Iridium-catalyzed regioselective decarboxylative allylation of 
β-ketoacids: efficient construction of γ, δ-unsaturated ketones

Shu-Jie Chen, Guo-Ping Lu and Chun Cai *

School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, People’s Republic of China
c.cai@mail.njust.edu.cn

Supporting information
Table of contents

General information………………………………………………………….S-2
Preparation of allylic alcohols 2n and 2p………………………………………S-2
General procedure for the decarboxylative allylation of β-ketoacids with allylic alcohols….S-2
Controlled experiment and the procedure for capture of intermediate …. …. …. …. S-3
Analytical data for the products……………………………………………..…S-4
Copies of 1H and 13C NMR spectra…………………………………………………………..S-11
General information

All air-sensitive manipulations were carried out under the inert gas atmosphere using standard Schlenk techniques. Glassware was oven or flame dried immediately prior to use. 1,2-Dichloroethane (DME) was distilled from P2O5 under nitrogen and kept with 4A molecular sieves. 1H NMR, 19F NMR, and 13C NMR spectra were recorded on an AVANCE 500 Bruker spectrometer operating at 500 MHz, 470 MHz, and 125 MHz in CDCl3, respectively, and chemical shifts were reported in ppm relative to the center of the singlet at 7.26 ppm for CDCl3 or downfield from internal tetramethylsilane). GC/MS were performed on an ISQ Trace 1300 (electrospray ionization: EI). GC analysis were performed on an Agilent 7890A instrument (Column: Agilent 19091J-413: 30 m × 320 μm × 0.25 μm, carrier gas: N2, FID detector. Elemental analyses were performed on a Yanagimoto MT3CHN recorder. Preparative high performance liquid chromatography was performed on the column XDB-C18 (9.6 mm × 250 mm) with methanol/water as eluent.

Monosubstituted allylic alcohols were prepared by the reaction of the corresponding aldehyde with vinyl magnesium bromide. Allylic alcohols 2n and 2p were prepared by a 1,2-reduction of the corresponding α,β-unsaturated ketones. β-Ketoacids 1g-1h were prepared from the corresponding aryl ketones. β-Ketoacids 1i-1l were prepared from the commercially available β-ketoesters.

General procedure for the preparation of allylic alcohols 2n and 2p.

In an oven-dried round-bottom flask, a solution of the α,β-unsaturated ketone (2 mmol, 1 equiv) in 10 ml THF/MeOH (v/v=1/1) was stirred for 5 minutes at 0 ºC. Then NaBH4 (2.59 g, 2 mmol, 1.0 equiv) was added in one portion and the reaction mixture was maintained at this temperature for 1 h (monitored by TLC). Then the reaction was quenched with several mLs of 0.1 M HCl until no further hydrogen evolution was observed. The solution was then made basic using NaHCO3 and extracted with diethyl ether (15 ml ×3). The combined organic phase was washed by saturated solution of NaCl, dried over anhydrous MgSO4, and evaporated to leave the crude product which was purified by column chromatography over silica gel.

General procedure for the decarboxylative allylation of β-ketoacids with allylic alcohols.

A 10 ml schlenk tube was charged with [Ir(cod)Cl]2 (3.0 mg, 0.0045 mmol, 0.015 equiv), (+)-10-Camphorsulfonic Acid (CSA) (35 mg, 0.15 mmol, 0.5 equiv) and β-ketoacids (0.39 mmol, 1.3 equiv). The tube was flushed with nitrogen for three times. Then 1.5 ml of dry 1,2-dichloroethane (DCE) and allylic alcohol (0.3 mmol, 1.0 equiv) were added by syringe and the reaction was stirred at 25 ºC for 10 hours. After the indicated time, the solvent was removed by vacuum and the residue was analyzed by 1H NMR spectroscopy to determine the ratio of branched to linear regioisomers. The solvent was then removed again, and the residue was purified by flash column chromatography on silica gel with pentane and Et2O as elute.
Controlled experiment and the procedure for capture of intermediate. \(^5\)

A 10 ml schlenk tube was charged with \([\text{Ir} (\text{cod}) \text{Cl}]_2\) (3.0 mg, 0.0045 mmol, 0.015 equiv), (±)-10-Camphorsulfonic Acid (CSA) (35 mg, 0.15 mmol, 0.5 equiv) and acetophenone 1 (0.39 mmol, 1.3 equiv). The tube was flushed with nitrogen for three times. Then 1.5 ml of dry 1,2-dichloroethane (DCE) and allylic alcohol 2a (0.3 mmol, 1.0 equiv) were added by syringe and the reaction was stirred at 25 °C for 10 hours. The GC-MS of the crude mixture showed no conversion of 1a and no product 3 or 4 was observed.

A 10 ml schlenk tube was charged with \([\text{Ir} (\text{cod}) \text{Cl}]_2\) (3.0 mg, 0.0045 mmol, 0.015 equiv), (±)-10-Camphorsulfonic Acid (CSA) (35 mg, 0.15 mmol, 0.5 equiv) and benzoylacetic acid 1a (0.39 mmol, 1.3 equiv). The tube was flushed with nitrogen for three times. Then 1.5 ml of dry 1,2-dichloroethane (DCE) and allylic alcohol 2a (0.3 mmol, 1.0 equiv) were added by syringe and the reaction was stirred at 25 °C for 0.5 h. Then methanol/ether (1 ml/1 mL) and trimethylsilyldiazomethane solution (2.0 M in hexane, 0.9 mmol, 3 equiv) were added and the mixture was stirred at room temperature for 5 minutes. The reaction mixture was concentrated in vacuo and purified by flash column chromatography on silica gel with pentane/Et₂O as elute to get 1,3-diphenylpent-4-en-1-one 3a (8.5 mg, 12 %) and methyl 2-benzoyl-3-phenylpent-4-enoate B (53.8 mg, 61 %, dr = 7 : 3).

**Caution:** When adding the TMSCHN₂, the nitrogen is generated dramatically. Perform this process in an open system.

Methyl 2-benzoyl-3-phenylpent-4-enoate (B, one isomer, separated by preparative HPLC with acetonitrile/water as elute). White solid; \(^1\)H NMR (500 MHz, CDCl₃) δ 8.05 – 8.00 (m, 2H), 7.54 (t, \(J = 7.4\) Hz, 1H), 7.43 (t, \(J = 7.7\) Hz, 2H), 7.28 – 7.22 (m, 4H), 7.19 – 7.15 (m, 1H), 5.88 – 5.79 (m, 1H), 4.93 (d, \(J = 7.4\) Hz, 1H), 4.90 (d, \(J = 0.8\) Hz, 1H), 4.86 (d, \(J = 11.1\) Hz, 1H), 4.38 (dd, \(J = 11.0, 7.3\) Hz, 1H), 3.33 (s, 3H). \(^{13}\)C NMR (125 MHz, CDCl₃) δ 193.01, 168.04, 140.15, 138.07, 136.80, 133.74, 128.85, 128.79, 128.59, 128.33, 127.12, 116.50, 59.09, 52.42, 49.40. GCMS (EI) m/z: 294 (M⁺).
Analytical data for the products

1,3-Diphenylpent-4-en-1-one (3a). Colorless oil; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.98 – 7.89 (m, 2H), 7.55 (t, $J$ = 7.4 Hz, 1H), 7.45 (t, $J$ = 7.7 Hz, 2H), 7.31 (t, $J$ = 7.5 Hz, 2H), 7.27 (d, $J$ = 7.7 Hz, 2H), 7.21 (t, $J$ = 7.1 Hz, 1H), 6.06 (ddd, $J$ = 17.1, 10.3, 6.8 Hz, 1H), 5.06 (dd, $J$ = 18.6, 13.7 Hz, 2H), 4.15 (q, $J$ = 6.9 Hz, 1H), 3.41 (qd, $J$ = 16.6, 7.1 Hz, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 198.39, 143.27, 140.78, 137.25, 133.15, 128.71, 128.18, 127.83, 126.67, 114.84, 44.64, 44.14.

3-(2-Bromophenyl)-1-phenylpent-4-en-1-one (3b). Colorless oil; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.03 – 7.91 (m, 2H), 7.57 (ddd, $J$ = 8.6, 3.1, 2.0 Hz, 2H), 7.46 (dd, $J$ = 10.6, 4.8 Hz, 2H), 7.34 – 7.22 (m, 2H), 7.17 – 7.02 (m, 1H), 6.04 (ddd, $J$ = 17.0, 10.4, 6.4 Hz, 1H), 5.08 (ddt, $J$ = 61.1, 17.2, 1.2 Hz, 2H), 4.65 (ddd, $J$ = 9.9, 6.3, 1.3 Hz, 1H), 3.42 (qd, $J$ = 16.9, 7.1 Hz, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 197.71, 142.30, 138.98, 136.98, 133.37, 133.24, 128.82, 128.73, 128.22, 127.74, 124.68, 115.79, 43.22. GCMS (EI) m/z: 314 (M$^+$); Anal. Calcd for C$_{17}$H$_{15}$BrO: C, 64.78; H, 4.80. Found: C, 64.99; H, 4.66%.

3-(4-Chlorophenyl)-1-phenylpent-4-en-1-one (3c). Colorless oil; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.96 – 7.88 (m, 2H), 7.56 (dd, $J$ = 10.5, 4.3 Hz, 1H), 7.45 (t, $J$ = 7.7 Hz, 2H), 7.30 – 7.24 (m, 2H), 7.19 (d, $J$ = 8.4 Hz, 2H), 6.01 (ddd, $J$ = 17.1, 10.3, 6.6 Hz, 1H), 5.13 – 4.96 (m, 2H), 4.12 (q, $J$ = 6.9 Hz, 1H), 3.38 (qd, $J$ = 16.8, 7.1 Hz, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 198.00, 141.69, 140.40, 137.08, 133.29, 132.36, 129.27, 128.79, 128.76, 128.14, 115.18, 77.39, 77.14, 76.88, 43.91. GCMS (EI) m/z: 270 (M$^+$); Anal. Calcd for C$_{17}$H$_{15}$ClO: C, 75.41; H, 5.58. Found: C, 75.14; H, 5.69%.

3-(2,4-Dichlorophenyl)-1-phenylpent-4-en-1-one (3d). Colorless oil; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.97 (dt, $J$ = 8.5, 1.5 Hz, 2H), 7.67 – 7.52 (m, 1H), 7.51 – 7.44 (m, 2H), 7.43 – 7.38 (m, 1H), 7.26 – 7.18 (m, 2H), 6.02 (ddd, $J$ = 17.0, 10.4, 6.4 Hz, 1H), 5.09 (ddt, $J$ = 61.1, 17.2, 1.2 Hz, 2H), 4.62 (ddt, $J$ = 7.7, 6.3, 1.4 Hz, 1H), 3.43 (qd, $J$ = 17.0, 7.1 Hz, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 197.47, 139.27, 138.56, 136.87, 134.61, 133.36, 132.84, 129.77, 129.62, 128.78, 128.17, 127.37, 116.06, 42.82, 40.35. GCMS (EI) m/z: 304 (M$^+$); Anal. Calcd for C$_{17}$H$_{13}$ClO$_2$: C, 66.90; H, 4.62. Found: C, 67.20; H, 4.43%.

1-Phenyl-3-(p-tolyl)pent-4-en-1-one (3e). Colorless oil; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.97 – 7.89 (m, 2H), 7.55 (t, $J$ = 7.4 Hz, 1H), 7.44 (t, $J$ = 7.7 Hz, 2H), 7.13 (dd, $J$ = 20.5, 8.1 Hz, 4H), 6.03 (ddd, $J$ = 17.1, 10.3, 6.8 Hz, 1H), 5.21 – 4.90 (m, 2H), 4.10 (q, $J$ = 6.9 Hz, 1H), 3.38 (ddd, $J$ = 23.1, 16.6, 7.1 Hz, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 198.49, 140.98, 140.25, 137.27, 136.20, 133.13, 129.40, 128.69, 128.20, 127.67, 114.62, 44.27, 44.20, 21.12.
3-(3-Methoxyphenyl)-1-phenylpent-4-en-1-one (3f). Colorless oil; \( ^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.95 – 7.91 (m, 2H), 7.57 – 7.53 (m, 1H), 7.47 – 7.43 (m, 2H), 7.23 (t, \( J = 7.9 \) Hz, 1H), 6.87 (t, \( J = 5.7 \) Hz, 1H), 6.83 – 6.79 (m, 1H), 6.78 – 6.73 (m, 1H), 6.03 (dd, \( J = 17.1, 10.3, 6.8 \) Hz, 1H), 5.06 (ddt, \( J = 18.1, 17.1, 1.3 \) Hz, 2H), 4.12 (q, \( J = 6.7 \) Hz, 1H), 3.79 (s, 3H), 3.40 (ddd, \( J = 23.0, 16.6, 7.1 \) Hz, 2H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \) 198.34, 159.87, 144.97, 140.58, 137.27, 133.14, 129.69, 128.69, 128.17, 120.14, 114.90, 113.82, 111.81, 55.28, 44.67, 44.09.

3-(3,5-Dimethoxyphenyl)-1-phenylpent-4-en-1-one (3g). Colorless oil; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.94 (dd, \( J = 5.1, 3.4 \) Hz, 2H), 7.61 – 7.50 (m, 1H), 7.45 (dd, \( J = 10.6, 4.8 \) Hz, 2H), 6.42 (d, \( J = 2.2 \) Hz, 2H), 6.32 (t, \( J = 2.2 \) Hz, 1H), 6.02 (ddd, \( J = 17.1, 10.4, 6.8 \) Hz, 1H), 5.10 – 5.01 (m, 2H), 4.08 (dd, \( J = 14.2, 6.7 \) Hz, 1H), 3.77 (s, 6H), 3.38 (ddd, \( J = 22.9, 16.7, 7.1 \) Hz, 2H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \) 198.33, 160.99, 145.82, 140.37, 137.23, 133.17, 128.71, 128.19, 114.99, 105.98, 98.40, 55.39, 44.84, 44.00. GCMS (EI) m/z: 296 (M\(^+\)); Anal. Calcd for C\(_{19}\)H\(_{20}\)O\(_3\): C, 77.00; H, 6.80. Found: C, 77.25; H, 7.06%.

3-(2-Methoxyphenyl)-1-phenylpent-4-en-1-one (3h). Colorless oil; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.98 (d, \( J = 7.7 \) Hz, 2H), 7.56 (dd, \( J = 13.7, 6.8 \) Hz, 1H), 7.46 (t, \( J = 7.6 \) Hz, 2H), 7.21 (t, \( J = 7.8 \) Hz, 2H), 6.93 (t, \( J = 7.5 \) Hz, 1H), 6.87 (d, \( J = 8.0 \) Hz, 1H), 6.12 (ddd, \( J = 17.2, 10.3, 6.9 \) Hz, 1H), 5.05 (dd, \( J = 22.4, 13.8 \) Hz, 2H), 4.48 (q, \( J = 7.0 \) Hz, 1H), 3.83 (s, 3H), 3.44 – 3.34 (m, 2H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \) 198.91, 156.93, 139.91, 137.33, 132.93, 131.65, 128.58, 128.43, 128.25, 127.69, 120.76, 141.88, 110.90, 55.44, 43.30, 39.11. GCMS (EI) m/z: 266 (M\(^+\)); Anal. Calcd for C\(_{18}\)H\(_{18}\)O\(_2\): C, 81.17; H, 6.81. Found: C, 81.09; H, 7.14%.

1-Phenyl-3-(3-(trifluoromethyl)phenyl)pent-4-en-1-one (3i). Colorless oil; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.96 – 7.90 (m, 2H), 7.58 – 7.54 (m, 1H), 7.51 (s, 1H), 7.48 – 7.40 (m, 5H), 6.04 (dd, \( J = 17.1, 10.3, 6.7 \) Hz, 1H), 5.09 (ddt, \( J = 36.4, 17.2, 1.2 \) Hz, 2H), 4.22 (q, \( J = 6.9 \) Hz, 1H), 3.43 (ddd, \( J = 52.2, 16.9, 7.1 \) Hz, 2H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \) 197.79, 144.22, 139.96, 137.02, 131.48, 130.96 (q, \( J = 31.5 \) Hz), 129.11, 128.77, 128.42, 128.14, 124.58, 124.25 (q, \( J = 270.1 \) Hz), 123.58, 115.64, 44.27, 43.83. \(^{19}\)F NMR (470 MHz, CDCl\(_3\)) \( \delta \) -62.50. GCMS (EI) m/z: 304 (M\(^+\)); Anal. Calcd for C\(_{18}\)H\(_{15}\)F\(_3\)O: C, 71.04; H, 4.97. Found: C, 71.15; H, 4.68%.

3-(3-Nitrophenyl)-1-phenylpent-4-en-1-one (3j). Colorless oil; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 8.14 (t, \( J = 1.9 \) Hz, 1H), 8.07 (ddd, \( J = 8.2, 2.1, 0.9 \) Hz, 1H), 7.98 – 7.88 (m, 2H), 7.60 – 7.55 (m, 1H), 7.47 (dt, \( J = 7.6, 6.0 \) Hz, 3H), 6.04 (ddd, \( J = 17.1, 10.3, 6.7 \) Hz, 1H), 5.13 (dd, \( J = 35.1, 13.7 \) Hz, 2H), 4.28 (q, \( J = 6.9 \) Hz, 1H), 3.47 (qd, \( J = 17.1, 7.1 \) Hz, 2H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \) 197.40, 148.55, 145.36, 139.57, 136.81, 134.57, 133.49, 129.55, 128.82, 128.12, 122.70, 121.84, 116.11, 44.03, 43.63. GCMS (EI) m/z: 281 (M\(^+\)); Anal. Calcd for C\(_{18}\)H\(_{15}\)NO\(_3\): C, 72.58; H, 5.37. Found: C, 72.43; H, 5.44%.
4-(5-Oxo-5-phenylpent-1-en-3-yl)benzonitrile (3k). Colorless oil; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.92 (dt, $J = 8.5, 1.5$ Hz, 2H), 7.61 – 7.54 (m, 3H), 7.50 – 7.43 (m, 2H), 7.41 – 7.34 (m, 2H), 6.01 (ddd, $J = 17.1, 6.7$ Hz, 1H), 5.10 (ddt, $J = 40.7, 17.2, 1.2$ Hz, 2H), 4.21 (q, $J = 6.9$ Hz, 1H), 3.43 (qd, $J = 17.1, 7.1$ Hz, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 197.44, 148.78, 139.51, 136.84, 133.49, 132.51, 128.81, 128.11, 118.98, 116.01, 110.57, 44.47, 43.53. GCMS (EI) m/z: 261 (M$^+$); Anal. Calcd for C$_{18}$H$_{15}$NO: C, 82.73; H, 5.79. Found: C, 83.04; H, 5.62%.

1-Phenyl-3-(thiophen-2-yl)pent-4-en-1-one (3l). Colorless oil; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.02 – 7.90 (m, 2H), 7.57 (t, $J = 7.4$ Hz, 1H), 7.46 (t, $J = 7.7$ Hz, 2H), 7.16 (dd, $J = 5.1, 1.1$ Hz, 1H), 6.96 – 6.84 (m, 2H), 6.04 (ddd, $J = 17.2, 10.2, 7.2$ Hz, 1H), 5.12 (dd, $J = 13.5, 12.9$ Hz, 2H), 4.44 (q, $J = 6.9$ Hz, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 197.82, 146.94, 140.16, 137.12, 133.29, 128.75, 128.21, 126.90, 124.15, 123.76, 115.50, 45.08, 39.99. GCMS (EI) m/z: 242 (M$^+$); Anal. Calcd for C$_{15}$H$_{14}$OS: C, 74.34; H, 5.82. Found: C, 74.56; H, 5.98%.

3-(Furan-2-yl)-1-phenylpent-4-en-1-one (3m). Colorless oil; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.00 – 7.92 (m, 2H), 7.56 (t, $J = 7.4$ Hz, 1H), 7.49 – 7.43 (m, 2H), 7.32 (d, $J = 1.1$ Hz, 1H), 6.28 (dd, $J = 3.1, 1.9$ Hz, 1H), 6.07 (d, $J = 3.2$ Hz, 1H), 6.03 – 5.92 (m, 1H), 5.18 – 5.03 (m, 2H), 4.23 (q, $J = 6.9$ Hz, 1H), 3.41 (ddd, $J = 24.4, 16.7, 7.0$ Hz, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 197.88, 156.03, 141.52, 137.88, 137.10, 133.22, 128.71, 128.20, 116.22, 110.29, 105.50, 42.00, 38.58.

(E)-1,3-Diphenylundec-4-en-1-one (3n) and (E)-1-Phenyl-3-styrylnonan-1-one (4n). Mixture of 3n and 4n, the ratio is 75:25. Colorless oil; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.01 – 7.85 (m, 3H), 7.54 (dd, $J = 9.6, 5.2$ Hz, 1H), 7.49 – 7.39 (m, 3H), 7.35 – 7.22 (m, 6H), 7.22 – 7.14 (m, 1H), 6.38 (d, $J = 15.8$ Hz, 1H), 6.07 (dd, $J = 15.8, 8.7$ Hz, 1H), 5.62 (dd, $J = 15.3, 7.2$ Hz, 1H), 5.48 – 5.38 (m, 1H), 4.07 (q, $J = 7.1$ Hz, 1H), 3.36 (qd, $J = 16.2, 7.2$ Hz, 2H), 3.10 – 3.03 (m, 1H), 2.96 – 2.88 (m, 1H), 1.96 (q, $J = 7.0$ Hz, 2H), 1.40 – 1.08 (m, 13H), 0.88 – 0.83 (m, 4H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 199.49, 198.76, 144.25, 137.46, 133.73, 132.99, 132.25, 131.29, 130.21, 128.62, 128.20, 127.68, 127.10, 126.42, 126.20, 44.93, 44.50, 44.06, 39.26, 35.25, 32.58, 31.89, 31.76, 29.79, 29.36, 28.85, 27.37, 22.68, 14.15. GCMS (EI) m/z: 320 (M$^+$).
1-Phenyl-3-vinylnonan-1-one (3o). Colorless oil; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.93 (d, $J = 7.3$ Hz, 2H), 7.55 (t, $J = 7.4$ Hz, 1H), 7.45 (t, $J = 7.6$ Hz, 2H), 5.68 (ddd, $J = 17.3, 10.2, 8.3$ Hz, 1H), 4.98 (dd, $J = 13.7, 7.2$ Hz, 2H), 2.97 (d, $J = 6.8$ Hz, 2H), 2.80 – 2.67 (m, 1H), 1.30 – 1.23 (m, 8H), 0.87 (t, $J = 6.8$ Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 199.67, 141.75, 137.53, 132.97, 128.65, 128.22, 114.76, 44.06, 39.88, 34.84, 31.89, 29.37, 27.15, 22.72, 14.17. GCMS (EI) m/z: 244 (M$^+$); Anal. Calcd for C$_{17}$H$_{24}$O: C, 83.55; H, 9.90. Found: C, 83.24; H, 9.97%.

(O)-1,3-Diphenylhex-4-en-1-one (3p) and (E)-3-Methyl-1,5-diphenylpent-4-en-1-one (4p). Mixture of 3p and 4p, the ratio is 60:40. Colorless oil; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.95 (dd, $J = 19.9, 8.0$ Hz, 4H), 7.55 (dt, $J = 7.8, 4.0$ Hz, 2H), 7.51 – 7.41 (m, 4H), 7.37 – 7.23 (m, 8H), 7.19 (t, $J = 7.0$ Hz, 2H), 6.42 (d, $J = 15.9$ Hz, 1H), 6.23 (dd, $J = 15.9, 6.7$ Hz, 1H), 5.65 (dd, $J = 15.2, 7.2$ Hz, 1H), 5.51 – 5.41 (m, 1H), 4.07 (q, $J = 7.1$ Hz, 1H), 3.37 (qd, $J = 16.4, 7.1$ Hz, 2H), 3.16 – 3.05 (m, 1H), 3.00 (dd, $J = 14.4, 5.8$ Hz, 1H), 1.64 (d, $J = 6.4$ Hz, 3H), 1.20 (d, $J = 6.0$ Hz, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 199.33, 198.67, 144.20, 137.59, 137.36, 135.03, 133.66, 133.06, 128.66, 128.19, 127.69, 126.47, 126.20, 125.64, 45.69, 44.86, 43.97, 33.25, 20.37, 18.04. GCMS (EI) m/z: 250 (M$^+$).

(E)-1,5-Diphenyl-3-vinylpent-4-en-1-one (3q). Colorless oil; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.01 – 7.93 (m, 2H), 7.57 (t, $J = 7.4$ Hz, 1H), 7.47 (t, $J = 7.7$ Hz, 2H), 7.33 (d, $J = 7.4$ Hz, 2H), 7.28 (t, $J = 7.6$ Hz, 2H), 7.20 (t, $J = 7.2$ Hz, 1H), 6.45 (d, $J = 15.9$ Hz, 1H), 6.22 (dd, $J = 15.9, 7.4$ Hz, 1H), 5.93 (ddd, $J = 17.2, 10.3, 6.9$ Hz, 1H), 5.11 (dd, $J = 18.8, 13.8$ Hz, 2H), 3.69 (p, $J = 6.9$ Hz, 1H), 3.21 (d, $J = 7.0$ Hz, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 198.49, 139.77, 139.32, 133.18, 131.40, 130.53, 128.73, 128.58, 128.23, 127.35, 126.30, 115.32, 43.36, 42.24. GCMS (EI) m/z: 262 (M$^+$); Anal. Calcd for C$_{19}$H$_{18}$O: C, 86.99; H, 6.92. Found: C, 86.64; H, 7.09%.

3-Phenyl-1-(o-tolyl)pent-4-en-1-one (5a). Colorless oil; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.54 (d, $J = 7.6$ Hz, 1H), 7.35 (t, $J = 7.5$ Hz, 1H), 7.29 (t, $J = 7.6$ Hz, 2H), 7.25 – 7.18 (m, 5H), 6.02 (ddd, $J = 17.1, 10.3, 6.8$ Hz, 1H), 5.05 (dd, $J = 18.3, 13.8$ Hz, 2H), 4.07 (q, $J = 7.1$ Hz, 1H), 3.32 (qd, $J = 16.2, 7.4$ Hz, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 202.84, 143.01, 140.80, 138.52, 138.05, 131.96, 131.20, 128.68, 128.15, 127.84, 126.68, 125.67, 114.76, 47.19, 45.12, 20.91. GCMS (EI) m/z: 250 (M$^+$); Anal. Calcd for C$_{19}$H$_{18}$O: C, 86.36; H, 7.25. Found: C, 86.49; H, 7.01%.
3-Phenyl-1-(m-tolyl)pent-4-en-1-one (5b). Colorless oil; \(^{1}H\) NMR (500 MHz, CDCl\(_3\)) \(\delta 7.66\) (d, \(J = 7.0\) Hz, 2H), \(7.29\) (d, \(J = 5.3\) Hz, 1H), \(7.26 – 7.19\) (m, 5H), \(7.16 – 7.12\) (m, 1H), \(5.98\) (ddd, \(J = 17.1\), 10.3, 6.7 Hz, 1H), \(5.04 – 4.94\) (m, 2H), \(4.08\) (q, \(J = 6.7\) Hz, 1H), \(3.33\) (ddd, \(J = 23.1, 16.6, 7.1\) Hz, 2H), \(2.33\) (s, 3H). \(^{13}C\) NMR (125 MHz, CDCl\(_3\)) \(\delta 198.56, 143.34, 140.81, 138.49, 137.30, 133.89, 128.69, 128.55, 127.84, 126.63, 125.39, 114.80, 44.63, 44.19, 21.45. GCMS (EI) m/z: 250 (M\(^{+}\)); Anal. Calcld for C\(_{18}\)H\(_{18}\)O: C, 86.36; H, 7.25. Found: C, 86.54; H, 7.18%.

1-(4-Methoxyphenyl)-3-phenylpent-4-en-1-one (5c). Colorless oil; \(^{1}H\) NMR (500 MHz, CDCl\(_3\)) \(\delta 8.00 – 7.83\) (m, 2H), \(7.32 – 7.25\) (m, 4H), \(7.23 – 7.17\) (m, 1H), \(6.99 – 6.84\) (m, 2H), \(6.05\) (ddd, \(J = 17.1, 10.3, 6.8\) Hz, 1H), \(5.05\) (ddt, \(J = 20.8, 17.2, 1.3\) Hz, 2H), \(4.14\) (q, \(J = 6.7\) Hz, 1H), \(3.85\) (s, 3H), \(3.35\) (ddd, \(J = 22.9, 16.4, 7.1\) Hz, 2H). \(^{13}C\) NMR (125 MHz, CDCl\(_3\)) \(\delta 196.92, 163.56, 143.43, 140.93, 130.48, 130.36, 128.68, 127.85, 126.62, 114.75, 113.83, 55.57, 44.81, 43.77.

1-(4-Bromophenyl)-3-phenylpent-4-en-1-one (5d). Colorless oil; \(^{1}H\) NMR (500 MHz, CDCl\(_3\)) \(\delta 7.81 – 7.75\) (m, 2H), \(7.62 – 7.55\) (m, 2H), \(7.30\) (dd, \(J = 10.4, 4.6\) Hz, 2H), \(7.25\) (d, \(J = 7.0\) Hz, 2H), \(7.23 – 7.19\) (m, 1H), \(6.04\) (ddd, \(J = 17.1, 10.3, 6.8\) Hz, 1H), \(5.05\) (ddt, \(J = 27.8, 17.2, 1.2\) Hz, 2H), \(4.11\) (q, \(J = 6.9\) Hz, 1H), \(3.36\) (qd, \(J = 16.6, 7.1\) Hz, 2H). \(^{13}C\) NMR (125 MHz, CDCl\(_3\)) \(\delta 197.40, 143.02, 140.58, 135.93, 132.01, 129.71, 128.75, 128.34, 127.78, 126.77, 114.96, 44.67, 44.08. GCMS (EI) m/z: 314 (M\(^{+}\)); Anal. Calcld for C\(_{17}\)H\(_{15}\)BrO: C, 64.78; H, 4.80. Found: C, 65.09; H, 4.55%.

1-(4-Iodophenyl)-3-phenylpent-4-en-1-one (5e). Colorless oil; \(^{1}H\) NMR (500 MHz, CDCl\(_3\)) \(\delta 7.74\) (d, \(J = 8.5\) Hz, 2H), \(7.56\) (d, \(J = 8.5\) Hz, 2H), \(7.49\) (ddd, \(J = 24.9, 13.7\) Hz, 2H), \(4.19 – 4.17\) (m, 1H), \(4.03\) (q, \(J = 6.9\) Hz, 1H), \(3.28\) (qd, \(J = 16.6, 7.1\) Hz, 2H). \(^{13}C\) NMR (125 MHz, CDCl\(_3\)) \(\delta 197.70, 143.02, 140.58, 138.02, 136.48, 129.58, 128.75, 128.34, 127.78, 126.77, 114.96, 44.67, 44.03. GCMS (EI) m/z: 362 (M\(^{+}\)); Anal. Calcld for C\(_{17}\)H\(_{15}\)IO: C, 56.37; H, 3.98%.

1-(Naphthalen-2-yl)-3-phenylpent-4-en-1-one (5f). Colorless oil; \(^{1}H\) NMR (500 MHz, CDCl\(_3\)) \(\delta 8.45\) (s, 1H), \(8.01\) (dd, \(J = 8.6, 1.7\) Hz, 1H), \(7.95\) (d, \(J = 8.0\) Hz, 1H), \(7.88\) (dd, \(J = 8.2, 5.5\) Hz, 2H), \(7.58\) (ddd, \(J = 16.1, 6.9, 1.2\) Hz, 2H), \(7.34 – 7.29\) (m, 4H), \(7.22\) (ddd, \(J = 6.6, 5.7, 2.6\) Hz, 1H), \(6.10\) (ddd, \(J = 17.1, 10.4, 6.8\) Hz, 1H), \(5.09\) (ddt, \(J = 16.5, 15.3, 1.2\) Hz, 2H), \(3.55\) (ddd, \(J = 23.0, 16.5, 7.1\) Hz, 2H). \(^{13}C\) NMR (125 MHz, CDCl\(_3\)) \(\delta 198.34, 143.33, 140.81, 135.68, 134.59, 132.62, 129.82, 129.67, 128.74, 128.58, 127.88, 126.89, 126.71, 124.02, 114.91, 44.82, 44.22.
3-Phenyl-1-(thiophen-2-yl)pent-4-en-1-one (5g). Colorless oil; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.69 (dd, \(J = 3.8, 1.0\) Hz, 1H), 7.61 (dd, \(J = 4.9, 1.0\) Hz, 1H), 7.34 – 7.25 (m, 4H), 7.24 – 7.19 (m, 1H), 7.10 (dd, \(J = 4.9, 3.9\) Hz, 1H), 6.05 (ddd, \(J = 17.1, 10.4, 6.8\) Hz, 1H), 5.14 – 4.99 (m, 2H), 4.13 (q, \(J = 6.9\) Hz, 1H), 3.33 (ddd, \(J = 22.6, 15.9, 7.3\) Hz, 2H). 13C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 191.26, 144.64, 143.00, 140.50, 133.85, 131.98, 128.74, 128.21, 127.82, 126.76, 115.06, 44.96. GCMS (EI) m/z: 242 (M\(^+\)); Anal. Calcd for C\(_{15}\)H\(_{14}\)OS: C, 74.34; H, 5.82. Found: C, 74.62; H, 5.95%.

1-(Furan-2-yl)-3-phenylpent-4-en-1-one (5h). Colorless oil; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.56 (s, 1H), 7.29 (t, \(J = 7.5\) Hz, 2H), 7.25 (d, \(J = 6.6\) Hz, 2H), 7.20 (t, \(J = 7.1\) Hz, 1H), 7.15 (d, \(J = 3.6\) Hz, 1H), 6.50 (dd, \(J = 3.4, 1.4\) Hz, 1H), 6.03 (ddd, \(J = 17.1, 10.4, 6.9\) Hz, 1H), 5.11 – 4.97 (m, 2H), 4.10 (dd, \(J = 15.1, 7.5\) Hz, 1H), 3.25 (ddd, \(J = 22.6, 15.9, 7.4\) Hz, 2H). 13C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 187.61, 153.07, 146.41, 142.97, 140.51, 128.67, 127.78, 126.69, 117.17, 114.95, 112.34, 44.66, 43.96. GCMS (EI) m/z: 226 (M\(^+\)); Anal. Calcd for C\(_{15}\)H\(_{14}\)O\(_2\): C, 79.62; H, 6.24. Found: C, 79.36; H, 6.17%.

4-Phenylhex-5-en-2-one (5i). Colorless oil; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.32 – 7.28 (m, 2H), 7.21 (dd, \(J = 10.0, 4.4\) Hz, 3H), 5.97 (ddd, \(J = 17.1, 10.3, 6.8\) Hz, 1H), 5.10 – 4.96 (m, 2H), 3.91 (q, \(J = 7.1\) Hz, 1H), 2.85 (q, \(J = 16.2, 7.3\) Hz, 2H), 2.09 (s, 3H). 13C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 207.14, 142.89, 140.66, 128.72, 127.70, 126.72, 114.72, 49.11, 44.66, 30.75.

2-Methyl-5-phenylhept-6-en-3-one (5j). Colorless oil; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.33 – 7.26 (m, 2H), 7.23 – 7.16 (m, 3H), 5.98 (dt, \(J = 12.5, 10.3, 6.3\) Hz, 1H), 5.20 – 4.88 (m, 2H), 3.95 (dd, \(J = 12.5, 6.0\) Hz, 1H), 3.07 – 2.74 (m, 2H), 2.50 (dq, \(J = 13.7, 6.8\) Hz, 1H), 1.04 (t, \(J = 6.3\) Hz, 3H), 0.97 (t, \(J = 6.3\) Hz, 3H). 13C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 213.49, 143.24, 140.88, 128.64, 127.78, 126.61, 114.61, 46.05, 44.40, 41.45, 18.02, 17.91.

2,2-Dimethyl-5-phenylhept-6-en-3-one (5k). Colorless oil; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.29 (t, \(J = 7.5\) Hz, 2H), 7.23 – 7.16 (m, 3H), 5.97 (dddt, \(J = 17.1, 10.3, 6.8\) Hz, 1H), 5.11 – 4.91 (m, 2H), 3.99 (q, \(J = 7.0\) Hz, 1H), 2.95 – 2.84 (m, 2H), 1.05 (s, 9H). 13C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 213.49, 143.48, 141.03, 128.57, 127.89, 126.52, 114.55, 44.23, 44.09, 42.42, 26.20. GCMS (EI) m/z: 216 (M\(^+\)); Anal. Calcd for C\(_{15}\)H\(_{20}\)O: C, 83.28; H, 9.32. Found: C, 83.13; H, 9.46%.
6-Phenyl-6-endo-8-en-4-one (5l). Colorless oil; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 7.30 (dd, J = 10.6, 4.5\) Hz, 2H), 7.20 (dd, \(J = 7.1, 3.3, 2.4\) Hz, 3H), 5.97 (ddd, \(J = 17.1, 10.3, 6.8\) Hz, 1H), 5.03 (ddt, \(J = 22.1, 17.1, 1.3\) Hz, 2H), 3.93 (q, \(J = 7.1\) Hz, 1H), 2.82 (qd, \(J = 16.1, 7.3\) Hz, 2H), 2.31 (qt, \(J = 16.8, 7.3\) Hz, 2H), 1.59 – 1.47 (m, 2H), 0.84 (t, \(J = 7.4\) Hz, 3H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta 209.32, 143.07, 140.80, 128.68, 127.74, 126.65, 114.65, 48.22, 45.64, 44.61, 17.09, 13.75.\) GCMS (EI) \(m/z:\ 202 (M^+);\) Anal. Calcd for C\(_{14}H_{18}O:\) C, 83.12; H, 8.97. Found: C, 83.35; H, 8.81%.

References
Copies of $^1$H and $^{13}$C NMR spectra