow solid; mp: 91-92 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86-7.76 (m, 1H), 7.60-7.48 (comp, 2H), 7.47-7.35 (comp, 2H), 6.90 (s, 1H), 5.99 (d, *J* = 16.7 Hz, 1H), 2.51 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.6, 195.7, 150.6, 147.7, 135.5, 133.8, 130.9, 130.6, 125.7, 121.9, 121.3, 117.9, 102.6, 99.1, 90.8, 31.0, 27.1; HRMS (TOF MS CI$^+$) calculated for $C_{17}H_{14}NO_2$ [M+H]$^+$: 264.1025, found 264.1024.

*Ethyl (E)-3-(2-(4-acetyl-5-oxohex-3-en-1-yn-1-yl)phenyl)-but-2-enoate (**1y**)*. 311.2 mg, 32% yield. Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 6.90 (s, 1H), 5.89 (s, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.51 (s, 3H), 2.49 (s, 3H), 2.35 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.9, 195.7, 166.4, 155.6, 149.6, 146.9, 133.7, 130.3, 128.1, 127.7, 122.0, 120.8, 119.2, 105.4, 88.7, 60.2, 31.1, 27.5, 20.4, 14.4; HRMS (TOF MS CI$^+$) calculated for $C_{20}H_{21}O_4$ [M+H]$^+$: 325.1440, found 325.1441.

*3-(3-(2-(2-(4-methoxyphenyl)vinyl-2-d)phenyl)prop-2-yn-1-ylidene)pentane-2,4-dione (**1f-d**)*. *trans/cis* = 58/42; 482.2 mg, 47% yield. Yellow soild; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 1H), 7.61-7.55 (m, 2H), 7.50-7.44 (m, 1.7H), 7.42-7.34 (m, 2.1H), 7.33-7.28 (m, 0.8H), 7.24-7.16 (m, 2.6H), 7.13-7.07 (m, 1.5H), 6.99 (s, 1H), 6.96-6.90 (m, 2.8H), 6.75-6.69 (m, 1.5H), 6.63 (s, 0.7H), 3.83 (s, 3H), 3.76 (s, 2.1H), 2.53 (s, 2.1H), 2.52 (s, 3H), 2.38 (s, 3H), 2.35 (s, 2.1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.2, 201.1, 195.8, 195.7, 159.9, 159.0 149.19, 149.16 141.1, 140.4, 133.6, 133.1, 130.5, 130.3, 129.9, 129.7, 129.4, 129.0, 128.5, 127.2, 126.2, 124.7, 123.4, 122.5, 122.4, 121.1, 120.2, 114.3, 113.7, 106.2, 106.1, 89.9, 89.3, 55.4, 55.3, 31.2, 31.14, 27.4, 27.3; HRMS (TOF MS CI$^+$) calculated for $C_{23}H_{20}DO_3$ [M+H]$^+$: 346.1553, found 346.1548.

General Procedure for Copper-Catalyzed Cyclization Reaction of 1. To a 10-mL oven-dried vial containing a magnetic stirring bar, enynones **1** (0.2 mmol), $CuSO_4{\cdot}5H_2O$ (0.5 mg, 1.0 mol %) and anhydrous DCE (2.0 mL) was added in sequence under atmosphere of argon, and the reaction mixture was stirred at 55 °C. When the reaction was completed (monitored by TLC, 2~16 h), the solvent was evaporated *in vacuo* and the residue was purified by flash column chromatography on silica gel without additional treatment (hexanes/ethyl acetate = 10:1 to 5:1) to afford the pure products **2**.

*1-(2-Methyl-5-(2-phenyl-1H-inden-3-yl)furan-3-yl)ethan-1-one (**2a**)*. 59.4 mg, 95% yield. Yellow solid; mp: 74-77 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.6 Hz, 1H), 7.52 (d, *J* = 7.3 Hz, 1H), 7.42-7.26 (comp, 7H), 6.64 (s, 1H), 3.90 (s, 2H), 2.60 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 157.8, 147.5, 144.5, 144.2, 142.4, 136.8, 128.4, 128.3, 127.9, 127.9, 126.9, 125.5, 123.8, 122.8, 120.9, 109.6, 42.6, 29.3, 14.6; HRMS (TOF MS CI$^+$) calculated for $C_{22}H_{19}O_2$ $[M+H]^+$: 315.1385, found 315.1383.

*1-(2-Methyl-5-(2-(p-tolyl)-1H-inden-3-yl)furan-3-yl)ethan-1-one (**2b**)*. 62.2 mg, 95% yield. Yellow solid; mp: 110-112 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.63 (d, *J* = 7.6 Hz, 1H), 7.52 (d, *J* = 7.3 Hz, 1H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.26 (td, *J* = 7.4, 1.1 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.70 (s, 1H), 3.88 (s, 2H), 2.59 (s, 3H), 2.40 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 194.3, 157.9, 147.9, 145.1, 144.9, 142.8, 138.4, 134.2, 129.5, 128.6, 127.6, 127.1, 125.7, 124.2, 123.3, 121.0, 110.1, 42.8, 29.6, 21.6, 14.7; HRMS (TOF MS CI$^+$) calculated for $C_{23}H_{21}O_2$ $[M+H]^+$: 329.1542, found 329.1537.

*1-(5-(2-(4-Fluorophenyl)-1H-inden-3-yl)-2-methylfuran-3-yl)ethan-1-one (**2c**)*. 63.7 mg, 96% yield. Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 7.4 Hz, 1H), 7.41-7.32 (comp, 3H), 7.31-7.27 (m, 1H), 7.09-7.00 (m, 2H), 6.66 (s, 1H), 3.86 (s, 2H), 2.60 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 162.4 (d, *J* = 247.9 Hz), 157.9, 147.3, 144.0, 143.2, 142.2, 132.9 (d, *J* = 3.5 Hz), 130.0 (d, *J* = 8.0 Hz), 127.9, 126.9, 125.6, 123.8, 122.9, 120.9, 115.4 (d, *J* = 21.5 Hz), 109.7, 42.6, 29.3, 14.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.70; HRMS (TOF MS CI$^+$) calculated for $C_{22}H_{18}FO_2$ $[M+H]^+$: 333.1291, found 333.1286.

*1-(5-(2-(4-Chlorophenyl)-1H-inden-3-yl)-2-methylfuran-3-yl)ethan-1-one (**2d**)*. 67.4 mg, 97% yield. Yellow solid; mp: 103-105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 7.3 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.33-7.31 (comp, 4H), 7.31-7.26 (m, 1H), 6.69 (s, 1H), 3.86 (s, 2H), 2.60 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 158.0, 147.1, 144.0, 142.8, 142.2, 135.2, 133.7, 129.6, 128.6, 128.4, 127.0, 125.8, 123.9, 122.9, 121.0, 109.9, 42.4, 29.3, 14.6; HRMS (TOF MS CI$^+$) calculated for $C_{22}H_{18}ClO_2$ $[M+H]^+$: 349.0995, found 349.0997.

*1-(5-(2-(4-Bromophenyl)-1H-inden-3-yl)-2-methylfuran-3-yl)ethan-1-one (**2e**)*. 74.5 mg, 95% yield. Yellow solid; mp: 105-106 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.7 Hz, 1H), 7.51 (d, *J* = 7.3 Hz, 1H), 7.49-7.43 (m, 2H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.32-7.27 (m, 1H), 7.26-7.22 (m, 2H), 6.70 (s, 1H), 3.84 (s, 2H), 2.60 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 158.0, 147.0, 143.9, 142.8, 142.2, 135.7, 131.6, 129.9, 128.4, 126.9, 125.8, 123.9, 122.9, 121.8, 120.9, 109.9, 42.3, 29.3, 14.6; HRMS (TOF MS CI$^+$) calculated for $C_{22}H_{18}BrO_2$ $[M+H]^+$: 393.0490, found 393.0497.

*1-(5-(2-(4-Methoxyphenyl)-1H-inden-3-yl)-2-methylfuran-3-yl)ethan-1-one (**2f**)*. 64.4 mg, 94% yield. Yellow solid; mp: 112-113 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 7.3 Hz, 1H), 7.38-7.31 (comp, 3H), 7.28-7.23 (m, 1H), 6.92-6.86 (m, 2H), 6.67 (s, 1H), 3.86 (s, 2H), 3.84 (s, 3H), 2.62 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 159.4, 157.7, 147.6, 144.5, 144.4, 142.1, 129.6, 129.1, 126.8, 126.7, 125.2, 123.7, 122.8, 120.6, 113.9, 109.5, 55.4, 42.4, 29.3, 14.6; HRMS (TOF MS CI$^+$) calculated for $C_{23}H_{21}O_3$ $[M+H]^+$: 345.1491, found 345.1486.

*1-(2-Methyl-5-(2-(4-nitrophenyl)-1H-inden-3-yl)furan-3-yl)ethan-1-one (**2g**)*. 66.3 mg, 92% yield. Yellow solid; mp: 168-171 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24-8.13 (m, 2H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.55 (d, *J* = 7.4 Hz, 1H), 7.53-7.49 (m, 2H), 7.45-7.38 (m, 1H), 7.36-7.31 (m, 1H), 6.80 (s, 1H), 3.92 (s, 2H), 2.58 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.9, 158.5, 146.8, 146.4, 143.5, 143.4, 142.5, 141.0, 130.9, 129.0, 127.2, 126.6, 124.1, 123.7, 123.1, 121.4, 110.6, 42.2, 29.3, 14.6; HRMS (TOF MS CI$^+$) calculated for $C_{22}H_{18}NO_4$ $[M+H]^+$: 360.1236, found 360.1243.

*1-(2-Methyl-5-(2-(m-tolyl)-1H-inden-3-yl)furan-3-yl)ethan-1-one (**2h**)*. 62.8 mg, 96% yield. Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.7 Hz, 1H), 7.51 (d, *J* = 7.3 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.31-7.26 (m, 1H), 7.26-7.21 (m, 2H), 7.18 (d, *J* = 7.7 Hz, 1H), 7.13 (d, *J* = 7.5 Hz, 1H), 6.66 (s, 1H), 3.89 (s, 2H), 2.61 (s, 3H), 2.40 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.4, 157.7, 147.6, 144.6, 144.2, 142.4, 138.0, 136.7, 129.0, 128.6, 128.3, 127.7, 126.8, 125.48, 125.45, 123.8, 122.8, 120.9, 109.6, 42.6, 29.3, 21.6, 14.5; HRMS (TOF MS CI$^+$) calculated for $C_{23}H_{21}O_2$ $[M+H]^+$: 329.1542, found 329.1540.

*1-(2-Methyl-5-(2-(o-tolyl)-1H-inden-3-yl)furan-3-yl)ethan-1-one (**2i**)*. 59.2 mg, 90% yield. Yellow solid; mp: 77-79 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.7 Hz, 1H), 7.53 (d, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.34-7.25 (comp, 4H), 7.23-7.17 (m, 1H), 6.11 (s, 1H), 3.79 (s, 2H), 2.59 (s, 3H), 2.25 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 157.2, 148.5, 143.8, 142.9, 142.9, 137.7, 135.9, 130.3, 128.9, 128.7, 127.9, 126.8, 126.1, 125.3, 123.8, 122.6, 121.8, 108.7, 44.1, 29.1, 19.9, 14.5; HRMS (TOF MS CI$^+$) calculated for $C_{23}H_{21}O_2$ $[M+H]^+$: 329.1542, found 329.1547.

*1-(5-(2-(2-Bromophenyl)-1H-inden-3-yl)-2-methylfuran-3-yl)ethan-1-one (**2j**)*. 73.0 mg, 93% yield. Yellow solid; mp: 128-129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.7 Hz, 1H), 7.71-7.66 (m, 1H), 7.54 (d, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.40-7.35 (m, 1H), 7.35-7.30 (m, 1H), 7.30-7.23 (comp, 2H), 6.28 (s, 1H), 3.88 (s, 2H), 2.56 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 157.5, 147.8, 142.9, 142.6, 142.4, 139.3, 132.9, 130.5, 129.8, 129.3, 127.6, 126.8, 125.7, 123.9, 123.3, 122.7, 121.9, 109.1, 43.4, 29.1, 14.5; HRMS (TOF MS CI$^+$) calculated for $C_{22}H_{18}BrO_2$ $[M+H]^+$: 393.0490, found 393.0491.

*1-(5-(2-(Benzo[d][1,3]dioxol-5-yl)-1H-inden-3-yl)-2-methylfuran-3-yl)ethan-1-one (**2k**)*. 65.0 mg, 91% yield. Yellow solid; mp: 86-89 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.6 Hz, 1H), 7.48 (d, *J* = 7.3 Hz, 1H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.28-7.22 (m, 1H), 6.93-6.88 (m, 1H), 6.85 (d, *J* = 1.7 Hz, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 6.69 (s, 1H), 5.98 (s, 2H), 3.83 (s, 2H), 2.63 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 157.8, 147.7, 147.3, 144.4, 144.1, 142.0, 130.6, 127.2, 126.8, 125.4, 123.7, 122.9, 122.2, 120.7, 109.7, 108.6, 108.4, 101.3, 42.6, 29.3, 14.6; HRMS (TOF MS CI$^+$) calculated for $C_{23}H_{19}O_4$ $[M+H]^+$: 359.1283, found 359.1282.

*1-(2-Methyl-5-(2-(naphthalen-1-yl)-1H-inden-3-yl)furan-3-yl)ethan-1-one (**2l**)*. 67.0 mg, 92% yield. Yellow solid; mp: 82-84 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.7 Hz, 1H), 7.91 (t, *J* = 7.3 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.57 (comp, 2H), 7.47 (comp, 3H), 7.37 (comp, 2H), 6.04 (s, 1H), 3.97 (s, 2H), 2.45 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (10 MHz, $CDCl_3$) δ 194.2, 157.2, 148.0, 143.1, 142.9, 142.2, 136.1, 133.7, 131.4, 130.1, 128.4, 128.1, 126.9, 126.3, 126.2, 126.1, 125.7, 125.6, 125.5, 123.8, 122.4, 121.9, 109.3, 45.2, 28.9, 14.3; HRMS (TOF MS CI$^+$) calculated for $C_{26}H_{21}O_2$ $[M+H]^+$: 365.1542, found 365.1547.

*1-(2-Methyl-5-(2-(thiophen-2-yl)-1H-inden-3-yl)furan-3-yl)ethan-1-one (**2m**)*. 62.0 mg, 97% yield. Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.3 Hz, 1H), 7.44 (d, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.32-7.29 (m, 1H), 7.29-7.24 (comp, 2H), 7.05 (dd, *J* = 5.1, 3.7 Hz, 1H), 6.91 (s, 1H), 3.99 (s, 2H), 2.73 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 158.5, 145.9, 144.9, 141.2, 138.7, 138.6, 127.3, 127.0, 126.9, 126.8, 126.5, 125.7, 123.7, 123.0, 120.5, 111.0, 42.1, 29.4, 14.7; HRMS (TOF MS CI$^+$) calculated for $C_{20}H_{17}O_2S$ $[M+H]^+$: 321.0949, found 321.0947.

*(E)-1-(2-Methyl-5-(2-styryl-1H-inden-3-yl)furan-3-yl)ethan-1-one (**2n**)*. 60.1 mg, 88% yield. Yellow solid; mp: 139-142 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71-7.64 (m, 2H), 7.49 (comp, 3H), 7.32 (comp, 5H), 6.94 (d, *J* = 14.4 Hz, 2H), 3.85 (s, 2H), 2.76 (s, 3H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 158.3, 148.0, 143.4, 142.1, 142.0, 137.5, 131.7, 129.4, 128.9, 128.0, 126.9, 126.7, 125.9, 123.9, 123.6, 123.1, 121.0, 110.2, 38.3, 29.4, 14.9; HRMS (TOF MS CI$^+$) calculated for $C_{24}H_{21}O_2$ $[M+H]^+$: 341.1542, found 341.1543.

*1-(2-Methyl-5-(2-(phenylethynyl)-1H-inden-3-yl)furan-3-yl)ethan-1-one (**2o**)*. 63.5 mg, 94% yield. Yellow solid; mp: 136-138 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.7 Hz, 1H), 7.59-7.53 (comp, 3H), 7.47 (d, *J* = 7.3 Hz, 1H), 7.42-7.36 (comp, 4H), 7.35-7.30 (m, 1H), 3.77 (s, 2H), 2.75 (s, 3H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 157.7, 148.6, 142.7, 141.5, 136.0, 131.5, 128.7, 128.7, 127.1, 126.5, 123.8, 123.5, 122.9, 122.7, 120.4, 110.8, 100.2, 87.9, 42.8, 29.3, 14.8; HRMS (TOF MS CI$^+$) calculated for $C_{24}H_{19}O_2$ $[M+H]^+$: 339.1385, found 339.1382.

*1-(5-(2-Cyclopropyl-1H-inden-3-yl)-2-methylfuran-3-yl)ethan-1-one (**2p**)*. 52.7 mg, 95% yield. Yellow solid; mp: 81-82 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.7 Hz, 1H), 7.38 (d, *J* = 7.4 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.17 (td, *J* = 7.4, 1.0 Hz, 1H), 6.85 (s, 1H), 3.20 (s, 2H), 2.71 (s, 3H), 2.49 (s, 3H), 2.40-2.30 (m, 1H), 1.09-0.98 (m, 2H), 0.82-0.74 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 157.2, 148.9, 148.4, 143.9, 140.9, 127.5, 126.6, 124.4, 123.6, 122.8, 119.8, 108.6, 37.6, 29.4, 14.7, 12.4, 9.2; HRMS (TOF MS CI$^+$) calculated for $C_{19}H_{19}O_2$ $[M+H]^+$: 279.1385, found 279.1379.

*1-(5-(2-Cyclohexyl-1H-inden-3-yl)-2-methylfuran-3-yl)ethan-1-one (**2q**)*. 62.5 mg, 98% yield. Yellow solid; mp: 81-83 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 7.3 Hz, 1H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.21 (td, *J* = 7.4, 1.0 Hz, 1H), 6.73 (s, 1H), 3.50 (s, 2H), 3.15-2.80 (m, 1H), 2.71 (s, 3H), 2.50 (s, 3H), 1.93-1.75 (comp, 5H), 1.50-1.24 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 157.3, 153.5, 148.0, 143.7, 142.1, 126.5, 125.8, 124.5, 123.7, 122.8, 120.2, 108.5, 39.1, 38.1, 33.2, 29.3, 26.6, 26.2, 14.7; HRMS (TOF MS CI$^+$) calculated for $C_{22}H_{25}O_2$ $[M+H]^+$: 321.1855, found 321.1852.

*1-(5-(1H-inden-3-yl)-2-methylfuran-3-yl)ethan-1-one (**2r**)*. 40.0 mg, 84% yield. Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.5 Hz, 1H), 7.53 (d, *J* = 7.2 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.29 (t, *J* = 7.3 Hz, 1H), 6.93 (s, 1H), 6.84 (s, 1H), 3.54 (s, 2H), 2.68 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 157.8, 148.3, 144.4, 141.3, 133.4, 129.7, 126.5, 125.4, 124.2, 122.9, 120.6, 106.8, 38.3, 29.3, 14.6; HRMS (TOF MS CI$^+$) calculated for $C_{16}H_{15}O_2$ $[M+H]^+$: 239.1072, found 239.1069.

*Ethyl 3-(4-acetyl-5-methylfuran-2-yl)-1H-indene-2-carboxylate (**2s**)*. 56.4 mg, 91% yield. Yellow solid; mp: 87-90 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-7.99 (m, 1H), 7.71 (s, 1H), 7.55-7.49 (m, 1H), 7.42-7.37 (m, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 3.89 (s, 2H), 2.73 (s, 3H), 2.51 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.6, 165.0, 158.9, 146.4, 143.5, 142.4, 139.3, 130.0, 128.0, 127.1, 124.5, 124.2, 122.9, 115.8, 60.7, 40.5, 29.4, 14.7, 14.5; HRMS (TOF MS CI$^+$) calculated for $C_{19}H_{19}O_4$ $[M+H]^+$: 311.1283, found 311.1277.

*Ethyl 3-(4-benzoyl-5-phenylfuran-2-yl)-1H-indene-2-carboxylate (**2t**)*. 73.4 mg, 85% yield. Yellow solid; mp: 123-124 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17-8.10 (m, 1H), 8.00-7.94 (m, 2H), 7.89-7.83 (m, 2H), 7.72 (s, 1H), 7.58-7.53 (comp, 2H), 7.48-7.41 (comp, 4H), 7.41-7.35 (comp, 3H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.94 (s, 2H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 164.9, 155.6, 147.0, 143.4, 142.3, 138.8, 138.0, 133.2, 131.0, 130.0, 129.7, 129.5, 128.6, 128.6, 128.0, 127.7, 127.2, 124.3, 124.2, 122.5, 118.7, 60.7, 40.6, 14.4; HRMS (TOF MS CI$^+$) calculated for $C_{29}H_{23}O_4$ $[M+H]^+$: 435.1596, found 435.1587.

*Ethyl 3-(4-(4-chlorobenzoyl)-5-(4-chlorophenyl)furan-2-yl)-1H-indene-2-carboxylate (**2u**)*. 82.0 mg, 82% yield. Yellow solid; mp: 176-177 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09-8.03 (m, 1H), 7.94-7.89 (m, 2H), 7.88-7.81 (m, 2H), 7.68 (s, 1H), 7.58-7.53 (m, 1H), 7.47-7.40 (comp, 4H), 7.40-7.35 (m, 2H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.94 (s, 2H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.1, 164.8, 154.7, 147.3, 143.4, 142.1, 139.8, 138.7, 136.3, 135.7, 131.5, 131.4, 129.0, 129.0, 128.9, 128.2, 128.0, 127.2, 124.3, 124.1, 122.4, 118.7, 60.8, 40.6, 14.5; HRMS (TOF MS CI$^+$) calculated for $C_{29}H_{21}Cl_2O_4$ $[M+H]^+$: 503.0817, found 503.0812.

*Methyl 5-(2-(ethoxycarbonyl)-1H-inden-3-yl)-2-methylfuran-3-carboxylate (**2v**)*. 53.0 mg, 81% yield. Yellow solid; mp: 121-122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00-7.93 (m, 1H), 7.61 (s, 1H), 7.54-7.48 (m, 1H), 7.41-7.35 (comp, 2H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.871 (s, 2H), 3.865 (s, 3H), 2.72 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 164.5, 159.6, 146.4, 143.4, 142.4, 139.0, 130.3, 127.9, 127.0, 124.3, 124.1, 115.5, 115.1, 60.6, 51.6, 40.4, 14.4, 14.1; HRMS (TOF MS CI$^+$) calculated for $C_{19}H_{19}O_5$ $[M+H]^+$: 327.1232, found 327.1226.

*1-(5-(2-Benzoyl-1H-inden-3-yl)-2-methylfuran-3-yl)ethan-1-one (**2w**)*. 24.1 mg, 35% yield. Yellow solid; mp: 117-119 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (m, 1H), 7.78-7.71 (m,

2H), 7.60 (d, *J* = 6.9 Hz, 1H), 7.49-7.40 (comp, 3H), 7.32 (t, *J* = 7.7 Hz, 2H), 6.87 (s, 1H), 4.02 (s, 2H), 2.34 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5, 193.8, 158.9, 145.6, 143.5, 141.5, 140.0, 138.5, 135.5, 132.6, 128.9, 128.3, 127.7, 127.3, 124.6, 122.8, 122.5, 111.9, 41.2, 29.2, 14.1; HRMS (TOF MS CI$^+$) calculated for $C_{23}H_{19}O_3$ $[M+H]^+$: 343.1334, found 343.1331.

*3-(4-Acetyl-5-methylfuran-2-yl)-1H-indene-2-carbonitrile (**2x**).* 27.5 mg, 52% yield. Yellow solid; mp: 162-163 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17-8.03 (m, 1H), 7.58-7.50 (comp, 2H), 7.50-7.42 (comp, 2H), 3.83 (s, 2H), 2.77 (s, 3H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.9, 159.9, 145.8, 144.0, 143.3, 139.2, 128.9, 127.8, 124.4, 124.0, 123.3, 118.0, 113.4, 105.1, 40.8, 29.4, 14.8; HRMS (TOF MS CI$^+$) calculated for $C_{17}H_{14}NO_2$ $[M+H]^+$: 264.1025, found 264.1026.

General Procedure for Scale Up. To a 50-mL oven-dried round-bottom flask with a magnetic stirring bar, enynone **1j** (1.18 g, 3.0 mmol), $CuSO_4{\cdot}5H_2O$ (7.5 mg, 1.0 mol %), and anhydrous DCE (15.0 mL) was added in sequence under atmosphere of argon, and the reaction mixture was stirred at 55 °C for 2 h. When the reaction was completed (monitored by TLC), the solvent was evaporated *in vacuo* and the residue was purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 10:1 to 5:1) to give 1.11 g of pure **2j** (94% yield).

Procedure for the Preparation of 3j.[25] To a 10-mL oven-dried vial containing a magnetic stirring bar, **2j** (39.3 mg, 0.1 mmol), AIBN (32.8 mg, 0.2 mmol), *n*-Bu_3SnH (40 μL, 0.15 mmol) and anhydrous toluene (2.0 mL) was added in sequence under atmosphere of argon, and the reaction mixture was stirred at 110 °C for 30 minutes. When the reaction was completed (monitored by TLC), the solvent was evaporated *in vacuo* and the residue was purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 10:1 to 5:1) to afford 25.0 mg of pure **3j** (80% yield). Yellow solid; mp: 200-202 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67-8.59 (m, 1H), 8.10 (d, *J* = 7.5 Hz, 1H), 8.03-7.96 (m, 1H), 7.60 (d, *J* = 7.4 Hz, 1H), 7.56-7.49 (m, 2H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.39-7.32 (m, 1H), 4.12 (s, 2H), 2.78 (s, 3H), 2.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 157.5, 147.3, 143.5, 140.0, 138.8, 128.5, 127.1, 127.0, 126.5, 126.4, 125.8, 125.5, 125.1, 124.9, 124.7, 122.4, 121.9, 120.4, 36.7, 32.2, 15.4; HRMS (TOF MS CI$^+$) calculated for $C_{22}H_{17}O_2$ $[M+H]^+$: 313.1229, found 313.1224.

Procedure for the Preparation of 4j. To a 25-mL oven-dried round-bottom flask with a magnetic stirring bar, **2j** (78.4 mg, 0.2 mmol), 4-methoxyphenylboronic acid (60.8 mg, 0.4 mmol), Na_2CO_3 (53 mg, 0.5 mmol), $Pd(PPh_3)_4$ (11.6 mg, 5 mol %), water (0.5 mL) and DME (3.5 mL) was added in sequence under atmosphere of argon, and the reaction mixture was heated to reflux overnight. When the reaction was completed (monitored by TLC), the solvent was evaporated *in vacuo* and the residue was purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 10:1 to 4:1) to afford 65.5 mg of pure **4j** (78% yield). Yellow solid; mp: 78-80 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.6 Hz, 1H), 7.42 (comp, 2H), 7.33 (comp, 4H), 7.24-7.19 (m, 1H), 7.18-7.08 (m, 2H), 6.81-6.68 (m, 2H), 6.33 (s, 1H), 3.74 (s, 3H), 3.44 (s, 2H), 2.57 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194., 158.7, 157.4, 148.2, 144.9, 143.1, 143.0, 140.7, 136.4, 133.8, 130.3, 130.1, 129.9, 129.5, 128.2, 127.1, 126.6, 125.2, 123.7, 122.7, 121.3, 113.8, 109.1, 55.3, 43.2, 29.2, 14.6; HRMS (TOF MS CI$^+$) calculated for $C_{29}H_{25}O_3$ $[M+H]^+$: 421.1804, found 421.1802.

Procedure for the Preparation of 2y and 2y'. To a 10-mL oven-dried vial containing a magnetic stirring bar, **1y** (64.8 mg, 0.2 mmol), $CuSO_4{\cdot}5H_2O$ (0.5 mg, 1.0 mol %) and anhydrous DCE (2.0 mL) was added in sequence under atmosphere of argon, and the reaction mixture was stirred at 55 °C for 16 h. When the reaction was completed (monitored by TLC), the solvent was evaporated *in vacuo* and the residue was purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 10:1 to 7.5:1) to afford 41.0 mg of **2y** and 4.0 mg of **2y'** in total 70% yield.

To a 10-mL oven-dried vial containing a magnetic stirring bar, **1y** (64.8 mg, 0.2 mmol), CuCl (1.0 mg, 5.0 mol %) and anhydrous DCE (2.0 mL) was added in sequence under atmosphere of argon, and the reaction mixture was stirred at room temperature for 16 hours. When the reaction was completed (monitored by TLC), the solvent was evaporated *in vacuo* and the residue was purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 10:1 to 7.5:1) to afford 40.8 mg of **2y** and 12.3 mg of **2y'** in total 82% yield.

*Ethyl 3-(4-acetyl-5-methylfuran-2-yl)-1-methyl-1H-indene-2-carboxylate (**2y**).* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.89 (m, 1H), 7.55 (s, 1H), 7.51-7.45 (m, 1H), 7.43-7.35 (m, 2H), 4.42-4.24 (m, 2H), 3.98 (q, *J* = 7.4 Hz, 1H), 2.72 (s, 3H), 2.50 (s, 2H), 1.48 (d, *J* = 7.4 Hz, 3H), 1.36 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.4, 165.1, 158.9, 149.5, 146.2, 140.7, 137.7, 136.3, 128.2, 127.2, 124.2, 123.3, 122.9, 115.0, 60.7, 46.0, 29.4, 16.9, 14.7, 14.5; HRMS (TOF MS CI$^+$) calculated for $C_{20}H_{21}O_4$ $[M+H]^+$: 325.1440, found 325.1436.

*Ethyl 1-(4-acetyl-5-methylfuran-2-yl)-3-methyl-1H-indene-2-carboxylate (**2y'**).* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.49 (m, 1H), 7.43-7.32 (m, 3H), 6.31 (s, 1H), 4.94 (d, *J* = 2.1 Hz, 1H), 4.36-4.12 (m, 2H), 2.60 (d, *J* = 2.2 Hz, 3H), 2.50 (s, 3H), 2.34 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 165.2, 157.6, 152.9, 150.3, 145.1, 143.9, 131.0, 128.7, 127.8, 124.1, 122.3, 121.7, 106.5, 60.2, 48.9, 29.3, 14.6, 14.4, 12.8; HRMS (TOF MS CI$^+$) calculated for $C_{20}H_{21}O_4$ $[M+H]^+$: 325.1440, found 325.1436.

Control Experiment of 2y and 2y'. To a 10-mL oven-dried vial containing a magnetic stirring bar, **2y'** (32.4 mg, 0.1 mmol), $CuSO_4{\cdot}5H_2O$ (0.3 mg, 1.0 mol %) and anhydrous DCE (1.0 mL) was added in sequence under atmosphere of argon. After stirring for 16 hours at 55 °C, the reaction mixture was concentrated *in vacuo*. The residue was subjected to proton NMR analysis and only signals of compound **2y'** was observed.

To a 10-mL oven-dried vial containing a magnetic stirring bar, **2y** (32.4 mg, 0.1 mmol), $CuSO_4{\cdot}5H_2O$ (0.3 mg, 1.0 mol %) and anhydrous DCE (1.0 mL) was added in sequence under atmosphere of argon. After stirring for 16 hours at 55 °C, the reaction mixture was concentrated *in vacuo*. The residue was

subjected to proton NMR analysis and only signals of compound **2y** was observed.

Isotope-Labeled Experiment. To a 10-mL oven-dried vial containing a magnetic stirring bar, **1f-*d*** (> 95% D, 34.5 mg, 0.1 mmol), $CuSO_4{\cdot}5H_2O$ (0.3 mg, 1.0 mol %) and anhydrous DCE (2.0 mL) was added in sequence under atmosphere of argon, and the reaction mixture was stirred at 55 ^oC for 2 h. When the reaction was completed (monitored by TLC), the solvent was evaporated *in vacuo* and the residue was purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 10:1 to 7.5:1) to afford 31.8 mg of pure **2f-*d*** (92% yield, > 95% D, see Figure S1). **2f-*d*:** Yellow solid; mp: 113-114 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 7.6 Hz, 1H), 7.51 (d, J = 8.0 Hz, 1H), 7.37 (comp, 3H), 7.30-7.25 (m, 1H), 6.94-6.89 (m, 2H), 6.70 (s, 1H), 3.86 (s, 4H), 2.65 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 159.4, 157.7, 147.6, 144.6, 144.3, 142.0, 129.5, 129.1, 126.8, 126.7, 125.2, 123.7, 122.8, 120.5, 113.8, 109.5, 55.4, 29.3, 14.6; HRMS (TOF MS CI^+) calculated for $C_{23}H_{20}DO_3$ $[M+H]^+$: 346.1553, found 346.1549.

Computational Methods. All of the calculations were performed with the Gaussian 09 program.[26] Geometry optimizations of all the minima and transition states involved were carried out at the B3LYP level of theory[27] in the gas phase. The SDD basis set[28] and pseudopotential were used for Cu and the 6-31G(d) basis set[29] for the other atoms. The key word "5D" was used to specify that five d-type orbitals were used for all elements in the calculations. For open-shell species, (U)B3LYP method was used. Frequency calculations at the same level were performed to validate each structure as either a minimum or a transition state and to evaluate its zero-point energy and the thermal corrections at 298 K. Key transition-state structures were confirmed to connect corresponding reactants and products by intrinsic reaction coordinate (IRC) calculations.[30] Solvation energies in dichloroethane (ε = 10.125) were evaluated by IEFPCM calculations with radii and non-electrostatic terms for SMD solvation model[31] using the gas-phase optimized structures. Standard state concentrations of 1.0 mol/L were used for all species in calculations. To improve the calculation accuracy, single-point energies calculations were computed at the B3LYP level of theory with the SDD basis set and pseudopotential for Cu and the 6-311+G(d,p) basis set[32] for the other atoms.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge via the Internet at http://pubs.acs.org."

Computational results, ^1H and ^{13}C NMR spectra (PDF).

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Notes

The authors declare no competing financial interest.

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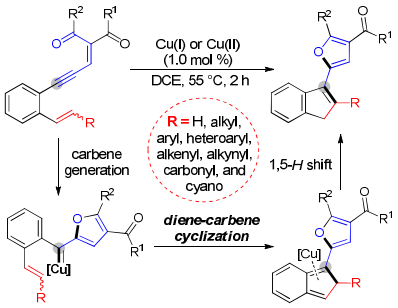
Cu(I) or Cu(II)
(1.0 mol %)
DCE, 55 °C, 2 h
R = H, alkyl, aryl, heteroaryl, alkenyl, alkynyl, carbonyl, and cyano
carbene generation
1,5-H shift
diene-carbene cyclization
[Cu]