# Transition-Metal-Free Superbase-Promoted Stereoselective $\alpha$ -Vinylation of Ketones with Arylacetylenes: A General Strategy for Synthesis of $\beta$ , $\gamma$ -Unsaturated Ketones

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**Supporting Information** 

**ABSTRACT:** A wide variety of  $\beta$ , $\gamma$ -unsaturated ketones of *E* configuration have been obtained in good to excellent yields via KO'Bu/DMSO promoted  $\alpha$ -vinylation of aliphatic, cycloaliphatic, and alkyl aromatic (heteroaromatic) ketones with diverse arylacetylenes.



The importance of the vinylation reactions of ketones stems not only from frequent appearance of the C-C double bondcarbonyl entities in natural products and biologically active compounds<sup>1</sup> but also from the rich and well-studied chemistry of  $\beta_{\gamma}$ -unsaturated ketones that enables expedient synthesis of complex structures.<sup>2</sup> Many synthetic approaches to  $\beta_{i}\gamma$ unsaturated ketones have been documented. Among these are palladium-catalyzed cross-coupling of ketones with alkenylbromides<sup>3</sup> or alkenyltriflates<sup>4</sup> and  $\alpha$ -iodoenones with alkenylzinc<sup>5</sup> and Yb-mediated coupling of oxonitriles with allylbromides.<sup>2b</sup> The InBr<sub>3</sub> reactions of acylchlorides with allyl silanes<sup>6</sup> or allylic mercuric iodides<sup>7</sup> in the presence of AlCl<sub>3</sub> were also employed to reach this aim. A series of  $\beta_{\gamma}$ -unsaturated ketones were synthesized by addition of allylzinc bromide to nitriles in the presence of AlCl<sub>2</sub>.<sup>8</sup> Also, there were reported a number of other syntheses including the alkenylation of enol silyl ethers with alkenylbismuth,<sup>9</sup> Et<sub>3</sub>B-catalyzed alkenylation of  $\alpha$ -halo ketones with alkenylindium<sup>10</sup> or allyltributyltin in the presence of SnCl<sub>2</sub>,<sup>11</sup> allylation of arylpentamethylcyclopentadienyl ketones with allyldimethylaluminum,<sup>2d</sup> and allylation of borolanes.<sup>12</sup> Moreover,  $\beta$ , $\gamma$ -unsaturated ketones were synthesized by the cross-coupling of allylic halides with acylstannanes,<sup>13</sup> -silanes,<sup>14</sup> and -zirconocenes.<sup>15</sup> Alternatives to the above syntheses were the oxidation of homoallylic alcohols,<sup>16</sup> ruthenium-catalyzed hydration dimerization of arylacetylenes,<sup>17</sup> and ruthenium hydride-catalyzed addition of aldehydes to dienes.<sup>18</sup> The list of efforts toward reasonably simple preparation of  $\beta_{,\gamma}$ -unsaturated ketones may be even further extended by cerium-mediated addition of organolithiums to silvlated enaminones<sup>19</sup> and acid-catalyzed transformation of 2-(1-hydroxyalkyl)-1-alkylcyclopropanols.<sup>20</sup> However, some of these methods are based on tedious procedures that narrow their applicability, and others require hardly accessible starting materials or transition metal catalysts. In view of the synthetic importance of  $\beta_{\gamma}$ -unsaturated ketones, it would be desirable to develop convenient methodologies for their synthesis from readily available starting materials. Along this line, most recently one-pot conversion of benzylic alcohols into  $\beta$ , $\gamma$ -



unsaturated ketones was developed.<sup>21</sup> The procedure included oxidation of the alcohols to aldehydes in the presence of an allylating reagent (allyl stannane with catalytic Yb(OTf)<sub>3</sub> or allyl trifluoroborate with boron trifluoride etherate) and in situ oxidation of the allylic alcohols.<sup>21</sup>

The base-promoted addition of ketones to acetylenes might be a convenient straightforward route to the chemistry of  $\beta$ , $\gamma$ unsaturated ketones, but such an addition seemed to be precluded because in the presence of basic catalysts the formation of propargyl alcohols usually took place (Favorsky reaction).<sup>22</sup> Recently, contrary to this common knowledge, we have found alkylarylketones to be capable of vinylation by arylacetylenes in the superbasic heterogeneous system KOH/ DMSO to give the  $\beta$ , $\gamma$ -unsaturated ketones in good yields.<sup>23</sup> However, for aliphatic and cycloaliphatic ketones this protocol happened to be inefficient; the yields of the adducts were from low to modest.

Therefore, a further search for a more efficient promoting system that would be suitable for both aliphatic, cycloaliphatic, and alkylaromatic ketones remained an obvious challenge.

# RESULTS AND DISCUSSION

To develop a general strategy of the superbase-induced vinylation of ketones with acetylenes, we have evaluated the catalytic activity of a series of DMSO-tailored superbases and found that the system of KO<sup>t</sup>Bu/DMSO secured efficient  $\alpha$ -vinylation of various ketones including aliphatic, cycloaliphatic, and alkylaromatic ones. Herein, we summarize the results of this study.

As models for the screening promoting systems, we have chosen two reactions: vinylation of acetone 1 and cyclohexanone 6 with phenylacetylene 15 (Tables 1, 2).

As seen from Table 1, the MOH/DMSO system (except for LiOH) promotes the formation of the expected  $\beta$ , $\gamma$ -unsaturated

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Table 1. Promoting Activity of the MOR/DMSO Systems in the  $\alpha$ -Vinylation of Acetone 1 with Phenylacetylene 15<sup>*a*</sup>

Me Me +	<u></u> —−Ph	OR/DMSO	Me
0 <b>1</b>	15		0 <b>21</b>
MOR	temp (°C)	time (min)	yield of <b>21</b> $(\%)^b$
LiOH	80-120	60-180	nd <sup>c</sup>
NaOH	80	120	traces
NaOH	100	120	10
КОН	80	120	17
КОН	100	60	20
KOH/ <sup>t</sup> BuOH	100	120	29
KO <sup>t</sup> Bu	100	60	63
KO <sup>t</sup> Bu	100	30	70

<sup>a</sup>Reaction conditions: acetone 1 (4 mmol, 230 mg), phenylacetylene 15 (4 mmol, 410 mg), 4 mmol MOR in 10 mL of DMSO. <sup>b</sup>Isolated yield after column chromatography. <sup>c</sup>Not detected.

Table 2. Promoting Activity of the MOR/DMSO Systems in the  $\alpha$ -Vinylation of Cyclohexanone 6 with Phenylacetylene  $15^{\alpha}$ 

+ =-Ph MOR/DMSO				
0 <b>6</b>	15		0 <b>28</b>	
MOR	temp (°C)	time (min)	yield of <b>28</b> $(\%)^b$	
LiOH	100-120	60	nd <sup>c</sup>	
NaOH	80	120	7	
NaOH	100	60	27	
КОН	80	60	57	
КОН	100	60	61	
LiOH/CsF	100	120	39	
KOH/ <sup>t</sup> BuOH	100	60	83	
KO <sup>t</sup> Bu	100	30	90	
			1	

"The reaction conditions were the same as Table 1. "Isolated yield after column chromatography. "Not detected.

ketone 21 (10–29% yields), and the system of KO<sup>t</sup>Bu/DMSO proved to be the most effective (yield of 21 being 70%).

In the case of  $\alpha$ -vinylation of cyclohexanone **6**, the same trend is observed (the reaction proceeds almost quantitatively, and yields of the corresponding ketone **28** reach 90%, Table 2), albeit KOH/DMSO systems ensure quite appropriate isolated yield (up to 61%) and the <sup>t</sup>BuOH additive provides for even further improvement (83% yield).

In all of the experiments presented in Tables 1 and 2, the vinylation proceeded as a regioselective and close to 100% stereoselective process, i.e., only *E* isomers of adducts were formed. The *E* configuration of  $\beta$ , $\gamma$ -ethylenic ketones was confirmed by <sup>3</sup>J values (16.1 Hz) between protons at the double bond.

For the reaction with the KO<sup>t</sup>Bu/DMSO system, the anticipated regioisomers, i.e., the corresponding  $\alpha_{,\beta}$ -unsaturated ketones (also exclusively of *E* configuration), originated from prototropic isomerization of ketones **21** and **28** were just minor admixtures (5–10%) in major  $\beta_{,\gamma}$ -isomers:



The *E* configuration of the minor  $\alpha_{,\beta}$ -ethylenic ketones was supported by the presence of characteristic cross-peaks in their NOESY spectra.

Meanwhile, other promoting systems facilitated the formation of  $\alpha_{,\beta}$ -unsaturated isomers, their content increasing to 20%. However, we obtained convincing experimental proof that these regioisomers are readily separable by the column chromatography (SiO<sub>2</sub>, eluent hexane/benzene with gradient from 1:0 to 0:1).

Notably, other potentially promoting superbase systems of the type KO<sup>t</sup>Bu/nonhydroxylic polar solvent appeared to be inefficient in the reaction studied. For example, with KO<sup>t</sup>Bu/ THF and KO<sup>t</sup>Bu/DMF pairs under the conditions of Table 1, none of the products were detected in the reaction mixtures, and in the KO<sup>t</sup>Bu/N-methylpyrrolidone system, a complicated mixture of inseparable components including vinylated acetone **21** was obtained.

With the optimal conditions in hand, we examined the KO<sup>t</sup>Bu/DMSO system for  $\alpha$ -vinylation of various ketones 1– 14 with acetylenes 15–20. Table 3 illustrates the wide generality and substrate scope of this reaction. As follows from Table 3, the methodology thus developed demonstrates excellent efficacy toward aliphatic, cycloaliphatic (including macrocyclic), alkyl aromatic, and alkyl heteroaromatic ketones and an appropriate range of arylacetylenes. Gratifyingly, acylated condensed aromatics and diphenyl derivatives as well as 1,4-diethynylbenzene tolerate the reaction conditions (entries 14 and 15).

Noteworthy, for all 18 ketone/acetylene pairs, good (or in some cases, total) regioselectivity and total stereoselectivity are preserved. In particular,  $\alpha$ -vinylation of alkylaryl(hetaryl) ketones (entries 10–18) resulted in the formation of  $\beta$ , $\gamma$ - unsaturated ketones exclusively. Regarding the predominance of  $\beta$ , $\gamma$ - versus  $\alpha$ , $\beta$ -unsaturated isomers, this is a well-known consequence of kinetic protonation of a dienolate (see below, Scheme 1). At the same time there is a contest between olefin conjugation with carbonyl versus with aryl, and the latter is likely thermodynamically favored, which is supported by quantum chemical calculations (see below).

When the CH<sub>3</sub> and CH<sub>2</sub> groups of a ketone competed for the addition to the triple bond, the latter in the case of 2butanone **2** won the competition (entry 2) to give the 4:1 mixture of the regioisomers. However, when the CH<sub>2</sub> moiety was sterically screened by two methyl groups, as in the case of 4-methyl-2-pentanone **39**, the methyl  $\alpha$ -group became equally competitive with the CH<sub>2</sub> group. The two expected regioisomeric  $\beta_i\gamma$ -unsaturated ketones **40** and **41** (both of *E* configuration) were formed in a ~1:1 ratio (77% total yield):



Surprisingly, 3,3-dimethyl-2-butanone 3 was capable of double vinylation to give along with the monoadducts 23 and 24 (entries 3, 4) also the divinyl derivative 42 in a yield of 34%

Table 3. Substrate Scope of  $\alpha$ -Vinylation of Ketones 1–14 with Acetylenes 15–20 in the Presence of the KO<sup>t</sup>Bu/DMSO System<sup>a</sup>



<sup>*a*</sup>The reaction conditions were the same as Table 1. <sup>*b*</sup>Isolated yield after column chromatography. <sup>*c*</sup>The sample contained 20% of admixture of the regioisomer formed over the methyl group. <sup>*d*</sup>Ketone/acetylene molar ratio was 2:1.

# Scheme 1. Plausible Mechanism



(when 2 equiv of phenylacetylene was employed and the reaction was carried out for a longer time):



The reaction mechanism obviously represents the nucleophilic attack of the enolate **A** at an acetylene. Such reactions are commonly known to proceed as a concerted trans-addition<sup>24</sup> to deliver the adduct **B** of *Z* configuration (Scheme 1), but a challenging issue here is the *E* stereoselectivity of the reaction under study. Apparently, the intermediate **B** tends to the  $Z \rightarrow E$ isomerization in its deprotonated form **C** in which a free rotation of the phenyl group around the former double bond becomes allowable. The driving force of such an isomerization might be chelating of the potassium cation in the enolate **D** with the participation of  $\pi$ -electrons of the arylethenyl moiety thus forming six-p-electron quasi-aromatic cycle **D**. Actually, the whole process is an equilibration, mediated by HO<sup>t</sup>Bu. The subsequent aqueous workup of this chelate leads to final adducts **21–38** of *E* configuration.

This mechanism is supported by the following experimental evidence: (i) the highest yields were reached only with the equimolar ratio of starting ketone and KO<sup>t</sup>Bu that fit with the binding of  $K^+$  in the chelate **D**, i.e., the neutralization of the promoting base in the reaction process; (ii) at a lower temperature (60 °C, 60 min) with KOH/DMSO, the E:Z isomer ratio for adduct 30 was 3:2, indicating the incomplete conversion of the intermediate B to chelate D; (iii) the replacement of K<sup>+</sup> by the bulkier diffuse Cs<sup>+</sup> (when CsOH/ DMSO was used instead of KOH/DMSO, 100 °C, 60 min) also led to the violation of the E stereoselectivity (the E and Zisomers of adduct 30 in a  $\sim$ 1:1 ratio were formed) thus corresponding to a lower rate of the D-type chelating; (iv) when  $\sim 1.1 E/Z$  mixture of adduct 30 obtained in the presence of Cs<sup>+</sup> as described above was treated with the KO<sup>t</sup>Bu/DMSO system under the same conditions, only E-adduct 30 was observed in the reaction mixture; (v) with NaOH/DMSO (other reaction conditions being as in Table 3) the E:Z ratio of adduct 30 was 9:1, likely due to the stronger Na-O bond that hindered the chelating of the type **D**; (vi) the energy difference between E and Z isomers of adduct 21 has been quantum chemically calculated [MP2/6-311++G(d,p)] to be 0.07 kcal/

mol, which corresponds to approximately equal population of the E and Z isomers at the thermodynamic equilibrium. Thus, the high E stereoselectivity observed in the reaction is kinetically controlled, i.e., is determined by the rate of chelate **D** formation.

To gain a better insight into of the mechanistic aspects of the reaction studied, we have carried out the synthesis of adduct **30a** in which the reaction mixture after 30 min has been quenched with D<sub>2</sub>O, and in the <sup>1</sup>H NMR spectrum of the crude, only the  $\beta_i\gamma$ -isomer having one deuterium atom in the CHD group has been discernible.



This selective isotope exchange supports our previous suggestion<sup>23</sup> that the dienolate C is present as the stable intermediate and that the  $\beta$ , $\gamma$ -unsaturated ketones of *E* configuration are kinetic products.

Also, we have performed the quantum chemical calculations [MP2/6-311++G(d,p)] of energy difference between  $\alpha,\beta$ - and  $\beta,\gamma$ -isomers of adduct **21**, both of *E* configuration, to theoretically determine their thermodynamical distribution. The energy difference has been found to be 0.36 kcal/mol. This corresponds to the 35:65 ratio of the above isomers in the equilibrium. This confirms that the observed  $\beta,\gamma$ - versus  $\alpha,\beta$ -selectivity is kinetically controlled.

### CONCLUSION

In conclusion, we have disclosed a novel general methodology of the transition-metal-free base-promoted stereoselective  $\alpha$ vinylation of ketones with arylacetylenes. The methodology provides a straightforward entry to a wide variety of  $\beta_i \gamma$ unsaturated ketones of *E* configuration that are obtained in good to excellent yields.

### EXPERIMENTAL SECTION

**General Information.** <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at 400.13 and 100.61 MHz, respectively, on an instrument equipped with an inverse gradient 5 mm probe in CDCl<sub>3</sub> with hexamethyldisiloxane (HMDS) as an internal standard. Coupling constants are given in Hertz. All 2D NMR spectra were recorded by using a standard gradient Bruker pulse program. Standard COSY spectra with a 90°, 45° pulse sequence were recorded.<sup>25</sup> The NOESY spectra were recorded in the phase-sensitive TPPI mode with amixing time of 1–1.4 s.<sup>26</sup> HSQC spectra via double INEPT transfer in the phase sensitive TPPI mode with GARP decoupling during acquisition were recorded.<sup>27</sup> HMBC spectra were obtained with the inverse technique and processed in the magnitude mode.<sup>28</sup> IR spectra were taken with FT-IR. All chemicals and solvents are commercially available and were used without further purification. The elaborated procedure does not require degassing of DMSO and use of inert atmosphere, and the benefit of DMSO as a solvent is that it is stable up to 150 °C for a long time (24 h, weight lost 0.1–1.0%).<sup>29</sup>

General Procedure for  $\alpha$ -Vinylation of Ketones with Acetylenes (Example of the Reaction of Acetone 1 with Phenylacetylene 15; Table 3, Entry 1). A mixture of acetone 1 (232 mg, 4.0 mmol), phenylacetylene 15 (409 mg, 4.0 mmol), and KO'Bu (449 mg, 4.0 mmol) in DMSO (10 mL) was heated (100 °C) and stirred at 100 °C for 30 min. The reaction mixture, after cooling (20–25 °C), was diluted with H<sub>2</sub>O (10 mL), neutralized with NH<sub>4</sub>Cl, and extracted with Et<sub>2</sub>O (10 mL × 4). The organic extract was washed with H<sub>2</sub>O (5 mL × 3) and dried (MgSO<sub>4</sub>). After removal of the Et<sub>2</sub>O, a crude residue (612 mg) was obtained. Column chromatography (SiO<sub>2</sub>, eluent hexane/benzene with gradient from 1:0 to 0:1) gave the pure  $\beta_i \gamma$ -unsaturated ketone **21** (449 mg, 70%) as yellow oil.

Compounds 22-38 and 40-41 were prepared analogously.

(*E*)-5-Phenylpent-4-en-2-one (21; Table 3, Entry 1). Yellow oil. Elemental Analysis Calcd (%) for  $C_{11}H_{12}O(160.21)$ : C 82.46; H 7.55. Found: C 82.15, H 7.59. IR (film):  $\nu_{max} = 3026$ , 2958, 1715, 1668, 1599, 1495, 1357, 1157, 1073, 965, 741, 694 cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  7.26–7.24 (m, 2H; H<sub>o</sub>), 7.20–7.18 (m, 2H; H<sub>m</sub>), 7.13–7.11 (m, 1H; H<sub>p</sub>), 6.49 (d, <sup>3</sup>J = 16.1 Hz, 1H; H5), 6.20 (dt, <sup>3</sup>J = 16.1 Hz, <sup>3</sup>J = 7.1 Hz, 1H; H4), 3.35 (d, <sup>3</sup>J = 7.1 Hz, 2H; H3), 2.22 ppm (s, 3H; H1). <sup>13</sup>C NMR:  $\delta$  206.6 (C=O), 137.0 (C<sub>i</sub>), 133.9 (CS), 128.7 (C<sub>m</sub>), 127.7 (C<sub>p</sub>), 126.4 (C<sub>o</sub>), 122.0 (C4), 47.9 (C3), 29.7 ppm (Me).

(*E*)-5-(3-Methoxyphenyl)-3-methylpent-4-en-2-one (22; Table 3, Entry 2). With admixture (~20%) of the regioisomer formed over the methyl group. Total yield: 539 mg, 66%. Yellow oil. Elemental Analysis Calcd (%) for  $C_{13}H_{16}O_2$  (204.27): C 76.44, H 7.90. Found: C 76.48, H 7.67. IR (film):  $\nu_{max}$ = 2972, 2934, 2836, 1716, 1600, 1582, 1489, 1459, 1434, 1356, 1265, 1160, 1046, 971, 779, 691 cm<sup>-1</sup>. <sup>1</sup>H NMR for 22:  $\delta$  7.24–7.21 (m, 1H; H<sub>5</sub>), 6.98–6.96 (m, 1H; H<sub>4</sub>), 6.81–6.82 (m, 1H; H<sub>6</sub>), 6.80–6.79 (m, 1H; H<sub>2</sub>), 6.50 (d, <sup>3</sup>*J* = 15.8 Hz, 1H; H5), 6.18 (dd, <sup>3</sup>*J* = 15.8 Hz, <sup>3</sup>*J* = 8.5 Hz, 1H; H4), 3.82 (s, 3H; OMe), 3.36–3.32 (m, 1H; H3), 2.21 (s, 3H; Me), 1.28 ppm (d, <sup>3</sup>*J* = 6.9 Hz, 3H; CHMe). <sup>13</sup>C NMR for 22:  $\delta$  209.3 (C=O), 159.9 (C<sub>3</sub>), 138.3 (C<sub>1</sub>), 132.1 (C5), 129.6 (C4), 129.1 (C<sub>5</sub>), 119.0 (C<sub>6</sub>), 113.4 (C<sub>2</sub>), 111.6 (C<sub>4</sub>), 55.2 (OMe), 51.3 (C3), 28.2 (C1), 16.2 ppm (CHMe).

(*E*)-2,2-Dimethyl-6-phenylhex-5-en-3-one (23; Table 3, Entry **3**). Yield: 744 mg, 92%. Yellow oil. Elemental Analysis Calcd (%) for  $C_{14}H_{18}O$  (202.29): C 83.12, H 8.97. Found: C 83.18, H 9.00. IR (film):  $\nu_{max}$  = 3027, 2969, 2934, 2871, 1706, 1599, 1496, 1478, 1449, 1394, 1366, 1294, 1206, 1094, 1072, 1053, 1028, 992, 965, 768, 733, 692 cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  7.31–7.29 (m, 2H; H<sub>o</sub>), 7.25–7.21 (m, 2H; H<sub>m</sub>), 7.18–7.14 (m, 1H; H<sub>p</sub>), 6.37 (d, <sup>3</sup>*J* = 16.0 Hz, 1H; H6), 6.29 (dt, <sup>3</sup>*J* = 16.0 Hz, <sup>3</sup>*J* = 6.4 Hz, 1H; H5), 3.37 (d, <sup>3</sup>*J* = 6.4 Hz, 2H; H4), 1.165 ppm (s, 9H; C(<u>Me</u>)<sub>3</sub>). <sup>13</sup>C NMR:  $\delta$ =212.6 (C=O), 137.2 (C<sub>i</sub>), 132.8 (C6), 128.4 (C<sub>o</sub>), 127.3 (C<sub>p</sub>), 126.2 (C<sub>m</sub>), 123.3 (C5), 44.4 (<u>C</u>(Me)<sub>3</sub>), 40.6 (C4), 26.5 ppm (C(<u>Me</u>)<sub>3</sub>).

(*E*)-6-(2,5-Dimethylphenyl)-2,2-dimethylhex-5-en-3-one (24; Table 3, Entry 4). Yield: 838 mg, 91%. Yellow oil. Elemental Analysis Calcd (%) for  $C_{16}H_{22}O$  (230.35): C 83.43, H 9.63. Found: C 83.20, H 9.60. IR (film):  $\nu_{max}$  = 3039, 3017, 2969, 2924, 2870, 1708, 1612, 1496, 1478, 1463, 1394, 1380, 1366, 1294, 1160, 1088, 1053, 994, 967, 910, 808, 734 cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  7.25–7.23 (m, 1H; H<sub>6</sub>), 6.99–6.96 (m, 1H; H<sub>3</sub>), 6.92–6.91 (m, 1H; H<sub>4</sub>), 6.59 (dt, <sup>3</sup>*J* = 15.9 Hz, <sup>4</sup>*J* = 1.1 Hz, 1H; H6), 6.17 (dt, <sup>3</sup>*J* = 15.9 Hz, <sup>3</sup>*J* = 7.0 Hz, 1H; H5), 3.44–3.42 (dd, <sup>3</sup>*J* = 7.0 Hz, <sup>4</sup>*J* = 1.1 Hz, 2H; H4), 2.27, 2.26 (s, 6H; C<sub>2</sub>-Me, C<sub>5</sub>-Me), 1.17 ppm (s, 9H; C(<u>Me</u>)<sub>3</sub>). <sup>13</sup>C NMR:  $\delta$  213.2 (C=O), 135.9 (C<sub>1</sub>), 135.0 (C<sub>5</sub>), 131.7 (C<sub>2</sub>), 130.6 (C6), 129.8 (C<sub>6</sub>), 127.8 (C<sub>4</sub>), 126.2 (C<sub>3</sub>), 124.3 (C5), 44.1 (<u>C</u>(Me)<sub>3</sub>), 40.7 (C4), 26.2 (C(<u>Me</u>)<sub>3</sub>), 20.8 (C<sub>5</sub>-<u>Me</u>), 19.1 ppm (C<sub>2</sub>-<u>Me</u>).

(*E*)-3-Ethyl-1-phenylhept-1-en-4-one (25; Table 3, Entry 5). Yield: 787 mg, 91%. Yellow oil. Elemental Analysis Calcd (%) for C<sub>15</sub>H<sub>20</sub>O (216.32): C 83.28, H 9.32. Found: C 83.26, H 9.41; IR (film):  $\nu_{max}$  = 3027, 2964, 2933, 2875, 1712, 1667, 1601, 1494, 1453, 1378, 1196, 1073, 1055, 1029, 968, 748, 697 cm<sup>-1</sup>. <sup>1</sup>H NMR: δ 7.37–7.35 (m, 2H; H<sub>o</sub>), 7.32–7.30 (m, 2H; H<sub>m</sub>), 7.28–7.26 (m, 1H; H<sub>p</sub>), 6.45 (d, <sup>3</sup>*J* = 15.9 Hz, 1H; H1), 6.04 (dd, <sup>3</sup>*J* = 15.9 Hz, <sup>3</sup>*J* = 9.3 Hz, 1H; H2), 3.16–3.10 (m, 1H; H3), 2.46–2.44 (m, 2H; H5), 1.82–1.79, 1.57–1.55 (m, 2H; CH<sub>2</sub>Me), 1.63–1.61 (m, 2H; H6), 0.90 (m, 3H; H7), 0.89–0.87 ppm (m, 3H; CH<sub>2</sub>Me). <sup>13</sup>C NMR: δ 211.0 (C=O), 136.9 (C<sub>i</sub>), 132.8 (C1), 128.5 (C<sub>m</sub>), 127.9 (C2), 127.0 (C<sub>p</sub>), 126.1 (C<sub>o</sub>), 58.5 (C3), 43.5 (C5), 24.4 (CH<sub>2</sub>Me), 16.9 (C6), 13.7 (C7), 11.7 ppm (CH<sub>2</sub>Me).

(*E*)-3-Ethyl-1-(3-methoxyphenyl)hept-1-en-4-one (26; Table 3, Entry 6). Yield: 798 mg, 81%. Yellow oil. Elemental Analysis Calcd (%) for  $C_{16}H_{22}O_2$  (246.35): C 78.01, H 9.00. Found: C 78.12, H 8.99. IR (film):  $\nu_{max}$  = 3026, 2963, 2932, 2875, 2834, 1711, 1666, 1599, 1489, 1464, 1455, 1434, 1289, 1262, 1156, 1048, 971, 871, 780, 690 cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  7.23–7.17 (m, 1H; H<sub>5</sub>), 6.93–6.91 (m, 1H; H<sub>6</sub>),

6.87–6.86 (m, 1H; H<sub>2</sub>), 6.77–6.75 (m, 1H; H<sub>4</sub>), 6.43 (d,  ${}^{3}J$  = 15.8 Hz, 1H; H1), 6.05 (dd,  ${}^{3}J$  = 15.8 Hz,  ${}^{3}J$  = 9.2 Hz, 1H; H2), 3.78 (s, 3H; O<u>Me</u>), 3.15–3.09 (m, 1H; H3), 2.50–2.33 (m, 2H; H5), 1.85–1.78, 1.59–1.54 (m, 4H; C<u>H</u><sub>2</sub>Me, H6), 0.89–0.85 ppm (m, 6H; CH<sub>2</sub><u>Me</u>, H7).  ${}^{13}$ C NMR: δ 210.8 (C=O), 159.7 (C<sub>3</sub>), 138.1 (C<sub>1</sub>), 132.5 (C1), 129.3 (C<sub>5</sub>), 128.0 (C2), 118.6 (C<sub>6</sub>), 112.3 (C<sub>4</sub>), 111.4 (C<sub>2</sub>), 58.3 (C3), 54.9 (O<u>Me</u>), 43.5 (C5), 24.4 (<u>C</u>H<sub>2</sub>Me), 16.8 (C6), 13.5 (C7), 11.6 ppm (CH<sub>2</sub><u>Me</u>).

(*E*)-4-StyryInonan-5-one (27; Table 3, Entry 7). With admixture (~20%) of the  $\alpha_{\beta}\beta$ -isomer. Total yield: 606 mg, 62%. Yellow oil. Elemental Analysis Calcd (%) for C<sub>17</sub>H<sub>24</sub>O (244.37): C 83.55, H 9.90. Found: C 83.68, H 9.98. IR (film):  $\nu_{max}$  = 3027, 2959, 2935, 2863, 1713, 1669, 1600, 1495, 1465, 1452, 1378, 1259, 1157, 1126, 1072, 1044, 1030, 968, 750, 694 cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  7.25–7.23 (m, 2H; H<sub>o</sub>), 7.23–7.21 (m, 2H; H<sub>m</sub>), 7.16–7.14 (m, 1H; H<sub>p</sub>), 6.38 (d, <sup>3</sup>*J* = 15.9 Hz, 1H; H $\gamma$ ), 6.01 (dd, <sup>3</sup>*J* = 15.9 Hz, <sup>3</sup>*J* = 9.3 Hz, 1H; H $\beta$ ), 3.18–3.12 (m, 1H; H4), 2.38–2.34 (m, 2H; H6), 1.72–1.68, 1.47–1.44 (m, 2H; H3), 1.49–1.42 (m, 2H; H7), 1.28–1.21 (m, 2H; H2), 1.22–1.18 (m, 2H; H8), 0.83 (m, 3H; H9), 0.82 ppm (m, 3H; H1). <sup>13</sup>C NMR: δ 209.9 (C=O), 136.5 (C<sub>1</sub>), 132.2 (C $\gamma$ ), 128.1 (C<sub>m</sub>), 128.0 (C $\beta$ ), 127.0 (C<sub>p</sub>), 125.6 (C<sub>o</sub>), 56.2 (C4), 40.9 (C6), 33.1 (C3), 25.5 (C7), 21.9 (C8), 20.0 (C2), 13.5 (C1), 13.5 ppm (C9).

(*E*)-2-Styrylcyclohexanone (28; Table 3, Entry 8). Yield: 721 mg, 90%. Yellow oil. Elemental Analysis Calcd (%) for  $C_{14}H_{16}O$  (200.28): C 83.96, H 8.05. Found: C 84.10, H 8.09. IR (film):  $\nu_{max}$  = 3027, 2937, 2863, 1951, 1709, 1613, 1495, 1450, 1249, 1143, 1127, 1071, 966, 748, 696, 495 cm<sup>-1</sup>. <sup>1</sup>H NMR: δ 7.40–7.39 (m, 2H; H<sub>o</sub>), 7.31–7.29 (m, 2H; H<sub>m</sub>), 7.23–7.22 (m, 1H; H<sub>p</sub>), 6.42 (dd, <sup>3</sup>*J* = 16.1 Hz, <sup>3</sup>*J* = 6.4 Hz, 1H; H $\beta$ ), 6.35 (d, <sup>3</sup>*J* = 16.1 Hz, 1H; H $\gamma$ ), 3.21–3.15 (m, 1H; H2), 2.45–2.34 (m, 2H; 6-CH<sub>2</sub>), 2.16–1.72 (m, 2H; 3-CH<sub>2</sub>), 2.01–1.72 (m, 2H; 4-CH<sub>2</sub>), 1.91–1.73 ppm (m, 2H; 5-CH<sub>2</sub>). <sup>13</sup>C NMR: δ 211.2 (C=O), 137.1 (C<sub>i</sub>), 131.3 (C $\gamma$ ), 128.6 (C<sub>m</sub>), 127.4 (C $\beta$ ), 126.4 (C<sub>p</sub>), 126.2 (C<sub>o</sub>), 53.8 (C2), 41.6 (C6), 34.3 (C3), 27.6 (C4), 24.3 ppm (C5).

(E)-2-Styrylcyclododecanone (29; Table 3, Entry 9). Yield: 717 mg, 63%. White powder: mp 58–60 °C. Elemental Analysis Calcd (%) for  $C_{20}H_{28}O$  (284.44): C 84.45, H 9.92. Found: C 84.31, H 9.67. IR (KBr):  $\nu_{max} = 2930$ , 2862, 1701, 1667, 1495, 1469, 1445, 1347, 1247, 1128, 1072, 1017, 968, 754, 731, 692 cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  7.22–7.21 (m, 2H; H<sub>o</sub>), 7.20–7.19 (m, 1H; H<sub>m</sub>), 7.12–7.11 (m, 2H; H<sub>p</sub>), 6.37 (d, <sup>3</sup>J = 15.8 Hz, 1H; H $\gamma$ ), 6.06 (dd, <sup>3</sup>J = 15.8 Hz, <sup>3</sup>J = 8.8 Hz, 1H; H $\beta$ ), 3.44–3.39 (m, 1H; H2), 2.57–2.48 (m, 2H; 12-CH<sub>2</sub>), 2.37–2.30 (m, 2H; 3-CH<sub>2</sub>), 1.98–1.92 (m, 2H; 11-CH<sub>2</sub>), 1.77–1.70 (m, 2H; 4-CH<sub>2</sub>), 1.53–1.42 (m, 2H; 5-CH<sub>2</sub>), 1.21–1.20 ppm (m, 10H; 6-CH<sub>2</sub>, 7-CH<sub>2</sub>, 8-CH<sub>2</sub>, 9-CH<sub>2</sub>, 10-CH<sub>2</sub>). <sup>13</sup>C NMR:  $\delta$  212.2 (C=O), 136.9 (C $\beta$ ), 131.9 (C<sub>i</sub>), 128.4 (C<sub>m</sub>), 127.6 (C<sub>p</sub>), 126.5 (C $\gamma$ ), 126.3 (C<sub>o</sub>), 55.1 (C2), 38.7 (C3), 30.7 (C12), 25.5, 24.9, 24.8, 24.7, 24.4, 24.3, 24.1, 23.4 ppm (C4–C11).

(*E*)-1,4-Diphenyl-3-buten-1-one (30; Table 3, Entry 10). Yield: 756 mg, 85%. White crystals: mp 92–94 °C. Elemental Analysis Calcd (%) for C<sub>16</sub>H<sub>14</sub>O (222.28): C 86.45, H 6.35. Found: C 86.67, H 6.57. IR (KBr):  $\nu_{max}$  = 3082, 3061, 3023, 1683, 1597, 1496, 1449, 1399, 1356, 1334, 1296, 1277, 1208, 1071, 983, 908, 749, 732, 688, 566, 501 cm<sup>-1</sup>. <sup>1</sup>H NMR: δ 8.00–7.98 (m, 2H; H<sub>o</sub>), 7.58–7.55 (m, 1H; H<sub>p</sub>), 7.47–7.44 (m, 2H; H<sub>m</sub>), 7.37–7.34 (m, 2H; H<sub>o'</sub>), 7.30–7.27 (m, 2H; H<sub>m'</sub>), 7.18–7.20 (m, 1H; H<sub>p'</sub>), 6.53 (d, <sup>3</sup>*J* = 16.1 Hz, 1H; Hγ), 6.45 (dt, <sup>3</sup>*J* = 16.1 Hz, <sup>3</sup>*J* = 6.1 Hz, 1H; Hβ), 3.90 ppm (d, <sup>3</sup>*J* = 6.1 Hz, 2H; CH<sub>2</sub>). <sup>13</sup>C NMR: δ 198.1 (C=O), 137.0 (C<sub>i</sub>'), 136.5 (C<sub>i</sub>), 133.5 (Cγ), 133.1 (C<sub>p</sub>), 128.6 (C<sub>m</sub>), 128.4 (C<sub>m'</sub>), 128.3 (C<sub>o</sub>), 127.3 (C<sub>p'</sub>), 126.2 (C<sub>o'</sub>), 122.6 (Cβ), 42.8 ppm (<u>C</u>H<sub>2</sub>).

(*E*)-4-(2,5-Dimethylphenyl)-1-phenylbut-3-en-1-one (31; Table 3, Entry 11). Yield: 801 mg, 80%. Pale yellow crystals: mp 58-60 °C. Elemental Analysis Calcd (%) for  $C_{18}H_{18}O$  (250.34): C 86.36, H 7.25. Found: C 86.51, H 7.21. IR (KBr):  $\nu_{max}$  = 3040, 3023, 2920, 1684, 1595, 1579, 1495, 1447, 1400, 1327, 1206, 1180, 1070, 983, 958, 797, 753, 692, 558 cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  8.01-7.99 (m, 2H; H<sub>o</sub>), 7.58-7.54 (m, 1H; H<sub>p</sub>), 7.49-7.45 (m, 2H; H<sub>m</sub>), 7.27-7.26 (m, 1H; H<sub>6</sub>), 7.01-6.99 (m, 1H; H<sub>3</sub>), 6.95-6.92 (m, 1H; H<sub>4</sub>), 6.72 (d, <sup>3</sup>J = 16.1 Hz, 1H; H $\gamma$ ), 6.45 (dt, <sup>3</sup>J = 16.1 Hz, <sup>3</sup>J = 6.8 Hz, 1H; H $\beta$ ), 3.91 (dd, <sup>3</sup>J = 6.8 Hz, <sup>3</sup>J = 1.5 Hz, 2H; CH<sub>2</sub>), 2.28 (s, 3H; C<sub>5</sub>-Me), 2.27 ppm (s, 3H; C<sub>2</sub>-<u>Me</u>). <sup>13</sup>C NMR:  $\delta$  198.1 (C=O), 136.7 (C<sub>i</sub>), 135.9 (C<sub>1</sub>), 135.4 (C<sub>5</sub>), 133.2 (C $\gamma$ ), 132.1 (C<sub>2</sub>), 131.6 (C<sub>p</sub>), 130.1 (C<sub>6</sub>), 128.6 (C<sub>m</sub>), 128.4 (C<sub>o</sub>), 128.2 (C<sub>4</sub>), 126.4 (C<sub>3</sub>), 123.6 (C $\beta$ ), 43.1 (<u>CH<sub>2</sub></u>), 21.1 (C<sub>5</sub>-<u>Me</u>), 19.4 ppm (C<sub>2</sub>-<u>Me</u>).

(*E*)-4-(4-Methoxyphenyl)-1-phenylbut-3-en-1-one (32; Table 3, Entry 12). Yield: 686 mg, 68%. Yellow crystals: mp 96–98 °C. Elemental Analysis Calcd (%) for  $C_{17}H_{16}O_2$  (252.31): C 80.93, H 6.39. Found: C 80.89, H 6.43. IR (KBr):  $\nu_{max}$  = 3062, 2957, 2836, 1679, 1606, 1578, 1510, 1449, 1398, 1357, 1327, 1283, 1206, 1174, 1108, 1032, 978, 837, 812, 758, 743, 688 cm<sup>-1.</sup> <sup>1</sup>H NMR:  $\delta$  8.03–8.01 (m, 2H; H<sub>o</sub>), 7.60–7.58 (m, 1H; H<sub>p</sub>), 7.50–7.48 (m, 2H; H<sub>m</sub>), 7.34–7.32 (m, 2H; H<sub>o</sub>'), 6.86–6.84 (m, 2H; H<sub>m</sub>'), 6.51 (d, <sup>3</sup>J = 15.9 Hz, 1H; H $\gamma$ ), 6.34 (dt, <sup>3</sup>J = 15.9 Hz, <sup>3</sup>J = 6.9 Hz, 1H; H $\beta$ ), 3.90 (dd, <sup>3</sup>J = 6.9 Hz, <sup>3</sup>J = 1.5 Hz, 2H; CH<sub>2</sub>), 3.81 ppm (s, 3H; OMe). <sup>13</sup>C NMR:  $\delta$  198.3 (C=O), 159.3 (C<sub>p</sub>'), 136.8 (C<sub>i</sub>), 133.3 (C<sub>p</sub>), 133.1 (C $\gamma$ ), 130.0 (C<sub>i</sub>'), 128.8 (C<sub>m</sub>), 128.4 (C<sub>o</sub>), 127.5 (C<sub>o</sub>'), 120.4 (C $\beta$ ), 114.0 (C<sub>m</sub>'), 55.4 (OMe), 42.8 ppm (<u>CH</u><sub>2</sub>).

(*E*)-1-(4-Fluorophenyl)-4-phenylbut-3-en-1-one (33; Table 3, Entry 13). Yield: 836 mg, 87%. White crystals: mp 117–119 °C. Elemental Analysis Calcd (%) for C<sub>16</sub>H<sub>13</sub>FO (240.27): C 79.98, H 5.45, F 7.91. Found: C 80.00, H 5.48, F, 7.93. IR (KBr):  $\nu_{max}$  = 3064, 2872, 1686, 1597, 1505, 1449, 1408, 1393, 1357, 1298, 1272, 1232, 1207, 1158, 1092, 1069, 1030, 993, 975, 839, 805, 767, 731, 688, 599, 558, 499 cm<sup>-1.</sup> <sup>1</sup>H NMR: δ 8.03–8.00 (m, 2H; H<sub>o</sub>), 7.37–7.35 (m, 2H; H<sub>o'</sub>), 7.30–7.27 (m, 2H; H<sub>m'</sub>), 7.25–7.22 (m, 1H; H<sub>p'</sub>), 7.15– 7.11 (m, 2H; H<sub>m</sub>), 6.53 (d, <sup>3</sup>J = 16.1 Hz, 1H; Hγ), 6.43 (dt, <sup>3</sup>J = 16.1 Hz, <sup>3</sup>J = 6.1 Hz, 1H; Hβ), 3.90 ppm (d, <sup>3</sup>J = 6.1 Hz, 2H; CH<sub>2</sub>). <sup>13</sup>C NMR: δ 196.4 (C=O), 165.8 (d, <sup>1</sup>J = 254.9 Hz, C<sub>p</sub>), 136.9 (C<sub>i'</sub>), 133.7 (Cγ), 133.0 (d, <sup>4</sup>J = 3.1 Hz, C<sub>i</sub>), 130.9 (d, <sup>3</sup>J = 9.6 Hz, C<sub>o</sub>), 128.5 (C<sub>m'</sub>), 127.5 (C<sub>p'</sub>), 126.3 (C<sub>o'</sub>), 122.3 (Cβ), 115.8 (d, <sup>2</sup>J = 21.8 Hz, C<sub>m</sub>), 42.7 ppm (<u>C</u>H<sub>2</sub>).

(E)-1-[1,1.-Biphenyl]-4-yl-4-(4-pentylphenyl)-3-buten-1-one (34; Table 3, Entry 14). Yield: 1.31 g, 89%. White powder: mp 132 °C. Elemental Analysis Calcd (%) for C<sub>27</sub>H<sub>28</sub>O (368.51): C 88.00, H 7.66. Found: C 87.96, H 7.71. IR (KBr):  $\nu_{max}$  = 3033, 2927, 2857, 1681, 1603, 1512, 1486, 1399, 1202, 1119, 1022, 991, 974, 845, 823, 759, 688 cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  8.10–8.08 (m, 2H; Ho), 7.72–7.70 (m, 2H; Hm), 7.65–7.64 (m, 2H; Ho), 7.51–7.47 (m, 2H; Hm), 7.43–7.40 (m, 1H; Hp.), 7.33–7.31 (m, 2H; Ho-), 7.14–7.12 (m, 2H, Hm-), 6.57 (d, <sup>3</sup>J = 16.0 Hz, 1H, Hγ), 6.45 (dt, <sup>3</sup>J = 16.0 Hz, <sup>3</sup>J = 6.6 Hz, 2H, CH<sub>2</sub>), 2.59, 1.59, 1.33 (m, 8H, CH<sub>2</sub>), 0.90 ppm (m, 3H, Me). <sup>13</sup>C NMR:  $\delta$  197.6 (C=O), 145.9 (C<sub>p</sub>), 142.4 (C<sub>p</sub>°), 139.9 (C<sub>i</sub>), 135.3 (C<sub>i</sub>'), 134.4 (C<sub>i</sub>°), 133.5 (Cγ), 128.9, (C<sub>o</sub>° C<sub>m</sub>'), 128.6 (C<sub>m</sub>°), 128.2 (C<sub>p</sub>'), 127.3 (C<sub>o</sub>°, C<sub>m</sub>), 126.2 (C<sub>o</sub>°), 121.6 (Cβ), 42.9 (CO<u>C</u>H<sub>2</sub>), 35.6, 31.5, 31.1, 22.5 (4<u>C</u>H<sub>2</sub>), 14.0 ppm (Me).

(3*E*,3'*E*)-4,4'-(1,4-phenylene)bis(1-(naphthalen-2-yl)but-3en-1-one) (35; Table 3, Entry 15). Yield: 1.42 g, 76%. Yellow crystals: mp 163 °C. Elemental Analysis Calcd (%) for  $C_{34}H_{26}O_2$ (466.57): C 87.52, H 5.62. Found: C 87.55, H 5.67. IR (KBr):  $\nu_{max}$  = 3053, 1677, 1626, 1596, 1509, 1468, 1408, 1355, 1277, 1183, 1123, 989, 966, 944, 863, 819, 747, 476 cm<sup>-1.</sup> <sup>1</sup>H NMR: δ 8.51 (s, 2H; H<sub>1</sub>), 8.10–7.80 (m, 8H; H<sub>Naphth</sub>), 7.70–7.50 (m, 4H; H<sub>Naphth</sub>), 7.32 (s, 4H; H<sub>o</sub>), 6.55–6.52 (m, 4H; Hγ, Hβ), 4.03 ppm (d, <sup>3</sup>*J* = 5.4 Hz, 4H; C<u>H</u><sub>2</sub>). <sup>13</sup>C NMR: δ 198.0 (C=O), 136.4, 135.8, 134.1, 132.7, 130.1, 129.7, 127.9, 126.9, 126.6, 124.1 (20 C<sub>Naphth</sub>), 133.3 (Cβ), 122.6 (Cγ), 42.9 ppm (CO<u>C</u>H<sub>2</sub>);

(*E*)-1-(Furan-2-yl)-4-phenylbut-3-en-1-one (36; Table 3, Entry 16). Yield: 518 mg, 61%. White crystals: mp 78–80 °C. Elemental Analysis Calcd (%) for C<sub>14</sub>H<sub>12</sub>O<sub>2</sub> (212.24): C 79.22, H 5.70. Found: C 79.31, H 5.76. IR (KBr):  $\nu_{max}$  = 3142, 3127, 3057, 3024, 2893, 1689, 1564, 1495, 1468, 1450, 1395, 1306, 1249, 1236, 1161, 1089, 1079, 1070, 1032, 1021, 997, 973, 917, 882, 790, 769, 728, 690, 619, 596, 527, 498 cm<sup>-1</sup>. <sup>1</sup>H NMR: δ 7.54–7.53 (m, 1H; H5), 7.32–7.30 (m, 2H; H<sub>o</sub>), 7.26–7.22 (m, 2H; H<sub>m</sub>), 7.19–7.18 (m, 1H; H<sub>p</sub>), 6.50 (d, <sup>3</sup>*J* = 16.5 Hz, 1H; Hγ), 6.47–6.45 (m, 2H; H3, H4), 6.37 (dt, <sup>3</sup>*J* = 16.5 Hz, <sup>3</sup>*J* = 6.9 Hz, 1H; Hβ), 3.69 ppm (d, <sup>3</sup>*J* = 6.9 Hz, 2H; CH<sub>2</sub>). <sup>13</sup>C NMR: δ 186.8 (C=O), 152.3 (C<sub>2</sub>), 146.6 (C<sub>5</sub>), 136.9 (C<sub>i</sub>), 133.8 (Cγ), 128.6 (C<sub>m</sub>), 126.8 (C<sub>o</sub>), 127.5 (C<sub>p</sub>), 121.8 (Cβ), 117.6 (C<sub>3</sub>), 112.3 (C<sub>4</sub>), 42.6 ppm (<u>C</u>H<sub>2</sub>). (*E*)-4-Phenyl-1-thiophen-2-yl-3-buten-1-one (37; Table 3, Entry 17). Yield: 749 mg, 82%. Pale yellow crystals: mp 42 °C. Elemental Analysis Calcd (%) for C<sub>14</sub>H<sub>12</sub>OS (228.31): C 73.65, H 5.30, S 14.04. Found: C 73.74, H 5.45, S 14.00. IR (KBr):  $\nu_{max}$  = 3436, 3026, 1660, 1516, 1495, 1353, 1299, 1208, 1053, 963, 945, 859, 839, 765, 726, 692, 583, 498, 463 cm<sup>-1</sup>. <sup>1</sup>H NMR: δ 7.77 (dd, <sup>3</sup>*J* = 3.8 Hz, <sup>4</sup>*J* = 1.2 Hz, 1H; H3), 7.63 (dd, <sup>3</sup>*J* = 4.9 Hz, <sup>4</sup>*J* = 1.2 Hz, 1H; H5), 7.36 (m, 2H; H<sub>o</sub>), 7.29 (m, 2H; H<sub>m</sub>), 7.21 (m, 1H; H<sub>p</sub>), 7.13 (dd, <sup>3</sup>*J* = 3.8 Hz, <sup>3</sup>*J* = 4.9 Hz, 1H; H4), 6.56 (d, <sup>3</sup>*J* = 16.1 Hz, 1H; Hγ), 6.42 (dt, <sup>3</sup>*J* = 16.1 Hz, <sup>3</sup>*J* = 6.8 Hz, 1H; Hβ), 3.82 ppm (d, <sup>3</sup>*J* = 6.8 Hz, 2H; CH<sub>2</sub>). <sup>13</sup>C NMR: δ 190.8 (C=O), 143.8 (C<sub>2</sub>), 136.9 (C<sub>i</sub>), 133.9 (Cβ), 133.4 (C<sub>5</sub>), 132.4 (C<sub>3</sub>), 128.6 (C<sub>m</sub>), 128.2 (C<sub>4</sub>), 127.6 (C<sub>p</sub>), 126.4 (C<sub>o</sub>), 122.3 (Cγ), 43.7 ppm (<u>CH<sub>2</sub></u>).

(E)-4-(3-Methoxyphenyl)-2-methyl-1-(thiophen-2-yl)but-3en-1-one (38; Table 3, Entry 18). Yield: 872 mg, 80%. Yellow oil. Elemental Analysis Calcd (%) for C<sub>16</sub>H<sub>16</sub>O<sub>2</sub>S (272.36): C 70.56, H 5.92, S 11.77. Found: C 70.61, H 5.96, S 11.75. IR (film):  $\nu_{max} = 3102$ , 3026, 2972, 2933, 2835, 1661, 1599, 1579, 1518, 1490, 1464, 1454, 1433, 1415, 1355, 1318, 1289, 1266, 1242, 1203, 1157, 1042, 969, 936, 853, 780, 726, 689, 656, 565, 452 cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  7.82 (dd, <sup>3</sup>*J* = 3.9 Hz,  ${}^{4}J$  = 1.0 Hz, 1H; H3), 7.60 (dd,  ${}^{3}J$  = 4.9 Hz,  ${}^{4}J$  = 1.0 Hz, 1H; H5), 7.21 (m, 1H; H<sub>5</sub>), 7.10 (dd,  ${}^{3}J$  = 3.9 Hz,  ${}^{4}J$  = 4.9 Hz, 1H; H4), 6.96 (m, 1H; H<sub>6</sub>), 6.92 (m, 1H; H<sub>2</sub>), 6.79 (m, 1H; H<sub>4</sub>), 6.56 (d,  ${}^{3}J$  = 15.9 Hz, 1H; H $\gamma$ ), 6.38 (dd, <sup>3</sup>J = 15.9 Hz, <sup>3</sup>J = 8.3 Hz, 1H; H $\beta$ ), 4.15 (m, 1H; C<u>H</u>Me), 3.77 (s, 3H; O<u>Me</u>), 1.46 ppm (d,  ${}^{3}J$  = 6.9 Hz, 3H; CH<u>Me</u>). <sup>13</sup>C NMR: δ 193.6 (C=O), 159.6 (C<sub>3</sub>), 143.4 (C2), 138.1  $(C_1)$ , 133.6 (C5), 132.2 (C3), 131.59 (C $\gamma$ ), 129.4 (C $_5$ ), 129.7 (C $\beta$ ), 128.1 (C4), 118.8 (C6), 113.2 (C4), 111.3 (C2), 54.9 (OMe), 46.5 (CHMe), 17.6 ppm (CHMe).

(*E*)-6-Methyl-1-phenylhept-1-en-4-one (40). Yield: 307 mg, 38%. Yellow oil. Elemental Analysis Calcd (%) for C<sub>14</sub>H<sub>18</sub>O (202.29): C 83.12, H 8.97. Found: C 83.17, H 8.92. IR (film):  $\nu_{max}$  = 3027, 2957, 2931, 2872, 1714, 1673, 1599, 1495, 1467, 1450, 1366, 1294, 1170, 1072, 1031, 966, 746, 695 cm<sup>-1</sup>. <sup>1</sup>H NMR: δ 7.40–7.39 (m, 2H; H<sub>o</sub>), 7.33–7.32 (m, 2H; H<sub>m</sub>), 7.26–7.24 (m, 1H; H<sub>p</sub>), 6.49 (d, <sup>3</sup>*J* = 16.1 Hz, 1H; H1), 6.34 (dt, <sup>3</sup>*J* = 16.1 Hz, <sup>3</sup>*J* = 7.1 Hz, 1H; H2), 3.32 (d, <sup>3</sup>*J* = 7.1 Hz, 2H; H3), 2.39 (d, <sup>3</sup>*J* = 7.1 Hz, 2H; H5), 2.20–2.19 (m, 1H; H6), 0.95 ppm (d, <sup>3</sup>*J* = 6.6 Hz, 6H; H7, C6-Me). <sup>13</sup>C NMR: δ 208.5 (C=O), 137.0 (C<sub>i</sub>), 133.6 (C1), 128.6 (C<sub>m</sub>), 127.5 (C<sub>p</sub>), 126.3 (C<sub>o</sub>), 122.2 (C2), 51.5 (CS), 47.4 (C3), 24.5 (C6), 22.6 ppm (C6-Me, C7).

(E)-3-Isopropyl-5-phenylpent-4-en-2-one (41). Yield: 316 mg, 39%. Yellow oil. Elemental Analysis Calcd (%) for  $C_{14}H_{18}O$  (202.29): C 83.12, H 8.97. Found: C 83.08, H 8.64. IR (film):  $\nu_{max} = 3027, 2959, 2930, 2871, 1711, 1673, 1599, 1495, 1466, 1450, 1367, 1354, 1158, 970, 747, 695 cm<sup>-1</sup>. <sup>1</sup>H NMR: <math>\delta$  7.40–7.39 (m, 2H; H<sub>o</sub>), 7.33–7.32 (m, 2H; H<sub>m</sub>), 7.26–7.24 (m, 1H; H<sub>p</sub>), 6.50 (d, <sup>3</sup>J = 15.6 Hz, 1H; H5), 6.34 (dd, <sup>3</sup>J = 15.6 Hz, <sup>3</sup>J = 9.8 Hz, 1H; H4), 2.98 (dd, <sup>3</sup>J = 9.8 Hz, <sup>3</sup>J = 9.3 Hz, 1H; H3), 2.21 (s, 3H; C1), 2.19–2.17 (m, 1H; CH(Me)<sub>2</sub>), 0.96, 0.94 ppm (d, <sup>3</sup>J = 6.6 Hz, 6H; CH(<u>Me</u>)<sub>2</sub>). <sup>13</sup>C NMR:  $\delta$  209.6 (C=O), 136.9 (C<sub>1</sub>), 133.7 (C5), 128.7 (C<sub>m</sub>), 128.2 (C<sub>p</sub>), 127.9 (C4), 126.4 (C<sub>0</sub>), 65.4 (C3), 30.2 (<u>C</u>H(Me)<sub>2</sub>), 29.7 (C1), 21.2, 20.0 ppm (CH-(<u>Me</u>)<sub>2</sub>).

(E)-2,2-Dimethyl-6-phenyl-4-styrylhex-5-en-3-one (42). Yield: 414 mg, 34%. Yellow powder: mp 70–72 °C. Elemental Analysis Calcd (%) for  $C_{22}H_{24}O$  (304.43): C 86.80, H 7.95. Found: C 86.91, H 7.99. IR (film):  $\nu_{max} = 3059$ , 3027, 2969, 2932, 2870, 1704, 1599, 1495, 1477, 1448, 1394, 1366, 1293, 1068, 1052, 1029, 985, 968, 897, 775, 743, 693 cm<sup>-1.</sup> <sup>1</sup>H NMR:  $\delta$  7.40–7.38 (m, 4H; H<sub>o</sub>), 7.33– 7.31 (m, 4H; H<sub>m</sub>), 7.25–7.23 (m, 2H; H<sub>p</sub>), 6.60 (d, <sup>3</sup>*J* = 15.9 Hz, 2H; Hγ), 6.44 (dd, <sup>3</sup>*J* = 15.9 Hz, <sup>3</sup>*J* = 8.3 Hz, 2H; Hβ), 4.72 (t, <sup>3</sup>*J* = 8.3 Hz, 1H; H4), 1.31 ppm (s, 9H; C(Me)<sub>3</sub>). <sup>13</sup>C NMR:  $\delta$  213.8 (C=O), 136.9 (C<sub>i</sub>), 131.6 (Cγ), 128.6 (C<sub>m</sub>), 128.3 (Cβ), 127.7 (C<sub>p</sub>), 126.4 (C<sub>o</sub>), 54.3 (C4), 45.5 (<u>C</u>(Me)<sub>3</sub>), 26.2 ppm (C(Me)<sub>3</sub>).

# ASSOCIATED CONTENT

#### **S** Supporting Information

<sup>1</sup>H and <sup>13</sup>C NMR spectra of products. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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