JOC The Journal of Organic Chemistry

ARTICLE

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Cyclization Reaction for the Synthesis of Polysubstituted Naphthalenes in the Presence of Au(I) Precatalysts

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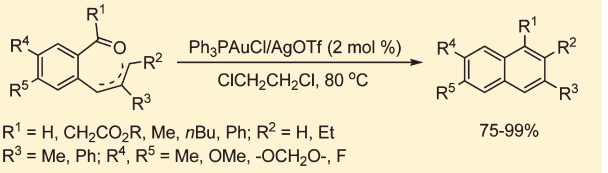
Supporting Information

ABSTRACT: Au(I)-catalyzed cyclization of alkenyl carbonyl compounds leading to a variety of substituted naphthalenes has been developed. This process exploits a dual function of the Au(I) catalyst: (1) the oxophilic nature of the Au(I) catalyst, counterintuitive to the π-acidic reactivities generally associated with Au catalysts, and (2) olefin isomerization supported by the outcome of isotope scrambling experiments. It cannot be completely excluded that TfOH is a true operative catalyst in this protocol. In view of the practicality, the unnecessity of isomerically pure starting material in this reaction is particularly attractive and valuable.



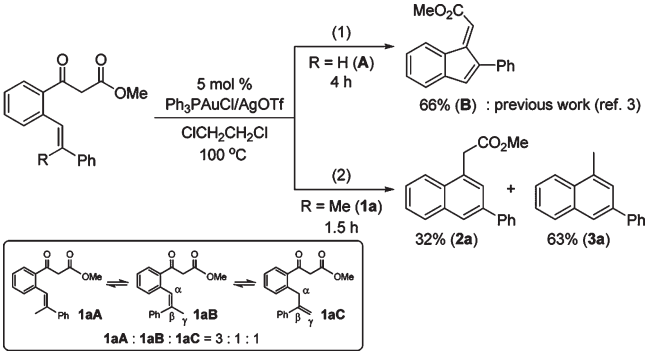
INTRODUCTION

Substituted naphthalenes have attracted considerable attention owing to their prevalence in a variety of compounds possessing important physical and biological properties.[1] Consequently, a number of synthetic strategies have been reported for the construction of these privileged structural motifs.[2] Recently, we reported a Au(I)-catalyzed[3] cyclization of 2-alkenylphenyl carbonyl compounds to afford a variety of indenes, indenols, and indanones (Scheme 1(1)).[4] In this process, Au(I) exhibited oxophilic Lewis acidity[5] to activate the carbonyl group of aldehydes, ketones, and β-keto esters in the presence of C−C multiple bonds. During the course of this study, we also uncovered the influence of olefin substitution in determining the reaction pathways. In this context, while disubstituted styrenes (type **A**) led to the indene product (type **B**) as previously described, trisubstituted styrenes (type **1a**) underwent C−C bond formation at γ (allylic) position to furnish the corresponding naphthalenes derivatives **2a** and **3a** (Scheme 1, (1) vs (2)).

Before proceeding with the discussion, a few cursory words from the mechanistic perspective will be instructive and serve to highlight the novelty of this unexpected transformation. First and foremost, the formation of naphthalenes (**2a** and **3a**) suggested that the methyl substituent of substrate **1a** (i.e., R = Me) had participated in the carbon−carbon bond forming process, presumably through the intermediacy of **1aC** (an isomeric form of **1a**).

The γ-carbon in **1aC** then undergoes nucleophilic attack to the keto carbon of the proximal β-keto ester motif, thereby leading to the naphthalene backbone of products **2a** and **3a** (Scheme 2, path b).[6] This observation is indeed counterintuitive in the context of Au(I) catalysis, where **1aC** is expected to undergo a 6-*exo*-*trig* cyclization originating from the nucleophilic attack of the 1,3-dicarbonyl to the π-activated alkene, a net process generally referred to as the Conia-ene reaction[7] (Scheme 2, path a).

Scheme 1. Au(I)-Catalyzed Reactions of Alkenyl β-Keto Esters

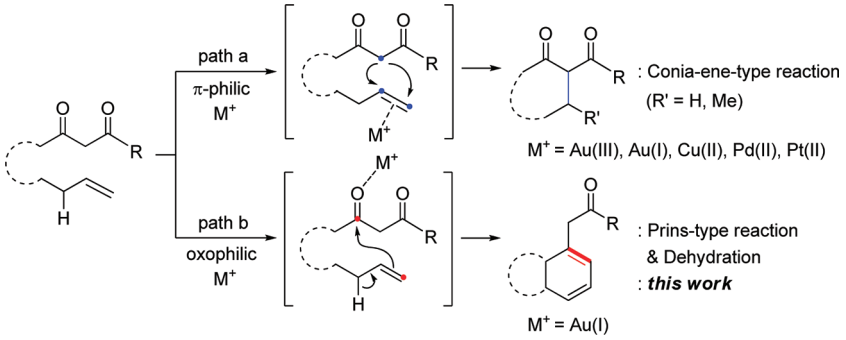


RESULTS AND DISCUSSION

Having uncovered this unexpected and novel transformation, we set out to explore the utility and scope of this process (Tables 1 and 2). Indeed, our initial result was particularly encouraging, where a reaction condition consists of 5 mol % of $Ph_3PAuCl/AgOTf$ (1:1) in $ClCH_2CH_2Cl$ (0.025 M) at 100 °C for 1.5 h to afford naphthalene products **2a**/**3a** with a combined yield of 95%. The cyclization process could also take place uneventfully at higher concentrations (0.1 M), and both catalyst loading and reaction temperature could be reduced without incurring penalty on the reaction yield, albeit a longer reaction time was required (Table 1, entry 1). Substrates bearing either electron-donating or electron-withdrawing substituents on the aromatic moiety were well tolerated, leading to the corresponding products in good to excellent yields. We also discovered that the isomeric form of the starting alkene substrates is

Received: July 4, 2011
Published: July 22, 2011

Scheme 2. Transition-Metal-Catalyzed Reactions between 1,3-Dicarbonyl and Olefin Functionalities



inconsequential to the reaction outcome, where both isomerically pure 2-methyl-1-propenyl- (**1g**, **6h**) and 2-methylallyl-substituted (**1h**, **6i**) substrates afforded the same products in comparable yields. Allylic substrates with no substituents at β position (**1i**, **6j**−**l**) failed to undergo any productive cyclizations. Lastly, the reactions of **1g** and **1h** afforded significant amount of isochromane (**4a**), presumably through the competitive intramolecular nucleophilic addition of β-keto ester oxygen to alkene group.[8]

Next, we examined the reaction of **6h** in the presence of other Lewis acids and protic acids (Table 3). With the exception of AgOTf, $Cu(OTf)_2$, $Bi(OTf)_3$, and TfOH, most of the Lewis and Brønsted acids examined were ineffective with the recovery of **6h**. It is noteworthy that the reaction did not take place in the absence of cationic Au(I) catalyst (Table 3, entry 2). On the other hand, $AuCl_3$ did not promote the reaction at all (Table 3, entry 3). Considering the well-known π-philic Lewis acidity of Au(I) that activates the alkene moiety toward nucleophlic attack by 1,3-dicarbonyls,[7c−e] and recognizing Au(III) is more oxophilic than Au(I),[9] our findings are particularly noteworthy. We suspected that trace amounts of protic acid could conceivably be generated in situ and thereby catalyze the reaction.[10] Indeed, TfOH did result in the production of **7h**, albeit in moderate yield (45%, Table 3, entry 12). In sharp contrast, other protic acids such as trifluoroacetic acid (CF_3CO_2H) did not show the ability to produce the desired product **7h**. In addition, $Sc(OTf)_3$ and $Zn(OTf)_2$ were totally ineffective and other triflate salts (e.g., AgOTf, $Cu(OTf)_2$, and $Bi(OTf)_3$) gave lower conversions than the combination of Ph_3PAuCl and AgOTf. These results suggest that cationic Au(I) plays a somehow important role in this transformation, although the catalytic system consisting of Ph_3PAuCl/AgOTf could serve as a precatalyst for the generation of the likely operative catalyst, TfOH.

To gain further mechanistic insights into this reaction, an isotope scrambling experiment was performed as shown in Scheme 3. In sharp contrast to the use of only either Ph_3PAuCl or AgOTf, upon treatment of α-methylstilbene **8** with D_2O in the presence of Ph_3PAuCl/AgOTf, significant deuterium exchange was observed along with a trace amount of the thermodynamically less stable alkene derivative **8′**. These findings are in support of a Au(I)-catalyzed olefin isomerization,[11] where 2-alkyl-1-propenyl-substituted substrates (e.g., **1b**−**g**, **5d**, **6c**,**d**,**f**−**h**) also led to the corresponding naphthalene products.

On the basis of our experimental findings and by analogy with the mechanism proposed for the related cyclization reaction of alkenyl carbonyl compounds,[12] a plausible mechanism is outlined in Scheme 4. Although the exact mechanism for this process is yet to be fully elucidated, a plausible starting point may involve a Au(I)-promoted olefin isomerization to generate a small amount of the required alkene isomer. Activation of the carbonyl functionality through the participation of the Lewis acidic Au(I) catalyst (or TfOH) (**C**) precedes the intramolecular nucleophilic attack by the pendant alkene moiety, thereby generating a newly formed carbon−carbon bond (**D**). Subsequent proton transfer leads to tertiary alcohol **E** and regenerates the Au(I) (or H^+) catalyst, where the former species undergoes further aromaticity-driven dehydration to give the naphthalenes. Considering allylic substrates bearing no substituents at the β position (**1i**, **6j**−**l**) failed to give any of the desired products, the stabilization of a charge-delocalized species (i.e., **C** to **D**) appears to be an essential feature for the cyclization reaction to take place.

CONCLUSION

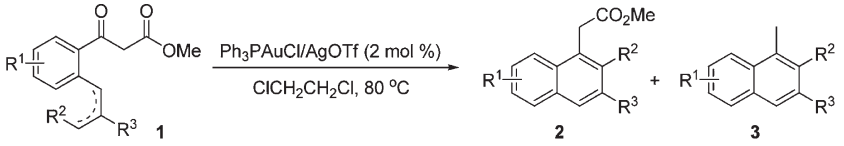
In summary, we have developed a Au(I)-catalyzed cyclization reaction of alkenyl carbonyl compounds to afford a variety of substituted naphthalenes.[13−15] In this process, Au(I) served to activate the carbonyl group of β-keto esters as well as aldehydes and ketones, preferentially exhibiting oxophilicity in the presence of C−C multiple bonds that is counterintuitive to the π-philic nature of Au(I) catalyst.[16] Furthermore, we also secured evidence pointing toward a Au(I)-catalyzed olefin isomerization. An alternative or synergistic mechanistic pathway involving TfOH as a true operative catalyst cannot be completely excluded. In addition, the isomeric mixture of starting material is inconsequential, where an isomerization process was believed to have taken place during the reaction and thereby funneling all isomeric reactants to the naphthalene products. This is particularly attractive on the practical standpoint where the preparation of isomerically pure starting material is not necessary. It is much anticipated that these findings and the associated new reactivities unveiled will lead to further advancements in the field of Au-catalyzed reaction, and our continued efforts in this area will be reported in due course.

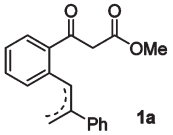
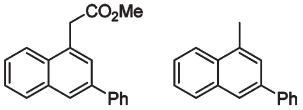
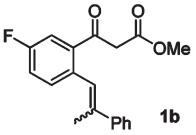
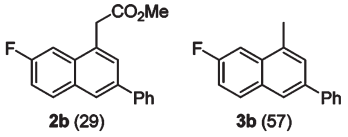
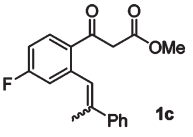
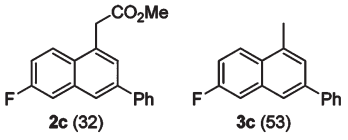
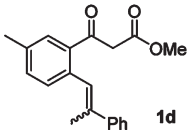
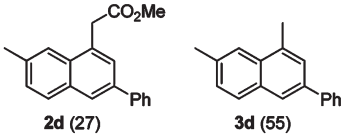
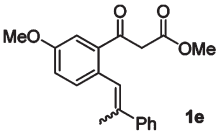
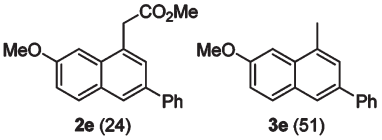
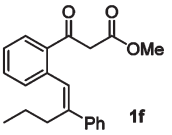
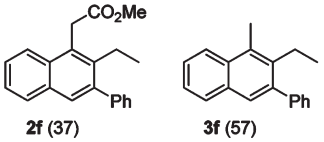
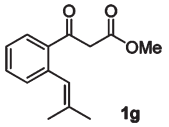
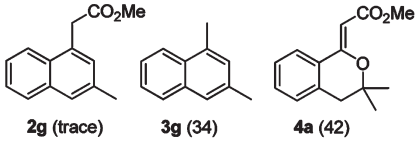
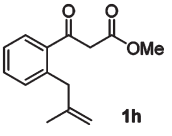
EXPERIMENTAL SECTION

General Information. Nuclear magnetic resonance spectra were recorded on 400 MHz instrument. Spectra were recorded in $CDCl_3$ solutions referenced to TMS or solvent residual peak. High-resolution mass spectra were measured using EI at 70 eV. GC−MS spectra were recorded with EI ionization and an Elite-1 column (0.25 mm × 30 m, film: 0.25 μm). For control of the conversion and characterization of the products, the following method was used: The method starts with the injection temperature T_0 (50 °C); after holding this temperature for 20 min, the column is heated to the temperature T_1 (ramp, 300 °C) and held for an additional 3 min. Flash chromatography was performed on silica gel 230−400 mesh. All catalysts were purchased as higher quality and used as received. Unless otherwise

dx.doi.org/10.1021/jo201339z |J. Org. Chem. 2011, 76, 7204–7215

Table 1. Au(I)-Catalyzed Cyclization Reaction of Alkenyl β-Keto Esters 1



entry	substrate	time (h)	product (%)
1	 1a (*E*:Z:allyl = 60:20:20)	12	 **2a** (33) **3a** (53)[a]
2	 1b (*E*:Z = 82:18)	12	 **2b** (29) **3b** (57)
3	 1c (*E*:Z = 77:23)	15	 **2c** (32) **3c** (53)
4	 1d (*E*:Z = 91:9)	13	 **2d** (27) **3d** (55)
5	 1e (*E*:Z = 87:13)	11	 **2e** (24) **3e** (51)
6	 1f	18	 **2f** (37) **3f** (57)
7	 1g	12	 **2g** (trace) **3g** (34) **4a** (42)
8	 1h	13	**2g** (trace), **3g** (49), **4a** (42)

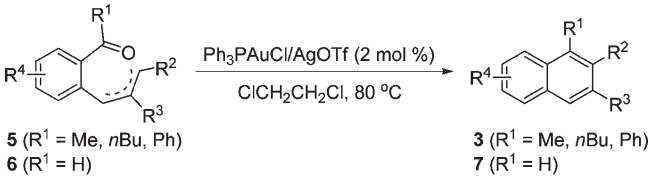
[a] Performed in CH_2Cl_2 at 60 °C.

noted, all commercially obtained reagents were used as received. THF and benzene were distilled from sodium benzophenone ketyl immediately prior to use. CH_2Cl_2 was distilled from CaH_2 immediately prior to use. Thin layer chromatograms (TLC) were visualized via UV and anisaldehyde stain.

General Procedures for the Preparation of Alkenylbenzaldehydes. *Method A.* To the solution of the corresponding 2-bormobenzaldehyde, α-methylstyrene (5.0 equiv), and DIPEA (1.5 equiv) in DMA (0.1 M) in a round-bottom flask were added

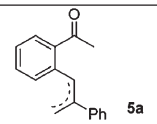
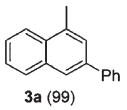
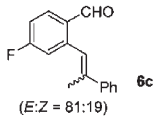
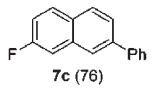
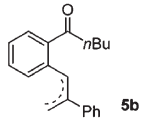
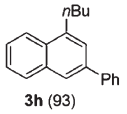
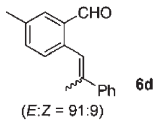
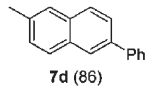
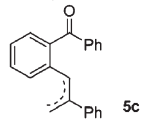
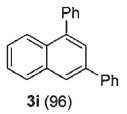
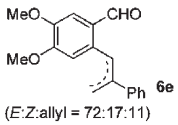
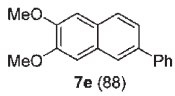
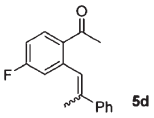
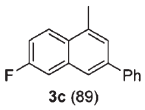
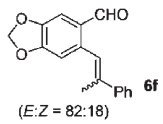
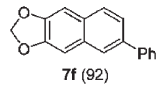
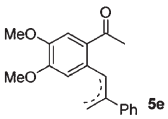
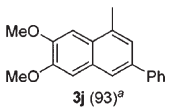
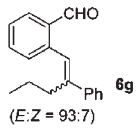
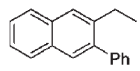
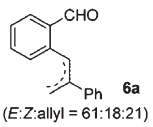
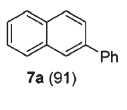
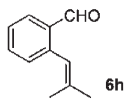
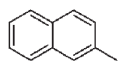
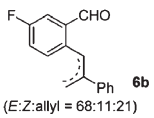
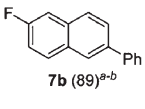
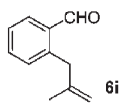
dx.doi.org/10.1021/jo201339z |*J. Org. Chem.* 2011, 76, 7204–7215

Table 2. Au(I)-Catalyzed Cyclization Reaction of Alkenylaryl Ketones 5 and Alkenylbenzaldehydes 6

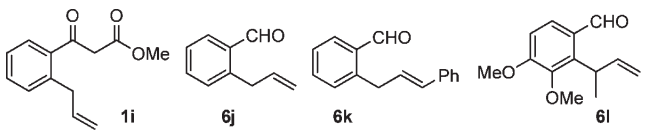


5 (R^1 = Me, *n*Bu, Ph)
6 (R^1 = H)

3 (R^1 = Me, *n*Bu, Ph)
7 (R^1 = H)

entry	substrate	time (h)	product (%)	entry	substrate	time (h)	product (%)
1	 **5a** (*E*:*Z*:allyl = 58:18:24)	13	 **3a** (99)	8	 **6c** (*E*:*Z* = 81:19)	24	 **7c** (76)
2	 **5b** (*E*:*Z*:allyl = 62:18:20)	16	 **3h** (93)	9	 **6d** (*E*:*Z* = 91:9)	21	 **7d** (86)
3	 **5c** (*E*:*Z*:allyl = 57:19:24)	39	 **3i** (96)	10	 **6e** (*E*:*Z*:allyl = 72:17:11)	25	 **7e** (88)
4	 **5d** (*E*:*Z* = 79:21)	24	 **3c** (89)	11	 **6f** (*E*:*Z* = 82:18)	15	 **7f** (92)
5	 **5e** (*E*:*Z*:allyl = 65:18:17)	24	 **3j** (93)[a]	12	 **6g** (*E*:*Z* = 93:7)	10	 **7g** (88)
6	 **6a** (*E*:*Z*:allyl = 61:18:21)	39	 **7a** (91)	13	 **6h**	12	 **7h** (76)
7	 **6b** (*E*:*Z*:allyl = 68:11:21)	24	 **7b** (89)[a-b]	14	 **6i**	12	**7h** (78)

[a] Performed at 100 °C. [b] Performed with 4 mol % $Ph_3PAuCl/AgOTf$.



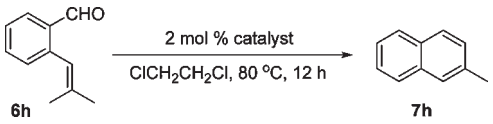
1i **6j** **6k** **6l**

$Pd(OAc)_2$ (2 mol %) and P(*o*-Tol)$_3$ (2 mol %) under argon atmosphere. The reaction mixture was heated at 135 °C for 2−12 h. The reaction mixture was quenched with H_2O and extracted with CH_2Cl_2 (three times). The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc/*n*-hexane = 1:10−1:50) to afford the desired product.

Method B. To the suspension of phosphonium salt (1.2 equiv) in THF was slowly added *n*-BuLi (1.6 M solution in hexane, 1.2 equiv) at 0 °C. The resulting solution was stirred for 30 min at 0 °C, and the corresponding 2-bormobenzaldehyde (1.0 equiv) was added to form a light red solution. After 2 h, the reaction mixture was quenched with satd NH_4Cl/water (1:1) and extracted with CH_2Cl_2 (three times). The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford the desired 1-alkenyl-2-bromobenzene product. To a solution of the corresponding 1-alkenyl-2-bromobenzene in THF was added *n*-BuLi (1.6 M solution in hexane, 1.5 equiv) dropwise slowly at −78 °C. The resulting solution was stirred for 3 h at −78 °C, and DMF (1.5 equiv) was slowly added.

dx.doi.org/10.1021/jo201339z |*J. Org. Chem.* 2011, 76, 7204–7215

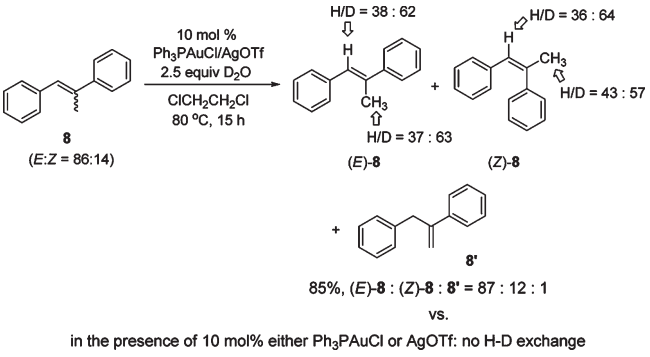
Table 3. Cyclization Reaction of 6h Catalyzed by Various Lewis Acids and Brønsted Acids



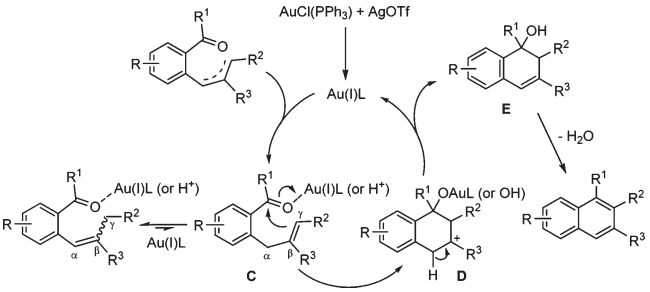
entry	catalyst	yield[a] (%)
1	$Ph_3PAuCl/AgOTf$ (1:1)	80
2	Ph_3PAuCl	0
3	$AuCl_3$	0
4	AgOTf	54
5	$Sc(OTf)_3$	7
6	$Cu(OTf)_2$	57
7	$Bi(OTf)_3$	51
8	$Zn(OTf)_2$	8
9	$AlCl_3$	0
10	$ZnCl_2$	0
11	$BF_3 \cdot Et_2O$	0
12	TfOH	45
13	CF_3CO_2H	0

[a] Yields were determined by ^1H NMR using trichloroethylene as an internal standard.

Scheme 3. Deuterium Exchange Experiment



Scheme 4. Proposed Mechanism for the Au(I)-Catalyzed Cyclization Reaction of Alkenyl Carbonyl Compounds



After 0.25−1 h, the reaction mixture was quenched with satd NH_4Cl solution and extracted with CH_2Cl_2 (three times). The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc/*n*-hexane = 1:20−1:50) to afford the desired product.

Method C. To a solution of the 2-formylphenylboronic acid and corresponding allyl halide (1−1.2 equiv) in THF (0.2 M) in a round-bottom flask were added $PdCl_2(PPh_3)_2$ (2.5 mol %) and aq Na_2CO_3 (1 M, 2 equiv) solution. The reaction mixture was heated at reflux for 3−4 h. The reaction mixture was quenched with H_2O and extracted with CH_2Cl_2 (three times). The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc/*n*-hexane = 1:50) to afford the desired product.

*2-(2-Phenylprop-1-enyl)benzaldehyde (**6a**).*[13e] Following method A using 2-bormobenzaldehyde (1.851 g, 10 mmol) for 12 h, **6a** was obtained: 1.325 g (60%, *E*/*Z*/allyl = 61:18:21); ^1H NMR ($CDCl_3$, 400 MHz) δ 2.09 (d, J = 1.2 Hz, 3H, *E*), 2.32 (d, J = 1.6 Hz, 3H, *Z*), 4.25 (s, 2H, allyl), 4.72 (s, 1H, allyl), 5.47 (s, 1H, allyl), 6.94 (s, 1H, *Z*), 7.01 (d, J = 7.6 Hz, 1H, *Z*), 7.04 (dd, J = 2.2, 7.4 Hz, 2H, *Z*), 7.14−7.18 (m, 2H, allyl), 7.21 (s, 1H, *E*), 7.28−7.53 (m, 5H of *E*, 5H of *Z*, and 6H of allyl), 7.58 (d, J = 7.2 Hz, 2H, *E*), 7.61 (td, J = 1.4, 7.8 Hz, 1H, *E*), 7.75 (dd, J = 1.2, 7.6 Hz, 1H, *Z*), 7.88 (dd, J = 1.2, 7.6 Hz, 1H, allyl), 7.95 (d, J = 7.6 Hz, 1H, *E*), 10.23 (s, 1H, *Z*), 10.24 (s, 1H, allyl), 10.28 (s, 1H, *E*); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.1, 25.7, 37.4, 114.7, 123.0, 123.6, 125.8, 126.6, 126.9, 127.0, 127.1, 127.58, 127.61, 128.0, 128.2, 128.3, 128.4, 128.8, 128.9, 130.5, 131.1, 131.3, 131.4, 133.0, 133.3, 133.4, 133.6, 133.8, 140.2, 140.7, 141.2, 141.4, 141.5, 142.0, 142.3, 147.3, 191.8, 192.0, 192.1 (3 carbons are missing due to overlapping).

*5-Fluoro-2-(2-phenylprop-1-enyl)benzaldehyde (**6b**).* Following method A using 2-bromo-5-fluorobenzaldehyde (1.01 g, 5 mmol) for 2 h, **6b** was obtained: 571.0 mg (48%, *E*/*Z*/allyl = 68:11:21); ^1H NMR ($CDCl_3$, 400 MHz) δ 2.06 (s, 3H, *E*), 2.31 (d, J = 0.8 Hz, 3H, *Z*), 4.19 (s, 2H, allyl), 4.71 (s, 1H, allyl), 5.48 (s, 1H, allyl), 6.85 (s, 1H, *Z*), 6.98−7.07 (m, 1H of *Z* and 2H of allyl), 7.10 (s, 1H, *E*), 7.15−7.18 (m, 2H, allyl), 7.22 (dd, J = 2.6, 8.2 Hz, 1H, allyl), 7.29−7.46 (m, 5H of *E*, 6H of *Z*, and 1H of allyl), 7.56 (d, J = 7.2 Hz, 2H, *E*), 7.55−7.59 (m, 2H, allyl), 7.63 (dd, J = 2.8, 8.8 Hz, 1H, *E*), 7.97 (dd, J = 6.0, 8.8 Hz, 1H, *Z*), 10.18 (d, J = 2.8 Hz, 1H, *Z*), 10.19 (d, J = 2.4 Hz, 1H, allyl), 10.23 (d, J = 2.8 Hz, 1H, *E*); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.1, 25.6, 36.7, 114.1 (d, J = 22.0 Hz), 114.2 (d, J = 22.0 Hz), 115.0, 116.4 (d, J = 21.2 Hz), 120.5 (d, J = 21.2 Hz), 120.77 (d, J = 21.3 Hz), 120.81 (d, J = 22.0 Hz), 121.6, 122.3, 125.8, 127.2, 127.80, 127.84, 128.2, 128.3, 128.4, 128.5, 132.4 (d, J = 6.8 Hz), 133.0 (d, J = 6.8 Hz), 133.3 (d, J = 6.8 Hz), 135.38, 135.44, 135.47, 135.52, 137.3, 137.4, 137.5, 137.6, 137.7, 139.9, 140.4, 141.2, 142.0, 142.9, 147.4, 161.3 (d, J = 247.4 Hz), 161.7 (d, J = 247.4 Hz), 165.6 (d, J = 255.8 Hz), 190.4, 190.5, 190.8; HRMS (EI) $[M]^+$ m/z calcd for $C_{16}H_{13}FO$ 240.0950, found 240.0953.

*4-Fluoro-2-(2-phenylprop-1-enyl)benzaldehyde (**6c**).* Following method B using 2-bromo-5-fluorobenzaldehyde (807.9 mg, 4 mmol) and triphenyl-(1-phenylethyl)phosphonium bromide (2.230 g, 5.0 mmol), **6c** was obtained: 511.2 mg (53%, *E*/*Z* = 81:19); ^1H NMR ($CDCl_3$, 400 MHz) δ 2.11 (s, 3H, *Z*), 2.32 (s, 3H, *E*), 6.67 (dd, J = 2.6, 9.8 Hz, 1H, *E*), 6.89 (s, 1H, *E*), 6.93 (td, J = 2.8, 8.4 Hz, 1H, *E*), 7.03−7.07 (m, 2H of *E* and 1H of *Z*), 7.12 (td, J = 1.8, 8.4 Hz, 1H, *Z*), 7.15 (s, 1H, *Z*), 7.18−7.21 (m, 3H, *E*), 7.35 (d, J = 6.8 Hz, 1H, *Z*), 7.41 (t, J = 7.4 Hz, 2H, *Z*), 7.57 (d, J = 7.2 Hz, 2H, *Z*), 7.77 (dd, J = 6.2, 8.6 Hz, 1H, *E*), 7.97 (dd, J = 6.0, 8.4 Hz, 1H, *Z*), 10.15 (s, 1H, *E*), 10.20 (s, 1H, *Z*); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.3, 25.9, 114.3 (d, J = 22.0 Hz), 114.7 (d, J = 22.0 Hz), 117.3 (d, J = 22.0 Hz), 117.7 (d, J = 22.0 Hz), 121.8, 122.5, 127.5, 128.0, 128.32, 128.35, 128.5, 130.1, 131.7 (d, J = 9.9 Hz), 139.8, 141.4, 142.0, 143.6, 144.3 (d, J = 9.8 Hz), 144.5 (d, J = 9.9 Hz), 165.4 (d, J = 254.3 Hz), 165.6 (d, J = 255.7 Hz), 190.3, 190.6 (3 carbons are missing due to overlapping); HRMS (EI) $[M]^+$ m/z calcd for $C_{16}H_{13}FO$ 240.0950, found 240.0952.

*5-Methyl-2-(2-phenylprop-1-enyl)benzaldehyde (**6d**).* Following method B using 2-bromo-4-methylbenzaldehyde (399.9 mg, 2.0 mmol) and triphenyl(1-phenylethyl)phosphonium bromide (1.07 g, 2.4 mmol),

6d was obtained: 272.9 mg (60%, *E*/*Z* = 91:9); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.08 (s, 3H, *Z*), 2.30 (s, 3H, *E*), 2.31 (s, 3H, *E*), 2.43 (s, 3H, *Z*), 6.89 (d, *J* = 7.6 Hz, 1H, *E*), 6.90 (s, 1H, *E*), 7.04−7.06 (m, 2H, *E*), 7.12 (d, *J* = 7.6 Hz, 1H, *E*), 7.16−7.20 (m, 3H, *E*), 7.26−7.43 (m, 7H, *Z*), 7.55 (s, 1H, *E*), 7.57 (d, *J* = 9.6 Hz, 1H, *Z*), 7.75 (s, 1H, *Z*), 10.20 (s, 1H, *E*), 10.25 (s, 1H, *Z*); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.2, 20.8, 20.9, 25.8, 122.9, 123.6, 125.8, 127.0, 127.6, 128.1, 128.4, 128.5, 129.1, 129.2, 130.5, 131.1, 133.2, 133.7, 134.1, 134.5, 136.5, 137.1, 138.6, 138.8, 140.1, 140.4, 141.7, 192.2, 192.5 (1 carbon is missing due to overlapping); HRMS (EI) $[M]^+$ *m*/*z* calcd for $C_{17}H_{16}O$ 236.1201, found 236.1204.

*5-Methoxy-2-(2-phenylprop-1-enyl)benzaldehyde (**F**).* Following method A using 2-bromo-5-methoxybenzaldehyde (1.060 g, 5 mmol) for 2 h, **F** was obtained: 298.0 mg (24%, *E*/*Z*/allyl = 80:6:14); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.07 (s, 3H, *E*), 2.30 (s, 3H, *Z*), 3.80 (s, 3H, *Z*), 3.86 (s, 3H, allyl), 3.89 (s, 3H, *E*), 4.15 (s, 2H, allyl), 4.70 (s, 1H, allyl), 5.46 (s, 1H, allyl), 6.85 (s, 1H, *Z*), 6.89 (dd, *J* = 2.4, 8.4 Hz, 1H, *Z*), 6.93 (d, *J* = 8.4 Hz, 1H, *Z*), 7.05 (d, *J* = 8.0 Hz, 1H, allyl), 7.08 (dd, *J* = 2.4, 8.4 Hz, 1H, allyl), 7.13 (s, 1H, *E*), 7.17 (dd, *J* = 2.8, 8.4 Hz, 1H, *E*), 7.16−7.47 (m, 6H of *Z* and 6H of allyl), 7.26 (d, *J* = 2.8 Hz, 1H, *E*), 7.33−7.42 (m, 3H, *E*), 7.44 (d, *J* = 2.4 Hz, 1H, *E*), 7.56 (d, *J* = 7.6 Hz, 2H, *E*), 10.20 (s, 2H, *Z*), 10.21 (s, 2H, allyl), 10.24 (s, 2H, *E*); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.0, 25.6, 36.4, 55.23, 55.24, 110.7, 111.9, 113.5, 114.5, 120.5, 120.7, 121.0, 122.2, 123.0, 125.69, 125.73, 126.9, 127.5, 127.6, 128.0, 128.19, 128.24, 128.4, 129.8, 131.7, 132.3, 132.6, 133.8, 134.1, 134.3, 134.4, 134.6, 140.0, 140.2, 140.6, 141.4, 142.3, 147.8, 158.1, 158.4, 158.6, 191.3, 191.7, 191.8 (1 carbon is missing due to overlapping); HRMS (EI) $[M]^+$ *m*/*z* calcd for $C_{17}H_{16}O_2$ 252.1150, found 252.1151.

*4,5-Dimethoxy-2-(2-phenylprop-1-enyl)benzaldehyde (**6e**).* Following method A using 2-bromo-4,5-dimethoxybenzaldehyde (1.225 g, 5 mmol) for 3 h, **6e** was obtained: 790.0 mg (56%, *E*/*Z*/allyl = 72:17:11); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.07 (s, 3H, *E*), 2.31 (s, 3H, *Z*), 3.51 (s, 3H, *Z*), 3.88 (s, 3H, *Z*), 3.89 (s, 3H, allyl), 3.93 (s, 3H, allyl), 3.965 (s, 3H, *E*), 3.972 (s, 3H, *E*), 4.18 (s, 2H, allyl), 4.78 (s, 1H, allyl), 5.48 (s, 1H, allyl), 6.37 (s, 1H, *Z*), 6.75 (s, 1H, allyl), 6.77 (s, 1H, *E*), 6.95 (s, 1H, *Z*), 7.08 (s, 1H, *Z*), 7.10 (s, 1H of *E* and 1H of allyl), 7.16−7.22 (m, 2H of *Z* and 1H of allyl), 7.29−7.62 (m, 3H of *Z* and 4H of allyl), 7.34−7.42 (m, 3H, *E*), 7.46 (s, 1H, *E*), 7.56 (d, *J* = 7.6 Hz, 2H, *E*), 10.13 (s, 1H, *E*), 10.15 (s, 1H, allyl), 10.20 (s, 1H, *Z*); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.1, 25.7, 36.5, 55.3, 55.5, 55.70, 55.74, 55.86, 108.6, 108.9, 110.1, 110.8, 111.9, 113.0, 113.3, 114.7, 121.9, 122.8, 125.6, 125.7, 126.5, 126.9, 127.0, 127.5, 128.07, 128.14, 128.2, 136.2, 136.6, 137.0, 140.5, 140.56, 140.64, 141.85, 141.94, 147.5, 147.6, 148.1, 152.8, 153.37, 153.43, 189.6, 189.9, 190.3 (4 carbons are missing due to overlapping); HRMS (EI) $[M]^+$ *m*/*z* calcd for $C_{18}H_{18}O_3$ 282.1256, found 282.1253.

*4,5-Methylenedioxy-2-(2-phenylprop-1-enyl)benzaldehyde (**6f**).* Following method B using 2-bromo-4,5-methylenedioxybenzaldehyde (227.9 mg, 1.0 mmol) and triphenyl(1-phenylethyl)phosphonium bromide (446 mg, 1.0 mmol), **6f** was obtained: 152.5 mg (58%, *E*/*Z* = 82:18); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.06 (d, *J* = 1.2 Hz, 3H, *Z*), 2.29 (d, *J* = 1.2 Hz, 3H, *E*), 5.95 (s, 2H, *E*), 6.08 (s, 2H, *Z*), 6.42 (s, 1H, *E*), 6.76 (s, 1H, *Z*), 6.81 (s, 1H, *E*), 7.07 (s, 1H, *Z*), 7.07 (dd, *J* = 7.6 Hz, 2H, *E*), 7.14−7.21(m, 3H, *E*), 7.21 (s, 1H, *E*), 7.33 (t, *J* = 7.2 Hz, 1H, *Z*), 7.40 (t, *J* = 7.4 Hz, 2H, *Z*), 7.40 (s, 1H, *Z*), 7.54 (d, *J* = 7.6 Hz, 2H, *Z*), 10.10 (s, each 1H of *E* and *Z*); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.2, 25.6, 101.6, 101.9, 106.3, 106.4, 109.7, 110.19, 110.21, 122.1, 122.9, 125.7, 127.1, 127.7, 128.1, 128.28, 128.33, 128.8, 139.0, 139.2, 140.0, 140.9, 142.0, 142.3, 146.9, 147.3, 151.9, 152.2, 189.7, 190.0; HRMS (EI) $[M]^+$ *m*/*z* calcd for $C_{17}H_{14}O_3$ 266.0943, found 266.0945.

*2-(2-Phenylpent-1-enyl)benzaldehyde (**6g**).* Following method B using 2-bromobenzaldehyde (555.1 mg, 3.0 mmol) and triphenyl (1-phenylbutyl)phosphonium bromide (1.707 g, 3.6 mmol), **6g** was obtained: 298.5 mg (66%, *E*/*Z* = 93:7); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.74 (t, *J* = 7.4 Hz, 3H, *E*), 0.97 (t, *J* = 7.4 Hz, 3H, *Z*), 1.32 (sextet, *J* = 7.2 Hz, 2H, *E*), 1.48 (sextet, *J* = 7.2 Hz, 2H, *Z*), 2.48 (t, *J* = 7.6 Hz, 2H, *E*), 2.60 (t, *J* = 7.4 Hz, 2H, *Z*), 6.91 (s, 1H, *Z*), 6.97 (d, *J* = 7.6 Hz, 2H, *Z*), 7.03 (s, 1H, *E*), 7.15−7.23 (m, 3H, *Z*), 7.28−7.45 (m, 3H, *Z*), 7.33−7.36 (m, 2H, *E*), 7.40 (t, *J* = 7.4 Hz, 2H, *E*), 7.44 (t, *J* = 7.6 Hz, 1H, *E*), 7.51 (d, *J* = 7.6 Hz, 2H, *E*), 7.61 (t, *J* = 7.0 Hz, 1H, *E*), 7.74 (d, *J* = 6.4 Hz, 1H, *Z*), 7.94 (d, *J* = 7.6 Hz, 1H, *E*), 10.26 (s, 1H, *Z*), 10.32 (s, 1H, *E*); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.7, 16.1, 17.7, 21.3, 32.1, 38.2, 124.3, 125.3, 126.6, 127.2, 127.4, 127.5, 128.0, 128.4, 128.6, 128.9, 129.0, 129.8, 130.4, 131.2, 133.7, 133.9, 134.2, 139.5, 140.6, 141.7, 141.8, 145.8, 192.39, 192.42 (2 carbons are missing due to overlapping); HRMS (EI) $[M]^+$ *m*/*z* calcd for $C_{18}H_{18}O$ 250.1358, found 250.1356.

*2-(2-Methylprop-1-enyl)benzaldehyde (**6h**)*[13e]. Following method B using 2-bromobenzaldehyde (370.1 mg, 2.0 mmol) and isopropyltriphenylphos-phonium iodide (950.5 mg, 2.2 mmol), **6h** was obtained: 152.5 mg (69%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.65 (s, 3H), 1.96 (s, 3H), 6.58 (s, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 10.21 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.4, 26.0, 121.2, 126.8, 128.0, 130.7, 133.5, 133.7, 139.2, 142.2, 192.7.

*2-(2-Methylallyl)benzaldehyde (**6i**)*[17]. Following method C using 3-bromo-2-methylprop-1-ene (334.9 mg, 2.5 mmol, 1.2 equiv), **6i** was obtained: 142.2 mg (44%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.77 (s, 3H), 3.73 (s, 2H), 4.45 (s, 1H), 4.84 (s, 1H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 10.24 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 22.8, 40.1, 112.4, 126.9, 130.5, 131.6, 133.8, 134.3, 142.0, 145.2, 192.0.

*2-Allylbenzaldehyde (**6j**)*[13e]. Following method C using allyl bromide (303 μL, 2.5 mmol, 1 equiv), **6j** was obtained: 223.0 mg (61%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.82 (d, *J* = 6.0 Hz, 2H), 4.99 (dd, *J* = 1.8, 17.0 Hz, 1H), 5.09 (dd, *J* = 1.4, 10.2 Hz, 1H), 6.04 (ddt, *J* = 6.2, 10.4, 17.2 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.53 (td, *J* = 1.4, 7.4 Hz, 1H), 7.85 (d, *J* = 7.6 Hz, 1H), 10.26 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 36.3, 116.2, 126.7, 130.9, 131.4, 133.7, 133.8, 136.8, 142.0, 192.1.

*2-Cinnamylbenzaldehyde (**6k**)*[18]. Following method C using cinnamyl bromide (492.7 mg, 2.5 mmol, 1.2 equiv), **6k** was obtained: 253.2 mg (57%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.99−4.00 (m, 1H), 6.39−6.41 (m, 2H), 7.20 (t, *J* = 7.0 Hz, 1H), 7.28 (t, *J* = 7.2 Hz, 2H), 7.33 (d, *J* = 7.2 Hz, 2H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.55 (td, *J* = 1.2, 7.4 Hz, 1H), 7.86 (dd, *J* = 1.0, 7.4 Hz, 1H), 10.30 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 35.7, 126.1, 126.9, 127.2, 128.4, 128.5, 131.0, 131.5, 132.1, 133.8, 133.9, 137.1, 142.4, 192.4.

*2-(But-3-en-2-yl)-3,4-dimethoxybenzaldehyde (**6l**).* Prepared following the procedure in the literature:[19] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.50 (d, *J* = 7.2 Hz, 3H), 3.81 (s, 3H), 3.94 (s, 3H), 4.55−4.61 (m, 1H), 5.03 (d, *J* = 17.2 Hz, 1H), 5.08 (d, *J* = 10.4 Hz, 1H), 6.24 (ddd, *J* = 4.6, 10.0, 17.2 Hz, 1H), 6.91 (d, *J* = 8.8 Hz, 1H), 7.71 (d, *J* = 8.8 Hz, 1H), 10.26 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.7, 33.7, 55.7, 60.9, 109.9, 113.6, 127.8, 128.1, 142.0, 143.1, 147.0, 157.4, 191.1; HRMS (EI) $[M]^+$ *m*/*z* calcd for $C_{13}H_{16}O_3$ 220.1099, found 220.1095.

Synthesis of α*-Methylstilbene **8**.*[20] Following method B using benzaldehyde (204 μL, 2.0 mmol) and triphenyl(1-phenylethyl)phosphonium bromide (892.2 mg, 2.0 mmol), **8** was obtained 226.3 mg (58%, *E*/*Z* = 86:14): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.22 (d, *J* = 1.2 Hz, 3H, *Z*), 2.30 (d, *J* = 0.8 Hz, 3H, *E*), 6.49 (s, 1H, *Z*), 6.85 (s, 1H, *E*), 6.95 (d, *J* = 6.4 Hz, 2H, *Z*), 7.08−7.13 (m, 3H, *Z*), 7.20 (dd, *J* = 1.6, 7.6 Hz, 2H, *Z*), 7.24−7.30 (m, 3H, *E*), 7.27−7.32 (m, 2H of *E* and 3H of *Z*), 7.37−7.41 (m, 6H, *E*), 7.54 (d, *J* = 7.6 Hz, 2H, *E*); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.4 (*E*), 27.0 (*Z*), 125.9 (*E*), 126.0 (*Z*), 126.4 (*E*), 126.5 (*Z*), 126.8 (*Z*), 127.1 (*E*), 127.6 (*E*), 127.8 (*Z*), 128.1 (*E*), 128.2 (*E*), 128.4 (*Z*), 128.9 (*Z*), 129.1 (*E*), 137.3 (*E*), 137.5 (*Z*), 138.3 (*E*), 138.6 (*Z*), 142.0 (*Z*), 143.8 (*E*) (1 carbon is missing due to overlapping).

General Procedures for the Preparation of Alkenylaryl β-Keto Esters. To a solution of the corresponding 2-alkenylbenzaldehyde and Zn (1.5 equiv) in benzene (0.2 M) in a two-neck round-bottom flask was added methyl bromoacetate (1.2−2.0 equiv). The resulting mixture was heated at 90−100 °C for 1−2 h. The reaction mixture was quenched with satd NH_4Cl and extracted with CH_2Cl_2 (three times). The combined organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel to give the corresponding alkenyl β-hydroxy ester product. To a solution of the corresponding alkenyl β-hydroxy ester in CH_2Cl_2 (0.1 M) in a round-bottom flask was added PCC (2.5 equiv) at 25 °C. The reaction mixture was stirred at 25 °C for 0.25−9.5 h. After the reaction was completed, ∼1 g of Celite was added and the mixture stirred for 5−10 min. The rection mixture was flitered through Celite and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc/*n*-hexane =1:20) to give the corresponding product **1**.

*Methyl 3-oxo-3-(2-(2-phenylprop-1-enyl)phenyl)propanoate (**1a**):* step 1, 84% (from **6a**); step 2, 60% (6 h), *E*/*Z*/allyl = 60 (keto 45 + enol 15):20 (keto 15 + enol 5):20 (keto 15 + enol 5), keto/enol = 3:1: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.09 (s, 3H, *E* of keto), 2.16 (s, 3H, *E* of enol), 2.25 (s, 3H, *Z* of enol), 2.26 (s, 3H, *Z* of keto), 3.69 (s, 3H, *E* of keto), 3.73 (s, 3H, *Z* of keto), 3.76 (s, 3H, *E* of enol), 3.77 (s, 3H, allyl of keto), 3.79 (s, 3H, allyl of enol), 3.82 (s, 3H, *Z* of enol), 3.94 (s, each 2H, *Z* of keto and allyl of keto), 3.96 (s, 2H, *E* of keto), 4.03 (s, 2H, allyl of enol), 4.14 (s, 2H, allyl of keto), 4.78 (s, 1H, allyl of keto), 4.85 (s, 1H, allyl of enol), 5.33 (s, 1H, allyl of enol), 5.435 (s, 1H, allyl of keto), 5.444 (s, 1H, *E* of enol), 5.48 (s, 1H, *Z* of enol), 5.49 (s, 1H, allyl of enol), 6.63 (s, 1H, *Z* of enol), 6.79 (s, 1H, *Z* of keto), 6.84 (d, *J* = 8.0 Hz, 1H, *Z* of enol), 6.91 (d, *J* = 7.2 Hz, 1H, *Z* of keto), 6.97 (s, 1H, *E* of enol), 7.12 (s, 1H, *E* of keto), 7.03−7.60 (m, 6H of *E* of keto, 8H of *E* of enol, 7H of *Z* of keto, 8H of *Z* of enol, 9H of allyl of keto, 9H of allyl of enol), 7.58 (d, *J* = 7.6 Hz, 2H, *E* of keto), 7.66 (d, *J* = 7.6 Hz, each 1H, *E* of enol and *Z* of keto), 7.74 (d, *J* = 7.6 Hz, 1H, *E* of keto), 12.42 (s, 1H, allyl of enol), 12.43 (s, 1H, *Z* of enol), 12.44 (s, 1H, *E* of enol); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.3, 17.4, 25.9, 26.0, 39.0, 39.1, 48.0, 48.3, 48.4, 51.6, 52.47, 52.54, 91.7, 91.9, 92.4, 114.5, 115.0, 126.08, 126.12, 126.17, 126.25, 126.33, 126.5, 126.6, 126.8, 126.9, 127.1, 127.2, 127.5, 127.66, 126.70, 128.25, 128.30, 128.46, 128.53, 128.57, 128.62, 128.8, 128.9, 129.0, 129.2, 129.4, 129.8, 130.1, 130.3, 130.89, 130.94, 131.4, 131.6, 131.8, 132.0, 132.1, 132.3, 132.4, 133.7, 134.0, 134.9, 136.7, 136.9, 137.07, 137.11, 137.2, 137.9, 138.0, 138.7, 138.9, 139.0, 139.4, 140.2, 141.1, 141.2, 141.3, 143.0, 143.4, 147.1, 147.4, 168.0, 168.2, 173.28, 173.34, 173.37, 173.44, 173.6, 174.9, 195.5, 195.85, 195.93; HRMS (EI) $[M]^+$ *m*/*z* calcd for $C_{19}H_{18}O_3$ 294.1256, found 294.1253.

*Methyl 3-(5-fluoro-2-(2-phenylprop-1-enyl)phenyl)-3-oxopropanoate (**1b**):* step 1, 67% (from **6b**); step 2, 66% (8 h), *E*/*Z* = 82 (keto 53 + enol 29):18 (keto 11 + enol 7); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.06 (s, 3H, *E* of keto), 2.14 (s, 3H, *E* of enol), 2.24 (s, 3H, *Z* of enol), 2.25 (s, 3H, *Z* of keto), 3.68 (s, 3H, *E* of keto), 3.768 (s, 3H, *Z* of keto), 3.774 (s, 3H, *E* of enol), 3.82 (s, 3H, *Z* of enol), 3.90 (s, 2H, *Z* of keto), 3.92 (s, 2H, *E* of keto), 5.46 (s, 1H, *E* of enol), 5.54 (s, 1H, *Z* of enol), 6.54 (s, 1H, *Z* of enol), 6.69 (s, 1H, *Z* of keto), 6.75−6.79 (m, 1H, *Z* of keto), 6.87 (s, 1H of *E* of enol and 2H of *Z* of keto), 7.01 (s, 1H, *E* of keto), 7.04−7.49 (m, 6H of *E* of keto, 6H of *E* of enol, 5H of *Z* of keto, 7H of *Z* of enol), 7.52 (d, *J* = 8.0 Hz, 2H, *E* of enol), 7.55 (d, *J* = 7.6 Hz, 2H, *E* of keto), 7.97 (d, *J* = 8.0 Hz, 1H, *Z* of enol), 12.43 (s, each 1H, *Z* of enol and *E* of enol); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.09, 17.14, 25.7, 47.7, 48.0, 51.5, 52.3, 92.2, 92.7, 114.7 (d, *J* = 23.5 Hz), 115.1 (d, *J* = 22.8 Hz), 115.2 (d, *J* = 22.0 Hz), 115.8 (d, *J* = 22.8 Hz), 116.7 (d, *J* = 20.5 Hz), 116.8 (d, *J* = 20.5 Hz), 118.7 (d, *J* = 21.2 Hz), 118.9 (d, *J* = 21.2 Hz), 124.7, 124.9, 125.3, 125.6, 125.8, 125.9, 126.99, 127.03, 127.4, 127.6, 128.1, 128.25, 128.32, 128.35, 128.38, 128.5, 132.4 (d, *J* = 7.6 Hz), 132.876 (d, *J* = 7.6 Hz), 132.883, 133.1, 133.2 (d, *J* = 7.6 Hz), 133.9 (d, *J* = 6.8 Hz), 134.2 (d, *J* = 3.8 Hz), 134.5, 135.4 (d, *J* = 7.6 Hz), 137.2, 138.0, 138.48, 138.54, 138.7, 138.9, 139.9, 140.6, 140.8, 142.4, 142.9, 160.6 (d, *J* = 246.7 Hz), 161.2 (d, *J* = 247.4 Hz), 161.3 (d, *J* = 245.8 Hz), 162.1, 167.4, 167.6, 171.2 (d, *J* = 2.2 Hz), 171.5, 173.0, 173.1, 194.2, 194.7 (d, *J* = 1.5 Hz); HRMS (EI) $[M]^+$ *m*/*z* calcd for $C_{19}H_{17}FO_3$ 312.1162, found 312.1164.

*Methyl 3-(4-fluoro-2-(2-phenylprop-1-enyl)phenyl)-3-oxopropanoate (**1c**):* step 1, 66% (from **6c**); step 2, 77% (5 h), *E*/*Z* = 77 (keto 57 + enol 20):23 (keto 18 + enol 5); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.11 (s, 3H, *Z* of keto), 2.18 (s, 3H, *Z* of enol), 2.24 (s, 3H, *E* of enol), 2.26 (s, 3H, *E* of keto), 3.69 (s, 3H, *Z* of keto), 3.76 (s, each 3H, *E* of keto and *Z* of enol), 3.81 (s, 3H, *E* of enol), 3.92 (s, 2H, *E* of keto), 3.94 (s, 2H, *Z* of keto), 5.41 (s, 1H, *Z* of enol), 5.46 (s, 1H, *E* of enol), 6.50 (dd, *J* = 2.4, 10.4 Hz, 1H, *Z* of keto), 6.56 (dd, *J* = 2.4, 10.0 Hz, each 1H, *E* of keto and *E* of enol), 6.76 (s, 1H, *E* of keto), 6.81−6.90 (m, each 1H, *E* of keto, *E* of enol, and *Z* of keto), 7.05−7.22 (m, 5H of *E* of keto, 2H of *E* of enol, 4H of *Z* of keto, 5H of *Z* of enol), 7.31 (t, *J* = 7.4 Hz, 1H of *E* of enol and 2H of *Z* of enol), 7.39 (t, *J* = 7.4 Hz, 2H of *E* of enol and 1H of *Z* of keto), 7.50−7.54 (m, 2H, *Z* of keto), 7.57 (d, *J* = 8.0 Hz, 2H, *E* of enol), 7.63 (dd, *J* = 6.0, 8.8 Hz, 1H of *E* of keto and 2H of *Z* of enol), 7.79 (dd, *J* = 5.6, 9.2 Hz, 1H, *Z* of keto), 12.44 (s, 1H, *E* of enol), 12.46 (s, 1H, *Z* of enol); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 16.9, 17.0, 25.5, 25.6, 47.5, 47.7, 51.2, 52.06, 52.14, 91.6, 92.0, 113.2 (d, *J* = 22.0 Hz), 113.3 (d, *J* = 22.0 Hz), 113.7 (d, *J* = 22.0 Hz), 117.2 (d, *J* = 22.0 Hz), 117.6 (d, *J* = 22.0 Hz), 117.9 (d, *J* = 21.3 Hz), 118.7 (d, *J* = 22.0 Hz), 124.6, 125.1, 125.4, 125.67, 125.71, 125.8, 127.06, 127.12, 127.4, 127.5, 128.01, 128.04, 128.1, 128.2, 129.6, 130.0 (d, *J* = 8.3 Hz), 130.3 (d, *J* = 9.1 Hz), 131.4 (d, *J* = 9.1 Hz), 131.9 (d, *J* = 9.8 Hz), 132.5 (d, *J* = 3.0 Hz), 132.8, 137.8, 138.2, 139.4 (d, *J* = 9.2 Hz), 139.9, 140.2 (d, *J* = 8.8 Hz), 140.4, 141.8 (d, *J* = 9.1 Hz), 142.1 (d, *J* = 9.1 Hz), 142.3, 142.6, 162.8 (d, *J* = 248.2 Hz), 163.8 (d, *J* = 252.7 Hz), 164.1 (d, *J* = 253.5 Hz), 167.5, 167.7, 171.8, 172.1, 172.9, 173.0, 193.5, 193.7; HRMS (EI) $[M]^+$ *m*/*z* calcd for $C_{19}H_{17}FO_3$ 312.1162, found 312.1166.

*Methyl 3-(5-methyl-2-(2-phenylprop-1-enyl)phenyl)-3-oxopropanoate (**1d**):* step 1, 79% (from **6d**); step 2, 76% (6 h); *E*/*Z* = 91 (keto 68 + enol 23):9 (keto 7 + enol 2); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.08 (s, 3H, *Z* of keto), 2.16 (s, 3H, *Z* of enol), 2.23 (s, 3H, *E* of enol), 2.24 (s, 3H, *E* of keto), 2.27 (s, 3H, *E* of enol), 2.29 (s, 3H, *E* of keto), 2.40 (s, 3H, *Z* of enol), 2.42 (s, 3H, *Z* of keto), 3.68 (s, 3H, *Z* of keto), 3.76 (s, each 3H, *E* of keto and *Z* of enol), 3.81 (s, 3H, *E* of enol), 3.93 (s, 2H, *E* of keto), 3.95 (s, 2H, *Z* of keto), 5.43 (s, 1H, *Z* of enol), 5.49 (s, 1H, *E* of enol), 6.58 (s, 1H, *E* of enol), 6.72 (s, 1H, *E* of enol), 6.73 (s, 1H, *E* of keto), 6.79 (d, *J* = 7.6 Hz, 1H, *E* of keto), 6.86 (d, *J* = 7.2 Hz, 1H, *E* of enol), 6.97 (d, *J* = 8.0 Hz, 1H, *E* of keto), 7.07−7.53 (m, 5H of *E* of keto, 6H of *E* of enol, 6H of *Z* of keto, 9H of *Z* of enol), 7.38 (s, 1H, *E* of keto), 7.56 (d, *J* = 7.6 Hz, 2H, *Z* of keto), 7.97 (d, *J* = 7.2 Hz, 1H, *Z* of keto), 12.43 (s, 1H, *E* of enol), 12.44 (s, 1H, *Z* of enol); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.00, 17.04, 20.8, 20.9, 25.61, 25.64, 26.4, 47.7, 48.0, 51.2, 52.2, 91.5, 125.6, 125.8, 126.4, 126.7, 127.2, 127.9, 128.0, 128.1, 128.2, 128.3, 128.4, 128.5, 128.7, 129.1, 129.5, 130.3, 130.5, 130.9, 131.1, 131.9, 132.3, 132.5, 132.9, 133.2, 133.9, 135.3, 135.6, 135.86, 135.90, 136.4, 136.6, 136.8, 137.9, 138.6, 141.0, 141.2, 167.9, 173.1, 173.4, 195.4, 195.8; HRMS (EI) $[M]^+$ *m*/*z* calcd for $C_{20}H_{20}O_3$ 308.1412, found 308.1411.

*Methyl 3-(5-methoxy-2-(2-phenylprop-1-enyl)phenyl)-3-oxopropanoate (**1e**):* step 1, 72% (from **F**); step 2, 63% (0.5 h); *E*/*Z*/allyl = 87 (keto 62 + enol 25):13 (keto 9 + enol 4):trace; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.07 (s, 3H, *E* of keto), 2.15 (d, *J* = 1.2 Hz, 3H, *E* of enol), 2.22 (d, *J* = 1.2 Hz, 3H, *Z* of enol), 2.24 (d, *J* = 1.6 Hz, 3H, *Z* of keto), 3.67 (s, 3H, *E* of keto), 3.76 (s, each 3H, *Z* of keto and *Z* of enol), 3.77 (s, each 3H, *Z* of keto and *E* of enol), 3.82 (s, 3H, *Z* of enol), 3.86 (s, 3H, *E* of enol), 3.87 (s, 3H, *E* of keto), 3.92 (s, 2H, *Z* of keto), 3.93 (s, 2H, *E* of keto), 5.45 (s, 1H, *E* of enol), 5.51 (s, 1H, *Z* of enol), 6.54 (s, 1H, *Z* of enol), 6.61 (dd, *J* = 2.4, 8.8 Hz, 1H, *Z* of enol), 6.68 (s, 1H, *Z* of keto), 6.72 (dd, *J* = 2.8, 8.8 Hz, 1H, *Z* of keto), 6.75 (d, *J* = 8.8 Hz, 1H, *Z* of enol), 6.82 (d, *J* = 8.8 Hz, 1H, *Z* of keto), 6.89 (s, 1H, *E* of enol), 7.00

(dd, J = 2.8, 8.8 Hz, 1H, E of enol), 7.02 (s, 1H, E of keto), 7.08 (dd, J = 3.0, 8.6 Hz, each 1H, E of keto and E of enol), 7.12−7.31 (m, 2H of E of enol, 6H of Z of keto, 6H of Z of enol), 7.17 (d, J = 7.6 Hz, 1H, E of enol), 7.21 (d, J = 2.4 Hz, 1H, E of enol), 7.24 (d, J = 2.4 Hz, 1H, E of keto), 7.29 (d, J = 7.6 Hz, 1H, E of keto), 7.38 (t, J = 7.4 Hz, 3H, E of keto), 7.52 (d, J = 7.4 Hz, 2H, E of enol), 7.55 (d, J = 7.2 Hz, 2H, E of keto), 12.44 (s, 1H, Z of enol), 12.45 (s, 1H, E of enol); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 16.98, 17.04, 25.6, 47.9, 48.1, 51.3, 52.1, 52.2, 55.1, 55.18, 55.24, 55.3, 91.8, 92.3, 112.4, 112.9, 113.5, 113.8, 115.9, 117.3, 117.6, 125.3, 125.7, 125.8, 125.9, 126.1, 126.7, 127.0, 127.3, 128.0, 128.20, 128.22, 128.5, 129.2, 129.3, 130.4, 130.7, 131.8, 132.2, 132.5, 133.1, 134.7, 135.9, 137.6, 138.1, 138.4, 141.0, 141.2, 142.7, 143.2, 157.6, 158.2, 167.6, 167.8, 172.5, 172.8, 173.0, 195.2, 195.7; HRMS (EI) $[M]^+$ m/z calcd for $C_{20}H_{20}O_4$ 324.1362, found 324.1365.

*Methyl 3-oxo-3-(2-(2-phenylpent-1-enyl)phenyl)propanoate (**1f**):* step 1, 86% (from **6g**); step 2, 83% (9.5 h); E/Z = >99:1, keto/enol = 71:29; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.74 (t, J = 7.2 Hz, 3H, keto), 0.79 (t, J = 7.4 Hz, 3H, enol), 1.24−1.39 (m, each 2H, keto and enol), 2.49 (t, J = 7.8 Hz, 2H, keto), 2.57 (t, J = 7.6 Hz, 2H, enol), 3.68 (s, 3H, keto), 3.77 (s, 3H, enol), 3.95 (s, 2H, keto), 5.47 (s, 1H, enol), 6.79 (s, 1H, enol), 6.94 (s, 1H, keto), 7.28−7.47 (m, 5H of keto and 8H of enol), 7.51 (d, J = 7.2 Hz, 2H, keto), 7.53 (t, J = 8.0 Hz, 1H, keto), 7.66 (d, J = 7.6 Hz, 1H, enol), 7.74 (d, J = 7.6 Hz, 1H, keto), 12.41 (s, 1H, enol); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.6, 13.8, 21.3, 21.4, 31.7, 31.8, 47.9, 51.1, 52.0, 92.0, 126.5, 126.6, 126.7, 126.8, 127.0, 127.1, 127.3, 127.5, 127.9, 128.2, 128.8, 129.1, 129.8, 130.2, 130.8, 131.8, 133.6, 136.6, 136.9, 138.4, 141.9, 142.26, 142.32, 142.8, 167.6, 172.9, 173.0, 195.2; HRMS (EI) $[M]^+$ m/z calcd for $C_{21}H_{22}O_3$ 322.1569, found 322.1564.

*Methyl 3-(2-(2-methylprop-1-enyl)phenyl)-3-oxopropanoate (**1g**):* step 1, 84% (from **6h**); step 2, 77% (8 h); keto/enol = 75:25; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.67 (s, 3H, keto), 1.75 (s, 3H, enol), 1.90 (s, 3H, enol), 1.92 (s, 3H, keto), 3.73 (s, 3H, keto), 3.79 (s, 3H, enol), 3.91 (s, 2H, keto), 5.39 (s, 1H, enol), 6.34 (s, 1H, enol), 6.47 (s, 1H, keto), 7.23 (d, J = 7.2 Hz, 1H, keto), 7.23−7.33 (m, 2H, enol), 7.31 (t, J = 7.8 Hz, 1H, keto), 7.37 (t, J = 7.0 Hz, 1H, enol), 7.46 (t, J = 7.2 Hz, 1H, keto), 7.59 (d, J = 8.0 Hz, 1H, enol), 7.64 (d, J = 8.0 Hz, 1H, keto), 12.39 (s, 1H, enol); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.2, 25.98, 26.04, 48.2, 51.2, 52.12, 52.14, 91.8, 123.9, 124.0, 124.1, 126.2, 126.4, 128.0, 128.6, 129.6, 130.6, 131.0, 131.5, 133.3, 135.4, 137.1, 137.2, 138.1, 167.8, 173.1, 173.2, 196.4; HRMS (EI) $[M]^+$ m/z calcd for $C_{14}H_{16}O_3$ 232.1099, found 232.1101.

*Methyl 3-(2-(2-methylallyl)phenyl)-3-oxopropanoate (**1h**):* step 1, 86% (from **6i**); step 2, 68% (7 h); keto/enol = 74:26; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.70 (s, 3H, enol), 1.73 (s, 3H, keto), 3.51 (s, 2H, enol), 3.60 (s, 2H, keto), 3.74 (s, 3H, keto), 3.80 (s, 3H, enol), 3.93 (s, 2H, keto), 4.44 (s, 1H, keto), 4.55 (s, 1H, enol), 4.80 (s, 1H, keto), 4.83 (s, 1H, enol), 5.30 (s, 1H, enol), 7.24−7.33 (m, each 2H, keto and enol), 7.37 (t, J = 7.0 Hz, 1H, enol), 7.42 (d, J = 8.0 Hz, 1H, enol), 7.45 (t, J = 7.0 Hz, 1H, keto), 7.62 (d, J = 7.6 Hz, 1H, keto), 12.39 (s, 1H, enol); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 22.4, 22.7, 41.0, 41.2, 48.2, 51.2, 52.2, 91.3, 111.7, 112.2, 126.1, 126.2, 128.57, 128.63, 129.9, 130.6, 131.7, 134.6, 137.0, 137.8, 139.9, 144.6, 145.0, 167.7, 173.0, 174.6, 195.8 (1 carbon is missing due to overlapping); HRMS (EI) $[M]^+$ m/z calcd for $C_{14}H_{16}O_3$ 232.1099, found 232.1097.

*Methyl 3-(2-allylphenyl)-3-oxopropanoate (**1i**):* step 1, 62% (from **6j**); step 2, 59% (6 h); keto/enol = 77:23; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.57 (d, J = 6.4 Hz, 2H, enol), 3.66 (d, J = 6.5 Hz, 2H, keto), 3.74 (s, 3H, keto), 3.80 (s, 3H, enol), 3.95 (s, 2H, keto), 3.97 (s, 2H, keto), 4.98−5.07 (m, each 2H, keto and enol), 5.31 (s, 1H, enol), 5.93−6.05 (m, each 1H, keto and enol), 7.23−7.27 (m, 2H, enol), 7.31 (t, J = 7.2 Hz, 1H, keto), 7.32 (d, J = 7.6 Hz, 1H, keto), 7.33−7.36 (m, 1H, enol), 7.39 (t, J = 7.1 Hz, 1H, enol), 7.45 (t, J = 7.2 Hz, 1H, keto), 7.64 (d, J = 7.6 Hz, 1H, keto), 12.40 (s, 1H, enol); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 37.6, 37.8, 48.0, 51.2, 52.2, 91.4, 115.76, 115.84, 126.1, 126.2, 128.6, 128.8, 130.1, 130.2, 131.3, 132.1, 134.2, 136.2, 137.0, 138.3, 140.6, 167.7, 172.9, 174.7, 195.6 (1 carbon is missing due to overlapping); HRMS (EI) $[M]^+$ m/z calcd for $C_{13}H_{14}O_3$ 218.0943, found 218.0943.

General Procedures for the Preparation of Alkenylaryl Ketones. To a solution of the corresponding 2-alkenylbenzaldehyde in dry THF (0.2 M) in a two-neck round-bottom flask was added MeMgBr, PhMgBr, or n-BuLi (1.5 equiv) at −78 °C. After being stirred at −78 °C for 0.5−1 h, the reaction mixture was quenched with satd NH_4Cl and extracted with CH_2Cl_2 (three times). The combined organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel to give the corresponding 2-alkenylaryl alcohol product. To a solution of the corresponding 2-alkenylaryl alcohol in CH_2Cl_2 (0.1 M) in a round-bottom flask was added PCC (2.5 equiv) at 25 °C. The reaction mixture was stirred at 25 °C for 2−3 h. After the reaction was completed, ∼1 g of Celite was added and the mixture stirred for 5−10 min. The rection mixture was flitered through Celite and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc/n-hexane = 1:20−1:50) to give the corresponding product **5**.

*1-(2-(2-Phenylprop-1-enyl)phenyl)ethanone (**5a**):* step 1, 85% (from **6a**); step 2, 86%; E/Z/allyl = 58:18:24; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.09 (d, J = 1.2 Hz, 3H, E), 2.25 (d, J = 1.6 Hz, 3H, Z), 2.49 (s, 3H, Z), 2.55 (s, 3H, allyl), 2.57 (s, 3H, E), 4.12 (s, 2H, allyl), 4.74 (d, J = 1.2 Hz, 1H, allyl), 5.39 (s, 1H, allyl), 6.77 (s, 1H, Z), 6.91 (dd, J = 2.4, 6.8 Hz, 1H, Z), 7.06 (dd, J = 2.0, 7.2 Hz, 2H, Z), 7.14 (s, 1H, E), 7.14−7.18 (m, 2H of Z and 3H of allyl), 7.25−7.40 (m, 5H of E, 4H of Z, and 3H of allyl), 7.44 (d, J = 7.2 Hz, 2H, allyl), 7.51 (t, J = 6.8 Hz, 1H, E), 7.57 (d, J = 7.2 Hz, 2H, E), 7.66 (d, J = 7.6 Hz, 1H, allyl), 7.75 (dd, J = 1.2, 7.4 Hz, 1H, E); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.0, 25.6, 29.3, 29.5, 29.7, 38.7, 113.9, 125.8, 126.0, 126.1, 126.3, 126.7, 127.20, 127.21, 127.4, 127.9, 128.1, 128.2, 128.45, 128.53, 128.88, 128.91, 130.7, 130.8, 131.1, 131.2, 131.6, 131.7, 136.8, 137.8, 138.1, 138.17, 138.21, 138.4, 138.8, 141.0, 141.1, 142.9, 147.7, 201.4, 201.6, 202.0 (3 carbons are missing due to overlapping); HRMS (EI) $[M]^+$ m/z calcd for $C_{17}H_{16}O$ 236.1201, found 236.1205.

*1-(2-(2-Phenylprop-1-enyl)phenyl)pentan-1-one (**5b**):* step 1, 77% (from **6a**); step 2, 81%; E/Z/allyl = 62:18:20; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.88 (t, J = 7.2 Hz, 3H, E), 0.92 (t, J = 7.2 Hz, 3H, allyl), 0.95 (t, J = 7.4 Hz, 3H, E), 1.23−1.42 (m, each 2H of E, Z, and allyl), 1.65 (sextet, J = 7.2 Hz, each 2H of E, Z, and allyl), 2.08 (d, J = 1.2 Hz, 3H, E), 2.24 (d, J = 1.2 Hz, 3H, Z), 2.82 (t, J = 7.4 Hz, 2H, allyl), 2.84 (t, J = 7.4 Hz, 3H, Z), 2.87 (t, J = 7.4 Hz, 3H, E), 4.07 (s, 2H, allyl), 4.77 (d, J = 0.8 Hz, 1H, allyl), 5.40 (s, 1H, allyl), 6.72 (s, 1H, Z), 6.89 (d, J = 7.6 Hz, 1H, Z), 7.07−7.21 (m, each 2H of E, Z, and allyl), 7.24−7.57 (m, 5H of E, 6H of Z, and 7H of allyl), 7.55 (d, J = 7.6 Hz, 2H, E), 7.65 (dd, J = 1.2, 7.6 Hz, 1H, E); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.7, 13.79, 13.82, 17.0, 22.26, 22.29, 25.6, 26.2, 26.3, 26.5, 38.5, 41.1, 41.5, 41.6, 114.1, 125.8, 125.9, 125.98, 126.00, 126.1, 126.6, 126.9, 127.2, 127.3, 127.7, 127.8, 127.9, 128.0, 128.1, 128.2, 128.4, 130.2, 130.5, 130.6, 131.3, 131.6, 137.0, 137.2, 137.4, 138.23, 138.24, 138.6, 138.9, 139.0, 141.00, 141.03, 142.9, 147.5, 204.4, 204.8, 205.0 (3 carbons are missing due to overlapping); HRMS (EI) $[M]^+$ m/z calcd for $C_{20}H_{22}O$ 278.1671, found 278.1672.

*Phenyl(2-(2-phenylprop-1-enyl)phenyl)methanone (**5c**):* step 1, 76% (from **6a**); step 2, 79%; E/Z/allyl = 57:19:24; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.05 (d, J = 1.2 Hz, 3H, E), 2.06 (d, J = 1.6 Hz, 3H, Z), 3.96 (s, 2H, allyl), 4.91 (d, J = 1.2 Hz, 1H, allyl), 5.36 (s, 1H, allyl), 6.51 (s, 1H, Z), 6.68 (s, 1H, E), 6.97 (dd, J = 3.6, 6.0 Hz, 1H, Z), 7.07−7.30 (m, each 6H of E, Z, and allyl), 7.35−7.46 (m, 4H of E, 3H of Z, and 4H of allyl), 7.51−7.60 (m, each 2H of E, Z, and allyl), 7.73−7.77 (m, each 2H of E, Z, and allyl); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.2, 25.9, 38.3, 115.0, 124.6, 125.4, 125.6, 125.97, 126.04, 126.4, 126.7, 127.0, 127.2, 127.9, 128.0, 128.09, 128.13, 128.2, 128.3, 128.55, 128.61, 129.5, 129.6, 128.8, 129.9, 130.0, 130.1, 130.55, 130.63, 132.7, 132.9, 137.18, 137.24, 137.45, 137.51, 137.8, 138.2, 138.3, 138.4, 138.5, 138.7, 139.7, 140.4, 141.0, 142.9,

dx.doi.org/10.1021/jo201339z |*J. Org. Chem.* 2011, 76, 7204–7215

146.6, 197.7, 198.0, 198.1 (5 carbons are missing due to overlapping); HRMS (EI) $[M]^+$ m/z calcd for $C_{22}H_{18}O$ 298.1358, found 298.1360.

*1-(4-Fluoro-2-(2-phenylprop-1-enyl)phenyl)ethanone (**5d**):* step 1, 76% (from **6c**); step 2, 88%; *E*/*Z* = 79:21; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.10 (d, J = 1.2 Hz, 3H, *Z*), 2.25 (d, J = 1.6 Hz, 3H, *E*), 2.49 (s, 3H, *E*), 2.56 (s, 3H, *Z*), 6.57 (dd, J = 2.6, 10.2 Hz, 1H, *E*), 6.75 (s, 1H, *E*), 6.84 (dt, J = 2.8, 8.2 Hz, 1H, *E*), 7.03−7.07 (m, each 2H of *E* and *Z*), 7.11 (s, 1H, *Z*), 7.15−7.22 (m, 3H, *E*), 7.31 (t, J = 7.4 Hz, 1H, *Z*), 7.39 (t, J = 7.6 Hz, 2H, *Z*), 7.57 (d, J = 7.2 Hz, 2H, *Z*), 7.62 (dd, J = 6.0, 8.8 Hz, 1H, *E*), 7.80 (dd, J = 5.4, 9.2 Hz, 1H, *Z*); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 16.9, 25.6, 29.1, 29.4, 113.1 (d, J = 21.3 Hz), 113.5 (d, J = 21.3 Hz), 117.6 (d, J = 21.3 Hz), 118.3 (d, J = 21.2 Hz), 125.5, 125.8, 126.3 (d, J = 2.5 Hz), 127.0, 127.4, 128.0, 128.2, 128.3, 131.1 (d, J = 9.2 Hz), 131.7 (d, J = 9.9 Hz), 134.1 (d, J = 3.1 Hz), 134.2 (d, J = 3.1 Hz), 137.3, 139.5, 140.4, 141.16 (d, J = 9.1 Hz), 141.20 (d, J = 9.1 Hz), 142.6, 163.5 (d, J = 250.4 Hz), 163.8 (d, J = 251.9 Hz), 199.5 (1 carbon is missing due to overlapping); HRMS (EI) $[M]^+$ m/z calcd for $C_{17}H_{15}FO$ 254.1107, found 254.1103.

*1-(4,5-Dimethoxy-2-(2-phenylprop-1-enyl)phenyl)ethanone (**5e**):* step 1, 92% (from **6e**); step 2, 70%; *E*/*Z*/allyl = 65:18:17; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.08 (s, 3H, *E*), 2.27 (s, 3H, *Z*), 2.53 (s, 3H, *E*), 2.55 (s, 3H, *Z*), 2.58 (s, 3H, allyl), 3.37 (s, 3H, allyl), 3.83 (s, 3H, allyl), 3.87 (s, 3H, *Z*), 3.91 (s, 3H, *Z*), 3.95 (s, 3H, *E*), 3.96 (s, 3H, *E*), 4.14 (s, 2H, allyl), 4.80 (s, 1H, allyl), 5.39 (s, 1H, allyl), 6.31 (s, 1H, allyl), 6.76 (s, 1H, allyl), 6.78 (s, 1H, *E*), 6.82 (s, 1H, *Z*), 7.10 (s, 1H, *Z*), 7.12 (s, 1H, *E*), 7.10−7.32 (m, 4H of *Z* and 5H of allyl), 7.30 (t, J = 7.2 Hz, 1H, *E*), 7.35 (s, 1H, *E*), 7.39 (t, J = 7.6 Hz, 2H, *E*), 7.45 (d, J = 7.2 Hz, 2H, *Z*), 7.57 (d, J = 7.2 Hz, 2H, *E*); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.1, 25.7, 29.5, 29.8, 30.1, 39.0, 55.4, 55.9, 56.0, 56.1, 111.6, 112.0, 113.0, 113.2, 113.8, 114.2, 114.7, 125.8, 126.1, 126.7, 126.8, 127.4, 127.5, 127.7, 128.2, 128.3, 128.4, 128.5, 130.0, 130.3, 130.8, 132.6, 132.8, 134.1, 136.8, 138.3, 141.3, 141.6, 142.8, 146.5, 146.7, 147.4, 147.9, 150.8, 151.4, 151.5, 199.7, 199.88, 199.92 (2 carbons are missing due to overlapping); HRMS (EI) $[M]^+$ m/z calcd for $C_{19}H_{20}O_3$ 296.1412, found 296.1415.

General Procedure for Au(I)-Catalyzed Cyclization Reaction of Alkenyl Carbonyl Compounds. The mixture of Ph_3PAuCl (2 mol %, 1.9 mg, 0.00391 mmol) and AgOTf (2 mol %, 1.0 mg, 0.00391 mmol) in $ClCH_2CH_2Cl$ (977 μL, 0.2 M) was stirred vigorously for 1 h. To the resulting solution was added alkenyl carbonyl compound **1**, **5**, or **6** (0.195 mmol) in $ClCH_2CH_2Cl$ (977 μL, 0.2 M). The resulting mixture was stirred at the 80 °C for the reported time. After the reaction was complete, solvent was evaporated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc/*n*-hexane = 1:20 (for **2**), 1:50−1:100 (for **3**, **7a**−**g**), 1:10 (for **4a**); only *n*-hexane (for **7h**)) to afford the corresponding product.

*Methyl 2-(3-phenylnaphthalen-1-yl)acetate (**2a**):* ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.71 (s, 3H), 4.15 (s, 2H), 7.40 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.6 Hz, 2H), 7.53−7.58 (m, 2H), 7.71 (s, 1H), 7.74 (d, J = 7.6 Hz, 2H), 7.93 (dd, J = 2.0, 6.4 Hz, 1H), 8.01 (s, 1H), 8.02 (dd, J = 2.4, 6.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 39.1, 52.2, 123.7, 125.8, 126.2, 126.4, 127.37, 127.42, 127.8, 128.8, 129.0, 131.0, 131.3, 134.1, 138.1, 140.7, 171.9; HRMS (EI) $[M]^+$ m/z calcd for $C_{19}H_{16}O_2$ 276.1150, found 276.1153.

*Methyl 2-(7-fluoro-3-phenylnaphthalen-1-yl)acetate (**2b**):* ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.72 (s, 3H), 4.08 (s, 2H), 7.31 (td, J = 2.0, 8.4 Hz, 1H), 7.39 (t, J = 7.2 Hz, 1H), 7.49 (t, J = 7.4 Hz, 2H), 7.63 (dd, J = 1.8, 11.0 Hz, 1H), 7.71 (d, J = 8.4 Hz, 2H), 7.72 (s, 1H), 7.91(dd, J = 6.0, 8.8 Hz, 1H), 7.99 (s, J = 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 39.1, 52.3, 107.6 (d, J = 22.2 Hz), 116.6 (d, J = 25.0 Hz), 125.7, 127.3, 127.5, 128.8, 128.9, 130.6 (d, J = 6.1 Hz), 131.1, 131.4 (d, J = 9.1 Hz), 132.2 (d, J = 8.3 Hz), 137.5 (d, J = 3.1 Hz), 140.4, 161.0 (d, J = 245.2 Hz), 171.6; HRMS (EI) $[M]^+$ m/z calcd for $C_{19}H_{15}FO_2$ 294.1056, found 294.1055.

*Methyl 2-(6-fluoro-3-phenylnaphthalen-1-yl)acetate (**2c**):* ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.70 (s, 3H), 4.12 (s, 2H), 7.31 (td, J = 2.4, 8.8 Hz, 1H), 7.40 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 8.0 Hz, 2H), 7.53 (dd, J = 2.4, 10.0 Hz, 1H), 7.64 (s, 1H), 7.71 (d, J = 7.2 Hz, 2H), 7.93 (s, 1H), 8.01 (dd, J = 5.4, 9.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 39.3, 52.3, 111.9 (d, J = 20.5 Hz), 116.5 (d, J = 25.1 Hz), 125.2 (d, J = 5.4 Hz), 126.3 (d, J = 9.1 Hz), 127.2, 127.4, 127.7, 128.3, 128.9, 131.3, 135.2 (d, J = 9.1 Hz), 139.4, 140.3, 160.8 (d, J = 245.2 Hz), 171.7; HRMS (EI) $[M]^+$ m/z calcd for $C_{19}H_{15}FO_2$ 294.1056, found 294.1058.

*Methyl 2-(7-methyl-3-phenylnaphthalen-1-yl)acetate (**2d**):* ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.57 (s, 3H), 3.71 (s, 3H), 4.12 (s, 2H), 7.37 (d, J = 8.0 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H), 7.67 (s, 1H), 7.72 (d, J = 7.2 Hz, 2H), 7.77 (s, 1H), 7.83 (d, J = 8.4 Hz, 1H), 7.96 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 22.2, 39.1, 52.2, 122.7, 125.6, 127.25, 127.29, 127.8, 128.5, 128.8, 128.9, 130.3, 131.4, 132.3, 136.2, 137.2, 140.8, 172.0; HRMS (EI) $[M]^+$ m/z calcd for $C_{20}H_{18}O_2$ 290.1307, found 290.1307.

*Methyl 2-(7-methoxy-3-phenylnaphthalen-1-yl)acetate (**2e**):* ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.70 (s, 3H), 3.96 (s, 3H), 4.09 (s, 2H), 7.20 (dd, J = 2.0, 9.2 Hz, 1H) 7.30 (s, 1H), 7.37 (t, J = 7.2 Hz, 1H), 7.48 (t, J = 7.2 Hz, 2H), 7.68 (s, 1H), 7.71 (d, J = 7.2 Hz, 2H), 7.83 (d, J = 8.8 Hz, 1H), 7.94 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 39.6, 52.2, 55.3, 102.4, 118.7, 125.6, 127.1, 127.2, 128.3, 128.8, 129.5, 129.8, 130.5, 132.4, 135.9, 140.8, 158.1, 172.0; HRMS (EI) $[M]^+$ m/z calcd for $C_{20}H_{18}O_3$ 306.1256, found 306.1256.

*Methyl 2-(2-ethyl-3-phenylnaphthalen-1-yl)acetate (**2f**):* ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.02 (t, J = 7.4 Hz, 3H), 2.83 (t, J = 7.2 Hz, 3H), 3.72 (s, 3H), 4.24 (s, 2H), 7.38−7.48 (m, 6H), 7.53 (t, J = 7.6 Hz, 1H), 7.64 (s, 1H), 7.80 (d, J = 8.0 Hz, 1H), 8.00 (d, J = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 15.1, 23.7, 34.5, 52.1, 123.6, 125.3, 126.4, 126.9, 127.7, 127.9, 128.5, 129.1, 129.4, 131.7, 132.3, 139.6, 141.0, 142.4, 172.3; HRMS (EI) $[M]^+$ m/z calcd for $C_{21}H_{20}O_2$ 304.1463, found 304.1470.

*1-Methyl-3-phenylnaphthalene (**3a**):* ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.80 (s, 3H), 7.41 (t, J = 7.4 Hz, 1H), 7.50−7.56 (m, 4H), 7.64 (s, 1H), 7.76 (d, J = 7.2 Hz, 2H), 7.92−7.95 (m, 2H), 8.03−8.06 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.5, 124.0, 124.2, 125.8, 126.0, 126.3, 127.2, 127.4, 128.77, 128.82, 131.8, 133.8, 134.8, 138.2, 141.2; GC/MS R_t = 15.83 min; MS (EI) m/z 218 (M^+), 202, 189, 165, 141, 115, 108, 101, 77, 65, 51, 39. Spectral data of **3a** were consistent with data reported in the literature.[21]

*7-Fluoro-1-methyl-3-phenylnaphthalene (**3b**):* ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.71 (s, 3H), 7.30 (td, J = 2.4, 8.6 Hz, 1H), 7.38 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.8 Hz, 2H), 7.61 (dd, J = 2.0, 11.0 Hz, 1H), 7.63 (s, 1H), 7.71 (d, J = 7.6 Hz, 2H), 7.87−7.91 (m, 1H), 7.90 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.5, 107.7 (d, J = 21.2 Hz), 116.2 (d, J = 25.1 Hz), 124.0, 127.21, 127.29, 127.32, 128.8, 130.8, 131.1 (d, J = 9.1 Hz), 132.7 (d, J = 8.4 Hz), 134.2 (d, J = 6.1 Hz), 137.5 (d, J = 3.1 Hz), 140.9, 160.7 (d, J = 244.3 Hz); HRMS (EI) $[M]^+$ m/z calcd for $C_{17}H_{13}F$ 236.1001, found 236.1002.

*6-Fluoro-1-methyl-3-phenylnaphthalene (**3c**):* ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.76 (s, 3H), 7.30 (td, J = 2.6, 8.8 Hz, 1H), 7.41 (t, J = 7.4 Hz, 1H), 7.49−7.54 (m, 1H), 7.51 (t, J = 8.0 Hz, 2H), 7.57 (s, 1H), 7.73 (d, J = 6.8 Hz, 2H), 7.85 (s, 1H), 8.01 (dd, J = 5.6, 9.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.6, 111.6 (d, J = 19.7 Hz), 115.8 (d, J = 25.0 Hz), 123.5, 123.6, 125.7 (d, J = 2.2 Hz), 126.5 (d, J = 8.4 Hz), 127.4, 127.5, 128.8, 134.8 (d, J = 9.1 Hz), 135.0, 139.4, 140.8, 160.8 (d, J = 244.4 Hz); HRMS (EI) $[M]^+$ m/z calcd for $C_{17}H_{13}F$ 236.1001, found 236.0996.

*1,7-Dimethyl-3-phenylnaphthalene (**3d**):* ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.59 (s, 3H), 2.76 (s, 3H), 7.38 (d, J = 8.4 Hz, 1H), 7.39 (t, J = 7.8 Hz, 1H), 7.50 (t, J = 7.6 Hz, 2H), 7.60 (s, 1H), 7.74 (d, J = 7.6 Hz, 2H), 7.80 (s, 1H), 7.83 (d, J = 8.8 Hz, 1H), 7.90 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.5, 22.1, 123.1, 124.0, 126.3, 127.1, 127.3, 128.2, 128.6, 128.7, 131.95, 132.01, 134.1, 135.4, 137.2, 141.3; GC/MS t_R = 16.34 min; EI m/z 232 (M^+), 215, 202, 189, 165, 152, 125, 108, 101, 94, 75, 65, 51. Spectral data of **3d** were consistent with data reported in the literature.[21a]

*7-Methoxy-1-methyl-3-phenylnaphthalene (**3e**):* ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.74 (s, 3H), 3.99 (s, 3H), 7.22 (d, J = 8.8 Hz, 1H), 7.26

(s, 1H), 7.38 (t, J = 7.0 Hz, 1H), 7.49 (t, J = 7.4 Hz, 2H), 7.61 (s, 1H), 7.73 (d, J = 7.6 Hz, 2H), 7.83 (d, J = 8.8 Hz, 1H), 7.88 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.7, 55.3, 102.6, 118.3, 124.0, 126.8, 126.9, 127.2, 128.7, 129.2, 130.4, 132.9, 133.4, 135.9, 141.3, 157.7; HRMS (EI) $[M]^+$ m/z calcd for $C_{18}H_{16}O$ 248.1201, found 248.1198.

*2-Ethyl-1-methyl-3-phenylnaphthalene (**3f**):* ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.07 (t, J = 7.2 Hz, 3H), 2.75 (s, 3H), 2.80 (t, J = 7.6 Hz, 3H), 7.38−7.48 (m, 6H), 7.53 (t, J = 7.4 Hz, 1H), 7.58 (s, 1H), 7.80 (d, J = 7.6 Hz, 1H), 8.09 (d, J = 8.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.7, 15.1, 23.8, 123.9, 125.1, 125.7, 126.7, 127.1, 127.8, 128.3, 129.4, 131.2, 131.5, 132.4, 138.1, 141.1, 142.9; HRMS (EI) $[M]^+$ m/z calcd for $C_{19}H_{18}$ 246.1409, found 246.1406.

*1,3-Dimethylnaphthalene (**3g**):* ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.49 (s, 3H), 2.68 (s, 3H), 7.19 (s, 1H), 7.45 (dd, J = 3.2, 6.4 Hz, 2H), 7.50 (s, 1H), 7.77 (dd, J = 3.2, 6.0 Hz, 1H), 7.96 (dd, J = 3.4, 5.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.2, 21.6, 123.9, 124.8, 125.2, 125.6, 127.8, 128.9, 130.8, 133.8, 134.0, 135.0; GC/MS t_R = 12.12 min; EI m/z 156 (M^+), 141, 128, 115, 102, 89, 77, 63, 51, 39. Spectral data of **3g** were consistent with data reported in the literature.[22]

*1-Butyl-3-phenylnaphthalene (**3h**):* ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.04 (t, J = 7.4 Hz, 3H), 1.54 (sextet, J = 7.4 Hz, 2H), 1.83 (quintet, J = 7.6 Hz, 2H), 3.18 (t, J = 7.6 Hz, 2H), 7.41 (t, J = 7.2 Hz, 1H), 7.51−7.56 (m, 4H), 7.65 (s, 1H), 7.77 (d, J = 7.6 Hz, 2H), 7.94 (d, J = 7.2 Hz, 1H), 7.95 (s, 1H), 8.10 (dd, J = 2.6, 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.0, 22.9, 33.0, 33.1, 123.8, 124.3, 125.6, 125.7, 125.8, 127.2, 127.4, 128.8, 129.0, 131.1, 134.2, 138.1, 139.6, 141.3; HRMS (EI) $[M]^+$ m/z calcd for $C_{20}H_{20}$ 260.1565, found 260.1565.

*1,3-Diphenylnaphthalene (**3i**):* ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.39 (t, J = 7.4 Hz, 1H), 7.42−7.57 (m, 9H), 7.72 (d, J = 1.6 Hz, 1H), 7.76 (d, J = 7.2 Hz, 2H), 7.91 (d, J = 8.4 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H), 8.07 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 125.4, 125.9, 126.1, 126.2, 126.7, 127.36, 127.43, 128.3, 128.6, 128.9, 130.1, 130.8, 134.2, 138.0, 140.7, 140.8, 140.9 (1 carbon is missing due to overlapping); GC/MS t_R = 18.17 min; EI m/z 280 (M^+), 263, 252, 239, 202, 189, 176, 165, 150, 138, 125, 113, 89, 75, 65, 51. Spectral data of **3i** were consistent with data reported in the literature.[23]

*6,7-Dimethoxy-1-methyl-3-phenylnaphthalene (**3j**):* ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.71 (s, 3H), 4.03 (s, 3H), 4.06 (s, 3H) 7.21 (s, 1H), 7.23 (s, 1H), 7.36 (t, J = 7.4 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.49 (s, 1H), 7.72 (d, J = 7.6 Hz, 2H), 7.80 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.7, 55.8, 102.8, 107.2, 122.8, 124.7, 126.9, 127.2, 127.4, 128.7, 129.6, 133.2, 136.7, 141.4, 149.3, 149.4 (1 carbon is missing due to overlapping); HRMS (EI) $[M]^+$ m/z calcd for $C_{19}H_{18}O_2$ 278.1307, found 278.1310.

*(Z)-Methyl 2-(3,3-dimethylisochroman-1-ylidene)acetate (**4a**):* ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.40 (s, 6H), 2.91 (s, 2H), 3.71 (s, 3H), 5.64 (s, 1H), 7.14 (d, J = 7.6 Hz, 1H), 7.26 (t, J = 7.6 Hz, 1H), 7.36 (t, J = 7.4 Hz, 1H), 7.63 (d, J = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 27.0, 40.1, 50.6, 76.7, 91.8, 124.9, 127.1, 128.1, 128.8, 130.7, 134.2, 161.7, 166.4; HRMS (EI) $[M]^+$ m/z calcd for $C_{14}H_{16}O_3$ 232.1099, found 232.1097. The chemical structure of compound **4a** was assigned on the basis of spectral correlation with its ethyl ester congener.[24]

*2-Phenylnaphthalene (**7a**):* ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.41 (t, J = 7.2 Hz, 1H), 7.50−7.56 (m, 4H), 7.76 (d, J = 8.4 Hz, 1H), 7.77 (t, J = 9.0 Hz, 2H), 7.89−7.96 (m, 3H), 8.08 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 125.6, 125.8, 125.9, 126.3, 127.3, 127.4, 127.6, 128.2, 128.4, 128.8, 132.6, 133.7, 138.5, 141.1; GC/MS t_R = 15.22 min; EI m/z 204 (M^+), 204, 176, 150, 126, 101, 89, 74, 63, 51, 39. Spectral data of **7a** were consistent with data reported in the literature.[25]

*2-Fluoro-6-phenylnaphthalene (**7b**):* ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.30 (td, J = 2.4, 8.8 Hz, 1H), 7.40 (t, J = 7.4 Hz, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.50 (t, J = 7.6 Hz, 2H), 7.72 (d, J = 7.6 Hz, 2H), 7.79 (d, J = 8.8 Hz, 1H), 7.87 (d, J = 8.4 Hz, 1H), 7.89 (dd, J = 5.6, 9.2 Hz, 1H), 8.04 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 110.7 (d, J = 20.5 Hz), 116.7 (d, J = 25.1 Hz), 125.7, 126.6, 127.3, 127.4, 127.7 (d, J = 5.4 Hz), 128.9, 130.5 (d, J = 9.1 Hz), 130.7, 133.2 (d, J = 9.1 Hz), 137.9 (d, J = 3.0 Hz), 140.8, 160.6 (d, J = 244.3 Hz); HRMS (EI) $[M]^+$ m/z calcd for $C_{16}H_{11}F$ 222.0845, found 222.0840.

*2-Fluoro-7-phenylnaphthalene (**7c**):* ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.28 (td, J = 2.4, 8.8 Hz, 1H), 7.41 (t, J = 7.2 Hz, 1H), 7.51 (t, J = 7.8 Hz, 2H), 7.52 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 7.2 Hz, 2H), 7.72−7.74 (m, 1H), 7.86 (dd, J = 5.6, 8.8 Hz, 1H), 7.92 (d, J = 8.8 Hz, 1H), 7.99 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 111.1 (d, J = 20.5 Hz), 116.2 (d, J = 25.0 Hz), 124.9 (d, J = 2.3 Hz), 125.1 (d, J = 5.3 Hz), 127.4, 127.6, 128.4, 128.9, 129.6, 130.0 (d, J = 9.1 Hz), 134.4 (d, J = 9.8 Hz), 139.6, 140.7, 160.9 (d, J = 245.1 Hz); HRMS (EI) $[M]^+$ m/z calcd for $C_{16}H_{11}F$ 222.0845, found 222.0848.

*2-Methyl-6-phenylnaphthalene (**7d**):* ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.55 (s, 3H), 7.36 (d, J = 7.2 Hz, 1H), 7.39 (t, J = 7.2 Hz, 1H), 7.50 (t, J = 7.8 Hz, 2H), 7.65 (s, 1H), 7.74 (d, J = 7.2 Hz, 3H), 7.82 (d, J = 10.4 Hz, 1H), 7.84 (d, J = 8.8 Hz, 1H), 8.02 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.7, 125.5, 125.6, 126.6, 127.2, 127.3, 127.7, 128.0, 128.6, 128.8, 131.9, 132.8, 135.6, 137.6, 141.2; GC/MS t_R = 15.80 min; EI m/z 218 (M^+), 218, 202, 189, 179, 165, 152, 141, 115, 109,101, 94, 87, 75, 63, 51. Spectral data of **7d** were consistent with data reported in the literature.[26]

*2,3-Dimethoxy-6-phenylnaphthalene (**7e**):* ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.03 (s, 6H), 7.16 (s, 1H), 7.19 (s, 1H), 7.37 (t, J = 7.2 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.62 (d, J = 8.4 Hz, 1H), 7.71 (d, J = 7.0 Hz, 2H), 7.77 (d, J = 8.4 Hz, 1H), 7.92 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 55.8, 106.0, 106.5, 123.8, 124.3, 126.8, 127.0, 127.2, 128.3, 128.8, 129.4, 137.0, 141.3, 149.5, 149.8 (1 carbon is missing due to overlapping); HRMS (EI) $[M]^+$ m/z calcd for $C_{18}H_{16}O_2$ 264.1150, found 264.1143.

*2,3-Methylenedioxy-6-phenylnaphthalene (**7f**):* ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.05 (s, 2H), 7.15 (s, 1H), 7.18 (s, 1H), 7.38 (t, J = 7.4 Hz, 1H), 7.48 (t, J = 7.8 Hz, 2H), 7.60 (dd, J = 1.4, 8.6 Hz, 1H), 7.70 (d, J = 7.2 Hz, 2H), 7.74 (d, J = 8.4 Hz, 1H), 7.88 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 101.0, 103.6, 104.1, 124.0, 125.0, 127.1, 127.2, 127.4, 128.8, 129.6, 130.7, 137.2, 141.1, 147.7, 147.9; GC/MS t_R = 17.11 min; EI m/z 248 (M^+), 218, 202, 189, 178, 163, 150, 139, 124, 111, 94, 81, 75, 63. Spectral data of **7f** were consistent with data reported in the literature.[25a]

*2-Ethyl-3-phenylnaphthalene (**7g**):* ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.22 (t, J = 7.6 Hz, 3H), 2.82 (q, J = 7.6 Hz, 2H), 7.43−7.54 (m, 7H), 7.74 (s, 1H), 7.81 (s, 1H), 7.86 (d, J = 9.6 Hz, 1H), 7.89 (d, J = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 15.2, 26.6, 125.4, 125.8, 126.4, 126.9, 127.1, 127.5, 128.0, 128.6, 129.3, 131.7, 133.0, 140.1, 140.7, 141.8; HRMS (EI) $[M]^+$ m/z calcd for $C_{18}H_{16}$ 232.1252, found 232.1255.

*2-Methylnaphthalene (**7h**):* ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.53 (s, 3H), 7.34 (d, J = 8.0 Hz, 1H), 7.42 (t, J = 7.0 Hz, 1H), 7.46 (t, J = 6.2 Hz, 1H), 7.63 (s, 1H), 7.76 (d, J = 8.4 Hz, 1H), 7.77 (d, J = 7.6 Hz, 1H), 7.81 (d, J = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.7, 124.9, 125.8, 126.8, 127.2, 127.6, 127.7, 128.1, 131.7, 133.6, 135.4; GC/MS t_R = 11.22 min; EI m/z 142 (M^+), 128, 115, 102, 89, 77, 69, 63, 57, 51, 39. Spectral data of **7h** were consistent with data reported in the literature.[26,27]

■ ASSOCIATED CONTENT

Supporting Information. Copies of NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

This work was supported by the Mid-career Researcher Program (No. R01-2009-008-3940) and Basic Science Research Program (Nos. 2010-0017149 and 2010-0007737) through the National Research Foundation of Korea (NRF) grant funded by the Ministry of Education, Science and Technology (MEST). A.R.J. is grateful for 2009 NRF Postdoctoral Fellowship Program for Foreign Researchers (No. K20802001473-10B120004500). We gratefully acknowledge Professor Juyoung Yoon (Department of Chemistry and Nano Science, Ewha Womans University) for his generous support.

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