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Gold-Catalyzed Approach to Multisubstituted Fulvenes via Cycloisomerization of Furan/Ynes

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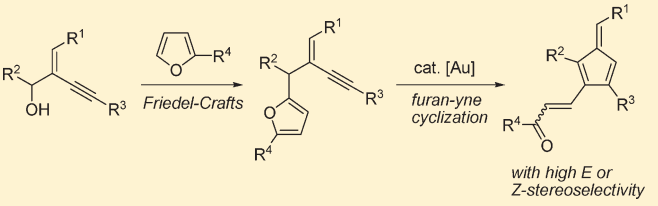
Supporting Information

ABSTRACT: A new approach to functionalized fulvenes with an enone or enal moiety has been developed through gold-catalyzed intramolecular cycloisomerization of furan/ynes with a two-carbon tether in between the furan and the triple bond. The reaction proceeds with complete regioselectivity via a 6-*endo*-cyclization and high stereoselectivity. Moreover, the *E*- or *Z*-stereochemistry of the double bond in fulvene products can be easily controlled by performing the reaction in different solvents.



INTRODUCTION

Fulvenes, which exhibit intriguing cross-conjugated molecular structures, have attracted much attention in theoretical studies,[1] as precursors of cyclopentadienyl ligands for metallocene synthesis,[2] and in natural product synthesis.[3] They can also undergo a diverse array of cycloaddition reactions such as [4 + 2],[4a,b] [6 + 2],[4c−e] and [6 + 3][4f] cyclizations for the construction of fused ring systems.[4] In general, fulvenes are prepared by the condensation reactions of cyclopentadienes with ketones or aldehydes in the presence of an alkali metal base[5,6] or through pyrrolidine-promoted reactions.[7] However, strongly alkaline conditions limit the substrate scope of these methodologies. Fulvenes could also be prepared by transition-metal-catalyzed reactions, such as Pd-catalyzed cross-coupling reactions of alkynes with vinyl halides,[8] Pd-catalyzed cyclotrimerization of alkynes,[9] or Ti-catalyzed cyclotrimerization of *tert*-butylacetylene.[10] However, these reactions were restricted to internal alkynes or special substituted terminal alkynes. Recently, a silver-catalyzed Nazarov-type cyclization of α-hydroxyallenes to benzofulvenes has been reported.[11] Despite progress in this area, the development of synthetic routes that allow the facile assembly of functionalized fulvenes under mild reaction conditions still remains an important objective. Recently, we have developed a new domino approach for the synthesis of substituted benzenes bearing enone or enal functionalities with excellent *Z*-stereoselectivity through gold(I)-catalyzed reactions of (*Z*)-2-en-4-yn-1-ols with furans (Scheme 1, eq 1).[12a] The gold catalyst was found to be quite efficient in catalyzing both the Friedel−Crafts and furan/alkyne[12−14] cyclization reactions with a highly regioselective manner of 7-*endo-dig* cyclization. We envisioned that the readily available enynols of 2-ylidene-buta-3-yn-1-ols **1** might also undergo the Friedel−Crafts reactions with furans to deliver the furanyl group in a close proximity to the alkyne moiety. We hypothesize that a new type of 6-*endo-dig* cyclization of the thus formed enynyl furans **2** might take place to generate fulvene derivatives via the π-complex between the gold catalyst and the alkyne (Scheme 1, eq 2). In this paper, we report our success in gold-catalyzed cycloisomerization reactions of enynyl furans **2** to functionalized fulvenes with controllable *E*- or *Z*-stereoselectivity. It is noted that there is no report for the ring-opening cyclization of furan/ynes with a two-carbon tether in between the furan and the alkyne moiety.[15]

RESULTS AND DISCUSSION

Initially, we focused on the development of a straightforward synthesis directly from enynols **1** and furan derivatives that combines the Friedel−Crafts and furan/alkyne cyclization reactions in a one-pot procedure. However, although much effort has been made, no satisfactory results were obtained. For example, reactions of enynol **1a** ($R^1 = R^2 = R^3 = Ph$) with 2 equiv of 2-methylfuran in the presence of 5 mol % gold catalysts such as $PPh_3AuCl/AgOTf$, $PPh_3AuCl/AgBF_4$, or PPh_3AuNTf_2 in CH_2Cl_2 gave a complicated mixture. We then decided to first synthesize the furanylated substrates **2** by Lewis-acid-catalyzed allylic substitution reactions. Optimization studies indicated that in the presence of 20 mol % of $BF_3 \cdot Et_2O$ the Friedel−Crafts reactions could be completed within 3−40 min, and good to high yields were achieved in most cases (Table 1). 2-Methylfuran, 2,3-disubstituted furan, 2-phenylfuran, and furan are all suitable for substitution reactions. The (*Z*)-configuration of the enyne double bond in **2** was determined by the 2D NOESY spectrum of compound **2h**. However, when enynol bearing two different substituents (R^1 and R^2) at both ends of the allylic moiety was employed, two regioisomers of **2l** were formed, which could not be separated by column chromatography (Table 1, entry 12). The failure of the regioselective substitution reactions of

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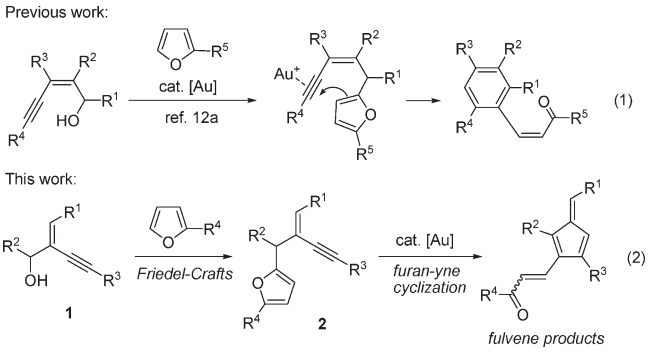
Scheme 1

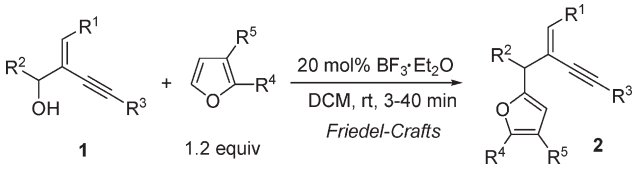


unsymmetrically substituted enynol **1** with furans was the limitations of the substrate synthesis.

With furan-ynes **2** in hand, we were interested in exploring the feasibility of **2** in gold-catalyzed cycloisomerization reactions. We first tried the cyclization reaction of **2a** with PPh_3AuTf_2 (5 mol %) as the catalyst in CH_2Cl_2. It was found that fulvene **3a** with an enone moiety was formed in 52% yield as a single geometric isomer (Table 2, entry 1). Unlike the previously reported benzene formation,[12a] in this case, the *E*-isomer of the enone moiety instead of the *Z*-isomer was obtained. Cyclization of **2a** with PPh_3AuOTf as the catalyst in CH_2Cl_2 at 50 °C led to 72% yield of **3a** as an *E*-isomer exclusively within 30 min (entry 3). The reaction could also be performed in DCE or toluene to produce the desired **3a** in 58% and 68% yields, respectively (entries 4 and 5). PPh_3AuBF_4 and PPh_3AuSbF_6 could also be used as the catalysts, furnishing **3a** in 52−59% yield, whereas gold(III) of $NaAuCl_4 \cdot 2H_2O$ afforded a low yield of **3a** (entries 6−8). Interestingly, switching the solvent to coordinating solvents such as 1,4-dioxane or THF provided the (*Z*)-isomer **4a** in high yields of 89−97% with high stereoselectivity (entries 9 and 10). It is probably due to the coordination of the electrophilic gold cation species by the solvent molecule, which would decrease the Lewis acidity of the gold catalyst to prevent the sequential *Z*−*E* isomerization reactions.[16] The *Z*/*E* ratio changed only slightly in THF when elevating the reaction temperature to 50 °C (entry 11). As a control, the reaction was run in the absence of a gold catalyst (entry 12). As expected, AgOTf alone did not promote any transformation. The above results indicated that by choosing the appropriate solvents it is possible to obtain either the *E*- or *Z*-isomer of the desired fulvenes.

After establishing the optimized conditions for both of the double bond isomers **3** and **4** (Table 2, entry 3 for *E*-isomer **3**, entry 10 for *Z*-isomer **4**), we proceeded to examine the scope of this novel approach for the synthesis of fulvene derivatives. The results are shown in Table 3. In all cases, the *E*/*Z* isomers **3** and **4** were obtained with high levels of stereoselectivity regardless of the substitution patterns of enynes **2**. Generally, *Z*-isomer **4** was obtained in better yields than that of the *E*-isomer **3**. The structure of **3b** was unambiguously determined by X-ray crystallographic analysis.[17] The substituent effects (R^4, R^5) on the furan moiety were first investigated. 2-Phenyl and 2,3-dimethyl substituents were all compatible under the cyclization conditions, yielding multisubstituted fulvenes in good yields (Table 3, entries 2 and 3). In the reaction of R^4-phenyl-substituted **2b** in THF, Luche reduction was performed to allow for product purification after the cyclization was completed (entry 2, for product **5b**). When enyne **2c** unsubstituted

Table 1. Lewis-Acid-Catalyzed Substitution of Enynols 1 with Furans



entry	R^1	R^2	R^3	R^4	R^5	product	yield (%)[a]
1	Ph	Ph	Ph	Me	H	**2a**	95
2	Ph	Ph	Ph	Ph	H	**2b**	94
3	Ph	Ph	Ph	Me	Me	**2c**	88
4	Ph	Ph	Ph	H	H	**2d**	42
5	Ph	Ph	*p*-MeC_6H_4	Me	H	**2e**	74
6	Ph	Ph	3,4,5-$(OMe)_3C_6H_2$	Me	H	**2f**	56
7	Ph	Ph	*p*-ClC_6H_4	Me	H	**2g**	94
8	Ph	Ph	*p*-$NO_2C_6H_4$	Me	H	**2h**	—[b]
9	Ph	Ph	H	Me	H	**2i**	—[c]
10	Ph	Ph	cyclohexenyl	Me	H	**2j**	55
11	Ph	Ph	cyclopropyl	Me	H	**2k**	89
12	Ph	*p*-ClC_6H_4	Ph	Me	H	**2l**	97[d]

[a] Isolated yields. [b] Prepared by Sonogashira coupling of 1-iodo-4-nitrobenzene with **2i**. [c] Not calculated. [d] Two regioisomers were obtained in a ratio of 1.3:1.

both at C-2 and C-3 on the furan ring was subjected to this gold-catalyzed reaction, the expected cyclization occurred smoothly to generate *E*- or *Z*-enals **3d** and **4d** in high yields of 80% and 83%, respectively (entry 4). The substituent effects of the aryl groups on the alkyne terminus (R^3) were also examined. It was found that the functionalities of Me, MeO, Cl, and NO_2 were well tolerated. The electronic properties of these aryl substituents had an influence on the reaction process for the formation of the *E*-isomer **3**, and enynes with an electron-withdrawing group usually afforded higher yields of fulvenes **3** than that of the substrates with an electron-donating group (entries 5−8). Notably, when terminal alkyne **2i** was employed, the desired furans **3i** and **4i** were still obtained in moderate yield via an *endo*-cyclization (entry 9). The result is in sharp contrast with the analogous gold-catalyzed cycloisomerization of furan/ynes bearing a terminal alkyne moiety reported previously, which proceeded with *exo*-type cyclization exclusively.[13a−g] Perhaps in our case, less strained intermediates were generated upon *endo*-cyclization during the reaction. Cyclohexenyl or cyclopropyl tethered alkynes also underwent the cyclization reactions readily in THF to give the corresponding fulvenes **4j** and **4k** in 62−79% yields (entries 10 and 11). However, when the reactions were performed in CH_2Cl_2, either complicated results or low yield (**3k**) of the desired product was observed.

The apparent ring opening of furans to enone-type products led us to propose the mechanism depicted in Scheme 2.[12a,13g] Initial coordination of the gold catalyst to the triple bond affords intermediate **6**. This is followed by intramolecular furan/yne cyclization in a highly regioselective 6-*endo*-*dig* manner to form a cyclopropyl gold carbenoid **8**.[18] Rearrangement of **8** followed by deprotonation and deauration leads to fulvene **4** with a *Z*-enone moiety. It should be noted that the *endo*-type cyclization in furan/yne cycloisomerization is quite rare.[12,13h] The *E*-isomer **3**

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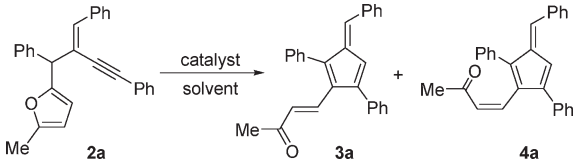
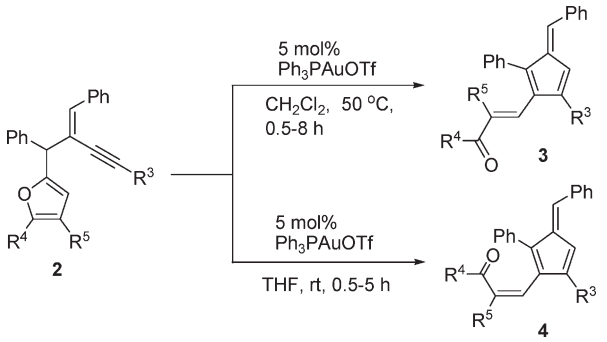
Table 2. Optimization Studies for the Formation of Fulvenes



entry	catalyst (5 mol %)	solvent	temp (°C)	time (h)	yield (%)[a] of **3a** and/or **4a**
1	PPh_3AuNTf_2	CH_2Cl_2	rt	2	52 (**3a**)
2	PPh_3AuOTf	CH_2Cl_2	rt	2	65 (95:5)[b]
3[c]	PPh_3AuOTf	CH_2Cl_2	50	0.5	72 (**3a**)
4	PPh_3AuOTf	DCE	50	2	58 (**3a**)
5	PPh_3AuOTf	toluene	50	2	68 (**3a**)
6	PPh_3AuBF_4	CH_2Cl_2	rt	4	59 (**3a**)
7	PPh_3AuSbF_6	CH_2Cl_2	rt	4	52 (**3a**)
8	$NaAuCl_4 \cdot 2H_2O$	CH_2Cl_2	rt	6	37 (**3a**)[d]
9	PPh_3AuOTf	1,4-dioxane	rt	4	89 (3:97)[b]
10	PPh_3AuOTf	THF	rt	4	97 (**4a**)
11	PPh_3AuOTf	THF	50	4	95 (5:95)[b]
12	AgOTf	CH_2Cl_2	rt	2	NR[e]
13	$PtCl_2$	DCE	80	5	[f]

[a] Isolated yield. [b] The ratio of **3a**:**4a** is shown in parentheses. [c] In a sealed tube. [d] 40% of starting material was recovered. [e] NR = no reaction. [f] Most of **2a** remained.

Table 3. Synthesis of Fulvenes through Gold(I)-Catalyzed Cyclization of Furan/Ynes

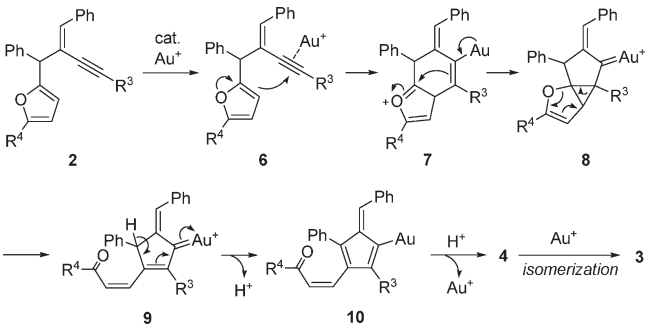


entry	substrate	R^3	R^4	R^5	yield (%)[a] of **3**		yield (%)[a] of **4**	
1	**2a**	Ph	Me	H	**3a**	72	**4a**	97
2	**2b**	Ph	Ph	H	**3b**	59	**5b**[b]	58
3	**2c**	Ph	Me	Me	**3c**	65	**4c**	77[c]
4	**2d**	Ph	H	H	**3d**	80[d]	**4d**	83[e,f]
5	**2e**	*p*-MeC_6H_4	Me	H	**3e**	51	**4e**	97
6	**2f**	3,4,5-$(OMe)_3C_6H_2$	Me	H	**3f**	55	**4f**	82
7	**2g**	*p*-ClC_6H_4	Me	H	**3g**	70	**4g**	93[e]
8	**2h**	*p*-$NO_2C_6H_4$	Me	H	**3h**	82	**4h**	87[e,f]
9	**2i**	H	Me	H	**3i**	45	**4i**	48[f]
10	**2j**	cyclohexenyl	Me	H	-		**4j**	79
11	**2k**	cyclopropyl	Me	H	**3k**	30	**4k**	62

[a] Isolated yield. [b] After Luche reduction. **5b** is (*Z*)-3-((*E*)-3-benzylidene-2,5-diphenylcyclopenta-1,4-dienyl)-1-phenylprop-2-en-1-ol. [c] *Z*:*E* = 20:1. [d] *E*:*Z* = 25:1. [e] *Z*:*E* = 50:1. [f] The reaction was performed at 50 °C.

might be formed by gold-assisted isomerization of **4** through the formation of zwitterionic intermediates.[16]

Scheme 2



CONCLUSION

In summary, we have developed an efficient gold-catalyzed intramolecular furan/yne cyclization reaction to form functionalized fulvenes with an enone or enal moiety under mild reaction conditions. Notably, the reactions reported here represent the first examples of gold-catalyzed ring-opening cyclizations of furan/ynes with a shortest tether in between furan and the alkyne moiety. The stereochemistry of the enone double bond can be easily controlled by simply changing the solvents. A variety of furan/yne substrates turned out to be applicable to this catalytic system.

EXPERIMENTAL SECTION

General Methods. All reactions were carried out under argon. DCE and DCM were distilled from P_2O_5. THF and Toluene were distilled from sodium and benzophenone. Unless noted, all commercial reagents were used without further purification. Ph_3PAuCl[19] and $Ph_3PAuNTf_2$[20] were

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prepared according to the published method. AgOTf was used as a 0.05 M solution in THF.

^{1}H NMR spectra were recorded at 300 or 400 MHz, and ^{13}C NMR spectra were recorded at 75.4 or 100.6 MHz, in $CDCl_3$ (containing 0.03% TMS). ^{1}H NMR spectra were recorded with tetramethylsilane (δ = 0.00 ppm) as internal reference; ^{13}C NMR spectra were recorded with $CDCl_3$ (δ = 77.00 ppm) as internal reference.

General Procedure for the Synthesis of Enynols 1. *Typical Procedure for the Synthesis of (E)-2-Benzylidene-1,4-diphenylbut-3-yn-1-ol (**1a**).* To a solution of *Z*-α-bromocinnamaldehyde (2.11 g, 10 mmol) in triethylamine (10 mL) and THF (10 mL) were added phenylacetylene (1.22 g, 1.32 mL, 12 mmol), $Pd(PPh_3)_4$ (0.12 g, 0.10 mmol), and CuI (0.095 g, 0.50 mmol) at room temperature, and then the mixture was stirred overnight. After the starting material was consumed, the solvent was removed in vacuo, and the residue was purified by chromatography on silica gel (petroleum:ethyl acetate = 20:1 to 10:1) to afford compound (*E*)-2-benzylidene-4-phenylbut-3-ynal (**s-1a**) (2.31 g, 99%) as yellow oil. The spectroscopic data are in agreement with that previously reported.[21]

To a solution of bromobenzene (3.96 g, 2.7 mL, 25.2 mmol) in THF (50 mL) was added *n*-BuLi (10.0 mL, 25.2 mmol, 2.5 M solution in hexanes) at −78 °C. After stirring at the same temperature for 1 h, **s-1a** (4.88 g, 21.0 mmol in 50 mL of THF) was added. The resulting solution was warmed to room temperature and stirred for 8 h. Then the mixture was quenched with saturated ammonium chloride solution. The reaction mixture was extracted with ether and dried over anhydrous Na_2SO_4. The solvent was evaporated, and the residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to afford compound **1a** (6.49 g, 99%) as brown oil. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 3.11 (s, 1H), 5.36 (s, 1H), 6.95 (s, 1H), 7.19−7.33 (m, 11H), 7.47 (d, *J* = 7.2 Hz, 2H), 7.86 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si) δ 77.6, 87.1, 97.9, 122.9, 124.3, 126.5, 127.6, 128.10, 128.12, 128.2, 128.26, 128.32, 128.8, 131.3, 133.8, 135.8, 141.8. HRMS (EI) calcd for $C_{23}H_{18}O$: 310.1358, found 310.1357.

*(E)-2-Benzylidene-4-p-tolylbut-3-ynal (**s-1b**).* Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1) afforded the title product in 77% yield (5 mmol scale, 944 mg) as a brown oil. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 2.36 (s, 3H), 7.17 (d, *J* = 7.8 Hz, 2H), 7.45−7.49 (m, 6H), 8.12−8.14 (m, 2H), 9.61 (s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$, Me_4Si) δ 21.5, 82.6, 101.2, 119.4, 122.7, 128.7, 129.2, 130.6, 131.5, 131.7, 134.1, 139.3, 150.9, 191.0. HRMS (EI) calcd for $C_{18}H_{14}O$: 246.1045, found 246.1050.

*(E)-2-Benzylidene-4-(3,4,5-trimethoxyphenyl)but-3-ynal (**s-1c**).* Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1 to 5:1) afforded the title product in 87% yield (8 mmol scale, 2.25 g) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 3.88 (s, 9H), 6.82 (s, 2H), 7.48−7.54 (m, 4H), 8.12−8.14 (m, 2H), 9.64 (s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$, Me_4Si) δ 56.1, 60.9, 82.2, 100.9, 108.9, 117.4, 122.6, 128.7, 130.6, 131.6, 134.1, 139.4, 151.5, 153.1, 191.0. HRMS (EI) calcd for $C_{20}H_{18}O_4$: 322.1205, found 322.1206.

*(E)-2-Benzylidene-4-(4-chlorophenyl)but-3-ynal (**s-1d**).* Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1) afforded the title product in 90% (3 mmol scale, 717 mg) yield as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 7.33 (d, *J* = 9.0 Hz, 2H), 7.46−7.52 (m, 6H), 8.08−8.11 (m, 2H), 9.61 (s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$, Me_4Si) δ 84.0, 99.6, 120.9, 122.3, 128.75, 128.76, 130.6, 131.7, 132.9, 133.9, 135.1, 151.8, 190.8. HRMS (EI) calcd for $C_{17}H_{11}ClO$: 266.0498, found 266.0500.

*(E)-2-Benzylidene-4-(trimethylsilyl)but-3-ynal (**s-1e**).* Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 15:1) afforded the title product in 69% yield (5 mmol scale, 783 mg) as a yellow oil. The spectroscopic data are in agreement with that previously reported.[22]

*(E)-2-Benzylidene-4-cyclohexenylbut-3-ynal (**s-1f**).* Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 25:1) afforded the title product in 93% yield (8 mmol scale, 1.76 g) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 1.62−1.73 (m, 4H), 2.17−2.19 (m, 2H), 2.27−2.30 (m, 2H), 6.33−6.36 (m, 1H), 7.43−7.46 (m, 4H), 8.09 (dd, *J* = 5.7, 3.6 Hz, 2H), 9.57 (s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$, Me_4Si) δ 21.2, 22.0, 25.7, 28.6, 80.6, 103.1, 120.3, 122.9, 128.5, 130.4, 131.2, 134.1, 137.2, 150.2, 191.1. HRMS (EI) calcd for $C_{17}H_{16}O$: 236.1201, found 236.1203.

*(E)-2-Benzylidene-1-phenyl-4-p-tolylbut-3-yn-1-ol (**1b**).* Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1) afforded the title product in 85% yield (3.6 mmol scale, 996.2 mg) as a brown oil. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 2.31 (s, 3H), 2.70 (d, *J* = 3.9 Hz, 1H), 5.41 (d, *J* = 4.8 Hz, 1H), 6.94 (s, 1H), 7.08 (d, *J* = 8.1 Hz, 2H), 7.24−7.37 (m, 8H), 7.51 (d, *J* = 7.2 Hz, 2H), 7.89 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$, Me_4Si) δ 21.5, 77.7, 86.3, 98.4, 119.9, 124.5, 126.5, 127.8, 128.20, 128.24, 128.3, 128.8, 129.1, 131.3, 133.7, 135.9, 138.7, 141.9. HRMS (EI) calcd for $C_{24}H_{20}O$: 324.1514, found 324.1510.

*(E)-2-Benzylidene-1-phenyl-4-(3,4,5-trimethoxyphenyl)but-3-yn-1-ol (**1c**).* Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 3:1) afforded the title product in 69% yield (2.9 mmol scale, 805.4 mg) as a brown oil. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 2.45 (d, *J* = 5.7 Hz, 1H), 3.83 (s, 6H), 3.85 (s, 3H), 5.48 (d, *J* = 5.1 Hz, 1H), 6.58 (s, 2H), 7.00 (s, 1H), 7.32−7.39 (m, 6H), 7.54 (d, *J* = 7.2 Hz, 2H), 7.90 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 56.0, 60.9, 77.6, 86.2, 98.1, 108.6, 117.9, 124.3, 126.6, 127.7, 128.15, 128.20, 128.4, 128.8, 134.0, 135.9, 138.9, 141.9, 152.9. HRMS (EI) calcd for $C_{26}H_{24}O_4$: 400.1675, found 400.1672.

*(E)-2-Benzylidene-4-(4-chlorophenyl)-1-phenylbut-3-yn-1-ol (**1d**).* Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1) afforded the title product in 59% yield (3.7 mmol scale, 753.7 mg) as a brown oil. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 3.27 (d, *J* = 0.6 Hz, 1H), 5.34 (s, 1H), 6.94 (s, 1H), 7.14−7.31 (m, 10H), 7.44 (d, *J* = 7.5 Hz, 2H), 7.81 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$, Me_4Si) δ 77.5, 88.0, 96.6, 121.3, 124.0, 126.4, 127.7, 128.1, 128.4, 128.5, 128.8, 132.5, 134.27, 134.29, 135.7, 141.6. HRMS (EI) calcd for $C_{23}H_{17}ClO$: 344.0968, found 344.0962.

*(E)-2-Benzylidene-1-phenyl-4-(trimethylsilyl)but-3-yn-1-ol (**1e**).* Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 3:1) afforded the title product in 84% yield (3.1 mmol scale, 798.7 mg) as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 0.34 (s, 9H), 2.72 (d, *J* = 5.2 Hz, 1H), 5.49 (d, *J* = 4.8 Hz, 1H), 7.05 (s, 1H), 7.43−7.52 (m, 6H), 7.61−7.63 (m, 2H), 8.03−8.05 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si) δ −0.4, 77.4, 102.3, 105.0, 124.3, 126.6, 127.8, 128.06, 128.2, 128.6, 128.9, 134.8, 135.6, 141.7. HRMS (EI) calcd for $C_{20}H_{22}OSi$: 306.1440, found 306.1438.

*(E)-2-Benzylidene-4-cyclohexenyl-1-phenylbut-3-yn-1-ol (**1f**).* Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20:1 to 10:1) afforded the title product in 33% yield (7.2 mmol scale, 806.8 mg) as a brown oil. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 1.55−1.61 (m, 4H), 2.09−2.11 (m, 4H), 2.63 (s, 1H), 5.33 (s, 1H), 6.08 (s, 1H), 6.85 (s, 1H), 7.24−7.35 (m, 6H), 7.46 (d, *J* = 7.5 Hz, 2H), 7.84 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$, Me_4Si) δ 21.3, 22.1, 25.7, 28.6, 77.7, 84.2, 100.5, 120.7, 124.7, 126.4, 127.6, 128.06, 128.11, 128.13, 128.7, 132.8, 135.9, 136.0, 142.0. HRMS (EI) calcd for $C_{23}H_{22}O$: 314.1671, found 314.1674.

*(E)-2-Benzylidene-1-(4-chlorophenyl)-4-phenylbut-3-yn-1-ol (**1g**).* Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 7:1) afforded the title product in 77% yield (3 mmol scale, 792.5 mg) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 2.79 (bs, 1H), 5.38 (s, 1H), 6.94 (s, 1H), 7.26−7.37 (m, 10H), 7.42−7.44 (m, 2H), 7.87−7.89 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$, Me_4Si) δ 77.2, 86.6, 98.3, 122.7, 123.9, 127.9, 128.3, 128.36, 128.37, 128.61, 128.63,

128.9, 131.4, 133.5, 134.4, 135.6, 140.3. HRMS (EI) calcd for $C_{23}H_{17}ClO$: 344.0968, found 344.0969.

Typical Procedure for the Synthesis of (*Z*)-2-(2-Benzylidene-1,4-diphenylbut-3-ynyl)-5-methylfuran (2a). To a solution of (*E*)-2-benzylidene-1,4-diphenylbut-3-yn-1-ol **1a** (62 mg, 0.2 mmol) in DCM (2 mL) were added 2-methylfuran (19.7 mg, 22 μL, 0.24 mmol) and $BF_3 \cdot Et_2O$ (5.0 μL, 0.04 mmol). The resulting solution was stirred at room temperature until the reaction was complete as monitored by thin-layer chromatography. The solvent was evaporated in vacuo, and the residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1) to afford the title product **2a** (70.7 mg, 95%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 2.25 (s, 3H), 5.07 (s, 1H), 5.91 (d, *J* = 2.0 Hz, 1H), 6.08 (d, *J* = 2.8 Hz, 1H), 6.63 (s, 1H), 7.23−7.26 (m, 5H), 7.31−7.34 (m, 6H), 7.40 (d, *J* = 7.6 Hz, 1H), 7.88 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si) δ 13.6, 53.5, 89.3, 97.0, 106.1, 109.1, 122.7, 123.4, 127.0, 128.1, 128.25, 128.27, 128.8, 131.4, 135.9, 136.3, 140.2, 151.4, 153.1. HRMS (EI) calcd for $C_{28}H_{22}O$: 374.1671, found 374.1673.

(Z)-2-(2-Benzylidene-1,4-diphenylbut-3-ynyl)-5-phenylfuran (***2b***). Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1) afforded the title product in 94% yield (2 mmol scale, 821.1 mg) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 5.18 (s, 1H), 6.29 (d, *J* = 3.3 Hz, 1H), 6.57 (d, *J* = 3.3 Hz, 1H), 6.68 (s, 1H), 7.11−7.31 (m, 14H), 7.43 (d, *J* = 7.8 Hz, 2H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.88 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$, Me_4Si) δ 53.6, 89.2, 97.2, 105.7, 110.7, 122.4, 123.1, 123.5, 127.0, 127.1, 128.1, 128.19, 128.22, 128.27, 128.31, 128.5, 128.7, 130.8, 131.3, 136.1, 136.2, 139.9, 153.3, 154.6. HRMS (EI) calcd for $C_{33}H_{24}O$: 436.1827, found 436.1833.

(Z)-5-(2-Benzylidene-1,4-diphenylbut-3-ynyl)-2,3-dimethylfuran (***2c***). It was synthesized from (*Z*)-2-benzylidene-1,4-diphenylbut-3-yn-1-ol **1a** (0.62 g, 2 mmol), DCM (20 mL), 2,3-dimethylfuran (0.25 mL, 2.4 mmol), and $BF_3 \cdot Et_2O$ (50 μL, 0.4 mmol) according to the procedure described for **2a**. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1) afforded the title product (0.68 g, 88%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 1.87 (s, 3H), 2.14 (s, 3H), 5.04 (s, 1H), 5.98 (s, 1H), 6.64 (s, 1H), 7.18−7.22 (m, 5H), 7.27−7.31 (m, 6H), 7.39−7.41 (m, 2H), 7.86−7.88 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si) δ 9.9, 11.3, 53.5, 89.4, 97.0, 111.7, 114.3, 122.8, 123.3, 126.9, 128.06, 128.08, 128.18, 128.20, 128.22, 128.7, 128.8, 131.3, 135.9, 136.3, 140.3, 146.6, 151.9. HRMS (EI) calcd for $C_{29}H_{24}O$: 388.1827, found 388.1826.

(Z)-2-(2-Benzylidene-1,4-diphenylbut-3-ynyl)furan (***2d***). It was synthesized from (*Z*)-2-benzylidene-1,4-diphenylbut-3-yn-1-ol **1a** (0.31 g, 1 mmol in 10 mL of DCM), furan (0.37 mL, 5.0 mmol), and $BF_3 \cdot Et_2O$ (25 μL, 0.2 mmol) according to the procedure described for **2a**. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1) afforded the title product (151.3 mg, 42%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 5.12 (s, 1H), 6.23 (d, *J* = 3.6 Hz, 1H), 6.40 (dd, *J* = 3.0, 1.6 Hz, 1H), 6.63 (s, 1H), 7.26−7.40 (m, 14H), 7.88 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si) δ 53.4, 89.1, 97.2, 108.3, 110.2, 122.4, 123.2, 127.1, 128.1, 128.17, 128.23, 128.27, 128.31, 128.72, 128.73, 131.3, 136.1, 136.2, 140.0, 141.8, 155.1. HRMS (EI) calcd for $C_{27}H_{20}O$: 360.1514, found 360.1518.

(Z)-2-(2-Benzylidene-1-phenyl-4-p-tolylbut-3-ynyl)-5-methylfuran (***2e***). Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1) afforded the title product in 74% yield (2.9 mmol scale, 834.6 mg) as a blue oil. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 2.25 (s, 3H), 2.30 (s, 3H), 5.06 (s, 1H), 5.90 (d, *J* = 1.2 Hz, 1H), 6.08 (d, *J* = 2.7 Hz, 1H), 6.61 (s, 1H), 7.07 (d, *J* = 7.8 Hz, 2H), 7.24 (t, *J* = 7.5 Hz, 4H), 7.32 (t, *J* = 6.9 Hz, 4H), 7.40 (d, *J* = 7.5 Hz, 2H), 7.88 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$, Me_4Si) δ 13.6, 21.5, 53.6, 88.7, 97.4, 106.1, 109.1, 120.3, 122.8, 126.9, 128.0, 128.1, 128.2, 128.7, 128.8, 129.0, 131.3, 135.5, 136.4, 138.4, 140.3, 151.4, 153.2. HRMS (EI) calcd for $C_{29}H_{24}O$: 388.1827, found 388.1833.

(Z)-2-(2-Benzylidene-1-phenyl-4-(3,4,5-trimethoxyphenyl)but-3-ynyl)-5-methylfuran (***2f***). Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) afforded the title product in 56% yield (1 mmol scale, 260.8 mg) as a yellow oil. ^{1}H NMR 400 MHz, $CDCl_3$, Me_4Si) δ 2.25 (s, 3H), 3.77 (s, 6H), 3.82 (s, 3H), 5.09 (s, 1H), 5.91 (d, *J* = 0.8 Hz, 1H), 6.08 (d, *J* = 3.2 Hz, 1H), 6.52 (s, 2H), 6.63 (s, 1H), 7.23−7.25 (m, 2H), 7.32 (t, *J* = 7.6 Hz, 4H), 7.40 (d, *J* = 7.2 Hz, 2H), 7.86 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si) δ 13.5, 53.2, 55.9, 60.7, 88.4, 97.1, 106.0, 108.4, 109.0, 118.2, 122.5, 126.8, 128.0, 128.1, 128.6, 128.7, 135.7, 136.2, 140.2, 151.3, 152.9, 153.0. HRMS (EI) calcd for $C_{31}H_{28}O_4$: 464.1988, found 464.1991.

(Z)-2-(2-Benzylidene-4-(4-chlorophenyl)-1-phenylbut-3-ynyl)-5-methylfuran (***2g***). Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1) afforded the title product in 94% yield (1 mmol scale, 384.3 mg) as a yellow oil. ^{1}H NMR 400 MHz, $CDCl_3$, Me_4Si) δ 2.22 (s, 3H), 5.07 (s, 1H), 5.89−5.90 (m, 1H), 6.07 (d, *J* = 3.2 Hz, 1H), 6.64 (s, 1H), 7.18−7.23 (m, 6H), 7.27−7.32 (m, 4H), 7.37−7.39 (m, 2H), 7.82−7.84 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si) δ 13.6, 53.4, 90.3, 95.7, 106.1, 109.2, 121.7, 122.4, 127.0, 128.1, 128.2, 128.3, 128.6, 128.7, 132.5, 134.2, 136.2, 136.4, 140.1, 151.4, 153.0. HRMS (EI) calcd for $C_{28}H_{21}ClO$: 408.1281, found 408.1280.

Synthesis of (Z)-2-(2-Benzylidene-4-(4-nitrophenyl)-1-phenylbut-3-ynyl)-5-methylfuran (***2h***). To a solution of (*Z*)-2-(2-benzylidene-1-phenylbut-3-ynyl)-5-methylfuran **2i** (see below, 0.33 g, 1.1 mmol) in triethylamine (5 mL) were added 1-iodo-4-nitrobenzene (0.25 g, 1.0 mmol), $PdCl_2(PPh_3)_2$ (14 mg, 0.02 mmol), and CuI (9.5 mg, 0.05 mmol) at room temperature, and then the mixture was heated at 50 °C for 5 h. After the starting material was consumed, the solvent was removed in vacuo, and a saturated NH_4Cl solution was added. The reaction mixture was extracted with ether and dried over anhydrous Na_2SO_4. The solvent was evaporated, and the residue was purified by chromatography on silica gel (petroleum:dichloromethane = 10:1) to afford the title compound (278.9 mg, 66%) as a yellow solid. Mp 86−87 °C. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 2.26 (s, 3H), 5.10 (s, 1H), 5.93(s, 1H), 6.07 (d, *J* = 1.6 Hz, 1H), 6.74 (s, 1H), 7.26−7.40 (m, 10 H), 7.81 (d, *J* = 8.0 Hz, 2H), 8.08 (d, *J* = 9.2 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si) δ 13.5, 53.0, 94.5, 94.6, 106.1, 109.3, 121.9, 123.4, 127.1, 128.2, 128.3, 128.60, 128.64, 128.8, 129.6, 131.8, 135.8, 138.0, 139.8, 146.7, 151.6, 152.7. HRMS (EI) calcd for $C_{28}H_{21}NO_3$: 419.1521, found 419.1528.

Synthesis of (Z)-2-(2-Benzylidene-1-phenylbut-3-ynyl)-5-methylfuran (***2i***). To a solution of (*E*)-2-benzylidene-1-phenyl-4-(trimethylsilyl)but-3-yn-1-ol (0.45 g, 1.47 mmol) in methanol (20 mL) was added K_2CO_3 (0.24 g, 1.76 mmol) at room temperature. After the starting material was consumed, the solvent was removed in vacuo. The mixture was extracted with ether and dried over anhydrous Na_2SO_4. The crude product was used in the next step without purification. To a solution of the above crude product in DCM (15 mL) were added 2-methylfuran (0.15 g, 158 μL, 1.76 mmol) and $BF_3 \cdot Et_2O$ (37 μL, 0.29 mmol). The mixture was stirred at room temperature, and the reaction was monitored by TLC. After 30 min, the reaction completed. The solvent was evaporated in vacuo, and the residue was purified by flash column chromatography on silica gel (eluent: petroleum ether) to afford the title product (0.37 g, 84%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 2.25 (s, 3H), 3.25 (s, 1H), 4.99 (s, 1H), 5.90 (d, *J* = 0.8 Hz, 1H), 6.00 (s, 1H), 6.59 (s, 1H), 7.24−7.33 (m, 8H), 7.81 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si) δ 13.6, 53.3, 82.9, 85.1, 106.1, 109.3, 121.6, 127.0, 128.1, 128.28, 128.31, 128.67, 128.70, 135.7, 137.6, 139.7, 151.5, 152.7. HRMS (EI) calcd for $C_{22}H_{18}O$: 298.1358, found 298.1355.

(Z)-2-(2-Benzylidene-4-cyclohexenyl-1-phenylbut-3-ynyl)-5-methylfuran (***2j***). Column chromatography on silica gel (eluent: petroleum ether/

ethyl acetate = 10:1) afforded the title product in 55% yield (2.4 mmol scale, 491.3 mg) as a yellow oil. ^{1}H NMR 400 MHz, $CDCl_3$, Me_4Si) δ 1.47−1.56 (m, 4H), 1.99−2.07 (m, 4H), 2.20 (s, 3H), 4.97 (s, 1H), 5.86 (dd, J = 0.8, 2.8 Hz, 1H), 5.99−6.01 (m, 1H), 6.04 (d, J = 2.8 Hz, 1H), 6.52 (s, 1H), 7.13−7.28 (m, 6H), 7.33−7.35 (m, 2H), 7.81 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si) δ 13.5, 21.3, 22.1, 25.6, 28.5, 53.6, 86.8, 99.3, 106.0, 108.9, 120.9, 123.0, 126.7, 127.7, 127.9, 128.1, 128.5, 128.6, 134.6, 135.2, 136.4, 140.3, 151.1, 153.2. HRMS (EI) calcd for $C_{28}H_{26}O$: 378.1984, found 378.1987.

*Synthesis of (Z)-2-(2-Benzylidene-4-cyclopropyl-1-phenylbut-3-ynyl)-5-methylfuran (**2k**).* To a solution of *Z*-α-bromocinnamaldehyde (2.11 g, 10 mmol) in triethylamine (10 mL) and THF (10 mL) were added ethynylcyclopropane (1.02 mL, 12 mmol), $Pd(PPh_3)_4$ (0.12 g, 0.10 mmol), and CuI (95 mg, 0.50 mmol) at room temperature, and then the mixture was stirred for 20 h. After the starting material was consumed, the solvent was removed in vacuo, and the residue was purified by chromatography on silica gel (petroleum: ethyl acetate = 20:1 to 10:1) to afford (*E*)-2-benzylidene-4-cyclopropylbut-3-ynal (1.85 g, 94%) as yellow oil.

To a solution of the above ynal (1.84 g, 9.36 mmol) in THF (10.0 mL) was added PhLi (5.2 mL, 10.3 mmol, 2.0 M in dibutylether) at −78 °C. The resulting solution was warmed to room temperature and stirred for 2 h. Then the mixture was quenched with saturated ammonium chloride solution. The reaction mixture was extracted with ether and dried over anhydrous Na_2SO_4. The solvent was evaporated, and the residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to afford (*E*)-2-benzylidene-4-cyclopropyl-1-phenylbut-3-yn-1-ol (2.16 g, 84%) as brown oil.

To a solution of the above enynol (274 mg, 1.0 mmol) in DCM (10.0 mL) were added 2-methylfuran (108 μL, 98.5 mg, 1.2 mmol) and $BF_3 \cdot Et_2O$ (25.0 μL, 0.20 mmol). The mixture was kept at room temperature and the reaction was monitored by TLC. After 20 min, the reaction completed. The solvent was evaporated in vacuo, and the residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1) to afford the title product (301 mg, 89%) as yellow oil. The combined yield for three steps was 70%. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.59−0.64 (m, 2H), 0.72−0.77 (m, 2H), 1.31−1.36 (m, 1H), 2.24 (s, 3H), 4.92 (s, 1H), 5.88 (d, J = 1.8 Hz, 1H), 5.99 (d, J = 3.0 Hz, 1H), 6.46 (s, 1H), 7.18−7.31 (m, 8H), 7.79 (d, J = 7.8 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$, Me_4Si) δ 0.7, 8.7, 13.6, 53.8, 75.3, 102.1, 106.0, 108.9, 123.2, 126.8, 127.7, 128.0, 128.2, 128.3, 128.7, 134.4, 136.5, 140.4, 151.3, 153.3. HRMS (EI) calcd for $C_{25}H_{22}O$: 338.1671, found 338.1672.

*(Z)-2-(2-Benzylidene-1-(4-chlorophenyl)-4-phenylbut-3-ynyl)-5-methylfuran and (Z)-2-(2-(4-Chlorobenzylidene)-1,4-diphenylbut-3-ynyl)-5-methylfuran (**2l**).* It was synthesized from (*E*)-2-benzylidene-1-(4-chlorophenyl)-4-phenylbut-3-yn-1-ol and 2-methylfuran according to the procedure described for **2a**. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1) afforded the product **2l** as a mixture of two regioisomers in 97% yield in the ratio of 1.3:1 (0.33 mmol scale, 131.2 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ two isomers: 2.26 (s), 5.03 (s), 5.06 (s), 5.92 (s), 6.07 (t, J = 3.2 Hz), 6.57 (s), 6.62 (s), 7.28−7.40 (m), 7.80 (d, J = 8.4 Hz), 7.88 (d, J = 7.2 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$, Me_4Si) δ two isomers: 13.6, 13.7, 52.9, 53.5, 88.86, 88.89, 97.2, 97.7, 106.09, 106.13, 109.2, 109.3, 122.1, 123.05, 123.12, 123.4, 127.1, 128.17, 128.26, 128.31, 128.40, 128.44, 128.72, 128.74, 129.9, 130.1, 131.3, 132.7, 133.5, 134.4, 134.8, 136.06, 136.09, 138.8, 140.0, 151.5, 151.7, 152.5, 152.9. HRMS (EI) calcd for $C_{28}H_{21}ClO$: 408.1281, found 408.1283.

Typical Procedure for Gold(I)-Catalyzed Cyclization of Enynyl Furans 2 to Fulvene Derivatives. *Method A.* To a solution of (*Z*)-2-(2-benzylidene-1,4-diphenylbut-3-ynyl)-5-methylfuran (**2a**) (74.9 mg, 0.2 mmol) in DCM (2 mL) were added PPh_3AuCl (5.0 mg, 0.01 mmol) and AgOTf (0.2 mL, 0.01 mmol, used as a 0.05 M solution in THF). The flask was sealed and immersed in an oil bath at 50 °C and stirred at this temperature until the reaction was complete as monitored by thin-layer chromatography. The solvent was evaporated under the reduced pressure, and the residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to afford (*E*)-4-((*E*)-3-benzylidene-2,5-diphenylcyclopenta-1,4-dienyl)but-3-en-2-one **3a** (53.8 mg, 72%) as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 2.07 (s, 3H), 5.89 (d, J = 16.0 Hz, 1H), 6.82 (s, 1H), 7.11 (s, 1H), 7.35−7.51 (m, 14H), 7.57−7.59 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si) δ 27.5, 120.6, 127.85, 127.88, 128.2, 128.3, 128.4, 128.8, 129.6, 129.7, 130.8, 131.0, 134.0, 135.0, 136.3, 136.5, 136.6, 140.6, 143.8, 144.9, 148.0, 198.5. HRMS (EI) calcd for $C_{28}H_{22}O$: 374.1671, found 374.1667.

Method B. To a solution of enyne **2a** (74.9 mg, 0.2 mmol) in THF (2 mL) were added PPh_3AuCl (5.0 mg, 0.01 mmol) and AgOTf (0.2 mL, 0.01 mmol, used as a 0.05 M solution in THF). The resulting solution was stirred at room temperature until the reaction was complete as monitored by thin-layer chromatography. The solvent was evaporated under the reduced pressure, and the residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to afford (*Z*)-4-((*E*)-3-benzylidene-2,5-diphenylcyclopenta-1,4-dienyl)but-3-en-2-one **4a** (72.4 mg, 97%) as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 1.70 (s, 3H), 6.06 (d, J = 11.6 Hz, 1H), 6.72 (d, J = 12.4 Hz, 1H), 6.89 (s, 1H), 7.13 (s, 1H), 7.13−7.43 (m, 13H), 7.58 (d, J = 6.8 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si) δ 29.0, 118.3, 127.2, 127.3, 127.8, 128.0, 128.1, 128.6, 129.2, 130.6, 130.8, 131.5, 134.4, 134.6, 136.2, 136.7, 136.9, 138.9, 139.4, 143.6, 148.2, 199.2. HRMS (EI) calcd for $C_{28}H_{22}O$: 374.1671, found 374.1670.

*(E)-3-((E)-3-Benzylidene-2,5-diphenylcyclopenta-1,4-dienyl)-1-phenylprop-2-en-1-one (**3b**).* Method A. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20:1) afforded the title product in 59% yield (0.3 mmol scale, 77.4 mg) as a brown solid. Mp 165−166 °C. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 6.77 (d, J = 15.9 Hz, 1H), 6.86 (s, 1H), 7.15 (s, 1H), 7.29−7.60 (m, 20H), 7.80 (d, J = 15.9 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$, Me_4Si) δ 120.6, 124.4, 127.7, 127.8, 128.1, 128.24, 128.28, 128.33, 128.7, 128.8, 129.6, 130.8, 131.1, 132.4, 134.0, 135.8, 136.5, 137.0, 137.1, 138.2, 140.7, 143.9, 145.4, 148.1, 189.7. HRMS (EI) calcd for $C_{33}H_{24}O$: 436.1827, found 436.1830.

*(E)-4-((E)-3-Benzylidene-2,5-diphenylcyclopenta-1,4-dienyl)-3-methylbut-3-en-2-one (**3c**).* Method A. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1) afforded the title product in 65% yield (0.2 mmol scale, 50.3 mg) as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 1.26 (s, 3H), 2.28 (s, 3H), 6.93 (s, 1H), 7.21 (s, 1H), 7.28−7.46 (m, 14H), 7.60 (d, J = 7.2 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si) δ 13.8, 26.0, 118.1, 127.2, 127.5, 127.7, 128.3, 128.4, 128.7, 129.3, 130.3, 130.7, 135.1, 135.3, 136.2, 136.3, 136.7, 139.3, 139.4, 139.5, 143.7, 148.7, 199.8. HRMS (EI) calcd for $C_{29}H_{24}O$: 388.1827, found 388.1823.

*(Z)-4-((E)-3-Benzylidene-2,5-diphenylcyclopenta-1,4-dienyl)-3-methylbut-3-en-2-one (**4c**).* Method B. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1) afforded the title product in 77% yield (*Z*:*E* = 20:1) (0.2 mmol scale, 59.8 mg) as a brown oil. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 1.81 (s, 3H), 1.87 (s, 3H), 6.62 (s, 1H), 6.90 (s, 1H), 7.13 (s, 1H), 7.29−7.46 (m, 13H), 7.58 (d, J = 7.2 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$, Me_4Si) δ 20.7, 28.3, 118.2, 127.0, 127.5, 128.0, 128.1, 128.2, 128.6, 129.1, 130.0, 130.6, 130.8, 134.6, 135.9, 136.8, 137.6, 138.2, 138.6, 140.3, 143.6, 148.3, 202.1. HRMS (EI) calcd for $C_{29}H_{24}O$: 388.1827, found 388.1833.

*(E)-3-((E)-3-Benzylidene-2,5-diphenylcyclopenta-1,4-dienyl)acrylaldehyde (**3d**).* Method A. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1) afforded the title product in 80% yield (0.15 mmol scale, 43.4 mg) as a brown solid (*E*:*Z* = 25:1). Mp 163−165 °C. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 5.90 (dd, J = 16.05, 7.8 Hz, 1H), 6.83 (s, 1H), 7.13 (s, 1H), 7.34−7.59 (m, 16H), 9.34 (dd, J = 8.1 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$, Me_4Si) δ 120.7, 128.0,

128.1, 128.29, 128.31, 128.4, 128.8, 129.9, 130.6, 130.9, 133.6, 134.7, 136.2, 136.3, 141.7, 143.6, 145.8, 146.2, 147.9, 194.4. HRMS (EI) calcd for $C_{27}H_{20}O$: 360.1514, found 360.1515.

*(Z)-3-((E)-3-Benzylidene-2,5-diphenylcyclopenta-1,4-dienyl)acrylaldehyde (**4d**).* Method B. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1) afforded the title product in 83% yield (0.2 mmol scale, 60.1 mg) as a brown oil (*Z*:*E* = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 5.88 (dd, J = 11.8, 8.0 Hz, 1H), 6.96 (s, 1H), 7.21 (s, 1H), 7.25 (d, J = 11.6 Hz, 1H), 7.30−7.45 (m, 13H), 7.60 (d, J = 6.8 Hz, 2H), 9.39 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si) δ 118.5, 127.6, 127.9, 128.2, 128.4, 128.5, 128.8, 129.68. 129.73, 130.8, 131.0, 133.7, 134.8, 135.2, 136.4, 141.0, 141.9, 142.7, 143.4, 148.3, 191.7. HRMS (EI) calcd for $C_{27}H_{20}O$: 360.1514, found 360.1518.

*(E)-4-((E)-3-Benzylidene-2-phenyl-5-p-tolylcyclopenta-1,4-dienyl)-but-3-en-2-one (**4e**).* Method A. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20:1) afforded the title product in 51% yield (0.3 mmol scale, 59.1 mg) as a brown oil. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 2.08 (s, 3H), 2.39 (s, 3H), 5.94 (d, J = 16.5 Hz, 1H), 6.80 (s, 1H), 7.08 (s, 1H), 7.18−7.58 (m, 15H); ^{13}C NMR (75.5 MHz, $CDCl_3$, Me_4Si) δ 21.3, 27.3, 120.1, 127.8, 128.21, 128.23, 128.7, 128.9, 129.5, 129.7, 130.7, 130.9, 133.5, 133.9, 135.0, 136.4, 136.5, 137.6, 140.2, 143.8, 144.8, 148.0, 198.6. HRMS (EI) calcd for $C_{29}H_{24}O$: 388.1827, found 388.1831.

*(Z)-4-((E)-3-Benzylidene-2-phenyl-5-p-tolylcyclopenta-1,4-dienyl)-but-3-en-2-one (**4e**).* Method B. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1) afforded the title product in 97% yield (0.2 mmol scale, 75.6 mg) as a brown oil. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 1.74 (s, 3H), 2.34 (s, 3H), 6.04 (d, J = 12.3 Hz, 1H), 6.74 (d, J = 12.3 Hz, 1H), 6.87 (s, 1H), 7.11−7.15 (m, 3H), 7.32−7.43 (m, 10H), 7.57 (d, J = 7.2 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$, Me_4Si) δ 21.2, 29.0, 117.6, 127.1, 127.7, 128.0, 128.6, 128.8, 129.1, 130.6, 130.8, 131.6, 133.1, 134.4, 134.8, 136.7, 136.8, 137.2, 138.6, 139.3, 143.6, 148.1, 199.3. HRMS (EI) calcd for $C_{29}H_{24}O$: 388.1827, found 388.1832.

*(E)-4-((E)-3-Benzylidene-2-phenyl-5-(3,4,5-trimethoxyphenyl)cyclopenta-1,4-dienyl)but-3-en-2-one (**3f**).* Method A. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 3:1) afforded the title product in 55% yield (0.2 mmol scale, 51.2 mg) as a brown oil. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 2.11 (s, 3H), 3.87 (s, 6H), 3.92 (s, 3H), 6.01 (d, J = 16.5 Hz, 1H), 6.66 (s, 2H), 6.84 (s, 1H), 7.12 (s, 1H), 7.36−7.54 (m, 9H), 7.59−7.64 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$, Me_4Si) δ 27.6, 56.1, 60.9, 105.6, 120.1, 127.9, 128.3, 128.8, 129.4, 129.7, 130.7, 130.9, 132.0, 133.8, 134.7, 136.1, 136.3, 137.8, 140.8, 143.6, 144.9, 147.9, 152.9, 198.3. HRMS (EI) calcd for $C_{31}H_{28}O_4$: 464.1988, found 464.1992.

*(Z)-4-((E)-3-Benzylidene-2-phenyl-5-(3,4,5-trimethoxyphenyl)cyclopenta-1,4-dienyl)but-3-en-2-one (**4f**).* Method B. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 3:1) afforded the title product in 82% yield (0.2 mmol scale, 76.1 mg) as a brown solid. Mp 149−150 °C. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 1.77 (s, 3H), 3.86 (s, 9H), 6.10 (d, J = 12.3 Hz, 1H), 6.67 (s, 2H), 6.73 (d, J = 12.3 Hz, 1H), 6.87 (s, 1H), 7.13 (s, 1H), 7.32−7.46 (m, 8H), 7.60 (d, J = 7.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 29.2, 56.2, 60.9, 105.3, 117.8, 127.3, 128.1, 128.7, 129.3, 130.7, 130.9, 131.5, 131.9, 134.4, 134.7, 136.7, 136.8, 137.7, 139.1, 139.7, 143.5, 148.1, 152.9, 199.1. HRMS (EI) calcd for $C_{31}H_{28}O_4$: 464.1988, found 464.1990.

*(E)-4-((E)-3-Benzylidene-5-(4-chlorophenyl)-2-phenylcyclopenta-1,4-dienyl)but-3-en-2-one (**3g**).* Method A. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1) afforded the title product in 70% yield (0.2 mmol scale, 57.3 mg) as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 2.09 (s, 3H), 5.89 (d, J = 16.4 Hz, 1H), 6.81 (s, 1H), 7.13 (s, 1H), 7.33−7.49 (m, 13H), 7.55−7.57 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si) δ 27.4, 120.9, 127.9, 128.3, 128.4, 128.8, 129.57, 129.62, 129.8, 130.8, 130.9, 133.7, 134.6, 134.9, 136.1, 136.3, 141.1, 143.5, 145.0, 146.6, 198.3. HRMS (EI) calcd for $C_{28}H_{21}ClO$: 408.1281, found 408.1266.

*(Z)-4-((E)-3-Benzylidene-5-(4-chlorophenyl)-2-phenylcyclopenta-1,4-dienyl)but-3-en-2-one (**4g**).* Method B. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1) afforded the title product in 93% yield (*Z*:*E* = 50:1) (0.2 mmol scale, 75.7 mg) as a brown solid. Mp 120−123 °C. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 1.72 (s, 3H), 6.08 (d, J = 12.0 Hz, 1H), 6.68 (d, J = 12.0 Hz, 1H), 6.87 (s, 1H), 7.14 (s, 1H), 2.28−7.44 (m, 12H), 7.56−7.58 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si) δ 29.2, 118.6, 127.3, 128.1, 128.2, 128.7, 129.0, 129.3, 130.6, 130.8, 131.3, 133.1, 134.3, 134.5, 134.8, 136.55, 136.60, 139.4, 139.6, 143.4, 147.0, 198.8. HRMS (EI) calcd for $C_{28}H_{21}ClO$: 408.1281, found 408.1284.

*(E)-4-((E)-3-Benzylidene-5-(4-nitrophenyl)-2-phenylcyclopenta-1,4-dienyl)but-3-en-2-one (**3h**).* Method A. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 7:1) afforded the title product in 82% yield (0.1 mmol scale, 34.2 mg) as a brown solid. Mp 158−159 °C. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 2.11 (s, 3H), 5.82 (d, J = 16.4 Hz, 1H), 6.94 (s, 1H), 7.23 (s, 1H), 7.36−7.52 (m, 9H), 7.59−7.61 (m, 4H), 8.25−8.27 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si) δ 27.4, 122.8, 123.5, 128.2, 128.4, 128.9, 129.1, 129.8, 130.2, 130.8, 130.9, 133.4, 134.1, 135.8, 136.0, 142.8, 143.2, 143.3, 145.37, 145.41, 147.1, 198.1. HRMS (EI) calcd for $C_{28}H_{21}NO_3$: 419.1521, found 419.1517.

*(Z)-4-((E)-3-Benzylidene-5-(4-nitrophenyl)-2-phenylcyclopenta-1,4-dienyl)but-3-en-2-one (**4h**).* Method B. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 8:1) afforded the title product in 87% yield (*Z*:*E* = 50:1) (0.2 mmol scale, 72.8 mg) as a brown solid. Mp 138−139 °C. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 1.71 (s, 3H), 6.16 (d, J = 12.0 Hz, 1H), 6.70 (d, J = 12.0 Hz, 1H), 6.99 (s, 1H), 7.23 (s, 1H), 7.32−7.45 (m, 8H), 7.56−7.60 (m, 4H), 8.17 (d, J = 8.7 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$, Me_4Si) δ 29.6, 120.7, 123.3, 127.5, 128.0, 128.1, 128.8, 129.7, 130.6, 130.7, 130.8, 133.9, 134.4, 136.3, 140.4, 141.0, 143.0, 143.3, 146.0, 146.4, 198.3. HRMS (EI) calcd for $C_{28}H_{21}NO_3$: 419.1521, found 419.1524.

*(E)-4-((E)-3-Benzylidene-2-phenylcyclopenta-1,4-dienyl)but-3-en-2-one (**3i**).* Method A. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1) afforded the title product in 45% yield (0.22 mmol scale, 29.7 mg) as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 2.26 (s, 3H), 6.51 (d, J = 16.0 Hz, 1H), 6.90 (d, J = 5.6 Hz, 1H), 6.95 (dd, J = 5.6, 1.2 Hz, 1H), 7.16 (s, 1H), 7.31−7.34 (m, 2H), 7.39−7.51 (m, 7H), 7.55−7.57 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si) δ 27.3, 122.3, 127.7, 127.8, 128.3, 128.8, 129.7, 130.8, 130.90, 130.94, 133.6, 136.4, 136.5, 136.6, 140.7, 143.3, 145.3, 198.7. HRMS (EI) calcd for $C_{22}H_{18}O$: 298.1358, found 298.1360.

*(Z)-4-((E)-3-Benzylidene-2-phenylcyclopenta-1,4-dienyl)but-3-en-2-one (**4i**).* Method B. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1) afforded the title product in 48% yield (0.10 mmol scale, 14.3 mg) as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 2.31 (s, 3H), 6.10 (d, J = 12.4 Hz, 1H), 6.51 (d, J = 12.4 Hz, 1H), 6.80 (d, J = 4.8 Hz, 1H), 7.09 (s, 1H), 7.10 (d, J = 4.8 Hz, 1H), 7.29−7.45 (m, 8H), 7.55−7.57 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si) δ 31.4, 120.3, 126.2, 127.6, 128.0, 128.7, 129.4, 130.8, 131.4, 134.1, 134.3, 135.1, 136.6, 136.9, 139.8, 143.6, 144.8, 199.3. HRMS (EI) calcd for $C_{22}H_{18}O$: 298.1358, found 298.1360.

*(Z)-4-((E)-3-Benzylidene-5-cyclohexenyl-2-phenylcyclopenta-1,4-dienyl)but-3-en-2-one (**4j**).* Method B. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1) afforded the title product in 79% yield (0.2 mmol scale, 59.3 mg) as a brown oil. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 1.61−1.75 (m, 4H), 2.02 (s, 3H), 2.14 (bs, 2H), 2.37 (bs, 2H), 6.01 (s, 1H), 6.03 (d, J = 12.3 Hz, 1H), 6.70 (s, 1H), 6.82 (d, J = 12.3 Hz, 1H), 6.98 (s, 1H), 7.25−7.41 (m, 8H), 7.54 (d, J = 8.4 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$, Me_4Si) δ 21.9, 22.7, 25.8,

27.3, 29.4, 114.8, 127.0, 128.0, 128.4, 128.6, 128.9, 130.5, 130.8, 131.2, 132.4, 134.4, 136.3, 136.7, 136.9, 137.3, 139.3, 143.6, 149.0, 199.7. HRMS (EI) calcd for $C_{28}H_{26}O$: 378.1984, found 378.1982.

*(E)-4-((E)-3-Benzylidene-5-cyclopropyl-2-phenylcyclopenta-1,4-dienyl)but-3-en-2-one (**3k**).* Method A. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1) afforded the title product in 30% yield (0.2 mmol scale, 20.1 mg) as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 0.75−0.79 (m, 2H), 0.97−1.02 (m, 2H), 1.86−1.89 (m, 1H), 2.23 (s, 3H), 6.44 (s, 1H), 6.91 (d, J = 16.8 Hz, 1H), 6.97 (s, 1H), 7.30−7.53 (m, 11H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si) δ 8.2, 11.7, 26.7, 116.0, 127.8, 128.2, 128.5, 128.7, 129.3, 130.7, 131.0, 134.0, 136.1, 136.6, 137.6, 138.9, 143.5, 145.4, 150.8, 199.3. HRMS (EI) calcd for $C_{25}H_{22}O$: 338.1671, found 338.1667.

*(Z)-4-((E)-3-Benzylidene-5-cyclopropyl-2-phenylcyclopenta-1,4-dienyl)but-3-en-2-one (**4k**).* Method B. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1) afforded the title product in 62% yield (0.2 mmol scale, 42.0 mg) as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 0.71−0.73 (m, 2H), 0.92−0.95 (m, 2H), 1.49−1.52 (m, 1H), 2.15 (s, 3H), 6.17 (d, J = 12.4 Hz, 1H), 6.26 (s, 1H), 6.81 (d, J = 12.4 Hz, 1H), 6.98 (s, 1H), 7.29−7.42 (m, 8H), 7.51 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si) δ 9.7, 10.2, 29.7, 111.1, 127.1, 128.1, 128.6, 128.8, 130.5, 130.6, 132.4, 134.4, 135.7, 136.9, 137.9, 138.2, 143.5, 152.7, 200.2. HRMS (EI) calcd for $C_{25}H_{22}O$: 338.1671, found 338.1676.

*Synthesis of (Z)-3-((E)-3-Benzylidene-2,5-diphenylcyclopenta-1,4-dienyl)-1-phenylprop-2-en-1-ol (**5b**).* To a solution of (*Z*)-2-(2-benzylidene-1,4-diphenylbut-3-ynyl)-5-phenylfuran (**2b**) (87.3 mg, 0.2 mmol) in THF (2 mL) were added PPh_3AuCl (5.0 mg, 0.01 mmol) and AgOTf (0.2 mL, 0.01 mmol, used as a 0.05 M solution in THF) at 50 °C. After stirring for 10 min, the reaction was quenched by 2 drops of Et_3N. The solvent was evaporated under the reduced pressure, and the residue was dissolved in methanol (2 mL). To the above mixture were added $CeCl_3\cdot 7H_2O$ (149.0 mg, 0.4 mmol) and $NaBH_4$ (14.9 mg, 0.4 mmol) at 0 °C. The resulting solution was kept at 0 °C and stirred for 2 h. Then the mixture was quenched with water, extracted with ether, and dried over anhydrous Na_2SO_4. The solvent was evaporated under the reduced pressure, and the residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to afford **5b** (50.6 mg, 58%) as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 0.54 (d, J = 2.0 Hz, 1H), 5.09 (d, J = 9.6 Hz, 1H), 5.60 (td, J = 10.0, 0.8 Hz, 1H), 6.33 (d, J = 8.4 Hz, 1H), 6.95 (s, 1H), 7.12−7.24 (m, 6H), 7.31−7.47 (m, 11H), 7.58 (dd, J = 18.4, 8.0 Hz, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$, Me_4Si) δ 70.9, 118.1, 124.4, 125.4, 127.0, 127.2, 127.8, 128.0, 128.2, 128.4, 128.7, 129.1, 130.6, 131.0, 135.2, 135.5, 136.2, 138.8, 137.0, 137.1, 138.4, 142.3, 143.8, 148.6. HRMS (EI) calcd for $C_{33}H_{26}O$: 438.1984, found 438.1992.

■ ASSOCIATED CONTENT

Supporting Information. X-ray crystallography of compound **3b** and spectroscopic characterization of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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