Electronic Supplementary Information

1. General Information

All solvents were used as obtained from commercial suppliers. Zinc powder was used after washing with 10% HCl according to the reported procedure. Chromatographic purification of products was accomplished using forced-flow chromatography on Kanto Chemical Co., INC. Silica gel 60 N (spherical, neutral).

$^1$H NMR spectra were recorded on Varian UNIRY INOVA-500 (500 MHz) or (Varian Gemini-2000 (300 MHz) instrument and are internally referenced to residual protio solvent signals. Data for $^1$H is reported as chemical shift ($\delta$ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), integration, and assignment.

Bis(iodozincio)methane (2a): A mixture of Zn (150 mmol) powder, diiodomethane (1.0 mmol), and PbCl$_2$ (0.01 mmol) in THF (2.0 mL) was sonicated for 1 h in an ultrasonic cleaner bath under Ar. To the mixture, diiodomethane (49 mmol) in THF (48 mL) was added dropwise over 20 min at 0 °C under vigorous stirring. The mixture was stirred for 2 h at 25 °C. After the stirring was stopped, the reaction vessel was stood undisturbed for several hours. Excess zinc powder was separated by sedimentation. $^1$H NMR spectra of the obtained supernatant showed a broad singlet at -1.2 ppm at 0 °C, which corresponded to the methylene proton of 2a. The supernatant was used for the further reaction as a solution of 2a in THF (0.5-0.6 M: The concentration was determined by $^1$H NMR analysis using 2,2,3,3-tetramethylbutane as the internal standard.). The obtained bis(iodozincio)methane in THF can be kept unchanged at least for a month in the sealed reaction vessel.

1,1-Bis(iodozincio) ethane (2b): A mixture of Zn (60 mmol) powder, 1,1-diiodoethane (1.0 mmol), and PbCl$_2$ (0.01 mmol) in THF (2.0 mL) was sonicated for 1 h in an ultrasonic cleaner bath under Ar. To the mixture, 1,1-diiodoethane (19 mmol) in THF (18 mL) was added dropwise over 15 min at 0 °C under vigorous stirring. The mixture was stirred for 1 h at 25 °C. After the stirring was stopped, the reaction vessel was stood undisturbed for several hours. Excess zinc powder was separated by sedimentation. $^1$H NMR spectra of the obtained supernatant showed two
signals at 1.45 (d, $J = 7.8$ Hz, 3H) and -0.08 ppm (q, $J = 7.8$ Hz, 1H) at 0 °C, which corresponded to the methylene proton of 1. The supernatant was used for the further reaction as a solution of 2b in THF (0.4-0.5 M). The concentration was determined by $^1$H NMR analysis using 2,2,3,3-tetramethylbutane as the internal standard. The obtained bis(iodozincio)methane in THF can be kept unchanged for a day in the sealed reaction vessel at 0 °C.

**Preparation of 3:** To a solution of Pd$_2$dba$_3$ (0.02 mmol) in THF (1.0 mL), tri(2-furyl)phosphine (0.082 mmol) in THF (1.0 mL) was added at 25 °C. The mixture was stirred for 15 min. To a solution, 1,1-bis(iodozincio)ethane in THF (2b, 0.40 M, 3.0 mmol) and p-nitrobenzene thiol ester of carboxylic acid (1, 2.0 mmol, 0.18 g) in THF (1.0 ml) and were added subsequently at 0 °C. The resulting mixture was stirred for 15 min at the same temperature. Silylation reagent (3.0 mmol) was added to the reaction mixture. The resulting mixture was stirred for 6 h at 25 °C. Et$_3$N (1.0 mL) was added to the mixture. Saturated aqueous solution of sodium bicarbonate (5.0 mL) was added to the reaction mixture. The mixture was extracted with ether. The combined organic layers were washed with sat.NaHCO$_3$aq and brine, and dried over anhydrous sodium sulfate. After rapid column chromatography on silica gel with hexane/ethyl acetate as the eluent, 3 was obtained.

**Preparation of 5:** To a solution of Pd$_2$dba$_3$ (0.02 mmol) in THF (1.0 mL), tri(2-furyl)phosphine (0.082 mmol) in THF (1.0 mL) was added at 25 °C. The mixture was stirred for 10 min. To a solution, chlorotrimethylsilane (3.0 mmol, 0.4 mL) and p-nitrobenzene thiol ester of keto acid (2.0 mmol) in THF (2.0 mL) were added subsequently at 0 °C. A solution of bis(iodozincio)methane in THF (2a, 0.40 M, 3.0 mmol) was added dropwise at 0 °C. The resulting mixture was stirred for 5 min at the same temperature. The mixture was stirred for additional 15 min at 25 °C. Et$_3$N (1.0 mL) was added to the mixture. Saturated aqueous solution of sodium bicarbonate (5.0 mL) was added to the reaction mixture. The mixture was extracted with ether. The combined organic layers were washed with brine, and dried over anhydrous sodium sulfate. The product was isolated by bulb-to-bulb distillation.

2. Characterization data

**3-β-Butyldimethylsiloxy-5-phenyl-2-pentene (3b):** $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ = 7.24-7.30 (m, 2H), 7.16-7.22 (m, 3H), 4.62 (q, $J=$7.0Hz, 0.07H, E isomer), 4.54 (q, $J=$6.5Hz, 0.93H, Z isomer), 2.75-2.80 (m, 2H), 2.35 (dd, $J=$8.5, 6.0Hz, 0.14H, E isomer), 2.29 (dd, $J=$8.5, 6.0Hz, 1.86H, Z isomer), 1.53 (d, $J=$6.5Hz, 2.79H, Z isomer), 1.44 (d, $J=$7.0Hz, 0.21H, E isomer), 0.99 (s, 8.37H, Z isomer), 0.95 (s, 0.63H, E isomer), 0.16 (s, 5.58H, Z isomer), 0.14 (s, 0.42H, E isomer) ppm.
2-Trimethylsiloxy-1,6-heptadiene (3c): $^1$H NMR (300 MHz, CDCl$_3$) $\delta = 5.81$ (ddt, $J=17.0, 10.0, 2.0$ Hz, 1H), 5.01 (dd, $J=17.0, 2.0$Hz, 1H), 4.96 (dd, $J=10.0, 2.0$ Hz, 1H), 4.05 (s, 2H), 2.06 (dt, $J=7.5, 6.5$Hz, 2H), 2.02 (t, $J=7.5, 2$H), 1.55 (tt, $J=7.5, 7.5$Hz, 2H), 0.20 (s, 9H) ppm.

2-Trimethylsiloxy-3-benzylthio-1-propene (3f): $^1$H NMR (300 MHz, CDCl$_3$) $\delta = 7.28-7.35$ (m, 4H), 7.21-7.27 (m, 1H), 4.21 (d, $J=1.0$Hz, 1H), 4.20 (d, $J=1.0$Hz, 1H), 3.73 (s, 2H), 2.94 (s, 2H), 0.25 (s, 9H) ppm.

Ethyl 7-trimetylsiloxy-7-octenoate (3g): $^1$H NMR (300 MHz, CDCl$_3$) $\delta = 4.12$ (q, $J=7.0$Hz, 2H), 4.03 (bs, 2H), 2.29 (t, $J=7.5$Hz, 2H), 2.00 (t, $J=7.5$Hz, 2H), 1.63 (tt, $J=7.5, 7.5$Hz, 2H), 1.47 (tt, $J=7.5, 7.5$Hz, 2H), 1.33 (tt, $J=7.5, 7.5$Hz, 2H), 1.25 (t, $J=7.5, 3$ H), 0.20 (s, 9H).

2-Trimethylsiloxy-9-bromo-1-nonene (3i): $^1$H NMR (300 MHz, CDCl$_3$) $\delta = 4.03$ (bs, 2H), 3.40 (t, $J=7.0$Hz, 2H), 2.00 (dd, $J=7.5, 7.5$Hz, 2H), 1.85 (dd, $J=7.5, 7.5$Hz, 2H), 1.38-1.48 (m, 4H), 1.26-1.36 (m, 4H), 0.20 (s, 9H).

Ethyl 7-t-butyldimethylsiloxy-7-nonenoate (3k): $^1$H NMR (300 MHz, CDCl$_3$) $\delta = 4.61$ (q, $J=7.0$Hz, 0.07H, $E$ isomer), 4.48 (q, $J=7.0$Hz, 0.93H, $Z$ isomer), 4.12 (q, $J=7.0$Hz, 2H), 2.29 (t, $J=8.0$Hz, 2H), 1.98 (dd, $J=8.0, 8.0$Hz, 2H), 1.62 (tt, $J=8.0, 7.5$Hz, 2H), 1.51 (d, $J=6.5$Hz, 3H), 1.47 (tt, $J=8.0, 8.0$Hz, 2H), 1.31 (tt, $J=8.0 , 7.5$Hz, 2H), 1.25 (t, $J=7.0$Hz, 3H), 0.95 (s, 9H), 0.11 (s, 6H).

5-($p$-Bromophenyl)-3-t-butyldimethylsiloxy-2-pentene (3l): $^1$H NMR (300 MHz, CDCl$_3$) $\delta = 7.38$ (d, $J=8.5$Hz, 2H), 7.04 (d, $J=8.5$Hz, 2H), 4.61 (q, $J=7.0$Hz, 0.07H, $E$ isomer), 4.48 (q, $J=6.5$Hz, 0.93H, $Z$ isomer), 2.67-2.77 (m, 2H), 2.32 (dd, $J=8.0, 7.5$Hz, 0.14H, $E$ isomer), 2.25 (dd, $J=8.0, 7.5$Hz, 1.86H, $Z$ isomer), 1.51 (d, $J=6.5$Hz, 2.79H), 1.41 (d, $J=7.0$Hz, 0.21H), 0.98 (s, 8.37H), 0.94 (s, 0.63H), 0.14 (s, 5.58H), 0.13 (s, 0.42H) ppm.

3-t-butyldimethylsiloxy-2-hexene (3m): $^1$H NMR (300 MHz, CDCl$_3$) $\delta = 4.63$ (q, $J=6.5$Hz, 0.05H, $E$ isomer), 4.48 (q, $J=6.5$Hz, 0.95H, $Z$ isomer), 2.03 (t, $J=7.0$Hz, 0.10H, $E$ isomer), 1.96 (t, $J=7.5$Hz, 1.90H, $Z$ isomer), 1.52 (d, $J=6.5$Hz, 3H), 1.47 (dt, $J=7.5, 7.5$Hz, 2H), 0.95 (s, 9H), 0.89 (t, $J=7.5$Hz, 3H), 0.12 (s, 5.70H), 0.11 (s, 0.30H) ppm.

2-Trimethylsiloxy-8-oxo-1-nonene (5a): $^1$H NMR (300 MHz, CDCl$_3$) $\delta = 4.03$ (bs, 2H), 2.42 (t, $J=7.5$Hz, 2H), 2.13 (s, 3H), 2.00 (t, $J=7.5$Hz, 2H), 1.58 (tt, $J=7.5, 7.5$Hz, 2H), 1.46 (tt, $J=7.5, 7.5$Hz,
2-Trimethylsiloxy-4-(p-acylphenyl)-1-butene (5b): $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ = 7.88 (d, $J$=8.5Hz, 2H), 7.28 (d, $J$=8.5Hz, 2H), 4.04 (d, $J$=1.0Hz, 1H), 4.03 (d, $J$=1.0Hz, 1H), 2.84 (dd, $J$=8.0, 6.5Hz, 2H), 2.58 (s, 3H), 2.34 (dd, $J$=8.0, 6.5Hz, 2H), 0.21 (s, 9H) ppm.

2-Trimethylsiloxy-7-oxo-1-octene (5c): $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ = 4.04 (bs, 2H), 2.43 (t, $J$=7.5Hz, 2H), 2.13 (s, 3H), 2.02 (t, $J$=7.5Hz, 2H), 1.59 (tt, $J$=7.5, 7.5Hz, 2H), 1.45 (tt, $J$=7.5, 7.5Hz, 2H), 0.20 (s, 9H) ppm.

2-Trimethylsiloxy-4-methyl-5-oxo-1-hexene (5d): $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ = 4.05 (bs, 1H), 4.04 (bs, 1H), 2.6-2.8 (m, 1H), 2.35-2.5 (m, 2H), 2.15 (s, 3H), 1.08 (d, $J$=6.5Hz, 3H), 0.20 (s, 9H) ppm.

2-Trimethylsiloxy-3-methyl-5-oxo-1-hexene (5e): $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ = 4.06 (bs, 1H), 3.99 (bs, 1H), 2.6-2.7 (m, 2H), 2.25-2.32 (m, 1H), 2.14 (s, 3H), 1.04 (d, $J$=6.5Hz, 3H), 0.20 (s, 9H) ppm.

3-t-Butyldimethylsiloxy-4-[4-(1-oxopropyl)phenyl]-2-pentene (5f): $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ = 7.88 (d, $J$=8.5Hz, 2H), 7.25 (d, $J$=8.5Hz, 2H), 4.62 (q, $J$=6.5Hz, 0.12H, $E$ isomer), 4.50 (q, $J$=6.5Hz, 0.88H, $Z$ isomer), 2.98 (q, $J$=7.0Hz, 2H), 2.83 (dd, $J$=10.0, 8.0Hz, 2H), 2.36 (dd, $J$=8.0, 7.5Hz, 0.24H, $E$ isomer), 2.29 (dd, $J$=10.0, 8.0Hz, 1.76H, $Z$ isomer), 1.51 (d, $J$=6.5Hz, 2.64H, $Z$ isomer), 1.40 (d, $J$=6.5Hz, 0.36H, $E$ isomer), 1.21 (t, $J$=7.0Hz, 3H), 0.99 (s, 7.92H, $Z$ isomer), 0.95(s, 1.08H, $E$ isomer), 0.15 (s, 5.28H, $Z$ isomer), 0.14 (s, 0.72H, $E$ isomer) ppm.