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Utilization of $Bu_3SnSiMe_3$ in organic synthesis

II *. New cyclization by a stannyl anion generated from $Bu_3SnSiMe_3$ and R_4NX

Miwako Mori [a], Naotake Kaneta [a] and Masakatsu Shibasaki [b]

[a] *Faculty of Pharmaceutical Sciences, Hokkaido University, Sapporo 060 (Japan)*
[b] *Faculty of Pharmaceutical Sciences, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113 (Japan)*

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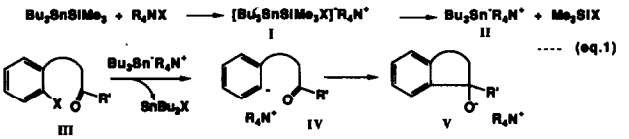
Abstract

A new cyclization reaction of an aryl or vinyl halide bearing a carbonyl group such as ketone or ester has been developed by use of a stannyl anion generated in DMF from $Bu_3SnSiMe_3$ and Bu_4NCl.

Key words: Trimethylsilyl; Stannyl anion

1. Introduction

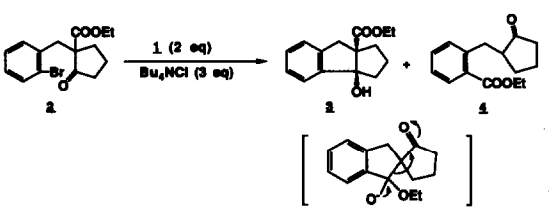
In a previous paper [1], we described a new cyclization reaction using $Bu_3SnSiMe_3$ (**1**) and R_4NX of an aryl halide bearing a carbonyl group and proposed a reaction mechanism. When **2** was treated with **1** in the presence of Bu_4NCl in DMF at room temperature, the cyclized product **3** was obtained in 53% yield along with the ester **4** (19% yield). The former alcohol **3** was provided by the reaction of an aryl halide with the keto-carbonyl group and the latter compound **4** was obtained by the reaction of the aryl halide with the ester carbonyl followed by ring opening as shown in Scheme 1. The reaction mechanism is not clear, but a stannyl anion would be expected to be generated from $Bu_3SnSiMe_3$ and R_4NX. The halide ion of the ammonium salt, such as Bu_4NX or $BnEt_3NX$, coordinates to the silyl group of $Bu_3SnSiMe_3$ to afford the hypervalent silicate (**I**), which would generate the stannyl anion, $Bu_3Sn^-R_4N^+$ (**II**), as shown in eqn. (1). The stannyl anion thus generated then attacks an aryl halide (**III**) to produce an aryl anion (**IV**) via the so-called halogen-metal exchange process [2]; this does not react with the stannyl halide but reacts with the carbonyl group to yield the cyclized product (**V**). In this reaction, the order of reactivity of the aryl halides was ArI > ArBr > ArCl. The aryl chloride did not produce the aryl anion. We now report the development of a new cyclization reaction using $Bu_3SnSiMe_3$ in the presence of R_4NX in DMF.



2. Results and discussion

2.1. Reaction of a stannyl anion with an aryl halide bearing a carbonyl group

The first attempt at cyclization using a stannyl anion generated from $Bu_3SnSiMe_3$ and R_4NX was the reaction of an aryl halide with the keto-carbonyl group.



Scheme 1.

Correspondence to: Dr. M. Mori.

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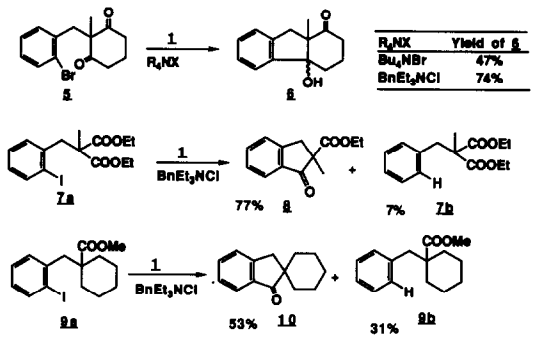


Scheme 2.

When a DMF solution of the ketone **5**, $Bu_3SnSiMe_3$, and Bu_4NBr was stirred at 60°C for 15.5 h, the cyclized product **6** was obtained in 47% yield along with the starting material. The yield was improved to 74% when the reaction was carried out in the presence of $BnEt_3NCl$ instead of Bu_4NBr as the ammonium salt. Since the generated aryl anion can react with an ester group, compound **7a** having the ester group in a chain was treated with $Bu_3SnSiMe_3$ in the presence of $BnEt_3NCl$. The reaction proceeded smoothly to give the five-membered ketone **8** in good yield. Moreover, the reaction of compound **9a** with $Bu_3SnSiMe_3$ in the presence of $BnEt_3NCl$ also afforded the *spiro*-compound **10** in 53% yield along with the dehalogenation product **9b** (31% yield). The results indicate that the stannyl anion generated from $Bu_3SnSiMe_3$ and R_4NX plays an important part in the formation of the aryl anion, which reacts with the keto or ester carbonyl to give the cyclized product in good to moderate yield.

2.2. *Reaction of the stannyl anion with vinyl halides having the carbonyl group*

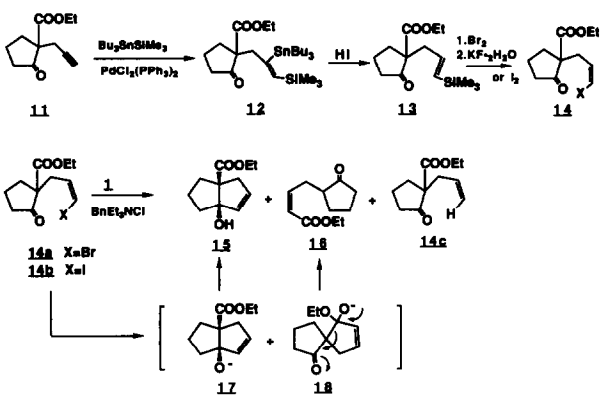
Vinyl anions are important in synthetic organic chemistry. However, generation of the vinyl anion is troublesome and various methods have been tried with this anion. In general, vinyl lithium is prepared by the reaction of lithium with vinyl chloride [3], by the metal–halogen exchange of RLi with vinyl bromide [4] or by transmetallation of vinyl stannane with RLi [5]. Formation of an aryl anion from the stannyl anion generated from $Bu_3SnSiMe_3$ and R_4NX prompted us to form a vinyl anion under mild conditions. The starting vinyl halide was prepared from the *E*-vinyl silane **13**, the synthetic procedure for which was developed by our group [6]. The reaction of the alkyne **11** with $Bu_3SnSiMe_3$ in the presence of a palladium catalyst [7] gave the bisfunctionalized compound **12** in good yield. Destannylation of **12** with HI proceeded smoothly to give the *E*-vinyl silane **13** in good yield, which was easily converted to the *Z*-vinyl bromide **14a** by treatment with bromine and then with $KF \cdot 2H_2O$.

TABLE 1. Percentage yields from reaction of **14** with $Bu_3SnSiMe_3$ in the presence of $BnEt_3NCl$

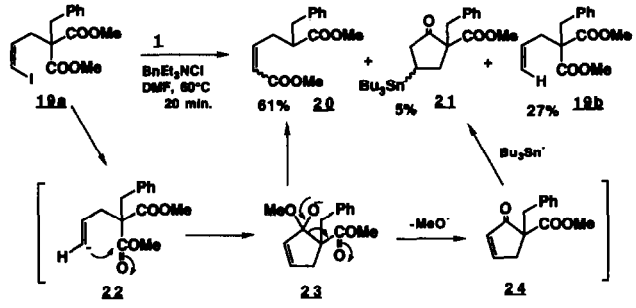
Run	X	Solvent	Temp. °C	Time h	Yield (%)		
					15	**16**	**14c**
1	Br	DMF	60	10	–	–	–
2	I	DMF	60	1	41	21	–
3	I	DMF	rt	22	19	10	–
4	I	THF	rt	12	41	17	23

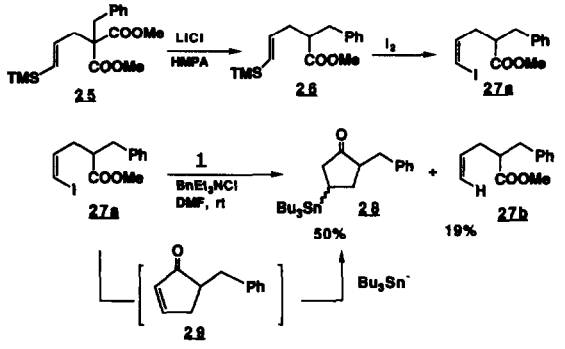
On the other hand, the *Z*-vinyl iodide **14b** was obtained by the reaction of the *E*-vinyl silane **13** with iodine. Treatment of the vinyl bromide **14a** with $Bu_3SnSiMe_3$ (2 equiv) and Bu_4NCl (3 equiv) in DMF at 60°C did not afford the desired product **15** (Table 1, run 1). However, treatment of the vinyl iodide **14b** with $Bu_3SnSiMe_3$ (2 equiv) and Bu_4NCl (3 equiv) provided the desired compound **15** in 41% yield along with the ester **16** (21% yield). Compound **15** was the reaction product of the vinyl anion with the keto-carbonyl group and the ester **16** was obtained by the reaction of the vinyl anion with the ester followed by ring opening as shown in Scheme 3. The reaction proceeded even at room temperature (run 3), but the yield was low; THF can be used as solvent (run 4).

The reaction of the stannyl anion generated from $Bu_3SnSiMe_3$ and R_4NX with the vinyl iodide having the ester group was examined subsequently. A DMF solution of **19a** and $Bu_3SnSiMe_3$ was warmed in the presence of $BnEt_3NCl$ at 60°C for 20 min. However, the cyclopentenone derivative **24** was not obtained and the major product was the unsaturated ester **20** (61% yield, $E/Z = 2/1$) while only a small amount (5% yield) of the desired cyclopentanone derivative **21** was obtained. The former compound **20** was obtained from the cyclized product **23** followed by ring opening as shown in Scheme 4. Isomerization of the *Z*-isomer of **20** to the *E*-isomer would be expected under basic



Scheme 3.

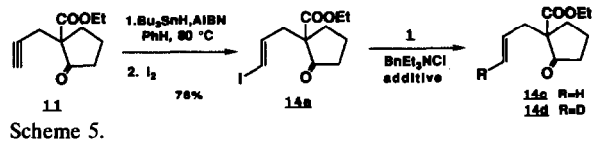




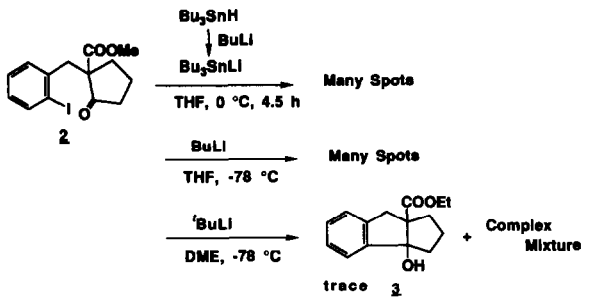
Scheme 4.

conditions because the methoxide ion was generated from **23** for the formation of **24**.

Compound **21** was the product of the 1,4-addition of stannyl anion to give the desired cyclopentenone **24**. To examine the reaction of the vinyl iodide-bearing monoester with $Bu_3SnSiMe_3$ in the presence of R_4NX, the monoester **27a** was prepared. Decarbomethoxylation of compound **25** by LiCl in HMPA [8] proceeded smoothly to give the monoester **26**, which was followed by treatment with iodine to afford the *Z*-vinyl iodide **27a** in good yield. Though compound **27a** was treated with $Bu_3SnSiMe_3$ in the presence of $BnEt_3NCl$ in DMF at room temperature, the major product was the dehalogenation product **27b** (Table 2, run 1). Since the formation of **27b** was considered to be due to a trace of water in the solvent, the reaction was carried out in the presence of dehydrating agents, such as 4 Å molecular sieves (MS 4A) or $MgSO_4$. The desired stannylated product **28** was obtained in moderate yield.



Scheme 5.



Scheme 6.

2.3. *Confirmation of the generation of the aryl or vinyl anion*

The reaction of the *Z*-vinyl iodide **14b** with $Bu_3SnSiMe_3$ (2 equiv) in the presence of Bu_4NCl (3 equiv) provided the cyclized product **15** in 41% yield along with the ester **16** (21% yield). If this reaction proceeds through the vinyl radical, the reaction of the *E*-vinyl iodide with $Bu_3SnSiMe_3$ in the presence of Bu_4NCl affords the same compounds because isomerization of the *E*-vinyl radical to the *Z*-vinyl radical would be easy. However, the reaction of the *E*-vinyl iodide with $Bu_3SnSiMe_3$ and Bu_4NCl afforded only the dehalogenation product **14c** (R = H) in 66% yield. The results indicate that the reaction proceeded via the vinyl anion, not via the vinyl radical. Generation of an aryl or vinyl anion was also supported by the following results (Table 3). (i) The reaction of **14e** with $Bu_3SnSiMe_3$ and $BnEt_3NCl$ in the presence of D_2O (5 equiv) gave the deuterated product **14d** (R = D) (Run 2). (ii) The reaction of **14e** with $Bu_3SnSiMe_3$ and $BnEt_3NCl$ in the presence of ^iPrOD afforded **14d** (R = D). If this reaction proceeds through the radical mechanism, **14c** (R = H) should be obtained.

Subsequently, the reaction of the aryl halide bearing the carbonyl group with Bu_3SnLi was tried. However,

TABLE 2. Percentage yields from reaction of **27a** with $Bu_3SnSiMe_3$–$BnEt_3Cl$ in the presence of dehydrating reagents

Run	Additive	28	27b
1	–	–	51
2	MS 4A	50	–
3	$MgSO_4$	26	26

TABLE 3. Reaction of **14e** with $Bu_3SnSiMe_3$–$BnEt_3NCl$ in the presence of additive

Run	Additive	R	Yield of 14 (%)
1	–	H	83 (**14c**)
2	D_2O	D	74 (**14d**)
3	^iPrOD	D	50 (**14d**)

the reaction of compound **2** with Bu_3SnLi, prepared from Bu_3SnH and LDA, did not afford the desired cyclized product and many spots appeared on TLC. On the other hand, in order to generate the aryl anion from an aryl or vinyl halide, compound **2** was treated with BuLi in THF or ^tBuLi in DME. However, only a trace of the desired product **3** was detected on TLC in each case. It was considered that the difference in the reactivities of Bu_3SnLi and $Bu_3Sn^-R_4N^+$ generated from $Bu_3SnSiMe_3$ and R_4NX is due to the difference in the counter cation of the stannyl anion or of the solvent.

The remarkable characteristics of this reaction are as follows: For the formation of the hypervalent silicate derived from $Bu_3SnSiMe_3$ and R_4NX in DMF, the chloride ion shows sufficient reactivity and the stannyl anion is generated. The aryl or vinyl anions generated the so-called halogen-metal exchange process of the aryl or vinyl halides with the stannyl anion which react with carbonyl groups such as aldehydes, ketones and even with ester carbonyls to give the cyclized products in good to moderate yields. Since the procedure for the generation of the stannyl anion from $Bu_3SnSiMe_3$ and R_4NX is easy and the stannyl anion thus generated is very reactive, it could be used for various chemical reactions.

3. Experimental section

All manipulations were performed under argon using standard Schlenk techniques, and all reaction solutions were degassed through freeze-pump-thaw cycle. Solvents were distilled under an argon atmosphere from sodium benzophenone (THF, Et_2O, dioxane), CaH_2 (HMPA, DMF, Et_3N, ^tBuOH), Na (toluene), or P_2O_5 (CH_2Cl_2, $ClCH_2CH_2Cl$). All other reagents and solvents were purified when necessary by standard procedures. NMR spectra were recorded on either a JEOL JNM-FX100. IR spectra were recorded on a JASCO A-300 spectrophotometer. Mass spectra were obtained from a JEOL JMS-DX303 or JMS-HX110. Melting points were determined by Yanagimoto Special No. 815 or Ishii Melting point Apparatus and were not corrected. $Me_3SiSnBu_3$ was prepared by the method reported [1,3a].

3.1. Preparations

3.1.1. Ethyl 2-oxo-1-((Z)-2-tributylstannyl-3-trimethylsilyl-2-propenyl)cyclopentanecarboxylate (12)

A solution of **11** (307 mg, 1.58 mmol), $Bu_3SnSiMe_3$ (700 mg, 1.9 mmol) and $PdCl_2(PPh_3)_2$ (34 mg, 0.048 mmol, 3 mol%) in THF (2.3 ml) was warmed at 60°C for 5 h. After cooling, the reaction mixture was passed through short column chromatography on silica gel (ether). The ether fraction was concentrated and the residue purified by column chromatography on silica gel (hexane/EtOAc, 20:1) to afford **12** (685 mg, 78%). IR (neat) 1760, 1720 cm^{-1}; ^{1}H-NMR δ ($CDCl_3$) 0.07 (s, 9H), 0.81–1.02 (m, 15H), 1.14–1.58 (m, 12H), 1.22 (t, $J = 7.1$ Hz, 3H), 1.92–2.80 (m, 6H), 2.52 and 3.03 (ABdq, $J = 15.6$, 1.5 Hz, 2H), 4.12 (q, $J = 7.1$ Hz, 2H), 6.25 (t, $J = 1.5$ Hz, 1H); MS m/z 543 ($M^+ - Me$), 501 ($M^+ - Bu$). HR-MS m/z Calcd. for $C_{26}H_{50}O_3SiSn$: 558.2552, found: 558.2538.

3.1.2. Ethyl 2-oxo-1-((E)-3-trimethylsilyl-2-propenyl) cyclopentanecarboxylate (13)

To a solution of **12** (130 mg, 0.23 mmol) in toluene (1 ml) was added aqueous hydriodic acid (0.30 ml, 57% solution, 2.3 mmol) and Bu_4NI (86 mg, 0.23 mmol) at 0°C. After 2 h, saturated $NaHCO_3$ was added and the whole solution was extracted with EtOAc. The organic layer was washed with 10% $Na_2S_2O_3$ and brine, dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc, 20:1) to afford **13** (61 mg, 99%). IR (neat) 1750, 1720 cm^{-1}; ^{1}H-NMR δ ($CDCl_3$) 0.03 (s, 9H), 1.24 (t, $J = 7.1$ Hz, 3H), 1.39–2.84 (m, 8H), 4.16 (q, $J = 7.1$ Hz, 2H), 5.60–7.10 (m, 2H); MS m/z 268 (M^+). HR-MS m/z Calcd. for $C_{14}H_{24}O_3Si$: 268.1495, Found: 268.1516.

3.1.3. Ethyl 2-oxo-1-((Z)-3-iodo-2-propenyl)cyclopentanecarboxylate (14b)

To a solution of **13** (253 mg, 0.897 mmol) in CH_2Cl_2 (3 ml) was added iodine (276 mg, 1.09 mmol) at room temperature. After 1 h, 10% $Na_2S_2O_3$ was added and the whole solution was extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc, 5:1) to afford **14b** (281 mg, 97%). IR (neat) 1750, 1724, 1609 cm^{-1}; ^{1}H-NMR δ ($CDCl_3$) 1.25 (t, $J = 7.1$ Hz, 3H), 1.8–2.2 (m, 3H), 2.2–2.9 (m, 5H), 4.17 (q, $J = 7.1$ Hz, 2H), 6.18 (ddd, $J = 7.6$, 6.4, 7.3 Hz, 1H), 6.39 (ddd, $J = 7.6$, 1.2, 1.2 Hz, 1H); MS m/z 323 ($M^+ + 1$), 195 ($M^+ - I$), 149 ($M^+ - I - OEt + 1$), 121 ($M^+ - I - COOEt + 1$, bp), 111, 93, 79; HR-MS m/z Calcd. for $C_{11}H_{15}O_3I$: 322.0069, Found: 322.0067.

3.1.4. Methyl (E)-2-benzyl-5-trimethylsilyl-4-pentenoate (26)

A solution of **25** (202 mg, 0.605 mmol) and LiCl (52 mg, 1.24 mmol) in HMPA (10 ml) was heated at 120°C for 24 h. After cooling, the mixture was diluted with EtOAc and 10% HCl was added. The aqueous layer was separated and the organic layer was washed with

brine, dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc, 20:1) to afford **26** (100 mg, 60%). IR (neat) 1740, 1620 cm^{-1}; ^{1}H-NMR δ ($CDCl_3$) 0.03 (s, 9H), 2.2–2.5 (m, 1H), 2.6–3.0 (m, 2H), 3.58 (s, 3H), 5.66 (d, J = 18 Hz, 1H), 5.96 (dt, J = 18, 6 Hz, 1H), 7.0–7.4 (m, 5H).

3.1.5. Methyl (Z)-2-benzyl-5-iodo-4-pentenoate (27a)

To a solution of **26** (90 mg, 0.33 mmol) in CH_2Cl_2 (2 ml) was added iodine (101 mg, 0.40 mmol) at room temperature. After 1 h, 10% $Na_2S_2O_3$ was added and the whole solution was extracted with EtOAc. The organic layer was washed H_2O and brine, dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc, 10:1) to afford **27a** (54 mg, 50%). IR (neat) 1736 cm^{-1}; ^{1}H-NMR δ ($CDCl_3$) 2.2–2.4 (m, 2H), 2.4–3.1 (m, 3H), 3.62 (s, 3H), 6.15 (dt, J = 7.5, 6.5 Hz, 1H), 6.33 (d, J = 7.5 Hz, 1H), 7.0–7.4 (m, 5H); MS m/z 331 (M^+ + 1), 299 (M^+ − OMe), 271 (M^+ − COOMe), 255, 239 (M^+ − $PhCH_2$), 203 (M^+ − I), 143 (M^+ − COOMe − I + 1, bp), 91. HR-MS m/z Calcd. for $C_{13}H_{15}IO_2$: 330.0117, Found: 330.0123.

3.2. Cyclizations

3.2.1. General procedure for the reaction of an aryl or vinyl halide with $Bu_3SnSiMe_3$

To a solution of halide (1 equiv) and $BnEt_3NCl$ (2 equiv) in DMF was added $Bu_3SnSiMe_3$ (2 equiv) and the solution was stirred under Ar for several hours. 10% NH_4OH was added and the mixture was stirred for 30 min. The whole mixture was extracted with EtOAc. The organic layer was washed with 10% HCl, brine, saturated $NaHCO_3$ and brine, dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel.

3.2.2. Cyclization of 2-(2-Bromobenzyl)-2-methylcyclohexane-1,3-dione (5)

The crude product obtained by reacting a mixture of **5** (61 mg, 0.21 mmol), $BnEt_3NCl$ (93 mg, 0.41 mmol) and $Bu_3SnSiMe_3$ (151 mg, 0.41 mmol) in DMF (1 ml) at room temperature for 12 h was purified by column chromatography on silica gel (hexane/EtOAc, 10:1 then 3:1) to afford cyclized product **6** (33 mg, 74%). IR; ^{1}H-NMR δ ($CDCl_3$) 1.32 (s, 3H), 1.2–2.6 (m, 6H), 2.67 and 3.56 (ABq, J = 15.6 Hz, 2H), 7.25 (s, 4H); MS m/z 216 (M^+), 198 (M^+ − H_2O), 183 (M^+ − H_2O − Me), 170, 146 (bp), 142, 131, 115, 91; HR-MS m/z Calcd for $C_{14}H_{16}O_2$: 216.1150, Found: 216.1128. Anal. Calcd. for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46, Found: C, 77.57; H, 5.77%.

3.2.3. Cyclization of diethyl 2-(2-iodobenzyl)-2-methylmalonate (7a)

The crude product obtained by reacting a mixture of **7a** (58 mg, 0.15 mmol), $BnEt_3NCl$ (84 mg, 0.37 mmol) and $Bu_3SnSiMe_3$ (110 mg, 0.300 mmol) in DMF (1 ml) at room temperature for 3 h was purified by column chromatography on silica gel (hexane/EtOAc, 5:1) to afford cyclized product **8** (25 mg, 77%) and deiodinated product **7b** (2.6 mg, 7%). **8**: IR (neat) 1741, 1713, 1607, 1589 cm^{-1}; ^{1}H-NMR δ ($CDCl_3$) 1.18 (t, J = 7.1 Hz, 3H), 1.30 (s, 3H), 2.99 and 3.72 (ABq, J = 17.2 Hz, 2H), 4.15 (q, J = 7.1 Hz, 2H), 7.08–7.88 (m, 4H); MS m/z 218 (M^+), 190, 173, 145 (M^+ − COOEt, bp), 117, 115, 91; HR-MS m/z Calcd for $C_{13}H_{14}O_3$: 218.0943. Found: 218.0952. Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47, Found: C, 71.35; H, 6.53%.

3.2.4. Cyclization of methyl 1-(2-iodobenzyl)cyclohexanecarboxylate (9a)

The crude product obtained by reacting a mixture of **9a** (53 mg, 0.15 mmol), $BnEt_3NCl$ (84 mg, 0.37 mmol) and $Bu_3SnSiMe_3$ (110 mg, 0.300 mmol) in DMF (1 ml) at room temperature for 6 h was purified by column chromatography on silica gel (hexane/EtOAc, 20:1) to afford cyclized product **10** (16 mg, 53%) and deiodinated product **9b** (11 mg, 31%). **10**: IR (neat) 1711, 1608 cm^{-1}; ^{1}H-NMR δ ($CDCl_3$) 1.0–2.0 (m, 10H), 3.03 (s, 2H), 7.2–7.8 (m, 4H); MS m/z 200 (M^+), 185, 171, 158, 145 (bp), 132, 115. HR-MS m/z Calcd for $C_{14}H_{16}O$: 200.1202, Found: 200.1200. Anal. Calcd. for $C_{14}H_{16}O$: C, 83.96; H, 8.05, Found: C, 83.73; H, 8.22%.

3.2.5. Cyclization of diethyl 2-benzyl-2-(2-iodobenzyl) malonate (19a)

The crude product obtained by reacting a mixture of **19a** (78 mg, 0.20 mmol), $BnEt_3NCl$ (112 mg, 0.492 mmol) and $Bu_3SnSiMe_3$ (146 mg, 0.404 mmol) in DMF at 60°C for 30 min was purified by column chromatography on silica gel (hexane/EtOAc, 5:1) to afford **20E** (21 mg, 40%), **20Z** (11 mg, 21%), **21** (5 mg, 5%) and **19b** (14 mg, 27%). **20**: IR (neat) 1735, 1720, 1645 cm^{-1}; MS m/z 262 (M^+), 230 (M^+ − MeOH), 202, 199, 63 (bp). Anal. Calcd. for $C_{15}H_{18}O_4$: C, 68.69; H, 8.12, Found: C, 68.78; H, 8.12%. ^{1}H-NMR **20E**: δ ($CDCl_3$, 270 MHz) 2.33–2.60 (m, 2H), 2.72–2.89 (m, 2H), 2.91–3.06 (m, 1H), 3.62 (s, 3H), 3.72 (s, 3H), 5.86 (dt, J = 15.4, 1.5 Hz, 1H), 6.87 (dt, J = 15.4, 7.3 Hz, 1H), 7.12–7.35 (m, 5H); **20Z**: δ ($CDCl_3$, 270 MHz) 2.75–3.08 (m, 5H), 3.61 (s, 3H), 3.69 (s, 3H), 5.83 (dt, J = 11.4, 1.8 Hz, 1H), 6.20 (dt, J = 11.4, 2.9 Hz, 1H), 7.10–7.35 (m, 5H); **21**: IR (neat) 1750, 1730 cm^{-1}; ^{1}H-NMR δ ($CDCl_3$) 0.64–2.01 (m, 29H), 2.10–2.70 (m, 3H), 3.17 and 3.19 (s, 2H), 3.72 (s, 3H), 7.00–7.40 (m, 5H); MS m/z 522 (M^+), 465 (M^+ − Bu, bp); HR-MS m/z Calcd.

for $C_{22}H_{33}O_3Sn$ (M^+ – Bu): 465.1451, Found: 465.1433. Anal. Calcd. for $C_{26}H_{42}O_3Sn$: C, 59.90; H, 8.12, Found: C, 59.90; H, 8.23%. **19b**: IR (neat) 1750, 1735, 1640 cm^{-1}; ^{1}H-NMR δ ($CDCl_3$) 2.57 (dt, J = 7.0, 1.2 Hz, 2H), 3.24 (s, 2H), 3.71 (s, 6H), 5.00–5.30 (m, 2H), 5.56–6.00 (m, 1H), 7.10–7.40 (m, 5H); MS m/z 262 (M^+), 221 (M^+-allyl), 202, 189, 91 (bp).

3.2.6. Cyclization of ethyl 1-((Z)-3-iodo-2-propenyl)-2-oxocyclopentanecarboxylate (14b)

The crude product obtained by reacting a mixture of **14b** (45 mg, 0.15 mmol), $BnEt_3NCl$ (117 mg, 0.511 mmol) and $Bu_3SnSiMe_3$ (104 mg, 0.289 mmol) in DMF at 60°C for 1 h was purified by column chromatography on silica gel (hexane/EtOAc, 10:1) to afford alcohol product **15** (11 mg, 41%) and ketone product **16** (5.7 mg, 21%). **15**: IR (neat) 3500, 1730, 1710, 1630 cm^{-1}; ^{1}H-NMR δ ($CDCl_3$, 270 MHz) 1.28 (t, J = 7.3 Hz, 3H), 1.42 (m, 1H), 1.77 (m, 3H), 1.97 (m, 1H), 2.23 (ddd, J = 17.6, 2.2, 2.2 Hz, 1H), 2.46 (m, 1H), 2.68 (brs, 1H), 3.20 (ddd, J = 17.6, 2.2, 2.2 Hz, 1H), 4.19 (q, J = 7.3 Hz, 2H), 5.54 (ddd, J = 5.5, 2.2, 2.2 Hz, 1H), 5.85 (ddd, J = 5.5, 2.2, 2.2 Hz, 1H); ^{13}C-NMR δ ($CDCl_3$) 14.3, 20.6, 29.7, 31.7, 32.5, 36.2, 61.0, 78.9, 110.3, 130.3, 167.3; MS m/z 196 (M^+), 178 ($M^+ - H_2O$), 167, 151, 150, 149, 123, 105, 57 (bp); HR-MS Calcd. for $C_{11}H_{16}O_3$: 196.1100, Found: 196.1127. **16**: IR (neat) 1740, 1720, 1645 cm^{-1}; ^{1}H-NMR δ ($CDCl_3$, 270 MHz) 1.28, (t, J = 7.3 Hz, 3H), 1.59 (m, 1H), 1.80 (m, 1H), 2.18 (m, 5H), 2.87 (m, 2H), 4.16 (q, J = 7.3 Hz), 5.83 (ddd, J = 11.4, 1.5, 1.5 Hz, 1H), 6.24 (ddd, J = 11.4, 8.1, 7.3 Hz, 1H); MS m/z 196 (M^+), 181, 167, 149, 113, 97, 83, 71, 57, 55; HR-MS Calcd. for $C_{11}H_{16}O_3$: 196.1100, Found: 196.1122.

3.2.7. Cyclization of ethyl 1-((E)-3-iodo-2-propenyl)-2-oxocyclopentanecarboxylate (14e) in the presence of D_2O

The crude product obtained by reacting a mixture of **14e** (52 mg, 0.16 mmol), $BnEt_3NCl$ (74.3 mg, 0.326 mmol) D_2O (15 μl, 0.829 mmol), and $Bu_3SnSiMe_3$ (118 mg, 0.329 mmol) in DMF (1 ml) at 60°C for 1 h was purified by column chromatography on silica gel (hexane/EtOAc, 10:1) to afford ethyl 1-((*E*)-3-deutero-2-oxocyclopentanecarboxylate (**14d**) (26.4 mg, 83%). ^{1}H-NMR δ ($CDCl_3$) 1.20 (t, J = 7.3 Hz, 3H), 1.20–2.76 (m, 8H), 4.12 (q, J = 7.3 Hz, 2H), 5.07 (bd, J = 17.8 Hz, 1H), 5.76 (m, 1H); MS m/z 197 (M^+), 169 (M^+ – Et), 152 (M^+ – OEt), 124 (M^+ – COOEt).

3.2.8. Cyclization of methyl (Z)-2-benzyl-5-iodo-4-pentenoate (27a)

A solution of $BnEt_3NCl$ (66 mg, 0.20 mmol) and MS-4A (67 mg) in DMF (1 ml) ws stirred at room temperature for 30 min. The solution (filtered by cannula) was added to **27a** (19 mg, 0.058 mmol) and $Bu_3SnSiMe_3$ (62 mg, 0.172 mmol) was added to the DMF solution. The whole solution was stirred at room temperature for 15 h and was then extracted with EtOAc. The organic layer was washed with 10% HCl, brine, saturated $NaHCO_3$ and brine, dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc, 10:1) to afford **28** (13 mg, 50%) and deiodinated product **27b** (2.3 mg, 19%). **28**: IR (neat) 1738, 1603 cm^{-1}; ^{1}H-NMR δ ($CDCl_3$) 0.8–1.0 (m, 15H), 1.0–1.6 (m, 12H), 1.6–3.2 (m, 8H), 7.1–7.4 (m, 5H); MS m/z 464 (M^+), 407 (M^+ – Bu), 235, 179, 155, 91 (bp). HR-MS m/z Calcd for $C_{24}H_{40}OSn$: 464.2101, Found: 464.2114. Anal. Calcd. for $C_{24}H_{40}OSn$: C, 62.22; H, 8.70, Found: C, 61.99; H, 8.60%.

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