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# Generation of Organotantalum Reagents and Conjugate Addition to Enones

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## Experimental Section

**Analysis.** IR spectra were recorded as thin film on a Horiba FT-720 spectrometer. All the $^{1}H$ and $^{13}C$ spectra were recorded with a JEOL JNM-GSX-270 (270 and 67.8 MHz, respectively) in deuteriochloroform ($CDCl_3$) containing 0.03% (w/v) of tetramethylsilane. Mass spectra were recorded on a JEOL JMS-DS-303 spectrometer. GLC analyses was performed on a Shimadzu GC-8A with FID using a 2m x 3 mm column packed with and SE-52 on UniportHP (15%, 60-80 mesh). Column chromatography was performed by using Fuji Davison silica gel FL-100DX. Preparative TLC was carried out on Wakogel B-5F silica gel.

**Materials.** Allyl-, crotyl- cinnamyl and prenyl tri-*n*-butyltin were prepared by the reaction of tri-*n*-butyltin chloride ($n$-$Bu_3SnCl$) with the corresponding Grignard reagents.[1] $TaCl_5$ was used as a commercially available one (Aldrich). THF was freshly distilled from sodium benzophenone ketyl. All reactions were carried out under dry nitrogen.

1) Y. Naruta, Y. Nishigaichi, K. Maruyama, *Chem. Lett*. **1986**, 1857.

**1. Sn-Ta exchange**

**GLC analysis of Generated *n*$Bu_3$SnCl**: To a dry nitrogen-filled 10 mL round bottomed flask containing $TaCl_5$ (0.358g, 1 mmol) in MeCN (1 mL) was added allyltri-*n*-butyltin (0.662 g, 2 mmol) at -40 °C. The resulting solusion was used for GLC analyses with SE-52. The peak of *n*$Bu_3$SnCl was detected at 2.5 min. Column tempetature 180 °C, flow pressure: 1.5 kg/$cm^3$, injector temp: 250 °C, detector temp: 250 °C.

**NMR Measurement of Generated *n*$Bu_3$SnCl**; Allyltri-*n*-butyltin (0.331 g, 1 mmol) and $TaCl_5$ (0.358 g, 1 mmol) were mixed at -40 °C under dry $N_2$ in 0.75 mL of $CH_3CN$. The resulting solution was transferred to a nitrogen filled 5 mm $\phi$ NMR tube, which was fixed into a 10 mm $\phi$ NMR tube containing $CDCl_3$ and $Me_4Sn$ as a standard, and the 10 mm $\phi$ tube was set in the NMR instrument. Measurement was performed at –40 °C. *n*$Bu_3$SnCl was detected at 123 ppm, and starting allyltri-*n*-butyltin was not detected at all.

**2. Conjugate addition**

**Representative procedure of conjugate addition**.

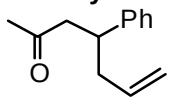
To a dry nitrogen-filled 10 mL round bottomed flask containing $TaCl_5$ (0.358g, 1 mmol) in MeCN (1 mL) was added allyltri-*n*-butyltin (0.662 g, 2 mmol) at –40 °C. $TaCl_5$ was partly insoluble at -40 °C, although which dissolved completely at r.t.. After stirring at -40 °C for 30 min, to the resulting solution was added benzalacetone (**1a**) (0.146 g, 1 mmol). As the reaction proceeded, the mixture gradually turned out to be homogeneous. During the reaction, the solution indicated a slight pale yellow color, and drastic change of color could not be detected. After stirring the mixture at -40 °C for 2 h, MeOH (2 mL) was added and volatiles were removed under reduced pressure. The residue was chromatographed on silica-gel column (FL100-DX (Fuji silysia)) eluting with hexane/EtOAc (3/1) to give conjugate adduct **2a** (0.171 g, 91%).

Conjugate addition using other substrates were performed in a similar manner (Tables 1 and 3, Scheme 2). Spectral data of products obtained are listed from the following pages.

**Representative procedure of conjugate allylation by using a catalytic amount of $TaCl_5$** (Scheme 4).

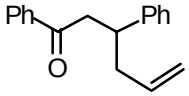
To a dry nitrogen-filled 10 mL round bottomed flask containing $TaCl_5$ (0.072g, 0.2 mmol), allyltri-*n*-butyltin (0.331 g, 1 mmol) in MeCN (1 mL) were added chalcone (**1b**) (0.208 g, 1 mmol) and chlorotrimethylsilane (0.108g, 1 mmol) at -40 °C. After stirring the mixture at -40 °C for 2 h, MeOH (2 mL) was added and volatiles were removed under reduced pressure. $^1$H NMR of this residue indicated the formation of conjugate adduct as a silyl enolate form, which was chromatographed on silica-gel column (FL100-DX (Fuji silysia)) eluting with hexane/EtOAc (3/1) to give conjugate adduct **2b** selectively (0.247 g, 99%).

**4-Phenyl-6-hepten-2-one (2a)**



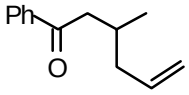

The product was obtained by the reaction of allyltri-*n*-butyltin with **1a**. IR (neat) 1712 (C=O), 1643, 1604, 1496, 1419, 950, 756, 701, 539 $cm^{-1}$; $^{1}H$ NMR (270 MHz, $CDCl_3$, 25 °C, TMS) δ2.00 (s, 3H, $CH_3$), 2.32-2.37 (m, 2H, $CH_2$), 2.69 (dd, 1H, $^{3}J$ (H, H)= 7.3 Hz and $^{2}J$ (H, H)= 16.1 Hz, one of $CH_2$), 2.76 (dd, 1H, $^{3}J$ (H, H)= 6.4 Hz and $^{2}J$ (H, H)= 16.1 Hz, one of $CH_2$), 3.25 (ddt, 1H, $^{3}J$ (H, H)= 6.4, 7.3 and 7.3 Hz, CHPh), 4.95-4.97 (m, 2H, C=$CH_2$), 5.64 (ddt, 1H, $^{3}J$ (H, H)= 9.8, 17.1 and 7.3 Hz, CH=C), 7.10-7.30 (m, 5H, arom); $^{13}C$ NMR (67.8 MHz, $CDCl_3$, 25 °C) δ30.52, 40.61, 40.76, 49.38, 116.63, 126.32, 127.35, 128.35, 136.04, 143.95, 207.47; HRMS calcd for $C_{13}H_{16}O$: 188.1200, found 188.1196.

**1,3-Diphenyl-5-hexen-1-one (2b)**




The product was obtained by the reaction of allyltri-*n*-butyltin with **1b**. IR (neat) 1681 (C=O), 1643, 1596, 1496, 1450, 995, 756, 694 $cm^{-1}$; $^{1}H$ NMR (270 MHz, $CDCl_3$, 25 °C, TMS) δ2.43-2.48 (m, 2H, $CH_2$), 3.27-3.30 (m, 2H, $CH_2$), 3.42-3.52 (m, 1H, CHPh), 4.93-5.03 (m, 2H, C=$CH_2$), 5.61-5.77 (m, 1H, CH=C), 7.13-7.55 (m, 8H, arom), 7.89 (d, 2H, $^{3}J$ (H, H)= 6.8 Hz, arom); $^{13}C$ NMR (67.8 MHz, $CDCl_3$, 25 °C) δ40.63, 40.70, 44.53, 116.73, 126.80, 127.50, 127.96, 128.37, 128.46, 132.88, 136.21, 137.16, 144.29, 198.88; HRMS calcd for $C_{18}H_{18}ON$ 250.1400, found 250.1358.

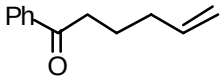
**3-Methyl-1-phenyl-5-hexen-1-one (2c)**




The product was obtained by the reaction of allyltri-*n*-butyltin with **1c**. IR (neat) 1689 (C=O), 1643, 1596, 1450 $cm^{-1}$; $^{1}H$ NMR (270 MHz, $CDCl_3$, 25 °C, TMS) δ1.00 (d, 3H, $^{3}J$ (H, H)= 6.4

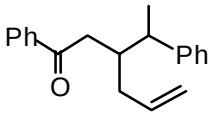
Hz, $CH_3$), 2.00-2.20 (m, 2H, $CH_2$), 2.20-2.35 (m, 1H, CH), 2.73 (dd, 1H, $^3J$ (H, H)= 8.3 Hz and $^2J$ (H, H)= 16.2 Hz, one of $CH_2$), 3.00 (dd, 1H, $^3J$ (H, H)= 5.9 Hz and $^2J$ (H, H)= 16.2 Hz, one of $CH_2$), 5.01-5.12 (m, 2H, C=$CH_2$), 5.73-5.89 (m, 1H, CH=C), 7.43-7.63 (m, 3H, arom), 7.92-8.03 (m, 2H, arom); $^{13}$C NMR (67.8 MHz, $CDCl_3$, 25 °C) δ19.88, 30.90, 41.29, 45.00, 116.56, 128.05, 128.53, 132.87, 136.67, 137.40, 200.19; HRMS calcd for $C_{13}H_{16}O$ 188.1200, found 188.1206.

**1-Phenyl-5-hexen-1-one (2d)**




The product was obtained by the reaction of allyltri-*n*-butyltin with **1d**. IR (neat) 1674 (C=O), 1596, 1450, 995, 571 $cm^{-1}$; $^1$H NMR (270 MHz, $CDCl_3$, 25 °C, TMS) δ1.85 (tt, 2H, $^3J$ (H, H)= 7.3 and 7.3 Hz, $CH_2$), 2.16 (dt, 2H, $^3J$ (H, H)= 7.3 and 7.3 Hz, C$H_2$CH=C), 2.98 (t, 2H, $^3J$ (H, H)= 7.3 Hz, $CH_2$C=O), 4.97-5.09 (m, 2H, C=$CH_2$), 5.75-5.90 (m, 1H, CH=C), 7.42-7.60 (m, 3H, arom), 7.94-7.99 (m, 2H, arom); $^{13}$C NMR (67.8 MHz, $CDCl_3$, 25 °C) δ23.25, 33.16, 37.67, 115.26, 127.99, 128.52, 132.89, 137.00, 138.03, 200.22; HRMS calcd for $C_{12}H_{14}O$: 174.1045, found 174.1041.

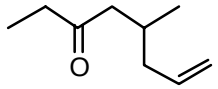
**1-Phenyl-3-(1-phenylethyl)-5-hexen-1-one (2e)**




The product was obtained by the reaction of allyltri-*n*-butyltin with **1e** (ds= 89:11 mixture). IR (neat) 1681 (C=O), 1596, 1450, 910, 701 $cm^{-1}$; $^1$H NMR (270 MHz, $CDCl_3$, 25 °C, TMS) δ1.25 (d, 3x0.89H, $^3J$ (H, H)= 6.9 Hz, $CH_3$ (major isomer)), 1.30 (d, 3x0.11H, $^3J$ (H, H)= 6.9 Hz, $CH_3$ (minor isomer)), 1.79-1.88 (m, 1H, CH), 2.03-2.13 (m, 1H, CH), 2.36-2.48 (m, 1H, one of $CH_2$), 2.73-2.90 (m, 3H, one of $CH_2$ and $CH_2$), 4.83-4.95 (m, 2H, C=$CH_2$), 5.57-5.73 (m, 1H, CH=C), 7.04-7.53 (m, 8H, arom), 7.80 (d, 2H, $^3J$ (H, H)= 6.8 Hz, arom); $^{13}$C NMR (67.8 MHz, $CDCl_3$, 25 °C) δ17.0, 18.18 (minor isomer), 34.92 (minor isomer), 36.17, 39.14 (minor isomer), 39.32,

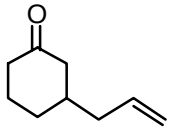
39.93, 40.07 (minor isomer), 41.47, 41.83 (minor isomer), 116.77, 126.07, 127.88, 127.94, 128.19, 128.32, 128.40, 132.74, 136.72, 145.25, 200.13, 211.75 (minor isomer); Anal Calcd calcd for $C_{20}H_{22}O$: C, 86.29; H 7.97. Found C, 86.60; H, 8.13.

**5-Methyl-7-octen-3-one (2f)**



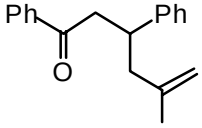
The product was obtained by the reaction of allyltri-*n*-butyltin with **1f**. IR (neat) 2977, 1712 (C=O), 1457, 1373, 1110, 917 $cm^{-1}$; $^1H$ NMR (270 MHz, $CDCl_3$, 25 °C, TMS) δ0.90 (d, 3H, $^3J$ (H, H)= 6.4 Hz, $CH_3$), 1.04 (d, 3H, $^3J$ (H, H)= 7.3 Hz, $CH_3$), 1.93-2.20 (m, 5H, CHMe and $2CH_2$), 2.40 (q, 2H, $^3J$ (H, H)= 7.3 Hz, $CH_2$), 4.94-5.06 (m, 2H, C=$CH_2$), 5.66-5.84 (m, 1H, CH=C); $^{13}C$ NMR (67.8 MHz, $CDCl_3$, 25 °C) 7.72, 19.73, 28.90, 36.49, 41.14, 48.89, 116.33, 136.65, 211.41; HRMS calcd for $C_9H_{16}O$ 140.1201, found 140.1211.

**3-Allylcyclohexanone (2h)**



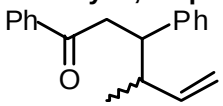
The product was obtained by the reaction of allyltri-*n*-butyltin with **1g**. IR (neat) 1712, 1643, 1442, 995, 617 $cm^{-1}$; $^1H$ NMR (270 MHz, $CDCl_3$, 25 °C, TMS) δ1.23-2.45 (m, 11H, $CH_2$ and CH), 4.95-5.08 (m, 2H, C=$CH_2$), 5.65-5.75 (m, 1H, CHC=C); $^{13}C$ NMR (67.8 MHz, $CDCl_3$, 25 °C) δ25.11, 30.84, 38.73, 40.77, 41.35, 47.71, 116.76, 135.64, 211.69; HRMS calcd for $C_9H_{14}ON$ 138.1000, found 138.1042.

**5-Methyl-1,3-diphenyl-5-hexen-1-one (3a)**



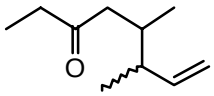
The product was obtained by the reaction of metharyltri-*n*-butyltin with **1b**. IR (neat) 1682 (C=O), 1598, 1496 $cm^{-1}$; $^{1}H$ NMR (270 MHz, $CDCl_3$, 25 °C, TMS) δ1.68 (s, 3H, $CH_3$), 2.34 (dd, 1H, $^{3}J$ (H, H)= 7.3 Hz and $^{2}J$ (H, H)= 13.7 Hz, one of $CH_2$), 2.42 (dd, 1H, $^{3}J$ (H, H)= 7.3 Hz and $^{2}J$ (H, H)= 13.7 Hz, one of $CH_2$), 3.21-3.25 (m, 2H, $CH_2$), 3.61 (tt, 1H, $^{3}J$ (H, H)= 7.3 and 7.3 Hz, CH), 4.65 (d, 1H, $^{2}J$ (H, H)= 1.0 Hz, one of C=$CH_2$), 4.69 (d, 1H, $^{2}J$ (H, H)= 1.0 Hz, one of C=$CH_2$), 7.08-7.45 (m, 8H, arom), 7.81-7.86 (m, 2H, arom); $^{13}C$ NMR (67.8 MHz, $CDCl_3$, 25 °C) δ21.99, 38.68, 44.58, 44.71, 112.65, 126.05, 127.24, 127.68, 128.12, 128.21, 132.59, 136.96, 143.10, 144.44, 198.49; HRMS calcd for $C_{19}H_{20}O$ 264.1514, found 264.1518.

**4-Methyl-1,3-diphenyl-5-hexen-1-one (3b)**




The product was obtained by the reaction of crotyltri-*n*-butyltin with **1b** (ds= 56:44 mixture). IR (neat) 1681 (C=O), 1596 $cm^{-1}$; $^{1}H$ NMR (270 MHz, $CDCl_3$, 25 °C, TMS) (major isomer): δ0.84 (d, 3H, $^{3}J$ (H, H)= 6.8 Hz, $CH_3$), 2.44 (qdd, 1H, $^{3}J$ (H, H)= 3.8, 6.8 and 9.3 Hz, CH), 3.17-3.46 (m, 3H, $CH_2$ and CH), 4.90-5.12 (m, 2H, C=$CH_2$), 5.57-5.80 (m, 1H, CHC=C), 7.10-7.57 (m, 8H, arom), 7.81-7.85 (m, 2H, arom). (minor isomer): δ1.00 (d, 3H, $^{3}J$ (H, H)= 6.8 Hz, $CH_3$), 2.53 (qdd, 1H, $^{3}J$ (H, H)= 3.8, 4.9 and 6.8 Hz, CH), 3.17-3.46 (m, 3H, $CH_2$ and CH), 4.90-5.12 (m, 2H, C=$CH_2$), 5.57-5.80 (m, 1H, CHC=C), 7.10-7.57 (m, 8H, arom), 7.89-7.93 (m, 2H, arom); $^{13}C$ NMR (67.8 MHz, $CDCl_3$, 25°C) (major isomer) δ19.69, 41.64, 43.78, 46.24, 114.93, 126.26-143.45 (arom), 199.22. (minor isomer): δ17.94, 42.42, 44.55, 45.57, 114.93, 126.26-143.45 (arom), 199.09; HRMS calcd for $C_{19}H_{20}O$ 264.1514, found 264.1502.

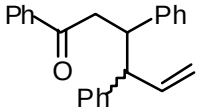
**5-Methyl-6-phenyl-7-octen-3-one (3c)**




The product was obtained by the reaction of crotyltri-*n*-butyltin with **1f**. IR (neat) 2958, 1708 (C=O), 1461, 698 $cm^{-1}$; $^{1}H$ NMR (270 MHz, $CDCl_3$, 25 °C, TMS) δ0.84 (d, 3H, $^{3}J$ (H, H)= 6.8

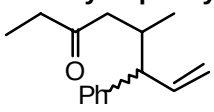
Hz, $CH_3$, (major isomer)), 0.86 (d, 3H, $^3J$ (H, H)= 6.4 Hz, $CH_3$ (minor isomer)), 0.97 (d, 3H, $^3J$ (H, H)= 6.4 Hz, $CH_3$ (minor isomer)), 0.98 (d, 3H, $^3J$ (H, H)= 6.8 Hz, $CH_3$ (major isomer)), 1.04 (t, 3H, $^3J$ (H, H)= 7.3 Hz, $CH_3$), 2.04-2.22 (m, 4H, 2CH and $CH_2$), 2.36-2.46 (m, 2H, $CH_2$), 4.99-4.93 (m, 2H, C=$CH_2$), 5.64-5.77 (m, 1H, CHC=C); $^{13}$C NMR (67.8 MHz, $CDCl_3$, 25 °C) (major isomer) δ7.75, 16.11, 16.80, 33.43, 36.46, 41.99, 46.93, 114.34, 141.48, 211.55. (minor isomer) δ7.75, 16.42, 16.97, 33.58, 36.51, 42.80, 47.14, 113.93, 142.69, 211.60; HRMS calcd for $C_{10}H_{18}O$ 154.1358, found 154.1366.

**1,3,4-Triphenyl-5-hexen-1-one (3d)**



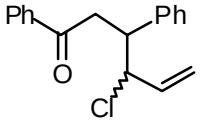

The product was obtained by the reaction of cinnamyltri-*n*-butyltin with **1b** (ds= 82:18 mixture). IR (neat) 1681, 1596, 1488, 1450 $cm^{-1}$; $^1$H NMR (270 MHz, $CDCl_3$, 25 °C, TMS) δ3.10 (dd, 1x0.18H, $^3J$ (H, H)= 4.3 Hz and $^2J$ (H, H)= 16.5 Hz, one of $CH_2$ (minor isomer)), 3.35 (dd, 1x0.82H, $^3J$ (H, H)= 8.4 Hz and $^2J$ (H, H)= 16.8 Hz, one of $CH_2$ (major isomer)), 3.48-3.59 (m, 2H, one of $CH_2$ and CHPh), 3.73-3.88 (m, 1H, CHPh), 4.75-4.90 (m, 2x0.18H, C=$CH_2$ (minor isomer)), 5.03-5.21 (m, 2x0.82H, C=$CH_2$ (major isomer)), 5.77-5.91 (m, 1x0.18H, CHC=C (minor isomer)), 6.02-6.16 (m, 1x0.82H, CHC=C (major isomer)), 7.00-7.53 (m, 13H, arom), 7.70 (d, 2x0.18H, $^3J$ (H, H)= 8.4 Hz, arom (minor isomer)), 7.85 (d, 2x0.82H, $^3J$ (H, H)= 8.9 Hz, arom (major isomer)); $^{13}$C NMR (67.8 MHz, $CDCl_3$, 25 °C) δ43.44 (minor isomer ), 43.45, 45.69, 46.39 (minor isomer), 55.62 (minor isomer), 57.34, 116.19, 126.08−142.58 (arom), 198.83 (minor isomer), 198.93 (major isomer); HRMS calcd for $C_{24}H_{22}O$ 326.1800, found 326.1664.

**5-Methyl-6-phenyl-7-octen-3-one (3e)**



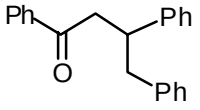
The product was obtained by the reaction of cinnamyltri-*n*-butyltin with **1f** (ds= 69:31 mixture).. IR (neat) 3023, 1712 (C=O), 1457, 1373, 1110, 917, 701 $cm^{-1}$; $^{1}H$ NMR (270 MHz, $CDCl_3$, 25 °C, TMS) δ0.74 (d, 1x0.31H, $^{3}J$ (H, H)= 6.8 Hz, $CH_3$ (minor isomer)), 0.93 (d, 1x0.69H, $^{3}J$ (H, H)= 6.8 Hz, $CH_3$ (major isomer)), 0.96 (d, 3x0.69H, $^{3}J$ (H, H)= 7.3 Hz, $CH_3$ (major isomer)), 1.04 (d, 3x0.69H, $^{3}J$ (H, H)= 7.3 Hz, $CH_3$ (minor isomer)), 2.03-2.69 (m, 5H, CH and $2CH_2$), 2.93-3.09 (m, 1H, PhCH), 5.00-5.09 (m, 2H, $C=CH_2$), 5.84-6.06 (m, 1H, CHC=C), 7.12-7.35 (m, 5H, arom); $^{13}C$ NMR (67.8 MHz, $CDCl_3$, 25°C) (major isomer) δ7.65, 17.79, 33.51, 36.48, 47.53, 56.19, 115.86, 126.28, 127.84, 128.51, 139.86, 143.41, 211.24. (minor isomer): δ7.74, 18.36, 33.35, 36.63, 47.53, 57.08, 115.54, 126.27, 127.84, 128.51, 140.81, 143.10, 211.31. ;HRMS calcd for $C_{15}H_{20}O$ 216.1514, found 216.1508.

**4-Chloro-1,3-diphenyl-5-hexen-1-one (3f)**




The product was obtained by the reaction of γ-chloroallyltri-*n*-butyltin with **1b**. IR (neat) 1666 (C=O), 1604, 1488, 1496 $cm^{-1}$; $^{1}H$ NMR (270 MHz, $CDCl_3$, 25 °C, TMS) (major isomer) δ3.53 (dd, 1H, $^{3}J$ (H, H)= 8.8 Hz and $^{2}J$ (H, H)= 17.6 Hz, one of $CH_2$), 3.67 (dd, 1H, $^{3}J$ (H, H)= 4.9 Hz and $^{2}J$ (H, H)= 17.6 Hz, one of $CH_2$), 3.82 (ddd, 1H, *J*= 4.9, 6.8 and 8.8 Hz, CHPh), 4.64 (dd, 1H, $^{3}J$ (H, H)= 6.8 and 7.8 Hz, CHCl), 5.06-5.21 (m, 2H, $C=CH_2$), 5.74-5.87 (m, 1H, CHC=C), 7.26-8.00 (m, 8H, arom), 8.00-8.05 (m, 2H, arom). $^{13}C$ NMR (67.8 MHz, $CDCl_3$, 25 °C) δ41.31, 47.43, 66.85, 122.11, 128.45-138.21 (arom), 144.86, 190.58.

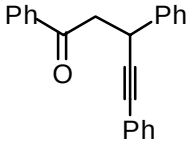
**1,3,4-Triphenylbutan-1-one (3g)**




The product was obtained by the reaction of benzyltri-*n*-butyltin with **1b**. IR (neat) 1673 (C=O), 1597, 1450 $cm^{-1}$; $^{1}H$ NMR (270 MHz, $CDCl_3$, 25 °C, TMS) δ2.93 (dd, 1H, $^{3}J$ (H, H)= 7.3 Hz

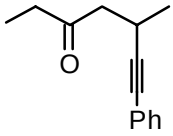
and $^{2}J$ (H, H)= 13.2 Hz, one of $CH_2$), 3.00 (dd, 1H, $^{3}J$ (H, H)= 7.3 Hz and $^{2}J$ (H, H)= 13.2 Hz, one of $CH_2$), 3.24 (dd, 1H, $^{3}J$ (H, H)= 7.3 Hz and $^{2}J$ (H, H)= 17.1 Hz, one of $CH_2$), 3.33 (dd, 1H, $^{3}J$ (H, H)= 7.3 Hz and $^{2}J$ (H, H)= 17.1 Hz, one of $CH_2$), 3.61-3.72 (m, 1H, CHPh), 7.00-7.50 (m, 13H, arom), 7.80-7.90 (m, 2H, arom); $^{13}$C NMR (67.8 MHz, $CDCl_3$, 25 °C) δ42.88, 43.14, 44.01, 125.99, 126.38, 127.55, 127.88, 128.08, 128.25, 128.40, 128.88, 132.92, 137.01, 139.71, 144.00, 198.73; HRMS calcd for $C_{22}H_{20}O$ 300.1514, found 301.1595 (CI, $(M^{+})$+1).

**1,3,5-Triphenyl-4-pentyn-1-one (3h)**




The product was obtained by the reaction of 2-phenylethynyltri-*n*-butyltin with **1b**. IR (neat) 2222, 1681 (C=O), 1596, 1488, 959, 755, 694 $cm^{-1}$; $^{1}$H NMR (270 MHz, $CDCl_3$, 25 °C, TMS) δ3.40 (dd, 1H, $^{3}J$ (H, H)= 6.4 Hz and $^{2}J$ (H, H)= 16.6 Hz, one of $CH_2$), 3.66 (dd, 1H, $^{3}J$ (H, H)= 7.8 Hz and $^{2}J$ (H, H)= 16.6 Hz, one of $CH_2$), 4.64 (dd, 1H, $^{3}J$ (H, H)= 6.4 and 7.8 Hz, CHPh), 7.23-7.58 (m, 13H, arom), 7.96 (d, 2H, $^{3}J$ (H, H)= 6.8 Hz, arom); $^{13}$C NMR (67.8 MHz, $CDCl_3$, 25 °C) δ33.73, 47.27, 83.30, 90.72, 123.37, 127.05, 127.57, 127.83, 128.09, 128.19, 128.58, 128.67, 131.62, 133.17, 136.86, 141.23, 197.06; HRMS calcd for $C_{23}H_{18}O$ 310.1400, found 310.1358.

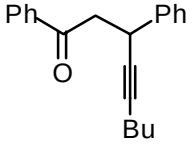
**5-Methyl-7-phenyl-6-heptyn-3-one (3i)**




The product was obtained by the reaction of 2-phenylethynyltri-*n*-butyltin with **1f**. IR (neat) 2977, 2229, 1712 (C=O). 1357, 755, 694 $cm^{-1}$; $^{1}$H NMR (270 MHz, $CDCl_3$, 25 °C, TMS) δ1.08 (t, 3H, *J*= 7.3 Hz, $CH_3$), 1.27 (d, 3H, $^{3}J$ (H, H)= 6.8 Hz, $CH_3$), 2.45 (q, 2H, $^{3}J$ (H, H)= 7.3 Hz, $CH_2$), 2.55 (dd, 1H, $^{3}J$ (H, H)= 7.3 Hz and $^{2}J$ (H, H)= 16.1 Hz, one of $CH_2$), 2.74 (dd, 1H, $^{3}J$ (H, H)= 6.8 Hz and $^{2}J$ (H, H)= 16.1 Hz, one of $CH_2$), 3.16-3.24 (m, 1H, CH), 7.23-7.39 (m, 5H,

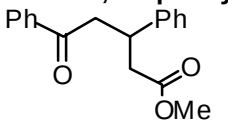
arom); $^{13}$C NMR (67.8 MHz, $CDCl_3$, 25 °C) δ7.63, 20.88, 22.28, 36.57, 49.02, 80.79, 93.14, 123.51, 127.65, 128.13, 131.50, 209.29; HRMS calcd for $C_{14}H_{16}O$ 200.1201, found 200.1212.

**1,3-Diphenyl-4-nonyn-1-one (3j)**




The product was obtained by the reaction of 2-*n*-butylethynyltri-*n*-butyltin with **1b**. IR (neat) 2237, 1689, 1596, 1496, 748, 694 $cm^{-1}$; $^1$H NMR (270 MHz, $CDCl_3$, 25 °C, TMS) δ0.85 (t, 3H, $^3J$ (H, H)= 6.8 Hz, $CH_3$), 1.27-1.48 (m, 4H, $CH_2$), 2.15 (t, 1H, $^3J$ (H, H)= 6.8 Hz, $CH_2$), 3.26 (dd, 1H, $^3J$ (H, H)= 6.4 Hz and $^2J$ (H, H)= 16.6 Hz, one of $CH_2$), 3.53 (dd, 1H, $^3J$ (H, H)= 8.3 Hz and $^2J$ (H, H)= 16.6 Hz, one of $CH_2$), 4.39 (dd, 1H, $^3J$ (H, H)= 6.4 and 8.3 Hz, CHPh), 7.20-7.57 (m, 8H, arom), 7.93 (d, 2H, $^3J$ (H, H)= 8.3 Hz, arom); $^{13}$C NMR (67.8 MHz, $CDCl_3$, 25 °C) δ13.56, 18.45, 21.87, 30.93, 33.35, 47.63, 80.88, 83.54, 126.83, 127.45, 128.19, 128.52 (d), 133.04, 137.02, 141.97, 197.49; HRMS calcd for $C_{21}H_{22}O$ 290.1700, found 290.1675.

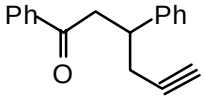
**5-Oxo-3,5-diphenylpentanoic acid methyl ester (3k)**




The product was obtained by the reaction of carbomethoxymethyl-*n*-butyltin with **1b**. IR (neat) 2946, 1727, 1678, 1438, 1361, 1265, 1226, 995, 701 $cm^{-1}$; $^1$H NMR (270 MHz, $CDCl_3$, 25 °C, TMS) δ2.68 (dd, 1H, $^3J$ (H, H)= 6.8 Hz and $^2J$ (H, H)= 15.1 Hz, one of $CH_2$), 2.82 (dd, 1H, $^3J$ (H, H)= 6.8 Hz and $^2J$ (H, H)= 15.1 Hz, one of $CH_2$), 3.32 (dd, 1H, $^3J$ (H, H)= 6.8 Hz and $^2J$ (H, H)= 17.1 Hz, one of $CH_2$), 3.40 (dd, 1H, $^3J$ (H, H)= 6.8 Hz and $^2J$ (H, H)= 17.1 Hz, one of $CH_2$), 3.57 (s, 3H, $OCH_3$), 3.85-3.92 (m, 1H, CHPh), 7.18-7.56 (m, 8H, arom), 7.90-7.92 (m, 2H, arom); $^{13}$C NMR (67.8 MHz, $CDCl_3$, 25 °C) δ37.40, 40.47, 44.45, 51.48, 126.74, 127.24,

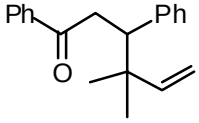
127.97, 128.51, 128.54, 133.03, 136.79, 143.25, 172.21, 198.03; HRMS calcd for $C_{18}H_{18}O_3$ 248.1256, found 248.1248.

**1,3-Diphenyl-5-hexyn-1-one (3l)**



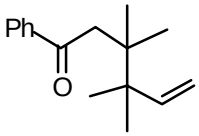

The product was obtained by the reaction of allenyltri-*n*-butyltin with **1b**. IR (neat) 1943, 1689, 1596, 1488 $cm^{-1}$; $^1H$ NMR (270 MHz, $CDCl_3$, 25 °C, TMS) δ2.00 (t, 1H, $^3J$ (H, H)= 2.4 Hz, CH), 2.50-2.70 (m, 2H, $CH_2$), 3.31-3.42 (m, 1H, CHPh), 3.55-3.69 (m, 2H, $CH_2$), 7.15-7.80 (m, 8H, arom), 7.90-8.00 (m, 2H, arom); $^{13}C$ NMR (67.8 MHz, $CDCl_3$, 25 °C) δ25.57, 39.29, 47.33, 70.55, 82.16, 126.80, 127.38, 128.48 (d), 128.55, 133.04, 137.02, 143.36, 198.33; HRMS calcd for $C_{18}H_{16}O$ 248.1201, found 248.1193.

**4,4-Dimethyl-1,3-diphenyl-5-hexen-1-one (3m)**



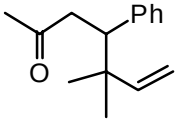

The product was obtained by the reaction of prenyltri-*n*-butyltin with **1b**. IR (neat) 1674, 1597, 1496 $cm^{-1}$; $^1H$ NMR (270 MHz, $CDCl_3$, 25 °C, TMS) δ0.98 (s, 3H, $CH_3$), 1.00 (s, 3H, $CH_3$), 3.26-3.53 (m, 3H, $CH_2$ and CH), 4.97-5.08 (m, 2H, C=$CH_2$), 5.91 (dd, 1H, $^3J$ (H, H)= 6.5 and 10.7 Hz, CHC=C), 7.13-7.54 (m, 8H, arom), 7.82-7.88 (m, 2H, arom); $^{13}C$ NMR (67.8 MHz, $CDCl_3$, 25 °C) δ22.95, 27.13, 40.07, 40.11, 49.88, 112.32, 126.29, 127.61, 127.90, 128.41, 129.55, 132.72, 137.38, 141.38, 146.82, 199.21; Anal Calcd calcd for $C_{20}H_{22}O$: C, 86.29; H 7.97. Found C, 86.17; H, 7.98.

**3,3,4,4-Tetramethyl-1-phenyl-5-hexen-1-one (3n)**



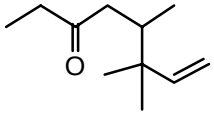
The product was obtained by the reaction of prenyltri-*n*-butyltin with 3-methyl-1-phenyl-2-buten-1-one. IR (neat) 1674 (C=O), 1581, 1473, 918, 602 $cm^{-1}$; $^{1}H$ NMR (270 MHz, $CDCl_3$, 25 °C, TMS) δ0.99 (s, 6H, $CH_3$), 1.06 (s, 6H, $CH_3$), 2.91 (s, 2H, $CH_2$), 5.00-5.12 (m, 2H, C=$CH_2$), 6.03 (dd, 1H, $^{3}J$ (H, H)= 10.7 and 17.6 Hz, CHC=C), 7.41-7.53 (m, 3H, arom), 7.88-7.93 (m, 2H, arom); $^{13}C$ NMR (67.8 MHz, $CDCl_3$, 25 °C) δ21.97, 22.27, 38.81, 42.69, 43.54, 112.61, 128.27-139.59 (arom), 145.41, 201.85; Anal Calcd calcd for $C_{16}H_{22}O$: C, 83.43; H 9.63. Found C, 83.22; H, 9.75.

**5,5-Dimethyl-4-phenyl-6-hepten-2-one (3o)**




The product was obtained by the reaction of prenyltri-*n*-butyltin with **1a**. IR (neat) 1720 (C=O), 1604, 1496, 918, 548 $cm^{-1}$; $^{1}H$ NMR (270 MHz, $CDCl_3$, 25 °C, TMS) δ0.92 (s, 3H, $CH_3$), 0.93 (s, 3H, $CH_3$), 1.96 (s, 3H, $CH_3$), 2.79 (dd, 1H, $^{3}J$ (H, H)= 4.4 Hz and $^{2}J$ (H, H)= 16.6 Hz, one of $CH_2$), 2.85 (dd, 1H, $^{3}J$ (H, H)= 10.3 Hz and $^{2}J$ (H, H)= 16.6 Hz, one of $CH_2$), 3.10 (dd, 1H, $^{3}J$ (H, H)= 4.4 and 10.3 Hz, CHPh), 4.92-5.04 (m, 2H, C=$CH_2$), 5.83 (dd, 1H, $^{3}J$ (H, H)= 10.7 and 17.6 Hz, CHC=C), 7.14-7.29 (m, 5H, arom); $^{13}C$ NMR (67.8 MHz, $CDCl_3$, 25 °C) δ22.63, 26.89, 30.50, 39.78, 45.17, 50.01, 112.19, 126.40, 127.64, 129.44, 140.96, 146.55, 208.01; HRMS calcd for $C_{15}H_{20}O$ 216.1514, found 217.1582.

**5-Ethyl-6,6-dimethyl-7-octen-3-one (3p)**




The product was obtained by the reaction of prenyltri-*n*-butyltin with **1f**. IR (neat) 2963, 1712 (C=O), 1457, 1373, 1002, 910 $cm^{-1}$; $^{1}H$ NMR (270 MHz, $CDCl_3$, 25 °C, TMS) δ 3H $^{3}J$ (H, H)= 6.8 Hz, $CH_3$) 0.95 (s, 3H, $CH_3$), 0.97 (s, 3H, $CH_3$), 1.04 (t, 3H, $^{3}J$ (H, H)= 7.3 Hz, $CH_3$), 1.90-2.01 (m, 1H, CHMe), 2.32-2.53 (m, 4H, 2$CH_2$), 4.92-5.01 (m, 2H, C=$CH_2$), 5.75 (dd, 1H, $^{3}J$

(H, H)= 11.0 and 17.4 Hz, CH=C); $^{13}$C NMR (67.8 MHz, $CDCl_3$, 25 °C) δ7.84, 14.93, 26.8, 27.8, 36.5, 37.4, 39.1, 45.4, 111.4, 147.3, 211.9; HRMS calcd for $C_{11}H_{20}O$ 168.1514, found 158.1544.