Supporting Information

$W(CO)_5$(L)-Catalyzed Tandem Intramolecular Cyclopropanation / Cope Rearrangement for the Stereoselective Cnstruction of Bicyclo[5.3.0]decane Framework

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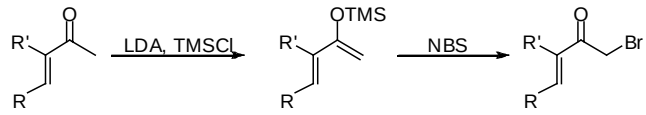
General. All operations were performed under an argon atmosphere. ^{1}H NMR spectra were recorded on a Bruker DRX–500 (500 MHz) or a JEOL AL–400 (400 MHz) spectrometer in $CDCl_3$ [using residual $CHCl_3$ (for ^{1}H, δ_H = 7.26) as internal standard] or bezene-d_6 [using residual benzene (for ^{1}H, δ_H = 7.15) as internal standard]. ^{13}C NMR spectra were recorded on a Bruker DRX–500 (125 MHz) or a JEOL AL–400 (100 MHz) spectrometer in $CDCl_3$ [using $CDCl_3$ (for ^{13}C, δ_C = 77.0) as internal standard] or bezene-d_6 [using bezene-d_6 (for ^{13}C, δ_C = 128.0) as internal standard]. IR spectra were recorded on an IR–810 or FT/IR–460 plus (JASCO Co., Ltd.). 250W super high–pressure Hg lamp, SX–UI 250HQ (USHIO Co. Ltd.) was used for photoirradiation. Silica Gel 60N or Silica Gel 60 (Kanto Chemical Co., Inc.) was used for silica–gel flash column chromatography. Merck Kieselgel 60 F_{254} (0.25 mm thickness, coated on glass 20×20 cm^2) plate was used for thin layer chromatography (TLC), and Wakogel B–5F coated on glass in a thickness of 0.9 mm was used for preparative TLC. THF was dried by passing over a column of activated alumina (A-2, Purify) followed by a column of Q-5 scavenger (Engelhard), and all other solvents were distilled according to the usual procedures and stored over molecular sieves. MS4A was heated by heat-gun under reduced pressure before use. Elemental analyses were performed on a Perkin-Elmer 2400 instrument.

(1) Preparation of α,β-unsaturated ketones (12, 13, 14)

1) Preparation of α-bromoketones (18, 19, 20)

Scheme 1



15 (R = Ph, R' = H)
16 (R = *i*-Pr, R' = H)
17 (R, R' = -$CH_2CH_2CH_2CH_2$-)

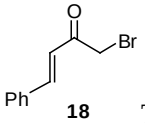
18 (R = Ph, R' = H) 94%
19 (R = *i*-Pr, R' = H) 79%
20 (R, R' = -$CH_2CH_2CH_2CH_2$-) 78%

A typical procedure for the preparation of α-bromoketone (**18**, **19**, **20**) is described for the reaction using benzalacetone **15** as substrate:

To a 0.35 M THF solution (200 mL) of LDA (70 mmol) was added a THF solution (20 mL) of benzalacetone **15** (10.0 g, 68.4 mmol) at –78 °C. The reaction mixture was stirred for 80 min, and then TMSCl (8.9 mL, 70.1 mmol) was added at the same temperature. The mixture was further stirred for 3 h at room temperature, and then the solvent was removed *in vacuo*. The residual suspension was filtered quickly, and the remaining solids were washed with hexane (20 mL × 3). The filtrate was evaporated, and the resulting crude silyl enol ether (6.6 g) was pure enough for the following bromination.

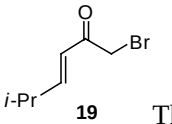
N-bromosuccinimide (13.3 g, 74.7 mmol) was added to a THF solution (100 mL) of the above silyl enol ether at –40 °C, and the mixture was stirred overnight at the same temperature. Then the mixture was poured into sat. $Na_2S_2O_3$ solution, and organic materials were extracted with ethyl acetate twice. The combined organic layer was washed with brine and was dried over anhydrous $MgSO_4$. The filtrate was concentrated and the resulting crude product was purified by silica gel column chromatography (5% ethyl acetate in hexane) to give 13.1 g of 1-bromo-4-phenylbut-3-en-2-one **18** as brown solids (94% 2 steps).

(3*E*)-1-Bromo-4-phenylbut-3-en-2-one (18)



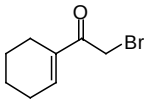
18 The spectral data were consistent with those of the literature.[1]

(3*E*)-1-Bromo-5-methylhex-3-en-2-one (19)



19 The spectral data were consistent with those of the literature.[2]

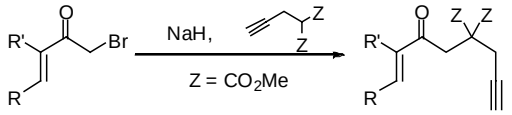
1-Bromo-2-(cyclohex-1-enyl)-2-one (20)



20 The spectral data were consistent with those of the literature.[2]

2) Preparation of α,β-unsaturated ketones (12, 13, 14)

Scheme 2

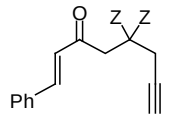


18 (R = Ph, R = H) **12** (R = Ph, R = H) 59%
19 (R = *i*-Pr, R = H) **13** (R = *i*-Pr, R = H) 51%
20 (R, R' = -$CH_2CH_2CH_2CH_2$-) **14** (R, R' = -$CH_2CH_2CH_2CH_2$-) 76%

A typical procedure for the preparation of the α,β-unsaturated ketone (**12**, **13**, **14**) is described for the reaction using **18** as substrate:

To a THF suspension (50 mL) of NaH (260 mg, 10.9 mmol) was added a THF solution (50 mL) of dimethyl prop-2-ynylmalonate at 0 °C. The reaction mixture was stirred for 100 min at the same temperature, and then a THF solution (10 mL) of bromoketone **18** (2.28 g, 10.1 mmol) was added. After the mixture was stirred overnight, the reaction was quenched with phosphate buffer (pH 7). Organic materials were extracted with ethyl acetate, and then dried over $MgSO_4$. After filtration of the drying agent, the filtrate was evaporated, and the crude product was purified by silica gel column chromatography (5% ethyl acetate in hexane) to give 1.84 g of the ketone **12** (59%).

Dimethyl [(3*E*)-2-Oxo-4-phenylbut-3-enyl](prop-2-ynyl)malonate (12)

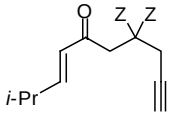


Z = CO_2Me
12

White solid
IR (KBr) 3290, 2950, 2120, 1740, 1610, 1200 cm^{-1}
^{1}H–NMR (500 MHz in $CDCl_3$) δ = 2.03 (t, *J* = 2.7 Hz, 1H), 3.08 (d, *J* = 2.7 Hz, 2H), 3.61 (s, 2H), 3.76 (s, 6H), 6.73 (d, *J* = 16.3 Hz, 1H), 7.39–7.41 (m, 3H), 7.53–7.57 (m, 2H), 7.62 (d, *J* = 16.3 Hz, 1H).
^{13}C–NMR (125 MHz in $CDCl_3$) δ = 23.4, 42.8, 53.1, 54.6, 71.8, 79.3, 125.7, 128.4, 129.0, 130.8, 134.2, 143.6, 169.7, 196.4.

Anal. Calcd for $C_{18}H_{18}O_5$: C, 68.78; H, 5.77 Found: C, 68.88, H, 6.02

Dimethyl [(3*E*)-2-Oxo-5-methylhex-3-enyl](prop-2-ynyl)malonate (13)

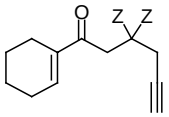


Z = CO_2Me
13

Colorless oil
IR (neat) 3280, 2959, 2121, 1742, 1672, 1628, 1436, 1201 cm^{-1}
^{1}H–NMR (400 MHz in $CDCl_3$) δ = 1.08 (d, *J* = 6.8 Hz, 6H), 2.01 (t, *J* = 2.6 Hz, 1H), 2.44-2.52 (m, 1H), 3.03 (d, *J* = 2.6 Hz, 2H), 3.45 (s, 2H), 3.75 (s, 6H), 6.04 (dd, *J* = 16.0 Hz, 1.6 Hz, 1H), 6.89 (dd, *J* = 16.0 Hz, 6.6 Hz, 1H).
^{13}C–NMR (100 MHz in $CDCl_3$) δ = 21.2, 23.3, 31.2, 42.1, 53.1, 54.4, 71.6, 79.3, 127.0, 154.6, 169.6, 196.8.

Anal. Calcd for $C_{15}H_{20}O_5$: C, 64.27; H, 7.19 Found: C, 64.40, H, 7.33

Dimethyl [2-Oxo-2-(cyclohex-1-enyl)ethyl](prop-2-ynyl)malonate (14)



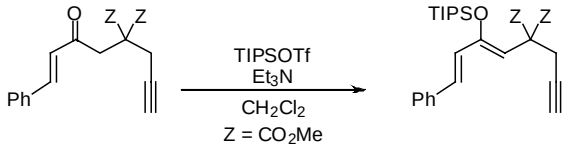
Z = CO_2Me
14

White solid
IR (KBr) 3283, 2937, 1738, 1664, 1430, 1197 cm^{-1}
^{1}H–NMR (400 MHz in $CDCl_3$) δ = 1.58-1.67 (m, 4H), 2.00 (t, *J* = 2.6 Hz, 1H), 2.17-2.23 (m, 2H), 2.24-2.30 (m, 2H), 3.02 (d, *J* = 2.6 Hz, 2H), 3.57 (s, 2H), 3.74 (s, 6H), 7.02-7.06 (m, 1H).
^{13}C–NMR (100 MHz in $CDCl_3$) δ = 21.5, 21.9, 22.9, 23.4, 26.2, 39.7, 53.1, 54.6, 71.5, 79.4, 138.8, 141.0, 169.8, 197.3.

Anal. Calcd for $C_{16}H_{20}O_5$: C, 65.74; H, 6.90 Found: C, 65.51, H, 6.91

(2) Preparation of terminal alkynes possessing siloxydiene moiety (21, 22)

Dimethyl [(1*Z*, 3*E*)-4-Phenyl-2-(triisopropylsiloxy)buta-1,3-dienyl](prop-2-ynyl) malonate (21)



12 **21**

68%

TIPSOTf (10 mL, 37.1 mmol) was added to a CH_2Cl_2 solution (50 mL) of ketone **12** (9.27 g, 29.5 mmol) and Et_3N (8.0 mL, 57.4 mmol) at room temperature, and the reaction mixture was stirred overnight. The mixture was quenched with phosphate buffer (pH 7), and then the organic materials were extracted with ethyl acetate. Combined organic layer was washed with brine, and dried over $MgSO_4$. After filtration of the drying agent, the filtrate was evaporated. Resulting crude silyl enol ether **21** was recrystallized from hexane to give 9.51 g of **21** as white solid (68%).

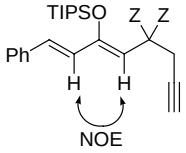
IR (KBr) 2950, 2120, 1740, 1220, 1200, 1180 cm^{-1}

^{1}H–NMR (500 MHz in $CDCl_3$) δ = 1.07-1.12 (m, 18H), 1.15-1.22 (m, 3H), 1.97 (t, J = 2.7 Hz, 1H), 3.20 (d, J = 2.7 Hz, 2H), 3.76 (s, 6H), 5.71 (s, 1H), 6.45 (d, J = 15.8 Hz, 1H), 6.94 (d, J = 15.8 Hz, 1H), 7.25–7.29 (m, 1H), 7.32–7.39 (m, 4H).

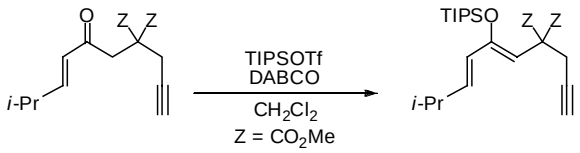
^{13}C–NMR (125 MHz in $CDCl_3$) δ = 13.9, 17.9, 24.7, 52.9, 56.4, 70.3, 80.0, 102.1, 125.5, 126.7, 128.1, 128.8, 132.1, 136.4, 151.8, 169.8.

Anal. Calcd for $C_{27}H_{38}O_5Si$: C, 68.90; H, 8.14. Found: C, 68.65; H, 8.40

The geometry was confirmed by NOE experiment as shown below.



Dimethyl [(1*Z*, 3*E*)-5-Methyl-2-(triisopropylsiloxy)hexa-1,3-dienyl](prop-2-ynyl) malonate (22)



13 **22**

41%

TIPSOTf (0.74 mL, 2.75 mmol) was added to a CH_2Cl_2 solution (8 mL) of ketone **13** (503 mg, 1.79 mmol) and DABCO (383 mg, 3.41 mmol) at room temperature, and the reaction mixture was stirred overnight. The mixture was quenched with phosphate buffer (pH 7), and then the organic materials were extracted with ethyl acetate. Combined organic layer was washed with brine, and dried over $MgSO_4$. Resulting crude silyl enol ether **22** was purified by silica gel column chromatography (3% ethyl acetate in hexane) to give 318 mg of **22** as colorless oil (41%).

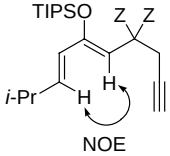
IR (neat) 3284, 2956, 2867, 2122, 1742, 11674, 1630, 437, 1291, 1203 cm^{-1}

^{1}H–NMR (400 MHz in $CDCl_3$) δ = 1.01 (d, J = 6.8 Hz, 6H), 1.06–1.17 (m, 21H), 1.94 (t, J = 2.6 Hz, 1H), 2.28–2.37 (m, 1H), 3.14 (d, J = 2.6 Hz, 2H), 3.73 (s, 6H), 5.44 (s, 1H), 5.71 (d, J = 15.6 Hz, 1H), 6.05 (dd, d, J = 15.6, 6.8 Hz, 1H).

^{13}C–NMR (100 MHz in $CDCl_3$) δ = 13.9, 18.0, 21.8, 24.7, 31.1, 52.9, 56.3, 70.1, 80.2, 100.6, 124.3, 141.7, 152.3, 169.8.

Anal. Calcd for $C_{24}H_{40}O_5Si$: C, 66.01; H, 9.23 Found: C, 66.00; H, 9.51

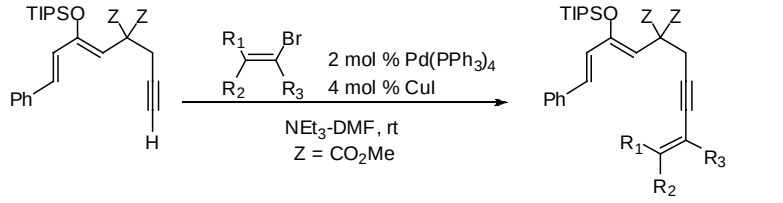
The geometry was confirmed by NOE experiment as shown below.



(3) Preparation of enynes possessing siloxydiene moiety

A. Preparation of enynes (1a, 1b, 1d, 3)

Scheme 3



21

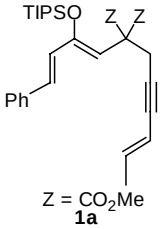
1a	(R_1 = H, R_2 = Me, R_3 = H)	87%
1b	(R_1 = H, R_2 = H, R_3 = H)	68%
1d	(R_1 = H, R_2 = H, R_3 = Me)	70%
3*	(R_1 = H, R_2, R_3 = -$CH_2CH_2CH_2CH_2$-)	50%

*The reaction was performed at 50 °C

A typical procedure for the preparation of enynes (**1a, 1b, 1d**, **3**) is described for the reaction using *trans*-1-bromoprop-1-ene as substrate:

To a mixture of **21** (425 mg, 0.90 mmol), $Pd(PPh_3)_4$ (15 mg, 0.013 mmol, 1.5 mol %) and CuI (6 mg, 0.032 mmol, 3.5 mol %) in NEt_3/DMF (4 : 1, 5 mL) was added *trans*-1-bromoprop-1-ene (0.11 mL, 1.28 mmol) at room temperature. After the mixture was stirred overnight, the reaction was quenched with sat. NH_4Cl solution and then was extracted with ether twice. The combined organic layer was washed with brine and was dried over $MgSO_4$. After filtration of the drying agent, the filtrate was evaporated, and the crude product was purified by silica gel column chromatography (7% ethyl acetate in hexane) to give 398 mg of the enyne **1a** (87%).

Dimethyl [(4*E*)-Hex-4-en-2-ynyl][(1*Z*, 3*E*)–4-phenyl-2-(triisopropylsiloxy)buta-1,3-dienyl]malonate (<u>1a</u>)



1a

Colorless oil

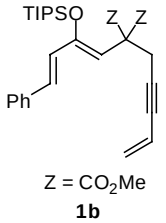
IR (neat) 2949, 2868, 2256, 1740, 1645, 1434 cm^{-1}

^{1}H–NMR (400 MHz in $CDCl_3$) δ= 1.11-1.22 (m, 21H), 1.73 (d, *J* = 6.6 Hz, 3H), 3.27 (s, 2H), 3.75 (s, 6H), 5.42 (brd, *J* = 15.6 Hz, 1H), 5.70 (s, 1H), 6.27 (dq, *J* =15.6, 6.6 Hz, 1H), 6.45 (d, *J* = 15.8 Hz, 1H), 6.92 (d, *J* = 15.8 Hz, 1H), 7.25–7.28 (m, 1H), 7.32–7.39 (m, 4H).

^{13}C–NMR (100 MHz in $CDCl_3$) δ= 13.9, 18.0, 18.5, 25.8, 52.9, 56.7, 81.2, 83.5, 102.6, 110.9, 125.6, 126.6, 128.0, 128.7, 131.9, 136.4, 138.5, 151.4, 169.8.

Anal. Calcd for $C_{30}H_{42}O_5Si$: C, 70.55; H, 8.29. Found: C, 70.27; H, 8.35

Dimethyl (Pent-4-en-2-ynyl)[(1*Z*, 3*E*)–4-phenyl-2-(triisopropylsiloxy)buta-1,3-dienyl]malonate (<u>1b</u>)



1b

Colorless oil

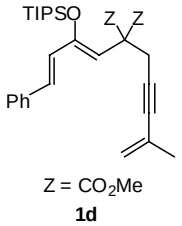
IR (neat) 2950, 2869, 2230, 1742, 1645, 1434, 1197 cm^{-1}

^{1}H–NMR (400 MHz in $CDCl_3$) δ= 1.08-1.22 (m, 21H), 3.31 (s, 2H), 3.75 (s, 6H), 5.38 (dd, *J* = 11.2, 2.4 Hz, 1H), 5.53 (dd, *J* = 17.6, 2.4 Hz, 1H), 5.70 (s, 1H), 5.72-5.78 (m, 1H), 6.45 (d, *J* = 15.6 Hz, 1H), 6.93 (d, *J* = 15.6 Hz, 1H), 7.25–7.39 (m, 5H).

^{13}C–NMR (100 MHz in $CDCl_3$) δ= 13.9, 18.0, 25.7, 52.9, 56.6, 81.3, 86.2, 102.4, 117.4, 125.5, 126.0, 126.6, 128.0, 128.7, 132.0, 136.4, 151.5, 169.8.

Anal. Calcd for $C_{29}H_{40}O_5Si$: C, 70.12; H, 8.12. Found: C, 69.87; H, 7.95

Dimethyl (4-Methylpent-4-en-2-yny)[(1*Z*, 3*E*)-4-phenyl-2-(triisopropylsiloxy)buta-1,3-dienyl]malonate (<u>1d</u>)



1d

Colorless oil

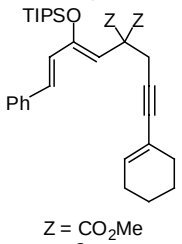
IR (neat) 2950, 2869, 2229, 1742, 1645, 1196 cm^{-1}

^{1}H–NMR (400 MHz in $CDCl_3$) δ= 1.08-1.22 (m, 21H), 1.84 (s, 3H), 3.30 (s, 2H), 3.75 (s, 6H), 5.13 (brs, 1H), 5.18 (brs, 1H), 5.71 (s, 1H), 6.46 (d, *J* = 15.8 Hz, 1H), 6.93 (d, *J* = 15.8 Hz, 1H), 7.25–7.28 (m, 1H), 7.32–7.38 (m, 4H).

^{13}C–NMR (100 MHz in $CDCl_3$) δ= 13.9, 18.0, 23.8, 25.6, 52.9, 56.6, 83.9, 84.7, 102.6, 120.7, 125.6, 126.6, 126.9, 128.0, 128.7, 132.0, 136.4, 151.4, 169.8.

Anal. Calcd for $C_{30}H_{42}O_5Si$: C, 70.55; H, 8.29. Found: C, 70.46; H, 8.48

Dimethyl [3-(Cyclohex-1-enyl)-prop-2-ynyl][(1*Z*, 3*E*)–4-phenyl-2-(triisopropylsiloxy)buta-1,3-dienyl]malonate (<u>3</u>)



3

Colorless oil

IR (neat) 2946, 2868, 1741, 1645, 1434, 1344, 1195 cm^{-1}

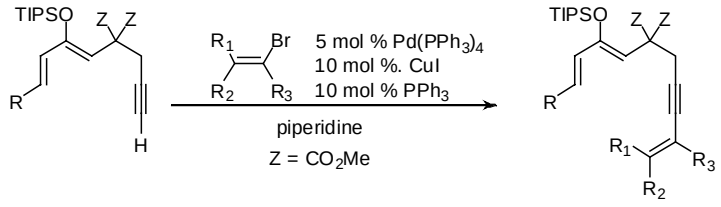
^{1}H–NMR (400 MHz in $CDCl_3$) δ= 1.09-1.22 (m, 21H), 1.51-1.63 (m, 4H), 2.00-2.09 (m, 4H), 3.28 (s, 2H), 3.75 (s, 6H), 5.72 (s, 1H), 5.95-6.00 (m, 1H), 6.45 (d, *J* = 15.8 Hz, 1H), 6.92 (d, *J* = 15.8 Hz, 1H), 7.25–7.28 (m, 1H), 7.32–7.39 (m, 4H).

^{13}C–NMR (100 MHz in $CDCl_3$) δ= 13.9, 18.0, 21.6, 22.4, 25.6, 25.7, 29.5, 52.9, 56.8, 82.5, 84.4, 102.8, 120.7, 125.7, 126.6, 128.0, 128.7, 131.9, 133.5, 136.4, 151.3, 169.8.

Anal. Calcd for $C_{33}H_{46}O_5Si$: C, 71.96; H, 8.42 Found: C, 72.20; H, 8.71

B. Preparation of enynes (<u>1c</u> , <u>1e</u>, <u>1g</u>, <u>1h</u>)

Scheme 4



21 (R = Ph)

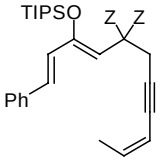
22 (R = *i*-Pr)

1c (R = Ph, R_1 = Me, R_2 = H, R_3 = H) 75%
1e (R = Ph, R_1 = Me, R_2 = Me, R_3 = H) 63%
1g (R = *i*-Pr, R_1 = H, R_2 = Me, R_3 = H) 67%
1h (R = *i*-Pr, R_1 = H, R_2 = H, R_3 = Me) 67%

A typical procedure[3] for the preparation of enynes (**1c, 1e**, **1g, 1h**) is described for the reaction using *cis*-1-bromoprop-1-ene as substrate:

To a mixture of **21** (140 mg, 0.30 mmol), $Pd(PPh_3)_4$ (13 mg, 0.011 mmol, 4 mol %), CuI (4 mg, 0.021 mmol, 7 mol %) and PPh_3 (7 mg, 0.027 mmol, 9 mol %) in degassed piperidine (2 mL) was added *cis*-1-bromoprop-1-ene (0.05 mL, 0.59 mmol) at room temperature. After the mixture was heated at 60 °C for 3 h, the reaction was quenched with sat. NH_4Cl solution and then was extracted with ethyl acetate twice. The combined organic layer was washed with brine and was dried over $MgSO_4$. After filtration of the drying agent, the filtrate was evaporated, and the crude product was purified by PTLC (10% ethyl acetate in hexane) to give 115 mg of the enyne **1c** (75%).

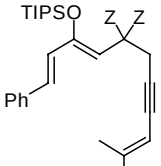
Dimethyl [(4*Z*)-Hex-4-en-2-ynyl][(1*Z*, 3*E*)–4-phenyl-2-(triisopropylsiloxy)buta-1,3-dienyl]malonate (<u>1c</u>)



1c

Colorless oil
IR (neat) 2949, 2868, 2255, 1742, 1645, 1434, 1345 cm^{-1}
^{1}H–NMR (400 MHz in $CDCl_3$) δ = 1.08-1.22 (m, 21H), 1.83 (dd, *J* = 6.8, 1.2 Hz, 3H), 3.35 (s, 2H), 3.75 (s, 6H), 5.42 (dd, *J* = 10.6, 1.2 Hz, 1H), 5.74 (s, 1H), 5.89 (dq, *J* =10.6, 6.8 Hz, 1H), 6.45 (d, *J* = 15.8 Hz, 1H), 6.92 (d, *J* = 15.8 Hz, 1H), 7.25–7.28 (m, 1H), 7.32–7.39 (m, 4H).
^{13}C–NMR (100 MHz in $CDCl_3$) δ = 13.9, 15.8, 18.0, 26.0, 52.9, 56.7, 79.2, 90.0, 102.6, 110.2, 125.6, 126.6, 128.0, 128.7, 131.9, 136.4, 137.6, 151.4, 169.8.
Anal. Calcd for $C_{30}H_{42}O_5Si$: C, 70.55; H, 8.29. Found: C, 70.73; H, 8.56

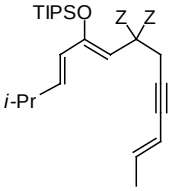
Dimethyl (5-Methylhex-4-en-2-ynyl)[(1*Z*, 3*E*)–4-phenyl-2-(triisopropylsiloxy)buta-1,3-dienyl]malonate (<u>1e</u>)



1e

Colorless oil
IR (neat) 2949, 2868, 2255, 1742, 1645, 1434, 1345 cm^{-1}
^{1}H–NMR (400 MHz in $CDCl_3$) δ = 1.09-1.22 (m, 21H), 1.75 (s, 3H), 1.84 (s, 3H), 3.32 (s, 2H), 3.76 (s, 6H), 5.19 (s, 1H), 5.73 (s, 1H), 6.45 (d, *J* = 15.6 Hz, 1H), 6.92 (d, *J* = 15.6 Hz, 1H), 7.25–7.28 (m, 1H), 7.32–7.39 (m, 4H).
^{13}C–NMR (100 MHz in $CDCl_3$) δ = 13.9, 18.0, 20.8, 24.7, 26.0, 52.9, 56.8, 80.5, 87.1, 102.8, 105.4, 125.6, 126.6, 128.0, 128.7, 131.8, 136.4, 147.4, 151.3, 169.8.
Anal. Calcd for $C_{31}H_{44}O_5Si$: C, 70.95; H, 8.45. Found: C, 70.84; H, 8.36

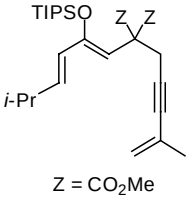
Dimethyl [(4*E*)-Hex-4-en-2-ynyl][(1*Z*, 3*E*)-5-methyl-2-(triisopropylsiloxy)hexa-1,3-dienyl]malonate (<u>1g</u>)



1g

Colorless oil
IR (neat) 2952, 2869, 2222, 1743, 1652, 1464, 1434, 1198 cm^{-1}
^{1}H–NMR (400 MHz in $CDCl_3$) δ = 1.01 (d, *J* = 6.4 Hz, 6H), 1.06–1.17 (m, 21H), 1.73 (dd, *J* = 6.4, 1.8 Hz, 3H), 2.28–2.37 (m, 1H), 3.22 (s, 2H), 3.72 (s, 6H), 5.41 (dq, *J* = 15.6, 1.8 Hz, 1H), 5.42 (s, 1H), 5.71 (d, *J* = 15.6 Hz, 1H), 5.96-6.06 (m, 2H).
^{13}C–NMR (100 MHz in $CDCl_3$) δ = 13.9, 18.0, 18.5, 21.8, 25.8, 31.1, 52.8, 56.6, 81.0, 83.7, 101.1, 111.0, 124.5, 138.4, 141.6, 152.0, 170.0.
Anal. Calcd for $C_{27}H_{44}O_5Si$: C, 68.02; H, 9.30 Found: C, 67.84; H, 9.47

Dimethyl (4-Methylpent-4-en-2-ynyl)[(1*Z*, 3*E*)-5-methyl-2-(triisopropylsiloxy)hexa-1,3-dienyl]malonate (<u>1h</u>)

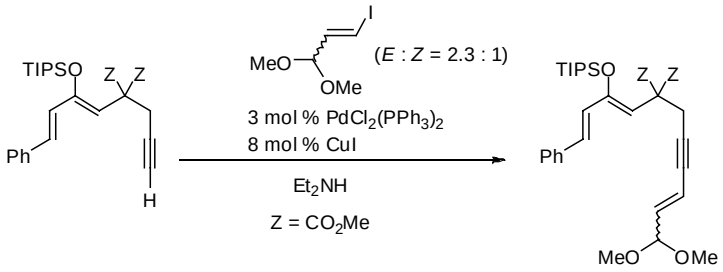


1h

Colorless oil
IR (neat) 2954, 2869, 2229, 1743, 1652, 1464, 1279, 1197, 1008 cm^{-1}
^{1}H–NMR (400 MHz in $CDCl_3$) δ = 1.01 (d, *J* = 6.4 Hz, 6H), 1.06–1.17 (m, 21H), 1.82 (s, 3H), 2.28–2.37 (m, 1H), 3.24 (s, 2H), 3.73 (s, 6H), 5.11 (s, 1H),), 5.16 (s, 1H), 5.43 (s, 1H), 5.72 (d, *J* = 15.6 Hz, 1H), 6.03 (dd, 15.6, 6.8 Hz, 1H).

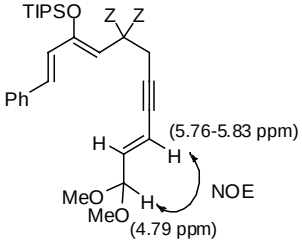
^{13}C–NMR (100 MHz in $CDCl_3$) δ = 13.9, 18.0, 21.8, 23.8, 25.6, 31.1, 52.8, 56.6, 83.7, 84.9, 101.1, 120.5, 124.5, 127.0, 141.7, 152.0, 169.9.
Anal. Calcd for $C_{27}H_{44}O_5Si$: C, 68.02; H, 9.30 Found: C, 68.17; H, 9.15

C. Preparation of dimethyl (6,6-dimethoxyhex-4-en-2-ynyl)[(1*Z*, 3*E)*–4-phenyl-2-(triisopropylsiloxy)buta-1,3-dienyl]malonate (1f)



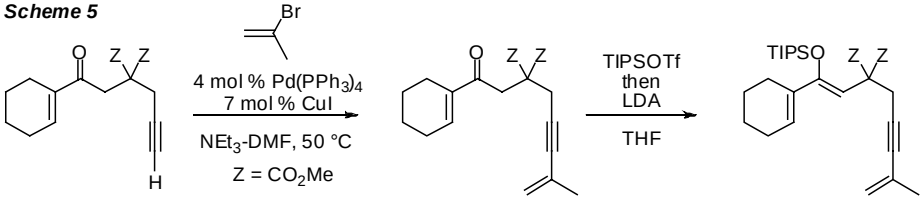
21 **1f** 80% (*E* : *Z* = 85 : 15)

To a mixture of $PdCl_2(PPh_3)_2$ (6 mg, 0.0085 mmol, 3 mol %) and CuI (4 mg, 0.021 mmol, 8 mol %) was added a Et_2NH (2.5 mL) solution of **21** (121 mg, 0.25 mmol) and 1-iodo-3,3-dimethoxyprop-1-ene[4] (*E* : *Z* = 2.3 : 1) (194 mg, 0.85 mmol) at room temperature. After the mixture was stirred overnight, the reaction was quenched with sat. NH_4Cl solution and then was extracted with ethyl acetate twice. The combined organic layer was washed with brine and was dried over $MgSO_4$. After filtration of the drying agent, the filtrate was evaporated, and the crude product was purified by silica gel column chromatography (10% ethyl acetate in hexane) to give 114 mg of the enyne **1f** as pale yellow oil (80%).
1f–*Z* and **1f –*E*** were obtained as an inseparable mixture in a ratio of 15 : 85.
IR (neat) 2950, 2869, 2251, 1741, 1645, 1463, 1346 cm^{-1}
^{1}H–NMR (400 MHz in $CDCl_3$) δ = 1.08-1.22 (m, 21H), 3.29 (s, 5.1H), 3.31-3.33 (m, 2H), 3.35 (s, 0.9H), 3.75 (s, 6H), 4.79 (d, *J* = 4.4 Hz, 0.85H), 5.18 (d, *J* = 7.6 Hz, 0.15H), 5.64-5.70 (m, 0.15H), 5.68 (s, 0.85H), 5.72 (s, 0.15H), 5.76-5.83 (m, 1H), 5.92 (dd, *J* = 16.0, 4.4 Hz, 0.85H), 6.39-6.45 (m, 0.15H), 6.44 (d, *J* = 15.8 Hz, 0.85H), 6.91 (d, *J* = 15.8 Hz, 0.85H), 6.94 (d, *J* = 15.8 Hz, 0.15H), 7.24–7.39 (m, 5H).
^{13}C–NMR (100 MHz in $CDCl_3$) δ = 13.9, 18.0, 25.7, 25.8, 52.6, 52.9, 53.7, 56.5, 56.6, 77.2, 78.0, 79.9, 88.0, 101.3, 101.7, 102.2, 102.3, 113.2, 114.2, 125.3, 125.4, 126.5, 126.6, 128.0, 128.1, 128.6, 128.7, 132.0, 136.2, 136.3, 137.2, 137.6, 151.5, 151.6, 169.6, 169.7.
Anal. Calcd for $C_{32}H_{46}O_7Si$: C, 67.34; H, 8.12 Found: C, 67.45; H, 8.20
The geometry of the major product was confirmed by NOE experiment as shown below.



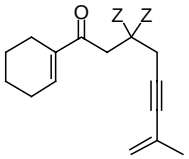
D. Preparation of
dimethyl (4-methylpent-4-en-2-ynyl)[(1*Z)*–2-(cyclohex-1-enyl)-2-(triisopropylsiloxy)ethyl]malonate (5)

Scheme 5



14 **23** (86%) **5** (23%)

To a mixture of **14** (405 mg, 1.38 mmol), $Pd(PPh_3)_4$ (63 mg, 0.045 mmol, 4 mol %) and CuI (19 mg, 0.10 mmol, 8 mol %) in NEt_3/DMF (4 : 1, 5 mL) was added 2-bromopropene (0.30 mL, 3.37 mmol) at room temperature. After the mixture was heated at 50 ˚C for 4 h, the reaction was quenched with sat. NH_4Cl solution and then was extracted with ether twice. The combined organic layer was washed with brine and was dried over $MgSO_4$. After filtration of the drying agent, the filtrate was evaporated, and the crude product was purified by silica gel column chromatography (8% ethyl acetate in hexane) to give 393 mg of the enyne **23** (86%).
Dimethyl (4-Methylpent-4-en-2-ynyl)[2-oxo-2-(cyclohex-1-enyl)ethyl]malonate (23)

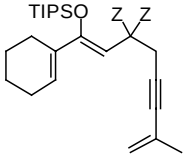


23

Colorless oil
IR (neat) 2951, 2863, 2226, 1742, 1667, 1435, 1284, 1200 cm^{-1}
^{1}H–NMR (400 MHz in $CDCl_3$) δ = 1.56-1.68 (m, 4H), 1.82 (s, 3H), 2.15–2.33 (m, 4H), 3.09 (s, 2H), 3.54 (s, 2H), 3.74 (s, 6H), 5.15 (s, 1H), 5.17 (s, 1H),), 7.02-7.09 (m, 1H).
^{13}C–NMR (100 MHz in $CDCl_3$) δ = 21.5, 21.9, 22.9, 23.6, 24.2, 26.2, 39.8, 53.0, 54.9, 83.8, 84.9, 121.2, 126.5, 138.8, 140.9, 169.9, 197.4.
Anal. Calcd for $C_{19}H_{24}O_5$: C, 68.66; H, 7.28 Found: C, 68.42; H, 7.58

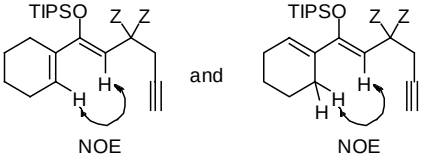
TIPSOTf (0.65 mL, 2.41 mmol) was added dropwise to a ketone **23** (614 mg, 1.85 mmol) in THF (8 mL) at 0 °C over 2 minutes and the reaction mixture was stirred for 30 minutes. A THF solution (1 mL) of LDA (2.03 mmol) was added and the mixture was stirred overnight at room temperature. Et_3N was added to the reaction mixture and then the reaction was quenched with phosphate buffer (pH 7). The mixture was extracted with ethyl acetate, and the combined organic layer was washed with brine, and was dried over $MgSO_4$. Evaporation under reduced pressure gave the crude product, which was purified by silica gel column chromatography (4% ethyl acetate in hexane) to give 207 mg of the dienol silyl ether **5** (23%).

Dimethyl (4-Methylpent-4-en-2-ynyl)[(1*Z*)–2-(cyclohex-1-enyl)-2-(triisopropylsiloxy)ethenyl]malonate (**5**)



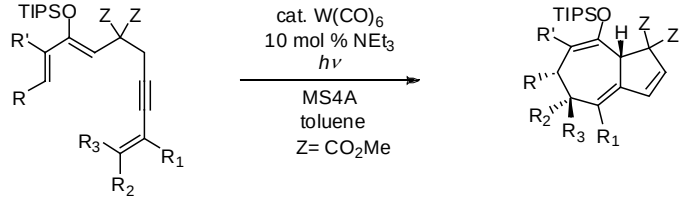
5

Colorless oil
IR (neat) 2948, 2868, 2229, 1743, 1644, 1435, 1232 cm^{-1}
^{1}H–NMR (400 MHz in $CDCl_3$) δ = 1.06–1.20 (m, 21H), 1.55-1.65 (m, 4H), 1.81 (s, 3H), 2.06–2.10 (m, 2H), 2.15-2.20 (m, 2H), 3.24 (s, 2H), 3.72 (s, 6H), 5.10-5.12 (m, 1H), 5.15 (brs, 1H), 5.24 (s, 1H), 5.83-5.86 (m, 1H).
^{13}C–NMR (100 MHz in $CDCl_3$) δ = 14.2, 18.2, 21.9, 22.6, 23.8, 25.0, 25.6, 27.8, 52.8, 56.3, 83.8, 84.7, 102.0, 120.5, 126.6, 127.0, 136.5, 155.0, 169.9.
Anal. Calcd for $C_{28}H_{44}O_5Si$: C, 68.81; H, 9.07 Found: C, 68.59; H, 9.15
The geometry was confirmed by NOE experiment as shown below.



(4) Tandem cyclization of enynes (1a ~ 1h, 3, 5)

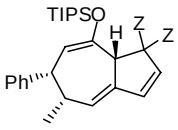
Scheme 6



1a	(R = Ph, R' = H, R_1 = H, R_2 = Me, R_3 = H)	**2a**	83%
1b	(R = Ph, R' = H, R_1 = H, R_2 = H, R_3 = H)	**2b**	63%
1c	(R = Ph, R' = H, R_1 = H, R_2 = H, R_3 = Me)	**2c**	80%
1d	(R = Ph, R' = H, R_1 = Me, R_2 = H, R_3 = H)	**2d**	79%
1e	(R = Ph, R' = H, R_1 = H, R_2 = Me, R_3 = Me)	**2e**	78%
1f	(R = Ph, R' = H, R_1 = H, R_2, R_3 = $CH(OMe)_2$, H *E* : *Z* = 6 : 1)	**2f**	71% (6 : 1 mixture of diastereomer)
1g	(R = *i*-Pr, R' = H, R_1 = H, R_2 = Me, R_3 = H)	**2g**	83%
1h	(R = *i*-Pr, R' = H, R_1 = Me, R_2 = H, R_3 = H)	**2h**	61%
3	(R = Ph, R' = H, R_1, R_2 = -$CH_2CH_2CH_2CH_2$-, R_3 = H)	**4**	81%
5	(R, R' = -$CH_2CH_2CH_2CH_2$-, R_1 = Me, R_2, R_3 = H)	**6**	67%

A typical procedure for the cyclization of enynes (**1a ~ 1h**, **3, 5**) is described for the reaction of **1a** as substrate:
To a mixture of $W(CO)_6$ (2.3 mg, 0.0065 mmol, 5 mol %) and activated MS4A were added **1a** (64 mg, 0.125 mmol) and NEt_3 (1.8 μL, 0.013 mmol, 10 mol %) in degassed toluene (1.3 mL). After the mixture was photoirradiated (250W super high–pressure Hg lamp) for 2 h at room temperature, the suspension was filtered and then the solvent was removed under reduced pressure to give crude product, which was purified by PTLC (10% ethyl acetate in hexane) to give 53 mg of **1a** (0.104 mmol, 83%).

Dimethyl (3*S, 4*S**, 7*S**)– 3–Methyl–4–phenyl–6–(triisopropylsiloxy)bicyclo[5.3.0]deca–1,5,9–triene–8,8–dicarboxylate (2a)**



Z = CO_2Me

2a

White crystal

IR (KBr) 2953, 2866, 1751, 1732, 1656, 1451, 1264 cm^{-1}

^{1}H–NMR (400 MHz in $CDCl_3$) δ = 1.01 (d, *J* = 7.2 Hz, 3H), 1.07–1.11 (m, 18H), 1.17–1.26 (m, 3H), 3.00-3.08 (m, 1H), 3.42-3.47 (m, 1H), 3.70 (s, 3H), 3.81 (s, 3H), 4.86 (brs, 1H), 5.09 (dd, *J* = 8.0, 2.0 Hz, 1H), 5.12 (dd, *J* = 3.2, 2.4 Hz, 1H), 6.05 (d, *J* = 5.4 Hz, 1H), 6.20 (d, *J* = 5.4 Hz, 1H), 7.19–7.28 (m, 3H), 7.34 (d, *J* = 7.2 Hz, 2H).

^{13}C–NMR (100 MHz in $CDCl_3$) δ = 13.3, 18.2, 20.1, 36.5, 49.7, 51.7, 52.3, 52.7, 70.7, 111.3, 126.1, 127.1, 128.3, 130.3, 132.4, 136.9, 141.3, 143.9, 149.2, 169.1, 170.3.

Anal. Calcd for $C_{30}H_{42}O_5Si$: C, 70.55; H, 8.29. Found: C, 70.36; H, 8.54

The relative stereochemistry was confirmed by X-ray analysis as shown below.

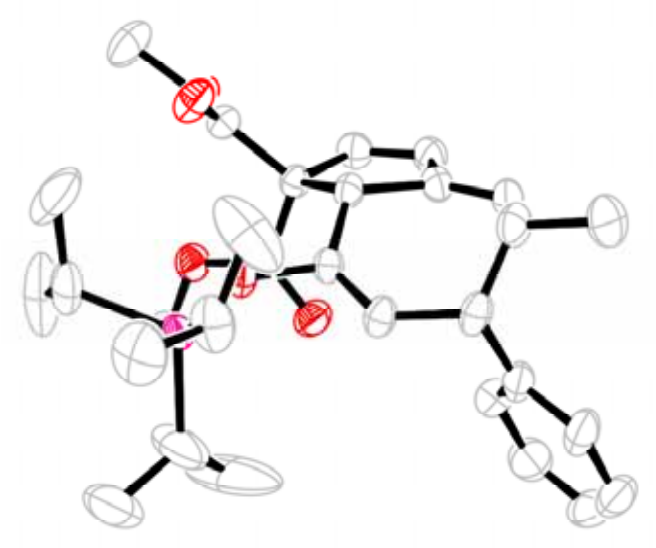
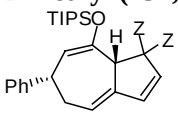


Figure S1. ORTEP plot of **2a** (hydrogen atoms are omitted for clarity). Full table of data are provided in the cif. file.

Dimethyl (4*S, 7*S**)–4–Phenyl–6–(triisopropylsiloxy)bicyclo[5.3.0]deca–1,5,9–triene–8,8–dicarboxylate (2b)**



Z = CO_2Me

2b

White solid

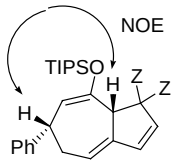
IR (KBr) 2945, 2867, 1743, 1654, 1432, 1198 cm^{-1}

^{1}H–NMR (500 MHz in $CDCl_3$) δ = 1.10 (d, *J* = 7.5 Hz, 18H), 1.16–1.25 (m, 3H), 2.41 (dt, *J* = 14.8, 7.0 Hz, 1H), 2.74-2.80 (m, 1H), 3.73 (s, 3H), 3.76-3.80 (m, 1H), 3.81 (s, 3H), 4.84-4.87 (m, 1H), 5.04 (dd, *J* = 7.5, 2.0 Hz, 1H), 5.49-5.52 (m, 1H), 6.02 (d, *J* = 5.5 Hz, 1H), 6.18 (d, *J* = 5.5 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.26–7.30 (m, 2H), 7.34 (d, *J* = 7.5 Hz, 2H).

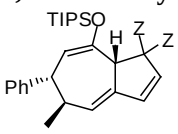
^{13}C–NMR (125 MHz in $CDCl_3$) δ = 13.2, 18.1, 18.2, 34.0, 42.6, 51.3, 52.3, 52.7, 70.3, 109.8, 121.9, 126.0, 127.9, 128.4, 131.9, 137.2, 144.9, 145.6, 150.3, 169.3, 170.4.

Anal. Calcd for $C_{29}H_{40}O_5Si$: C, 70.12; H, 8.12. Found: C, 69.85; H, 8.41

The relative stereochemistry was confirmed by NOE experiment as shown below.



Dimethyl (3*R, 4*S**, 7*S**)–3–Methyl–4–phenyl–6–(triisopropylsiloxy)bicyclo[5.3.0]deca–1,5,9–triene–8,8–dicarboxylate (2c)**



Z = CO_2Me

2c

White solid

IR (KBr) 2951, 2867, 1745, 1655, 1451, 1204 cm^{-1}

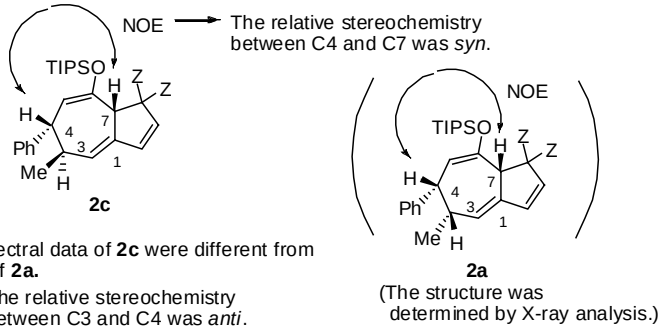
^{1}H–NMR (500 MHz in $CDCl_3$) δ = 1.07-1.10 (m, 18H), 1.17–1.26 (m, 3H), 1.21 (d, *J* = 7.1 Hz, 3H), 2.54-2.61 (m, 1H), 3.50-3.54 (m, 1H), 3.73 (s, 3H), 3.80 (s, 3H), 4.80-4.83 (m, 1H), 4.88 (dd, *J* = 5.2, 2.1 Hz, 1H), 5.59 (dd, *J* = 7.4, 2.9 Hz, 1H), 6.01 (d, *J* = 5.4 Hz, 1H), 6.16 (d, *J* = 5.4 Hz, 1H), 7.16-7.21 (m, 1H), 7.25-7.29 (m, 2H), 7.34 (d, *J* = 7.1 Hz, 2H).

^{13}C–NMR (100 MHz in $CDCl_3$) δ = 13.3, 18.08, 18.10, 19.1, 38.5, 49.5, 51.4, 52.3, 52.7, 70.3, 107.2, 125.9, 127.1, 127.9, 128.6, 131.5, 138.0, 144.0, 145.8, 149.7, 169.3, 170.5.

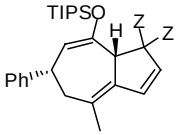
Anal. Calcd for $C_{30}H_{42}O_5Si$: C, 70.55; H, 8.29. Found: C, 70.30; H, 8.21

The relative stereochemistry was confirmed as follows: The relative stereochemistry between C4 and C7 was

determined as *syn* by NOE experiment (see below). The relative stereochemistry between C3 and C4 was determined as *anti* because the spectral data of **2c** were different from those of **2a**, whose relative stereochemistry was unambiguously determined by X-ray analysis.



Dimethyl (4*S, 7*S**)–2-Methyl-4–phenyl–6–(triisopropylsiloxy)bicyclo[5.3.0]deca–1,5,9–triene–8,8–dicarboxylate (2d)**



2d

White solid

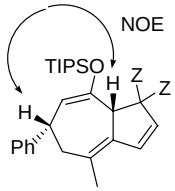
IR (KBr) 2951, 2866, 1739, 1656, 1462, 1195 cm^{-1}

^{1}H–NMR (500 MHz in $CDCl_3$) δ = 1.08-1.11 (m, 18H), 1.17–1.26 (m, 3H), 1.25 (d, *J* = 2.0 Hz, 3H), 2.18 (dd, *J* = 13.8, 6.2 Hz, 1H), 2.93 (brd, *J* = 13.8 Hz, 1H), 3.74 (s, 3H), 3.77-3.80 (m, 1H), 3.80 (s, 3H), 4.84 (brs, 1H), 5.01 (dd, *J* = 7.4, 1.7 Hz, 1H), 5.98 (d, *J* = 5.7 Hz, 1H), 6.42 (d, *J* = 5.7 Hz, 1H), 7.19 (t, *J* = 7.3 Hz, 1H), 7.25–7.30 (m, 2H), 7.36 (d, *J* = 7.3 Hz, 2H).

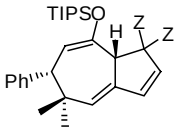
^{13}C–NMR (125 MHz in $CDCl_3$) δ = 13.3, 18.1, 18.2, 22.5, 41.3, 42.4, 51.3, 52.3, 52.7, 70.2, 109.2, 125.9, 127.8, 128.5, 129.5, 130.4, 133.8, 138.2, 143.9, 151.2, 169.5, 170.7.

Anal. Calcd for $C_{30}H_{42}O_5Si$: C, 70.55; H, 8.29. Found: C, 70.34; H, 8.29

The relative stereochemistry was confirmed by NOE experiment as shown below.



Dimethyl (4*S, 7*S**)– 3,3–Dimethyl–4–phenyl–6–(triisopropylsiloxy)bicyclo[5.3.0]deca–1,5,9–triene–8,8–dicarboxylate (2e)**



2e

White solid

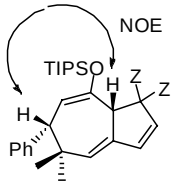
IR (KBr) 2950, 2867, 1747, 1655, 1467, 1209 cm^{-1}

^{1}H–NMR (500 MHz, 330 K in $CDCl_3$) δ = 0.94 (s, 3H), 1.06-1.10 (m, 18H), 1.17–1.26 (m, 3H), 1.28 (s, 3H), 3.25-3.29 (m, 1H), 3.66 (s, 3H), 3.81 (s, 3H), 4.78-4.81 (m, 1H), 4.99 (dd, *J* = 7.7, 2.3 Hz, 1H), 5.40 (d, *J* = 3.0 Hz, 1H), 6.03 (d, *J* = 5.5 Hz, 1H), 6.20 (d, *J* = 5.5 Hz, 1H), 7.15–7.25 (m, 3H), 7.35 (d, *J* = 7.0 Hz, 2H).

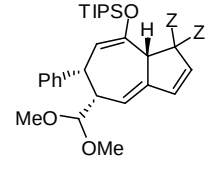
^{13}C–NMR (125 MHz, 330 K in $CDCl_3$) δ = 13.2, 18.1, 18.2, 28.1, 29.8, 37.3, 51.9, 52.1, 52.5, 55.2, 70.7, 109.6, 126.1, 127.3, 130.2, 131.9, 133.0, 138.4, 142.8, 143.4, 148.0, 169.1, 170.4.

Anal. Calcd for $C_{31}H_{44}O_5Si$: C, 70.95; H, 8.45. Found: C, 70.69; H, 8.34

The relative stereochemistry was confirmed by NOE experiment as shown below.



Dimethyl (3*S, 4*R**, 7*S**)–3–Dimethoxymethyl–4–phenyl–6–(triisopropylsiloxy)bicyclo[5.3.0]deca–1,5,9–triene–8,8–dicarboxylate (2f-*cis*)**



2f-*cis*

White crystal

IR (KBr) 2949, 2868, 1748, 1654, 1459, 1197 cm^{-1}

^{1}H–NMR (400 MHz in $CDCl_3$) δ = 1.06-1.11 (m, 18H), 1.17–1.26 (m, 3H), 3.20–3.27 (m, 1H), 3.27 (s, 3H), 3.39 (s, 3H), 3.70 (s, 3H), 3.78-3.83 (m, 1H), 3.81 (s, 3H), 4.12 (d, *J* = 9.6 Hz, 1H), 4.88 (brs, 1H), 5.10 (dd, *J* = 8.2, 2.2 Hz, 1H), 5.23 (dd, *J* = 5.8, 3.0 Hz, 1H), 6.08 (d, *J* = 5.6 Hz, 1H),

6.24 (d, *J* = 5.6 Hz, 1H), 7.18-7.29 (m, 3H), 7.39 (d, *J* = 6.8 Hz, 2H).
^{13}C–NMR (100 MHz in $CDCl_3$) δ = 13.3, 18.2, 18.3, 43.46, 43.53, 50.9, 51.6, 52.3, 52.8, 53.1, 70.9, 103.6, 111.3, 121.8, 126.3, 127.4, 130.4, 132.8, 136.7, 140.9, 145.1, 149.4, 169.0, 170.1.
Anal. Calcd for $C_{32}H_{46}O_7Si$: C, 67.34; H, 8.12. Found: C, 67.47; H, 8.41
The relative stereochemistry was confirmed by X-ray analysis as shown below.

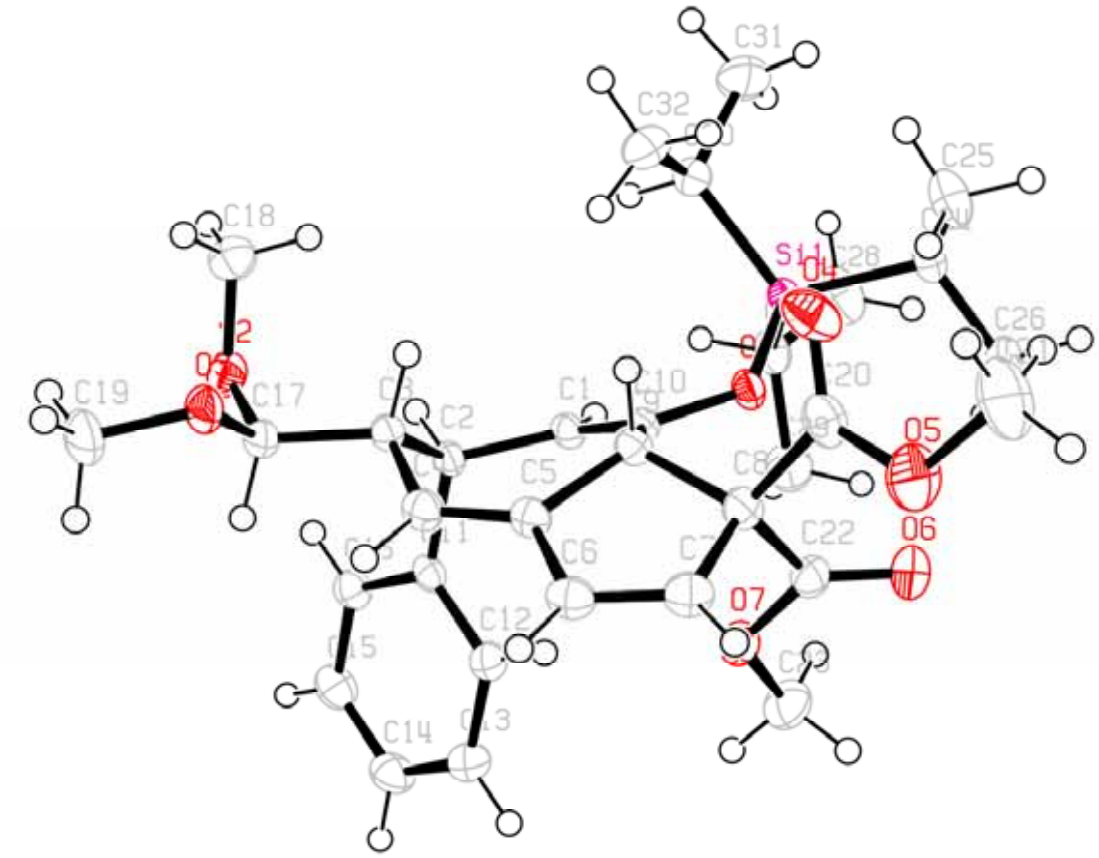
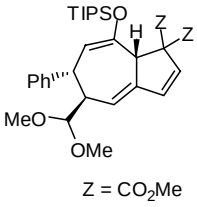


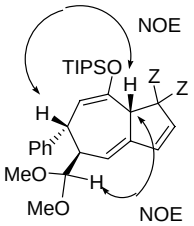
Figure S2. ORTEP plot of **2f-*cis***. Full table of data are provided in the cif. file.

Dimethyl (3*R, 4*R**, 7*S**)–3–dimethoxymethyl–4–phenyl–6–(triisopropylsiloxy)bicyclo[5.3.0]deca–1,5,9–triene–8,8–dicarboxylate (2f-*trans*)**

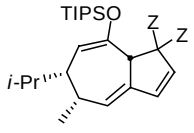


Z = CO_2Me
2f-*trans*

White solid
IR (KBr) 2922, 2866, 1742, 1656, 1459, 1200 cm^{-1}
^{1}H–NMR (500 MHz in $CDCl_3$) δ = 1.07-1.12 (m, 18H), 1.19–1.26 (m, 3H), 2.70 (td, *J* = 8.5, 4.2 Hz, 1H), 3.29 (s, 3H), 3.43 (s, 3H), 3.74 (s, 3H), 3.80 (s, 3H), 3.83-3.87 (m, 1H), 4.71 (d, *J* = 8.5 Hz, 1H), 4.74.79 (m, 1H), 4.90 (dd, *J* = 7.7, 2.1 Hz, 1H), 5.52 (dd, *J* = 8.5, 3.0 Hz, 1H), 6.02 (d, *J* = 5.5 Hz, 1H), 6.20 (d, *J* = 5.5 Hz, 1H), 7.17-7.21 (m, 1H), 7.25-7.29 (m, 2H), 7.40 (d, *J* = 7.2 Hz, 2H).
^{13}C–NMR (125 MHz in $CDCl_3$) δ = 13.1, 18.16, 18.20, 43.5, 47.0, 52.2, 52.4, 52.7, 53.1, 53.9, 70.8, 103.6, 107.4, 121.1, 126.0, 127.9, 129.0, 132.2, 138.2, 144.7, 145.5, 149.2, 169.2, 170.3.
Anal. Calcd for $C_{32}H_{46}O_7Si$: C, 67.34; H, 8.12. Found: C, 67.11; H, 8.20
The relative stereochemistry was confirmed by NOE experiment as shown below.



Dimethyl (3*R, 4*S**, 7*S**)-4–Isopropy-3–methyl-6-(triisopropylsiloxy)bicyclo[5.3.0]deca–1,5,9–triene–8,8–dicarboxylate (2g)**



Z = CO_2Me

2g

Pale yellow oil

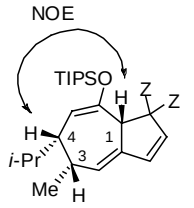
IR (neat) 2952, 2869, 1746, 1651, 1464, 1434, 1261 cm^{-1}

^1H–NMR (500 MHz, 330 K in $CDCl_3$) δ = 0.94 (d, *J* = 6.7 Hz, 3H), 0.95 (d, *J* = 6.7 Hz, 3H), 0.99 (d, *J* = 7.0 Hz, 3H), 1.09-1.13 (m, 18H), 1.20-1.28 (m, 3H), 1.63-1.70 (m, 1H), 2.17-2.22 (m, 1H), 2.58-2.65 (m, 1H), 3.63 (s, 3H), 3.76 (s, 3H), 4.60-4.63 (m, 1H), 4.66 (brs, 1H), 5.61 (dd, *J* = 7.0, 2.8 Hz, 1H), 5.97 (d, *J* = 5.5 Hz, 1H), 6.16 (d, *J* = 5.5 Hz, 1H).

^{13}C–NMR (125 MHz, 330 K in $CDCl_3$) δ = 13.2, 16.1, 18.1, 21.5, 21.9, 30.4, 33.6, 46.9, 50.9, 52.1, 52.4, 69.0, 107.2, 130.2, 131.3, 137.9, 142.7, 150.5, 169.6, 170.5.

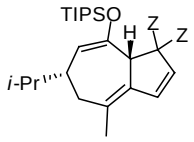
Anal. Calcd for $C_{27}H_{44}O_5Si$: C, 68.02; H, 9.30. Found: C, 67.80; H, 9.51

The relative stereochemistry was confirmed by NOE experiment as shown below.



The relative stereochemistry of C3 could not be determined by NOE experiment, but was temporary assigned to be *R** in comparison with that of **2a** derived from (*E*)-propenyl derivative **1a**.

Dimethyl (4*R, 7*S**)-4–Isopropyl 2–methyl–6-(triisopropylsiloxy)bicyclo[5.3.0]deca–1,5,9–triene–8,8–dicarboxylate (2h)**



Z = CO_2Me

2h

Pale yellow oil

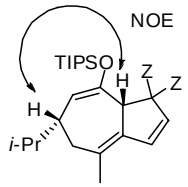
IR (neat) 2951, 2868, 1742, 1643, 1464, 1262 cm^{-1}

^1H–NMR (500 MHz in $CDCl_3$) δ = 0.93 (d, *J* = 6.7 Hz, 3H), 0.95 (d, *J* = 6.7 Hz, 3H), 1.03-1.08 (m, 18H), 1.14-1.21 (m, 3H), 1.57-1.63 (m, 1H), 1.78 (s, 3H), 1.94 (dd, *J* = 16.5, 9.6 Hz, 1H), 2.23-2.30 (m, 1H), 2.45 (d, *J* = 16.5 Hz,1H), 3.65 (s, 3H), 3.74 (s, 3H), 4.67 (d, *J* = 7.4 Hz, 1H), 4.77 (brs, 1H), 5.99 (d, *J* = 5.7 Hz, 1H), 6.50 (d, *J* = 5.7 Hz, 1H).

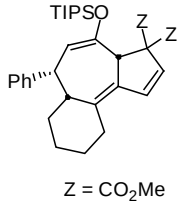
^{13}C–NMR (125 MHz in $CDCl_3$) δ = 13.1, 17.9, 18.1, 20.7, 21.3, 22.5, 32.4, 37.1, 42.0, 49.9, 52.1, 52.8, 68.4, 106.8, 129.2, 130.2, 133.8, 138.2, 151.2, 169.4, 170.8.

Anal. Calcd for $C_{27}H_{44}O_5Si$: C, 68.02; H, 9.30. Found: C, 68.07; H, 9.50

The relative stereochemistry was confirmed by NOE experiment as shown below.



Dimethyl (6*S, 9*S**, 10*R**)-7– (Triisopropylsiloxy)-9–phenyltricyclo[8.4.0.0^{2,6}]tetradeca–1,3,7–triene –5,5–dicarboxylate (4)**



Z = CO_2Me

4

White crystal

IR (KBr) 2934, 2864, 1737, 1655, 1459, 1210 cm^{-1}

^1H–NMR (500 MHz, 330 K in $CDCl_3$) δ = 1.09-1.13 (m, 18H), 1.20–1.40 (m, 5H), 1.44–1.54 (m, 2H), 1.56–1.65 (m, 2H), 1.71–1.80 (m, 1H), 2.01-2.08 (m, 1H), 2.68-2.73 (m, 1H), 3.69 (s, 3H), 3.79 (s, 3H), 3.79-3.84 (m, 1H), 4.95 (brs, 1H), 5.09 (dd, *J* = 8.0, 2.1 Hz, 1H), 6.03 (d, *J* = 5.8 Hz, 1H), 6.55 (d, *J* = 5.8 Hz, 1H), 7.18-7.22 (m, 1H), 7.25-7.29 (m, 2H), 7.33-7.36 (m, 2H).

^{13}C–NMR (125 MHz, 330 K in $CDCl_3$) δ = 13.2, 18.22, 18.23, 23.5, 24.6, 27.5, 30.1, 45.6, 47.0, 51.2, 52.1, 52.5, 69.5, 107.8, 126.1, 127.7, 129.4, 130.6, 133.7, 136.4, 136.6, 142.6, 151.2, 169.5, 170.7.

Anal. Calcd for $C_{33}H_{46}O_5Si$: C, 71.96; H, 8.42. Found: C, 72.19; H, 8.66

The relative stereochemistry was confirmed by X-ray analysis as shown below.

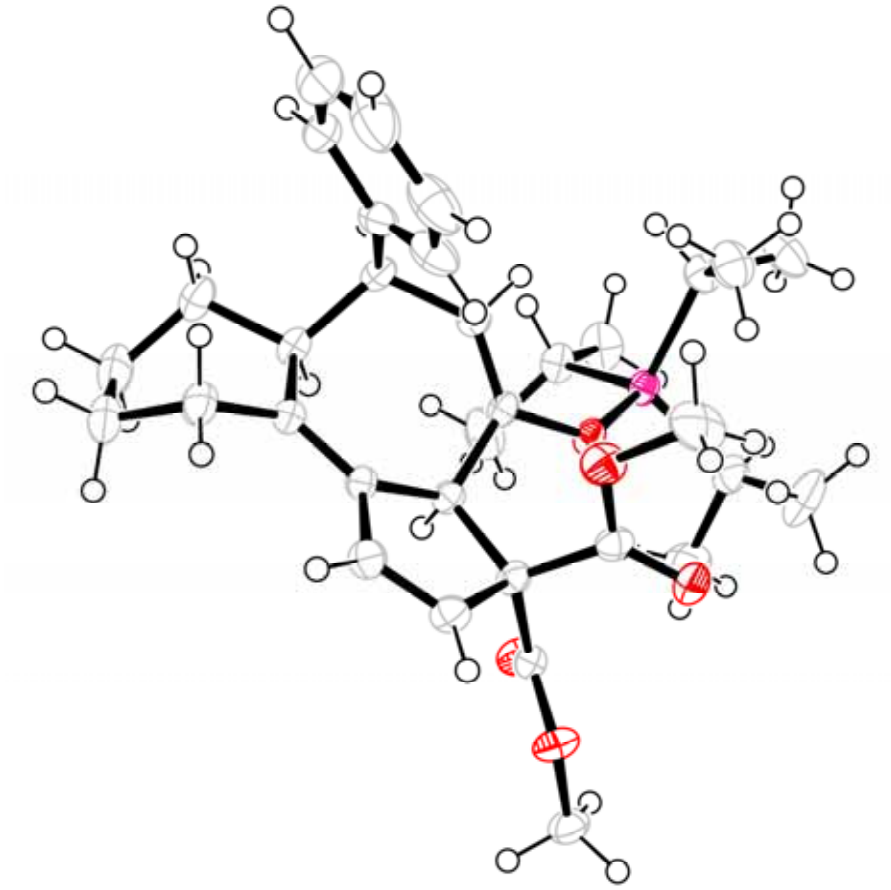
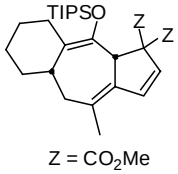


Figure S3. ORTEP plot of **4**. Full table of data are provided in the cif. file.

Dimethyl (3*S, 10*S**)-2–(Triisopropylsiloxy)-8–methyltricyclo[8.4.0.0^{3,7}]tetradeca–1,5,7–triene –4,4–dicarboxylate (6)**



6

White solid

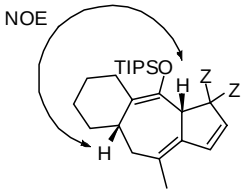
IR (KBr) 2926, 2866, 1743, 1646, 1434, 1260 cm^{-1}

^{1}H–NMR (500 MHz in $CDCl_3$) δ = 1.10-1.13 (m, 18H), 1.20-1.32 (m, 4H), 1.39-1.80 (m, 7H), 1.83 (dd, *J* = 13.8, 5.1 Hz, 1H), 1.85 (d, *J* = 2.2 Hz, 3H), 2.18-2.23 (m, 1H), 2.66 (brd, *J* = 12.1 Hz, 1H), 2.79 (d, *J* = 13.5 Hz, 1H), 3.64 (s, 3H), 3.78 (s, 3H), 4.92 (brs, 1H), 5.83 (d, *J* = 5.7 Hz, 1H), 6.49 (d, *J* = 5.7 Hz, 1H)

^{13}C–NMR (125 MHz, 350 K in benzene-d_6) δ = 14.2, 18.5, 18.9, 22.7, 27.3, 28.5, 32.4, 33.6, 39.4, 43.5, 51.5, 52.1, 53.5, 72.2, 124.5, 129.9, 131.1, 133.7, 138.9, 142.2, 169.1, 171.2.

Anal. Calcd for $C_{28}H_{44}O_5Si$: C, 68.81; H, 9.07. Found: C, 68.60; H, 8.78

The relative stereochemistry was confirmed by NOE experiment as shown below.



Reference

[1] Kuse, M.; Isobe, M. *Tetrahedron*, **2000**, *56*, 2629.
[2] Mitani, M.; Kobayashi, T.; Koyama, K. *J. Chem. Soc., Chem. Commun.* **1991**, 1418.
[3] Crisp, G. T.; Jiang, Y. -L.; Pullman, P. J.; Savi, C. D. *Tetrahedron*, **1997**, *53*, 17489.
[4] 1-Iodo-3,3-dimethoxyprop-1-ene was prepared from ethyl prop-2-ynoate according to the literature. See; Meyer, C.; Marek, I.; Normant, J. F. *Synlett*, **1993**, 386.