

Supporting Information

Table of Contents

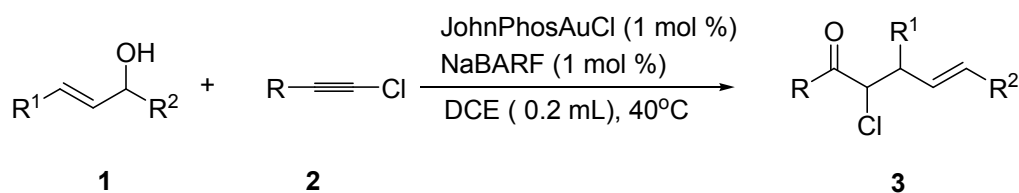
General Information.....	S-2
General Procedure for the Synthesis of γ,δ -Unsaturated α -Chloroketones via a Tandem Intermolecular Hydroalkoxylation/Claisen Rearrangement (Tables 2 and 3).....	S-2
Analytical data for the products shown in tables 2 and 3.....	S-3
References.....	S-9
Copies of ^1H and ^{13}C NMR Spectra.....	S-10

General Information

^1H and ^{13}C NMR Spectra were recorded on a Bruker AC-500 FT spectrometer (500 MHz and 125 MHz, respectively), a Bruker AC-400 FT spectrometer (400 MHz and 100 MHz, respectively) and a AC-300 FT spectrometer (300 MHz and 75 MHz, respectively) using tetramethylsilane as internal reference. Chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. IR spectra were recorded on a Perkin-Elmer 2000 FTIR spectrometer. High resolution mass spectra were recorded on a LC-TOF spectrometer (Micromass). The UV detection was monitored at 254 nm. Melting points were uncorrected.

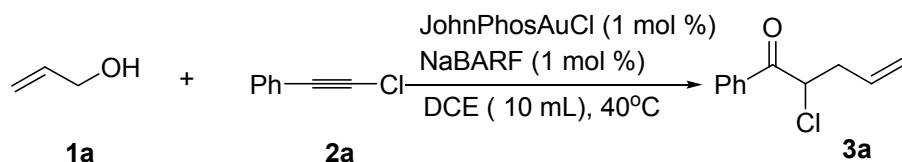
Analytical grade solvents for the column chromatography were used as received. 1,2-Dichloroethane, acetonitrile and CH_2Cl_2 were dried over CaH_2 and distilled prior to use. DMSO and MeNO_2 were dried over 4A molecular sieves and distilled prior to use. All the gold complexes ¹ and the substrates ² were prepared following the literature reports. The rest of chemicals were purchased from the Sinopharm Chemical Reagent Co., Meryer, Acros, and Alfa Aesar, and used as received.

General Procedure for the Synthesis of γ,δ -Unsaturated α -Chloroketones via a Tandem Intermolecular Hydroalkoxylation/Claisen Rearrangement (Tables 2 and 3)



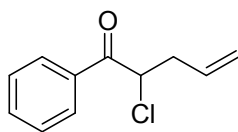
To a solution of allylic alcohol **1** (0.20 mmol) in dry DCE (0.20 mL) were added chloroalkyne **2** (0.24 mmol), JohnPhosAuCl (1.42 mg, 0.0020 mmol) and NaBARF (1.77 mg, 0.0020 mmol) subsequently. The resulting mixture was stirred at 40 °C until no further transformation was detected by TLC analysis. The mixture was cooled to room temperature, and purified by silica gel column chromatography, eluting with petroleum ether/ethyl acetate (100:0 to 10:1), to give γ,δ -unsaturated α -chloroketones **3**.

A 10 mmol Scale Reaction

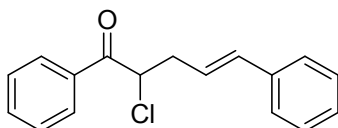


To a solution of allylic alcohol **1a** (0.58 g, 1.3 mL, 10.0 mmol) in dry DCE (10.0 mL) were added chloroalkyne **2a** (1.63 g, 12.0 mmol), JohnPhosAuCl (71.0 mg, 0.10 mmol) and NaBARF (88.5 mg, 0.10 mmol) subsequently. The resulting mixture was stirred at 40 °C for 3 hours. The mixture was cooled to room temperature, and purified by silica gel column chromatography, eluting with petroleum ether, to give γ,δ -unsaturated α -chloroketones **3a** (1.89 g) in 97% yield.

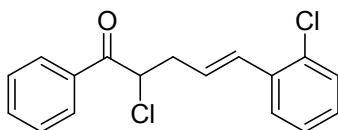
Analytical Data for The Products Shown in Tables 2 and 3



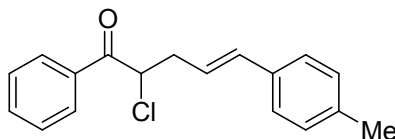
2-chloro-1-phenylpent-4-en-1-one (**3a**),³ colorless oil (52.0 mg); ¹H NMR (500 MHz, CDCl₃) δ 8.06 (d, *J* = 8.5 Hz, 2H), 7.63-7.60 (m, 1H), 7.51-7.47 (m, 2H), 5.88-5.82 (m, 1H), 5.22-5.14 (m, 2H), 5.12 (dd, *J* = 7.5 Hz, 6.0 Hz, 2H), 2.97-2.89 (m, 1H), 2.79-2.72 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): 193.0, 134.3, 133.8, 132.9, 128.9, 128.8, 119.0, 56.2, 37.7.



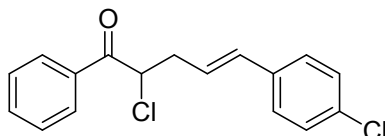
(*E*)-2-chloro-1,5-diphenylpent-4-en-1-one (**3b**),⁴ white solid (52.4 mg), m.p. 126-128 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.02 (d, *J* = 7.2 Hz, 2H), 7.70-7.48 (m, 3H), 7.35-7.20 (m, 5H), 6.54 (d, *J* = 15.9 Hz, 1H), 6.28-6.20 (m, 1H), 5.21 (dd, *J* = 7.5 Hz, 6.6 Hz, 1H), 3.13-3.03 (m, 1H), 2.96-2.85 (m, 1H); ¹³C NMR (75 MHz, CDCl₃): 193.0, 136.9, 134.1, 133.8, 129.0, 128.8, 128.5, 127.6, 126.3, 124.4, 118.4, 56.5, 37.0.



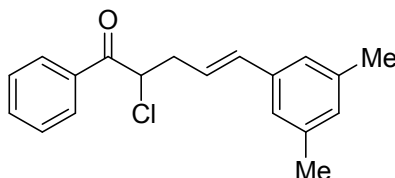
(*E*)-2-chloro-5-(2-chlorophenyl)-1-phenylpent-4-en-1-one (**3c**), white solid (55.3 mg), m.p. 137-138 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.03 (d, *J* = 7.5 Hz, 2H), 7.63-7.48 (m, 4H), 7.39-7.17 (m, 3H), 6.94 (d, *J* = 15.9 Hz, 1H), 6.32-6.18 (m, 1H), 5.23 (dd, *J* = 7.2 Hz, 6.3 Hz, 1H), 3.17-3.06 (m, 1H), 3.00-2.92 (m, 1H); ¹³C NMR (75 MHz, CDCl₃): 192.4, 138.0, 135.6, 133.9, 130.3, 129.6, 129.0, 128.8, 128.6, 127.7, 127.3, 126.9, 125.7, 56.4, 37.1; IR (film): ν 3059, 3020, 2921, 1600, 1583, 1491, 1450 cm⁻¹; HRMS (EI) Calcd for C₁₇H₁₄Cl₂O (M): 304.0422. Found: 304.0431.



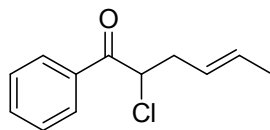
(*E*)-2-chloro-1-phenyl-5-p-tolylpent-4-en-1-one (**3d**),⁴ white solid (56.2 mg), m.p. 130-132 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.02 (d, *J* = 7.2 Hz, 2H), 7.69-7.40 (m, 3H), 7.19 (d, *J* = 6.3 Hz, 2H), 7.11 (d, *J* = 6.6 Hz, 2H), 6.48 (d, *J* = 15.9 Hz, 1H), 6.30-6.12 (m, 1H), 5.09 (dd, *J* = 7.2 Hz, 6.6 Hz, 1H), 3.11-3.03 (m, 1H), 3.98-2.84 (m, 1H), 2.03 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): 193.0, 136.8, 134.0, 133.7, 128.9, 128.7, 128.4, 127.4, 127.3, 126.1, 124.2, 57.0, 37.3, 29.7.



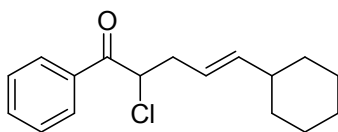
(*E*)-2-chloro-5-(4-chlorophenyl)-1-phenylpent-4-en-1-one (**3e**),⁵ white solid (58.0 mg), m.p. 134-136 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.02 (d, *J* = 7.2 Hz, 2H), 7.65-7.45 (m, 3H), 7.35-7.25 (m, 4H), 6.52 (d, *J* = 15.9 Hz, 1H), 6.25-6.15 (m, 1H), 5.32 (dd, *J* = 7.2 Hz, 6.3 Hz, 1H), 3.11-3.01 (m, 1H), 2.95-2.85 (m, 1H) ; ¹³C NMR (75 MHz, CDCl₃): 193.0, 138.4, 133.8, 132.9, 130.0, 129.7, 129.0, 128.8, 128.7, 127.5, 125.0, 118.7, 56.3, 36.9.



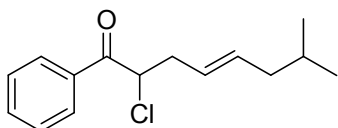
(*E*)-2-chloro-5-(3,5-dimethylphenyl)-1-phenylpent-4-en-1-one (**3f**), white solid (55.4 mg), m.p. 127-129 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.02 (d, *J* = 7.2 Hz, 2H), 7.59 (d, *J* = 7.5 Hz, 1H), 7.52-7.46 (m, 1.2 Hz, 1H), 7.31 (s, 1H), 7.17 (s, 2H), 6.57 (d, *J* = 15.6 Hz, 1H), 6.24-6.14 (m, 1H), 5.20 (dd, *J* = 7.2 Hz, 6.9 Hz, 1H), 3.14-3.04 (m, 1H), 2.94-2.84 (m, 1H), 1.85 (s, 6H) ; ¹³C NMR (75 MHz, CDCl₃): 193.2, 135.2, 134.0, 131.2, 129.0, 128.7, 126.6, 124.2, 123.4, 122.0, 120.7, 56.5, 37.1, 29.7; IR (film): ν 3055, 3021, 2923, 1600, 1582, 1491, 1459 cm⁻¹; HRMS (EI) Calcd for C₁₉H₁₉ClO (M): 298.8066. Found: 298.8057.



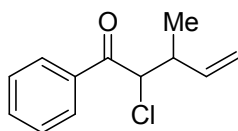
(*E*)-2-chloro-1-phenylhex-4-en-1-one (**3g**),⁴ colorless oil (39.5 mg); ¹H NMR (500 MHz, CDCl₃) δ 8.00 (d, *J* = 8.0 Hz, 2H), 7.62-7.58 (m, 1H), 7.51-7.47 (m, 2H), 5.65-5.57 (m, 1H), 5.48-5.42 (m, 1H), 5.08 (dd, *J* = 7.5 Hz, 6.5 Hz, 1H), 2.89-2.82 (m, 1H), 2.70-2.64 (m, 1H), 1.65 (d, *J* = 6.5 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): 193.2, 134.4, 133.7, 130.0, 128.9, 125.3, 56.8, 36.7, 18.0.



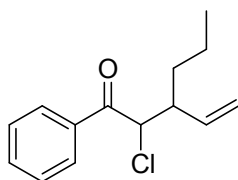
(*E*)-2-chloro-5-cyclohexyl-1-phenylpent-4-en-1-one (**3h**), colorless oil (51.0 mg); ¹H NMR (300 MHz, CDCl₃) δ 7.99 (d, *J* = 7.8 Hz, 2H), 7.63-7.57 (m, 1H), 7.50 (dd, *J* = 7.8 Hz, 6.9 Hz, 2H), 5.57-5.49 (m, 1H), 5.43-5.30 (m, 1H), 5.08 (dd, *J* = 7.5 Hz, 6.6 Hz, 1H), 2.90-2.80 (m, 1H), 2.72-2.64 (m, 1H), 2.15-2.03 (m, 1H), 1.92-1.65 (m, 6H), 1.34-1.25 (m, 4H); ¹³C NMR (75 MHz, CDCl₃): 193.4, 141.4, 134.8, 133.6, 128.9, 128.7, 121.5, 57.1, 40.6, 37.0, 32.8, 29.7, 25.9; IR (film): ν 3059, 3025, 2926, 1598, 1580, 1492, 1451 cm⁻¹; HRMS (EI) Calcd for C₁₇H₂₁ClO (M): 276.1281. Found: 276.1276.



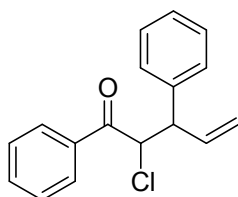
(*E*)-2-chloro-7-methyl-1-phenyloct-4-en-1-one (**3i**),⁴ colorless oil (48.5 mg); ¹H NMR (300 MHz, CDCl₃) δ 8.00 (d, *J* = 8.1 Hz, 2H), 7.70-7.46 (m, 3H), 5.50-5.32 (m, 2H), 5.11 (dd, *J* = 7.5 Hz, 6.9 Hz, 1H), 2.92-2.81 (m, 1H), 2.73-2.63 (m, 1H), 2.05-1.92 (m, 2H), 1.10-1.04 (m, 1H), 0.93 (d, *J* = 3.3 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃): 191.1, 134.3, 134.0, 128.9, 128.5, 124.8, 120.8, 62.2, 45.9, 36.8, 29.7.



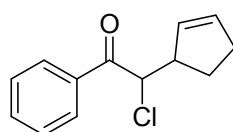
2-chloro-3-methyl-1-phenylpent-4-en-1-one (**3j**),⁵ colorless oil (41.2 mg); dr: 80:20; ¹H NMR (500 MHz, CDCl₃) δ 7.98 (d, *J* = 8.0 Hz, 2H), 7.62-7.59 (m, 1H), 7.50-7.48 (m, 2H), 5.92-5.84 (m, 0.8H), 5.79-5.72 (m, 0.2H), 5.15-4.99 (m, 3H), 3.08-2.99 (m, 1H), 1.24 (d, *J* = 6.5 Hz, 0.6H), 1.14 (d, *J* = 6.5 Hz, 2.4H); ¹³C NMR (100 MHz, CDCl₃): 193.4, 138.2, 135.0, 133.8, 128.8, 128.7, 116.7, 62.2, 40.9, 40.3, 17.7, 16.2.



2-chloro-1-phenyl-3-vinylhexan-1-one (**3k**), colorless oil (44.5 mg); dr > 99:1; ¹H NMR (500 MHz, CDCl₃) δ 7.95 (d, *J* = 8.5 Hz, 2H), 7.63-7.59 (m, 1H), 7.51-7.48 (m, 2H), 5.75-5.62 (m, 1H), 5.18-5.14 (m, 2H), 5.03 (d, *J* = 7.5 Hz, 1H), 2.90-2.79 (m, 1H), 1.47-1.28 (m, 4H), 0.95-0.86 (m, 3H); ¹³C NMR (100 MHz, CDCl₃): 193.5, 136.5, 135.2, 133.7, 128.9, 128.6, 118.3, 62.0, 46.9, 34.2, 20.3, 13.9; IR (film): ν 3056, 3020, 2925, 1587, 1588, 1490, 1454 cm⁻¹; HRMS (EI) Calcd for C₁₄H₁₇ClO (M): 236.0968. Found: 236.0975.

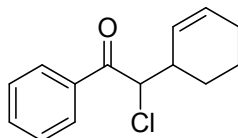


2-chloro-1,3-diphenylpent-4-en-1-one (**3l**), colorless oil (49.7 mg); dr = 60:40; ¹H NMR (500 MHz, CDCl₃) δ 7.95 (d, *J* = 8.5 Hz, 2H), 7.63-7.59 (m, 1H), 7.51-7.48 (m, 2H), 6.27-6.19 (m, 0.6H), 5.96-5.93 (m, 0.4H), 5.45-5.06 (m, 3H), 4.30-4.17 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): 193.0, 139.6, 136.8, 133.9, 128.9, 128.8, 128.6, 128.2, 127.3, 126.2, 118.4, 59.4, 58.6, 52.3, 52.2; IR (film): ν 3057, 3018, 2926, 1600, 1580, 1489, 1453 cm⁻¹; HRMS (EI) Calcd for C₁₇H₁₅ClO (M): 270.0811. Found: 270.0823.

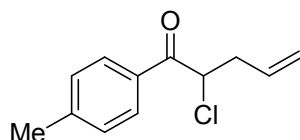


2-chloro-2-(cyclopent-2-enyl)-1-phenylethanone (**3m**),⁵ colorless oil (38.7 mg); dr =

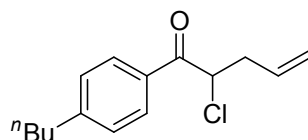
55:45; ^1H NMR (500 MHz, CDCl_3) δ 8.03-7.98 (m, 2H), 7.62-7.58 (m, 1H), 7.51-7.48 (m, 2H), 5.94-5.92 (m, 1H), 5.91-5.88 (m, 0.55H), 5.51-5.49 (m, 0.45H), 4.97 (d, $J = 8.5$ Hz, 0.55H), 4.92 (d, $J = 8.5$ Hz, 0.45H), 3.58-3.49 (m, 1H), 2.47-2.33 (m, 2H), 2.24-2.12 (m, 1H), 2.10-1.93 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): 193.7, 134.5, 133.7, 130.8, 130.2, 128.9, 128.8, 61.0, 49.0, 32.3, 27.8.



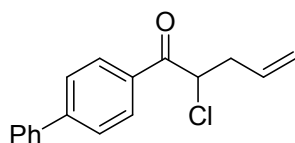
2-chloro-2-(cyclohex-2-enyl)-1-phenylethanone (**3n**),⁶ colorless oil (42.1 mg); dr = 50:50; ^1H NMR (500 MHz, CDCl_3) δ 8.00 (d, $J = 8.0$ Hz, 2H), 7.62-7.58 (m, 1H), 7.51-7.47 (m, 2H), 5.95-5.89 (m, 1H), 5.82-5.78 (m, 0.5H), 5.44-5.41 (m, 0.5H), 5.00 (d, $J = 9.0$ Hz, 0.5H), 4.94 (d, $J = 8.5$ Hz, 0.5H), 3.03-2.94 (m, 1H), 2.07-2.00 (m, 2H), 1.83-1.70 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): 193.6, 135.1, 133.7, 131.1, 130.1, 128.8, 128.3, 61.4, 60.9, 38.2, 26.8, 25.0, 21.1, 20.2.



2-chloro-1-p-tolylpent-4-en-1-one (**3o**), colorless oil (41.2 mg); ^1H NMR (300 MHz, CDCl_3) δ 7.86 (d, $J = 8.1$ Hz, 2H), 7.30 (d, $J = 8.1$ Hz, 2H), 6.07-5.94 (m, 1H), 5.22 (dd, $J = 7.2$ Hz, 6.6 Hz, 1H), 2.98-2.86 (m, 1H), 2.73-2.64 (m, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): 192.4, 140.3, 132.4, 128.6, 128.3, 126.4, 119.1, 61.9, 41.3, 29.6; IR (film): ν 3057, 3021, 2920, 1600, 1580, 1495, 1451 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{12}\text{H}_{13}\text{ClO}$ (M): 208.0655. Found: 208.0670.

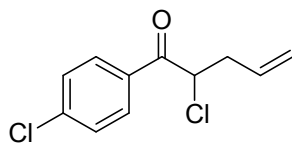


1-(4-butylphenyl)-2-chloropent-4-en-1-one (**3p**), colorless oil (52.5 mg); ^1H NMR (300 MHz, CDCl_3) δ 7.85 (d, $J = 8.1$ Hz, 2H), 7.32 (d, $J = 8.4$ Hz, 2H), 5.85-5.70 (m, 1H), 5.14-5.01 (m, 3H), 2.98-2.86 (m, 1H), 2.90-2.54 (m, 4H), 1.57-1.51 (m, 2H), 1.32-1.26 (m, 2H), 0.85 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): 192.6, 143.8, 133.9, 133.0, 129.1, 128.9, 118.7, 56.2, 37.7, 35.7, 33.1, 22.3, 13.8; IR (film): ν 3059, 3020, 2921, 1600, 1583, 1491, 1450 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{15}\text{H}_{19}\text{ClO}$ (M): 250.1124. Found: 250.1133.

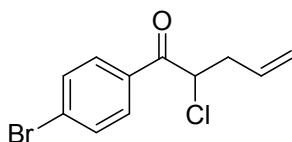


1-(4-phenylphenyl)-2-chloropent-4-en-1-one (**3q**), white solid (48.6mg), m.p. 89-91 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 8.09 (d, $J = 8.5$ Hz, 2H), 7.72 (d, $J = 8.5$ Hz, 2H), 7.64 (d, $J = 8.5$ Hz, 1H), 7.50-7.46 (m, 2H), 7.44-7.41 (m, 1H), 5.93-5.83 (m, 1H),

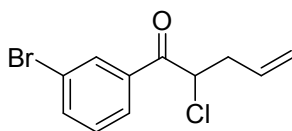
5.24-5.14 (m, 3H), 2.98-2.92 (m, 1H), 2.82-2.75 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): 192.3, 134.4, 132.3, 129.0, 127.7, 127.4, 125.6, 125.0, 124.7, 122.2, 114.7, 55.8, 32.6; IR (film): ν 3059, 3022, 2924, 1600, 1581, 1490, 1450 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{17}\text{H}_{15}\text{ClO}$ (M): 270.0811. Found: 270.0800.



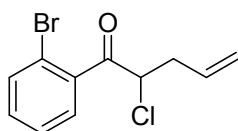
2-chloro-1-(4-chlorophenyl)pent-4-en-1-one (**3r**), white solid (39.8 mg), m.p. 76-78 $^{\circ}\text{C}$; ^1H NMR (300 MHz, CDCl_3) δ 7.92 (d, $J = 8.1$ Hz, 2H), 7.29 (d, $J = 8.4$ Hz, 2H), 5.91-5.78 (m, 1H), 5.21-5.08 (m, 3H), 2.97-2.87 (m, 1H), 2.80-2.72 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): 192.7, 138.5, 132.4, 129.0, 127.6, 125.0, 118.1, 55.8, 34.4; IR (film): ν 3050, 3015, 2926, 1600, 1581, 1490, 1459 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{11}\text{H}_{10}\text{Cl}_2\text{O}$ (M): 228.0109. Found: 228.0122.



1-(4-bromophenyl)-2-chloropent-4-en-1-one (**3s**), white solid (46.1 mg), m.p. 107-109 $^{\circ}\text{C}$; ^1H NMR (300 MHz, CDCl_3) δ 7.95 (d, $J = 8.7$ Hz, 2H), 7.47 (d, $J = 8.4$ Hz, 2H), 5.92-5.79 (m, 1H), 5.23-5.10 (m, 2H), 5.07 (dd, $J = 7.8$ Hz, 6.3 Hz, 1H), 2.96-2.86 (m, 1H), 2.80-2.71 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): 191.8, 134.1, 132.7, 130.3, 129.1, 128.8, 119.1, 56.1, 37.5; IR (film): ν 3059, 3020, 2921, 1600, 1583, 1491, 1450 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{11}\text{H}_{10}\text{BrClO}$ (M): 271.9604. Found: 271.9620.

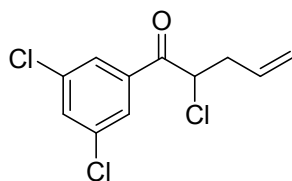


1-(3-bromophenyl)-2-chloropent-4-en-1-one (**3t**), white solid (48.1 mg), m.p. 102-104 $^{\circ}\text{C}$; ^1H NMR (300 MHz, CDCl_3) δ 7.96 (d, $J = 7.2$ Hz, 1H), 7.81 (s, 1H), 7.50-7.49 (m, 1H), 7.41-7.36 (m, 1H), 6.06-5.94 (m, 1H), 5.18-5.10 (m, 3H), 2.96-2.86 (m, 1H), 2.82-2.71 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): 192.9, 138.5, 134.3, 132.6, 131.6, 128.5, 128.0, 123.6, 118.8, 55.8, 36.9; IR (film): ν 3060, 3022, 2924, 1602, 1580, 1496, 1450 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{11}\text{H}_{10}\text{BrClO}$ (M): 271.9604. Found: 271.9615.

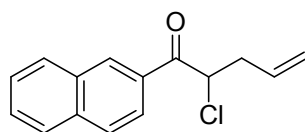


1-(2-bromophenyl)-2-chloropent-4-en-1-one (**3u**), white solid (45.6 mg), m.p. 97-99 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 8.00 (dd, $J = 8.0$ Hz, 1.0 Hz, 1H), 7.62 (d, $J = 7.5$ Hz, 1H), 7.51-7.47 (m, 2H), 5.88-5.83 (m, 1H), 5.15-5.07 (m, 3H), 2.94-2.91 (m, 1H), 2.74-2.68 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): 191.7, 134.3, 132.2, 128.7, 127.6, 127.5, 125.5, 122.6, 111.4, 55.8, 32.7; IR (film): ν 3058, 3020, 2920, 1600, 1580,

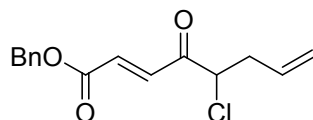
1495, 1456 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{11}\text{H}_{10}\text{BrClO}$ (M): 271.9604. Found: 271.9624.



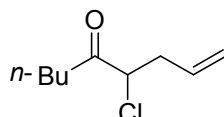
2-chloro-1-(3,5-dichlorophenyl)pent-4-en-1-one (**3v**), white solid (45.0 mg), m.p. 122-124 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 7.85 (s, 2H), 7.59 (s, 1H), 5.87-5.77 (m, 1H), 5.23-5.16 (m, 2H), 4.96 (dd, $J = 8.5$ Hz, 8.0 Hz, 1H), 2.94-2.81 (m, 1H), 2.78-2.70 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): 190.5, 135.8, 133.4, 132.3, 127.3, 119.5, 112.1, 56.1, 37.2, 23.7; IR (film): ν 3056, 3030, 2928, 1600, 1581, 1493, 1452 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{11}\text{H}_9\text{Cl}_3\text{O}$ (M): 261.9719. Found: 261.9707.



2-chloro-1-(naphthalen-2-yl)pent-4-en-1-one (**3w**), white solid (48.2 mg), m.p. 118-120 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 8.54 (s, 1H), 8.10-7.88 (m, 4H), 7.64-7.50 (m, 2H), 5.96-5.85 (m, 1H), 5.30 (dd, $J = 8.5$ Hz, 7.5 Hz, 1H), 5.26-5.16 (m, 2H), 3.03-2.98 (m, 1H), 2.86-2.78 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): 192.5, 146.5, 139.6, 129.5, 129.0, 128.4, 127.4, 127.3, 119.1, 56.2, 37.7; IR (film): ν 3059, 3022, 2920, 1600, 1580, 1488, 1460 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{15}\text{H}_{13}\text{ClO}$ (M): 244.0655. Found: 244.0639.

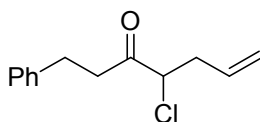


(*E*)-benzyl 5-chloro-4-oxoocta-2,7-dienoate (**3x**), white solid (47.7 mg), m.p. 93-95 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 7.45-7.34 (m, 5H), 6.89 (d, $J = 15.5$ Hz, 1H), 5.81-5.72 (m, 1H), 5.26 (s, 2H), 5.19-5.15 (m, 2H), 4.41-4.30 (dd, $J = 8.0$ Hz, 6.5 Hz, 1H), 2.81-2.75 (m, 1H), 2.68-2.63 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): 192.1, 164.8, 135.7, 135.1, 132.9, 131.8, 128.7, 128.6, 128.4, 119.6, 67.3, 61.0, 37.3; IR (film): ν 3065, 3030, 2926, 1600, 1585, 1495, 1462 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{15}\text{H}_{15}\text{ClO}_3$ (M): 278.0710. Found: 278.0701.



4-chloronon-1-en-5-one (**3y**),⁴ colorless oil (32.2 mg); ^1H NMR (500 MHz, CDCl_3) δ 5.81-5.74 (m, 1H), 5.23-5.15 (m, 2H), 4.35 (dd, $J = 8.0$ Hz, 7.5 Hz, 1H), 2.80-2.74 (m, 1H), 2.67-2.62 (m, 1H), 2.59-2.51 (m, 2H), 1.45-1.41 (m, 2H), 1.37-1.32 (m, 2H), 1.01-0.97 (t, 3H); ^{13}C NMR (100 MHz, CDCl_3): 199.7, 133.2, 117.8, 61.7, 35.0, 32.6,

26.4, 21.3, 13.9.



4-chloro-1-phenylhept-6-en-3-one (**3z**),⁵ colorless oil (42.7 mg); ¹H NMR (300 MHz, CDCl₃) δ 7.30 (d, J = 6.9 Hz, 2H), 7.22-7.16 (m, 3H), 6.07-5.94 (m, 1H), 5.31-5.24 (m, 1H), 5.17-5.12 (m, 1H), 4.14 (dd, J = 7.8 Hz, 6.5 Hz, 1H), 3.01-2.91 (m, 2H), 2.87-2.83 (m, 2H), 2.71-2.64 (m, 1H), 2.61-2.50 (m, 1H); ¹³C NMR (75 MHz, CDCl₃): 199.1, 136.5, 131.0, 128.6, 127.9, 126.5, 117.1, 67.0, 39.6, 36.8, 33.5.

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Copies of ^1H and ^{13}C NMR Spectra

