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Direct Preparation of Lanthanoid Ester Homoenolates from 3-Halo Esters and Lanthanoid Metals: Their Homo-Reformatsky-Type Reaction with Carbonyl Compounds

Shin-ichi Fukuzawa,* Norifumi Sumimoto, Tatsuo Fujinami, and Shizuyoshi Sakai

Department of Materials Science, Faculty of Engineering, Shizuoka University, Hamamatsu 432, Japan

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The direct reaction of ethyl 3-bromopropionate (**2a**) or 3-iodopropionate (**2b**) with lanthanoid metals (La, Ce, Nd, Sm) in tetrahydrofuran produces lanthanoid ester homoenolates (**3**), which react with ketones to give γ-lactones in good yields under mild conditions. The isolation of 3-phenylseleno (**8a**), 3-phenyltelluro (**8b**), and 3-tri-*n*-butylstannyl esters (**10**) from the reaction with diphenyl diselenide (**7a**), ditelluride (**7b**), and tri-*n*-butyltin iodide (**9**), respectively, suggests the formation of the lanthanoid ester homoenolate.

Lanthanoid compounds have been of interest in the area of synthetic organic chemistry for the last decade, and some characteristic reactions have been developed.[1] Organolanthanoid σ-complexes are among the most efficient reagents for high regio- and stereoselective carbon–carbon bond formation, and they have been applied to natural products synthesis.[2] Special characteristics of organolanthanoids include high oxophilicity and strong nucleophilicity, but weak basicity for a carbonyl group. Existing examples, however, seem to be relatively limited to date because organolanthanoid σ-complexes are not easily prepared from readily available organic bromides, and some organolanthanoid compounds do not undergo carbon–carbon bond formation with organic compounds.[3] On the other hand, inorganic lanthanoid salts such as samarium(II) diiodide[4] and lanthanoid(III) trihalides[5] are intensively employed in organic synthesis. Generally, organolanthanoic σ-complexes are easily prepared by the direct reaction of organic iodide with lanthanoid metals,[6] by transmetalation of organolithium reagents with lanthanoid halides,[7] and also from organomercury compounds by oxidative–reductive transmetalation with lanthanoid metals.[8]

Scheme I

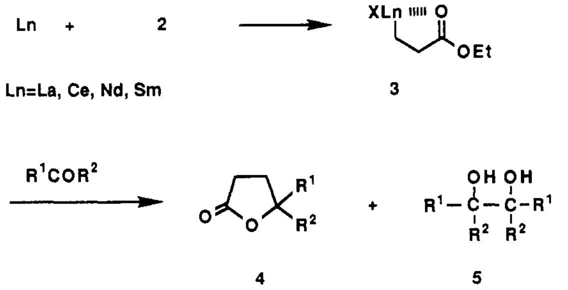

Table I. Reactions of 3-Halo Ester (2) with Acetophenone Mediated by Lanthanoid Metals[a]

entry	3-halo ester	Ln	product and isolated yield, % 4	5[b]
1	**2a**	La	68	20
2		Ce	70	21
3[c]		Ce	52	25
4[d]		Ce	50	23
5[e]		Ce	55	29
6[f]		Ce	55	19
7		Nd	68	20
8		Sm	71	22
9	**2b**	La	68	10
10		Ce	71	5
11		Nd	61	9
12		Sm	0	63
13[g]		Sm	57	30[15]

[a] 2 (4 mmol), acetophenone (4 mmol), Ln (4 mmol), THF (10 mL); room temperature, 2 h. [b] Determined by GLC. [c] HMPA (1 mL) was added. [d] TMEDA (1 mL) was added. [e] TEGDME (1 mL) was added. [f] 18-Crown-6 (1 mL) was added. [g] Acetophenone was added to the organosamarium reagent at −78 °C.

The chemistry of metal homoenolates (β-metal-substituted carbonyl compounds) has been rapidly advanced, especially aiming at their use in organic synthesis, leading to the design of several synthetic equivalents.[9] The ring opening of a siloxycyclopropane (**1**)[10] is one of the most

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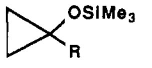
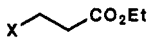
efficient methods for preparation of a metal homoenolate, but direct reaction of 3-halo carbonyl compounds and a metal would be preferable. The direct synthesis of β-lithiopropionate from 3-bromopropionic acid and lithium naphthalenide has been reported.[11] The lithium homoenolate reacts with carbonyl compounds at −70 °C to give γ-lactones in moderate yields. Zinc ester homoenolates have recently been prepared by the direct reaction of ethyl 3-iodopropionate (**2b**) with zinc–copper couple in benzene–dimethylformamide or dimethylacetamide, and their reaction with carbonyl compounds in the presence of a metal complex catalyst has been studied.[12] In a preliminary communication, we have reported the lanthanoid metal mediated reaction of 3-bromo ester (**2a**) with ketones leading to a facile γ-lactone synthesis, where a lanthanoid ester homoenolate was assumed to be an intermediate.[13] We describe here the details of the formation of lanthanoid ester homoenolates by the direct reaction of 3-halo esters (**2**) with lanthanoid metals.



1

R=OEt or alkyl



2a; X=Br
2b; X=I

Results and Discussion

The reaction of ethyl 3-bromopropionate (**2a**) with cerium metal in tetrahydrofuran (THF) proceeded smoothly in the presence of a trace of iodine with a slight temperature rise to give a dark brown homogeneous solution,[14] even though cerium metal has been reported to be unreactive toward alkyl bromides.[6a] Treatment of acetophenone with the resulting solution at room temperature for 2 h afforded 4-methyl-4-phenyl-γ-butyrolactone (4; R^1 = Ph, R^2 = Me) as the major product (70%), contaminated by a pinacol-coupled product (5) (18–20%) (Scheme I). The cerium ester homoenolate (3; Ln = Ce, X = Br) was thought to be a likely intermediate in the reaction. Similar results were obtained when lanthanum, neodymium, or samarium[15] was employed as a lanthanoid metal in the place of cerium. The results of the reaction of acetophenone with 2 in the presence of lanthanoid metals are summarized in Table I. To improve the yield of the γ-lactone and suppress the formation of the pinacol, some additives such as hexamethylphosphoric triamide (HMPA), tetramethylethylenediamine (TMEDA), tetraethylene glycol dimethyl ether (TEGDME), and 18-crown-6 were tested (entries 3–6). The results however, were disappointing; these additives were not effective for the reaction and rather spoiled the γ-lactone synthesis. 3-Iodo ester (**2b**) reacted more rapidly with lanthanoid metals to form the lanthanoid ester homoenolate, which also reacted with acetophenone to give the γ-lactone in equal yields to those utilizing **2a**. In the case of **2b**, the formation of a pincaol **5** was suppressed except using samarium. These results are also shown in Table I (entries 9–12).

Table II. Reaction of 3-Halo Ester (2) with Various Carbonyl Compounds Mediated by Cerium[a]

entry	3-halo ester	carbonyl compound	product and isolated yield, % 4	5[b]
1	**2a**	acetophenone	70	20
2		benzophenone	46	–[c]
3		diethyl ketone	51	20
4		2-octanone	61	20
5		cyclohexanone	55	32
6		cycloheptanone	60	–[c]
7		cyclododecanone	40	–[c]
8		5-hexen-2-one	69	–[c]
9		benzaldehyde	0	–[c]
10		isobutyraldehyde	0	–[c]
11	**2b**	acetophenone	71	5
12		benzophenone	32	–[c]
13		diethyl ketone	49	10
14		2-octanone	65	8
15		cyclohexanone	60	11
16		5-hexen-2-one	71	–[c]
17		benzaldehyde	0	–[c]
18		hexanal	0	–[c]

[a] 2 (4 mmol), carbonyl compound (4 mmol), cerium (4 mmol), THF (10 mL); the reaction was carried out at room temperature, 2 h. [b] Determined by GLC. [c] Not determined.

Scheme II

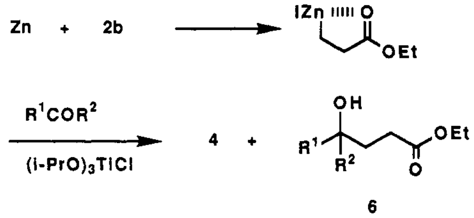


Table II shows the reaction of various ketones with **2** by using cerium as a lanthanoid component. For both aliphatic and aromatic ketones, the γ-lactones were produced in good yields from either **2a** or **2b**. From the olefinic ketone, 5-hexen-2-one, the olefinic γ-lactone derivative was obtained without any side reactions, e.g. intramolecular cyclization (entry 8). Unfortunately in the case of aldehydes such as benzaldehyde and hexanal, γ-lactones could not be obtained even at lower temperatures (−78 to 0 °C).[16]

On the other hand, the use of magnesium instead of lanthanoid metals did not give any γ-lactones even under ultrasonic irradiation or on heating, and instead resulted in the recovery of unreacted metal and starting organic compounds. The zinc ester homoenolate, which reacts with carbonyl compounds in the presence of a titanium(IV) complex to give γ-lactones and/or γ-hydroxy esters, has recently been prepared by the direct reaction of zinc–copper couple with **2b** (Scheme II).[12d] We confirmed that zinc did not react with **2a** and that the use of **2b** was always required for the direct preparation of the zinc ester homoenolate.

The characteristics of the lanthanoid-mediated reaction of 3-halo esters with ketones may be concluded as follows.

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[14] We occasionally had difficulties to initiate the reaction. In this case, the reaction mixture was gently warmed at 35 °C, and then the reaction started within 10 min.

[15] The reaction solution was deep green before the addition of a ketone, indicating the presence of divalent samarium.[6a] When the reaction with a ketone was carried out at room temperature, the major product was a pinacol coupling product. The reaction must be carried out at lower temperature (−78 °C). Namy, J. L.; Souppe, J.; Kagan, H. B. *Tetrahedron Lett.* **1983**, *24*, 765.

[16] Some organolanthanoids do not undergo simple nucleophilic addition with aldehydes. References 3a–b and 6e.

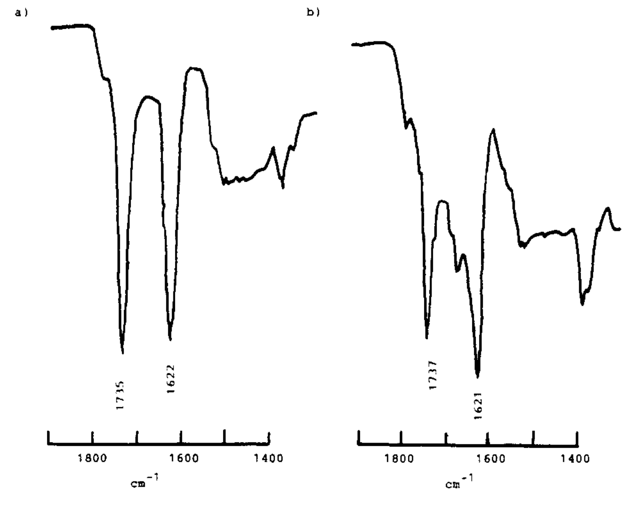
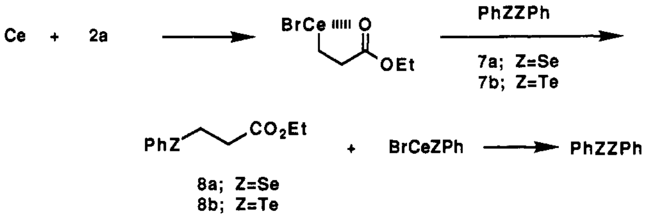


Figure 1. IR spectra of 0.25 M THF solution of (a) cerium ester homoenolate (3; Ln = Ce, X = Br) and (b) samarium ester homoenolate (3; Ln = Sm, X = Br).

Scheme III



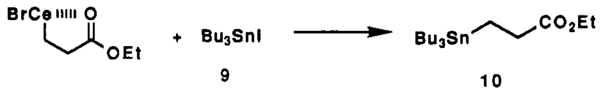
(1) Lanthanoid ester homoenolates can easily be prepared from 3-bromo esters. This has the advantage that the organic substrate is commercially available and is able to be stored for a longer period than the corresponding iodo ester. (2) The reaction with carbonyl compounds proceeds without any additives or catalysts such as Lewis acids. This fact is compatible with the high reactivity of organolanthanoid σ-complexes toward a carbonyl group.[6b] (3) The reaction conditions are mild; the γ-lactone synthesis via the lithium homoenolate must be carried out at −70 °C, while the lanthanoid ester homoenolate method can normally be carried out at ambient conditions.[11]

As we have described, the reaction intermediate is thought to be a lanthanoid ester homoenolate. It was difficult to isolate the extremely air and moisture sensitive lanthanoid ester homoenolate, but we could know its formation by a spectroscopic method. In the IR spectra of THF solution of "3 (Ln = Ce, Sm; X = Br)" (Figure 1), two strong carbonyl bands were observed at 1621–1622 and 1735–1737 cm^{-1}. As the IR spectrum of the zinc ester homoenolate in diethyl ether has been reported to show the similar two strong carbonyl absorptions at 1662 and 1740 cm^{-1},[10c] the bands appearing in Figure 1 can be considered as the characteristic carbonyl absorptions of metal ester homoenolates: the lower wavenumber carbonyl absorption due to the chelated carbonyl group and the higher wavenumber due to the nonchelated ester.[10b]

The formation of the metal homoenolate was further confirmed by GLC analyses of the reaction of **2a** with cerium or samarium followed by acid hydrolysis, which indicated the disappearance of the starting compound and the formation of ethyl propionate.

On treatment of diphenyldiselenide (**7a**) or -ditelluride (**7b**) with the dark gray solution prepared from cerium and **2a** in THF, 3-phenylseleno (**8a**) or 3-phenyltelluro (**8b**) ester was produced (Scheme III). It is reasonable to assume that the lanthanoid ester homoenolate reacts with **7a** or **7b** like Grignard reagents and organolithium reagents.[17] These results may also suggest that the lanthanoid ester homoenolate is an intermediate. The formation of organolanthanoid species was further supported by isolation of 3-tri-*n*-butylstannyl ester (**10**) resulting from the interaction of **3** (Ln = Ce, X = Br) with tri-*n*-butyltin iodide (**9**) at room temperature (Scheme IV).[18]

Scheme IV



Experimental Section

General. ^{1}H NMR (60 MHz) spectra were recorded on a Hitachi R-24 spectrometer as solutions in $CDCl_3$. ^{13}C NMR spectra were determined on a Fourier transform NMR system (JEOL JNM EX-90) in $CDCl_3$. Chemical shifts are reported in δ units down field from the internal reference Me_4Si. IR spectra were taken on a Shimadzu IR-410 instrument. GLC analyses were carried out by using a Shimadzu GC 8A gas chroamtograph apparatus equipped with 2 m silicone DC QF-1 (5% Chromosorb-W 60–80 mesh) and 2-m EGSS-X (3% Chromosorb-W 60–80 mesh) columns (nitrogen as carrier gas). Column chroamtography was performed with Wakogel C-300 (200–300 mesh). Combustion analyses were carried out at Microanalytical Center of Kyoto University, Kyoto, Japan.

Materials. Cerium powder was purchased from Nippon Yttrium Co., Ltd. Lanthanum and Neodymium powders packed with oil were obtained from the Aldrich Chemical Co. Samarium was provided by Shin-Etsu Chemical Co., Ltd. Commercial **2a** (Tokyo Kasei Chemicals) was used without purification. **2b** was prepared by a displacement reaction of the corresponding chloro compounds (Alrich) with sodium iodide in acetone. THF was distilled under nitrogen from sodium benzophenone ketyl prior to use. Commercial HMPA was dried over calcium hydride, distilled in vacuo, and stored on 5-Å molecular sieves. TMEDA was dried over NaOH. 18-Crown-6 and tetraethylene glycol dimethyl ether were stored on 5-Å molecular sieves. All carbonyl compounds were commercially available and used without further purification unless otherwise noted. Authentic pinacols for GLC analyses were prepared by the reported method.[15] Diphenyldiselenide (**7a**)[19] and -ditelluride (**7b**)[20] were prepared by the reaction of phenylmagnesium bromide with selenium and tellurium powders, respectively. Tri-*n*-butyltin iodide was prepared from the corresponding chloride (commercially available) and sodium iodide in refluxing acetone.[21]

Warning! Lanthanum and cerium powders must be treated carefully under nitrogen, since they are pyrophor metal and tend to burn spontaneously when they are in contact with air.

Reaction of Ethyl 3-Bromo- or 3-Iodopropionate (2a,b) with Carbonyl Compounds Mediated by Lanthanoid Metal. All reactions were carried out under nitrogen by standard tech-

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(17) The reaction of Grignard reagents or organolithium compounds with diorganyl dichalcogenides affords the unsymmetric diorganyl chalcogenides.

$$\text{RZZR} + \text{R'M} \rightarrow \text{RZR'} + \text{RZM}$$

$$\text{Z} = \text{Se, Te} \qquad \text{M} = \text{MgBr, Li}$$

(a) O'Brien, D. H.; Dereu, N.; Huang, C.-K.; Irgolic, K. J. *Organometallics* **1983**, *2*, 305. (b) Petragnani, N. *Chem. Ber.* **1963**, *96*, 247.

(18) The only one example of a substitution reaction of aryl lanthanoid compounds with triphenyltin chloride is reported. Syutkina, O. P.; Rybakova, L. F.; Petrov, E. S.; Beletskaya, I. P. *J. Organomet. Chem.* **1985**, *280*, C-67.

(19) (a) Foster, D. G. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III, p 777. (b) Sharpless, K. B.; Young, M. W. *J. Org. Chem.* **1975**, *40*, 947.

(20) Haller, W. S.; Irgolic, K. J. *J. Organomet. Chem.* **1972**, *38*, 97.

(21) For example, Davies, A. G.; Smith, P. J. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Eds.; Pergamon Press: Oxford, 1982; Vol. 2, pp 519–627.

niques for air-sensitive materials. The following example provides a general procedure for the reaction of **2** with carbonyl compounds mediated by lanthanoid metal. Cerium powder (0.56 g, 4 mmoL) and a trace of iodine (10 mg, 0.04 mmoL) were placed in a 50-mL two-neck round-bottom flask equipped with a magnetic stirring bar. The flask was flushed with nitrogen several times. **2a** (0.72 g, 4 mmoL) in THF (2 mL) was added to cerium through a rubber septum with a syringe. The mild exothermic reaction started in a few minutes, and then acetophenone (0.48 g, 4 mmol) in 3 mL of THF was injected into the solution. The mild exothermic reaction continued, and additional THF (5 mL) was introduced. The resulting solution was stirred at room temperature for 2 h, during which time the cerium powder was consumed almost completely and a fine black precipitate was formed. The mixture was treated with dilute HCl and extracted with diethyl ether (30 mL × 3). The extract was washed with brine and dried over $MgSO_4$. GLC analysis of the ethereal solution revealed the presence of γ-lactone (**4**; R^1 = Ph, R^2 = Me) and the pinacol coupled product (**5**; R^1 = Ph, R^2 = Me).

The solvent was removed by evaporation, and the γ-lactone was isolated by column chromatography on silica gel (hexane–diethyl ether, 1:1).

4-Methyl-4-phenyl-γ-butyrolactone: yield 0.50 g, 70%; ^1H NMR δ 1.58 (s, 3 H), 2.30 (br s, 4 H), 7.14 (br s, 5 H); IR $\nu_{C=O}$ 1787 cm^{-1}. Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86. Found: C, 74.83; H, 5.71.

4,4-Diphenyl-γ-butyrolactone: yield 0.44 g, 46%; ^1H NMR δ 2.32 (m, AA′BB′, 2 H), 2.80 (m, AA′BB<<sp, 2 H), 6.8–7.4 (m, 5 H); IR $\nu_{C=O}$ 1782 cm^{-1}. Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.39; H, 5.71.

4,4-Diethyl-γ-butyrolactone: yield 0.29 g, 51%; ^1H NMR δ 0.85 (t, *J* = 7.0 Hz, 3 H), 1.53 (q, *J* = 7.0 Hz, 2 H), 1.86 (m, AA′BB′, 2 H), 2.39 (m, AA′BB′, 2 H); IR $\nu_{C=O}$ 1782 cm^{-1}. Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.93. Found: C, 67.05; H, 9.88.

4-Hexyl-4-methyl-γ-butyrolactone: yield 0.45 g, 61%; ^1H NMR δ 0.89 (t, *J* = 7.0 Hz, 3 H), 1.37 (s, 3 H), 1.1–1.7 (m, 10 H), 2.00 (m, AA′BB′, 2 H), 2.62 (m, AA′BB′, 2 H); IR $\nu_{C=O}$ 1783 cm^{-1}. Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94. Found: C, 71.04; H, 11.07.

1-Oxaspiro[4.5]decan-2-one: yield 0.34 g, 55%; ^1H NMR δ 1.2–1.8 (m, 10 H), 2.01 (m, AA′BB′, 2 H), 2.53 (m, AA′BB′, 2 H); IR $\nu_{C=O}$ 1779 cm^{-1}. Anal. Calcd for $C_9H_{14}O_2$: C, 70.09; H, 9.15. Found: C, 70.56; H, 9.69.

1-Oxaspiro[4.6]undecan-2-one: yield 0.40 g, 60%; ^1H NMR δ 0.8–1.5 (m, 12 H), 1.61 (m, AA′BB′, 2 H), 1.95 (m, AA′BB′, 2 H); IR $\nu_{C=O}$ 1741, 1760 cm^{-1}. Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 70.86; H, 9.85.

1-Oxaspiro[4.11]hexadecan-2-one: yield 0.38 g, 40%; mp 84–85 °C; ^1H NMR δ 0.9–1.3 (m, 12 H), 1.60 (m, AA′BB′, 2 H), 2.01 (m, AA′BB′, 2 H); IR $\nu_{C=O}$ 1705, 1762 cm^{-1}. Anal. Calcd for $C_{15}H_{26}O_2$: C, 75.58; H, 10.99. Found: C, 75.18; H, 11.24.

4-(1′-Butenyl)-4-methyl-γ-butyrolactone: yield 0.43 g, 69%; ^1H NMR δ 1.41 (s, 3 H), 1.5–2.7 (m, 8 H), 5.1–5.2 (m, 2 H), 5.8–6.4 (m, 1 H); IR $\nu_{C=O}$ 1776 cm^{-1}. Anal. Calcd for $C_9H_{14}O_2$: C, 70.09; H, 9.21. Found: C, 70.68; H, 9.85.

Reaction of Diphenyl Diselenide (7a) or Ditelluride (7b) with the Cerium Ester Homoenolate. A THF (2 mL) solution of **2a** (181 mg, 1 mmoL) was added to cerium powder (170 mg, 1.2 mmoL) treated with a trace of iodine under nitrogen at room temperature with stirring. The mild exothermic reaction started in a few minutes, and the stirring was continued for 30 min. Then the reaction mixtures was gently warmed at 35 °C to complete the reaction and stirred for another 30 min. To the resulting dark brown homogeneous solution was added **7a** (312 mg, 1 mmoL) in one portion, and the solution was stirred at 25–35 °C for 5 h.

After acid hydrolysis of the solution with diluted HCl, the product was extracted with diethyl ether (30 mL × 2), washed with aqueous $Na_2S_2O_3$, and dried ($MgSO_4$). Evaporation of the solvent left a yellow oil, which was subjected to column chromatography; petroleum ether–diethyl ether (5:1) eluted the recovered **7a** (198 mg, 0.63 mmoL) (first fraction) and **8a** (second fraction).

Ethyl 3-(Phenylseleno)propionate (8a): pale yellow oil; yield 196 mg, 0.76 mmoL, 76%; R_f = 0.65 (silica gel, petroleum ether–diethyl ether, 5:1); ^1H NMR δ 1.18 (t, *J* = 7.0 Hz, 3 H), 2.60–2.95 (m, 4 H), 4.07 (q, *J* = 7.0 Hz, 2 H), 7.1–7.7 (m, 5 H); ^{13}C NMR δ 15.5 (q, CH_3), 23.1 (t, $SeCH_2$), 36.7 (t, CH_2CO), 62.0 (t, OCH_2), 128.6 (d), 130.5 (d), 130.7 (s), 134.6 (d), 173.5 (s, C=O); IR (neat) $\nu_{C=O}$ 1728 cm^{-1}. Anal. Calcd for $C_{11}H_{14}O_2Se$: C, 51.37; H, 5.49. Found: C, 51.44; H, 5.54.

Ethyl 3-(Phenyltelluro)propionate (8b): yellow oil; yield 237 mg, 0.78 mmoL, 78%; R_f = 0.65 (silica gel, petroleum, ether–diethyl ether, 5:1); ^1H NMR δ 1.18 (t, *J* = 7.0 Hz, 3 H), 2.92 (t, *J* = 4.5 Hz, 4 H), 4.07 (q, *J* = 7.0 Hz, 2 H), 7.2–7.4 (m, 3 H), 7.7–7.9 (m, 2 H); ^{13}C NMR δ 1.9 (t, $TeCH_2$), 15.5 (q, CH_3), 38.1 (t, CH_2CO), 61.9 (t, OCH_2), 112.9 (s), 129.0 (d), 130.5 (d), 140.0 (d), 174.2 (s, C=O); IR (neat) $\nu_{C=O}$ 1725 cm^{-1}. Anal. Calcd for $C_{11}H_{14}O_2Te$: C, 43.20; H, 4.61. Found: C, 43.38; H, 4.53. Recovered **7b**, 158 mg, 0.38 mmoL.

Reaction of Tri-*n*-butyltin Iodide (9) with Cerium Ester Homoenolate. The dark brown homogeneous solution of **3** (Ln = Ce, X = Br) prepared from cerium (1.4 g, 10 mmoL) and **2a** (1.81 g, 10 mmoL) in THF (20 mL) as described above was treated with **9** (2.1 g, 5 mmoL) at 0 °C. To complete the reaction, the mixture was allowed to warm to room temperature and stirred for 10 h. The solution was diluted with 50 mL of diethyl ether, and the precipitate was removed by filtration through a Celite pad. The filtrate was treated with aqueous $NaHCO_3$ (50 mL × 2) and dried ($MgSO_4$). Evaporation of the solvent left a yellow oil, which was subjected to column chromatography on silica gel; hexane–ethyl acetate (50:1) eluted ethyl 3-(tri-*n*-butylstannyl)propionate (**10**). Kugelrol distillation (oven temperature 180 °C/5 mmHg) gave pure **10** as a colorless oil (630 mg, 1.7 mmol, 34% yield based on **9**): ^1H NMR δ 0.6–1.7 (m, 32 H including t, *J* = 7.7 Hz at 1.25 ppm), 2.47 (t, *J* = 7.7 Hz, 2 H), 4.12 (q, *J* = 7.0 Hz, 2 H); ^{13}C NMR δ 4.7 (t, $SnCH_2CH_2CO_2$), 10.2 (t, $SnCH_2$), 15.0 (q), 15.6 (q, OCH_2CH_3), 28.7 (t), 30.5 (t), 32.8 (t, CH_2CO_2), 61.6 (t, OCH_2), 176.7 (s, C=O); IR (neat) $\nu_{C=O}$ 1735 cm^{-1}. Anal. Calcd for $C_{17}H_{36}O_2Sn$: C, 52.20; H, 9.27. Found: C, 52.46; H, 9.51.

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