Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Rhenium(I)-Catalyzed Intramolecular Geminal Carbo-functionalization of Alkynes: Tandem Cyclization of *ω*-Acetylenic Dienol Silyl Ethers**

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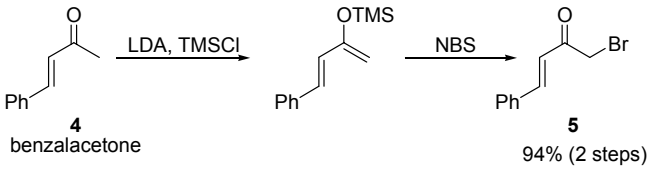
General. All operations were performed under an argon atmosphere. ^{1}H and ^{13}C–NMR spectra were recorded on a Bruker DRX–500 (500 MHz for H[1] and 125 MHz for ^{13}C) or a JEOL AL–400 (400 MHz for ^{1}H and 100 MHz for ^{13}C) spectrometer in $CDCl_3$ (99.8% atom enriched, Acros Co., Ltd.). Chemical shifts are expressed in parts per million (ppm) downfield from tetramethylsilane and are referenced to residual $CHCl_3$ (δ_H 7.26) for ^{1}H spectra and $CDCl_3$ (δ_C 77.0) for ^{13}C spectra. 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. LC–918 (Japan Analytical Industry Co. Ltd.) was used for further purifications. THF was freshly distilled from benzophenone ketyl, and all other solvents were distilled according to the usual procedures and stored over molecular sieves.

A. Preparation of dienol silyl ether 1a

1) 1-bromo-4-phenylbut-3-en-2-one (5)



To a 0.35 M THF solution (200 mL) of LDA (70 mmol) was added a THF solution (20 mL) of benzalacetone **4** (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.

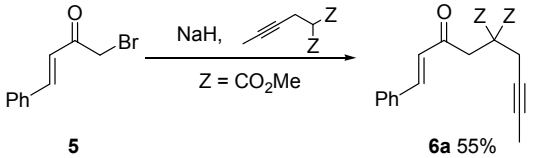
N-bromosuccinimide (13.3 g, 74.7 mmol) was added to a THF solution (100 mL) of the above silyl enol ether at –40 °C, and the mixture was stirred overnight at the same temperature. Then the mixture was poured into sat. $Na_2S_2O_3$ solution, and organic materials were extracted with ethyl acetate twice. 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 (**5**) as brown solids (94% 2 steps). Spectral data were consistent with those of the literature.[1]

^{1}H–NMR(400 MHz, $CDCl_3$) δ= 4.09 (s, 2H), 6.96 (d, J = 16.0 Hz, 1H), 7.41–7.43 (m, 3H), 7.58–7.60 (m, 2H), 7.71 (d, J = 16.1 Hz, 1H).

^{13}C–NMR(100 MHz, $CDCl_3$) δ=33.1, 122.1, 128.6, 129.0, 131.0, 133.9, 145.3, 190.8.

2) dimethyl (but-2-ynyl)(2-oxo-4-phenylbut-3-enyl)malonate (<u>6a</u>)



5 **6a** 55%

To a THF suspension (50 mL) of NaH (260 mg, 10.9 mmol) was added a THF solution (50 mL) of dimethyl but-2-ynylmalonate[2] at 0 °C. The reaction mixture was stirred for 100 min at the same temperature, and then a THF solution (10 mL) of bromoketone **5** (2.28 g, 10.1 mmol) was added. After the mixture was stirred overnight, the reaction was quenched with phosphate buffer. Organic materials were extracted with ethyl acetate, and then dried over $MgSO_4$. After the 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 **6a** (55%).

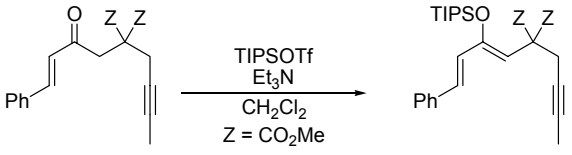
IR (KBr) 1740, 1729, 1207 cm^{-1}

^{1}H–NMR (400 MHz) δ = 1.75 (t, J = 2.7 Hz, 3H), 2.99 (q, J = 2.7 Hz, 2H), 3.59 (s, 2H), 3.76 (s, 3H), 6.74 (d, J = 16.4 Hz, 1H), 7.40–7.41 (m, 3H), 7.55–7.57 (m, 2H), 7.62 (d, J = 16.4 Hz, 1H).

^{13}C–NMR (100 MHz) δ = 3.65, 23.9, 42.9, 53.1, 73.7, 79.3, 125.8, 128.3, 128.9, 130.6, 134.2, 143.3, 169.9, 196.5.

Anal. Calcd for $C_{19}H_{30}O_5$: C, 69.50; H, 6.14 Found: C, 69.23, H, 6.13

3) dimethyl (but-2-ynyl)[4-phenyl-2- (triisopropylsiloxy)but-1,3-dienyl]malonate (<u>1a</u>)



6a **1a** 72%

TIPSOTf (1.5 mL, 5.5 mmol, 1.7 eq.) was added to a CH_2Cl_2 solution (50 mL) of ketone **6a** (1.01 g, 3.2 mmol) and Et_3N (1.35 mL, 9.7 mmol, 3 eq.) at –78 °C. After the mixture was stirred for 4 h at the same temperature, the mixture was slowly warmed up to room temperature and was further stirred overnight. The mixture was quenched with phosphate buffer, and then the organic materials were extracted with ether. Combined organic layer was washed with brine, and dried over $MgSO_4$. Resulting crude silyl enol ether **1a** was recrystallized from hexane to give 1.10 g of **1a** as white crystals (72%).

IR (neat) 1740, 1220, 1200, 1180 cm^{-1}

^{1}H–NMR(500 MHz) δ= 1.10–1.11 (m, 18H), 1.12–1.22 (m, 3H), 1.75 (t, J = 2.5 Hz, 3H), 3.11 (q, J = 2.4 Hz, 2H), 3.74 (s, 6H), 5.69 (s, 1H), 6.46 (d, J = 15.8 Hz, 1H), 6.93 (d, J = 15.8 Hz, 1H), 7.25–7.29 (m,

1H), 7.33–7.39 (m, 4H).

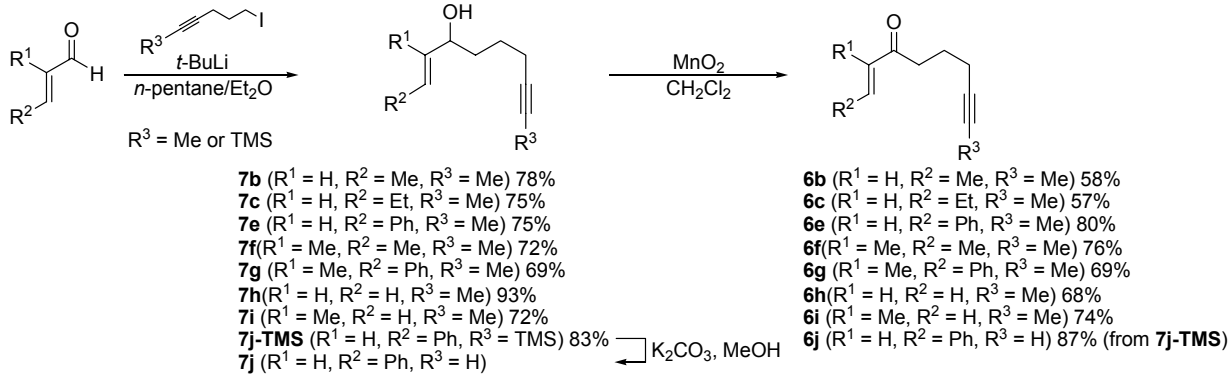
^{13}C–NMR(125 MHz) δ= 3.57, 13.8, 17.9, 25.2, 52.8, 56.8, 74.5, 77.7, 102.8, 125.8, 126.7, 128.1, 128.7, 131.8, 136.5, 151.3, 170.1.

Anal. Calcd for $C_{28}H_{40}O_5Si$: C, 69.38; H, 8.32 Found: C, 69.28; H, 8.27

B. Preparation of dienol silyl ethers (1b, 1c, 1e~1l)

The α, β-unsaturated ketones (**1b, 1c, 1e~1l)** were prepared as shown in Scheme 1.

Scheme 1



1) Preparation of allyl alcohol (7b, 7c, 7e~7j).

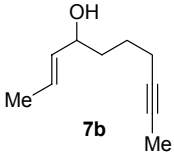
A typical procedure for the preparation of the allylic alcohols (**7b, 7c, 7e~7j**) is described for the reaction using cinnamaldehyde and 1-iodohex-4-yne[3, 4] as substrate:

A 1.47 M pentane solution (7.0 mL, 10 mmol) of *t*-BuLi was added to a pentane/ether (3 : 2, 50 mL) solution of 1-iodohex-4-yne (1.02 g, 4.88 mmol) at –78 °C. After the reaction mixture was stirred for 15 minutes, *trans*-cinnamaldehyde (0.77 mL, 6.1 mmol) was added. The reaction mixture was maintained at –78 °C for 40 min, and then was quenched with phosphate buffer (pH 7). Organic layer was extracted with ether twice, and the combined ether was washed with brine. After the organic layer was dried over $MgSO_4$, the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography (10% ethyl acetate in hexane) to give the allylic alcohol **7e** (781 mg, 75%).

The terminal acetylenic substrate **7j** was prepared by desilylation of **7j-TMS**:

K_2CO_3 (4.40 g, 31.9 mmol) was added to the methanol solution (30 mL) of allylic alcohol **7j-TMS** (1.72 g, 6.37 mmol). The reaction mixture was stirred for 6 h, and then was quenched with sat. $NaHCO_3$ solution. Organic material was extracted with ethyl acetate three times, and the combined organic layer was washed with water and brine. After the organic layer was dried over $MgSO_4$, the solvent was removed under reduced pressure to give allylic alcohol **7j**, which was sufficiently pure for the next step.

(2*E*)-dec-2-en-8-yn-4-ol (7b)



7b

IR (neat) 3366, 2919, 2052, 1673, 1450, 1065 cm^{-1}

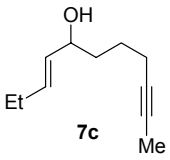
^{1}H–NMR (400 MHz) δ= 1.42–1.43 (m, 1H), 1.47–1.65 (m, 4H), 1.70 (ddd, J = 6.4, 1.6, 0.8 Hz 3H), 1.77

(t, *J* = 2.4 Hz, 3H), 2.15 (tq, *J* = 7.2, 2.4 Hz, 2H), 4.05 (m, 1H), 5.48 (ddq, *J* = 15.6, 6.6, 1.6 Hz, 1H), 5.66 (ddq, *J* = 15.6, 0.8, 6.6 Hz, 1H).

^{13}C–NMR (100 MHz) δ = 3.56, 17.7, 18.7, 25.1, 36.4, 72.8, 75.8, 78.9, 126.9, 134.0.

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.87; H, 10.48

(3*E*)-undec-3-en-9-yn-5-ol (7c)



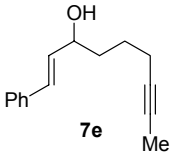
IR (neat) 3366, 2920, 2871, 1669, 1457, 1067 cm^{-1}

^{1}H–NMR (400 MHz) δ = 0.99 (t, *J* = 7.2 Hz, 3H), 1.43–1.66 (m, 5H), 1.78 (t, *J* = 2.4 Hz, 3H), 2.01–2.09 (m, 2H), 2.14–2.15 (m, 2H), 4.03–4.06 (m, 1H), 5.45 (ddt, *J* = 15.2, 7.0, 1.6 Hz, 1H), 5.68 (ddt, *J* = 15.2, 0.8, 7.0 Hz, 1H).

^{13}C–NMR (100 MHz) δ = 3.52, 13.5, 18.7, 25.1, 25.2, 36.5, 72.8, 75.7, 78.9, 131.7, 133.7.

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91 Found: C, 79.21; H, 10.93

(1*E*)-1-phenylnon-1-en-7-yn-3-ol (7e)



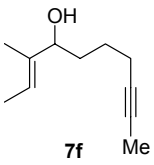
IR (neat) 3410, 2921, 2249, 1727, 1494, 1449, 1384, 1102 cm^{-1}

^{1}H–NMR (400 MHz) δ = 1.56–1.76 (m, 5H), 1.78 (t, *J* = 2.4 Hz, 3H), 2.19 (tq, *J* = 4.8, 2.4 Hz, 2H), 4.28–4.34 (m, 1H), 6.23 (dd, *J* = 16.0, 6.8 Hz, 1H), 6.58 (d, *J* = 16.0 Hz, 1H), 7.22− 7.40 (m, 5H).

^{13}C–NMR (100 MHz) δ = 3.52, 18.7, 25.0, 36.4, 72.6, 75.9, 78.8, 126.3, 127.5, 128.5, 130.2, 132.2, 136.5.

Anal. Calcd for $C_{15}H_{18}O$: C, 84.06; H, 8.47 Found: C, 84.31; H, 8.73

(2*E*)-3-methyldec-2-en-8-yn-4-ol (7f)



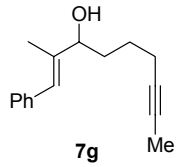
IR (neat) 3582, 2920, 2862, 1734, 1670, 1439, 1381 cm^{-1}

^{1}H–NMR (400 MHz) δ = 1.35–1.67 (m, 11H), 1.75 (t, *J* = 2.4 Hz, 3H), 2.12–2.17 (m, 2H), 4.00 (t, *J* = 6.8 Hz, 1H), 5.41–5.49 (m, 1H).

^{13}C–NMR (100 MHz) δ = 3.54, 10.9, 13.1, 18.7, 25.4, 34.0, 75.7, 77.6, 79.0, 120.9, 137.7.

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91 Found: C, 79.18; H, 11.19

(1*E*)-2-methyl-1-phenylnon-1-en-7-yn-3-ol (7g)



7g

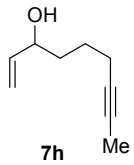
IR (neat) 3366, 3024, 2918, 2051, 1718, 1654, 1600, 1443, 1066 cm^{-1}

^{1}H–NMR (400 MHz) δ = 1.50–1.79 (m, 8H), 1.88 (s, 3H), 2.17–2.22 (m, 2H), 4.19–4.22 (m, 1H), 6.50 (s, 1H), 7.20–7.36 (m, 5H).

^{13}C–NMR (100 MHz) δ = 3.56, 13.2, 18.7, 25.3, 34.2, 75.9, 77.8, 78.9, 125.8, 126.4, 128.0, 128.9, 137.4, 140.1.

Anal. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83 Found: C, 84.25; H, 9.05

non-1-en-7-yn-3-ol (7h)



7h

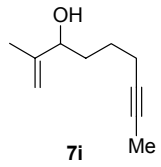
IR (neat) 3376, 2920, 2231, 1644, 1435 cm^{-1}

^{1}H–NMR (400 MHz) δ = 1.50− 1.67 (m, 5H), 1.77 (t, J = 2.4 Hz, 3H), 2.14− 2.19 (m, 2H), 4.1 (br, 1H), 5.11 (dt, J = 10.6, 1.6 Hz, 1H), 5.23 (dt, J = 17.6, 1.6 Hz, 1H), 5.87 (ddd, J = 17.6, 10.6, 6.4 Hz, 1H).

^{13}C–NMR (100 MHz) δ = 3.54, 18.7, 24.9, 36.1, 72.9, 75.9, 78.8, 114.7, 141.0.

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21 Found: C, 77.87; H, 10.44

2-methylnon-1-en-7-yn-3-ol (7i)



7i

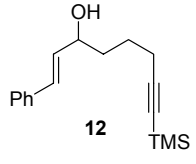
IR (neat) 3389, 3072, 2945, 2864, 2231, 1651, 1453, 1373 cm^{-1}

^{1}H–NMR (400 MHz) δ = 1.43− 1.70 (m, 5H), 1.72 (br, 3H), 1.77 (t, J = 2.4 Hz, 3H), 2.16 (tq, J = 7.2, 2.4 Hz, 2H), 4.06− 4.09 (m, 1H), 4.83 (t, J = 1.0 Hz, 1H), 4.94 (t, J = 1.0 Hz, 1H).

^{13}C–NMR (100 MHz) δ = 3.52, 17.6, 18.7, 25.1, 34.0, 75.5, 75.8, 78.9, 111.0, 147.3.

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59 Found: C, 78.65; H, 10.86

(1*E*)-8-Trimethylsilyl-1-phenyloct-1-en-7-yn-3-ol (7j-TMS)



12

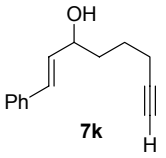
IR(neat) 3350, 2960, 2180, 1250 cm^{-1}

^{1}H–NMR (400 MHz) δ = 0.13 (s, 9H), 1.58–1.76 (m, 5H), 2.27 (t, J = 6.6 Hz, 2H), 4.31, (dt, J = 6.8, 6.6 Hz, 1H), 6.21 (dd, J = 15.9, 6.8 Hz, 1H), 6.57 (d, J = 15.9 Hz, 1H), 7.21–7.38 (m, 5H).

^{13}C–NMR (100 MHz) δ = 0.14, 19.7, 24.5, 36.3, 72.6, 84.9, 107.0, 126.4, 127.7, 128.6, 130.5, 132.2, 136.6.

Anal. Calcd for $C_{17}H_{24}OSi$: C, 74.94; H, 8.88 Found: C, 74.82; H, 9.15

(1*E*)-1-phenyloct-1-en-7-yn-3-ol (7j)



IR (neat) 3300, 2940, 1490, 1450 cm^{-1}

^{1}H–NMR (400 MHz) δ = 1.56 (d, *J* = 3.6 Hz, 1H), 1.60–1.77 (m, 4H), 1.95 (t, *J* = 2.7 Hz, 1H), 2.24 (dt, *J* = 6.6, 2.7 Hz, 2H), 4.27–4.32 (m, 1H), 6.21 (dd, *J* = 15.9, 6.8 Hz, 1H), 6.56 (d, *J* = 15.9 Hz, 1H), 7.21–7.38 (m, 5H).

^{13}C–NMR (100 MHz) δ = 13.4, 24.4 36.2, 68.6, 72.6, 84.2, 126.4, 127.6, 128.5, 130.4, 132.0, 136.4.

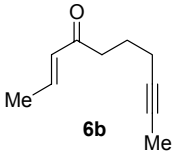
Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05 Found: C, 83.66; H, 7.78

2) Preparation of α, β-unsaturated ketones (<u>6b</u>, <u>6c</u>, <u>6e</u> ~ <u>6j</u>).

A typical procedure for the oxidation of (**6b, 6c, 6e** ~ **6j**) is described for the reaction using **7e** as substrate:

A mixture of allylic alcohol **7e** (781 mg, 3.65 mmol) and MnO_2 (9.95 g 115 mmol) in CH_2Cl_2 (50 mL) was stirred for 5.5 hours at room temperature. The reaction mixture was filtered through a pad of Celite®, and the resulting solution was evaporated under reduced pressure. The residue was purified by silica gel chromatography (10% ethyl acetate in hexane) to give α, β-unsaturated ketone **6e** (622 mg, 80%).

(2*E*)-dec-2-en-8-yn-4-one (<u>6b</u>)



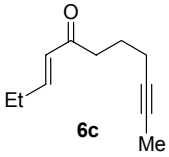
IR (neat) 2938, 2920, 1697, 1671, 1633, 1442 cm^{-1}

^{1}H–NMR (400 MHz) δ = 1.74–1.81 (m, 5H), 1.90 (dd, *J* = 6.8, 1.6 Hz, 3H), 2.17 (tq, *J* = 7.2, 2.4 Hz, 2H), 2.64 (t, *J* = 7.2 Hz, 2H), 6.13 (dq, *J* = 16.0, 1.6 Hz, 1H), 6.87 (dq, *J* = 16.0, 6.8 Hz, 1H).

^{13}C–NMR (100 MHz) δ = 3.55, 18.3, 23.4, 38.7, 76.2, 78.4, 131.9, 142.4, 199.9.

Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39 Found: C, 79.70; H, 9.50

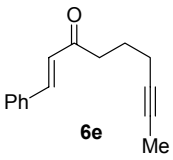
(3*E*)-undec-3-en-9-yn-5-one (<u>6c</u>)



IR (neat) 3380, 2966, 2225, 1673, 1630, 1438 cm^{-1}

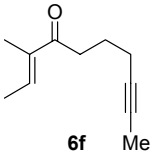
^{1}H–NMR (400 MHz) δ = 1.08 (t, J = 7.2 Hz, 3H), 1.75–1.82 (m, 5H), 2.15–2.29 (m, 4H), 2.66 (t, J = 7.2 Hz, 2H), 6.10 (dt, J = 15.8, 1.6 Hz, 1H), 6.90 (dt, J = 15.8, 6.4 Hz, 1H).
^{13}C–NMR (100 MHz) δ = 3.56, 12.3, 18.3, 23.5, 25.6, 38.8, 76.2, 78.4, 129.4, 148.6, 200.2.
Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82 Found: C, 80.36; H, 9.62

(1*E*)-1-phenylnon-1-en-7-yn-3-one (6e)



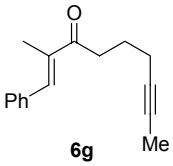
IR (neat) 2919, 2856, 2051, 1663, 1610, 1449 cm^{-1}
^{1}H–NMR (400 MHz) δ = 1.79 (t, J = 2.4 Hz, 3H), 1.85 (quintet, J = 7.2 Hz, 2H), 2.24 (tq, J = 7.2, 2.4 Hz, 2H), 2.80 (t, J = 7.2 Hz, 2H), 6.75 (d, J = 16.1 Hz, 1H), 7.38–7.41 (m, 3H), 7.54–7.61 (m, 3H).
^{13}C–NMR (100 MHz) δ = 3.56, 18.3, 23.5, 39.6, 76.4, 78.4, 126.2, 128.1, 128.8, 130.3, 134.4, 142.3, 199.8.
Anal. Calcd for $C_{15}H_{16}O$: C, 84.86; H, 7.60 Found: C, 84.90; H, 7.73

(2*E*)-3-methyldec-2-en-8-yn-4-one (6f)



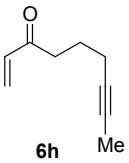
IR (neat) 2921, 2857, 2052, 1668, 1644, 1439 cm^{-1}
^{1}H–NMR (400 MHz) δ = 1.72–1.79 (m, 8H), 1.86 (dq, J = 6.9, 1.0 Hz, 3H), 2.18 (tq, J = 6.9, 2.3 Hz, 2H), 2.76 (t, J = 7.4 Hz, 2H), 6.78 (qq, J = 6.9, 1.3 Hz, 1H).
^{13}C–NMR (100 MHz) δ = 3.52, 11.1, 14.8, 18.4, 24.0, 36.0, 76.1, 78.5, 137.0, 138.1, 201.1
Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82 Found: C, 80.18; H, 10.03

(1*E*)-2-methyl-1-phenylnon-1-en-7-yn-3-one (6g)



IR (neat) 3025, 2919, 1666, 1626, 1445, 1366 cm^{-1}
^{1}H–NMR (400 MHz) δ = 1.79 (t, J = 2.4 Hz, 3H), 1.86 (quintet, J = 7.2 Hz, 2H), 2.06 (d, J = 1.6 Hz, 3H), 2.24 (tq, J = 7.2, 2.4 Hz, 2H), 2.93 (t, J = 7.2 Hz, 2H), 7.33–7.44 (m, 5H), 7.57 (d, J = 1.6 Hz, 1H).
^{13}C–NMR (100 MHz) δ = 3.58, 13.2, 18.4, 24.1, 36.4, 76.3, 78.5, 128.3, 129.6, 135.9, 137.3, 138.5, 201.8.
Anal. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02 Found: C, 84.61; H, 8.03

non-1-en-7-yn-3-one (6h)



6h

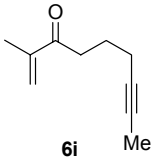
IR (neat) 2921, 1700, 1682, 1616, 1403 cm^{-1}

^{1}H–NMR (400 MHz) δ = 1.76− 1.83 (m, 5H), 2.19 (tq, J = 7.2, 2.4 Hz, 2H), 2.71 (t, J = 7.2 Hz, 2H), 5.83 (dd, J = 10.8, 1.6 Hz, 1H), 6.24 (dd, J = 17.6, 1.6 Hz, 1H), 6.36 (dd, J = 17.6, 10.8 Hz, 1H).

^{13}C–NMR (100 MHz) δ = 3.52, 18.2, 23.2, 38.3, 76.4, 78.3, 127.9, 136.5, 200.3.

HRMS for $C_9H_{12}O$: 136.0888 Found: m/z 136.0858

2-methylnon-1-en-7-yn-3-one (6i)



6i

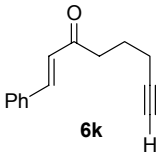
IR (neat) 2922, 1767, 1680, 1631, 1453, 1370cm^{-1}

^{1}H–NMR (400 MHz) δ = 1.76− 1.82 (m, 5H), 1.87–1.88 (m 3H), 2.18 (tq, J = 6.8, 2.4 Hz, 2H), 2.80 (t, J = 7.2 Hz, 2H), 5.76 (br, 1H), 6.00 (br, 1H).

^{13}C–NMR (100 MHz) δ = 3.53, 17.7, 18.3, 23.7, 36.3, 76.2, 78.4, 124.4, 144.4, 201.5.

Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39 Found: C, 79.69; H, 9.29

(1*E*)-1-phenyloct-1-en-7-yn-3-one (6j)



6k

IR (neat) 3300, 2940, 1690, 1660, 1620, 1550, 750 cm^{-1}

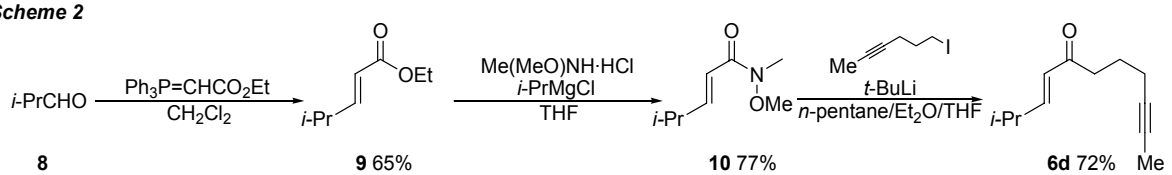
^{1}H–NMR (400 MHz) δ = 1.89 (tt, J = 7.1 Hz, 7.1 Hz, 2H), 1.98 (t, J = 2.4 Hz, 1H), 2.28 (dt, J = 7.1, 2.4 Hz, 2H), 2.82 (t, J = 7.1 Hz, 2H), 6.73 (d, J = 16.4 Hz, 1H), 7.37 (m, 3H), 7.52–7.55 (m, 2H), 7.56 (d, J = 16.4 Hz, 1H).

^{13}C–NMR (100 MHz) δ = 18.0, 22.8, 39.2, 69.1, 83,7, 126.1, 128.2, 128.9, 130.4, 134.4, 142.5, 199.5.

Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12 Found: C, 84.55; H, 7.33

The ketones **6d** was prepared as shown in Scheme 2.

Scheme 2



3) Preparation of α, β-unsaturated ester (9).

Ester **9** was prepared according to the literature, [5] and was obtained in 65% yield.

4) Preparation of Weinreb amide (10).

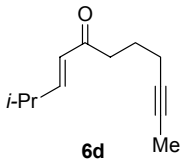
Weinreb amide **10** was prepared according to the method of Williams'.[6]

An ether solution of *i*-PrMgCl (1.73 M, 9.8 mL, 17.0 mmol) was added slowly to a mixture of Me(MeO)NH· HCl (828 mg, 8.49 mmol) and ester **9** (777 mg, 5.47 mmol) in THF (10 mL) at –4 °C over 5 min. The reaction temperature was raised gradually to room temperature, and the mixture was stirred for 80 minutes. The reaction was quenched with 20 %wt aq. NH_4Cl solution and then was extracted with ether twice. The combined organic layer was washed with brine and was dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by silica gel chromatography (30% ether in pentane). Weinreb amide **10** (662 mg) was obtained as a yellowish oil in 77% yield. Spectral data of **10** were consistent with those of the literature.

5) Preparation of α, β-unsaturated ketone (6d).

A pentane solution of *t*-BuLi (1.53 M, 5.1 mL, 7.80 mmol) was added to an ether/pentane solution (2 : 3, 25 mL) of 6-iodohex-2-yne (810 mg, 3.89 mmol) at –78 °C. The reaction mixture was stirred until 6-iodohex-2-yne was consumed completely as checked by an analytical TLC (for 30 min ~ 2 h). Resulting lithiated solution was added dropwise to a THF solution (25 mL) of Weinreb amide **10** (468 mg, 2.98 mmol) at –78 °C over 10 min *via* cannula. The reaction mixture was maintained at the same temperature for additional 2 hours. The reaction was quenched with phosphate buffer (pH 7), and was extracted with ethyl acetate three times. The combined organic layer was washed with brine and was dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by silica gel chromatography (10% ethyl acetate in hexane). The ketone **6d** was obtained in 72% yield as colorless oil.

(3*E*)-2-methylundec-3-en-9-yn-5-one (6d)



6d

IR (neat) 2962, 2871, 1697, 1672, 1629, 1465, 1368 cm^{-1}

^{1}H–NMR (400 MHz) δ = 1.07 (d, J = 6.8 Hz, 6H), 1.58–1.82 (m, 5H), 2.18 (tq, J = 6.8, 2.4 Hz, 2H), 2.42–2.51 (m, 1H), 2.66 (t, J = 7.2 Hz, 2H), 6.05 (dd, J = 16.0, 1.2 Hz, 1H), 6.82 (dd, J = 16.0, 6.4 Hz, 1H).

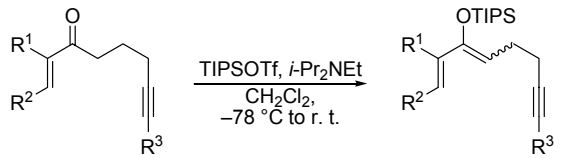
^{13}C–NMR (100 MHz) δ = 3.56, 18.3, 21.4, 23.5, 31.2, 38.9, 76.7, 77.3, 127.5, 153.3, 200.4.

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18 Found: C, 80.73; H, 10.19

6) Preparation of dienol silyl ethers (1d, 1e, 1g~1j).

Dienol silyl ethers **1d**, **1e**, **1g~1j** were prepared by using *i*-Pr_2NEt as a base (Scheme 3).

Scheme 3

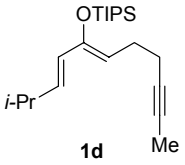


6d (R^1 = H, R^2 = *i*-Pr, R^3 = Me)	**1d** (R^1 = *i*-Pr, R^2 = H, R^3 = Me)	84%	(*Z* isomer only)
6e (R^1 = H, R^2 = Ph, R^3 = Me)	**1e** (R^1 = Ph, R^2 = H, R^3 = Me)	79%	(*E* : *Z* = 6 : 94)
6g (R^1 = Me, R^2 = Ph, R^3 = Me)	**1g** (R^1 = Ph, R^2 = Me, R^3 = Me)	92%	(*E* : *Z* = 17 : 83)
6h (R^1 = H, R^2 = H, R^3 = Me)	**1h** (R^1 = H, R^2 = H, R^3 = Me)	40%	(*E* : *Z* = 5 : 95)
6i (R^1 = Me, R^2 = H, R^3 = Me)	**1i** (R^1 = Me, R^2 = H, R^3 = Me)	35%	(*Z* isomer only)
6j (R^1 = H, R^2 = Ph, R^3 = H)	**1j** (R^1 = H, R^2 = Ph, R^3 = H)	83%	(*E* : *Z* = 9 : 91)

A typical procedure for the preparation of dienol silyl ethers (**1d**, **1e**, **1g~1j**) is described for the reaction of **6d** as substrate:

TIPSOTf (0.22 mL, 0.82 mmol) was added dropwise to a mixture of ketone **6d** (109 mg, 0.61 mmol), *i*-Pr_2NEt (0.21 mL, 1.21 mmol) in CH_2Cl_2 (6 mL) at –78 °C over 2 min, and the reaction mixture was stirred overnight (the reaction temperature gradually rose to 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 ether, 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 using silica gel deactivated with water (5 %wt) and eluent (hexane) cooled to –78 °C. Dienol silyl ether **1d** (171 mg) was obtained in 84% yield.

triisopropyl[(3*E*, 5*Z*)-2-methylundeca-3,5-dien-9-yn-5-yloxy]silane (1d)



1d

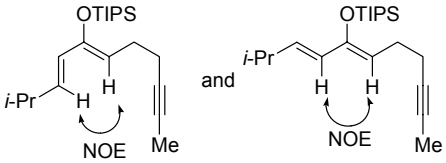
IR (neat) 2960, 2868, 2051, 1653, 1625, 1465, 1164 cm^{-1}

^{1}H–NMR (400 MHz) δ = 1.00 (d, *J* = 6.8 Hz, 6H), 1.09–1.12 (m, 18H), 1.15–1.22 (m, 3H), 1.78 (t, *J* = 2.4 Hz, 3H), 2.13–2.19 (m, 2H), 2.27–2.37 (m, 3H), 4.72 (t, *J* = 7.2 Hz, 1H), 5.76–5.85 (m, 2H).

^{13}C–NMR (100 MHz) δ = 3.65, 13.8, 18.1, 19.1, 22.4, 25.7, 30.8, 75.5, 79.0, 109.6, 126.0, 136.5, 149.7.

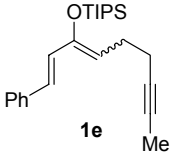
Anal. Calcd for $C_{21}H_{38}OSi$: C, 75.38; H, 11.45 Found: C, 75.58; H, 11.75

The geometry was confirmed by NOE experiments as shown blow.



triisopropyl[(1*E*, 3*Z*)-1-phenylnona-1,3-dien-7-yn-3-yloxy]silane (1e–*Z*)

triisopropyl[(1*E*, 3*E*)-1-phenylnona-1,3-dien-7-yn-3-yloxy]silane (1e–*E*)



1e

1e–*Z* and **1e–*E*** were obtained as an inseparable mixture in a ratio of 5 : 1.

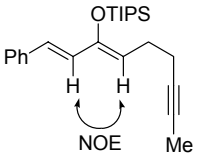
IR (neat) 2945, 2867, 2051, 1941, 1870, 1806, 1726, 1619, 1465, 1165 cm^{-1}

^{1}H–NMR (400 MHz) (*E* : *Z* = 6 : 94) δ = 1.05–1.19 (m, 18H), 1.21–1.31 (m, 3H), 1.75 (t, *J* = 2.4 Hz, 0.18H), 1.80 (t, *J* = 2.4 Hz, 2.82H), 2.17–2.23 (m, 2H), 2.38, (q, *J* = 6.8 Hz, 2H), 4.97 (t, *J* = 6.8 Hz, 1H), 6.57 (d, *J* = 15.9 Hz, 0.94H), 6.72 (d, *J* = 15.9 Hz, 0.94H), 6.89–7.00 (m, 0.12H), 7.19–7.44 (m, 5H).

^{13}C–NMR (100 MHz) (major isomer) δ = 3.64, 13.9, 18.2, 19.0, 26.0, 75.8, 78.8, 113.2, 126.3, 127,0, 127.2, 127.7, 128.5, 137.1, 149.8.

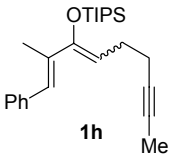
Anal. Calcd for $C_{24}H_{36}OSi$: C, 78.19; H, 9.84 Found: C, 78.04; H, 9.86

The geometry of the major isomer was confirmed by NOE experiment as shown blow.



triisopropyl[(1*E*, 3*Z*)-2-methyl-1-phenylnona-1,3-dien-7-yn-3-yloxy]- silane (1g–*Z*)

triisopropyl[(1*E*, 3*E*)-2-methyl-1-phenylnona-1,3-dien-7-yn-3-yloxy]- silane (1g–*E*)



1g–*Z* and **1g–*E*** were obtained as an inseparable mixture in a ratio of 87 : 13.

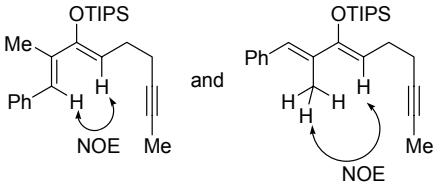
IR (neat) 2945, 2867, 1621, 1464, 1356, 1119 cm^{-1}

^{1}H–NMR (400 MHz) (*E* : *Z* = 17 : 83) δ = 1.10–1.15 (m, 18H), 1.19–1.29 (m, 3H), 1.77 (t, *J* = 2.4 Hz, 0.51H), 1.80 (t, *J* = 2.4 Hz, 2.49H), 2.00 (d, *J* = 0.8 Hz, 2.49H), 2.01 (d, *J* = 1.2 Hz, 0.51H), 2.17–2.25 (m, 2H), 2.30–2.42 (m, 2H), 4.86 (t, *J* = 7.6 Hz, 0.17H), 5.04 (t, *J* = 6.8 Hz, 0.83H), 6.52 (br, 0.17H), 6.86 (br, 0.83H), 7.20–7.36 (m, 5H).

^{13}C–NMR (100 MHz) (major isomer) δ = 3.65, 12.8, 14.0, 18.0, 19.1, 26.2, 75.6, 79.0, 109.4, 125.7, 126.2, 128.0, 129.0, 134.7, 138.1, 152.6.

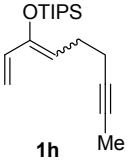
Anal. Calcd for $C_{25}H_{38}OSi$: C, 78.47; H, 10.01 Found: C, 78.57; H, 10.11

The geometry of the major isomer was confirmed by NOE experiments as shown blow.



[(*Z*)-nona-1,3-dien-7-yn-3-yloxy]triisopropylsilane (1h–*Z*)

[(*E*)-nona-1,3-dien-7-yn-3-yloxy]triisopropylsilane (1h–*E*)



1h–*Z* and **1h–*E*** were obtained as an inseparable mixture in a ratio of 95 : 5.

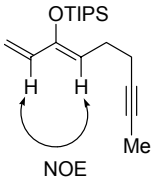
IR (neat) 2946, 2868, 1646, 1605, 1465, 1368 cm^{-1}

^{1}H–NMR (400 MHz)(major isomer) δ = 1.06− 1.25 (m, 21H), 1.78 (t, J = 2.4 Hz, 3H), 2.15− 2.20 (m, 2H), 2.32 (q, J = 7.2 Hz, 2H), 4.83 (t, J = 7.2 Hz, 1H), 4.97 (d, J = 10.4 Hz, 1H), 5.35 (d, J = 17.2 Hz, 1H), 6.16 (dd, J = 17.2, 10.4 Hz, 1H).

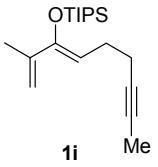
^{13}C–NMR (100 MHz)(major isomer) δ = 3.61, 13.9, 18.1, 18.9, 25.7, 75.7, 78.8, 112.2, 112.3, 136.0, 149.8.

HRMS Calcd for $C_{18}H_{32}O$: 292.2222 Found: m/z 292.2206

The geometry of the major isomer was confirmed by NOE experiments as shown blow.



[(*Z*)-2-methylnona-1,3-dien-7-yn-3-yloxy]triisopropylsilane (1i)



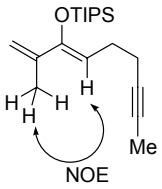
IR (neat) 2946, 2868, 2244, 1641, 1610, 1465, 1354, 1136 cm^{-1}

^{1}H–NMR (400 MHz) δ = 1.06− 1.25 (m, 21H), 1.78 (t, J = 2.6 Hz, 3H), 1.87 (br, 3H), 2.16− 2.20 (m, 2H), 2.32 (q, J = 6.8 Hz, 2H), 4.88 (br, 1H), 4.91 (t, J = 6.8 Hz, 1H), 5.24 (br, 1H).

^{13}C–NMR (100 MHz) δ = 3.61, 14.0, 18.2, 19.0, 20.5, 26.0, 75.6, 78.9, 109.1, 112.0, 141.1, 151.2.

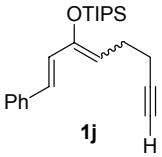
Anal. Calcd for $C_{11}H_{18}O$: C, 74.44; H, 11.18 Found: C, 74.27; H, 11.46

The geometry was confirmed by NOE experiments as shown blow.



triisopropyl[(1*E*, 3*Z*)-1-phenylocta-1,3-dien-7-yn-3-yloxy]silane (1j–*Z*)

triisopropyl[(1*E*, 3*E*)-1-phenylocta-1,3-dien-7-yn-3-yloxy]silane (1j–*E*)



1j–*Z* and **1j–*E*** were obtained as an inseparable mixture in a ratio of 10 : 1.

IR(neat) 3025, 2867, 2118, 1634, 1619, 1465, 1367 cm^{-1}

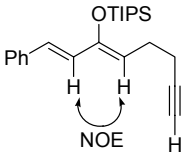
^{1}H–NMR (400 MHz) (E : Z = 1 : 10) δ = 1.06–1.18 (m, 18H), 1.20–1.31 (m, 3H), 1.97–2.00 (m, 1H), 2.25–2.32 (m, 2H), 2.41–2.48 (m, 2H), 4.96–5.02 (m, 1H), 6.57 (d, J = 15.6 Hz, 0.91 H), 6.74 (d, J = 15.6 Hz, 0.91H), 6.91 (d, J = 15.8 Hz, 0.09H), 7.01 (d, J = 15.8 Hz, 0.09H), 7.20–7.27 (m, 1H), 7.28–7.35 (m,

2H), 7.36–7.40 (m, 1.82H), 7.42–7.46 (m, 0.18H).

^{13}C–NMR (100 MHz) (major isomer)δ = 13.9, 18.1 18.7, 25.4, 68.5, 84.1, 112.3, 126.3, 126.7, 127.3, 127.3, 127.5, 128.5, 137.0, 150.2.

HRMS Calcd for $C_{23}H_{34}OSi$: 354.2379 Found: m/z 354.2374

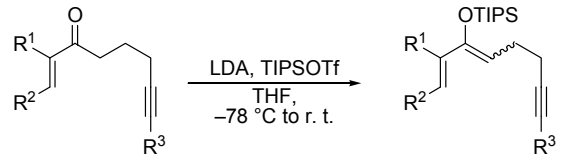
The geometry of the major product was confirmed by NOE experiment as shown blow.



7) Preparation of dienol silyl ethers (<u>1b</u>, <u>1c</u>, <u>1f</u>).

Dienol silyl ethers **1b**, **1c**, **1f** were prepared by using LDA as a base (Scheme 4).

Scheme 4



6b (R^1 = H, R^2 =Me, R^3 =Me) **1b** (R^1 = H, R^2 =Me, R^3 =Me) 65% (*E* : *Z* = 1 : 4)
6c (R^1 = H, R^2 =Et, R^3 =Me) **1c** (R^1 = H, R^2 =Et, R^3 =Me) 65% (*E* : *Z* = 1 : 3)
6f (R^1 = Me, R^2 = Me, R^3 =Me)[a] **1f** (R^1 = Me, R^2 = Me, R^3 =Me) 89% (*Z* isomer only)

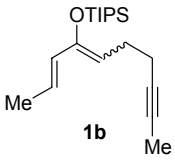
[a] The reaction proceeded at –98 °C.

A typical procedure for the preparation of dienol silyl ethers (**1b**, **1c**, **1f**) is described for the reaction of **6b** as substrate:

To a THF solution (4mL) of LDA (0.86 mmol) was added a THF solution (4 mL) of ketone **6b** (117 mg, 0.78 mmol) at –78 °C. The reaction mixture was stirred for 45 minutes, and then TIPSOTf (0.24 mL, 0.89 mmol) was added. The reaction mixture was stirred overnight (reaction temperature gradually rose to room temperature). Et_3N was added before quenching with phosphate buffer (pH 7), and then organic layer was extracted with ethyl acetate, and was washed with brine. The organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography using the deactivated silica gel and cooled eluent (hexane). Dienol silyl ether **1b** (156 mg) was obtained in 65% yield.

[(2*E,* 4*Z*)-deca-2,4-dien-8-yn-4-yloxy]triisopropylsilane (<u>1b–*Z*</u>)

[(2*E,* 4*E*)-deca-2,4-dien-8-yn-4-yloxy]triisopropylsilane (<u>1b–*E*</u>)



1b–*Z* and **1d–*E*** were obtained as an inseparable mixture in a ratio of 4 : 1.

IR (neat) 2945, 2922, 2868, 1654, 1626, 1465, 1166 cm$^{-1,}$

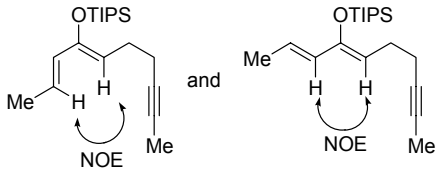
^{1}H–NMR (400 MHz) (*E* : *Z* = 1 : 4) δ = 1.04–1.25 (m, 21H), 1.73–1.81 (m, 6H), 2.13–2.18 (m, 2H), 2.24–2.32 (m, 2H), 4.69 (t, *J* = 7.2 Hz, 0.8H), 4.77 (t, *J* = 7.2 Hz, 0.2H), 5.77–5.90 (m, 1.6H), 6.05–6.23 (m, 0.4H).

^{13}C–NMR (100 MHz) (*E* : *Z* = 1 : 4) δ = 3.51, 3.63, 12.9, 13.8, 17.8, 18.1, 18.2, 19.1, 20.0, 25.6, 26.1,

75.5, 75.9, 79.0, 107.1, 109.3, 124.1, 124.2, 126.3, 130.2, 148.4, 149.6.

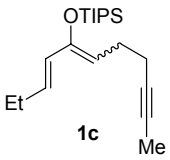
Anal. Calcd for $C_{19}H_{34}OSi$: C, 74.44; H, 11.18 Found: C, 74.58; H, 11.41

The geometry of the major product was confirmed by NOE experiments as shown blow.



triisopropyl[(3*E,* 5*Z*)-undeca-3,5-dien-9-yn-5-yloxy]silane (1c–*Z*)

triisopropyl[(3*E,* 5*E*)-undeca-3,5-dien-9-yn-5-yloxy]silane (1c–*E*)



1c–*Z* and **1e–*E*** were obtained as an inseparable mixture in a ratio of 3 : 1.

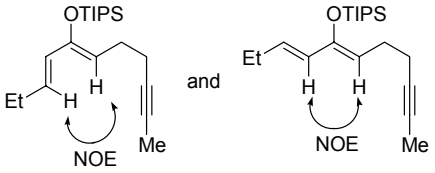
IR (neat) 2962, 2945, 2868, 1654, 1625, 1464, 1166 cm^{-1}

^{1}H–NMR (400 MHz) (*E* : *Z* = 1 : 3) δ = 0.98–1.04 (m, 3H), 1.10–1.12 (m, 18H), 1.14–1.24 (m, 3H), 1.76 (t, *J* = 2.4 Hz, 0.75H), 1.78 (t, *J* = 2.4 Hz, 2.25H), 2.08–2.18(m, 4H), 2.25–2.32 (m, 2H), 4.71 (t, *J* = 7.2 Hz, 0.75H), 4.79 (t, *J* = 7.6 Hz, 0.25H), 5.80–5.91 (m, 1.5H), 6.09–6.19 (m, 0.5H).

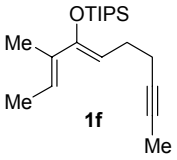
^{13}C–NMR (100 MHz) (*E* : *Z* = 1 : 3) δ = 3.52, 3.64, 12.9, 13.6, 13.7, 13.8, 18.1, 18.2, 19.1, 20.0, 25.4, 25.7, 26.2, 75.5, 75.9, 78.8, 79.0, 107.5, 109.5, 121.7, 127.9, 131.2, 133.3, 149.7.

Anal. Calcd for $C_{20}H_{36}OSi$: C, 74.93; H, 11.32 Found: C, 75.01; H, 11.37

The geometry of the major product was confirmed by NOE experiments as shown blow.



triisopropyl[(2*E,* 4*Z*)-3-methyldeca-2,4-dien-8-yn-4-yloxy]silane (1f)



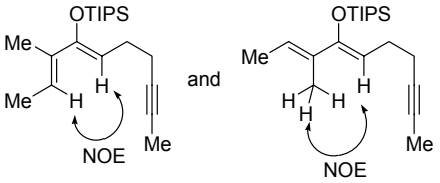
IR (neat) 2945, 2867, 1650, 1629, 1465, 1315, 1128 cm^{-1}

^{1}H–NMR (400 MHz) δ = 1.09 (d, *J* = 3.2 Hz, 18H), 1.12–1.20 (m, 3H), 1.67 (d, *J* = 7.0 Hz, 3H), 1.74 (br, 3H), 1.78 (t, *J* = 2.4 Hz, 3H), 2.13–2.18 (m, 2H), 2.31 (q, *J* = 7.2 Hz, 2H), 4.77 (t, *J* = 7.2 Hz, 1H), 5.82 (dq, *J* = 1.2, 7.0 Hz, 1H).

^{13}C–NMR (100 MHz) δ = 3.63, 13.5, 13.8, 13.9, 18.1, 19.2, 25.9, 75.4, 79.1, 106.8, 121.1, 133.5, 152.6.

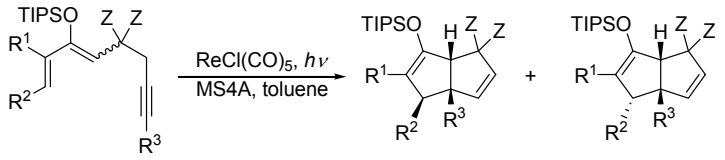
Anal. Calcd for $C_{20}H_{36}OSi$: C, 74.93; H, 11.32 Found: C, 75.15; H, 11.39

The geometry was confirmed by NOE experiments as shown blow.



D. Tandem cyclization of dienol silyl ethers (1a ~ 1j).

Scheme 5



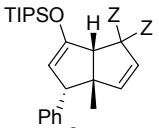
2–*α* **2–*β***

1a (R^1 = H, R^2 = Ph, R^3 = Me, Z = CO_2Me)
1b (R^1 = H, R^2 = Me, R^3 = Me, Z = H)
1c (R^1 = H, R^2 = Et, R^3 = Me, Z = H)
1d (R^1 = H, R^2 = *i*-Pr, R^3 = Me, Z = H)
1e (R^1 = H, R^2 = Ph, R^3 = Me, Z = H)
1f (R^1 = Me, R^2 = Me, R^3 = Me, Z = H)
1g (R^1 = Me, R^2 = Ph, R^3 = Me, Z = H)
1h (R^1 = H, R^2 = H, R^3 = Me, Z = H)
1i (R^1 = Me, R^2 = H, R^3 = Me, Z = H)
1j (R^1 = H, R^2 = Ph, R^3 = H, Z = H)

A typical procedure for the cyclization of dienol silyl ethers (**1a ~ 1l**) is described for the reaction of **1a** as substrate:

To a mixture of $ReCl(CO)_5$ (1.1 mg, 0.0030 mmol, 0.5 mol%) and activated MS4A was added **1a** (292 mg, 0.60 mmol) in degassed toluene (1.0 mL). After the mixture was photoirradiated (250W super high–pressure Hg lamp) overnight, the reaction mixture was directly passed through silica gel deactivated with 5 wt% of water (10% ethyl acetate in hexane) to give crude product, which was purified by PTLC (10% ethyl acetate in hexane) to give 269 mg (0.55 mmol, 92%) of **2a** and **3a** as a mixture of diastereomers (**2a-*α*** : **2a-*β*** : **3a** = 69 : 17 : 14). **2a-*α*** could be isolated by a further purification of this mixture.

(1*S, 5*R**, 6*S**)-dimethyl 5-methyl-6-phenyl-8- (triisopropylsiloxy)bicyclo[3.3.0]oct-3,7-diene-2,2-dicarboxylate (2a–*α*)**



2a–*α*
Z = CO_2Me

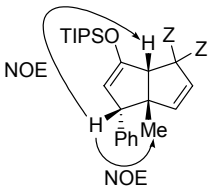
IR (neat) 1740, 1260, 1220 cm^{-1}

^{1}H–NMR(500 MHz) δ= 1.10–1.12(m, 18H), 1.18–1.22 (m, 3H), 1.32 (s, 3H), 3.64 (br, 1H), 3.73 (s, 3H), 3.74 (s, 3H), 3.90 (br, 1H), 4.68 (br, 1H), 4.82 (d, *J* = 5.6 Hz, 1H), 5.46 (d, *J* = 5.6 Hz, 1H), 7.18–7.31 (m, 5H).

^{13}C–NMR(125 MHz) δ= 12.5, 17.9, 18.0, 27.2, 52.5, 52.6, 57.4, 58.5, 61.5, 68.9, 107.0, 126.0, 126.4, 128.0, 128.6, 141.5, 142.2, 152.5, 170.6, 171.3.

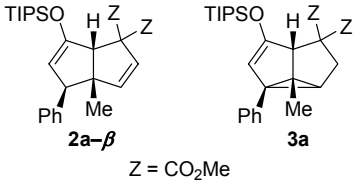
Anal. Calcd for $C_{28}H_{40}O_5Si$: C, 69.38; H, 8.46. Found: C, 69.26; H, 8.33

The relative stereochemistry was confirmed by NOE experiments and as shown blow.



(1*S, 5*R**, 6*R**)-dimethyl 5-methyl-6-phenyl-8-(triisopropylsiloxy)bicyclo[3.3.0]oct-3,7-diene-2,2-dicarboxylate (2a–*β*)**

dimethyl 8-methyl-5-phenyl-7-(triisopropylsiloxy)tricyclo[3.2.1.0^{4,8}]oct-6-ene-2,2-dicarboxylate (3a)



2a–*β* and **3a** were obtained as an inseparable mixture in a ratio of 1 : 1.

IR (neat) 2950, 2868, 1739, 1454, 1434 cm^{-1}

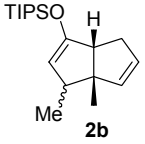
^{1}H–NMR(500 MHz) (**2b–*β*** : **3b** = 1 : 1) δ = 0.68 (s, 1.5H), 1.05 (s, 1.5H), 1.06–1.33 (m, 21H), 2.06 (dd, *J* = 6.8, 1.9 Hz, 0.5H), 2.69 (ddd, *J* = 14.4, 6.8, 1.6 Hz, 0.5H), 2.82 (dd, *J* = 14.4, 1.9 Hz, 0.5H), 3.31 (d, *J* = 1.6 Hz, 0.5H), 3.66 (s, 1.5H), 3.72 (s, 1.5H), 3.75 (s, 1.5H), 3.78 (s, 1.5H), 3.84 (dd, *J* = 2.0, 1.6 Hz, 0.5H), 3.87–3.88 (m, 0.5H), 4.71–4.72(m, 0.5H), 4.73 (s, 0.5H), 5.72 (d, *J* = 5.4 Hz, 0.5H), 5.97 (d, *J* = 5.4Hz, 0.5H), 7.16–7.23 (m, 3H), 7.26–7.31 (m, 2H).

^{13}C–NMR(125 MHz) δ = 12.4, 12.5, 15.5, 17.8, 17.9, 18.1, 23.7, 31.6, 33.7, 45.5, 48.7, 52.2, 52.5, 52.6, 55.8, 58.4, 61.2, 62.4, 68.2, 72.7, 106.5, 106.9, 126.0, 126.2, 126.4, 128.0, 128.1, 128.4, 128.8, 140.7, 142.7, 144.3, 152.6, 155.5, 168.7, 170.5, 171.1, 172.1.

Anal. Calcd for $C_{28}H_{40}O_5Si$: C, 69.38; H, 8.46. Found: C, 69.54 ; H, 8.46

(1*R, 4*R**, 5*R**)-[4,5-Dimethylbicyclo[3.3.0]oct-2,6-dien-2-yloxy]triisopropylsilane (2b–*α*)**

(1*R, 4*S**, 5*R**)-[4,5-Dimethylbicyclo[3.3.0]oct-2,6-dien-2-yloxy]triisopropylsilane (2b–*β*)**



2b–*α* and **2b–*β*** were obtained as an inseparable mixture in a ratio of 75 : 25.

IR (neat) 3051, 2946, 2867, 1648, 1464, 1334, 1215 cm^{-1}

^{1}H–NMR (500 MHz) (*α* : *β* = 75 : 25) δ = 0.91 (d, *J* = 7.2, 2.25H), 0.95 (d, *J* = 7.1 Hz, 0.75H), 1.03 (s, 0.75H), 1.05–1.09 (m, 18H), 1.10–1.21 (m, 3H), 1.13 (s, 2.25H), 2.37–2.44 (m, 1.5H), 2.48–2.52 (m, 1.5H), 2.70–2.71 (m, 0.25H), 2.77 (dq, *J* = 8.4, 1.8 Hz, 0.75H), 4.31 (t, *J* = 1.8 Hz, 0.75H), 4.44–4.45 (m, 0.25H), 5.47 (dt, *J* = 5.8, 2.1 Hz, 0.75 H), 5.49 (s, 0.5 H), 5.55 (dt, *J* = 5.8, 2.3 Hz, 0.75H).

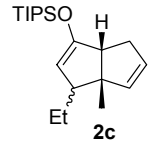
^{13}C–NMR (125 MHz) δ = 12.5, 16.8, 18.1, 18.5, 20.7, 25.6, 33.5, 34.8, 43.3, 46.1, 53.8, 55.3, 55.4, 56.9, 106.1, 106.6, 125.6, 127.4, 136.2, 141.3, 154.3.

Anal. Calcd for $C_{19}H_{34}OSi$: C, 74.44; H, 11.18. Found: C, 74.15; H, 11.13

The relative stereochemistry of the major product was assumed to be (1*R**, 4*R**, 5*R**) by a comparison with 4-ethyl derivative **2c**.

(1*R, 4*R**, 5*R**)-[4-Ethyl-5-methylbicyclo[3.3.0]oct-2,6-dien-2-yloxy]triisopropylsilane (2c–*α*)**

(1*R, 4*S**, 5*R**)-[4-Ethyl-5-methylbicyclo[3.3.0]oct-2,6-dien-2-yloxy]triisopropylsilane (2c–*β*)**



2c

2c–*α* and **2c**–*β* were obtained as an inseparable mixture in a ratio of 67 : 33.

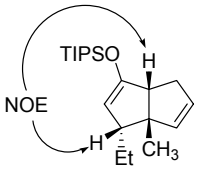
IR (neat) 3051, 2946, 2867, 1647, 1464, 1335, 1229 cm^{-1}

^{1}H–NMR (500 MHz) (*α* : *β* = 67 : 33) *δ* = 0.88 (t, *J* = 7.4 Hz, 0.99H), 0.92 (t, *J* = 7,4 Hz, 2.01H), 0.98–1.25 (m, 25.3H), 1.41–1.50 (m, 0.67H), 2.14–2.20 (m, 0.33H), 2.27–2.30 (m, 0.67H), 2.35–2.51 (m, 2H), 2.67–2.70 (m, 0.33H), 2.77 (dq, *J* = 9.1, 1.8 Hz, 0.67H), 4.45 (t, *J* = 1.8 Hz, 0.67 H), 4.59 (br, 0.33H), 5.48 (s, 0.66H), 5.51 (dt, *J* = 5.8, 2.0 Hz, 0.67H), 5.55 (dt, *J* = 5.7, 2.2 Hz, 0.67H).

^{13}C–NMR (125 MHz) (*α* : *β* = 67 : 33) *δ* = 12.5, 12.7, 13.5, 17.9, 20.5, 25.4, 26.1, 26.5, 33.5, 34.6, 50.4, 54.0, 54.0 55.6, 56.8, 103.8, 103.8, 125.4, 127.4, 136.3, 141.5, 154.8.

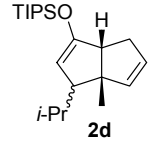
Anal. Calcd for $C_{20}H_{36}OSi$: C, 74.93; H, 11.32. Found: C, 74.65; H, 11.27

The relative stereochemistry of the major product was confirmed by NOE experiments as shown blow.



(1*R, 4*R**, 5*R**)-triisopropyl[5-methyl-4-(1-methylethyl)bicyclo[3.3.0]oct-2,6-dien-2-yloxy] silane (2d–*α*)**

(1*R, 4*S**, 5*R**)-triisopropyl[5-methyl-4-(1-methylethyl)bicyclo[3.3.0]oct-2,6-dien-2-yloxy] silane (2d–*β*)**



2d

2d–*α* and **2d**–*β* were obtained as an inseparable mixture in a ratio of 70 : 30.

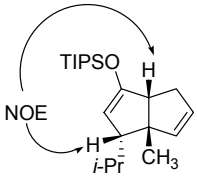
IR (neat) 3053, 2947, 2868, 1649, 1464, 1336, 1231, 1215 cm^{-1}

^{1}H–NMR (500 MHz) (*α* : *β* = 70 : 30) *δ* = 0.79 (d, *J* = 6.6 Hz, 0.9H), 0.85 (d, *J* = 6.6, 2.1 Hz, 2.1H), 0.90 (d, *J* = 4.1 Hz, 0.9H), 0.98 (d, *J* = 4.4 Hz, 2.1H), 1.14–1.30 (m, 24H), 1.47–1.53 (m, 0.7H), 1.84–1.93 (m, 0.3H), 2.13 (dt, *J* = 8.4, 1.9, 0.7 Hz, 0.7H), 2.22 (dd, *J* = 3.0, 2.8 Hz, 0.3H), 2.30–2.50 (m, 2H), 2.68–2.71 (m, 0.3H), 2.75 (dq, *J* = 8.5, 1.9 Hz, 0.7H), 4.41–4.42 (m, 0.3H), 4.47 (t, *J* = 1.9 Hz, 0.7H), 5.44–5.48 (m, 0.6H), 5.56 (dt, *J* = 5.8, 2.3 Hz, 0.7H), 5.62 (dt, *J* = 5.8, 2.2 Hz, 0.7H).

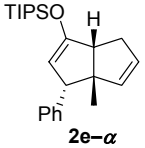
^{13}C–NMR (125 MHz) (*α* : *β* = 70 : 30) *δ* = 12.3, 12.5, 17.7, 18.0, 19.1, 20.1, 21.9, 23.1, 23.2, 28.1, 28.9, 30.1, 33.5, 34.5, 54.4, 55.2, 55.5, 56.3, 56.9, 59.4, 99.8, 102.7, 125.0, 127.7, 136.4, 142.2, 154.6, 155.5.

Anal. Calcd for $C_{21}H_{38}OSi$: C, 75.38; H, 11.45. Found: C, 75.11; H, 11.74

The relative stereochemistry of the major product was confirmed by NOE experiments as shown below.



(1*R, 4*S**, 5*R**)-triisopropyl[5-methyl-4-phenylbicyclo[3.3.0]oct-2,6-dien-2-yloxy]silane (2e–*α*)**



2e–*α*

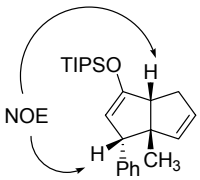
IR (neat) 3059, 2945, 2866, 1645, 1355, 1224 cm^{-1}

^{1}H–NMR (500 MHz) δ = 1.11–1.13 (m, 18H), 1.20–1.26 (m, 3H), 1.27 (s, 3H), 2.42 (ddt, *J* = 16.9, 8.4, 2.3 Hz, 1H), 2.60 (ddt, *J* = 16.9, 8.4, 1.8 Hz, 1H), 2.88 (dq, *J* = 8.4, 1.8 Hz, 1H), 3.76 (t, *J* = 1.8 Hz, 1H), 4.50 (t, *J* = 1.8 Hz, 1H), 4.63 (dt, *J* = 5.7, 2.3 Hz, 1H), 5.42 (dt, *J* = 5.7, 2.3 Hz, 1H), 7.10–7.30 (m, 5H).

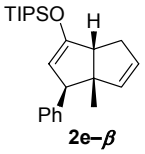
^{13}C–NMR (125 MHz) δ = 12.6, 18.1, 25.8, 34.7, 54.9, 57.9, 58.6, 103.2, 126.0, 126.5, 127.7, 128.3, 136.9, 143.0, 156.3.

Anal. Calcd for $C_{24}H_{36}OSi$: C, 78.19; H, 9.84. Found: C, 78.23; H, 10.14

The relative stereochemistry was confirmed by NOE experiments as shown blow.



(1*R, 4*R**, 5*R**)-triisopropyl[5-methyl-4-phenylbicyclo[3.3.0]oct-2,6-dien-2-yloxy]silane (2e–*β*)**



2e–*β*

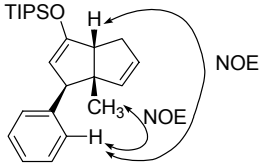
IR (neat) 3060, 2945, 2867, 1942, 1871, 1803, 1645, 1335, 1224 cm^{-1}

^{1}H–NMR (500 MHz) δ = 0.63 (s, 3H), 1.10–1.14 (m, 18H), 1.20–1.27 (m, 3H), 2.46 (ddt, *J* = 16.7, 7.9, 2.4 Hz, 1H), 2.56 (ddt, *J* = 16.7, 2.4, 1.7 Hz, 1H), 2.83 (ddt, *J* = 7.9, 2.5, 1.7 Hz, 1H), 3.60 (t, *J* = 2.5 Hz, 1H), 4.55 (dd, *J* = 2.5, 1.7 Hz, 1H), 5.57 (dt, *J* = 5.6, 2.4 Hz, 1H), 5.66 (dt, *J* = 5.6, 2.4 Hz, 1H), 7.15–7.30 (m, 5H).

^{13}C–NMR (125 MHz) δ = 12.5, 18.1, 23.0, 33.6, 54.1, 56.6, 57.2, 103.1, 125.9, 126.0, 127.8, 128.8, 141.0, 144.0, 156.4.

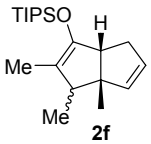
Anal. Calcd for $C_{24}H_{36}OSi$: C, 78.19; H, 9.84. Found: C, 78.13; H, 9.98

The relative stereochemistry was confirmed by NOE experiments as shown blow.



(1*R, 4*S**, 5*R**)-triisopropyl[3,4,5-trimethylbicyclo[3.3.0]oct-2,6-dien-2-yloxy]silane (2f–*α*)**

(1*R, 4*R**, 5*R**)-triisopropyl[3,4,5–trimethylbicyclo[3.3.0]oct-2,6-dien-2-yloxy]silane (2f–*β*)**



2f

2f–α and **2f–β** were obtained as an inseparable mixture in a ratio of 23 : 77.

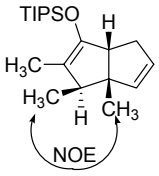
IR (neat) 2945, 2867, 1687, 1464, 1320, 1214 cm^{-1}

^{1}H–NMR (400 MHz) δ = 0.90 (d, J = 7.2 Hz, 0.69H), 0.95 (d, J = 7.2 Hz, 2.31H), 1.00–1.20 (m, 24H), 1.48–1.49 (m, 0.69H), 1.52 (dd, J = 2.0, 1.2 Hz, 2.31H), 2.17–2.30 (m, 0.54H), 2.42–2.45 (m, 2H), 2.68–2.77 (m, 1H), 5.44–5.55 (m, 2H).

^{13}C–NMR (100 MHz) (α : β = 23 : 77) δ = 10.5, 11.3, 13.0, 15.2, 15.8, 18.0, 21.3, 26.8, 34.9, 36.4, 47.5, 49.2, 54.5, 55.0, 56.1, 114.8, 115.5, 125.4, 127.3, 136.2, 141.0, 146.8, 147.1.

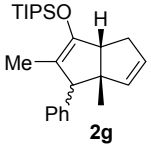
Anal. Calcd for $C_{20}H_{36}OSi$: C, 74.93; H, 11.32. Found: C, 74.92; H, 11.48

The relative stereochemistry of the major product was confirmed by NOE experiments as shown below.



(1*R, 4*S**, 5*R**)- [3,5–dimethyl-4-phenylbicyclo[3.3.0]oct-2,6-dien-2-yloxy]- triisopropylsilane (2g–α)**

(1*R, 4*R**, 5*R**)- [3,5–dimethyl-4-phenylbicyclo[3.3.0]oct-2,6-dien-2-yloxy]- triisopropylsilane (2g–β)**



2g

2g–α and **2g–β** were obtained as an inseparable mixture in a ratio of 20 : 80.

IR (neat) 3050, 2946, 1685, 1453, 1322, 1214 cm^{-1}

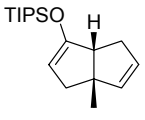
^{1}H–NMR (500 MHz) (α : β = 20 : 80) δ = 0.63 (s, 2.4H), 1.10–1.29 (m, 21.6H), 1.39–1.40 (m, 0.6H), 1.42 (m, 2.4H), 2.43–2.58 (m, 2H), 2.84–2.87 (m, 1H), 3.40 (d, J = 1.8 Hz, 0.8H), 3.48 (s, 0.2H), 4.58 (dt, J = 5.7, 2.3 Hz, 0.2H), 5.38 (dt, J = 5.7, 2.3 Hz, 0.2H), 5.57 (dt, J = 5.5, 2.3 Hz, 0.8H), 5.62 (dt, J = 5.5, 2.3 Hz, 0.8H), 7.00–7.30 (m, 5H).

^{13}C–NMR (125 MHz) (α : β = 20 : 80) δ = 11.0, 11.8, 13.0, 17.9, 18.0, 23.6, 27.6, 35.0, 36.6, 54.9, 55.1, 56.0, 57.4, 61.5, 62.6, 112.4, 113.0, 125.9, 126.0, 126.0, 126.5, 127.6, 127.8, 129.3, 137.3, 141.0, 141.5, 142.5, 149.4, 150.0.

Anal. Calcd for $C_{25}H_{38}OSi$: C, 78.47; H, 10.01. Found: C, 78.18; H, 9.98

The stereochemistry of the major product was assumed to be (1*R**, 4*R**, 5*R**) by a comparison with 4–phenyl derivative **2e**.

(1*R, 5*S**)- triisopropyl[5-methylbicyclo[3.3.0]oct-2,6-dien-2-yloxy]silane (2h)**



2h

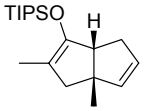
IR (neat) 3050, 2946, 2867, 1647, 1464, 1334, 1226 cm^{-1}

^{1}H–NMR (500 MHz) δ = 1.04− 1.08 (m, 18H), 1.14–1.19 (m, 6H), 2.16− 2.23 (m, 2H), 2.43− 2.46 (m, 2H), 2.71− 2.74 (m, 2H), 4.39 (q, *J* = 2.1 Hz, 1H), 5.47 (dt, *J* = 5.6, 2.1 Hz, 1H), 5.52 (dt, *J* = 5.6, 2.2 Hz, 1H).

^{13}C–NMR (125 MHz) δ = 12.5, 17.9, 26.5, 34.4, 41.6, 53.3, 54.5, 98.7, 126.4, 139.8, 155.1.

Anal. Calcd for $C_{18}H_{32}O$: C, 73.90; H, 11.03 Found: C, 73.64; H, 11.31

(1*R, 5*S**)-[3,5-dimethylbicyclo[3.3.0]oct-2,6-dien-2-yloxy] triisopropylsilane (2i)**



2i

IR (neat) 3048, 2946, 2868, 1688, 1464, 1323, 1220 cm^{-1}

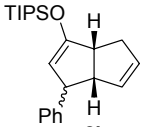
^{1}H–NMR (400 MHz) δ = 1.06− 1.15 (m, 21H), 1.16 (s, 3H), 1.53− 1.54 (m, 3H), 2.07− 2.17 (m, 2H), 2.39− 2.50 (m, 2H), 2.72− 2.79 (m, 2H), 5.47 (dt, *J* = 5.6, 2.0 Hz, 1H), 5.50 (dt, *J* = 5.6, 1.9 Hz, 1H).

^{13}C–NMR (100 MHz) δ = 12.5, 13.0, 18.0, 27.4, 36.0, 47.2, 51.8, 55.4, 109.9, 126.4, 139.5, 147.2.

Anal. Calcd for $C_{11}H_{18}O$: C, 74.44; H, 11.18 Found: C, 74.18; H, 11.0

(1*R, 4*S**, 5*R**)-triisopropyl[4-phenylbicyclo[3.3.0]oct-2,6-dien-2-yloxy]silane (2j–α)**

(1*R, 4*R**, 5*R**)-triisopropyl[4-phenylbicyclo[3.3.0]oct-2,6-dien-2-yloxy]silane (2j–β)**



2j

2j–α and **2j–β** were obtained as an inseparable mixture in a ratio of 85 : 15.

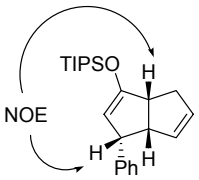
IR (neat) 2944, 2867, 1644, 1464, 1335 cm^{-1}

^{1}H–NMR (400 MHz) (**2j–α** : **2j–β** = 75 : 25) 1.06–1.15 (m, 18H), 1.20–1.29 (m, 3H), 2.35–2.47 (m, 1H), 2.58 (double– quintet, *J* = 16.4, 2.2 Hz, 0.25 H), 2.65 (double–quintet, *J* = 16.8, 2.2 Hz, 0.75 H), 3.11–3.15 (m, 0.25H), 3.28–3.34 (m, 0.75H), 3.37–3.42 (m, 0.25H), 3.53–3.62 (m, 1H), 4.15–4.18 (m, 0.75H), 4.53 (t, *J* = 1.6 Hz, 0.75H), 4.57 (t, *J* = 2.2 Hz, 0.25H), 4.76–4.79 (m, 0.75H), 5.51–5.54 (m, 0.75H), 5.67–5.70 (m, 0.25H), 5.75–5.78 (m, 0.25H), 7.12–7.30 (m, 5H)

^{13}C–NMR (100 MHz) (**2j–α** : **2j–β** = 75 : 25) 12.5, 12.6, 18.0, 18.0, 34.9, 35.7, 47.0, 47.8, 50.1, 52.1, 53.5, 56.8, 102.5, 102.7, 125.8, 127.0, 127.8, 128.2, 128.3, 128.5, 128.6, 131.6, 133.8, 143.5, 147.7, 157.0. 157.6.

HRMS Calcd for $C_{23}H_{34}OSi$: 354.2379 Found: 354.2365

The relative stereochemistry of the major product was confirmed by NOE experiments as shown blow.



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[4] 5-Iodo-1-(trimethylsilyl)pent-1-yne was prepared from 5-(trimethylsilyl)pent-4-yn-1-ol in the same manner as the preparation of 1-iodohex-4-yne (see ref. 3). 5-(trimetylsilyl)-pent-4-yn-1-ol was prepared by the method of Corchrane's, see: Corchrane, J. S.; Hanson, J. R. *J. Chem. Soc. Perkin Trans. I*, **1972**, 361.

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