Supporting Information

Auto-tandem Catalysis; Facile Synthesis of Substituted Alkylidenecyclohexanones by Domino (4 + 2) Cycloaddition-Elimination Raction

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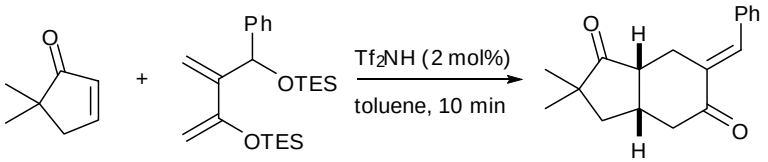
Solvent effects in the domino (4 + 2) cycloaddition-elimination reaction of **3d** and **4a** were examined. The results are summarized in Table S1. The results indicate that CH_2Cl_2 and toluene are appropriate solvents for the domino reaction. When the reaction was subjected in THF, ring-opening polymerization of THF solvent giving poly(tetramethylene ether glycol)s was observed.

Table S1. Solvent effects.[a]



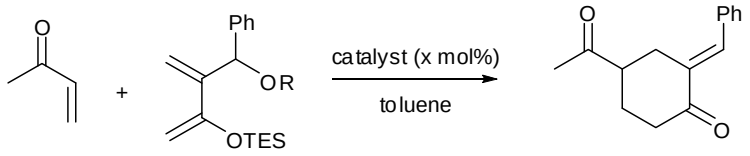
4a **3d** **5b**

entry	solvent	% yield of **5b**
1	toluene	66
2	chlorobenzene	35
3	CH_2Cl_2	65
4	hexane	10
5	CH_3CN	22
6	THF	0
7	Et_2O	0

[a] Conditions; **3d** (1.2 equiv.), **4a** (1.0 equiv.), Tf_2NH (2 mol%), toluene, -40 ^oC, 10 min.

A survey of the optimal catalyst was carried out in the reaction of **4a** and **3d** (or **3f**). The results are summarized in Table S1. Several acidic catalysts gave the desired *exo*-enone **5c**. Among the acidic catalysts tested, several representative element Lewis acids such as BF_3, $EtAlCl_2$, ZnI_2 and $TMSNTf_2$ activate the domino reaction to give **5c** albeit in low conversion.

Table S2. Results of catalyst screen.[a]



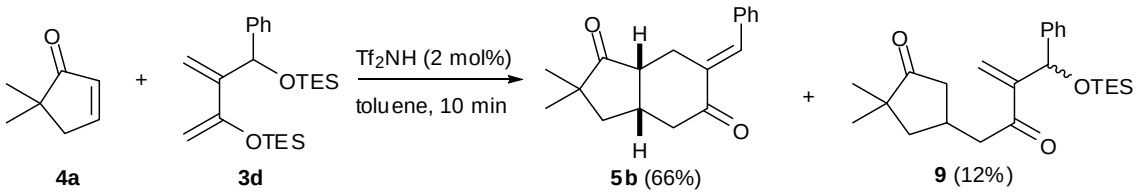
1 **3d** (R = TES) **3f** (R = Me) **5c**

entry	substrate **3**	catalyst (mol%)	time (h)	% yield of **5c**
1[b]	**3d**	BF_3-OEt_2 (20)	16	45
2	**3d**	BF_3-OEt_2 (100)	1	74
3	**3d**	$TMSNTf_2$ (10)	0.5	40
4[b]	**3d**	$Yb(OTf)_3$ (2.0)	2	0[c]
5[b]	**3d**	$PtCl_4$ (20)	12	0[d]
6	**3f**	Tf_2NH (2.0)	0.2	68
7	**3f**	TfOH (20)	0.2	0[e]
8	**3f**	$Sc(OTf)_3$ (20)	0.2	0[e]
9	**3f**	$EtAlCl_2$ (20)	0.2	20
10	**3f**	ZnI_2 (20)	0.2	37
11[b]	**3f**	$ZnBr_2$ (20)	2	31
12	**3f**	$TiCl_4$ (20)	0.2	0[e]
13	**3f**	$AgNTf_2$ (20)	2	0[c]

[a] Conditions; **3** (1.2 equiv.), **1** (1.0 equiv.), catalyst, toluene, -40 °C. [b] Reaction temperature was gradually warmed from -40 °C to rt. [c] No reaction (substrate **3** was completely recovered). [d] Complex mixture. [e] Decomposition (hydrolysis) of **3** was observed.

Tf_2NH-catalyzed (2 + 2) cycloaddition of siloxydiene with enone would promote via a stepwise mechanism. The stepwise mechanism is supported by the following observation: reaction of **3d** with **4a** in the presence of Tf_2NH (Table 2, entry 1 in maintext), Mukaiyama Michael adduct **9** was obtained in 12% yield (Scheme S1).

Scheme S1.

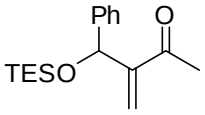


4a **3d** **5b** (66%) **9** (12%)

General Methods

Unless otherwise noted, all reactions were performed under argon atmosphere. Nominal (LR-MS) and exact mass (HR-MS) spectra were recorded on Shimazu GC-2010/PARVUM2 (for LRMSEI) and JEOL JMS-01SG-2 (for LRMSFAB) or JMS-HX/HX 110A (for HRMS) mass spectrometer. ^{1}H-NMR and ^{13}C-NMR spectra were registered on JEOL JNM-LA500 (500 MHz) or JEOL NMTC-400/54/SS (400 MHz), NMTC-500/54/SS (500 MHz) using TMS (0.00 ppm) and $CDCl_3$ (77.0) as internal standard for CDCl3. For column chromatography, Kanto Silica gel 60 (spherical, 63-210 μl) was employed. Analytical thin-layer chromatography was performed with "105715 TLC Silica gel 60 F_{254} (25 Glass plates 20 x 20 cm)" or "Merck 105554 TLC Silica gel 60 F_{254} (25 Aluminium sheets 20 x 20 cm)". Infrared spectroscopy was performed on JASCO FT/IR-410. Unless otherwise noted, materials were purchased from Tokyo Kasei Co., Aldrich Inc., Nacalai Tesque Inc. and other commercial suppliers, and were used without purification. Tf_2NH was purchased from Aldrich Chemical Company, Inc. An 80 mM solution of Tf_2NH in toluene was prepared as follows. A flame-dried, 50-ml, round-bottomed flask equipped with gas inlet is charged with Tf_2NH (675 mg, 2.40 mmol) under an atmosphere of argon, and toluene (anhydrous, Aldrich Sure-Seal) (30 ml) is quickly added under an atmosphere of argon. The solution can be stored for more than 1 month in the dark at ambient temperature.

3-[(Triethylsiloxy)phenylmethyl]-3-buten-2-one (**2d**)

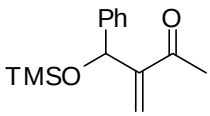


2d

To a stirred solution of 3-hydroxyphenylmethyl-3-buten-2-one (2.5 g, 14.2 mmol) and TESCl (3.1 ml, 18.4 mmol) and DMAP (173 mg, 1.4 mmol) in CH_2Cl_2 (50 mL), DIPEA (3.4 mL, 19.9 mmol) was added at 0 ℃. The reaction mixture was quenched with saturated $NaHCO_3$. The resulting mixture was extracted with Et_2O. The combined organic layers were dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane-AcOEt (95:5 v/v) as eluent, gave **2d** (4.14 g, quant.) as a colorless oil.

IR (neat) ν = 2955, 2911, 2876, 1678, 1084, 1067, 743, 699 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) 7.36-7.19 (5H, m), 6.29 (1H, s) , 6.11 (1H, s), 5.73 (1H, s), 2.25 (3H, s), 0.86 (9H, t, *J* = 8.0 Hz), 0.53 (6H, q, *J* = 8.0 Hz); ^{13}C-NMR (125 MHz, $CDCl_3$) 198.5, 152.1, 143.1, 127.9, 127.1, 126.6, 124.0, 70.9, 26.4, 6.7, 4.7; MS *m/z* 291 $(M + H)^+$; Anal. Calcd for $C_{17}H_{26}O_2Si$, C: 70.29; H: 9.02. Found, C: 70.09; H: 8.81.

3-[(Trimethylsiloxy)phenylmethyl]-3-buten-2-one (**2e**)



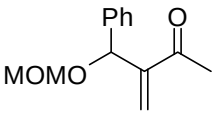
2e

2e was synthesized from 3-hydroxyphenylmethyl-3-buten-2-one and TMSCl according as the same procedure as above (119 mg, 94%, colorless oil).

IR (neat) ν = 2957, 1678, 1251, 1083, 1066, 888, 839, 699 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) 7.34-7.20 (5H, m) 6.20 (1H, s), 6.13 (1H, s) 5.73 (1H, s) 2.26 (3H, s) 0.04 (9H, s); ^{13}C-NMR (125 MHz, $CDCl_3$) 198.6, 151.9, 142.9, 128.1, 127.3, 126.9, 124.6, 71.3, 26.6, 0.0; MS *m/z* 249 $(M + H)^+$; Anal. Calcd for

$C_{14}H_{20}O_2Si$, C: 67.70; H: 8.12. Found, C: 67.99; H: 8.16.

3-[(Methoxymethyloxy)phenylmethyl]-3-buten-2-one (**2g**).

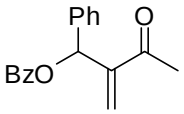


2g

2h was synthesized from 3-hydroxyphenylmethyl-3-buten-2-one and MOMCl in 79% yield as a colorless oil.

IR (neat) ν = 2950, 2888, 2822, 1678, 1150, 1098, 1038 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) 7.37-7.25 (5H, m), 6.20 (1H, s), 6.17 (1H, d, *J* = 1.2 Hz), 4.61 (1H, d, *J* = 3.9 Hz) , 4.59 (1H, d, *J* = 3.9 Hz), 3.32 (3H, s), 2.29 (3H, s); ^{13}C-NMR (125 MHz, $CDCl_3$) 198.2, 149.2, 139.6, 128.2, 127.7, 127.5, 125.1, 94.3, 74.0, 55.6, 26.3; MS *m/z* 221 $(M + H)^+$; Anal. Calcd for $C_{13}H_{16}O_3$, C: 70.89; H: 7.32. Found, C: 71.00; H: 7.46.

3-[(Benzoyloxy)phenylmethyl]-3-buten-2-one (**2h**).

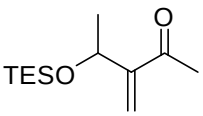


2h

2g was synthesized from 3-hydroxyphenylmethyl-3-buten-2-one and benzoyl chloride in 40% yield as white solids.

Mp. 112-113 °C, IR ($CHCl_3$) ν = 3028, 1722, 1678, 1274, 1108 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) 7.69-7.25 (10H, m) 6.99 (1H, s), 6.25 (1H, s), 6.19 (1H, d, *J* = 1.2 Hz), 2.34 (3H,s); ^{13}C-NMR (125 MHz, $CDCl_3$) 197.2, 165.0, 147.8, 138.2, 133.1, 129.9, 129.6, 128.4, 128.4, 128.2, 127.4, 125.2, 73.0, 26.2; MS *m/z* 281 $(M + H)^+$; Anal. Calcd for $C_{18}H_{16}O_3$, C: 77.12; H: 5.75. Found, C: 77.10; H: 5.82.

3-Methylene-4-triethylsiloxy-2-pentanone (**2i**).

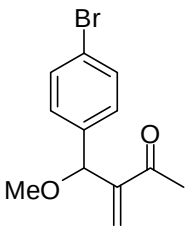


2i

2i was synthesized from 4-hydroxy-3-methylene-2-pentanone and TESCl in 90% yield as a colorless oil.

IR (neat) ν = 2956, 2912, 2877, 1678, 1374, 1088, 982, 742 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) 6.19 (1H, s), 6.07 (1H, s), 4.77 (1H, q, *J* = 6.1 Hz), 2.34 (3H, s), 1.22 (3H, d, *J* = 6.1 Hz), 0.93 (9H, t, *J* = 7.8 Hz), 0.58 (6H, q, *J* = 7.8 Hz); ^{13}C-NMR (125 MHz, $CDCl_3$) 198.7, 153.6, 123.7, 65.4, 26.1, 24.7, 6.6, 4.6; MS *m/z* 199 (M^+－Et); Anal. Calcd for $C_{12}H_{24}O_2Si$, C: 63.10; H: 10.59. Found, C: 63.34; H: 10.68.

3-[(Triethylsiloxy)-(*p*-bromophenyl)methyl]-3-buten-2-one (**2j**)



2j

To a stirred solution of methylvinylketone (2.0 mL, 24.7 mmol) and pyridine (2.2 mL, 27.1 mmol) in CH_2Cl_2 (100 mL), TMSOTf (5.8 mL, 32.1 mmol) was added at -78 ℃. To the mixture was added *p*-bromobenzaldehyde dimethylacetal (5.2 mL, 32.1 mmol), and then the mixture was warmed to -20 °C. After the mixture was stirred for 2 h at the same temperature, to the mixture was added DBU (8.8 mL, 59.2 mmol). After stirring for 30 min, the mixture was quenched with saturated $NaHCO_3$. The resulting mixture was extracted with AcOEt. The combined organic layers were dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure. The residue was

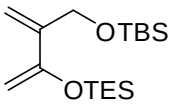
purified by column chromatography on silica gel with hexane-AcOEt (90:10 v/v) as eluent, gave **2j** (3.2 g, 48%) as a colorless oil.

IR (neat) ν = 2933, 2823, 1677, 1485, 1092 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) 7.43 (2H, d, *J* = 8.4 Hz), 7.22 (2H, d, *J* = 8.4 Hz) 6.18 (1H, s), 6.14 (1H, s), 5.18 (1H, s), 3.28 (3H, s), 2.29 (3H, s), ^{13}C-NMR (125 MHz, $CDCl_3$) 198.1, 148.9, 139.1, 131.3, 128.9, 124.9, 121.5, 78.9, 56.8, 26.1; MS *m/z* 269 $(M + H)^+$, 271 $(M + H + 2)^+$; Anal. Calcd for $C_{13}H_{15}BrO_2$, C: 53.55; H: 4.87. Found, C: 53.25; H: 4.87.

Synthsis of 3b (typical procedure)

To a stirred solution of dist. *i*Pr_2NH (1.8 mL, 12.9 mmol) in anhydrous THF (25 mL), *n*-buthyllithium (8.6 mL, 1.6 M in hexane 13.8 mmol) was added at -78 ^oC, and the mixture was stirred for 30 min. A solution of **2a** (2.0 g, 9.2 mmol) in anhydrous THF (5 mL) was slowly added. After the mixture was stired for 30 min at the same temperature, to the mixture was added TESCl (2.2 mL, 12.9 mmol). The resulting solution was stirred for 30 min at the same temperature and for additional 15 min at ambient temperature. After quenched with saturated $NaHCO_3$, the resulting mixture was extracted with AcOEt. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by short column chromatography on silica gel with hexane-AcOEt (98:2 v/v) as eluent, to afford **3b** (0.96 g, 32%) as a colorless oil.

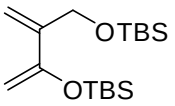
2-Triethylsiloxy-3-(*tert*-butyldimethylsiloxy)methyl-1,3-butadiene (3b)



3b

IR (neat) ν = 3120, 2956, 2878, 1590, 1461, 1252, 1098, 1017, 836, 779, 740 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) 5.56 (1H, s), 5.32 (1H, s), 4.34 (2H, m), 4.28 (2H, s), 0.98 (9H, t, *J* = 7.8 Hz), 0.92 (9H, s), 0.71 (6H, q, *J* = 7.8 Hz), 0.08 (6H, s), ^{13}C-NMR (500 MHz, $CDCl_3$) 154.0, 143.4, 111.9, 91.4, 62.5, 25.9, 18.3, 6.7, 6.4, 5.0, 3.9, -5.5; MS *m/z* 329 (M^+); HRMS (FAB^+): Calcd for $C_{17}H_{36}O_2Si_2$ $(M - H)^+$: 328.2254, Found: 328.2260.

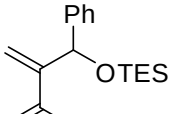
2-*tert*-Butyldimethylsiloxy-3-(*tert*-butyldimethylsiloxy)methyl-1,3-butadiene (3c)



3c

3c was obtained from **2a** in 70% yield as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) 5.55 (1H, s), 5.32 (1H,s), 4.36 (1H, m), 4.28 (1H, m), 0.96 (9H,s), 0.92 (9H, s), 0.16 (6H, s), 0.07 (6H, s).

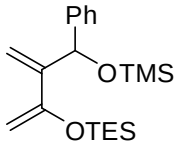
2-Triethylsiloxy-3-(triethylsiloxy)phenylmethyl-1,3-butadiene (3d)



3d

3d was obtained from **2d** in 65% yield as a colorless oil. IR (neat) ν = 3064, 3029, 2956, 2912, 2877, 1587, 1087, 1067, 1008, 743, 699 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) 7.36-7.20 (5H, m), 5.67 (1H, d, J = 2.4 Hz), 5.54 (1H, s), 5.44 (1H, s), 4.41 (1H, d, *J* = 1.5 Hz), 4.23 (1H, s), 0.92 (9H, t, *J* = 8.1 Hz), 0.90 (9H, t, *J* = 8.1 Hz), 0.63 (6H, q, *J* = 8.1 Hz), 0.60 (6H, q, *J* = 8.1 Hz); ^{13}C-NMR (125 MHz, $CDCl_3$) 153.7, 147.2, 143.4, 127.9, 126.9, 126.6, 113.5, 93.9, 74.1, 6.81, 6.68, 4.86, 4.83; MS *m/z* 405 $(M + H)^+$; Anal. Calcd for $C_{23}H_{40}O_2Si_2$, C: 68.25; H: 9.96. Found: C: 68.04; H: 9.94.

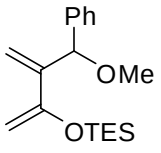
2-Triethylsiloxy-3-(trimethylsiloxy)phenylmethyl-1,3-butadiene (3e)



3e

3e was obtained from **2e** in 43% yield as a colorless oil. IR (neat) ν = 3063, 3029, 2956, 2911, 2877, 1587, 1456, 1250, 1087, 1067, 1015, 889, 840, 745, 699 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) 7.34-7.21 (5H, m), 5.70 (1H, s), 5.47 (1H, s), 5.43 (1H, s), 4.38 (1H, s), 4.24 (1H, s), 0.94 (9H, t, *J* = 8.0 Hz), 0.64 (6H, q, *J* = 8.0 Hz), 0.10 (9H, s), ^{13}C-NMR (125 MHz, $CDCl_3$) 153.7, 146.8, 143.1, 128.0, 127.0, 126.7, 114.0, 93.9, 74.1, 6.6, 4.8, 0.0; MS *m/z* 361 $(M + H)^+$; HRMS (FAB^+): Calcd for $C_{20}H_{33}O_2Si_2$ $(M + H)^+$: 361.2014, Found: 361.2026.

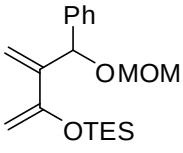
2-Triethylsiloxy-3-(methoxy)phenylmethyl-1,3-butadiene (3f)



3f

3f was obtained from **2f** in 78% yield as a colorless oil. IR (neat) ν = 3062, 3029, 2955, 2911, 2877, 2820, 1586, 1454, 1098, 1017, 744, 699 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) 7.37-7.23 (5H, m), 5.77 (1H, d, *J* = 2.0 Hz), 5.36 (1H, s), 4.93 (1H, s), 4.45 (1H, s), 4.29 (1H, s), 3.36 (3H, s), 0.95 (9H, t, *J* = 7.8 Hz), 0.66 (6H, q, *J* = 7.8 Hz); ^{13}C-NMR (125 MHz, $CDCl_3$) 153.8, 144.0, 140.4, 128.1, 127.5, 127.1, 114.8, 93.7, 82.9, 56.9, 6.69, 4.86; MS *m/z* 305 $(M + H)^+$; HRMS (FAB^+): Calcd for $C_{18}H_{27}O_2Si$ $(M + H)^+$: 303.1775, Found: 303.1773.

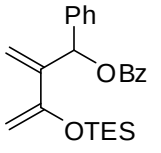
2-Triethylsiloxy-3-(methoxymethyloxy)phenylmethyl-1,3-butadiene (3g)



3g

3g was obtained from **2g** in 45% yield as a colorless oil. IR (neat) ν = 3063, 3029, 2955, 2912, 2878, 1587, 1149, 1039, 747, 700 cm^{-}; ^{1}H-NMR (400 MHz, $CDCl_3$) 7.39-7.24 (5H, m), 5.82 (1H, d, *J* = 2.2 Hz), 5.47 (1H, s), 5.43 (1H, s), 4.66 (1H, d, *J* = 3.9 Hz), 4.64 (1H, d, *J* = 3.9 Hz), 4.43 (1H, d, *J* = 1.7 Hz), 4.29 (1H, s), 3.39 (3H, s), 0.94 (9H, t, *J* = 8.0 Hz), 0.65 (6H, q, *J* = 8.0 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) 153.7, 143.8, 140.4, 128.2, 127.6, 127.4, 126.4, 115.1, 94.2, 76.4, 55.6, 6.58, 4.78; MS *m/z* 335 $(M + H)^+$; HRMS (FAB^+): Calcd for $C_{19}H_{30}O_3Si$ (M^+): 334.1959, Found: 334.1954.

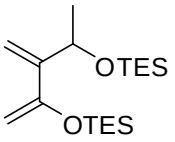
3-(Benzoyloxy)phenylmethyl-2-triethylsiloxy-1,3-butadiene (3h)



3h

3h was obtained from **2h** in 62% yield as a colorless oil. IR (neat) ν = 3033, 2958, 2913, 3877, 1717, 1588, 1274, 1006 cm^{-}; ^{1}H-NMR (400 MHz, $CDCl_3$) 8.09 (2H, m), 7.56 (1H, m), 7.44 (4H, m), 7.43 (3H, m), 6.84 (1H, s), 5.83 (1H, s), 5.40 (1H, s), 4.52 (1H, d, *J* = 2.0 Hz), 4.36 (1H, s), 0.95 (9H, t, *J* = 8.0 Hz), 0.67 (6H, q, *J* = 8.0 Hz); ^{13}C-NMR (125 MHz, $CDCl_3$) 165.2, 153.3, 143.2, 138.6, 132.9, 130.1, 129.6, 128.2, 128.0, 127.4, 115.2, 93.8, 74.4, 6.61, 4.78; MS *m/z* 395 $(M + H)^+$; Anal. Calcd for $C_{24}H_{30}O_3Si$, C: 73.05; H: 7.66. Found: C: 72.77; H: 7.76.

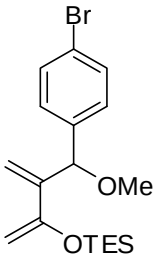
2-Triethylsiloxy-3-[1-(triethylsiloxy)ethyl]-1,3-butadiene (3i)



3i

3i was obtained from **2i** in 43% yield as a colorless oil. IR (neat) ν = 2956, 2912, 2878, 1585, 1459, 1098, 1008, 741 cm^{-}; ^{1}H-NMR (400 MHz, $CDCl_3$) 5.48 (1H, s), 5.36 (1H, s), 4.55 (1H, q, *J* = 6.4 Hz), 4.44 (1H, s), 4.32 (1H, s), 1.31 (3H, d, *J* = 6.4 Hz), 0.98 (9H, t, *J* = 7.8 Hz), 0.95 (9H, t, *J* = 7.8 Hz), 0.71 (6H, q, *J* = 7.8 Hz), 0.59 (6H, q, *J* = 7.8 Hz), ^{13}C-NMR (125 MHz, $CDCl_3$) 154.6, 149.6, 111.2, 92.0, 67.5, 25.3, 6.8, 6.7, 5.0, 4.8; MS *m/z* 343 $(M + H)^+$; HRMS $(M + H)^+$: Calcd for $C_{18}H_{37}O_2Si_2$ $(M - H)^+$: 341.2327, Found: 341.2326.

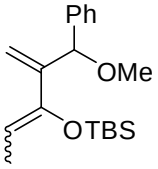
3-[(*p*-Bromophenyl)methoxymethyl]-2-triethylsiloxy-1,3-butadiene (3j)



3j

3j was obtained from **2j** in 56% yield as a colorless oil. IR (neat) ν = 2955, 2911, 2877, 2821, 1628, 1588, 1485, 1096, 1012, 745 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) 7.44-7.42 (2H, m), 7.24-7.22 (2H, m), 5.77 (1H, s), 5.34 (1H, s), 4.88 (1H, s), 4.41 (1H, s), 4.28 (1H, s), 3.35 (3H, s), 0.95 (9H, t, *J* = 7.8 Hz), 0.66 (6H, q, *J* = 7.8 Hz); ^{13}C-NMR (125 MHz, $CDCl_3$) 153.6, 143.8, 139.7, 131.2, 128.8, 121.4, 115.3, 93.8, 82.4, 56.9, 6.7, 4.8; MS *m/z* 381 $(M + H)^+$, 383 $(M + H + 2)^+$; HRMS (FAB^+): Calcd for $C_{18}H_{26}O_2Br_{81}Si$ $(M + H + 2)^+$: 383.0865, Found: 383.0870.

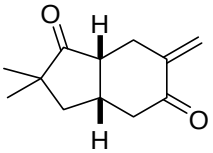
3-*tert*-Butyldimethylsiloxy 2-(phenylmethoxymethyl)-1,3-pentadiene (3k)



3k

(as a mixture of *E/Z* isomers, isomer ratio = 74 : 26): IR (neat) ν = 3029, 2955, 2930, 2887, 2858, 2821, 1471, 1254, 1101, 1073, 839, 779, 700 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) *Z* isomer; 7.40-7.27 (5H, m), 5.23 (1H, s), 5.32 (1H, s), 5.03 (1H, q, *J* = 6.8 Hz), 4.95 (1H, s), 3.40 (3H, s), 1.60 (3H, d, *J* = 6.8 Hz), 1.04 (9H, s), 0.04 (6H, s); *E* isomer; 7.40-7.27 (5H, m), 5.49 (1H, s), 5.12 (1H, s), 4.97 (1H, s), 4.82 (1H, q, *J* = 6.8 Hz), 3.38 (3H, s) 1.42 (3H, d, *J* = 6.8 Hz), 1.00 (9H, s), 0.18 (3H, s), 0.15 (3H, s); ^{13}C-NMR (125 MHz, $CDCl_3$) *Z* isomer; 148.0, 145.3, 140.7, 128.1, 127.4, 127.2, 112.8, 107.4, 83.3, 56.9, 25.9, 18.3, 11.6, -4.0; MS *m/z* 317 $(M + H)^+$; HRMS (FAB^+): Calcd for $C_{19}H_{29}O_2Si$ $(M + H)^+$: 317.1931, Found: 317.1935.

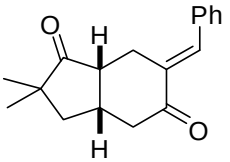
(1*S,6*R**)-8,8-Dimethyl-4-methylenebicyclo[4.3.0]nonan-3,7-dione** (**5a**)



5a

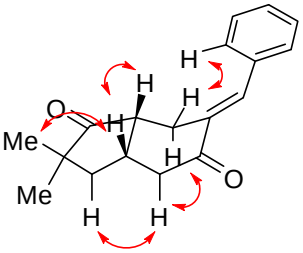
Colorless oil, IR (KBr) ν = 2962, 2864, 1741, 1703, 1624, 1461, 1228, 1145, 950 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) 6.00 (1H, s), 5.25 (1H, s), 2.97-2.90 (1H, m), 2.84-2.71 (4H, m), 2.42 (1H, dd, *J* = 10.7, 4.9 Hz), 2.07 (1H, dd, *J* = 7.6, 5.8 Hz), 1.25 (1H, *J* = 13.2, 10.3 Hz), 1.08 (3H, s), 1.02 (3H, s), ^{13}C-NMR (125 MHz, $CDCl_3$) 222.2, 200.0, 141.2, 122.2, 45.9, 43.9, 43.3, 42.4, 29.9, 28.5, 24.6, 22.3; MS *m/z* 193 $(M + H)^+$; HRMS (FAB^+): Calcd for $C_{12}H_{15}O_2$ $(M - H)^+$: 191.1067, Found: 191.1076.

(*E*,1*S,6*R**)-4-Benzylidene-8,8-dimethylbicyclo[4.3.0]nonan-3,7-dione** (**5b**)



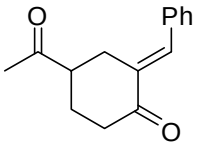
5b

Colorless solids, mp 78-79 ^{o}C, IR (neat) ν = 3058, 3022, 2961, 2866, 1742, 1687, 1614, 1446, 752, 696 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) 7.61 (1H, s), 7.41-7.33 (5H, m), 3.11-2.75 (5H, m), 2.46 (1H, dd, *J* = 6.1, 14.6 Hz), 2.14 (1H, dd, *J* = 7.3, 13.1 Hz) 1.42 (1H, dd, *J* = 9.8, 13.2 Hz), 1.08 (3H, s), 1.05 (3H, s), ^{13}C-NMR (125 MHz, $CDCl_3$) 222.1, 200.4, 136.3, 134.8, 133.1, 129.8, 128.8, 128.5, 45.9, 44.2, 43.3, 42.8, 28.5, 24.9, 24.7, 22.9; MS *m/z* 269 $(M + H)^+$; HRMS (FAB^+): Calcd for $C_{18}H_{19}O_2$ $(M - H)^+$: 267.1380, Found: 267.1380.



The stereochemistry of **5b** was determined by NOESY experiment. The representative NOE correlations were shown.

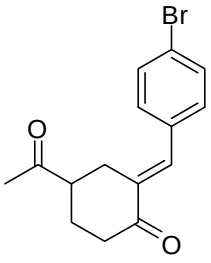
(*E*)-4-Acetyl-2-benzylidenecyclohexanone (**5c**)



5c

Colorless needles, mp 75 ^{o}C, IR (neat) ν = 3012, 2949, 1711, 1680, 1593, 1211 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) 7.58 (1H, s), 7.42-7.32 (5H, m), 3.13 (1H, m), 2.90-2.83 (1H, m), 2.81-2.76 (1H, m), 2.75-2.68 (1H, m), 2.54-2.45 (1H, m), 2.26-2.18 (1H, m), 2.20 (3H, s), 2.02-1.91 (1H, m), ^{13}C-NMR (100 MHz, $CDCl_3$) 209.4, 199.7, 137.2, 135.0, 133.8, 130.2, 128.9, 128.4, 47.8, 38.3, 29.8, 28.4, 25.2; MS *m/z* 229 $(M + H)^+$; HRMS (FAB^+): Calcd for $C_{15}H_{15}O_2$ $(M - H)^+$: 227.1067, Found: 227.1078.

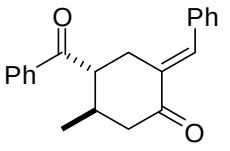
(*E*)- 4-Acetyl 2-(*p*-bromobenzylidene)cyclohexanone (**5d**)



5d

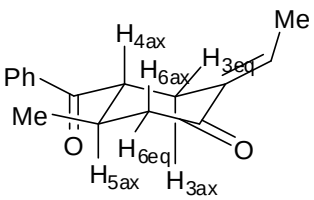
Colorless needles, mp 73-75 ^{o}C, IR (neat) ν = 2948, 2877, 1705, 1677, 1588, 1485, 1238, 1174, 810 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) 7.54-7.51 (2H, m), 7.48 (1H, s), 7.28-7.25 (2H, m), 3.07-3.03 (1H, m), 2.88-2.67 (3H, m), 2.55-2.45 (1H, m), 2.25-2.21 (4H, m), 2.02-1.94 (1H, m) ; ^{13}C-NMR (100 MHz, $CDCl_3$) 209.4, 199.6, 136.0, 134.5, 134.0, 131.8, 131.7, 123.3, 47.6, 38.3, 29.7, 28.3, 25.2; MS *m/z* 307 $(M + H)^+$, 309 $(M + H + 2)^+$; HRMS (FAB^+): Calcd for $C_{15}H_{14}BrO_2$ $(M + H)^+$: 307.0157, Found: 307.0156.

(*E*,4*R,5*R**)-4-Acetyl-2-benzylidene-5-methylcyclohexanone** (**5e**)



5e

Colorless solids, mp 104-105 ^{o}C, IR (neat) ν = 3057, 3023, 2958, 2930, 2873, 1677, 1594, 1446, 1250, 1201,761, 697 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) 7.97-7.95 (2H, m), 7.61-7.27 (8H, m), 3.52 (1H, ddd, *J* = 4.4, 9.8, 11.2 Hz), 3.16 (1H, ddd, *J* = 1.2, 4.4, 16.1 Hz), 2.96 (1H, ddd, *J* = 3.0, 11.2, 16.1 Hz) 2.81 (1H, dd, *J* = 4.9, 17.6 Hz), 2.55 (1H, m), 2.28 (1H, dd, *J* = 11.4, 17.6 Hz) 0.98 (3H, d, *J* = 6.3 Hz); ^{13}C-NMR (125 MHz, $CDCl_3$) 202.8, 200.0, 137.0, 136.7, 135.1, 133.9, 133.5,

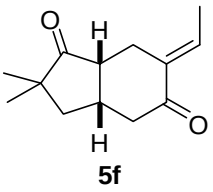


$J_{H3eq-H4ax}$ = 4.4 Hz
$J_{H3ax-H4ax}$ = 11.2 Hz
$J_{H4ax-H5ax}$ = 9.8 Hz
$J_{H5ax-H6eq}$ = 4.9 Hz
$J_{H5ax-H6ax}$ = 11.4 Hz

130.3, 128.8, 128.4, 128.2 (2C), 48.2, 46.9, 32.7, 31.6, 20.3; MS *m/z* 305 $(M + H)^+$; HRMS (FAB^+): Calcd for $C_{21}H_{20}O_2$ (M^+): 304.1458, Found: 304.1458.

The stereochemistry of **5e** was determined by J values.

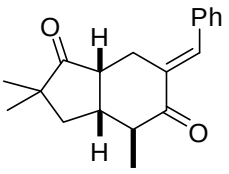
(*E*,1*S,6*R**)-4-Ethylidene-8,8-dimethylbicyclo[4.3.0]nonan-3,7-dione** (**5f**)



5f

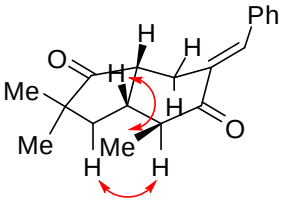
Colorless oil, IR (neat) ν = 2961, 2931, 2866, 1737, 1698, 1631 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) 6.76 (1H, ddq, *J* = 1.2, 1.7, 7.3 Hz), 2.95-2.81 (3H, m), 2.76 (1H, dd, *J* = 5.8, 15.4 Hz), 2.55 (1H, ddt, *J* = 1.4, 6.8, 14.6 Hz), 2.38 (1H, dd, *J* = 4.9, 15.4 Hz), 2.05 (1H, ddd, *J* = 1.2, 7.6, 13.2 Hz), 1.77 (3H, dd, *J* = 1.2, 7.3 Hz), 1.24 (1H, dd, *J* = 10.0, 13.2 Hz), 1.07 (3H, s), 1.00 (3H, s); ^{13}C-NMR (125 MHz, $CDCl_3$) 222.6, 200.0, 135.0, 134.6, 46.0, 44.0, 43.3, 42.4, 28.3, 24.7, 23.7, 22.5, 13.7; MS *m/z* 207 $(M + H)^+$; HRMS (FAB^+): Calcd for $C_{13}H_{17}O_2$ $(M - H)^+$: 205.1223, Found: 205.1223.

(*E*,1*S,2*S**,6*R**)-4-Benzylidene-2,8,8-trimethylbicyclo[4.3.0]nonan-3,7-dione** (**5g**)



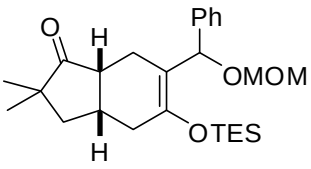
5g

Colorless needles, mp 85-87 °C, IR (neat) ν = 2966, 2930, 1735, 1693, 1614, 1447, 1166, 698 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) 7.65 (1H, s), 7.43-7.33 (5H, m), 3.39-3.29 (1H, m), 2.63-2.51 (2H, m), 2.47-2.40 (1H, m), 2.37-2.24 (2H, m), 1.60 (1H, dd, *J* = 7.8, 16.8 Hz), 1.22 (3H, d, *J* = 6.3 Hz), 1.14 (3H, s), 1.07 (3H, s); ^{13}C-NMR (125 MHz, $CDCl_3$) 221.7, 201.9, 135.4, 135.0, 133.5, 129.9, 128.7, 128.5, 46.9, 46.1, 45.5, 43.2, 36.0, 24.9, 24.6, 23.1, 12.5; MS *m/z* 283 $(M + H)^+$; Anal. Calcd for $C_{19}H_{22}O_2$, C: 80.82; H: 7.85. Found, C: 80.82; H: 7.76.



The stereochemistry of **5g** was determined by NOESY experiment. The representative NOE correlations were shown.

(1*S,6*R**)-3-Triethylsiloxy-4-(Methoxymethoxy)phenylmethyl-8,8-dimethylbicyclo[4.3.0]non-3-en-7-one** (**6g**)



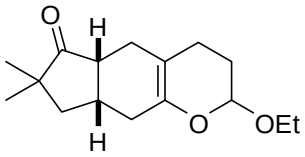
6g

Colorless oil, IR (neat) ν = 2956, 2877, 1739, 1677, 1038, 730 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) 7.37-7.19 (5H, m), 6.00 (1H, s), 4.66 (1H, d, *J* = 6.4 Hz), 4.59 (1H, d, *J* = 6.4 Hz), 3.37 (3H, s) 2.59-2.50 (1H, m), 2.44 (1H, dd, *J* = 7.3, 17.1 Hz), 2.32 (1H, dd, J = 7.8, 15.6 Hz), 2.12 (1H, dd, *J* = 7.3, 17.1 Hz) 2.00 (1H, d, *J* = 17.1 Hz), 1.95 (1H, d, *J* = 8.3 Hz) 1.91 (1H, dd, *J* = 6.8, 13.0 Hz), 1.70 (1H, dd, *J* = 9.5, 12.7 Hz), 1.14 (3H, s), 1.04 (3H, s), 1.01 (9H, t, *J* = 7.8 Hz) 0.72 (6H, q, *J* = 7.8 Hz); ^{13}C-NMR (500 MHz, $CDCl_3$) 223.1, 145.9, 141.7, 128.0, 126.6, 125.9, 111.7, 93.5, 71.9, 55.4, 44.6, 44.5, 42.8, 32.0, 31.0, 26.1, 19.5, 6.8, 5.8; MS *m/z* 443 $(M + H)^+$; Anal. Calcd for $C_{26}H_{40}O_4Si$, C: 70.23; H: 9.07. Found, C: 70.08; H: 8.95.

Domino (4 + 2) cycloaddition—elimination—oxa Diels-Alder reaction

To a stirred solution of **4a** (57.0 mg, 0.52 mmol) and $ZnBr_2$ (35.0 mg, 0.16 mmol) in CH_2Cl_2 (3.0 ml), a solution of **3c** (170.0 mg, 0.52 mmol) in CH_2Cl_2 (2.0 mL) was added at ambient temperature. After the solution was stirred for 10 min at the same temperature, ethylvinylether (**7**) (0.50 mL, 5.2 mmol) was added and the resulting solution was stirred for 40 min at the same temperature. The mixture was filtered through a short pad of Celite using AcOEt as eluent. Removal of the solvent under reduced pressure, followed by column chromatography with hexane-AcOEt (90:10 v/v) as an eluent, gave **8** (35 mg, 25 %) as a single diastereomer (its stereochemistry was not determined).

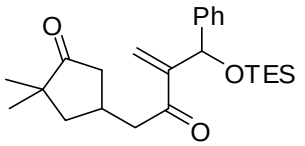
Compound 8.



8

Colorless oil, IR (neat) ν = 2960, 2933, 2867, 1739, 1705, 1122, 1100, 1078, 1055 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) diastereomixture 4.95-4.93 (1H, m), 3.86-3.78 (1H, m), 3.60-3.53 (1H, m), 2.62-2.53 (2H, m), 2.33-2.25 (1H, m), 2.12-1.72 (9H, m), 1.24-1.19 (3H, m), 1.16 (3H, s), 1.08 (3H, s); ^{13}C-NMR (125 MHz, $CDCl_3$) 223.5, 141.5, 102.1, 97.0, 63.6, 45.1, 44.3, 42.4, 30.7, 28.8, 27.2, 26.8, 26.3, 25.5, 21.6, 15.2; MS *m/z* 265 $(M + H)^+$; HRMS (FAB^+): Calcd for $C_{16}H_{24}O_3$ $(M)^+$: 264.1720, Found: 264.1722.

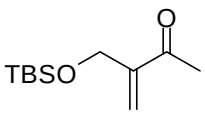
Compound 9



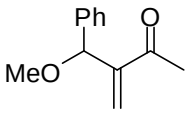
9

Colorless oil, IR (neat) ν = 2957, 2876, 1739, 1676, 1455, 1015, 743, 699 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) major isomer; 7.35-7.20 (5H, m), 6.27 (1H, s), 6.06 (1H, s), 5.72 (1H, s), 2.69 (2H, s), 2.54-2.35 (2H, m), 1.84-1.62 (2H, m), 1.27-1.20 (1H, m), 1.00 (3H, s), 0.95 (3H, s), 0.86 (9H, t, *J* = 7.8 Hz), 0.53 (6H, q, *J* = 7.8 Hz); ^{13}C-NMR (500 MHz, $CDCl_3$) 222.1, 199.9, 152.2, 143.0, 128.0, 127.3, 126.8, 122.8, 71.4, 46.0, 44.8, 44.6, 43.6, 28.6, 24.0, 6.7, 4.7; MS *m/z* 399 $(M + H)^+$; HRMS (FAB^+): Calcd for $C_{24}H_{35}O_3Si$ $(M + H)^+$: 399.2350, Found: 399.2369.

Compounds **2a**[S1] and **2f**[S2] were prepared according as reported proceudres.



2a



2f

References

S1 G. Mehta, B. A. Bhat, T. H. Suresha Kumara, *Tetrahedron Lett*., 2009, **50**, 6597.

S2 S. Kim, Y. G. Kim, J. H. Park, *Tetrahedron Lett.*, 1991, **32**, 2043.