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Graphical Abstract

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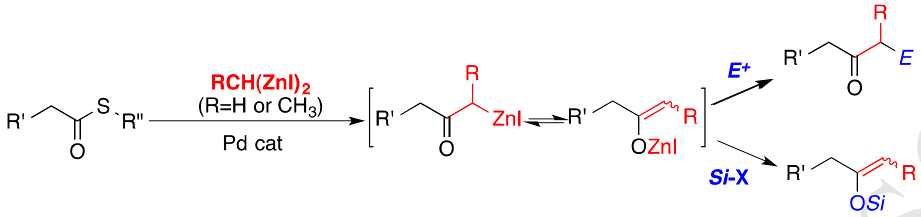

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ABSTRACT

The palladium catalyzed cross-coupling reaction of thiol esters with bis(iodozincio)methane or 1,1-bis(iodozincio)ethane gave Reformatsky-type enolates. They can react with some electrophiles to give the corresponding adducts and were also trapped by silylation reagents to afford silyl enol ethers. As the method applicable to the thiol ester carrying ketone moiety, it afforded zinc enolates carrying ketone in the same molecule.

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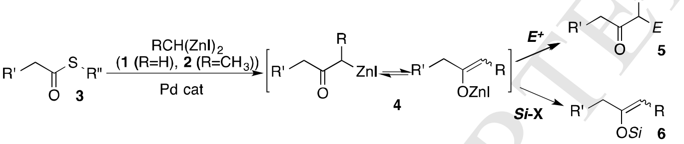
1. Introduction

Bis(iodozincio)methane (**1**) and 1,1-bis(iodozincio)ethane (**2**), which are easily prepared from the corresponding *gem*-diiodoalkane and zinc powder in the presence of Pb catalyst, have been utilized in organic reactions.[1,2] These reagetns work as a nucleophile to carbonyl compounds as a dianion equivalent with the function as a bidentate Lewis acid. Especially, bis(iodozincio)methane (**1**) has offered various specific and characteristic molecular transformations, such as Wittig-type methylenation reaction of easily enolizable ketones,[3] nucleophilic cyclopropanation reaction of 1,2-diketones,[4] ring contraction via 1,4-addition to cyclic enones,[5] and so on.[6] It can also work as a cross-coupling-partner with organic halides and their equivalents;[7] iodozinciomethylation of organic halides by a transition-metal catalyzed cross-coupling reaction resulted in the homologative organozinc reagent formation.[8] Using this strategy, we had tried to prepare a zinc enolate through the coupling reaction of **1** with acylating reagents. We had already reported syntheses of symmetrical 1,3-diketones by treatment of acyl chloride with *gem*-dizinc **1** in the presence of Pd catalysis.[9] The formation of the duplicated acylation of *gem*-dizinc **1** was observed, regardless of the stoichiometric relationship. The high reactivity of acyl chloride cannot ignore the existence of the formed zinc enolate equivalent, which was quenched immediately with the starting acyl chloride to give the symmetrical 1,3-diketone. In order to use the formed zinc enolate equivalent as a synthetic tool, the milder acylating reagent, which is hard to react with the zinc enolate, should be used. From this viewpoint, we chose a thiol ester, which had been used for the ketone synthesis by a cross-coupling with alklylzinc species.[10] As a result, we can perform chemoselective cross-coupling of *gem*-dizinc **1** or **2** with a thiol ester carrying various functional group;[11] the transformation gave a route to obtain the zinc enolate carrying even ketone moiety, that had been difficult to be prepared by the classical method.[12] The obtained zinc enolates **4** can be used as a *C*-nucleophile and also as a precursor for silyl enol ethers (Scheme 1).

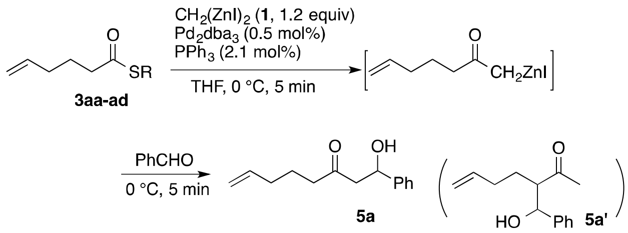


Scheme 1. Preparation and reaction of the zinc enolate by Pd-catalyzed zincioalkylation of a thiol ester.

2. Results and Discussion

According to palladium catalyzed cross-coupling reaction of *S*-ethy alkanethioate and ethylzinc iodide,[10,13] we started the cross-coupling reaction of bis(iodozincio)methane (**1**) and a thiol ester[14] using Pd/PPh$_3$ catalyst. As shown in Table 1, arenethiol esters of 5-hexenoic acid **3aa-ac** were treated with bis(iodozincio)methane (**1**) in the presence of the catalyst, prepared from Pd$_2$dba$_3$ and triphenylphosphine, and reacted subsequently with benzaldehyde. The electron density of the benzene ring of thiols affected the yield. The aldol product **5a** was obtained quantitatively, starting from 4-nitrobenzenethiol ester **3ac** (entry 3). Regioisomeric aldol product **5a'**, which may be formed by an isomerization of the initially formed enolate, was not observed. Use of the ethane thiol **3ad** ester as a substrate, which is a typical substrate for Fukuyama ketone synthesis,[9] resulted in the recovery of the starting material in this case (entry 4).

Table 1. Preparation and reaction with benzaldehyde of the zinc enolate from thiol ester **3aa-ad**.[a]

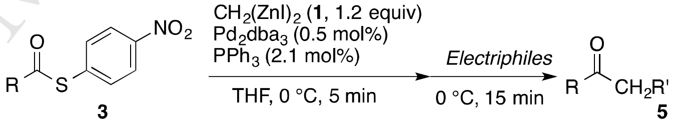


entry	R	**5a**[b]	**5a'**	Recovery
1	Ph (**3aa**)	90%	<1%	10%
2	4-MeOC$_6$H$_4$ (**3ab**)	74	<1	21
3	4-NO$_2$C$_6$H$_4$ (**3ac**)	>99	<1	<1
4	Et (**3ad**)	<1	<1	87

[a]**1** (1.2 mmol, 0.45 M in THF), **3aa-ad** (1.0 mmol), and benzaldehyde (1.5 mmol) were used. [b]Isolated yield.

Various electrophiles can be applied as a substrate to the obtained enolate, as shown in Table 2. A reaction with acyl cyanides gave 1,3-diketones. A conjugate addition was not observed in the reaction with (*E*)-MeCH=CHCOPh (entry 7). Tolerance of functional groups in this enolate formation was also appealed: Primary bromide (entry 11), silyl ether (entry 14), and ester (entry 15) were intact during the reaction. Bromobenzene (entry12) did not disturb the formation of the enolate, although it often interacts with palladium catalyst.

Table 2. Reaction of the enolate from thiol esters **3** with various electrophiles.[a]

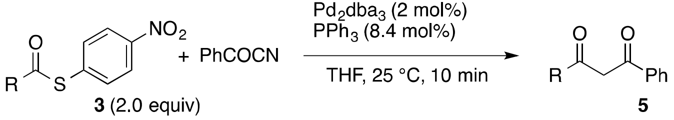


entry	**R**	Electrophile	**R'** in **5**	Yield %[b]
1	PhCH$_2$CH$_2$- (**3b**)	PhCOCN	PhCO-	89 (**5ba**)
2	**3b**	MeCOCN	MeCO-	70 (**5bb**)
3	**3b**	PhCHO	PhCH(OH)-	99 (**5bc**)
4	**3b**	EtCHO	EtCH(OH)-	99 (**5bd**)
5	**3b**	PhCOMe	PhCMe(OH)-	86 (**5be**)
6	**3b**	Cyclohexanone	1-Hydroxycyclohexyl	99 (**5bf**)
7	**3b**	(*E*)-MeCH=CHCOPh	(*E*)-MeCH=CHCPh(OH)-	62 (**5bg**)
8	Ph (**3c**)	PhCOCN	PhCO-	80 (**5c**)
9	CH$_2$=CH(CH$_2$)$_3$- (**3ac**)	PhCOCN	PhCO-	96 (**5aa**)
11	BrCH$_2$(CH$_2$)$_6$- (**3d**)	PhCOCN	PhCO-	93 (**5d**)
12	4-BrC$_6$H$_4$CH$_2$CH$_2$- (**3e**)	PhCOCN	PhCO-	80 (**5e**)
13	PhO(CH$_2$)$_{10}$- (**3f**)	PhCOCN	PhCO-	85 (**5f**)
14	TBDMSO(CH$_2$)$_{11}$- (**3g**)	PhCOCN	PhCO-	84 (**5g**)
15	EtO$_2$C(CH$_2$)$_5$- (**3h**)	PhCOCN	PhCO-	93 (**5h**)

[a]**1** (1.2 mmol, 0.45 M in THF), **3** (1.0 mmol), and benzaldehyde (1.5 mmol) were used. [b]Isolated yield.

The preparation of the zinc enolate, which has ketone group in the same molecule, is quite useful.[15] Treatment of a thiol ester carrying a keto group **3i** with bis(iodozincio)methane (**1**) in the presence of palladium catalyst gave a sluggish mixture, which might be formed by a reaction of the ketone group and the formed enolate. Mixing an electrophile, benzoyl cyanide, in advance, however, prevented this homo-condensation. As shown in Table 3, the results by the following procedure were shown: A mixture of thiol esters with keto group **3i-m** and benzoyl cyanide was treated with the dizinc **1** in the presence of palladium catalyst. These reactions gave triketones in excellent yields. The initially formed zinc enolate reacted with benzoyl cyanide, which is more electrophilic than ketone. It reacted with benzoyl cyanide without transposing to the other methyl ketone moiety in the same molecule. The formation and reaction of enolate from thiol esters proceeded chemo- and regioselectively.

Table 3. Preparation of triketone **5i-m** by a reaction of benzoyl cyanide with enolates from thiol esters carrying acyl group **3i-m**.[a]



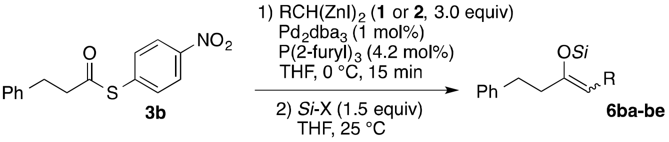
entry	R	Yield (%)[b]
1	$CH_3CO(CH_2)_5$– (**3i**)	92 (**5i**)
2	$CH_3CO(CH_2)_8$– (**3j**)	72 (**5j**)
3	4-CH_3CO-C_6H_4-$(CH_2)_2$– (**3k**)	83 (**5k**)
4	$CH_3COCH(CH_3)CH_2$– (**3l**)	94 (**5l**)
5[c]	$CH_3COCH_2CH(CH_3)$– (**3m**)	79 (**5m**)

[a] **1** (1.5 mmol, 0.45 M in THF), **3** (1.0 mmol), and benzoyl cyanide (0.5 mmol) were used. [b] Isolated yield. [c] Pd_2dba_3 (2.0 mol%) and P(2-furyl)$_3$ (8.4 mol%) were used.

To broaden the scope of this method, the formed zinc enolates were transformed into the silyl enol ethers. The silyl enol ethers have been important reagents especially for cross-aldol reactions, but the selective preparation of those compounds are still needed.[16] For example, it is not so easy to realize the regioselective preparation from an internal ketone, such as 3-hexanone. When we can trap the zinc enolates prepared from thiol ester and *gem*-dizinc **1** or **2**, it is possible to construct the silyl enol ether of methyl- and ethyl ketones carrying functional groups regio- and chemoselectively.

As shown in Table 4, *S*-(4-nitrophenyl) 3-phenylpropanethioate (**3b**) was treated with *gem*-dizinc **1** or **2** in the presence of palladium catalyst and the mixture were treated with various silylation reagents. In this preparation of silyl enol ether, the palladium catalyst prepared from Pd_2dba_3 and tris(2-furyl)phosphine gave the good yields. Trimethylsilyl triflate gave the best yield among the used trimethysilylation reagents (entries 1-3). The reactions of 1,1-bis(iodozincio)ethane (**2**) gave the corresponding silyl enol ethers **6** as a mixture of E/Z-iomers. Use of tert-butyldimethylsilylation gave the sterically less hindered Z-enolate more diastereoselectively compare to trimethylsilation or dimethylphenylsilation (entries 7-11).

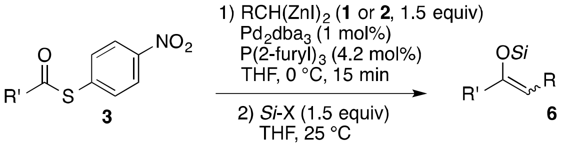
Table 4. Preparation of silyl enol ethers **6ba-be** by a reaction of silylation reagents with enolates from thiol ester **3b**.[a]



entry	$RCH(ZnI)_2$	*Si*X	Yield (%)[b]	*Z* : *E*
1	$CH_2(ZnI)_2$ (**1**)	Me_3SiCl	96 (**6ba**)	–
2	**1**	Me_3SiCN	92 (**6ba**)	–
3	**1**	Me_3SiOTf	>99 (**6ba**)	–
4	**1**	*t*-$BuMe_2SiCl$	32 (**6bb**)	–
5	**1**	*t*-$BuMe_2SiCN$	92 (**6bb**)	–
6	**1**	*t*-$BuMe_2SiOTf$	89 (**6bb**)	–
7	$CH_3CH(ZnI)_2$ (**2**)	Me_3SiCl	93 (**6bc**)	79:21
8	**2**	$PhMe_2SiCl$	34 (**6bd**)	70:30
9	**2**	*t*-$BuMe_2SiCl$	34 (**6be**)	96:4
10	**2**	*t*-$BuMe_2SiCN$	60 (**6be**)	93:7
11	**2**	*t*-$BuMe_2SiOTf$	72 (**6be**)	93:7

[a] Thiol ester (2.0 mmol), dizinc (0.45 M in THF, 3.0 mmol), *Si*-X (3.0 mmol), Pd_2dba_3 (0.02 mmol) and phosphine (0.84 mmol) were used. [b] Yields were determined by ^1H NMR using bromoform as an internal standard. The product was also isolated by bulb-to-bulb distillation in entries 1–3, 7 and by short silica gel column chromatography in entries 4–6, 8–11.

Table 5. Preparation of silyl enol ethers **6** by a reaction of silylation reagents with enolates from various thiol esters **3**.[a]



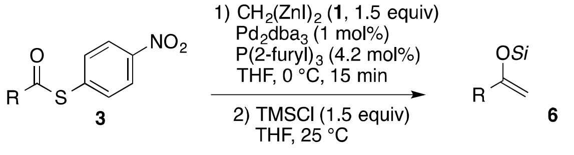
entry	R'	*gem*-dizinc	*Si*X	**6** (%)[b]	*Z* : *E*
1	$CH_2{=}CH(CH_2)_3$- (**3ac**)	**1**	Me_3SiCl	94 (**6aa**)	–
2	Ph (**3c**)	**1**	Me_3SiCl	70 (**6ca**)	–
3	$BrCH_2(CH_2)_6$- (**3d**)	**1**	Me_3SiCl	79 (**6da**)	–
4	4-$BrC_6H_4CH_2CH_2$- (**3e**)	**1**	Me_3SiCl	76 (**6ea**)	–
5	$PhO(CH_2)_{10}$- (**3f**)	**1**	Me_3SiCl	79 (**6fa**)	–
6	$EtO_2C(CH_2)_5$- (**3h**)	**1**	Me_3SiCl	96 (**6ga**)	–
7	$CH_2{=}CH(CH_2)_3$- (**3ac**)	**2**	*t*-$BuMe_2SiOTf$	66 (**6ab**)	90:10
8	4-$BrC_6H_4CH_2CH_2$- (**3e**)	**2**	*t*-$BuMe_2SiOTf$	67 (**6eb**)	93:7
9	$EtO_2C(CH_2)_5$- (**3h**)	**2**	*t*-$BuMe_2SiOTf$	60 (**6hb**)	93:7
10	$CH_3CH_2CH_2$- (**3n**)	**2**	*t*-$BuMe_2SiOTf$	58 (**6nb**)	90:10
11	3-Furanyl (**3o**)	**1**	Me_3SiCl	63 (**6oa**)	–
12	3-Thienyl (**3p**)	**1**	Me_3SiCl	59 (**6pa**)	–

[a] Thiol ester (2.0 mmol), dizinc (0.45 M in THF, 3.0 mmol), *Si*-X (3.0 mmol), Pd_2dba_3 (0.02 mmol) and phosphine (0.84 mmol) were used. [b] Yields were determined by ^1H NMR using bromoform as an internal standard. The product was also isolated by bulb-to-bulb distillation in entries 1–6, 12,13 and by short silica gel column chromatography in entries 8–11.

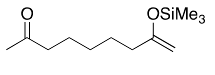
As shown in Table 5, various thiol esters were examined for the preparation of silyl enol ethers. Thiol esters carrying primary bromide (entry 3), aryl bromide (entries 4, 9), and ester (runs 6, 10) were transformed into the corresponding silyl enol ethers in good yields. When 1,1-bis(iodozincio)ethane was used, the produced silyl enol ethers had Z-configuration selectively.[17] Especially, the transformation shown in entry 11 gave (*Z*)-*tert*-butyl(hex-2-en-3-yloxy)dimethylsilane, which is hard to prepare selectively from the corresponding ketone, 3-hexanone.[18]

As shown in Table 6, treatment of a mixture of the thiol ester carrying keto group and chlorotrimethylsilane with bis(iodozincio)methane in the palladium catalyst gave the corresponding silyl enol ether carrying acyl group in the same molecule. In entries 3 and 4, two possible kinetic enolates from 3-methylhexane-2,5-dione **6k**,**l** were prepared selectively. The classical deprotonation method from 3-methylhexane-2,5-dione cannot yield selectively.

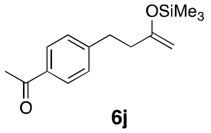
Table 6. Preparation of silyl enol ether having acyl group in the same molecule **6**.[a]



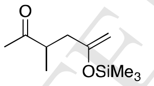
entry	R	**6**[b]
1	$CH_3CO(CH_2)_5$– (**3i**)	82 %(**6i**)
2	4-CH_3CO-C_6H_4-$(CH_2)_2$– (**3j**)	97 (**6j**)
3	$CH_3COCH(CH_3)CH_2$– (**3k**)	58 (**6k**)
4	$CH_3COCH_2CH(CH_3)$– (**3l**)	62 (**6l**)
5	$CH_3CO(CH_2)_4$– (**3q**)	65 (**6q**)



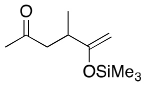
6i



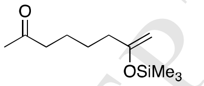
6j



6k



6l



6q

[a]**1** (1.5 mmol, 0.45 M in THF), **3** (1.0 mmol), and benzoyl cyanide (0.5 mmol) were used. [b]Isolated yield.

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3. Experimental

3.1. General

Nuclear magnetic resonance spectra were taken on Varian UNITY INOVA 500 (^1H, 500 MHz; ^{13}C, 125.7 MHz) spectrometer using tetramethylsilane for ^1H NMR as an internal standard (δ = 0 ppm), $CDCl_3$ for ^{13}C NMR as an internal standard (δ = 77.0 ppm). ^1H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz), and integration. High-resolution mass spectra were obtained with a Thermo Fisher SCIENTIFIC EXACTIVE (ESI, APCI). Infrared (IR) spectra were determined on a SHIMADZU FTIR-8200PC spectrometer. Melting points were determined using a YANAKO MP-500D. TLC analyses were performed by means of Merck Kieselgel 60 F254 (0.25 mm) Plates. Visualization was accomplished with UV light (254 nm) and an aqueous vanillin solution followed by heating. Flash column chromatography was carried out using Kanto Chemical silica gel (spherical, 40–100 μm). Unless otherwise noted, commercially available reagents were used without purification. Tetrahydrofuran, Dehydrated stabilizer free —Super— was purchased from Kanto Chemical Co., stored under argon, and used as it is. Zinc powder, which does not contain lead (electrolytic zinc), was purchased from Aldrich (>98% purity on label, <10um). Zinc powder, which contains 0.04-0.07 mol% Pb originally (distilled zinc), was purchased from Wako Pure Chemical Industries (>98% purity).[2a] Zinc powder was used after washing with 10% HCl according to the reported procedure.[19]

3.2. Experimental Procedure and Characterization Data for Substrates.

Preparation of bis(iodozincio)methane (**1**)[3]

A mixture of zinc powder (150 mmol), diiodomethane (1.0 mmol), and $PbCl_2$ (0.005 mmol) in THF (5.0 mL) was sonicated for 1 h in an ultrasonic cleaner bath under Ar. When the distilled zinc was used instead of the electrolytic zinc, it was not necessary to add $PbCl_2$. Diiodomethane (50 mmol) in THF (45 mL) was added dropwise to the mixture over 30 min at 0 °C with vigorous stirring. The mixture was then stirred for 4 h at 25 °C. After the stirring was stopped, the reaction vessel was allowed to stand undisturbed for several hours. Excess zinc was separated by sedimentation. ^1H NMR spectra of the obtained supernatant showed a broad singlet at –1.2 ppm at 0 °C, which corresponded to the methylene proton of **1**. The supernatant was used in further reactions as a solution of **1** in THF (0.4–0.5 M). The concentration of **1** was estimated by ^1H NMR analysis using 2,2,3,3-tetramethylbutane as an internal standard. Bis(iodozincio)methane in THF can be kept for at least a month in a sealed reaction vessel.

Preparation of 1,1-bis(iodozincio)ethane (**2**)[5b]

A mixture of zinc powder (150 mmol), 1,1-diiodoethane (1.0 mmol), and $PbCl_2$ (0.005 mmol) in THF (5.0 mL) was sonicated for 1 h in an ultrasonic cleaner bath under Ar. Zinc When the distilled zinc was used instead of the electrolytic zinc, it was not necessary to add $PbCl_2$. Both of pure zinc and pyrometallurgy zinc are commercially available. To the mixture, 1,1-diiodoethane (50 mmol) in THF (45 mL) was added dropwise over 30 min at 0 °C with vigorous stirring. The mixture was stirred for 4 h at 25 °C. After the stirring was stopped, the reaction vessel was allowed to stand undisturbed for several hours. Excess zinc was separated by sedimentation. ^1H NMR (300 MHz, 20°C) δ –0.08 (q, *J* = 7.8 Hz, 1H), 1.45 (d, *J* = 7.8 Hz, 3H). ^1H NMR spectra of the obtained supernatant showed a quartet at –0.08 ppm at 0 °C, which corresponded to the methyne proton of **2**. The supernatant was used for the further reaction as a solution of **2** in THF (0.1–0.5 M). The concentration of **2** was estimated by ^1H NMR analysis using 2,2,3,3-tetramethylbutane as an internal standard. 1.1-bis(iodozincio)ethane in THF can be kept unchanged at least for two days in a sealed reaction vessel.

General procedure for the preparation and reaction of zinc enolate from thiol ester (Preparation of **5***)*

To a solution of Pd_2dba_3 (0.005 mmol, 4.6 mg) in THF (0.8 mL), triphenylphosphine (0.021 mmol, 5.5 mg) was added at 25 °C. The mixture was stirred for 10 min. To a solution, *p*-nitrobenzene thiol ester of 5-hexenoic acid (**3ac**, 1.0 mmol, 0.25 g) in THF (1.0 ml) and bis(iodozincio)methane in THF (1, 0.45 M, 1.2 mmol, 2.7 mL) were added subsequently at 0 °C. The resulting mixture was stirred for 5 min at the same temperature. A solution of electrophile (1.5 mmol) in THF (1.0 mL) was added at 0 °C. The whole was stirred for 5 min at the same temperature. Saturated aqueous solution of ammonium chloride (1.0 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 a short silica-gel column chromatography using hexane/ethyl acetate as an eluent, **5** was isolated.

1-Hydroxy-1-phenyloct-7-en-3-one (**5a**).

^{1}H NMR (CDCl$_3$) δ 7.25 (m, 4H), 7.18 (m, 1H), 5.65 (ddt, *J* = 17.0, 10.5, 7.0 Hz, 1H), 5.06 (dt, *J* = 9.0, 3.0 Hz, 1H), 4.90 (m, 2H), 2.76 (dd, *J* = 17.0, 9.0 Hz, 1H), 2.68 (dd, *J* = 17.0, 3.0 Hz, 1H), 2.35 (t, *J* = 7.5 Hz, 2H), 1.96 (m, 2H), 1.60 (quint, *J* = 7.5 Hz, 2H). ^{13}C NMR (CDCl$_3$) δ 211.3, 142.7, 137.7, 128.5, 127.6, 125.6, 115.4, 69.9, 51.1, 42.7, 32.9, 22.4. TLC: R$_f$ 0.40 (hexane/EtOAc = 3:1). IR (KBr) 3417.0, 3073.7, 3031.3, 2931.9, 1707.1, 1640.5, 1517.1, 1452.5, 1405.2, 1371.5, 1338.7, 1089.8, 1062.8, 1001.1, 913.3, 760.0, 700.2 cm^{-1}. HRMS (ESI) Calcd for $C_{14}H_{18}O_2Na$: [M+Na]$^+$, 241.1199. Found: *m/z* 241.1194

1-Phenyloct-7-ene-1,3-dione (**5aa**): CAS RN [131223-44-4].

^{1}H NMR (CDCl$_3$) δ 7.90–7.87 (m, 2H), 7.54–7.51 (m, 1H), 7.47–7.43 (m, 2H), 6.18 (s, 1H), 5.82 (ddt, *J* = 17.0, 10.5, 6.5 Hz, 1H), 5.06 (dd, *J* = 17.0, 2.0 Hz, 1H), 5.01 (dd, *J* = 10.5, 2.0 Hz, 1H), 2.45 (t, *J* = 8.0. Hz, 2H), 2.14 (dt, *J* = 8.0, 6.5 Hz, 2H), 1.85-1.75 (m, 2H). ^{13}C NMR (CDCl$_3$) δ 196.6, 183.4, 137.8, 134.0, 132.2, 128.6, 127.0, 115.4, 96.2, 38.4, 33.1, 24.8

1,5-Diphenylpentane-1,3-dione (**5ba**): CAS RN [71298-03-8].

^{1}H NMR (CDCl$_3$) δ 7.86–7.85 (m, 2H), 7.54–7.51 (m, 1H), 7.46–7.43 (m, 2H), 7.32–7.29 (m, 2H), 7.24–7.21 (m, 3H), 6.14 (s, 1H), 3.02 (t, *J* = 8.0 Hz, 2H), 2.76 (t, *J* = 8.0 Hz, 2H). ^{13}C NMR (CDCl$_3$) δ 195.8, 183.1, 140.7, 134.8, 132.3, 128.6, 128.5, 128.3, 127.0, 126.2, 96.3, 41.0, 31.6.

6-Phenylhexane-2,4-dione (**5bb**): CAS RN [52393-50-7].

^{1}H NMR (CDCl$_3$) δ 7.31–7.27 (m, 2H), 7.22–7.18 (m, 3H), 5.48 (s, 0.84H), 3.56 (s, 0.32H), 2.95–2.90 (m, 2H), 2.86–2.83 (m, 0.32H), 2.60 (t, *J* = 7.5 Hz, 1.68H), 2.20 (s, 0.48H), 2.04 (s, 2.52H). ^{13}C NMR (CDCl$_3$) δ 203.2, 202.0, 193.2, 191.0, 140.7, 140.5, 128.53, 128.47, 128.30, 128.26, 126.23, 126.19, 100.0, 58.0, 45.2, 40.0, 31.4, 30.9, 29.4, 24.8.

1-Hydroxy-1,5-diphenylpentan-3-one (**5bc**): CAS RN [62731-45-7].

^{1}H NMR (CDCl$_3$) δ 7.34–7.33 (m, 4H), 7.30–7.27 (m, 3H), 7.22–7.19 (m, 1H), 7.18–7.16 (m, 2H), 5.16 (dd, *J* = 9.5, 3.0 Hz, 1H), 2.92 (t, *J* = 7.5 Hz, 2H), 2.85 (dd, *J* = 17.5, 9.5 Hz, 1H), 2.77 (t, *J* = 7.5 Hz, 2H), 2.76 (dd, *J* = 17.5, 3.0 Hz, 1H). ^{13}C NMR (CDCl$_3$) δ 210.3, 142.7, 140.6, 128.9, 128.5, 128.3, 127.7, 126.2, 125.6, 69.9, 51.3, 45.1, 29.4.

5-Hydroxy-1-phenylheptan-3-one (**5bd**).

^{1}H NMR (CDCl$_3$) δ 7.30–7.27 (m, 2H), 7.21–7.20 (m, 1H), 7.19–7.17 (m, 2H), 3.98–3.93 (m, 1H), 2.91 (t, *J* = 7.5 Hz, 2H), 2.77 (t, *J* = 7.5 Hz, 2H), 2.58 (dd, *J* = 17.5, 3.0 Hz, 1H), 2.49 (dd, *J* = 17.5, 9.0 Hz, 1H), 1.55–1.38 (m, 2H), 0.93 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (CDCl$_3$) δ 211.2, 140.7, 128.5, 128.2, 126.2, 68.9, 48.8, 45.0, 29.5, 29.3, 9.8. TLC: R$_f$ 0.30 (hexane/EtOAc = 3:1). IR (neat) 3467.2, 3026.4, 2964.7, 2918.4, 2878.9, 2850.0, 2308.9, 1710.9, 1700.3, 1654.0, 1559.5, 1540.2, 1507.4, 1457.3, 1339.6, 1110.1, 1030.0, 982.8, 745.5, 697.3, 668.4 cm^{-1}. HRMS (ESI) Calcd for $C_{13}H_{19}O_2$: [M+H]$^+$, 207.1380. Found: *m/z* 207.1378.

5-Hydroxy-1,5-diphenylhexan-3-one (**5be**): CAS RN [925421-43-8].

^{1}H NMR (CDCl$_3$) δ 7.41–7.40 (m, 2H), 7.35–7.31 (m, 2H), 7.27–7.23 (m, 3H), 7.20–7.17 (m, 1H), 7.07–7.06 (m, 2H), 3.16 (d, *J* = 16.5 Hz, 1H), 2.80 (d, *J* = 16.5. Hz, 1H), 2.81–2.67 (m, 3H), 2.62–2.55 (m, 1H), 1.51 (s, 3H). ^{13}C NMR (CDCl$_3$) δ 211.8, 147.1, 140.4, 128.5, 128.3, 128.2, 126.7, 126.1, 124.3, 73.3, 53.4, 46.0, 30.6, 29.0.

1-(1-Hydroxycyclohexyl)-4-phenylbutan-2-one (**5bf**).

^{1}H NMR (CDCl$_3$) δ 7.30–7.26 (m, 2H), 7.21–7.17 (m, 3H), 3.55 (bs, 1H), 2.89 (t, *J* = 7.5 Hz, 2H), 2.76 (d, *J* = 7.5. Hz, 2H), 2.56 (s, 2H), 1.70–1.60 (m, 4H), 1.55–1.49 (m, 1H), 1.42–1.31 (m, 4H), 1.29–1.21 (m, 1H). ^{13}C NMR (CDCl$_3$) δ 212.2, 140.6, 128.5, 128.3, 126.2, 70.7, 52.3, 46.2, 37.5, 29.3, 25.6, 21.9. TLC: R$_f$ 0.47 (hexane/EtOAc = 3:1). IR (neat) 3491.3, 3027.4, 2931.0, 2857.7, 1701.3, 1496.8, 1453.4, 1405.2, 1363.7, 1312.6, 1267.3, 1168.9, 1095.6, 969.3, 745.5, 699.2 cm^{-1}. HRMS (ESI) Calcd for $C_{16}H_{23}O_2$: [M+H]$^+$, 247.1693. Found: *m/z* 247.1690.

(E)-5-Hydroxy-1,5-diphenyloct-6-en-3-one (**5bg**).

^{1}H NMR (CDCl$_3$) δ 7.40–7.38 (m, 2H), 7.34–7.31 (m, 2H), 7.28–7.22 (m, 3H), 7.20–7.17 (m, 1H), 7.10–7.08 (m, 2H), 5.69 (dq, *J* = 15.0, 1.5 Hz, 1H), 5.57 (ddq, *J* = 15.0, 6.5, 1.5 Hz, 1H), 4.76 (bs, 1H), 3.09 (d, *J* = 16.5. Hz, 1H), 2.95 (d, *J* = 16.5. Hz, 1H), 2.86–2.71 (m, 3H), 2.68–2.61 (m, 1H), 1.69 (ddd, *J* = 6.0, 1.5, 1.0 Hz, 3H). ^{13}C NMR (CDCl$_3$) δ 211.5, 145.3, 140.5, 135.9, 128.5, 128.2, 128.2, 126.9, 126.2, 125.0, 124.6, 75.3, 52.2, 46.1, 29.0, 17.7. Mp. 59.5–60.2 °C. TLC: R$_f$ 0.40 (hexane/EtOAc = 10:1). IR (KBr) 3473.0, 2837.4, 1681.0, 1595.2, 1576.9, 1507.4, 1474.6, 1450.5, 1363.7, 1339.6, 1175.7, 1107.2, 1079.2, 979.9, 854.5, 840.0, 758.1, 737.8, 700.2, 690.6 cm^{-1}. HRMS (ESI) Calcd for $C_{20}H_{23}O_2$: [M+H]$^+$, 295.1693. Found: *m/z* 295.1691.

1,3-Diphenylpropane-1,3-dione (**5c**): CAS RN [120-46-7].

^{1}H NMR (CDCl$_3$) δ 8.01–7.99 (m, 4H), 7.58–7.55 (m, 2H), 7.52–7.48 (m, 4H), 6.87 (s, 1H). ^{13}C NMR (CDCl$_3$) δ 185.8, 135.5, 132.5, 128.7, 127.2, 93.1.

10-Bromo-1-phenyldecane-1,3-dione (**5d**).

^{1}H NMR (CDCl$_3$) δ 7.90–7.87 (m, 2H), 7.54–7.51 (m, 1H), 7.47–7.43 (m, 2H), 6.17 (s, 1H), 3.41 (t, *J* = 7.0 Hz, 2H), 2.43 (t, *J* = 7.5 Hz, 2H), 1.86 (tt, *J* = 7.0, 6.5 Hz, 2H), 1.69 (tt, *J* = 7.5, 6.5 Hz, 2H), 1.48–1.35 (m, 6H). ^{13}C NMR (CDCl$_3$) δ 196.9, 183.4, 135.0, 132.2, 128.6, 127.0, 96.1, 39.2, 33.9, 32.7, 29.0, 28.5, 28.0, 25.7. TLC: R$_f$ 0.70 (hexane/EtOAc = 10:1). IR (KBr) 2920.4, 2852.8, 1737.0, 1559.5, 1494.9, 1457.3, 1404.2, 1366.6, 1303.0, 1279.8, 1258.6, 1217.1, 1143.8, 1078.3, 929.7, 766.7, 691.5 cm^{-1}. HRMS (ESI) Calcd for $C_{16}H_{22}BrO_2$: [M+H]$^+$, 325.0798. Found: *m/z* 325.0787.

5-(4-Bromophenyl)-1-phenylpentane-1,3-dione (**5e**).

^{1}H NMR (CDCl$_3$) δ 7.86–7.84 (m, 2H), 7.54–7.51 (m, 1H), 7.47–7.43 (m, 2H), 7.43–7.34 (m, 2H), 7.12–7.10 (m, 2H), 6.12 (s, 1H), 2.97 (t, *J* = 7.5 Hz, 2H), 2.73 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (CDCl$_3$) δ 195.5, 183.0, 139.6, 134.6, 132.4, 131.6, 130.1, 128.6, 127.0, 120.0, 96.4, 40.7, 30.9. Mp. 51.5–52.0 °C. TLC: R$_f$ 0.64 (hexane/EtOAc = 10:1). IR (KBr) 3059.2, 2930.0, 1599.1, 1533.5, 1488.2, 1298.2, 1227.7, 1102.4, 1073.4, 1000.1, 925.9, 821.7, 755.2, 680.9 cm^{-1}. HRMS (ESI) Calcd for $C_{17}H_{16}BrO_2$: $[M+H]^+$, 331.0328. Found: *m/z* 331.0355.

13-Phenoxy-1-phenyltridecane-1,3-dione (**5f**).

^{1}H NMR ($CDCl_3$) δ 7.89–7.88 (m, 2H), 7.53–7.50 (m, 1H), 7.46–7.43 (m, 2H), 7.29–7.25 (m, 2H), 6.94–6.89 (m, 3H), 6.17 (s, 1H), 3.94 (t, *J* = 6.5 Hz, 2H), 2.42 (t, *J* = 7.5 Hz, 2H), 1.77 (tt, *J* = 6.5, 6.5 Hz, 2H), 1.68 (tt, *J* = 7.5, 7.5 Hz, 2H), 1.48–1.27 (m, 12H). ^{13}C NMR ($CDCl_3$) δ 197.0, 183.4, 159.0, 135.0, 132.2, 129.3, 128.5, 126.9, 120.4, 114.4, 96.0, 67.8, 39.2, 29.5, 29.3, 29.3, 29.2, 29.2, 26.0, 25.8. Mp. 70.5–71.0 °C. TLC: R_f 0.63 (hexane/EtOAc = 10:1). IR (KBr) 2932.9, 2916.5, 2850.9, 1602.9, 1575.9, 1497.8, 1473.7, 1337.7, 1303.0, 1274.0, 1251.9, 1172.8, 1146.7, 1080.2, 1012.7, 879.6, 749.4, 691.5 cm^{-1}. HRMS (ESI) Calcd for $C_{25}H_{33}O_3$: $[M+H]^+$, 381.2424. Found: *m/z* 381.2416.

14-((t-Butyldimethylsilyl)oxy)-1-phenyltetradecane-1,3-dione (**5g**).

^{1}H NMR ($CDCl_3$) δ 7.89–7.87 (m, 2H), 7.54–7.50 (m, 1H), 7.47–7.44 (m, 2H), 6.17 (s, 1H), 3.59 (t, *J* = 6.5 Hz, 2H), 2.42 (t, *J* = 7.5 Hz, 2H), 1.68 (tt, *J* = 7.5, 7.5 Hz, 2H), 1.52–1.47 (m, 2H), 1.38–1.25 (m, 14H), 0.89 (s, 9H), 0.04 (s, 6H). ^{13}C NMR ($CDCl_3$) δ 197.0, 183.5, 135.1, 132.2, 128.6, 127.0, 96.1, 63.2, 39.3, 32.9, 29.6, 29.5, 29.5, 29.4, 29.4, 29.3, 26.0, 25.9, 25.8, 18.4, −5.3. TLC: R_f 0.57 (hexane/EtOAc = 10:1). IR (neat) 3065.0, 2927.1, 2854.8, 2648.4, 1723.5, 1603.9, 1575.9, 1463.1, 1360.8, 1300.1, 1255.7, 1182.4, 1097.5, 1028.1, 1005.9, 954.8, 835.2, 774.5, 694.4 cm^{-1}. HRMS (ESI) Calcd for $C_{26}H_{45}O_3Si$: $[M+H]^+$, 433.3132. Found: *m/z* 433.3127.

Ethyl 7,9-dioxo-9-phenylnonanoate (**5h**).

^{1}H NMR ($CDCl_3$) δ 7.90–7.87 (m, 2H), 7.54–7.50 (m, 1H), 7.47–7.43 (m, 2H), 6.17 (s, 1H), 4.12 (q, *J* = 7.0 Hz, 2H), 2.43 (t, *J* = 7.5 Hz, 2H), 2.31 (t, *J* = 7.5 Hz, 2H), 1.74–1.64 (m, 4H), 1.44–1.38 (m, 2H), 1.25 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 196.6, 183.4, 173.6, 134.9, 132.2, 128.6, 127.0, 96.1, 62.2, 39.0, 34.1, 28.7, 25.4, 24.6, 14.2. TLC: R_f 0.40 (hexane/EtOAc = 5:1). IR (neat) 3082.4, 2918.4, 2850.9, 2369.7, 1735.0, 1599.1, 1570.1, 1459.2, 1412.9, 1369.5, 1340.6, 1291.4, 1260.5, 1181.5, 1087.9, 1028.1, 853.5, 767.7, 697.3 cm^{-1}. HRMS (ESI) Calcd for $C_{17}H_{23}O_4$: $[M+H]^+$, 291.1591. Found: *m/z* 291.1586.

Preparation of 1-phenyldecane-1,3,9-trione (**5i**).

To a solution of Pd_2dba_3 (0.01 mmol, 9.2 mg) in THF (1.0 mL), triphenylphosphine (0.042 mmol, 11.3 mg) was added at 25 °C. The mixture was stirred for 10 min. To a solution, benzoyl cyanide (0.5 mmol, 0.066 g) in THF (0.5 mL) and *p*-nitrobenzene thiol ester of 7-oxooctanoic acid (1.0 mmol, 0.29 g) in THF (1.0 mL), bis(iodozincio)methane in THF (1, 0.45 M, 1.5 mmol, 3.3 mL) was added dropwise at 0 °C. The resulting mixture was stirred for 1 h at the same temperature. Saturated aqueous solution of ammonium chloride (2.0 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 a short silica-gel column chromatography using hexane/ethyl acetate as an eluent, the title compound 3 was obtained in 92% yield. Triketone, **5k-m** were obtained by the same procedure. P(2-furyl)$_3$ was used instead of PPh_3 in the preparation of **5m**.

^{1}H NMR ($CDCl_3$) δ 7.89–7.87 (m, 2H), 7.54–7.51 (m, 1H), 7.47–7.43 (m, 2H), 6.17 (s, 1H), 2.45 (t, *J* = 7.5 Hz, 2H), 2.30 (t, *J* = 7.5 Hz, 2H), 2.14 (s, 3H), 1.70 (tt, *J* = 7.5, 7.5 Hz, 2H), 1.62 (tt, *J* = 7.5, 7.5 Hz, 2H), 1.40–1.34 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 209.0, 196.7, 183.4, 134.9, 132.3, 128.6, 127.0, 96.1, 43.4, 39.0, 29.9, 28.7, 25.5, 23.4. Mp. 57.5–58.2 °C. TLC: R_f 0.33 (hexane/EtOAc = 3:1). IR (KBr) 2937.7, 2866.3, 1705.2, 1614.5, 1598.1, 1575.9, 1462.1, 1411.0, 1360.8, 1345.4, 1295.3, 1261.5, 1144.8, 1088.9, 1069.6, 947.1, 774.5, 695.4 cm^{-1}. HRMS (ESI) Calcd for $C_{16}H_{21}O_3$: $[M+H]^+$, 261.1485. Found: *m/z* 261.1482.

1-Phenyltridecane-1,3,12-trione (**5j**).

^{1}H NMR ($CDCl_3$) δ 7.89–7.87 (m, 2H), 7.53–7.50 (m, 1H), 7.47–7.43 (m, 2H), 6.17 (s, 1H), 2.42 (t, *J* = 7.5 Hz, 2H), 2.41 (t, *J* = 7.5 Hz, 2H), 2.13 (s, 3H), 1.67 (tt, *J* = 7.5, 7.5 Hz, 2H), 1.56 (tt, *J* = 7.5, 7.5 Hz, 2H), 1.37–1.26 (m, 8H). ^{13}C NMR ($CDCl_3$) δ 209.4, 197.0, 183.4, 135.0, 132.2, 128.6, 127.0, 96.1, 43.7, 39.2, 29.9, 29.2, 29.2, 29.2, 29.1, 25.8, 23.8. Mp. 34.8–35.5 °C. TLC: R_f 0.60 (hexane/EtOAc = 3:1). IR (KBr) 3098.8, 2930.0, 2852.8, 2549.0, 1705.2, 1616.4, 1595.2, 1576.9, 1507.4, 1499.7, 1410.0, 1341.6, 1101.4, 950.0, 929.7, 854.5, 839.1, 740.7, 692.5 cm^{-1}. HRMS (ESI) Calcd for $C_{19}H_{27}O_3$: $[M+H]^+$, 303.1955. Found: *m/z* 303.1947.

5-(4-Acetylphenyl)-1-phenylpentane-1,3-dione (**5k**).

^{1}H NMR ($CDCl_3$) δ 7.91–7.89 (m, 2H), 7.86–7.83 (m, 1H), 7.54–7.51 (m, 2H), 7.47–7.43 (m, 2H), 7.33–7.32 (m, 2H), 6.13 (s, 1H), 3.08 (t, *J* = 7.5 Hz, 2H), 2.78 (t, *J* = 7.5 Hz, 2H), 2.58 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 197.8, 195.4, 182.9, 146.4, 135.4, 134.6, 132.4, 128.7, 128.6, 128.6, 127.0, 96.3, 40.4, 31.4, 26.6. Mp. 50.9–51.5 °C. TLC: R_f 0.53 (hexane/EtOAc = 2:1). IR (KBr) 3065.0, 2918.4, 1683.9, 1602.9, 1570.1, 1494.9, 1460.2, 1406.2, 1360.8, 1302.0, 1267.3, 1177.6, 1142.9, 1108.2, 1079.2, 1033.9, 1013.6, 957.7, 868.0, 824.6, 779.3, 697.3 cm^{-1}. HRMS (ESI) Calcd for $C_{19}H_{19}O_3$: $[M+H]^+$, 295.1329. Found: *m/z* 295.1322.

5-Methyl-1-phenylheptane-1,3,6-trione (**5l**).

^{1}H NMR ($CDCl_3$) δ 7.86–7.85 (m, 2H), 7.53–7.50 (m, 1H), 7.46–7.43 (m, 2H), 6.17 (s, 1H), 3.13 (ddq, *J* = 8.0, 7.0, 6.0 Hz, 1H), 2.94 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.44 (dd, *J* = 16.0, 6.0 Hz, 1H), 2.25 (s, 3H), 1.18 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 211.1, 196.6, 181.0, 134.3, 132.3, 128.6, 126.9, 96.7, 42.8, 42.3, 28.5, 16.6. Mp. 35.1–36.0 °C. TLC: R_f 0.60 (hexane/EtOAc = 2:1). IR (KBr) 3403.5, 3095.9, 2973.4, 2877.9, 1712.9, 1598.1, 1560.5, 1462.1, 1427.4, 1396.5, 1371.5, 1336.7, 1281.8, 1213.3, 1174.7, 1150.6, 1082.1, 1068.6, 951.9, 932.6, 834.4, 770.6, 692.5 cm^{-1}. HRMS (ESI) Calcd for $C_{14}H_{17}O_3$: $[M+H]^+$, 233.1172. Found: *m/z* 233.1171.

4-Methyl-1-phenylheptane-1,3,6-trione (**5m**).

^{1}H NMR ($CDCl_3$) δ 7.88–7.86 (m, 2H), 7.53–7.50 (m, 1H), 7.46–7.43 (m, 2H), 6.23 (s, 1H), 3.08 (ddq, *J* = 7.5, 7.5, 5.0 Hz, 1H), 3.02 (dd, *J* = 17.5, 7.5 Hz, 1H), 2.51 (dd, *J* = 17.5, 5.0 Hz, 1H), 2.18 (s, 3H), 1.22 (d, *J* = 7.5 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 206.9, 201.2, 181.3, 134.4, 132.2, 128.6, 126.9, 95.4, 46.5, 38.7, 30.3, 17.9. Mp. 30.5–31.0 °C. TLC: R_f 0.63 (hexane/EtOAc = 2:1). IR (KBr) 2968.6, 1781.3, 1710.9, 1612.6, 1576.9, 1516.1, 1464.0, 1392.7, 1373.4, 1339.6, 1275.0, 1153.5, 1122.6, 1067.7, 942.3, 853.5, 802.8, 781.2, 693.4 cm^{-1}. HRMS (ESI) Calcd for $C_{14}H_{17}O_3$: $[M+H]^+$, 233.1172. Found: *m/z* 233.1169.

Preparation of **6** *except* **6i-l,o***:*

Tri(2-furyl)phosphine (0.082 mmol) in THF (1.0 mL) was added at 25 °C to a solution of Pd$_2$dba$_3$ (0.02 mmol) in THF (1.0 mL) and the mixture was stirred for 15 min. *gem*-dizinc in THF (**1** or **2**, 0.45M, 3.0mmol) and p-nitrobenzene thiol ester of carboxylic acid (**3**, 2.0 mmol) in THF (1.0 ml) 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. A saturated aqueous solution of sodium bicarbonate (5.0 mL) was added to the reaction mixture and the mixture extracted with diethyl ether. The combined organic layers were washed with sat. aq. NaHCO$_3$ and brine, and dried over anhydrous sodium sulfate. After rapid column chromatography on silica gel with hexane–ethyl acetate as the eluent, **6** was obtained.

(Hepta-1,6-dien-2-yloxy)trimethylsilane (**6aa**).

^{1}H NMR (CDCl$_3$) δ 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 (dd, *J* = 7.5, 7.5 Hz, 2H), 1.55 (tt, *J* = 7.5, 7.5 Hz, 2H), 0.20 (s, 9H). ^{13}C NMR (CDCl$_3$) δ 159.4, 138.9, 114.8, 90.2, 36.1, 33.3, 26.3, 0.3. TLC: R$_f$ 0.30 (hexane/EtOAc = 1:1). IR (neat) 3077.6, 2957.0, 2863.5, 1638.6, 1458.3, 1437.0, 1251.9, 1225.8, 1172.8, 1100.4, 1035.8, 958.7, 911.4, 841.0, 752.3, 694.4 cm^{-1}. HRMS (ESI) Calcd for C$_{10}$H$_{20}$OSi: [M+K]$^{+}$, 223.0915. Found: *m/z* 223.0943.

Trimethyl((4-phenylbut-1-en-2-yl)oxy)silane (**6ba**) : CAS RN [59417-89-9].

^{1}H NMR (CDCl$_3$) δ 7.30–7.26 (m, 2H), 7.21–7.17 (m, 3H), 4.07 (d, *J* = 0.5 Hz, 1H), 4.06 (d, *J* = 0.5 Hz, 1H), 2.79 (dd, *J* = 8.0, 8.0 Hz, 2H), 2.34 (dd, *J* = 8.0, 8.0 Hz, 2H), 0.22 (s, 9H). ^{13}C NMR (CDCl$_3$) δ 158.9, 142.1, 128.6, 128.5, 125.9, 90.4, 38.5, 33.6, 0.3.

t-Butyldimethyl((4-phenylbut-1-en-2-yl)oxy)silane (**6bb**).

^{1}H NMR (CDCl$_3$) δ 7.30 (t, *J* = 7.5 Hz, 2H), 7.21 (m, 2H), 4.07 (bs, 2H), 2.83 (t, *J* = 8.0 Hz, 2H), 2.36 (t, *J* = 8.0 Hz, 2H), 0.98 (s, 9H), 0.20 (s, 6H). ^{13}C NMR (CDCl$_3$) δ 158.8, 141.9, 128.4, 128.3, 125.8, 90.1, 38.6, 3[3.4, 25.7, 18.1, –4.7. IR (neat) 3112.3, 3028.4, 2957.0, 2930.0, 2858.6, 2361.9, 1654.0, 1635.7, 1496.8, 1472.7, 1361.8, 1292.4, 1257.6, 1221.0, 1160.2, 1149.6, 1077.3, 1031.0, 1005.0, 838.1, 810.1, 780.2, 697.3 cm^{-1}. HRMS (EI) Calcd for C$_{14}$H$_{22}$OSi: [M]$^{+}$, 234.1440. Found: *m/z* 234.1431.

Trimethyl((5-phenylpent-2-en-3-yl)oxy)silane *(Z/E mixture, 79/21)* (**6bc**).

^{1}H NMR (CDCl$_3$) δ 7.29 (t, *J* = 7.5 Hz, 2H), 7.20 (m, 3H), 4.65 (q, *J* = 7.0 Hz, 0.21H), 4.59 (q, *J* = 7.0 Hz, 0.79H), 2.79 (t, *J* = 8.0 Hz, 2H), 2.37 (t, *J* = 8.0 Hz, 0.42H), 2.30 (t, *J* = 8.0 Hz, 1.58H), 1.53 (dt, *J* = 7.0, 1.0 Hz, 2.37H), 1.46 (d, *J* = 7.0 Hz, 0.63H), 0.23 (s, 7.11H), 0.20 (s, 1.89H). ^{13}C NMR (for *Z* isomer, CDCl$_3$) δ 150.4, 142.0, 128.3, 128.3, 125.8, 102.7, 38.8, 33.7, 10.7, 0.6. IR (neat) 2929.0, 1676.2, 1454.4, 1331.9, 1252.8, 1192.1, 1105.3, 1092.7, 1041.6, 995.3, 912.4, 898.9, 843.9, 750.3, 698.3 cm^{-1}. HRMS (EI) Calcd for C$_{16}$H$_{26}$OSi: [M]$^{+}$, 262.1753. Found: *m/z* 262.1748.

Dimethyl(phenyl)((5-phenylpent-2-en-3-yl)oxy)silane (**6bd**) *(Z/E mixture, 70/30)*.

^{1}H NMR (CDCl$_3$) δ 7.68 (dd, *J* = 4.0, 2.0 Hz, 2H), 7.43 (m, 3H), 7.24 (t, *J* = 7.5 Hz, 2H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 7.5 Hz, 2H), 4.65 (q, *J* = 7.0 Hz, 0.30H), 4.59 (q, *J* = 6.5 Hz, 0.70H), 2.79 (t, *J* = 8.0 Hz, 0.60H), 2.71 (t, *J* = 8.0 Hz, 1.40H), 2.37 (t, *J* = 8.0 Hz, 0.60H), 2.23 (t, *J* = 8.0 Hz, 1.40H), 1.54 (dt, *J* = 6.5, 1.0 Hz, 2.10H), 1.42 (d, *J* = 6.5 Hz, 0.90H), 0.51 (s, 4.20H), 0.47 (s, 1.80H). ^{13}C NMR (for *Z* isomer, CDCl$_3$) δ 150.4, 141.9, 137.9, 133.3, 129.8, 128.3, 128.2, 127.9, 125.7, 103.1, 38.7, 33.8, 10.8, –0.9. IR (neat) 3068.9, 2958.0, 2917.5, 2861.5, 1678.1, 1496.8, 1454.4, 1428.4, 1381.1, 1327.1, 1252.8, 1191.1, 1118.8, 1041.6, 998.2, 898.9, 832.3, 787.0, 743.6, 698.3 cm^{-1}. HRMS (EI) Calcd for C$_{19}$H$_{24}$OSi: [M]$^{+}$, 296.1596. Found: *m/z* 296.1588.

t-Butyldimethyl((5-phenylpent-2-en-3-yl)oxy)silane (Z/E mixture, 93/7) (**6be**).

^{1}H NMR (CDCl$_3$) δ 7.29 (t, *J* = 7.5 Hz, 2H), 7.19 (m, 3H), 4.64 (q, *J* = 7.0 Hz, 0.07H), 4.56 (q, *J* = 7.0 Hz, 0.93H), 2.80 (t, *J* = 8.5 Hz, 2H), 2.31 (t, *J* = 8.5 Hz, 2H), 1.55 (d, *J* = 7.0 Hz, 2.79H), 1.45 (d, *J* = 7.0 Hz, 0.21H), 1.01 (s, 8.37H), 0.97 (s, 0.63H), 0.17 (s, 5.58H), 0.09 (s, 0.42H). ^{13}C NMR (for *Z* isomer, CDCl$_3$) δ 150.5, 142.0, 128.3, 128.3, 125.8, 102.4, 38.8, 33.9, 25.8, 10.8, 1.0, –4.0. IR (neat) 3027.4, 2958.9, 2921.3, 2862.5, 2360.0, 2342.7, 1676.2, 1604.8, 1496.8, 1454.4, 1382.1, 1331.9, 1220.0, 1192.1, 1105.3, 1041.6, 993.4, 912.4, 844.9, 751.3, 698.3 cm^{-1}. HRMS (EI) Calcd for C$_{17}$H$_{28}$OSi: [M]$^{+}$, 276.1909. Found: *m/z* 276.1906.

Trimethyl((1-phenylvinyl)oxy)silane (**6ca**) : CAS RN [13735-81-4].

^{1}H NMR (CDCl$_3$) δ 7.62–7.52 (m, 2H), 7.25–7.35 (m, 3H), 4.92 (d, *J* = 2.0 Hz, 1H), 4.43 (d, *J* = 2.0 Hz, 1H), 0.27 (s, 9H). ^{13}C NMR (CDCl$_3$) δ 155.9, 137.7, 128.4, 128.2, 125.4, 91.3, 0.3.

((9-Bromonon-1-en-2-yl)oxy)trimethylsilane (**6da**).

^{1}H NMR (CDCl$_3$) δ 4.03 (bs, 2H), 3.40 (t, *J* = 7.0 Hz, 2H), 2.00 (dd, *J* = 7.5, 7.5 Hz, 2H), 1.85 (ddt, *J* = 7.5, 7.5, 7.0 Hz, 2H), 1.48–1.38 (m, 4H), 1.36–1.26 (m, 4H), 0.20 (s, 9H). ^{13}C NMR (CDCl$_3$) δ 159.7, 90.0, 36.6, 34.1, 33.0, 29.0, 28.8, 28.3, 26.9, 0.3. IR (neat) 2960.9, 2932.9, 2857.7, 2360.0, 2331.1, 1654.0, 1635.7, 1628.0, 1459.2, 1433.2, 1251.9, 1216.2, 1117.8, 1016.5, 844.9, 752.3, 666.4 cm^{-1}. HRMS (EI) Calcd for C$_{12}$H$_{25}$BrOSi: [M]$^{+}$, 292.0858. Found: *m/z* 292.0851.

((4-(4-Bromophenyl)but-1-en-2-yl)oxy)trimethylsilane (**6ea**).

^{1}H NMR (CDCl$_3$) δ 7.39 (d, *J* = 8.5 Hz, 2H), 7.06 (d, *J* = 8.5 Hz, 2H), 4.04 (d, *J* = 1.0 Hz, 1H), 4.02 (d, *J* = 1.0 Hz, 1H), 2.73 (dd, *J* = 8.0, 6.5 Hz, 2H), 2.30 (dd, *J* = 8.0, 6.5 Hz, 2H), 0.21 (s, 9H). ^{13}C NMR (CDCl$_3$) δ 158.4, 141.0, 131.5, 130.4, 119.7, 90.6, 38.3, 33.0, 0.3. IR (neat) 2958.9, 1654.0, 1631.9, 1617.4, 1488.2, 1349.3, 1340.6, 1292.4, 1252.8, 1219.1, 1152.5, 1100.4, 1072.5, 1031.0, 1011.7, 921.1, 846.8, 753.2, 684.8 cm^{-1}. HRMS (EI) Calcd for C$_{13}$H$_{18}$OBrSi: [M–H]$^{+}$, 297.0313. Found: *m/z* 297.0312.

Trimethyl((12-phenoxydodec-1-en-2-yl)oxy)silane (**6fa**).

^{1}H NMR (CDCl$_3$) δ 7.30–7.25 (m, 2H), 6.95–6.85 (m, 3H), 4.04 (bs, 2H), 3.95 (t, *J* = 6.5 Hz, 2H), 2.00 (dd, *J* = 7.0, 7.0 Hz, 2H), 1.78 (ddt, *J* = 7.0, 7.0, 6.5 Hz, 2H), 1.50–1.40 (m, 4H), 1.40–1.26 (m, 10H), 0.21 (s, 9H). ^{13}C NMR (CDCl$_3$) δ 159.8, 159.3, 129.6, 120.1, 114.7, 89.9, 68.0, 36.7, 29.7, 29.7, 29.6, 29.6, 29.5, 29.3, 27.0, 26.3, 0.3. IR (neat) 3109.4, 3040.9, 2927.1, 2854.8, 1632.8, 1602.0, 1497.8, 1468.9, 1387.8, 1301.0, 1251.9, 1171.8, 1107.2, 1014.6, 846.8, 814.0, 752.3, 690.6 cm^{-1}. HRMS (EI) Calcd for C$_{21}$H$_{36}$OSi: [M]$^{+}$, 348.2485. Found: *m/z* 348.2480.

Ethyl 7-((trimethylsilyl)oxy)oct-7-enoate (**6ga**).

^{1}H NMR ($CDCl_3$) δ 4.12 (q, *J* = 7.5 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 Hz, 3H), 0.20 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 159.5, 90.1, 60.4, 36.5, 34.5, 28.8, 26.7, 25.0, 14.6, 0.3. IR (neat) 2938.7, 2863.5, 2360.0, 2331.1, 1739.9, 1735.0, 1252.8, 1181.5, 1139.0, 1087.9, 1014.6, 916.2, 845.8, 752.3, 685.7, 673.2 cm^{-1}. HRMS (ESI) Calcd for $C_{13}H_{27}O_3Si$: [M+H]$^+$, 259.1724. Found: *m/z* 259.1722.

t-Butyldimethyl(octa-2,7-dien-3-yloxy)silane (Z/E mixture, 90/10) (**6ab**).

^{1}H NMR ($CDCl_3$) δ 5.80 (ddt, *J* = 17.0, 10.5, 6.5 Hz, 1H), 5.01 (dd, *J* = 17.0, 2.0 Hz, 1H), 4.95 (dd, *J* = 17.0, 2.0 Hz, 1H), 4.63 (q, *J* = 7.0 Hz, 0.10H), 4.49 (q, *J* = 7.0 Hz, 0.90H), 2.05 (dt, *J* = 7.5, 6.5 Hz, 2H), 2.00 (dd, *J* = 7.5, 7.5 Hz, 2H), 1.55 (tt, *J* = 7.5, 7.5 Hz, 2H), 1.52 (d, *J* = 7.0 Hz, 3H), 0.95 (s, 8.10H), 0.94 (s, 0.90H), 0.12 (s, 6H). ^{13}C NMR ($CDCl_3$) δ 151.1, 138.9, 114.7, 102.1, 36.2, 33.4, 26.5, 26.0, 18.5, 11.0, -3.8. IR (neat) 3067.0, 2956.0, 2858.6, 1642.5, 1472.7, 1383.0, 1361.8, 1330.9, 1254.8, 1193.0, 1045.5, 910.4, 837.1, 777.4 cm^{-1}. HRMS (EI) Calcd for $C_{14}H_{28}OSi$: [M]$^+$, 240.1909. Found: *m/z* 240.1906.

((5-(4-Bromophenyl)pent-2-en-3-yl)oxy)(t-butyl)dimethylsilane (Z/E mixture, 93/7) (**6eb**).

^{1}H NMR ($CDCl_3$) δ 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), 4.48 (q, *J* = 6.5 Hz, 0.93H), 2.77–2.67 (m, 2H), 2.32 (dd, *J* = 8.0, 7.5 Hz, 1.86H), 2.25 (dd, *J* = 8.0, 7.5 Hz, 0.14H), 1.51 (d, *J* = 6.5 Hz, 2.79H), 1.41 (d, *J* = 6.5 Hz, 0.21H), 0.98 (s, 8.37H), 0.94 (s, 0.63H), 0.14 (s, 5.58H), 0.13 (s, 0.42H). ^{13}C NMR (for *Z* isomer, $CDCl_3$) δ 150.1, 141.1, 131.5, 130.3, 119.7, 103.0, 38.7, 33.3, 26.0, 18.5, 11.0, –3.7. IR (neat) 3024.5, 2955.1, 2930.0, 2857.7, 1489.1, 1471.8, 1404.2, 1388.8, 1331.9, 1253.8, 1193.0, 1100.4, 1043.5, 1012.7, 904.7, 838.1, 806.3, 778.3, 697.3 cm^{-1}. HRMS (EI) Calcd for $C_{17}H_{26}BrOSi$: [M–H]$^+$, 353.0936. Found: *m/z* 353.0935.

Ethyl 7-((t-butyldimethylsilyl)oxy)non-7-enoate (Z/E mixture, 93/7) (**6hb**).

^{1}H NMR ($CDCl_3$) δ 4.61 (q, *J* = 7.0 Hz, 0.07H), 4.48 (q, *J* = 7.0 Hz, 0.93H), 4.12 (q, *J* = 7.0 Hz, 2H), 2.29 (t, *J* = 8.0 Hz, 2H), 1.98 (t, *J* = 8.0 Hz, 2H), 1.62 (tt, *J* = 8.0, 7.5 Hz, 2H), 1.51 (d, *J* = 7.0 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). ^{13}C NMR (for *Z* isomer, $CDCl_3$) δ 159.5, 151.2, 102.0, 60.4, 36.6, 34.5, 28.9, 26.9, 26.0, 25.1, 18.5, 14.4, 11.0, –3.8. IR (neat) 2951.2, 2930.0, 2858.6, 2361.9, 1739.9, 1676.2, 1601.0, 1472.7, 1465.0, 1462.1, 1330.9, 1302.0, 1252.8, 1193.0, 1181.5, 1099.5, 1036.8, 1005.9, 939.4, 894.0, 838.1, 806.3, 777.4, 692.5 cm^{-1}. HRMS (EI) Calcd for $C_{17}H_{33}O_3Si$: [M–H]$^+$, 313.2199. Found: *m/z* 313.2191.

t-Butyl(hex-2-en-3-yloxy)dimethylsilane (Z/E mixture, 95/5) (**6nb**).

^{1}H NMR ($CDCl_3$) δ 4.63 (q, *J* = 6.5 Hz, 0.05H), 4.48 (q, *J* = 6.5 Hz, 0.95H), 2.03 (t, *J* = 7.0 Hz, 0.10H), 1.96 (t, *J* = 7.5 Hz, 1.90H), 1.52 (d, *J* = 6.5 Hz, 3H), 1.47 (tq, *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). ^{13}C NMR (for *Z* isomer, $CDCl_3$) δ 151.3, 101.8, 38.9, 26.0, 20.5, 18.5, 13.9, 11.0, –3.8. IR (neat) 2958.9, 2930.0, 2859.6, 2808.5, 2360.0, 2331.1, 1672.4, 1465.0, 1253.8, 1194.0, 1110.1, 914.3, 837.1, 777.4, 665.5 cm^{-1}. HRMS (EI) Calcd for $C_{12}H_{26}OSi$: [M]$^+$, 214.1753. Found: *m/z* 214.1752.

((1-(Furan-3-yl)vinyl)oxy)trimethylsilane (**6oa**)

^{1}H NMR ($CDCl_3$) δ 7.49 (bs, 1H), 7.33 (t, *J* = 2.0 Hz, 1H), 6.45 (dd, *J* = 1.0, 1.0 Hz, 1H), 4.56 (d, *J* = 1.5 Hz, 1H), 4.30 (d, *J* = 1.5 Hz, 1H), 0.25 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 150.0, 143.2, 140.2, 125.3, 108.0, 90.8, 0.1. IR (neat) 2959.9, 2917.5, 2904.0, 2850.0, 2377.4, 1319.4, 1253.8, 1168.0, 1100.4, 1070.5, 1009.8, 956.7, 843.9, 795.7 cm^{-1}. HRMS (EI) Calcd for $C_9H_{14}O_2Si$: [M]$^+$, 182.0763. Found: *m/z* 182.0762.

Trimethyl((1-(thiophen-3-yl)vinyl)oxy)silane (**6pa**): CAS RN [101306-15-4]

^{1}H NMR ($CDCl_3$) δ 7.36 (dd, *J* = 3.0, 1.0 Hz, 1H), 7.24 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.20 (dd, *J* = 5.0, 1.5 Hz, 1H), 4.76 (d, *J* = 1.5 Hz, 1H), 4.37 (d, *J* = 1.5 Hz, 1H), 0.27 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 152.1, 140.3, 125.6, 125.2, 121.8, 90.8, 0.1. HRMS (ESI) Calcd for $C_9H_{14}OSSi$: [M+H]$^+$, 198.0535. Found: *m/z* 198.0533.

Preparation of **6i-l,q**:

To a solution of Pd_2dba_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 this solution, chlorotrimethylsilane (3.0 mmol, 0.4 mL) and p-nitrobenzene thiol ester of keto acid (**3i-l,o** 2.0 mmol) in THF (2.0 mL) were added subsequently at 0 °C and a solution of bis(iodozincio)methane in THF (**1**, 0.45 M, 3.0 mmol) was added dropwise at 0 °C. The resulting mixture was stirred for 5 min at the same temperature and then stirred for an additional 15 min at 25 °C. Et_3N (1.0 mL) was added to the mixture. A saturated aqueous solution of sodium bicarbonate (5.0 mL) was added to the reaction mixture and the mixture extracted with diethyl ether. The combined organic layers were washed with brine, and dried over anhydrous sodium sulfate. The product was isolated by bulb-to-bulb distillation.

8-((Trimethylsilyl)oxy)non-8-en-2-one (**6i**).

^{1}H NMR ($CDCl_3$) δ 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, 2H), 1.30 (tt, *J* = 7.5, 7.5 Hz, 2H), 0.20 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 209.3, 159.2, 89.9, 47.7, 36.2, 29.9, 28.5, 26.5, 23.6, 0.1. IR (neat) 3111.3, 2940.6, 2860.6, 2361.9, 2321.4, 1718.7, 1430.3, 1358.9, 1252.8, 1222.9, 1168.9, 1145.8, 1092.7, 1016.5, 895.0, 845.8, 755.2, 684.8 cm^{-1}. HRMS (ESI) Calcd for $C_{12}H_{25}O_2Si$: [M+H]$^+$, 229.1618. Found: *m/z* 229.1617.

1-(4-(3-((Trimethylsilyl)oxy)but-3-en-1-yl)phenyl)ethan-1-one (**6j**).

^{1}H NMR ($CDCl_3$) δ 7.88 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 4.04 (d, *J* = 1.0 Hz, 1H), 4.03 (d, *J* = 1.0 Hz, 1H), 2.84 (dd, *J* = 8.0, 6.5 Hz, 2H), 2.58 (s, 3H), 2.34 (dd, *J* = 8.0, 6.5 Hz, 2H), 0.21 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 198.0, 158.2, 147.9, 135.3, 128.8, 128.6, 90.6, 38.0, 33.0, 26.7, 0.3. IR (neat) 2958.9, 2931.9, 1685.9, 1635.7, 1607.7, 1430.3, 1412.9, 1338.7, 1290.4, 1268.3, 1252.8, 1221.0, 1182.4, 1154.5, 1112.0, 1032.0, 1005.9, 954.8, 923.9, 847.8, 755.2, 685.7 cm^{-1}. HRMS (EI) Calcd for $C_{15}H_{22}O_2Si$: [M]$^+$, 262.1389. Found: *m/z* 262.1388.

3-Methyl-5-((trimethylsilyl)oxy)hex-5-en-2-one (**6k**).

^{1}H NMR ($CDCl_3$) δ 4.05 (bs, 1H), 4.04 (bs, 1H), 2.74 (dd, *J* = 13.5, 6.5 Hz, 1H), 2.40 (dd, *J* = 13.5, 6.5 Hz, 1H), 2.16 (s, 3H), 2.06 (ddq, *J* = 13.5, 6.5, 6.5 Hz, 1H), 1.08 (d, *J* = 6.5 Hz, 3H), 0.20 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 212.0, 156.5, 91.3, 44.5, 39.8, 28.3, 15.7, –0.1. IR (neat) 2963.8, 2920.4, 2360.0, 2312.8, 1714.8, 1635.7, 1576.9, 1510.3, 1457.3, 1338.7, 1287.5, 1251.9, 1091.8, 1012.7, 842.9, 742.6, 668.4 cm^{-1}. HRMS (ESI) Calcd for $C_{10}H_{20}O_2Si$: [M+H]$^+$, 201.1305. Found: *m/z* 201.1302.

4-Methyl-5-((trimethylsilyl)oxy)hex-5-en-2-one (**6l**).

^{1}H NMR ($CDCl_3$) δ 4.06 (bs, 1H), 3.99 (bs, 1H), 2.67 (dd, *J* = 13.5, 6.5 Hz, 1H), 2.36 (dd, *J* = 13.5, 6.5 Hz, 1H), 2.16 (s, 3H), 2.07 (ddq, *J* = 13.5, 6.5, 6.5 Hz, 1H), 1.04 (d, *J* = 6.5 Hz, 3H), 0.20 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 208.3, 162.0, 88.3, 48.5, 36.0, 30.4, 18.4, 0.0. IR (neat) 2965.7, 2917.5, 2850.0, 2598.2, 2375.4, 2310.8, 1717.7, 1539.3, 1253.8, 1010.7, 844.9, 665.5 cm^{-1}. HRMS (ESI) Calcd for $C_{10}H_{20}O_2Si$: $[M+H]^+$, 201.1305. Found: *m/z* 201.1305.

7-((Trimethylsilyl)oxy)oct-7-en-2-one (**6q**).

^{1}H NMR ($CDCl_3$) δ 4.03 (bs, 2H), 2.43 (t, *J* = 7.5 Hz, 2H), 2.13 (s, 3H), 2.01 (t, *J* = 7.5 Hz, 2H), 1.58 (m, 2H), 1.45 (m, 2H), 0.19 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 209.2, 158.9, 90.1, 43.6, 36.2, 29.9, 26.3, 23.2, 0.1. IR (neat) 2942.5, 2859.6, 1718.7, 1715.8, 1672.4, 1635.7, 1433.2, 1412.0, 1357.9, 1252.8, 1222.9, 1169.9, 1145.8, 1016.5, 846.8, 755.2, 683.8 cm^{-1}. HRMS (EI) Calcd for $C_{11}H_{22}O_2Si$: $[M]^+$, 214.1389. Found: *m/z* 214.1386.

4. Conclusion

This zinciomethylation of thiol esters offers an efficient method to give zinc enolates carrying additional ketone regio-, chemo-, and stereoselectively. The enolates can be isolated as the corresponding silyl enol ethers, which are important nucleophilic reagents for organic synthesis. The preparation of the silyl enol ether, which carries ketone moiety in the same molecule, is one of the most useful applications of this method.

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