Supporting Information

Indium(III) Chloride-Promoted Intramolecular Addition of Allylstannanes to Alkynes

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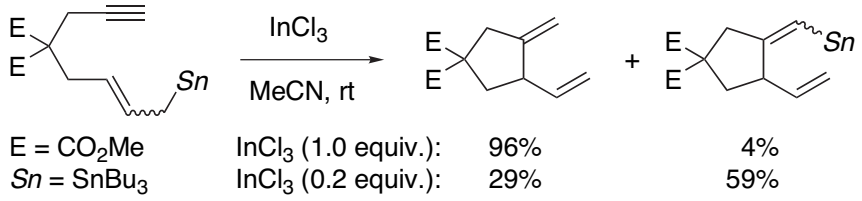

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1. General Method

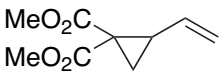
Unless otherwise noted, all reactions and distillation of solvents were carried out under N_2. Solvents were dried by distillation from sodium metal/benzophenone ketyl (THF, Et_2O, DME, 1,4-dioxane) and CaH_2 (benzene, CH_2Cl_2, MeCN, MeOH, acetone, DMF, hexane). 3-Bromo-1-propyne and dimethyl malonate were distilled from CaH_2. Me_3SiCl was distilled from *N*,*N*-dimethylaniline. 3-Buten-2-one was simply distilled before use. All other commercial reagents were used as received. Boiling points determined with Kugelrohr distillation apparatus are indicated by air-bath temperature (bath temp). ^1H and ^{13}C NMR were recorded in $CDCl_3$ or C_6D_6 at 270 and 67.7 MHz, respectively. The chemical shifts (δ) are reported with reference at 0.00 ppm (Me_4Si), 7.26 ppm ($CHCl_3$), or 7.15 ppm (C_6HD_5) for the proton and at 77.0 ppm (centered on the signal of $CDCl_3$) or 128.0 ppm (centered on the signal of C_6D_6) for the carbon. The coupling constant $J_{Sn\text{-}H}$ is corresponding to that between ^{119}Sn and ^1H nuclei.

2. Preparation of Substrates

Enynes **1a**-**c** and **1e**, bearing an allylstannane moiety, were prepared from vinylcyclopropanes **7a**-**c** by radical-mediated ring-opening reaction with Bu_3SnH followed by propargylation of the resultant allylstannanes **8a**-**c** with NaH and a propargyl bromide (Scheme S1).[1, 2] Vinylcyclopropane **7a** was derived from dimethyl malonate and 1,4-dichloro-2-butene in one step.[3a] Cyclopropanation of 3-buten-2-one (methyl vinyl ketone) and (*E*)-2-butenal (crotonaldehyde) with dimethyl bromomalonate[4, 5] and the subsequent Wittig methylenation were performed to synthesize vinylcyclopropanes **7b**-**c**. Enyne **1d** was obtained by reduction of **1a** with $LiAlH_4$ followed by methylation with MeI. Trimethylsilylation of **1a** with Me_3SiCl and *i*-Pr_2NLi afforded **1f**.

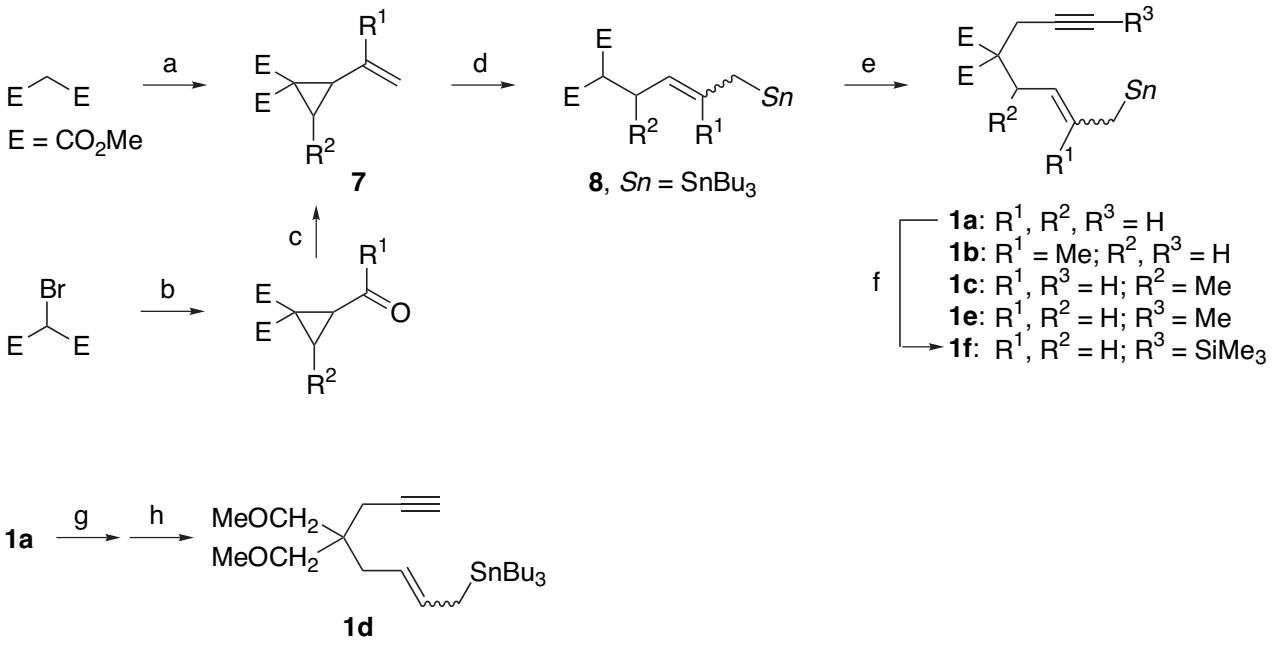
2. 1. Preparation of Cyclopropanes 7a-c

Dimethyl 2-Ethenylcyclopropane-1,1-dicarboxylate (7a): [17447-60-8].[3]



Dimethyl malonate (>95% pure, 24.1 ml, 200 mmol) was dropwise added to a solution of MeONa in MeOH, prepared from Na (9.2 g, 400 mmol) and MeOH (400 mL), over 10 min at 0 °C. The mixture was stirred at 0 °C for 10 min, then at room temperature for 20 min. The mixture was cooled to 0 °C again, and 1,4-dichloro-2-butene (25 g, 200 mmol, *E*:*Z* = *ca*. 1:1) was dropwise added over 10 min. The reaction was gradually warmed to room temperature over 12 h. The resultant mixture was evaporated and diluted with water (100 mL). The extract with *t*-BuOMe (100 mL and 50 mL) was washed by saturated aqueous NH_4Cl (50 mL), dried over Na_2SO_4, and evaporated. Purification of the

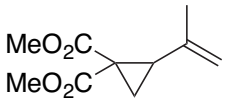
Scheme S1. Synthesis of Enynes **1a-f**



(a) NaOMe, MeOH, 1,4-dichloro-2-butene (*E*:*Z* = ca. 1:1); (b) 3-buten-2-one, DBU, benzene or (*E*)-2-butenal, NaOMe, MeOH; (c) Ph_3PCH_3Br, *t*-BuOK, THF; (d) Bu_3SnH, cat. AIBN, benzene; (e) NaH, 3-bromo-1-propyne or 1-bromo-2-butyne, DMF; (f) *i*-Pr_2NLi, Me_3SiCl, THF; (g) $LiAlH_4$, Et_2O; (h) NaH, MeI, DMF

crude product by distillation (77-82 °C, *ca*. 1 Torr) gave the title compounds (26.7 g, 96% pure, 139 mmol, 70%). ^{1}H NMR analysis of the purified product indicated 4% contamination with dimethyl 3-cyclopentene-1,1-dicarboxylate. For characterization data, see ref. 3b.

Dimethyl 2-(1-Methylethenyl)cyclopropane-1,1-dicarboxylate (7b): [61111-65-7].[6]

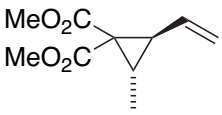


Dimethyl bromomalonate (90% pure, 21 g, 90 mmol) was dropwise added to a benzene (25 mL) solution of 3-buten-2-one (5.0 mL, 60 mmol) and DBU (16 mL, 110 mmol) over 30 min at ambient temperature (water bath).[4] The mixture was stirred for 24 h and filtered through a Celite® pad. After evaporation of the filtrate, purification of the residual oil by silica gel column chromatography (hexane-AcOEt 4:1) gave dimethyl 2-acetylcyclopropane-1,1-dicarboxylate (6.6 g, 33 mmol, 54%, [75073-94-8][7]).

THF (31 mL) was poured into a mixture of Ph_3PCH_3Br (4.82 g, 13.5 mmol) and *t*-BuOK (1.61 g,

13.5 mmol) at ambient temperature (water bath). After 1.5 h, dimethyl 2-acetylcyclopropane-1,1-dicarboxylate (2.25 g, 11.3 mmol) was added to the resultant yellow suspension. The mixture was warmed to 45 °C and stirred for 60 h. The reaction mixture was poured into saturated aqueous NH_4Cl. The extract with *t*-BuOMe was dried over Na_2SO_4 and evaporated. Purification of the crude product by silica gel column chromatography (hexane-AcOEt 7:1) gave the title compound (1.42 g, 7.16 mmol, 63%). For characterization data, see ref. 6.

Dimethyl *trans*-2-Ethenylcyclopropane-3-methyl-1,1-dicarboxylate (7c): [95054-55-0].[8]



MeONa (2.5 M in MeOH, 28 mL, 70 mmol) was dropwise added to a mixture of (*E*)-2-butenal (6.6 mL, 82 mmol), dimethyl bromomalonate (90% pure, 10 mL, 68 mmol), and MeOH (41 mL) over 30 min at 0 °C.[5] After being stirred for 16 h, the reaction mixture was evaporated and diluted with brine. The extract with *t*-BuOMe was dried over Na_2SO_4 and evaporated. Purification of the crude product by silica gel column chromatography (hexane-AcOEt 4:1) gave dimethyl *trans*-2-formyl-3-methylcyclopropane-1,1-dicarboxylate (8.48 g, 42.3 mmol, 62%).

THF (30 mL) was poured into a mixture of Ph_3PCH_3Br (6.43 g, 18.0 mmol) and *t*-BuOK (2.14 g, 18.0 mmol) at room temperature. After 1 h, a solution of dimethyl *trans*-2-formyl-3-methylcyclopropane-1,1-dicarboxylate (3.00 g, 15.0 mmol) in THF (10 mL) was dropwise added to the resultant yellow suspension at 0 °C. The mixture was stirred at 0 °C for 1 h, then at 45 °C for 4 h, and poured into saturated aqueous NH_4Cl. The extract with *t*-BuOMe was dried over Na_2SO_4 and evaporated. Purification of the crude product by silica gel column chromatography (hexane-AcOEt 7:1) gave the title compound (2.21 g, 11.1 mmol, 74%). Bp 70 °C (0.70 Torr, bath temp). IR (neat) 1732 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.14 (d, J = 6.3 Hz, 3H), 2.10 (dq, J = 7.7, 6.3 Hz, 1H), 2.41 (dd, J = 8.2, 7.7 Hz, 1H), 3.72 (s, 3H), 3.76 (s, 3H), 5.10 (dd, J = 10.0, 1.9 Hz, 1H), 5.28 (dd, J = 17.0, 1.9 Hz, 1H), 5.47 (ddd, J = 17.0, 10.0, 8.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 12.2 (CH_3), 27.0 (CH), 36.9 (CH), 41.8 (C), 52.5 (CH_3 × 2), 118.1 (CH_2), 133.1 (CH), 168.1 (C), 168.3 (C); MS *m*/*z* (relative intensity) 198 (M^+, 7.6), 167 (M^+ – OMe, 11), 59 (100).

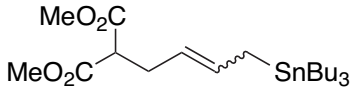
2. 2. Ring-Opening Reaction Leading to Allylstannanes 8a-c

Typical Procedure

A solution of cyclopropane **7a** (2.76 g, 15.0 mmol), Bu_3SnH (4.58 g, 15.8 mmol), and AIBN (123

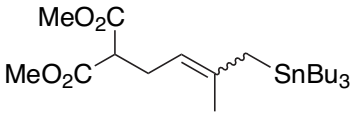
mg, 0.75 mmol) in benzene (75 mL) was stirred at 80 °C for 3 h. The resultant mixture was cooled to room temperature and evaporated. Purification of the residual oil by silica gel column chromatography (hexane-AcOEt 10:1) gave allylstannane **8a** (6.68 g, 14.1 mmol, 94%).

Dimethyl ((*E*)- and (*Z*)-4-Tributylstannyl-2-butenyl)propanedioate (8a, *E*:*Z* = 78:22)



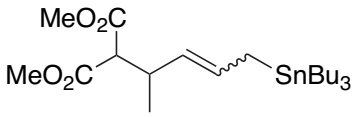
Bp 145 °C (0.40 Torr, bath temp). IR (neat) 1739 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.71–0.98 (m, 15H), 1.22–1.59 (m, 12H), 1.67 (d, *J* = 8.7 Hz, 1.56H), 1.74 (d, *J* = 9.6 Hz, 0.44H), 2.56 (dd, *J* = 7.6, 7.1 Hz, 1.56H), 2.61 (dd, *J* = 7.7, 6.9 Hz, 0.44H), 3.36 (t, *J* = 7.6 Hz, 0.78H), 3.39 (t, *J* = 7.7 Hz, 0.22H), 3.73 (s, 4.68H), 3.74 (s, 1.32H), 4.97 (dt, *J* = 10.7, 6.9 Hz, 0.22H), 5.13 (dtt, *J* = 15.0, 7.1, 1.2 Hz, 0.78H), 5.60–5.73 (m, 1H); ^{13}C NMR ($CDCl_3$) for the *E*-isomer δ 9.1 (CH_2 × 3), 13.7 (CH_3 × 3), 14.3 (CH_2), 27.3 (CH_2 × 3), 29.1 (CH_2 × 3), 32.1 (CH_2), 52.3 (CH_3 × 2), 52.5 (CH), 120.1 (CH), 133.2 (CH), 169.5 (C × 2), for the *Z*-isomer δ 9.3 (CH_2 × 3), 10.6 (CH_2), 13.7 (CH_3 × 3), 26.4 (CH_2), 27.3 (CH_2 × 3), 29.1 (CH_2 × 3), 51.8 (CH), 52.4 (CH_3 × 2), 118.5 (CH), 131.8 (CH), 169.6 (C × 2); MS *m*/*z* (relative intensity) for the *E*-isomer 419 (M^+ – Bu, 23), 417 (M^+ – 2 – Bu, 18), 415 (M^+ – 4 – Bu, 10), 179 (100), for the *Z*-isomer 419 (M^+ – Bu, 21), 417 (M^+ – 2 – Bu, 21), 415 (M^+ – 4 – Bu, 10), 73 (100). Anal. Calcd for $C_{21}H_{40}O_4Sn$: C, 53.07; H, 8.48. Found: C, 53.17; H, 8.43.

Dimethyl ((*E*)- and (*Z*)-3-Methyl-4-tributylstannyl-2-butenyl)propanedioate (8b, *E*:*Z* or *Z*:*E* = 65:35)



99% yield from **1b**. Bp 150 °C (0.40 Torr, bath temp). IR (neat) 1739 (C=O) cm^{-1}; ^1H NMR (C_6D_6) δ 0.82–1.06 (m, 15H), 1.29–1.70 (m, 15H), 1.79 (s, 0.70H), 1.86 (s, 1.30 H), 2.80–2.89 (m, 2H), 3.31 (s, 3.9H), 3.33 (s, 2.1H), 3.44 (t, *J* = 7.6 Hz, 0.35H), 3.51 (t, *J* = 7.8 Hz, 0.65H), 5.01 (tm, *J* = 7.0 Hz, 0.65H), 5.12 (tm, *J* = 7.4 Hz, 0.35H); ^{13}C NMR (C_6D_6) for the major isomer δ 10.0 (CH_2 × 3), 13.9 (CH_3 × 3), 15.6 (CH_2), 26.2 (CH_3), 27.8 (CH_2 × 3), 28.5 (CH_2), 29.5 (CH_2 × 3), 51.9 (CH_3 × 2), 52.3 (CH), 115.6 (CH), 138.7 (C), 169.5 (C × 2), for the minor isomer δ 9.7 (CH_2 × 3), 13.9 (CH_3 × 3), 18.7 (CH_3), 22.5 (CH_2), 27.8 (CH_2 × 3), 28.4 (CH_2), 29.5 (CH_2 × 3), 51.9 (CH_3 × 2), 52.7 (CH), 116.0 (CH), 138.7 (C), 169.4 (C × 2). Anal. Calcd for $C_{22}H_{42}O_4Sn$: C, 54.01; H, 8.65. Found: C, 54.18; H, 8.53.

Dimethyl ((*E*)- and (*Z*)-1-Methyl-4-tributylstannyl-2-butenyl)propanedioate (8c, *E*:*Z* = 87:13)



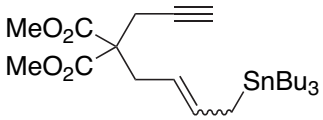
93% from **1c**. Bp 155 °C (0.40 Torr, bath temp). IR (neat) 1739 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.72–0.96 (m, 15H), 1.04 (d, *J* = 6.8 Hz, 3H), 1.19–1.73 (m, 14H), 2.80–2.94 (m, 1H), 3.24 (d, *J* = 9.1 Hz, 1H), 3.68 (s, 0.39H), 3.69 (s, 2.61H), 3.72 (s, 2.61H), 3.73 (s, 0.39H), 4.86–4.94 (m, 0.13H), 5.11 (dd, *J* = 15.0, 8.4 Hz, 0.87H), 5.55 (td, *J* = 10.7, 7.6 Hz, 0.13H), 5.64 (dt, *J* = 15.0, 8.9 Hz, 0.87H); ^{13}C NMR ($CDCl_3$) for the *E*-isomer δ 8.9 (CH_2 × 3), 13.5 (CH_3 × 3), 14.1 (CH_2), 18.8 (CH_3), 27.2 (CH_2 × 3), 29.0 (CH_2 × 3), 37.4 (CH), 51.9 (CH_3), 52.0 (CH_3), 58.1 (CH), 126.2 (CH), 130.8 (CH), 168.6 (C), 168.7 (C), for the *Z*-isomer δ 9.1 (CH_2 × 3), 10.4 (CH_2), 13.5 (CH_3 × 3), 18.8 (CH_3), 27.2 (CH_2 × 3), 29.0 (CH_2 × 3), 31.7 (CH), 51.9 (CH_3), 52.0 (CH_3), 57.7 (CH), 125.3 (CH), 129.8 (CH), 168.7 (C), 168.8 (C). Anal. Calcd for $C_{22}H_{42}O_4Sn$: C, 54.01; H, 8.65. Found: C, 54.16; H, 8.59.

2. 3. Preparation of Enynes 1a-f

Typical Procedure for Propargylation of Allylstannanes 8

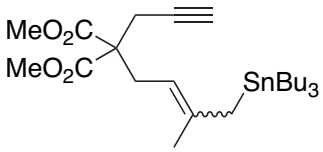
NaH (60% in mineral oil, 576 mg, 14.4 mmol) was washed with dry hexane (2 × 3 mL). After introduction of DMF (24 mL), the suspension was stirred at 0 °C, and allylstannane **8a** (*E*:*Z* = 78:22, 4.28 g, 9.00 mmol) was added slowly. After 30 min, the mixture was warmed to room temperature and stirred for 1.5 h. The resultant mixture was cooled to 0 °C again, and 3-bromo-1-propyne (1.36 mL, 18.0 mmol) was added. After 30 min, the mixture was warmed to room temperature and stirred for 11 h. The reaction mixture was poured into water. The extract with *t*-BuOMe was dried over Na_2SO_4 and evaporated. Purification of the residual oil by silica gel column chromatography (hexane-AcOEt 20:1) gave enyne **1a** (6.06 g, 11.8 mmol, 99%, *E*:*Z* = 81:19).

Dimethyl (2-Propynyl)((*E*)- and (*Z*)-4-tributylstannyl-2-butenyl)propanedioate (1a, *E*:*Z* = 81:19): [259879-46-4] for E-isomer.[9]



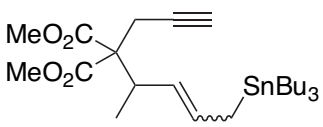
Bp 150 °C (0.45 Torr, bath temp). IR (neat) 3313 (sp-C-H), 1741 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.73–0.97 (m, 15H), 1.23–1.55 (m, 12H), 1.69 (d, *J* = 8.6 Hz, 1.6 H), 1.79 (d, *J* = 8.9 Hz, 0.4 H), 1.99 (t, *J* = 2.6 Hz, 1H), 2.73 (d, *J* = 7.1 Hz, 2H), 2.77 (d, *J* = 2.6 Hz, 1.6H), 2.81 (d, *J* = 2.6 Hz, 0.4H), 3.73 (s, 4.8H), 3.74 (s, 1.2H), 4.81 (dt, *J* = 10.7, 7.1 Hz, 0.2H), 4.94 (dtt, *J* = 14.8, 7.4, 1.2 Hz, 0.8H), 5.66–5.79 (m, 1H); ^{13}C NMR (C_6D_6) for the *E*-isomer δ 9.4 (CH_2 × 3), 13.9 (CH_3 × 3), 14.8 (CH_2), 23.0 (CH_2), 27.7 (CH_2 × 3), 29.5 (CH_2 × 3), 36.0 (CH_2), 52.2 (CH_3 × 2), 57.5 (C), 71.8 (CH), 79.4 (C), 118.4 (CH), 135.6 (CH), 170.2 (C × 2), for the *Z*-isomer δ 9.7 (CH_2 × 3), 11.1 (CH_2), 13.9 (CH_3 × 3), 23.1 (CH_2), 27.7 (CH_2 × 3), 29.5 (CH_2 × 3), 30.2 (CH_2), 52.3 (CH_3 × 2), 57.5 (C), 71.6 (CH), 79.8 (C), 116.7 (CH), 133.8 (CH), 170.2 (C × 2). Anal. Calcd for $C_{24}H_{42}O_4Sn$: C, 56.16; H, 8.25. Found: C, 56.07; H, 8.30.

Dimethyl ((*E*)- and (*Z*)-3-Methyl-4-tributylstannyl-2-butenyl)(2-propynyl)propanedioate (1b, *E*:*Z* = 65:35 or 35:65)



98% from **8b**. Bp 160 °C (0.40 Torr, bath temp). IR (neat) 3313 (sp-C-H), 1739 (C=O) cm^{-1}; ^1H NMR (C_6D_6) δ 0.81–1.09 (m, 15H), 1.30–1.78 (m, 16H), 1.83 (s, 0.7H), 1.97 (s, 1.3H), 3.11 (d, *J* = 2.8 Hz, 0.7H), 3.12 (d, *J* = 2.8 Hz, 1.3H), 3.18 (d, *J* = 7.5 Hz, 1.3H), 3.23 (d, *J* = 8.3 Hz, 0.7H), 3.34 (s, 3.9H), 3.35 (s, 2.1H), 4.92 (t, *J* = 7.5 Hz, 0.65H), 5.06 (t, *J* = 8.3 Hz, 0.35H); ^{13}C NMR (C_6D_6) for the major isomer δ 10.0 (CH_2 × 3), 13.9 (CH_3 × 3), 15.9 (CH_2), 23.1 (CH_2), 26.5 (CH_3), 27.8 (CH_2 × 3), 29.5 (CH_2 × 3), 31.6 (CH_2), 52.2 (CH_3 × 2), 57.7 (C), 71.6 (CH), 80.0 (C), 112.7 (CH), 140.8 (C), 170.4 (C × 2), for the minor isomer δ 9.7 (CH_2 × 3), 13.9 (CH_3 × 3), 19.0 (CH_3), 22.8 (CH_2), 23.0 (CH_2), 27.8 (CH_2 × 3), 29.5 (CH_2 × 3), 31.6 (CH_2), 52.2 (CH_3 × 2), 57.7 (C), 71.6 (CH), 79.8 (C), 113.2 (CH), 140.9 (C), 170.4 (C × 2). Anal. Calcd for $C_{25}H_{44}O_4Sn$: C, 56.94; H, 8.41. Found: C, 57.04; H, 8.17.

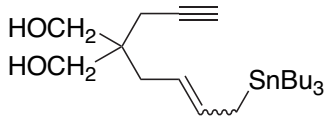
Dimethyl ((*E*)- and (*Z*)-1-Methyl-4-tributylstannyl-2-butenyl)(2-propynyl)propanedioate (1c, *E*:*Z* = 87:13)



95% from **1c**. Bp 160 °C (0.40 Torr, bath temp). IR (neat) 3313 (sp-C-H), 1736 (C=O) cm^{-1}; ^1H

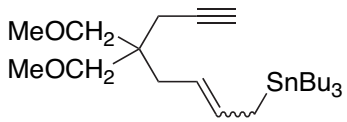
NMR (C_6D_6) δ 0.83–1.07 (m, 15H), 1.30–1.89 (m, 18H), 3.01 (dd, *J* = 17.0, 2.8 Hz, 0.87H), 3.03 (dd, *J* = 17.0, 2.8 Hz, 0.13H), 3.10 (dd, *J* = 17.0, 2.8 Hz, 0.87H), 3.19 (dd, *J* = 17.0, 2.8 Hz, 0.13H), 3.34–3.44 (m, 7H) including 3.34 (s) and 3.40 (s), 5.15 (t, *J* = 10.9 Hz, 0.13H), 5.31 (dd, *J* = 14.9, 9.3 Hz, 0.87H), 5.72 (td, *J* = 10.9, 7.3 Hz, 0.13H), 5.88 (dt, *J* = 14.9, 8.6 Hz, 0.87H); ^{13}C NMR (C_6D_6) for the *E*-isomer δ 9.4 (CH_2 × 3), 13.9 (CH_3 × 3), 14.6 (CH_2), 18.5 (CH_3), 24.9 (CH_2), 27.7 (CH_2 × 3), 29.6 (CH_2 × 3), 41.1 (CH), 51.7 (CH_3), 51.9 (CH_3), 60.9 (C), 71.6 (CH), 80.0 (C), 125.8 (CH), 132.5 (CH), 170.0(C), 170.2 (C), for the *Z*-isomer δ 9.7 (CH_2 × 3), 11.1 (CH_2), 13.9 (CH_3 × 3), 18.1 (CH_3), 24.5 (CH_2), 27.7 (CH_2 × 3), 29.6 (CH_2 × 3), 35.2 (CH), 51.7 (CH_3), 51.9 (CH_3), 61.1 (C), 71.5 (CH), 80.7 (C), 124.9 (CH), 131.0 (CH), 170.0 (C), 170.2 (C); MS *m/z* (relative intensity) for the *E*-isomer 471 (M^+ – Bu, 33), 469 (M^+ – 2 – Bu, 24), 467 (M^+ – 4 – Bu, 14), 73 (100). Anal. Calcd for $C_{25}H_{44}O_4Sn$: C, 56.94; H, 8.41. Found: C, 57.06; H, 8.35.

2-(2-Propynyl)-2-((*E*)- and (*Z*)-4-tributylstannyl-2-butenyl)-1,3-propanediol (*E*:*Z* = 80:20)



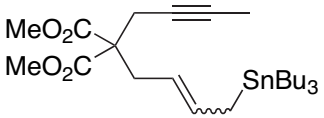
Enyne **1a** (2.57 g, 5.00 mmol) was slowly added to a suspension of $LiAlH_4$ (270 mg, 7.1 mmol) in Et_2O (15 mL) at 0 °C. The mixture was stirred at 0 °C for 1 h, then at room temperature for 2 h. The reaction mixture was subjected to an aqueous workup using aqueous NH_4Cl and *t*-BuOMe. Purification of the crude product by silica gel column chromatography (hexane-AcOEt 2:1) gave the title compound (2.08 g, 4.55 mmol, 91%, *E*:*Z* = 80:20). Bp 160 °C (0.40 Torr, bath temp). IR (neat) 3400 (br s, OH) 3311 (sp-C-H) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.78–0.98 (m, 15H), 1.23–1.57 (m, 12H), 1.71 (d, *J* = 8.2 Hz, 1.6H), 1.77 (d, *J* = 10.0 Hz, 0.4 H), 2.00–2.11 (m, 5H), 2.25 (d, *J* = 2.6 Hz, 1.6H), 2.31 (d, *J* = 2.6 Hz, 0.4H), 3.59–3.70 (m, 4H), 4.98–5.24 (m, 1H), 5.58–5.78 (m, 1H); ^{13}C NMR (C_6D_6) for the *E*-isomer δ 9.5 (CH_2 × 3), 13.9 (CH_3 × 3), 14.5 (CH_2), 21.6 (CH_2), 27.7 (CH_2 × 3), 29.6 (CH_2 × 3), 35.0 (CH_2), 42.7 (C), 67.3 (CH_2 × 2), 70.8 (CH), 81.6 (C), 120.3 (CH), 133.6 (CH), for the *Z*-isomer δ 9.7 (CH_2 × 3), 10.9 (CH_2), 13.9 (CH_3 × 3), 21.8 (CH_2), 27.7 (CH_2 × 3), 29.2 (CH_2), 29.6 (CH_2 × 3), 43.0 (C), 67.2 (CH_2 × 2), 70.8 (CH), 81.8 (C), 118.8 (CH), 131.9 (CH). Anal. Calcd for $C_{22}H_{42}O_2Sn$: C, 57.78; H, 9.26. Found: C, 57.96; H, 9.14.

(*E*)- and (*Z*)-4,4-Bis(methoxymethyl)-8-tributylstannyl-6-octen-1-yne (1d, *E*:*Z* = 80:20)



NaH (60% in mineral oil, 218 mg, 5.45 mmol) was washed with dry hexane (2 × 3 mL). After introduction of DMF (9.7 mL), the suspension was stirred at 0 °C, and 2-(2-propynyl)-2-((*E*)- and (*Z*)-4-tributylstannyl-2-butenyl)-1,3-propanediol (830 g, 1.81 mmol) was added slowly. The mixture was stirred at 0 °C for 10 min, then at room temperature for 30 min. MeI (0.56 mL, 9.0 mmol) was added to the mixture at 0 °C, which was warmed to room temperature after 10 min. After 36 h, the resultant mixture was subjected to an aqueous workup using aqueous NH_4Cl and *t*-BuOMe. Purification of the crude product by silica gel column chromatography (hexane-AcOEt 10:1) gave the title compound **1d** (822 mg, 1.69 mmol, 94%, *E*:*Z* = 80:20). Bp 145 °C (0.45 Torr, bath temp). IR (neat) 3311 (sp-C-H) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.76–0.97 (m, 15H), 1.23–1.37 (m, 6H), 1.43–1.56 (m, 6H), 1.71 (d, *J* = 8.9 Hz, 1.6 H), 1.78 (d, *J* = 9.0 Hz, 0.4 H), 1.93–1.96 (m, 1H), 2.07 (d, *J* = 7.3 Hz, 1.6H), 2.11 (d, *J* = 7.7 Hz, 0.4H), 2.17 (d, *J* = 2.6 Hz, 1.6H), 2.22 (d, *J* = 2.8 Hz, 0.4H), 3.19–3.27 (m, 4H), 3.33 (s, 6H), 5.00–5.22 (m, 1H), 5.55–5.73 (m, 1H); ^{13}C NMR (C_6D_6) for the *E*-isomer δ 9.5 (CH_2 × 3), 13.9 (CH_3 × 3), 14.7 (CH_2), 22.4 (CH_2), 27.8 (CH_2 × 3), 29.6 (CH_2 × 3), 35.4 (CH_2), 42.6 (C), 59.0 (CH_3 × 2), 70.4 (CH), 74.6 (CH_2 × 2), 81.7 (C), 121.0 (CH), 133.2 (CH), for the *Z*-isomer δ 9.7 (CH_2 × 3), 10.7 (CH_2), 13.9 (CH_3 × 3), 22.6 (CH_2), 27.8 (CH_2 × 3), 29.5 (CH_2), 29.6 (CH_2 × 3), 42.8 (C), 58.9 (CH_3 × 2), 70.4 (CH), 74.5 (CH_2 × 2), 81.9 (C), 119.3 (CH), 131.6 (CH). Anal. Calcd for $C_{24}H_{46}O_2Sn$: C, 59.39; H, 9.55. Found: C, 59.26; H, 9.37.

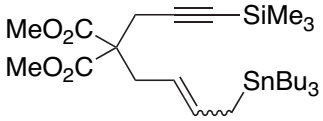
Dimethyl (2-Butynyl)((*E*)- and (*Z*)-4-tributylstannyl-2-butenyl)propanedioate (1e, *E*:*Z* = 79:21)



According to the typical procedure, the title compound can be synthesized from **1a** and 1-bromo-2-butyne in 95% yield (*E*:*Z* = 79:21). Bp 150 °C (0.45 Torr, bath temp). IR (neat) 1741 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.73–0.99 (m, 15H), 1.23–1.60 (m, 12H), 1.69 (d, *J* = 8.6 Hz, 1.58H), 1.74–1.81 (m, 3.42H), 2.66–2.78 (m, 4H), 3.72 (s, 6H), 4.81 (dt, *J* = 10.7, 7.4 Hz, 0.21H), 4.95 (dtt, *J* = 15.0, 7.4, 1.2 Hz, 0.79H), 5.64–5.79 (m, 1H); ^{13}C NMR ($CDCl_3$) for the *E*-isomer δ 3.4 (CH_3), 9.1 (CH_2 × 3), 13.7 (CH_3 × 3), 14.5 (CH_2), 22.7 (CH_2), 27.3 (CH_2 × 3), 29.1 (CH_2 × 3), 35.4 (CH_2), 52.5 (CH_3 × 2), 57.5 (C), 73.5 (C), 78.5 (C), 117.7 (CH), 135.0 (CH), 170.7 (C × 2), for the *Z*-isomer δ 3.4 (CH_3), 9.4 (CH_2 × 3), 10.7 (CH_2), 13.7 (CH_3 × 3), 22.9 (CH_2), 27.3 (CH_2 × 3), 29.1 (CH_2 × 3), 29.5 (CH_2), 52.5 (CH_3 × 2),

57.4 (C), 73.9 (C), 77.2 (C), 116.2 (CH), 133.3 (CH), 170.8 (C × 2); MS *m*/*z* (relative intensity) for the *E*-isomer 471 (M^+ – Bu, 40), 469 (M^+ – 2 – Bu, 27), 467 (M^+ – 4 – Bu, 15), 177 (100), for the *Z*-isomer 471 (M^+ – Bu, 14), 469 (M^+ – 2 – Bu, 9.2), 467 (M^+ – 4 – Bu, 5.1), 73 (100). Anal. Calcd for $C_{25}H_{44}O_4Sn$: C, 56.94; H, 8.41. Found: C, 56.89; H, 8.44.

Dimethyl ((*E*)- and (*Z*)-4-Tributylstannyl-2-butenyl)(3-trimethylsilyl-2-propynyl)propanedioate (1f, *E*:*Z* = 85:15): [259879-46-4] for *E*-isomer.[9]



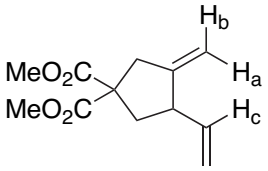
A THF solution of *i*-Pr_2NLi was prepared by the reaction of *i*-Pr_2NH (0.46 mL, 3.3 mmol) with BuLi (1.66 M in hexane, 2.0 mL, 3.3 mmol) in THF (3 mL) at 0 °C for 1 h. Enyne **1a** was dropwise added to the solution of *i*-Pr_2NLi at –78 °C. After 2 h, Me_3SiCl (0.42 mL, 3.3 mmol) was dropwise added to the mixture, which was gradually warmed to room temperature. After 48 h from the addition of Me_3SiCl, the resultant mixture was subjected to an aqueous workup using aqueous $NaHCO_3$ and *t*-BuOMe. Purification of the crude product by silica gel column chromatography (hexane-AcOEt 30:1) gave the title product (757 mg, 1.29 mmol, 43%, *E*:*Z* = 85:15). Bp 160 °C (0.40 Torr, bath temp). IR (neat) 1741 (C=O) cm^{-1}; ^1H NMR (C_6D_6) δ 0.18 (s, 7.65H), 0.19 (s, 1.35H), 0.82–1.05 (m, 15H), 1.30–1.68 (m, 12H), 1.75 (d, *J* = 8.4 Hz, 1.7H), 1.99 (d, *J* = 10.2 Hz, 0.3H), 3.17–3.29 (m, 4H), 3.34 (s, 0.9H), 3.35 (s, 5.1H), 5.11 (dt, *J* = 10.6, 7.4 Hz, 0.15H), 5.26 (dtt, *J* = 14.8, 7.7, 1.2 Hz, 0.85H), 5.79–6.03 (m, 1H); ^{13}C NMR (C_6D_6) for the *E*-isomer δ 0.1 (CH_3 × 3), 9.4 (CH_2 × 3), 13.9 (CH_3 × 3), 14.8 (CH_2), 24.4 (CH_2), 27.7 (CH_2 × 3), 29.5 (CH_2 × 3), 36.1 (CH_2), 52.2 (CH_3 × 2), 57.8 (C), 88.3 (C), 102.6 (C), 118.6 (CH), 135.5 (CH), 170.3 (C × 2), for the *Z*-isomer δ 0.1 (CH_3 × 3), 9.7 (CH_2 × 3), 11.2 (CH_2), 13.9 (CH_3 × 3), 24.4 (CH_2), 27.8 (CH_2 × 3), 29.6 (CH_2 × 3), 30.3 (CH_2), 52.2 (CH_3 × 2), 57.8 (C), 88.0 (C), 103.0 (C), 117.1 (CH), 133.8 (CH), 170.3 (C × 2). Anal. Calcd for $C_{27}H_{50}O_4SiSn$: C, 55.39; H, 8.61. Found: C, 55.15; H, 8.46.

3. $InCl_3$-Promoted Cyclization

Typical Procedure

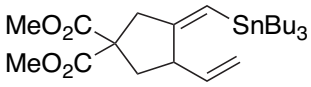
See the text.

Dimethyl 3-Ethenyl-4-methylenecyclopentane-1,1-dicarboxylate (2a): [109433-02-5].[9]



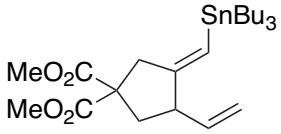
For the characterization data, see ref. 9. On the basis of NOE experiments, the chemical shifts of the *exo*-methylene protons H_a and H_b were determined to be 4.82 and 4.99 ppm, respectively. Irradiation of H_a showed a 2.4% enhancement of the internal vinyl proton H_c. This assignment agrees with the result of protiodestannylation of (*E*)-**3a** with DCl/D_2O (vide infra).

Dimethyl 3-Ethenyl-4-((*Z*)-tributylstannylmethylene)cyclopentane-1,1-dicarboxylate ((*Z*)-3a)



Bp 160 °C (0.40 Torr, bath temp). IR (neat) 1738 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.72–0.97 (m, 15H), 1.19–1.57 (m, 12H), 2.10 (dd, *J* = 13.2, 7.7 Hz, 1H), 2.66 (ddd, *J* = 13.2, 7.9, 1.3 Hz, 1H), 2.95 (d, *J* = 16.8 Hz, 1H), 3.11–3.21 (m, 2H), 3.71 (s, 3H), 3.73 (s, 3H), 4.99–5.11 (m, 2H), 5.68 (ddd, *J* = 17.1, 10.0, 7.4 Hz, 1H), 5.81 (q, *J* = 1.7 Hz, $^2J_{Sn-H}$ = 56.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 10.8 (CH_2 × 3), 13.7 (CH_3 × 3), 27.3 (CH_2 × 3), 29.1 (CH_2 × 3), 41.1 (CH_2), 44.7 (CH_2), 48.2 (CH), 52.7 (CH_3), 52.7 (CH_3), 58.7 (C), 115.7 (CH_2), 122.3 (CH), 140.4 (CH), 158.8 (C), 172.1 (C × 2). Anal. Calcd for $C_{24}H_{42}O_4Sn$: C, 56.16; H, 8.25. Found: C, 56.21; H, 8.37.

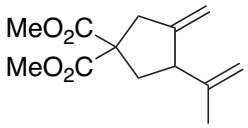
Dimethyl 3-Ethenyl-4-((*E*)-tributylstannylmethylene)cyclopentane-1,1-dicarboxylate ((*E*)-3a)



The analytical sample was prepared by homolytic intramolecular allylstannylation of **1a**.[1] Bp 160 °C (0.40 Torr, bath temp). IR (neat) 1738 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.78–1.03 (m, 15H), 1.23–1.58 (m, 12H), 2.02 (dd, *J* = 12.9, 11.0 Hz, 1H), 2.61 (ddd, *J* = 12.9, 7.7, 1.5 Hz, 1H), 2.90 (dt, *J* = 16.8, 2.3 Hz, 1H), 3.00 (d, J = 16.8 Hz, 1H), 3.11–3.23 (m, 1H), 3.73 (s, 3H), 3.74 (s, 3H), 5.04 (ddd, *J* = 16.6, 2.0, 0.8 Hz, 1H), 5.07 (ddd, *J* = 10.4, 2.0, 0.4 Hz, 1H), 5.61 (ddd, *J* = 16.6, 10.4, 8.2 Hz, 1H), 5.66 (q, *J* = 2.3 Hz, $^2J_{Sn-H}$ = 65.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 9.7 (CH_2 × 3), 13.6 (CH_3 × 3), 27.2 (CH_2 × 3), 29.1 (CH_2 × 3), 40.3 (CH_2), 42.3 (CH_2), 50.2 (CH), 52.7 (CH_3 × 2), 58.6 (C), 115.9 (CH_2), 120.6 (CH), 139.7 (CH), 158.9 (C), 172.0 (C), 172.1 (C); MS *m/z* (relative intensity) 457 (M^+ – Bu, 27), 455 (M^+ – 2 – Bu,

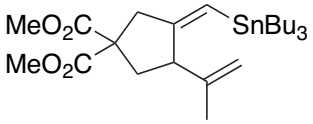
21), 453 (M^+ – 4 – Bu, 12), 73 (100). Anal. Calcd for $C_{24}H_{42}O_4Sn$: C, 56.16; H, 8.25. Found: C, 55.97; H, 8.23. The stereochemical assignment is based on NOE experiments in C_6D_6. Irradiation of the proton α to the stannyl group made a 7% enhancement of the internal vinyl proton.

Dimethyl 3-Methylene-4-(1-methylethenyl)cyclopentane-1,1-dicarboxylate (2b): [122941-18-8].[10]



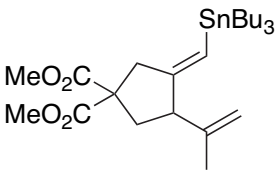
For the characterization data, see ref. 10.

Dimethyl 3-(1-Methylethenyl)-4-((*Z*)-tributylstannylmethylene)cyclopentane-1,1-dicarboxylate ((*Z*)-3b)



Bp 160 °C (0.40 Torr, bath temp). IR (neat) 1738 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.69–0.94 (m, 15H), 1.20–1.51 (m, 12H), 1.69 (s, 3H), 2.11 (dd, *J* = 13.1, 7.5 Hz, 1H), 2.66 (ddd, *J* = 13.2, 8.4, 1.6 Hz, 1H), 2.90 (d, *J* = 15.8 Hz, 1H), 3.12–3.21 (m, 2H), 3.69 (s, 3H), 3.71 (s, 3H), 4.74 (br s, 1H), 4.81 (br s, 1H), 5.90 (br s, $^2J_{Sn\text{-}H}$ = 57.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 10.0 (CH_2 × 3), 13.7 (CH_3 × 3), 19.6 (CH_3), 27.4 (CH_2 × 3), 29.1 (CH_2 × 3), 39.7 (CH_2), 46.0 (CH_2), 51.2 (CH), 52.6 (CH_3), 52.7 (CH_3), 59.1 (C), 112.5 (CH_2), 123.3 (CH), 146.4 (C), 158.3 (C), 172.0 (C × 2). Anal. Calcd for $C_{25}H_{44}O_4Sn$: C, 56.94; H, 8.41. Found: C, 57.11; H, 8.10.

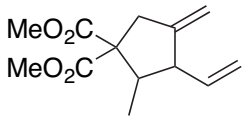
Dimethyl 3-(1-Methylethenyl)-4-((*E*)-tributylstannylmethylene)cyclopentane-1,1-dicarboxylate ((*E*)-3b): [313664-01-6].[11]



For the characterization data, see ref. 11.

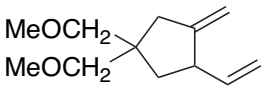
Dimethyl *cis*- and *trans*-3-Ethenyl-2-methyl-4-methylenecyclopentane-1,1-dicarboxylate (2c,

***cis*:*trans* = 47:53):** [95123-95-8] for *trans*-isomer; [95123-94-7] for *cis*-isomer.[12]



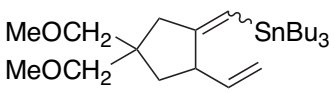
Bp 150 °C (0.45 Torr, bath temp). IR (neat) 1741 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.77 (d, J = 7.2 Hz, 1.41H), 1.04 (d, J = 6.8 Hz, 1.59H), 2.34 (dq, *J* = 11.7, 6.8 Hz, 0.53H), 2.74 (dq, *J* = 17.3, 2.5 Hz, 0.53H), 2.76–2.99 (m, 1.47H), 3.17 (dm, J = 17.3 Hz, 0.53H), 3.29 (dq, *J* = 18.0, 2.5 Hz, 0.47H), 3.37–3.45 (m, 0.47H), 3.72 (s, 1.41H), 3.73 (s, 3H), 3.74 (s, 1.59H), 4.78–4.82 (m, 1H), 4.92–4.99 (m, 1H), 5.03–5.18 (m, 2H), 5.51 (ddd, *J* = 16.8, 10.0, 8.6 Hz, 0.53H), 5.59 (ddd, *J* = 16.6, 10.4, 9.0 Hz, 0.47H); ^{13}C NMR ($CDCl_3$) for the *trans*-isomer δ 14.3 (CH_3), 40.4 (CH_2), 45.9 (CH), 52.0 (CH_3), 52.4 (CH_3), 55.1 (CH), 61.5 (C), 107.5 (CH_2), 117.7 (CH_2), 138.5 (CH), 150.0 (C), 171.6 (C), 172.1 (C), for the *cis*-isomer δ 11.5 (CH_3), 37.5 (CH_2), 43.4 (CH), 52.4 (CH_3), 52.5 (CH), 52.7 (CH_3), 62.9 (C), 109.3 (CH_2), 118.1 (CH_2), 136.5 (CH), 149.6 (C), 170.4 (C), 172.2 (C); MS *m*/*z* (relative intensity) for the *trans*-isomer 238 (M^+, 1.4), 119 (100), for the *cis*-isomer 238 (M^+, 1.2), 119 (100). Anal. Calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61. Found: C, 65.39; H, 7.48.

3-Ethenyl-1,1-bis(methoxymethyl)-4-methylenecyclopentane (2d)



Bp 95 °C (30 Torr, bath temp). IR (neat) 1110 (C-O-C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.36 (dd, *J* = 13.0, 10.4 Hz, 1H), 1.90 (dd, *J* = 13.0, 8.4 Hz, 1H), 2.19–2.35 (m, 2H), 3.06–3.18 (m, 1H), 3.21–3.28 (m, 4H), 3.33 (s, 3H), 3.34 (s, 3H), 4.76 (qd, *J* = 2.0, 1.0 Hz, 1H), 4.88–4.91 (m, 1H), 4.99–5.06 (m, 2H), 5.59–5.72 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 38.4 (CH_2), 39.2 (CH_2), 46.0 (C), 47.3 (CH), 59.20 (CH_3), 59.23 (CH_3), 75.5 (CH_2), 77.0 (CH_2), 106.9 (CH_2), 114.7 (CH_2), 140.7 (CH), 153.7 (C); MS *m*/*z* (relative intensity) 165 (M^+ – MeO, 0.17), 164 (M^+ – MeOH, 1.0), 45 (100). Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.62; H, 9.95.

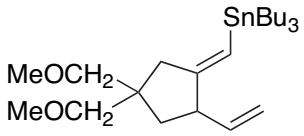
3-Ethenyl-1,1-bis(methoxymethyl)-4-((*E*)- and (*Z*)-tributylstannylmethylene)cyclopentane (3d, *E*:*Z* = 34:66)



Bp 165 °C (0.40 Torr, bath temp). IR (neat) 1115 (C-O-C) cm^{-1}; ^1H NMR (C_6D_6) δ 0.91–1.17 (m,

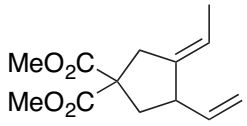
15H), 1.32–1.47 (m, 6H), 1.54–1.74 (m, 7H), 2.06–2.17 (m, 1H), 2.49–2.68 (m, 2H), 3.12 (s, 2H), 3.13 (s, 2H), 3.137 (s, 1H), 3.140 (s, 1H), 3.23–3.33 (m, 5H), 5.00 (ddd, J = 10.1, 1.8, 1.0 Hz, 0.66H), 5.03–5.16 (m, 1.34H), 5.72–5.92 (m, 1H), 5.97–6.10 (m, 1H); ^{13}C NMR ($CDCl_3$) for the *Z*-isomer δ 11.1 (CH_2 × 3), 14.0 (CH_3 × 3), 27.7 (CH_2 × 3), 29.7 (CH_2 × 3), 39.6 (CH_2), 44.4 (CH_2), 46.7 (C), 48.8 (CH), 58.9 (CH_3), 59.0 (CH_3), 75.5 (CH_2), 77.1 (CH_2), 114.3 (CH_2), 120.7 (CH), 142.8 (CH), 163.7 (C), for the *E*-isomer δ 10.1 (CH_2 × 3), 13.9 (CH_3 × 3), 27.7 (CH_2 × 3), 29.7 (CH_2 × 3), 38.9 (CH_2), 41.8 (CH_2), 46.6 (C), 50.7 (CH), 58.9 (CH_3), 59.0 (CH_3), 75.8 (CH_2), 77.2 (CH_2), 114.9 (CH_2), 118.9 (CH), 141.8 (CH), 163.7 (C). Anal. Calcd for $C_{24}H_{46}O_2Sn$: C, 59.39; H, 9.55. Found: C, 59.35; H, 9.36.

3-Ethenyl-1,1-bis(methoxymethyl)-4-((*E*)-tributylstannylmethylene)cyclopentane ((*E*)-3d)



The analytical sample was prepared by homolytic intramolecular allylstannylation of **1d**.[1] ^{1}H NMR (C_6D_6) δ 0.89–1.20 (m, 15H), 1.32–1.46 (m, 6H), 1.50–1.79 (m, 7H), 2.10 (dd, J = 12.9, 8.4 Hz, 1H), 2.48–2.63 (m, 2H), 3.14 (s, 6H), 3.26–3.36 (m, 5H), 5.01–5.09 (m, 2H), 5.79 (ddd, J = 17.5, 9.2, 8.1 Hz, 1H), 5.99 (q, J = 2.2 Hz, $^2J_{Sn\text{-}H}$ = 71.8 Hz, 1H). The geometry of the vinylstannane moiety was deduced from the result of the radical-induced cyclization of **1a** (see the characterization data for (*E*)-**3a**).[1]

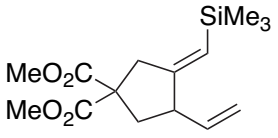
Dimethyl (*E*)-3-Ethenyl-4-ethylidenecyclopentane-1,1-dicarboxylate (2e)



Bp 70 °C (0.40 Torr, bath temp). IR (neat) 1736 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.60 (ddt, J = 6.8, 2.4, 1.7 Hz, 3H), 1.95 (dd, J = 12.8, 11.4 Hz, 1H), 2.54 (ddd, J = 12.8, 7.2, 1.6 Hz, 1H), 2.85 (dm, J = 17.3 Hz, 1H), 2.98–3.17 (m, 2H), 3.73 (s, 3H), 3.75 (s, 3H), 4.99–5.07 (m, 2H), 5.16–5.26 (m, 1H), 5.57 (ddd, J = 17.6, 9.4, 8.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.5 (CH_3), 36.8 (CH_2), 40.4 (CH_2), 47.8 (CH), 52.7 (CH_3), 52.7 (CH_3), 58.5 (C), 115.8 (CH_2), 117.9 (CH), 139.5 (CH), 141.1 (C), 172.2 (C), 172.2 (C); MS *m*/*z* (relative intensity) 238 (M^+, 5.6), 119 (100). Anal. Calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61. Found: C, 65.48; H, 7.52. The stereochemical assignment is based on NOE experiments. Irradiation of the olefinic proton of the ethylidene group showed a 2% enhancement of the internal vinyl proton. The signals of the allylic methylene protons were enhanced upon irradiation of the allylic

methyl protons (2.6 and 2.9%).

Dimethyl 3-Ethenyl-4-((*E*)-trimethylsilylmethylene)cyclopentane-1,1-dicarboxylate (2f): [131130-62-6].[9, 12]



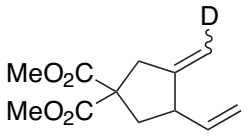
For the characterization data, see ref. 9.

4. Experiments for Mechanistic Insight

4. 1. Quenching with DCl/D_2O

After the reaction of allylstannane **1a** (154 mg, 0.300 mmol) with $InCl_3$ (66.4 mg, 0.300 mmol) was carried out in CH_3CN (1.5 mL) at room temperature for 2 h, DCl (35% in D_2O, 0.51 mL) was added to the reaction mixture. After being stirred for 3 min, the resultant mixture was subjected to the same workup as described in the typical procedure for the cyclization of enynes. Purification of the crude product gave deuterated methylenecyclopentane **2a-*d*** (67.5 mg, 0.300 mmol, quant., 77%*d*, *E*:*Z* = 3:97). The efficiency of deuteration (%*d*) was determined by ^{1}H NMR and GC-MS analyses. The isomeric ratio was also determined by ^{1}H NMR analysis. The stereochemical assignment is based on comparison with the authentic sample of (*E*)-**2a**-***d*** prepared from (*E*)-**3a**.

Dimethyl 3-((*E*)- and (Z)-2-Deuterioethenyl)-4-methylenecyclopentane-1,1-dicarboxylate (2a-*d*, *E*:*Z* = 85:15, >95%*d*)

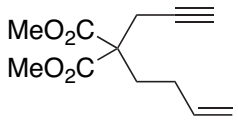


The title compound was obtained by protiodestannylation of (*E*)-**3a** with DCl/D_2O in CH_3CN (room temperature, 3 min, 97%). Protiodestannylation of vinylstannanes is known to proceed with stereochemical retention.[13] ^{1}H NMR ($CDCl_3$) δ 2.01 (dd, *J* = 13.0, 10.9 Hz, 1H), 2.58 (ddd, *J* = 13.0, 7.8, 1.2 Hz, 1H), 2.96 (dt, *J* = 17.0, 2.2 Hz, 1H), 3.06 (d, *J* = 17.0 Hz, 1H), 3.10–3.22 (m, 1H), 3.73 (s, 3H), 3.74 (s, 3H), 4.81 (q, *J* = 2.4 Hz, 0.85H), 4.95–5.00 (m, 0.15H), 5.03–5.11 (m, 2H), 5.64 (ddd, *J* = 17.5, 9.6, 8.1 Hz, 1H).

4. 2. An Attempt to Trap Allylindium Species

To ascertain the presence of an allylindium intermediate, the $InCl_3$-promoted reaction of **1a** was carried out at –40 °C for 30 min. According to the typical procedure, a mixture of **2a** and **6** was obtained in 44% yield (**2a**:**6** = 38:6), **1a** was recovered in 46% yield. When the reaction time was 10 min, the yields of **2a** and **6** were 18% and 4%, respectively, and the recovery of **1a** was 78%.

Dimethyl (3-Butenyl)(2-propynyl)propanedioate (6): [108561-17-7].[11]



For characterization data, see ref. 11.

4. 3. Reaction of Vinylstannane 3a with $InCl_3$

Vinylstannane **3a** (154 mg, 0.300 mmol, *E*:*Z* = 14:86) was added to a solution of $InCl_3$ (66 mg, 0.30 mmol) in CH_3CN (1.5 mL) at room temperature. After 30 seconds Et_3N (84 μL, 0.60 mmol) was added to the reaction mixture. The resultant mixture was subjected to the same workup as described in the typical procedure for the cyclization of enynes **1**. Purification of the crude product by silica gel column chromatography gave **2a** (61.9 mg, 0.276 mmol, 92%). A mixture of **3a** (*ca*. 6%) and unidentified impurities (14.1 mg) was also obtained. Et_3N was added with intention of suppressing protiodestannylation of **3a** in the aqueous workup. A similar result was obtained without addition of Et_3N.

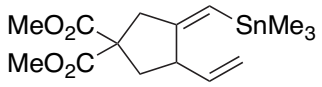
To examine the origin of the formation of (*E*)-**3a**, we performed the reaction of (*Z*)-**3a** (140 mg, 0.273 mmol) with $InCl_3$ (12 mg, 0.055 mmol) in MeCN (1.4 mL) at room temperature for 2 h. The reaction mixture was subjected to the same workup as described in the typical procedure for the cyclization of enynes **1**. Purification of the crude product by silica gel column chromatography gave destannylated product **2a** (24.0 mg, 0.107 mmol, 39%) with the recovery of (*Z*)-**3a** (73.8 mg, 0.144 mmol, 53%). The formation of (*E*)-**3a** was not observed.

4. 4. $InCl_3$-Catalyzed Cyclization in the Presence of Me_3SnCl

Allylstannane **1a** (154 mg, 0.300 mmol) was added to a solution of $InCl_3$ (66.4 mg, 0.060 mmol) and Me_3SnCl (120 mg, 0.600 mmol) in CH_3CN (1.5 mL) at room temperature. After being stirred for 2 h, the resultant mixture was subjected to the same workup as described in the typical procedure for the cyclization of enynes. Purification of the crude product by silica gel column chromatography (hexane-

AcOEt 30:1) gave a mixture of **2a** (18%) and (*Z*)-**3a'** (16%) along with (*Z*)-**3a** (<6%, including unidentified impurities).

Dimethyl 3-Ethenyl-4-((*Z*)-trimethylstannylmethylene)cyclopentane-1,1-dicarboxylate (3a')



Bp 115 °C (0.40 Torr, bath temp). IR (neat) 1736 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.10 (s, $^2J_{Sn-H}$ = 55.4 Hz, 9H), 2.09 (dd, *J* = 13.1, 8.2 Hz, 1H), 2.65 (ddd, *J* = 13.1, 8.2, 1.7 Hz, 1H), 2.96 (dt, *J* = 16.6, 1.6 Hz, 1H), 3.15 (dt, *J* = 16.6, 2.2 Hz, 1H), 3.17–3.27 (m, 1H), 3.71 (s, 3H), 3.74 (s, 3H), 5.01–5.12 (m, 2H), 5.66 (ddd, *J* = 17.0, 9.9, 7.7 Hz, 1H), 5.82 (q, *J* = 2.0 Hz, $^2J_{Sn-H}$ = 63.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ –7.6 (CH_3 × 3), 41.1 (CH_2), 44.6 (CH_2), 48.0 (CH), 52.7 (CH_3), 52.8 (CH_3), 58.6 (C), 116.3 (CH_2), 123.3 (CH), 140.3 (CH), 159.0 (C), 172.0 (C), 172.1 (C); MS *m/z* (relative intensity) 373 (M^+ – Me, 20), 371 (M^+ – 2 – Me, 20), 369 (M^+ – 4 – Me, 7), 59 (100). Anal. Calcd for $C_{15}H_{24}O_4Sn$: C, 46.55; H, 6.25. Found: C, 46.77; H, 6.25. The stereochemical assignment is based on NOE experiments and comparison with (*E*)- and (*Z*)-**3a** in ^1H NMR spectra. Irradiation of the olefinic proton α to the stannyl group showed a 6% enhancement of one allylic methylene proton. In addition, protiodestannylation of (*Z*)-**3a'** with DCl/D_2O gave (*Z*)-**2a-*d*** with high stereoselectivity (*E*:*Z* = <5:95).

4. 5. Reaction of Vinylindium 4 with Allyltrimethylstannane

After the $InCl_3$ (0.300 mmol)-promoted cyclization of **1a** (154 mg, 0.300 mmol) in CH_3CN (1.5 mL) was completed (room temperature, 2 h), allyltrimethylstannane (0.147 mL, 0.900 mmol) was added to the reaction mixture at room temperature. After being stirred for 2 h, the resultant mixture was subjected to the same workup as described in the typical procedure for the cyclization of enynes. Purification of the crude product gave a mixture of **2a** (35%) and (*Z*)-**3a'** (32%) along with (*Z*)-**3a** (5%).

5. References

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