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Iminyl Radical-Triggered 1,5-Hydrogen-Atom Transfer/Heck-Type Coupling by Visible-Light Photoredox Catalysis

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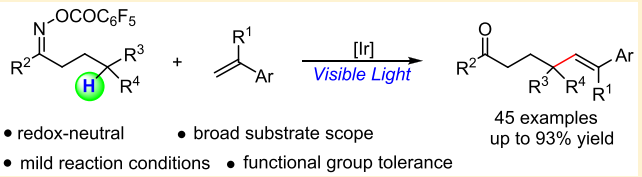
Supporting Information

ABSTRACT: An efficient iminyl radical-triggered 1,5-hydrogen-atom transfer/Heck-type coupling cascade has been achieved through visible-light photoredox catalysis. A variety of unactivated C(sp^3)−H bonds have been alkenylated efficiently and selectively with easily available alkenes, providing an elegant route to γ-alkenylated ketone.

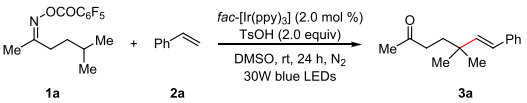


Alkenes are highly important and versatile building blocks in organic synthesis.[1,2] For instance, they are widely used in various Heck-type reactions to construct C−C bonds.[1] Moreover, the radical difunctionalization of unactivated alkenes has been developed as a powerful tool for the construction of various C−C and C−heteroatom bonds.[2] Therefore, continuous efforts have been devoted to developing new and efficient approaches for substituted alkenes.[3] Over the past few years, transition-metal-catalyzed alkyl-Heck reactions and direct alkenylation of unactivated C(sp^3)−H have been established for the alkene synthesis.[4] However, additional ligands, harsh reaction conditions, or directing groups were usually required therein. Recently, the radical-mediated alkenylation reactions have emerged as attractive alternatives, which overcome some drawbacks of traditional methods.[4c,d] Among them, the control of site selectivity could be accomplished through the hydrogen-atom transfer (HAT) strategy.[5] Especially, visible-light photoredox-induced alkenylation of inert C(sp^3)−H bonds provided an appealing and ideal synthetic method.

Iminyl radicals belong to an important class of reactive intermediates in radical chemistry, and their diverse transformations have been explored as an efficient tool for the C−C and C−heteroatom bonds formations.[6−8] For instance, iminyl radical-triggered 1,5-HAT has emerged as an elegant strategy for the distal unactivated C(sp^3)−H bond functionalization.[7] In 2018, the groups of Leonori and Studer and our group reported the intermolecular γ-halogenation, γ-alkylation, and γ-hydroxyalkylation of alkyl ketones through photoredox catalysis, respectively.[7f,g,j] Almost at the same time, Yu et al. described a photoredox-mediated γ-alkenylation of alkyl ketones with vinyl boronic acids, providing a new route to alkenes containing carbonyl groups.[7i] However, the application of this procedure would be probably limited due to the unavailability of vinyl boronic acids. We herein reveal an iminyl radical-mediated γ-alkenylation of alkyl ketones with styrenes via photoredox catalysis. Comparatively, styrenes are more easily available and atom economic as alternative alkenyl sources.[1,2] Remarkably, styrenes derived from natural products were also applicable.

Initially, we chose the oxime ester **1a** and styrene **2a** as model substrates for the optimization investigation under photoredox catalysis. When a mixture of **1a** and **2a** in DMSO was irradiated with 30 W blue LEDs in the presence of 2 mol % of *fac*-[Ir(ppy)$_3$] and 2.0 equiv of TsOH, the desired γ-alkenylated ketone **3a** was isolated in 68% yield after 24 h (Table 1, entry 1). Other photocatalysts such as [Ir(ppy)$_2$(dtbbpy)]PF$_6$, [Ru(bpy)$_3$]Cl$_2$, and eosin Y proved to be inefficient for this transformation. (For details, see the Supporting Information.) Solvent screening showed that the

Table 1. Optimization of the Reaction Conditions[a]



1a 2a 3a

entry	deviation from standard conditions	yield (%)[b]
1	none	68
2	DMAc instead of DMSO	61
3	without an additive	0
4	1.0 equiv of TsOH as additives	61
5	1.0 equiv of TFA as additives	56
6	1.0 equiv of HOAc as additives	0
7	1.0 equiv of K_2CO_3 as additives	0
8	1 mol % of *fac*-[Ir(ppy)$_3$] was used	73
9	0.5 mol % of *fac*-[Ir(ppy)$_3$] was used	20
10	without catalyst	nr[c]

[a]Reaction conditions: 2.0 mol % *fac*-[Ir(ppy)$_3$], **1a** (0.2 mmol, 1.0 equiv), **2a** (0.4 mmol, 2.0 equiv), and TsOH (0.4 mmol, 2.0 equiv) in DMSO (2.0 mL) were irradiated by 30 W blue light-emitting diodes (LEDs) for 24 h under N_2. [b]Yields of isolated product. [c]nr = no reaction.

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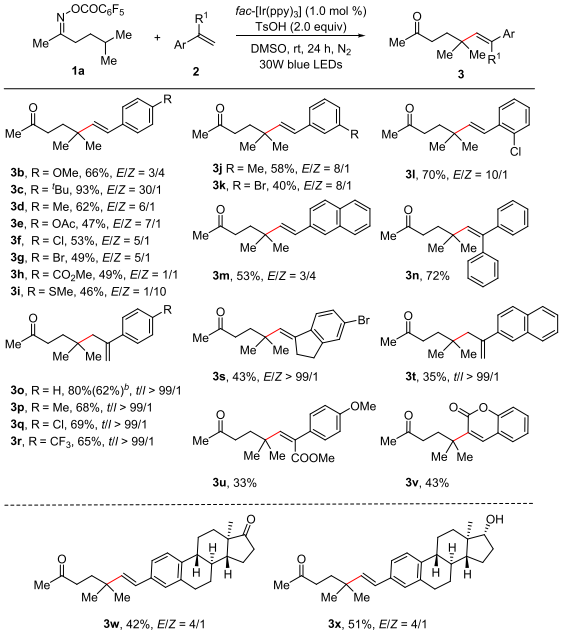
choice of polar aprotic solvents was crucial for this transformation (entry 2). Notably, the addition of strong acids such as TsOH and TFA as additives was indispensable for the success of this reaction.[9] No desired product could be observed without any additives, and even using a weak acid or base as additives (entries 3−7). Reducing the catalyst loading to 0.5 mol % resulted in an inferior yield (entry 9). Finally, no reaction occurred in the absence of the Ir catalyst (entry 10).

With the optimal conditions in hand, we set out to explore the generality of styrenes for this C(sp^3)−H alkenylation reaction. A variety of *para*-, *meta*-, and *ortho*-substituted styrenes reacted smoothly with **1a** to afford the corresponding γ-alkenylated ketones **3b**−**3l** in moderate to good yields (Scheme 1). It was found that the electronic effect of

Scheme 1. Scope of the Alkenes[a]

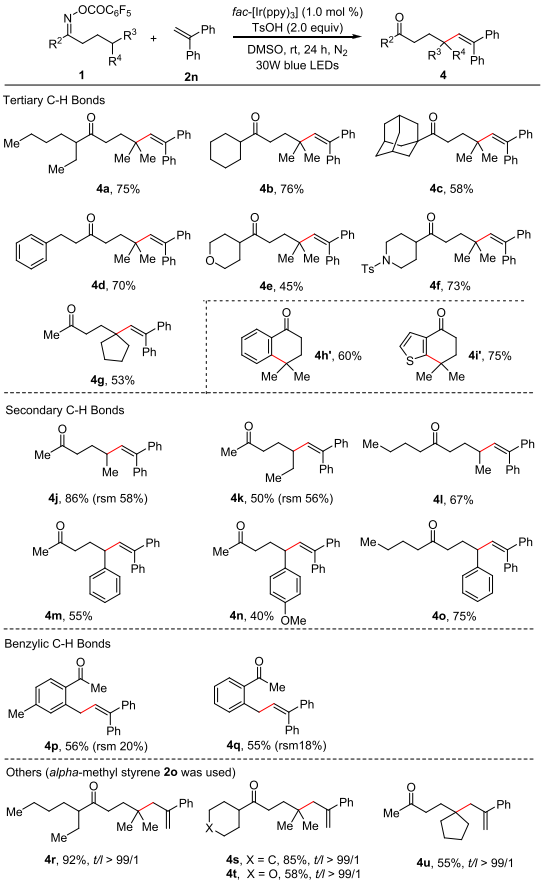


[a]See entry 8 in Table 1 for detailed conditions. *E*/*Z* and *t*/*l* ratios were determined by ^{1}H NMR analysis: *t* = terminal and *l* = linear. [b]The yield on a 1 mmol scale is given in parentheses.

substituents has a significant impact on the reaction efficiency (**3b**, **3c** vs **3g**, **3h**). Functional groups such as halogen (**3f**, **3g**, **3k**, **3l**), ether (**3b**, **3i**), and ester groups (**3e**, **3h**) were all well-tolerated. The Br group retained in **3g** and **3k** offers a platform for further modification by cross-couplings. 2-Vinylnaphthalene also delivered the desired product **3m** in 53% yield. Besides styrenes, 1,1-disubstituted alkenes **2n**−**2t** also gave the corresponding products **3n**−**3t** in 35−80% yields. Interestingly, the reactions of α-methylstyrenes **2o**−**2r** and α-methyl 2-vinylnaphthalene **2t** with **1a** provided unconventional terminal alkenes **3o**−**3r** and **3t** as the major products, probably due to the olefin isomerization and the balance between thermodynamic control or kinetic control.[10] The terminal olefin **2s** derived from cyclic ketone furnished the corresponding product **3s** in a slightly low yield. To our delight, the electron-deficient methyl 2-(4-methoxyphenyl) acrylate **2u** also afforded the **3u** in 33% yield. Coumarin **2v** delivered the anticipated product **3v** in 43% yield. Remarkably, the estrone-derived olefins **2w** and **2x** were efficiently engaged in this transformation to provide the products **3w** and **3x** in satisfactory yields, thus illustrating the potential utility of this protocol for a late-stage modification of complex molecules. However, other alkenes such as acrylonitrile, benzyl acrylate, benzyl crotonate, 4-cyanostyrene, and 4-(methylsulfonyl)-styrene were inefficient under the standard conditions (not shown).

Subsequently, we evaluated the reactions of various C(sp^3)−H bonds with terminal alkene **2n** (Scheme 2). Both acyclic and

Scheme 2. Scope of the Oxime Esters[a]



[a]See entry 8 in Table 1 for detailed conditions; rsm, recovery of the starting material. The *t*/*l* ratios were determined by ^{1}H NMR analysis.

cyclic tertiary C(sp^3)−H bonds in oxime esters underwent the 1,5-HAT/alkenylation efficiently to afford the products **4a**−**4g** in 45%−76% yields. The regioselective formation of **4a** indicates that the tertiary C(sp^3)−H bonds showed a better performance than secondary and primary C−H bonds, probably attributed to the stability of radicals. When a substrate containing the α-phenyl or α-thiophen-2-yl substituent was used, the competitive 1,5-HAT/cyclization product **4h**′ or **4i**′ was obtained in 60% or 75% yield as the sole product. The secondary C(sp^3)−H bonds and secondary benzylic C(sp^3)−H bonds converted into the anticipated products **4j**−**4o** in moderate to good yields, but low conversions were observed for the formations of **4j** and **4k**. Notably, substrates bearing both secondary C(sp^3)−H bonds and secondary benzylic C(sp^3)−H bonds could be alkenylated selectively, delivering the sole product **4o** in 75% yield. Unfortunately, the primary C(sp^3)−H bonds were invalid in

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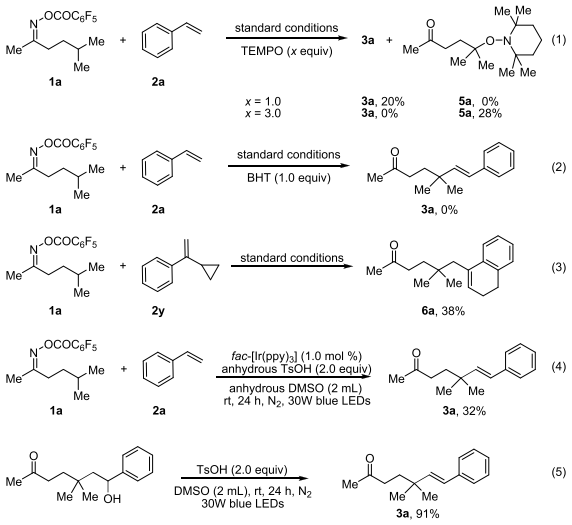
this transformation (not shown). While the substrate with benzylic C(sp^3)−H bonds could furnish the expected products, albeit in somewhat low yields (**4p** and **4q**). In addition, terminal olefin **2o** also reacted well with different tertiary C(sp^3)−H bonds (**4r**−**4u**).

To elucidate the mechanism, control experiments were conducted (Scheme 3). The addition of TEMPO and BTH,

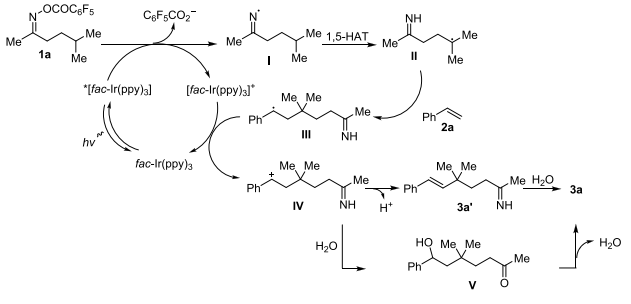
Scheme 3. Mechanistic Experiments



well-known radical scavengers, both inhibited this reaction significantly (eqs 1 and 2). Meanwhile, the TEMPO adduct **5a** was isolated in 28% yield, suggesting that a carbon center radical was involved in this transformation. Furthermore, treatment of **1a** with the α-cyclopropylstyrene **2y** resulted in the cyclic alkenylation product **6a** in 38% yield (eq 3), which also supports a radical pathway. Furthermore, the quantum yield was measured, and its value (0.56, λ = 468 nm) revealed that the radical chain propagation mechanism could be excluded. (For details, see the Supporting Information.) In addition, it was found that the crystalline water of TsOH had a significant effect on the reaction, which probably served as the hydroxyl source to give the corresponding alcohol (eq 4), and the alcohol delivered **3a** in 91% isolated yield under the standard conditions (eq 5), which indicates that γ-hydroxyalkylation of alkyl ketone might also be intermediate in this transformation.

Based on the above results and previous literature, a plausible mechanism was proposed (Scheme 4). First, the catalyst Ir^{III} is photoexcited to Ir^{III}* upon visible-light irradiation.[5] Subsequently, single-electron reduction of **1a** by

Scheme 4. Proposed Mechanism



excited species Ir^{III}* affords the iminyl radical **I** and generates the oxidizing catalyst Ir^{IV}.[7] Then, iminyl radical **I** undergoes a 1,5-HAT to give the C-centered radical **II**.[5] The radical **II** attacks the C=C bond of **2a** to provide the benzyl radial **III**, which is oxidized by Ir^{IV} to deliver the carbocation intermediate **IV** and regenerates the photocatalyst Ir^{III}. Finally, the carbocation **IV** loses a proton followed by hydrolysis to give the target product **3a**. Alternatively, H_2O might also capture the carbocation **IV** to give the alcohol **V**, which subsequently underwent dehydration to afford the desired product **3a**.

In conclusion, we have demonstrated a visible-light-driven γ-C(sp^3)−H alkenylation of alkyl ketones with styrenes via an iminyl radical-triggered 1,5-HAT strategy. This protocol was compatible with a wide range of styrenes and C(sp^3)−H bonds, producing structurally diverse γ-alkenyl ketones in moderate to good yields. Remarkably, this protocol was applicable to the late-stage modification of natural products.

EXPERIMENTAL SECTION

General Methods. Unless otherwise noted, reagents and solvents were obtained from commercial suppliers and were used without further purification. All catalytic reactions were carried out under nitrogen in reaction tubes. Reactions were monitored by thin-layer chromatography (TLC) and visualized using UV light. Column chromatography purifications were carried out using silica gel. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz (Bruker Avance III) instrument, and chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane (TMS). Chemical shifts are given in ppm, and the spectra are calibrated using the residual chloroform signals: 7.26 ppm for ^{1}H NMR and 77.16 ppm for ^{13}C NMR. Data were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, br = broad, etc.), coupling constant (Hz), integration. Infrared spectra were recorded on a Bruker V70 unit and only major peaks were reported in cm^{-1}. HRMS were obtained on a Q-TOF micro spectrometer. For the light source in detail and the material of the irradiation vessel, see the Supporting Information.

Starting Materials. All oxime esters **1** were synthesized from the corresponding cycloketones and carboxylic acids according to the literature.[7f,j,11] The alkenes **2a**−**v** and **2y** were purchased and used directly from commercial sources. Substrates **2w** and **2x** were prepared according to the literature.[7j] All of the NMR spectra were in full accordance with the data in the literatures.

Representative Procedure for the Coupling of Oxime Esters with Alkenes. An oven-dried 10 mL reaction tube equipped with a magnetic stir bar was charged with *fac*-[Ir(ppy)$_3$] (0.002 mmol, 1 mol %), oxime eaters **1** (0.2 mmol, 1.0 equiv), and TsOH (0.4 mmol, 2.0 equiv). Then, the tube was evacuated and backfilled with nitrogen (three times). Subsequently, alkenes **2** (0.4 mmol, 2.0 equiv) and DMSO (2.0 mL) were injected into the tube by syringe under a nitrogen atmosphere. The reaction mixture was stirred under the irradiation of a 30 W blue LED (distance app. 2.0 cm from the bulb) at room temperature for 24 h. After the reaction completed, the mixture was quenched with brine and extracted with ethyl acetate (3 × 10 mL). The combined organic phase was washed with brine (10 mL), dried over Na_2SO_4, and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel (petroleum ether/ethyl acetate 30:1 to 20:1) to give the corresponding products **3** or **4** in the yield list in Schemes 1 and 2.

(E)-5,5-Dimethyl-7-phenylhept-6-en-2-one (**3a**):[7i] colorless oil (73%, 31.6 mg, *E*/*Z* = 99:1), R_f = 0.50 (petroleum ether/ethyl acetate = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.29 (m, 4H), 7.23−7.19 (m, 1H), 6.28 (d, *J* = 16.3 Hz, 1H), 6.11 (d, *J* = 16.3 Hz, 1H), 2.41−2.37 (m, 2H), 2.11 (s, 3H), 1.71−1.67 (m, 2H), 1.11 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 209.4, 139.5, 137.7, 128.7,

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127.2, 126.7, 126.2, 39.6, 36.3, 36.0, 30.2, 27.2; IR (neat) υ_{max} (cm^{-1}) 3056, 3026, 2960, 2868, 1716, 1599, 1455, 1361, 1281, 1074, 1029, 974.

*7-(4-Methoxyphenyl)-5,5-dimethylhept-6-en-2-one (**3b**):*[7i] colorless oil (66%, 32.5 mg, *E*/*Z* = 3:4), R_f = 0.30 (petroleum ether/ethyl acetate = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$, *E* + *Z*) δ 7.29−7.26 (m, 1.7H, *E* + *Z*), 7.09−7.07 (m, 2H, *Z*), 6.85−6.80 (m, 3.4H, *E* + *Z*), 6.44 (d, *J* = 12.6 Hz, 1H, *Z*), 6.22 (d, *J* = 16.2 Hz, 0.7H, *E*), 5.96 (d, *J* = 16.2 Hz, 0.7H, *E*), 5.41 (d, *J* = 12.6 Hz, 1H, *Z*), 3.80 (s, 2H, *E*), 3.79 (s, 3H, *Z*), 2.39−2.35 (m, 3.4H, *E* + *Z*), 2.10 (s, 2.1H, *E*), 2.07 (s, 3H, *Z*), 1.69−1.65 (m, 1.4H, *E*), 1.59−1.55 (m, 2H, *Z*), 1.09 (s, 4.2H, *E*), 0.94 (s, 6H, *Z*); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, *E* + *Z*) δ 209.5, 209.4, 158.9, 158.3, 140.3, 137.4, 131.3, 130.5, 129.9, 128.5, 127.2, 126.1, 114.1, 113.2, 55.4, 55.3, 39.9, 39.6, 37.4, 36.8, 36.4, 35.8, 30.2, 29.9, 29.1, 27.3; IR (neat) υ_{max} (cm^{-1}) 2958, 2868, 1714, 1607, 1510, 1462, 1415, 1360, 1248, 1174, 1105, 1035.

*7-(4-(tert-Butyl)phenyl)-5,5-dimethylhept-6-en-2-one (**3c**):*[7i] colorless oil (93%, 50.7 mg, *E*/*Z* = 30:1), R_f = 0.55 (petroleum ether/ethyl acetate = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.29 (m, 4H), 6.27 (d, *J* = 16.3 Hz, 1H), 6.08 (d, *J* = 16.2 Hz, 1H), 2.41−2.37 (m, 2H), 2.11 (s, 3H), 1.70−1.66 (m, 2H), 1.32 (s, 9H), 1.11 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 209.4, 150.2, 138.7, 134.9, 126.5, 125.9, 125.6, 39.6, 36.4, 35.9, 34.6, 31.4, 30.2, 27.3; IR (neat) υ_{max} (cm^{-1}) 3025, 2960, 2869, 1716, 1510, 1464, 1415, 1361, 1267, 1166, 1108, 1023.

*5,5-Dimethyl-7-(p-tolyl)hept-6-en-2-one (**3d**):*[7i] colorless oil (62%, 28.6 mg, *E*/*Z* = 6:1), R_f = 0.50 (petroleum ether/ethyl acetate = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.26 (d, *J* = 16.3 Hz, 1H), 6.06 (d, *J* = 16.2 Hz, 1H), 2.40−2.36 (m, 2H), 2.33 (s, 3H), 2.11 (s, 3H), 1.70−1.66 (m, 2H), 1.10 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 209.4, 138.5, 136.9, 134.9, 129.3, 126.5, 126.0, 39.6, 36.4, 35.9, 30.2, 27.3, 21.2; IR (neat) υ_{max} (cm^{-1}) 3019, 2959, 2928, 2867, 1715, 1512, 1460, 1418, 1360, 1269, 1167, 1033, 974.

*4-(3,3-Dimethyl-6-oxohept-1-en-1-yl)phenyl Acetate (**3e**):* colorless oil (47%, 25.8 mg, *E*/*Z* = 7:1), R_f = 0.20 (petroleum ether/ethyl acetate = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.33 (m, 2H), 7.04−6.99 (m, 2H), 6.26 (d, *J* = 16.2 Hz, 1H), 6.05 (d, *J* = 16.2 Hz, 1H), 2.39−2.35 (m, 2H), 2.29 (s, 3H), 2.11 (s, 3H), 1.69−1.64 (m, 2H), 1.09 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 209.3, 169.7, 149.8, 139.8, 135.6, 127.1, 125.8, 121.7, 39.6, 36.3, 36.0, 30.2, 27.2, 21.2; IR (neat) υ_{max} (cm^{-1}) 2960, 2929, 2867, 1762, 1714, 1506, 1461, 1420, 1367, 1264, 1199, 1017; HRMS (ESI) calcd for $C_{17}H_{22}O_3Na$ [M + Na]$^+$ 297.1461, found 297.1461.

*7-(4-Chlorophenyl)-5,5-dimethylhept-6-en-2-one (**3f**):* colorless oil (53%, 26.6 mg, *E*/*Z* = 5:1), R_f = 0.48 (petroleum ether/ethyl acetate = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (s, 4H), 6.22 (d, *J* = 16.2 Hz, 1H), 6.07 (d, *J* = 16.2 Hz, 1H), 2.39−2.35 (m, 2H), 2.10 (s, 3H), 1.69−1.65 (m, 2H), 1.09 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 209.3, 140.3, 136.2, 132.7, 128.8, 127.4, 125.6, 39.5, 36.2, 36.0, 30.2, 27.1; IR (neat) υ_{max} (cm^{-1}) 2960, 2930, 2868, 1715, 1649, 1494, 1361, 1282, 1197, 1168, 1092; HRMS (ESI) calcd for $C_{15}H_{19}ClONa$ [M + Na]$^+$ 273.1017, found 273.1024.

*7-(4-Bromophenyl)-5,5-dimethylhept-6-en-2-one (**3g**):*[7i] colorless oil (49%, 28.9 mg, *E*/*Z* = 5:1), R_f = 0.48 (petroleum ether/ethyl acetate = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43−7.38 (m, 2H), 7.22−7.19 (m, 2H), 6.21 (d, *J* = 16.3 Hz, 1H), 6.09 (d, *J* = 16.3 Hz, 1H), 2.39−2.35 (m, 2H), 2.11 (s, 3H), 1.69−1.65 (m, 2H), 1.09 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 209.2, 140.4, 136.7, 131.7, 127.7, 125.6, 120.8, 39.5, 36.2, 36.1, 30.2, 27.1; IR (neat) υ_{max} (cm^{-1}) 2959, 2928, 2867, 1715, 1648, 1485, 1361, 1268, 1167, 1072, 1009.

*4-(3,3-Dimethyl-6-oxohept-1-en-1-yl)phenyl acetate (**3h**):* colorless oil (49%, 26.9 mg, *E*/*Z* = 1:1), R_f = 0.28 (petroleum ether/ethyl acetate = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$, *E* + *Z*) δ 7.98−7.93 (m, 3.9H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 6.49 (d, *J* = 12.8 Hz, 1H, *Z*), 6.32 (d, *J* = 16.3 Hz, 1H, *E*), 6.23 (d, *J* = 16.3 Hz, 1H, *E*), 5.52 (d, *J* = 12.8 Hz, 1H, *Z*), 3.91 (s, 3H), 3.90 (s, 3H), 2.40−2.36 (m, 4H, *E* + *Z*), 2.11 (s, 3H), 2.10 (s, 3H), 1.72−1.66 (m, 2H), 1.58−1.54 (m, 2H), 1.11 (s, 6H), 0.91 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, *E* + *Z*) δ 209.2, 209.2, 167.1, 167.1, 144.3, 142.4, 142.3, 141.5, 130.1, 129.1, 128.9, 128.6, 128.4, 127.9, 126.1, 52.2, 52.2, 39.8, 39.5, 37.6, 37.1, 36.3, 36.2, 30.2, 30.1, 28.9, 27.1; IR (neat) υ_{max} (cm^{-1}) 2958, 2869, 1719, 1607, 1438, 1362, 1279, 1180, 1107, 1022; HRMS (ESI) calcd for $C_{17}H_{22}O_3Na$ [M + Na]$^+$ 297.1461, found 297.1461.

*(E)-5,5-Dimethyl-7-(4-(methylthio)phenyl)hept-6-en-2-one (**3i**):* colorless oil (46%, 24.3 mg, *E*/*Z* = 1:10), R_f = 0.30 (petroleum ether/ethyl acetate = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20−7.15 (m, 2H), 7.09−7.07 (m, 2H), 6.43 (d, *J* = 12.7 Hz, 1H), 6.22 (d, *J* = 16.3 Hz, 1H), 6.06 (d, *J* = 16.2 Hz, 1H), 5.44 (d, *J* = 12.7 Hz, 1H), 2.47 (s, 3H), 2.39−2.35 (m, 2H), 2.08 (s, 3H), 1.59−1.55 (m, 2H), 0.93 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 209.4, 140.8, 136.5, 135.9, 129.3, 128.2, 126.1, 39.8, 37.5, 36.9, 30.0, 29.1, 16.1; IR (neat) υ_{max} (cm^{-1}) 3391, 2957, 1713, 1648, 1485, 1426, 1362, 1283, 1162, 1091; HRMS (ESI) calcd for $C_{16}H_{23}OS$ [M + H]$^+$ 263.1464, found 263.1454.

*5,5-Dimethyl-7-(m-tolyl)hept-6-en-2-one (**3j**):*[7i] colorless oil (58%, 26.7 mg, *E*/*Z* = 8:1), R_f = 0.50 (petroleum ether/ethyl acetate = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22−7.15 (m, 3H), 7.04−7.02 (m, 1H), 6.26 (d, *J* = 16.3 Hz, 1H), 6.10 (d, *J* = 16.3 Hz, 1H), 2.41−2.37 (m, 2H), 2.35 (s, 3H), 2.11 (s, 3H), 1.70−1.66 (m, 2H), 1.10 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 209.4, 139.3, 138.2, 137.7, 128.6, 127.9, 126.9, 126.8, 123.3, 39.6, 36.3, 35.9, 30.2, 27.2, 21.5; IR (neat) υ_{max} (cm^{-1}) 2958, 2926, 2867, 1715, 1606, 1459, 1361, 1268, 1163, 1042, 974.

*7-(3-Bromophenyl)-5,5-dimethylhept-6-en-2-one (**3k**):* colorless oil (40%, 23.6 mg, *E*/*Z* = 8:1), R_f = 0.48 (petroleum ether/ethyl acetate = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51−7.49 (m, 1H), 7.34−7.31 (m, 1H), 7.26−7.24 (m, 1H), 7.16−7.13 (m, 1H), 6.21 (d, *J* = 16.2 Hz, 1H), 6.11 (d, *J* = 16.2 Hz, 1H), 2.39−2.35 (m, 2H), 2.12 (s, 3H), 1.70−1.66 (m, 2H), 1.10 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 209.2, 141.2, 139.9, 130.2, 130.0, 129.0, 125.5, 124.9, 122.9, 39.6, 36.2, 36.1, 30.2, 27.1; IR (neat) υ_{max} (cm^{-1}) 3060, 2960, 2927, 2866, 1715, 1468, 1418, 1361, 1266, 1077, 1007; HRMS (ESI) calcd for $C_{15}H_{19}BrONa$ [M + Na]$^+$ 317.0511, found 317.0517.

*7-(2-Chlorophenyl)-5,5-dimethylhept-6-en-2-one (**3l**):* colorless oil (70%, 35.1 mg, *E*/*Z* = 10:1), R_f = 0.50 (petroleum ether/ethyl acetate = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.33 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.22−7.12 (m, 2H), 6.66 (d, *J* = 16.2 Hz, 1H), 6.06 (d, *J* = 16.2 Hz, 1H), 2.42−2.38 (m, 2H), 2.12 (s, 3H), 1.72−1.68 (m, 2H), 1.13 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 209.3, 142.4, 135.9, 132.9, 129.7, 128.2, 127.0, 126.8, 123.3, 39.5, 36.4, 36.1, 30.3, 27.2; IR (neat) υ_{max} (cm^{-1}) 3061, 2960, 2927, 2866, 1717, 1644, 1466, 1361, 1274, 1164, 1125, 1042; HRMS (ESI) calcd for $C_{15}H_{19}ClONa$ [M + Na]$^+$ 273.1017, found 273.1015.

*5,5-Dimethyl-7-(naphthalen-2-yl)hept-6-en-2-one (**3m**):* colorless oil (35%, 18.6 mg, *E*/*Z* = 3:4), R_f = 0.45 (petroleum ether/ethyl acetate = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$, *E* + *Z*) δ 7.84−7.75 (m, 5.3H, *E* + *Z*), 7.71 (s, 0.7H, *E*), 7.62 (s, 1H, *Z*), 7.60−7.57 (m, 0.7H, *E*), 7.49−7.39 (m, 3.6H, *E* + *Z*), 7.33−7.30 (m, 1H, *Z*), 6.65 (d, *J* = 12.7 Hz, 1H, *Z*), 6.46 (d, *J* = 16.2 Hz, 0.7H, *E*), 6.24 (d, *J* = 16.2 Hz, 0.7H, *E*), 5.55 (d, *J* = 12.7 Hz, 1H, *Z*), 2.44−2.40 (m, 3.4H, *E* + *Z*), 2.12 (s, 2H, *E*), 2.07 (s, 3H, *Z*), 1.75−1.71 (m, 1.4H, *E*), 1.62−1.58 (m, 2H, *Z*), 1.15 (s, 4.2H, *E*), 0.96 (s, 6H, *Z*); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, *E* + *Z*) δ 209.5, 209.4, 140.9, 140.0, 136.7, 135.2, 133.8, 133.1, 132.9, 132.2, 128.8, 128.3, 128.0, 127.9, 127.8, 127.5, 127.3, 127.2, 126.9, 126.3, 126.2, 125.8, 125.8, 125.7, 123.7, 39.9, 39.7, 37.6, 37.1, 36.4, 36.1, 30.2, 30.0, 29.1, 27.3; IR (neat) υ_{max} (cm^{-1}) 3053, 2959, 2927, 2865, 1713, 1503, 1461, 1417, 1360, 1265, 1161, 1088, 1025; HRMS (ESI) calcd for $C_{19}H_{22}ONa$ [M + Na]$^+$ 289.1563, found 289.1564.

*5,5-Dimethyl-7,7-diphenylhept-6-en-2-one (**3n**):* colorless oil (72%, 42.1 mg), R_f = 0.48 (petroleum ether/ethyl acetate = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.27 (m, 3H), 7.25−7.21 (m, 2H), 7.18−7.15 (m, 5H), 5.93 (s, 1H), 2.45−2.41 (m, 2H), 2.11 (s, 3H), 1.60−1.55 (m, 2H), 0.89 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 209.4, 143.9, 140.7, 140.5, 137.9, 130.2, 128.2, 128.0, 127.1, 126.9, 40.0, 38.0, 36.7, 30.1, 29.1; IR (neat) υ_{max} (cm^{-1}) 3055, 3024, 2959, 2868, 1714, 1598, 1492, 1447, 1362, 1263, 1162, 1076, 1031;

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HRMS (ESI) calcd for $C_{21}H_{24}ONa$ $[M + Na]^+$ 315.1719, found 315.1722.

*5,5-Dimethyl-7-phenyloct-7-en-2-one (**3o**):* colorless oil (80%, 36.9 mg, t/l = 99:1), R_f = 0.50 (petroleum ether/ethyl acetate = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.35 (m, 2H), 7.31−7.28 (m, 2H), 7.25−7.21 (m, 1H), 5.24 (d, 1H), 5.03 (s, 1H), 2.46 (s, 2H), 2.33−2.28 (m, 2H), 2.03 (s, 3H), 1.44−1.40 (m, 2H), 0.75 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 209.5, 147.1, 143.8, 128.3, 127.2, 126.7, 117.1, 46.9, 39.1, 35.9, 33.9, 29.8, 27.5; IR (neat) υ_{max} (cm^{-1}) 3078, 3026, 2958, 2928, 2868, 1714, 1624, 1462, 1361, 1163, 1072, 1033; HRMS (ESI) calcd for $C_{16}H_{22}ONa$ $[M + Na]^+$ 253.1563, found 253.1569.

*5,5-Dimethyl-7-(p-tolyl)oct-7-en-2-one (**3p**):* colorless oil (68%, 33.2 mg, t/l = 99:1), R_f = 0.50 (petroleum ether/ethyl acetate = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26−7.24 (m, 2H), 7.10 (d, J = 8.0 Hz, 2H), 5.21 (d, J = 2.0 Hz, 1H), 4.98 (d, J = 1.6 Hz, 1H), 2.44 (s, 2H), 2.34−2.29 (m, 5H), 2.04 (s, 3H), 1.45−1.41 (m, 2H), 0.75 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 209.7, 146.8, 140.9, 136.9, 129.0, 126.5, 116.4, 46.8, 39.2, 35.9, 33.9, 29.8, 27.5, 21.2; IR (neat) υ_{max} (cm^{-1}) 3080, 2958, 2927, 2867, 1715, 1621, 1512, 1462, 1361, 1163, 1031; HRMS (ESI) calcd for $C_{17}H_{24}ONa$ $[M + Na]^+$ 267.1719, found 267.1724.

*7-(4-Chlorophenyl)-5,5-dimethyloct-7-en-2-one (**3q**):* colorless oil (69%, 36.5 mg, t/l = 99:1), R_f = 0.45 (petroleum ether/ethyl acetate = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30−7.25 (m, 4H), 5.24 (d, J = 1.6 Hz, 1H), 5.04 (s, 1H), 2.43 (s, 2H), 2.35−2.31 (m, 2H), 2.07 (s, 3H), 1.46−1.42 (m, 2H), 0.73 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 209.3, 145.9, 142.3, 133.0, 128.5, 128.0, 117.7, 47.0, 39.0, 35.9, 33.9, 29.9, 27.4; IR (neat) υ_{max} (cm^{-1}) 3081, 2959, 2929, 2869, 1714, 1624, 1487, 1361, 1287, 1163, 1093, 1013; HRMS (ESI) calcd for $C_{16}H_{21}ClONa$ $[M + Na]^+$ 287.1173, found 287.1171.

*5,5-Dimethyl-7-(4-(trifluoromethyl)phenyl)oct-7-en-2-one (**3r**):* colorless oil (65%, 38.8 mg, t/l = 99:1), R_f = 0.47 (petroleum ether/ethyl acetate = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.3 Hz, 2H), 7.45 (d, J = 8.2 Hz, 2H), 5.30 (d, J = 1.5 Hz, 1H), 5.12 (s, 1H), 2.47 (s, 2H), 2.34−2.30 (m, 2H), 2.05 (s, 3H), 1.46−1.41 (m, 2H), 0.73 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 209.2, 147.5, 147.5, 146.0, 129.3 (q, J = 32.4 Hz), 127.0, 125.3 (q, J = 3.8 Hz), 124.3 (q, J = 272.9 Hz), 119.0, 47.0, 39.0, 35.8, 34.0, 29.9, 27.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.40 (s, 3F); IR (neat) υ_{max} (cm^{-1}) 3441, 2964, 1712, 1628, 1466, 1409, 1363, 1325, 1165, 1122, 1066, 1018; HRMS (ESI) calcd for $C_{17}H_{21}F_3ONa$ $[M + Na]^+$ 321.1437, found 321.1441.

*6-(5-Bromo-2,3-dihydro-1H-inden-1-ylidene)-5,5-dimethylhexan-2-one (**3s**):* colorless oil (43%, 27.6 mg, E/Z = 99:1), R_f = 0.43 (petroleum ether/ethyl acetate = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 1.3 Hz, 1H), 7.40 (dd, J = 8.1, 1.8 Hz, 1H), 7.21 (d, J = 8.1 Hz, 1H), 6.21−6.20 (m, 1H), 3.34 (s, 2H), 2.48−2.44 (m, 4H), 2.16 (s, 3H), 1.63−1.59 (m, 2H), 0.89 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 209.5, 146.3, 145.8, 141.1, 132.2, 129.0, 127.0, 121.0, 118.6, 39.3, 39.2, 37.9, 36.0, 34.0, 30.2, 27.1; IR (neat) υ_{max} (cm^{-1}) 3062, 2959, 2926, 1755, 1714, 1504, 1462, 1364, 1268, 1201, 1160, 1063; HRMS (ESI) calcd for $C_{17}H_{21}BrONa$ $[M + Na]^+$ 343.0668, found 343.0678.

*5,5-Dimethyl-7-(naphthalen-2-yl)oct-7-en-2-one (**3t**):* colorless oil (35%, 19.6 mg, t/l = 99:1), R_f = 0.40 (petroleum ether/ethyl acetate = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83−7.77 (m, 4H), 7.53−7.42 (m, 3H), 5.38 (d, J = 1.7 Hz, 1H), 5.14 (s, 1H), 2.57 (s, 2H), 2.35−2.31 (m, 2H), 1.98 (s, 3H), 1.50−1.46 (m, 2H), 0.77 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 209.6, 147.0, 141.2, 133.5, 132.8, 128.1, 127.9, 127.7, 126.3, 125.8, 125.4, 125.1, 117.8, 47.0, 39.2, 36.0, 34.0, 29.9, 27.5; IR (neat) υ_{max} (cm^{-1}) 3054, 2958, 2927, 2867, 1714, 1623, 1502, 1463, 1362, 1267, 1046; HRMS (ESI) calcd for $C_{20}H_{24}ONa$ $[M + Na]^+$ 303.1719, found 303.1715.

*Methyl-2-(4-methoxyphenyl)-4,4-dimethyl-7-oxooct-2-enoate (**3u**):* colorless oil (33%, 20.1 mg, E/Z = 99:1), R_f = 0.30 (petroleum ether/ethyl acetate = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25−7.21 (m, 2H), 6.87−6.83 (m, 2H), 5.66 (s, 1H), 3.80 (s, 3H), 3.79 (s, 3H), 2.50−2.46 (m, 2H), 2.15 (s, 3H), 1.72−1.68 (m, 2H), 1.13 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 209.3, 170.6, 159.6, 138.7, 132.9, 130.2, 127.2, 114.1, 55.5, 52.1, 39.7, 37.0, 36.7, 30.3, 27.3; IR (neat) υ_{max} (cm^{-1}) 3436, 2961, 1715, 1636, 1510, 1364, 1258, 1203, 1171, 1026; HRMS (ESI) calcd for $C_{18}H_{24}O_4Na$ $[M + Na]^+$ 327.1567, found 327.1574.

*3-(2-Methyl-5-oxohexan-2-yl)-2H-chromen-2-one (**3v**):* colorless oil (43%, 22.2 mg), R_f = 0.35 (petroleum ether/ethyl acetate = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52−7.46 (m, 3H), 7.31−7.24 (m, 2H), 2.25−2.15 (m, 4H), 2.09 (s, 3H), 1.36 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 208.9, 159.9, 153.4, 138.6, 134.9, 131.0, 127.8, 124.3, 119.3, 116.2, 40.0, 37.9, 33.5, 29.9, 27.1; IR (neat) υ_{max} (cm^{-1}) 3065, 2963, 2923, 1717, 1613, 1453, 1363, 1262, 1080, 1024; HRMS (ESI) calcd for $C_{16}H_{19}O_3$ $[M + H]^+$ 259.1329, found 259.1334.

*(8S,9R,13R,14R)-3-(3,3-Dimethyl-6-oxohept-1-en-1-yl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (**3w**):* colorless oil (42%, 33.0 mg, E/Z = 4:1), R_f = 0.40 (petroleum ether/ethyl acetate = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25−7.14 (m, 2H), 7.10 (s, 1H), 6.23 (d, J = 16.2 Hz, 1H), 6.06 (d, J = 16.2 Hz, 1H), 2.93−2.87 (m, 2H), 2.54−2.47 (m, 1H), 2.45−2.35 (m, 3H), 2.33−2.26 (m, 1H), 2.19−2.12 (m, 1H), 2.10 (s, 3H), 2.05−1.99 (m, 1H), 1.98−1.94 (m, 1H), 1.69−1.39 (m, 9H), 1.09 (s, 6H), 0.91 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 209.4, 138.9, 138.8, 136.7, 135.3, 126.7, 126.4, 125.7, 123.7, 50.6, 48.1, 44.5, 39.6, 38.3, 36.33, 6.0, 35.9, 31.7, 30.2, 29.5, 27.3, 26.6, 25.9, 21.7, 14.0; IR (neat) υ_{max} (cm^{-1}) 3447, 2956, 2928, 2866, 1738, 1715, 1502, 1460, 1373, 1265, 1079, 1050; HRMS (ESI) calcd for $C_{27}H_{36}O_2Na$ $[M + Na]^+$ 415.2608, found 415.2603.

*7-((8S,9R,13R,14R,17R)-17-Hydroxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)-5,5-dimethylhept-6-en-2-one (**3x**):* colorless oil (51%, 40.2 mg, E/Z = 4:1), R_f = 0.25 (petroleum ether/ethyl acetate = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25−7.13 (m, 2H), 7.08 (s, 1H), 6.22 (d, J = 16.2 Hz, 1H), 6.05 (d, J = 16.2 Hz, 1H), 3.73 (t, J = 8.5 Hz, 1H), 2.87−2.82 (m, 2H), 2.40−2.31 (m, 3H), 2.26−2.19 (m, 1H), 2.10 (s, 3H), 1.98−1.86 (m, 2H), 1.71−1.64 (m, 3H), 1.57−1.28 (m, 8H), 1.22−1.16 (m, 2H), 1.09 (s, 6H), 0.78 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 209.5, 139.5, 138.7, 137.0, 135.1, 126.7, 126.5, 125.7, 123.5, 82.0, 50.2, 44.5, 43.4, 39.7, 38.8, 36.8, 36.4, 35.9, 30.7, 30.2, 29.7, 27.3, 27.3, 26.3, 23.3, 11.2; IR (neat) υ_{max} (cm^{-1}) 3443, 2956, 2925, 2864, 1711, 1500, 1459, 1416, 1361, 1262, 1053, 1023; HRMS (ESI) calcd for $C_{27}H_{38}O_2Na$ $[M + Na]^+$ 417.2764, found 417.2766.

*7-Ethyl-3,3-dimethyl-1,1-diphenylundec-1-en-6-one (**4a**):* colorless oil (75%, 56.5 mg), R_f = 0.80 (petroleum ether/ethyl acetate = 30:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32−7.26 (m, 3H), 7.21−7.13 (m, 7H), 5.92 (s, 1H), 2.41−2.32 (m, 3H), 1.60−1.51 (m, 4H), 1.46−1.34 (m, 2H), 1.28−1.21 (m, 2H), 1.19−1.10 (m, 2H), 0.86 (s, 6H), 0.84−0.79 (m, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 215.2, 144.0, 140.7, 140.6, 138.1, 130.2, 128.2, 128.0, 127.1, 127.0, 126.9, 54.1, 38.5, 38.1, 36.7, 31.2, 29.8, 29.0, 29.0, 24.8, 23.0, 14.1, 12.1; IR (neat) υ_{max} (cm^{-1}) 3056, 3024, 2959, 2929, 2866, 1708, 1598, 1491, 1456, 1374, 1077, 1028; HRMS (ESI) calcd for $C_{27}H_{36}ONa$ $[M + Na]^+$ 399.2658, found 399.2656.

*1-Cyclohexyl-4,4-dimethyl-6,6-diphenylhex-5-en-1-one (**4b**):* colorless oil (76%, 54.8 mg), R_f = 0.70 (petroleum ether/ethyl acetate = 30:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32−7.26 (m, 3H), 7.22−7.13 (m, 7H), 5.92 (s, 1H), 2.43−2.39 (m, 2H), 2.32−2.26 (m, 1H), 1.79−1.73 (m, 4H), 1.65−1.62 (m, 1H), 1.55−1.51 (m, 2H), 1.33−1.16 (m, 5H), 0.86 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 214.5, 144.0, 140.6, 140.6, 138.1, 130.2, 128.2, 128.0, 127.1, 127.0, 126.9, 51.0, 38.1, 36.9, 36.8, 29.0, 28.8, 26.0, 25.8; IR (neat) υ_{max} (cm^{-1}) 3055, 3024, 2929, 2857, 1706, 1598, 1492, 1449, 1368, 1079, 1029; HRMS (ESI) calcd for $C_{26}H_{32}ONa$ $[M + Na]^+$ 383.2345, found 383.2351.

*1-((1R,3R,5S)-Adamantan-1-yl)-4,4-dimethyl-6,6-diphenylhex-5-en-1-one (**4c**):* colorless oil (58%, 47.9 mg), R_f = 0.80 (petroleum ether/ethyl acetate = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.29 (m, 3H), 7.25−7.16 (m, 7H), 5.96 (s, 1H), 2.47−2.43 (m, 2H), 2.05−2.03 (m, 3H), 1.80 (d, J = 2.7 Hz, 6H), 1.76−1.67 (m, 6H), 1.57−1.53 (m, 2H), 0.89 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 216.0, 144.1, 140.6, 140.5, 138.3, 130.3, 128.2, 128.0, 127.0, 127.0,

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126.9, 46.7, 38.5, 38.3, 36.9, 36.7, 32.1, 29.1, 28.1; IR (neat) υ_{max} (cm^{-1}) 3055, 3023, 2958, 2909, 2853, 1696, 1450, 1262, 1084, 1024; HRMS (ESI) calcd for $C_{30}H_{37}O$ $[M + H]^+$ 413.2839, found 413.2837.

6,6-Dimethyl-1,8,8-triphenyloct-7-en-3-one (**4d**): colorless oil (70%, 53.6 mg), R_f = 0.50 (petroleum ether/ethyl acetate = 20:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.34−7.15 (m, 15H), 5.92 (s, 1H), 2.87 (t, J = 7.6 Hz, 2H), 2.70 (t, J = 7.7 Hz, 2H), 2.41−2.37 (m, 2H), 1.59−1.55 (m, 2H), 0.88 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 210.4, 143.9, 141.2, 140.6, 140.5, 137.9, 130.2, 128.6, 128.4, 128.2, 128.0, 127.1, 126.9, 126.9, 126.2, 44.5, 39.3, 38.0, 36.7, 30.0, 29.0; IR (neat) υ_{max} (cm^{-1}) 3058, 3026, 2958, 2868, 1712, 1599, 1496, 1449, 1367, 1085, 1029; HRMS (ESI) calcd for $C_{28}H_{30}ONa$ $[M + Na]^+$ 405.2189, found 405.2192.

4,4-Dimethyl-6,6-diphenyl-1-(tetrahydro-2H-pyran-4-yl)hex-5-en-1-one (**4e**): colorless oil (45%, 32.6 mg), R_f = 0.30 (petroleum ether/ethyl acetate = 10:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.32−7.12 (m, 10H), 5.91 (s, 1H), 3.98−3.93 (m, 2H), 3.40−3.34 (m, 2H), 2.53−2.45 (m, 1H), 2.44−2.40 (m, 2H), 1.72−1.60 (m, 4H), 1.57−1.53 (m, 2H), 0.86 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 212.2, 143.9, 140.7, 140.5, 137.9, 130.2, 128.2, 128.0, 127.1, 127.0, 126.9, 67.4, 47.7, 37.9, 36.7, 36.5, 29.1, 28.4; IR (neat) υ_{max} (cm^{-1}) 3055, 3024, 2955, 2848, 1707, 1598, 1494, 1446, 1377, 1267, 1086, 1022; HRMS (ESI) calcd for $C_{25}H_{30}O_2Na$ $[M + Na]^+$ 385.2138, found 385.2139.

4,4-Dimethyl-6,6-diphenyl-1-(1-tosylpiperidin-4-yl)hex-5-en-1-one (**4f**): colorless oil (73%, 75.3 mg), R_f = 0.20 (petroleum ether/ethyl acetate = 10:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.65−7.63 (m, 2H), 7.33−7.13 (m, 12H), 5.90 (s, 1H), 3.73−3.68 (m, 2H), 2.43 (s, 3H), 2.41−2.33 (m, 4H), 2.27−2.19 (m, 1H), 1.88−1.83 (m, 2H), 1.75−1.65 (m, 2H), 1.55−1.51 (m, 2H), 0.88 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 211.7, 143.8, 143.7, 140.7, 140.4, 137.7, 133.1, 130.1, 129.8, 128.2, 128.0, 127.8, 127.1, 127.0, 126.9, 47.5, 45.7, 37.7, 36.8, 36.7, 29.1, 27.2, 21.7; IR (neat) υ_{max} (cm^{-1}) 3056, 3025, 2957, 2929, 2860, 1707, 1345, 1162, 1092, 931; HRMS (ESI) calcd for $C_{32}H_{37}NO_3SNa$ $[M + Na]^+$ 538.2386, found 538.2391.

4-(1-(2,2-Diphenylvinyl)cyclopentyl)butan-2-one (**4g**): colorless oil (53%, 33.8 mg), R_f = 0.30 (petroleum ether/ethyl acetate = 30:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.32−7.24 (m, 3H), 7.22−7.12 (m, 7H), 6.02 (s, 1H), 2.45−2.41 (m, 2H), 2.04 (s, 3H), 1.55−1.51 (m, 8H), 1.32−1.26 (m, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 209.5, 144.0, 141.2, 140.6, 137.2, 129.9, 128.2, 128.1, 127.2, 127.1, 127.0, 48.2, 40.7, 39.5, 33.8, 30.0, 23.7; IR (neat) υ_{max} (cm^{-1}) 3055, 3023, 2951, 2867, 1713, 1598, 1491, 1447, 1361, 1162, 1075, 1029; HRMS (ESI) calcd for $C_{23}H_{26}ONa$ $[M + Na]^+$ 341.1876, found 341.1869.

4,4-Dimethyl-3,4-dihydronaphthalen-1(2H)-one (**4h′**):[7f] colorless oil (60%, 20.9 mg), R_f = 0.52 (petroleum ether/ethyl acetate = 10:1); ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, J = 7.8, 1.4 Hz, 1H), 7.55−7.51 (m, 1H), 7.43 (dd, J = 7.9, 0.8 Hz, 1H), 7.32−7.28 (m, 1H), 2.75−2.72 (m, 2H), 2.04−2.01 (m, 2H), 1.39 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 198.6, 152.4, 134.0, 131.3, 127.5, 126.4, 126.0, 37.2, 35.3, 34.1, 29.9.

4,4-Dimethyl-5,6-dihydrobenzo[b]thiophen-7(4H)-one (**4i′**):[7j] colorless oil (75%, 27.0 mg), R_f = 0.51 (petroleum ether/ethyl acetate = 5:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 5.0 Hz, 1H), 7.04 (d, J = 5.0 Hz, 1H), 2.69−2.66 (m, 2H), 2.03−2.00 (m, 2H), 1.34 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 192.2, 160.9, 135.2, 134.5, 126.3, 38.7, 35.5, 34.1, 28.8.

5-Methyl-7,7-diphenylhept-6-en-2-one (**4j**): colorless oil (86%, 20.1 mg), R_f = 0.40 (petroleum ether/ethyl acetate = 20:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.40−7.31 (m, 3H), 7.26−7.15 (m, 7H), 5.82 (d, J = 10.3 Hz, 1H), 2.44−2.24 (m, 3H), 2.07 (s, 3H), 1.64−1.58 (m, 2H), 1.06 (d, J = 6.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 209.1, 142.4, 141.3, 140.4, 135.1, 129.8, 128.4, 128.3, 127.2, 127.1, 127.1, 42.0, 33.7, 31.4, 30.1, 21.5; IR (neat) υ_{max} (cm^{-1}) 3056, 3021, 2960, 2926, 2866, 1714, 1497, 1448, 1365, 1262, 1077, 1028; HRMS (ESI) calcd for $C_{20}H_{22}ONa$ $[M + Na]^+$ 301.1563, found 301.1562.

5-Ethyl-7,7-diphenylhept-6-en-2-one (**4k**): colorless oil (50%, 12.9 mg), R_f = 0.30 (petroleum ether/ethyl acetate = 20:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.43−7.15 (m, 10H), 5.79 (d, J = 10.5 Hz, 1H), 2.48−2.40 (m, 1H), 2.34−2.26 (m, 1H), 2.16−2.09 (m, 1H), 2.06 (s, 3H), 1.74−1.66 (m, 1H), 1.57−1.31 (m, 3H), 0.89 (t, J = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 209.2, 142.5, 142.5, 140.5, 133.9, 130.0, 128.4, 128.3, 127.1, 127.0, 41.9, 40.3, 30.1, 29.4, 28.9, 12.1; IR (neat) υ_{max} (cm^{-1}) 3055, 3020, 2960, 2925, 2862, 1714, 1496, 1450, 1365, 1074, 1033; HRMS (ESI) calcd for $C_{21}H_{24}ONa$ $[M + Na]^+$ 315.1719, found 315.1718.

2-Methyl-1,1-diphenylnon-1-en-5-one (**4l**): colorless oil (67%, 41.1 mg), R_f = 0.67 (petroleum ether/ethyl acetate = 20:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.42−7.17 (m, 10H), 5.85 (d, J = 10.3 Hz, 1H), 2.47−2.39 (m, 1H), 2.37−2.26 (m, 4H), 1.67−1.59 (m, 2H), 1.55−1.47 (m, 2H), 1.33−1.24 (m, 2H), 1.08 (d, J = 6.6 Hz, 3H), 0.90 (t, J = 7.3 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 211.5, 142.5, 141.2, 140.4, 135.2, 129.8, 128.4, 128.3, 127.2, 127.1, 127.1, 42.7, 41.0, 33.8, 31.4, 26.0, 22.5, 21.6, 14.0; IR (neat) υ_{max} (cm^{-1}) 3056, 3023, 2958, 2929, 2868, 1713, 1498, 1452, 1372, 1040, 1004; HRMS (ESI) calcd for $C_{23}H_{28}ONa$ $[M + Na]^+$ 343.2032, found 343.2031.

5,7,7-Triphenylhept-6-en-2-one (**4m**): colorless oil (55%, 37.5 mg), R_f = 0.28 (petroleum ether/ethyl acetate = 20:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.41−7.13 (m, 15H), 6.22 (d, J = 10.5 Hz, 1H), 3.40−3.34 (m, 1H), 2.42−2.23 (m, 2H), 2.07−1.94 (m, 5H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 208.6, 144.5, 142.3, 141.9, 140.0, 132.2, 129.9, 128.8, 128.4, 128.3, 127.5, 127.3, 126.5, 44.9, 41.7, 31.0, 30.1; IR (neat) υ_{max} (cm^{-1}) 3056, 3025, 2957, 2929, 1713, 1597, 1492, 1446, 1362, 1077, 1027; HRMS (ESI) calcd for $C_{25}H_{24}ONa$ $[M + Na]^+$ 363.1719, found 363.1718.

6-(4-Methoxyphenyl)-8,8-diphenyloct-7-en-3-one (**4n**): colorless oil (40%, 30.8 mg), R_f = 0.28 (petroleum ether/ethyl acetate = 20:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.40−7.31 (m, 3H), 7.27−7.19 (m, 5H), 7.14−7.07 (m, 4H), 6.86−6.82 (m, 2H), 6.18 (d, J = 10.5 Hz, 1H), 3.79 (s, 3H), 3.35−3.29 (m, 1H), 2.39−2.22 (m, 4H), 2.01−1.94 (m, 2H), 0.97 (t, J = 7.3 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 211.4, 158.1, 142.4, 141.4, 140.0, 136.6, 132.6, 129.9, 128.4, 128.3, 128.2, 127.3, 127.3, 127.3, 114.2, 55.4, 44.2, 40.4, 36.1, 31.2, 7.9; IR (neat) υ_{max} (cm^{-1}) 3055, 3023, 2935, 2840, 1713, 1608, 1507, 1451, 1367, 1249, 1178, 1033; HRMS (ESI) calcd for $C_{27}H_{28}O_2Na$ $[M + Na]^+$ 407.1982, found 407.1994.

8,10,10-Triphenyldec-9-en-5-one (**4o**): colorless oil (75%, 57.4 mg), R_f = 0.50 (petroleum ether/ethyl acetate = 20:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.44−7.17 (m, 15H), 6.26 (d, J = 10.5 Hz, 1H), 3.45−3.38 (m, 1H), 2.43−2.24 (m, 4H), 2.05 (q, J = 7.5 Hz, 2H), 1.54−1.47 (m, 2H), 1.32−1.23 (m, 2H), 0.90 (t, J = 7.3 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 211.0, 144.6, 142.3, 141.8, 140.0, 132.3, 129.9, 128.8, 128.4, 128.2, 127.5, 127.3, 127.3, 127.3, 126.4, 45.0, 42.7, 40.7, 31.1, 25.9, 22.4, 14.0; IR (neat) υ_{max} (cm^{-1}) 3057, 3026, 2956, 2931, 2869, 1712, 1598, 1493, 1450, 1369, 1074, 1029; HRMS (ESI) calcd for $C_{28}H_{30}ONa$ $[M + Na]^+$ 405.2189, found 405.2193.

1-(2-(3,3-Diphenylallyl)-4-methylphenyl)ethan-1-one (**4p**): colorless oil (56%, 29.2 mg), R_f = 0.35 (petroleum ether/ethyl acetate = 20:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 7.9 Hz, 1H), 7.43−7.33 (m, 3H), 7.28−7.23 (m, 7H), 7.10 (d, J = 7.9 Hz, 1H), 7.03 (s, 1H), 6.29 (t, J = 7.4 Hz, 1H), 3.75 (d, J = 7.4 Hz, 2H), 2.56 (s, 3H), 2.36 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 201.5, 142.7, 142.4, 142.3, 141.4, 140.1, 134.8, 131.9, 130.1, 130.0, 128.4, 128.2, 128.2, 127.4, 127.2, 127.1, 126.8, 34.3, 29.7, 21.6; IR (neat) υ_{max} (cm^{-1}) 3052, 3025, 2962, 2923, 1680, 1606, 1493, 1440, 1356, 1260, 1065, 1027; HRMS (ESI) calcd for $C_{24}H_{22}ONa$ $[M + Na]^+$ 349.1563, found 349.1562.

1-(2-(3,3-Diphenylallyl)phenyl)ethan-1-one (**4q**): colorless oil (55%, 28.2 mg), R_f = 0.35 (petroleum ether/ethyl acetate = 20:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 7.7 Hz, 1H), 7.44−7.40 (m, 3H), 7.37−7.23 (m, 10H), 6.28 (t, J = 7.4 Hz, 1H), 3.75 (d, J = 7.4 Hz, 2H), 2.58 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 202.2, 142.6, 140.9, 140.0, 138.0, 131.7, 131.0, 130.1, 129.3, 128.4, 128.2, 128.0, 127.4, 127.3, 127.1, 126.2, 34.1, 30.0; IR (neat) υ_{max} (cm^{-1}) 3057, 3025, 2963, 2925, 1684, 1522, 1489, 1439, 1356, 1254,

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1072, 1027; HRMS (ESI) calcd for $C_{23}H_{20}ONa$ $[M + Na]^+$ 335.1406, found 335.1413.

*5-Ethyl-9,9-dimethyl-11-phenyldodec-11-en-6-one (**4r**):* colorless oil (92%, 57.9 mg, *t*/*l* = 99:1), R_f = 0.80 (petroleum ether/ethyl acetate = 30:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.37−7.35 (m, 2H), 7.31−7.27 (m, 2H), 7.25−7.21 (m, 1H), 5.24 (d, *J* = 1.8 Hz, 1H), 5.03 (s, 1H), 2.46 (s, 2H), 2.33−2.27 (m, 3H), 1.58−1.48 (m, 2H), 1.44−1.39 (m, 3H), 1.30−1.25 (m, 3H), 1.18−1.11 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H), 0.80 (t, *J* = 7.4 Hz, 3H), 0.75 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 215.4, 147.2, 143.9, 128.3, 127.2, 126.7, 117.1, 54.0, 47.0, 37.7, 35.7, 33.9, 31.2, 29.8, 27.5, 24.8, 23.0, 14.1, 12.1; IR (neat) υ_{max} (cm^{-1}) 3078, 3026, 2958, 2928, 2864, 1708, 1459, 1376, 1078, 1024; HRMS (ESI) calcd for $C_{22}H_{34}ONa$ $[M + Na]^+$ 337.2502, found 337.2503.

*1-Cyclohexyl-4,4-dimethyl-6-phenylhept-6-en-1-one (**4s**).* colorless oil (85%, 50.7 mg, *t*/*l* = 99:1), R_f = 0.70 (petroleum ether/ethyl acetate = 30:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.36−7.34 (m, 2H), 7.31−7.27 (m, 2H), 7.25−7.21 (m, 1H), 5.23 (d, *J* = 1.8 Hz, 1H), 5.03 (s, 1H), 2.45 (s, 2H), 2.33−2.29 (m, 2H), 2.26−2.20 (m, 1H), 1.87−1.64 (m, 6H), 1.43−1.39 (m, 2H), 1.32−1.16 (m, 6H), 0.75 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 214.7, 147.1, 143.9, 128.3, 127.1, 126.7, 117.1, 50.9, 47.0, 36.0, 35.8, 34.0, 28.7, 27.5, 26.0, 25.8; IR (neat) υ_{max} (cm^{-1}) 3078, 3026, 2929, 2857, 1707, 1623, 1451, 1374, 1143, 1081, 897; HRMS (ESI) calcd for $C_{21}H_{30}ONa$ $[M + Na]^+$ 321.2189, found 321.2183.

*4,4-Dimethyl-6-phenyl-1-(tetrahydro-2H-pyran-4-yl)hept-6-en-1-one (**4t**):* colorless oil (58%, 34.9 mg, *t*/*l* = 99:1), R_f = 0.25 (petroleum ether/ethyl acetate = 20:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.36−7.34 (m, 2H), 7.31−7.27 (m, 2H), 7.25−7.21 (m, 1H), 5.23 (d, *J* = 1.7 Hz, 1H), 5.03 (s, 1H), 3.99−3.95 (m, 2H), 3.42−3.35 (m, 2H), 2.45 (s, 2H), 2.43−2.38 (m, 1H), 2.33−2.29 (m, 2H), 1.65−1.61 (m, 4H), 1.43−1.39 (m, 2H), 0.76 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 212.4, 147.0, 143.9, 128.3, 127.2, 126.7, 117.2, 67.4, 47.6, 47.0, 35.7, 35.6, 34.0, 28.4, 27.5; IR (neat) υ_{max} (cm^{-1}) 3059, 2963, 2923, 2350, 2316, 1718, 1638, 1150, 1049, 924; HRMS (ESI) calcd for $C_{20}H_{28}O_2Na$ $[M + Na]^+$ 323.1982, found 323.1988.

*4-(1-(2-Phenylallyl)cyclopentyl)butan-2-one (**4u**):* colorless oil (55%, 28.2 mg, *t*/*l* = 99:1), R_f = 0.50 (petroleum ether/ethyl acetate = 20:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.36−7.28 (m, 4H), 7.26−7.22 (m, 1H), 5.19 (d, *J* = 1.8 Hz, 1H), 5.06 (s, 1H), 2.51 (s, 2H), 2.29−2.25 (m, 2H), 1.96 (s, 3H), 1.57−1.49 (m, 4H), 1.46−1.42 (m, 2H), 1.40−1.34 (m, 2H), 1.23−1.17 (m, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 209.7, 147.9, 143.9, 128.3, 127.3, 126.8, 116.8, 45.9, 43.0, 39.7, 37.4, 31.8, 29.8, 23.9; IR (neat) υ_{max} (cm^{-1}) 3078, 3025, 2949, 2866, 1714, 1625, 1449, 1360, 1160, 1085, 1026; HRMS (ESI) calcd for $C_{18}H_{24}ONa$ $[M + Na]^+$ 279.1719, found 279.1721.

*5-Methyl-5-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)hexan-2-one (**5a**):*[7j] colorless oil (28%, 15.1 mg), R_f = 0.37 (petroleum ether/ethyl acetate = 20:1); ^1H NMR (400 MHz, $CDCl_3$) δ 2.67−2.63 (m, 2H), 2.18 (s, 3H), 1.86−1.82 (m, 2H), 1.64−1.39 (m, 6H), 1.26 (s, 6H), 1.09 (s, 6H), 1.06 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 209.9, 77.8, 59.4, 40.9, 38.9, 37.3, 34.9, 30.3, 27.1, 20.9, 17.3.

*6-(3,4-Dihydronaphthalen-1-yl)-5,5-dimethylhexan-2-one (**6a**):* colorless oil (38%, 19.5 mg), R_f = 0.32 (petroleum ether/ethyl acetate = 20:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 7.5 Hz, 1H), 7.18−7.08 (m, 3H), 5.82 (t, *J* = 4.6 Hz, 1H), 2.71 (t, *J* = 8.0 Hz, 2H), 2.47−2.42 (m, 2H), 2.41 (s, 2H), 2.24−2.19 (m, 2H), 2.12 (s, 3H), 1.56−1.52 (m, 2H), 0.80 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 209.8, 136.7, 136.3, 134.2, 129.3, 127.7, 126.5, 126.1, 123.5, 43.2, 39.3, 36.4, 33.9, 30.0, 29.1, 27.4, 23.5; IR (neat) υ_{max} (cm^{-1}) 3052, 2953, 2929, 2865, 1715, 1677, 1632, 1455, 1368, 1260, 1169, 1034; HRMS (ESI) calcd for $C_{18}H_{24}ONa$ $[M + Na]^+$ 279.1719, found 279.1714.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.9b00525.

^1H and ^{13}C spectra of all new compounds, the light source and the material of the irradiation vessel, optimization of oxime esters **1a** and styrene **2a**, and the primary mechanistic studies of the reactions (PDF)

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Notes

The authors declare no competing financial interest.

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