Supplementary Material (ESI) for Chemical Communications

Supporting Information for

Encapsulated Molecular Catalysts in Polysiloxane Gels: Ruthenium Cluster-Catalysed Isomerization of Alkenes

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General Methods: All reactions were carried out under a nitrogen or argon atmosphere. Dehydrated hexane and tetrahydrofuran (THF) were purchased from Kanto Chemical Co., Ltd., and used as received. Tetrahydropyran (THP) was distilled under an inert atmosphere from sodium/benzophenone prior to use. Dichloroethane was distilled under an inert atmosphere from CaH_2 prior to use. Sodium hydride was purchased from Kishida Chemical Co., Ltd. 3-Acetoxyphenol, allyl benzyl ether (**2a**), allyl bromide, allyl phenyl ether (**2b**), benzyl alcohol, benzyl bromide, 2,2'-biphenol, 3-buten-1-ol, cinnamyl alcohol, crotyl chloride, ethylene glycol, methallyl alcohol, 2-methoxyethanol, prenyl alcohol were purchased from Tokyo Chemical Industry Co., Ltd. Polymethylhydrosiloxane (PMHS) was purchased from AZmax Co., Ltd. Column chromatography was performed with silica gel (Merck, Art 7734). ^{1}H and ^{13}C NMR spectra were measured on JEOL GSX-270 (270 MHz) and Lambda 400 (395 MHz) spectrometers. Chemical shifts for ^{1}H NMR were described in parts per million downfield from tetramethylsilane as an internal standard ($\delta = 0$) in $CDCl_3$, unless otherwise noted. Chemical shifts for ^{13}C NMR were expressed in parts per million in $CDCl_3$ as an internal standard ($\delta = 77.1$), unless otherwise noted. IR spectra were measured on JASCO FT/IR-550 and -4200 spectrometers. ICP-MS and HRMS analyses were performed at the Analytical Center in Institute for Materials Chemistry and Engineering, Kyushu University. Analytical thin-layer chromatography (TLC) was performed on aluminum sheets precoated with aluminum oxide (Merck, aluminum oxide 150 F_{254}, neutral) and glass plates precoated with silica gel (Merck, Kieselgel 60 F_{254}). Visualization was accomplished by UV light (254 nm), anisaldehyde, and phosphomolybdic acid. ($\mu_3;\eta^2;\eta^3;\eta^5$-acenaphthylene)$Ru_3(CO)_7$ (**1**) was prepared by the method reported previously.[1]

Synthesis of [Ru_3]@Si Catalysts.

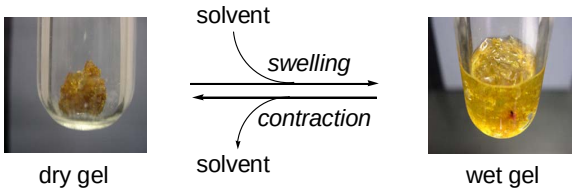
[Ru_3]@Si-O: To a solution of ($\mu_3;\eta^2;\eta^3;\eta^5$-acenaphthylene)$Ru_3(CO)_7$ (**1**) (6.5 mg, 0.01 mmol) and PMHS [M_w = 1500–1900; n = 25.6 (average); Si–H = 4 mmol] in tetrahydropyran (0.7 mL) was added dimethylformamide (1 mmol), and the mixture was heated at 50 °C. Deoxygenative reduction smoothly proceeded and [Ru_3]@Si-O was formed as a wet gel after 2 h. The wet gel was washed with ether and then dried under reduced pressure to afford the corresponding dry gel. ICP-MS analysis of the ether solution revealed that only 0.2 μg of ruthenium (<0.02% of charged [Ru_3] species) was contained; >99.98% of [Ru_3] species is immobilized into the polysiloxane networks. IR (KBr) ν 2167 (Si–H), 1280 (Si–Me), 1030 (Si–O) cm^{-1}.

[Ru_3]@Si-EG: To a solution of ($\mu_3;\eta^2;\eta^3;\eta^5$-acenaphthylene)$Ru_3(CO)_7$ (**1**) (6.5 mg, 0.01 mmol) and PMHS [M_w = 1500–1900; n = 25.6 (average); Si–H = 4 mmol] in tetrahydropyran (0.7 mL) was added ethylene glycol (EG: 2 mmol), and the mixture was heated at 50 °C. Dehydrogenative silylation smoothly proceeded and [Ru_3]@Si-EG was formed as a wet gel after 2 h. The wet gel was washed with ether and then dried under reduced pressure to afford the corresponding dry gel. ICP-MS analysis of the ether solution revealed that only 0.4 μg of ruthenium (<0.04% of charged [Ru_3] species) was contained; >99.96% of [Ru_3] species is immobilized into the polysiloxane networks. IR (KBr) ν 2173 (Si–H), 1272 (Si–Me), 1030 (Si–O) cm^{-1}.

[Ru_3]@Si-EG_{cap} and [Ru_3]@Si-BP_{cap}: To a solution of ($\mu_3;\eta^2;\eta^3;\eta^5$-acenaphthylene)$Ru_3(CO)_7$ (**1**) (6.5 mg, 0.01 mmol) and PMHS [M_w = 1500–1900; n = 25.6 (average); Si–H = 4 mmol] in tetrahydropyran (0.7 mL) was added 1 mmol of ethylene glycol (EG) or 2,2'-biphenol (BP), and 2-methoxyethanol (2 mmol), and the mixture was heated at 50 °C. Dehydrogenative silylation smoothly proceeded and [Ru_3]@Si-EG_{cap} and -BP_{cap} were formed as a wet gel after 2 h. The wet gel was washed with ether and then dried under reduced pressure to afford the corresponding dry gel. The Si–H groups remained in the siloxane gels are less than 1% (determined by IR). ICP-MS analysis of the ether solution revealed that only 0.4 μg of ruthenium (<0.04% of charged [Ru_3] species) was contained; >99.96% of [Ru_3] species is immobilized into the polysiloxane networks. IR (KBr) ν 1272 (Si–Me), 1030 (Si–O) cm^{-1}.

Mobility of Solvents in the Ruthenium-Containing Gel.

Solvents, substrates, and products facilely permeate through a gel membrane of [Ru_3]@Si. This is supported by the following experiments: [Ru_3]@Si obtained as above shows reversible swelling/contraction transition (Scheme S1). For example, dry [Ru_3]@Si-EG_{cap} (*ca.* 500 mg) absorbed 1.5 mL of 1,2-dimethoxyethane (DME) and swelled two or threefold within a few minutes (right photo). Removal of the solvent under reduced pressure regenerated a contracted dry gel (left photo).



Scheme S1. Photographs of contracted dry gel (left) and swelled wet gel (right) of [Ru_3]@Si-EG.

The diffusion velocity of organic molecules through the gel membrane is very fast. For example, addition of hexane (1.5 mL) to the dry [Ru_3]@Si-EG_{cap} gave hexane-swelled [Ru_3]@Si-EG_{cap}. Then, addition of DME (1.5 mL) to the hexane-swelled [Ru_3]@Si-EG_{cap} gave two phases, liquid phase and swelled gel. At this time, the liquid phase contains only DME determined by GLC analysis. After 5 min, the ratio of hexane/DME in the liquid phase attained equilibrium in a ratio of 54:46 (Figure S1, **A**). The time-content plots of the liquid phase obtained by treatment of DME-swelled [Ru_3]@Si-EG_{cap} with hexane are also shown in Figure S1, **B**. After 1 min, the ratio of hexane/DME was 65:35, and the liquid phase came to equilibrium after 5 min in a ratio of 52:48.

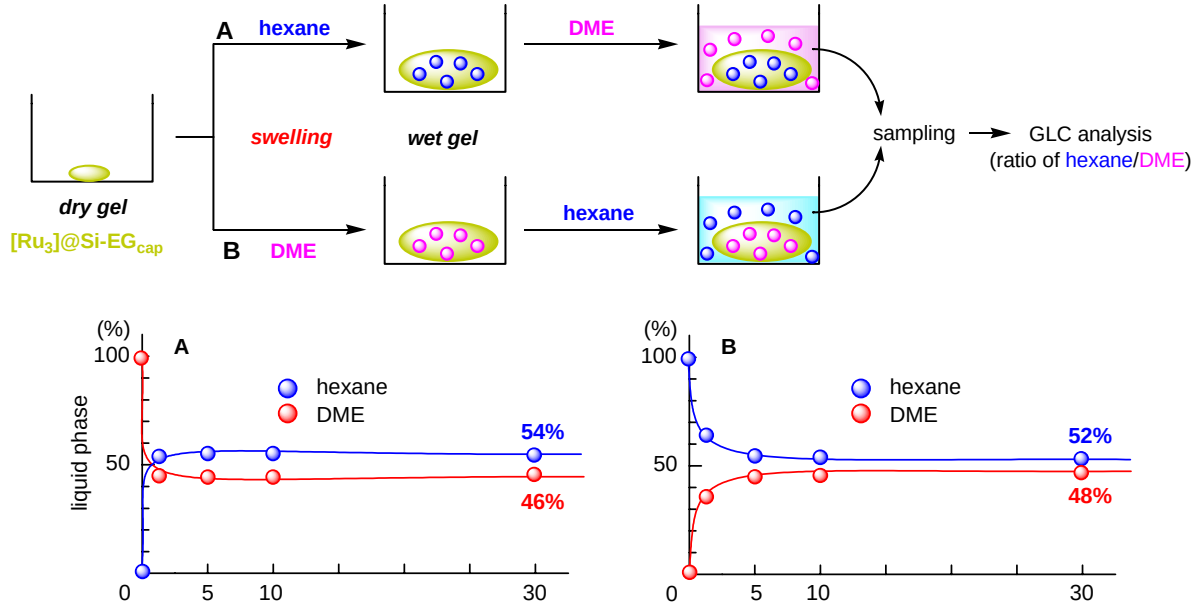


Figure F1. A: Addition of DME to the hexane-swelled gel. **B:** Addition of hexane to the DME-swelled gel.

Synthesis of Allyl and Homoallyl Ethers.

Benzyl crotyl ether (2c):[2] This compound was prepared from benzyl alcohol (15 mmol) and crotyl chloride (20 mmol; *E/Z* = 83:17) in the presence of sodium hydride (20 mmol) in THF at 70 °C. Purification by silica gel chromatography (hexane/ether = 10:1) gave **2c** in 98% yield (*E/Z* = 82:18); IR (neat) ν 3028, 2854, 1453, 1360, 1269, 1097, 1065, 967, 735, 697 cm^{-1}. ***E*-2c:** ^{1}H NMR (395 MHz, $CDCl_3$) δ 1.73 (dm, *J* = 6.3 Hz, 3H), 3.97 (dm, *J* = 6.3 Hz, 2H), 4.50 (s, 2H), 5.63 (dtm, *J* = 15.9, 6.3 Hz, 1H), 5.74 (dqm, *J* = 15.9, 6.3 Hz, 1H), 7.22-7.38 (m, 5H); ^{13}C NMR (99.4 MHz, $CDCl_3$) δ 17.8, 70.9, 71.9, 127.5, 127.6, 127.8, 128.4, 129.6, 138.5. ***Z*-2c:** 1.66 (dm, *J* = 6.3 Hz, 3H), 4.01 (dm, *J* = 6.3 Hz, 2H), 4.52 (s, 2H), 5.58-5.81 (m, 2H), 7.22-7.38 (m, 5H); GLC [TC-17 (30 m), column temperature 120 °C, detection FID] t_R = 21.1 min (*E*-**2c**), 21.4 min (*Z*-**2c**).

Benzyl methallyl ether (2d):[3] This compound was prepared from methallyl alcohol (20 mmol) and benzyl bromide (30 mmol) in the presence of sodium hydride (38 mmol) in THF at 70 °C. Purification by silica gel chromatography (hexane/ether = 4:1) gave **2d** in 82% yield; IR (neat) ν 2915, 2853, 1453, 1362, 1098, 1075, 900, 736, 696 cm^{-1}; ^{1}H NMR (395 MHz, $CDCl_3$) δ 1.78 (s, 3H), 3.94 (s, 2H), 4.50 (s, 2H), 4.93 (bs, 1H), 5.01 (bs, 1H), 7.26-7.39 (m, 5H); ^{13}C NMR (99.4 MHz, $CDCl_3$) δ 19.6, 71.9, 74.2, 112.4, 127.6, 127.8, 128.4, 142.3, 145.2; GLC [TC-17 (30 m), column temperature 120 °C, detection FID] t_R = 16.0 min.

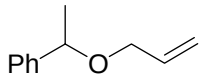
Benzyl cinnamyl ether (2e):[4] This compound was prepared from cinnamyl alcohol (12.7 mmol) and benzyl bromide (11.7 mmol) in the presence of sodium hydride (16.4 mmol) in THF at room temperature. Purification by silica gel chromatography (hexane/ether = 3:1) gave **2e** in 90% yield; IR (neat) ν 3027, 2852, 1495, 1451, 1360, 1115, 1072, 967, 735 cm^{-1}; ^{1}H NMR (395 MHz, $CDCl_3$) δ 4.21 (dd, *J* = 6.3, 1.5 Hz, 2H), 4.59 (s, 2H), 6.34 (dt, *J* = 15.8, 6.3 Hz, 1H), 6.65 (dt, *J* = 15.8, 1.5 Hz, 1H), 7.18-7.49 (m, 5); ^{13}C NMR (99.4 MHz, $CDCl_3$) δ 70.8, 72.2, 126.1, 126.5, 127.67, 127.69, 127.8, 128.4, 128.6, 132.5, 136.7, 138.3; GLC [TC-17 (30 m), column temperature 230 °C, detection FID] t_R = 15.1 min.

Benzyl prenyl ether (2f):[5] This compound was prepared from benzyl alcohol (20 mmol) and prenyl bromide (15 mmol) in the presence of sodium hydride (20 mmol) in THF at 70 °C. Purification by silica gel chromatography (hexane/ether = 10:1) gave **2f** in 93% yield; IR (neat) ν 2914, 2856, 1453, 1376, 1202, 1113, 1087, 1027, 735, 697 cm^{-1}; ^{1}H NMR (395 MHz, $CDCl_3$) δ 1.66 (bs, 3H), 1.76 (bs, 3H), 4.00 (d, *J* = 7.2 Hz, 2H), 4.51 (s, 2H), 5.41 (tm, *J* = 7.2 Hz, 1H), 7.25-7.38 (m, 5H); ^{13}C NMR (99.5 MHz, $CDCl_3$) δ 18.1, 25.8, 66.6, 72.1, 121.2, 127.5, 127.8, 128.4, 137.2, 138.7.

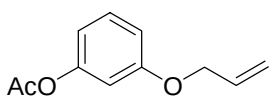
Benzyl homoallyl ether (2g):[6] This compound was prepared from 3-butene-1-ol (13 mmol) and benzyl bromide (11.7 mmol) in the presence of sodium hydride (16.4 mmol) in THF at

room temperature for 25 h. Purification by silica gel chromatography (hexane/ether = 10:1) gave **2g** in 88% yield; IR (neat) ν 2930, 2857, 1641, 1454, 1361, 1203, 1100, 914, 736, 697 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 2.39 (dtm, *J* = 6.8, 6.8 Hz, 2H), 3.54 (t, *J* = 6.8 Hz, 2H), 4.53 (s, 2H), 5.05 (dm, *J* = 10.2 Hz, 1H), 5.10 (dm, *J* = 17.2 Hz, 1H), 5.85 (ddt, *J* = 17.2, 10.2, 6.8 Hz, 1H), 7.24-7.37 (m, 5H); ^{13}C NMR (99.4 MHz, $CDCl_3$) δ 34.0, 69.3, 72.6, 116.0, 127.2, 127.3, 128.0, 135.0, 138.4; GLC [TC-17 (30 m), column temperature 120 °C, detection FID] t_R = 17.4 min.

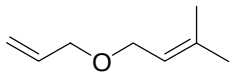
Allyl 1-phenylethyl ether (2h):[7] This compound was prepared from 1-phenylethyl alcohol (30 mmol) and allyl bromide (40 mmol) in the presence of sodium hydride (45 mmol) in THF at 70 °C. Purification by silica gel chromatography (hexane/ether = 10:1) gave **2h** in 97% yield; IR (neat) ν 2976, 2859, 1492, 1451, 1370, 1207, 1141, 1120, 1093, 1055, 921, 760, 700 cm^{-1}; ^1H NMR (395 MHz, $CDCl_3$) δ 1.39 (d, *J* = 6.3 Hz, 3H), 3.73 (ddm, *J* = 13.0, 5.8 Hz, 1H), 3.83 (ddm, *J* = 13.0, 5.3 Hz, 1H), 4.40 (q, *J* = 6.3 Hz, 1H), 5.08 (dm, *J* = 10.6 Hz, 1H), 5.17 (dm, *J* = 17.0 Hz, 1H), 5.84 (dddd, *J* = 17.0, 10.6, 5.8, 5.3 Hz, 1H), 7.17-7.31 (m, 5H); ^{13}C NMR (99.4 MHz, $CDCl_3$) δ 24.2, 69.5, 77.3, 116.7, 126.3, 127.5, 128.5, 135.1, 143.9; GLC [TC-17 (30 m), column temperature 120 °C, detection FID] t_R = 10.8 min; HPLC [Daicel CHIRALCEL OJ, flow rate 0.5 mL/min, UV detector 254 nm], t_R = 13.6 min (*S*-**2h**), 14.8 min (*R*-**2h**).



Allyl 3-acetoxyphenyl ether (2i):[8] This compound was prepared from 3-acetoxyphenol (66 mmol) and allylbromide (80 mmol) in the presence of sodium hydride (80 mmol) in THF at 70 °C. Purification by silica gel chromatography (hexane/ether = 5:1) gave **2i** in 93% yield; IR (neat) ν 3080, 2922, 1765, 1606, 1487, 1370, 1209, 1138, 1018, 927, 781, 688 cm^{-1}; ^1H NMR (395 MHz, $CDCl_3$) δ 2.29 (s, 3H), 4.52 (dm, *J* = 5.3 Hz, 2H), 5.29 (dm, *J* = 10.6 Hz, 1H), 5.41 (dm, *J* = 17.4 Hz, 1H), 6.04 (ddt, *J* = 17.4, 10.6, 5.3 Hz, 1H), 6.66 (bs, 1H), 6.69 (dm, *J* = 8.7 Hz, 1H), 6.80 (dm, *J* = 8.7 hz, 1H), 7.26 (t, *J* = 8.7 hz, 1H); ^{13}C NMR (99.4 MHz, $CDCl_3$) δ 21.2, 69.1, 108.6, 112.5, 114.0, 117.9, 129.9, 133.0, 159.6, 169.4, 177.0; GLC [TC-17 (30 m), column temperature 180 °C, detection FID] t_R = 10.5 min.



Allyl prenyl ether (5).[9] This compound was prepared from prenyl alcohol (20 mmol) and allyl bromide (30 mmol) in the presence of sodium hydride (24 mmol) in THF at 70 °C. Purification by silica gel chromatography (hexane/ether = 1:1) gave **5** in 93% yield; IR (neat) ν 2930, 2856, 1448, 1377, 1124, 1079, 921 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.67 (bs, 3H), 1.75 (bs, 3H), 3.93-3.99 (m, 4H), 5.17 (ddt, *J* = 10.4, 1.8, 1.2 Hz, 1H), 5.27 (ddt, *J* = 17.2, 1.8, 1.6 Hz, 1H), 5.36 (tm, *J* = 6.9 Hz, 1H), 5.93 (ddt, *J* = 17.3, 10.4, 5.6 Hz, 1H); ^{13}C NMR (99.4 MHz, $CDCl_3$) δ 18.1, 25.3, 66.6, 71.1, 116.9, 121.2, 135.2, 137.0; GLC [TC-17 (30 m), column temperature 80 °C, detection FID] t_R = 8.2 min.



Isomerization of Allyl Benzyl Ether 2a with [Ru_3]@Si Catalysts (Table 1).

A solution of allyl benzyl ether **2a** (148 mg, 1 mmol) in *n*-hexane (3 mL) was added to the dry [Ru_3]@Si catalyst ([Ru_3] = 1 mol%). After it was standing at 50 °C for 5 h without stirring, the liquid phase was separated and the residual [Ru_3]@Si catalyst was washed with *n*-hexane (totally 10 mL). The combined organic phases were evaporated under reduced pressure to afford benzyl 1-propenyl ether **3a**. The purity and the *E/Z* ratio of **3a** were determined by capillary GLC analysis.

Recycle Experiments and ICP-MS Analysis of the Product.

After the reaction of **2a** with [Ru_3]@Si-EG_{cap} described as above, the recovered catalyst was dried under reduced pressure and subjected to a further run of isomerization of **2a**. The ruthenium content in vinyl ether **3a** was determined by ICP-MS analysis: **3a** obtained by the above procedure was dissolved in an aqueous solution of HCl, and the concentration of HCl was adjusted to 5 x 10^{-3} wt%. The content of **3a** in this solution was 6.2 x 10^{-3} mol/L. The measurement was performed using this solution. The ruthenium content was calibrated with a commercially available standard reagent (ACROS: ruthenium atomic absorption standard solution, 1 mg/mL Ru in 5% HCl); five standard solutions, of which Ru concentration is in a rage from 5ppb to 200ppb, were used for calibration.

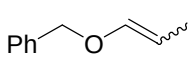
Table S1. Ru contents of **3a** in recycle experiments.

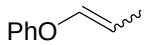
run	yield of **3a**	Ru amount in **3a**	calcd. catalyst leaching
1st	>95%	15 ppm	0.02%
2nd	>95%	25 ppm	0.04%
3rd	>95%	58 ppm	0.09%

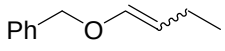
General Procedure for Isomerization of Allyl Ethers with [Ru_3]@Si-EG_{cap} or [Ru_3]@Si-BP_{cap} Followed by Hydrolisis (Table 2).

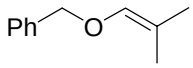
A solution of allyl ether (1 mmol) in *n*-hexane (3 mL) was added to the dry [Ru_3]@Si catalyst ([Ru_3] = 1 mol%), and it was standing at 50 °C without stirring. After the reaction completed, formed vinyl ether was obtained by filtration and washing the gel with hexane (10 mL). Treatment of vinyl ether with aq. HCl in MeOH at room temperature for 2 h gave the deallylated alcohol, which was purified by silica gel column chromatography.

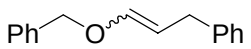
Spectral Data of Vinyl Ethers

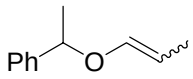
Benzyl 1-propenyl ether (3a).[10] ***E*-3a:** ^{1}H NMR (396 MHz, $CDCl_3$) δ 1.57 (dd, *J* = 6.8, 1.5 Hz, 3H),  4.71 (s, 2H), 4.90 (dq, *J* = 12.6, 6.8 Hz, 1H), 6.32 (dq, *J* = 12.6, 1.5 Hz, 1H), 7.27-7.40 (m, 5H); ***Z*-3a:** ^{1}H NMR (396 MHz, $CDCl_3$) δ 1.63 (dd, *J* = 6.8, 1.9 Hz, 3H), 4.45 (qd, *J* = 6.8, 6.3 Hz, 1H), 4.81 (s, 2H), 6.04 (dq, *J* = 6.3, 1.9 Hz, 1H), 7.27-7.40 (m, 5H); GLC [TC-17 (30 m), column temperature 120 °C, detection FID] t_R = 11.6 min (**3a**), 11.9 min (*Z*-**3a**), 13.7 min (*E*-**3a**).

Phenyl 1-propenyl ether (3b).[11] ***E*-3b:** ^{1}H NMR (396 MHz, $CDCl_3$) δ 1.67 (dd, *J* = 6.9, 1.7 Hz, 3H),  5.37 (dq, *J* = 12.0, 6.9 Hz, 1H), 6.42 (dq, *J* = 12.0, 1.7 Hz, 1H), 6.93-7.08 (m, 3H), 7.30 (m, 2H). ***Z*-3b:** ^{1}H NMR (396 MHz, $CDCl_3$) δ 1.72 (dd, *J* = 6.9, 1.8 Hz, 3H), 4.88 (qd, *J* = 6.9, 6.1 Hz, 1H), 6.38 (dq, *J* = 6.1, 1.8 Hz, 1H), 6.93-7.08 (m, 3H), 7.30 (m, 2H); GLC [TC-17 (30 m), column temperature 120 °C, detection FID] t_R = 7.8 min (*Z*-**3b**), 8.6 min (*E*-**3b**), 9.1 min (**2b**).

Benzyl 1-butenyl ether (3c). *E*-3c: ^{1}H NMR (396 MHz, $CDCl_3$) δ 0.97 (t, *J* = 7.6 Hz, 3H), 1.96 (qd, *J*  = 7.6, 6.9 Hz, 2H), 4.71 (s, 2H), 4.93 (dt, *J* = 12.5, 6.9 Hz, 1H), 6.34 (d, *J* = 12.5 Hz, 1H), 7.25-7.41 (m, 5H); ***Z*-3c:** ^{1}H NMR (396 MHz, $CDCl_3$) δ 0.98 (t, *J* = 7.6 Hz, 3H), 2.14 (qd, *J* = 7.6, 7.3 Hz, 2H), 4.41 (td, *J* = 7.3, 6.3 Hz, 1H), 4.79 (s, 2H), 5.99 (d, *J* = 6.3 Hz, 1H), 7.25-7.41 (m, 5H); GLC [TC-17 (30 m), column temperature 120 °C, detection FID] t_R = 17.1 min, 20.4 min. GLC [TC-17 (30 m), column temperature 120 °C, detection FID] t_R = 17.1 min (*Z*-**3c**), 20.4 min (*E*-**3c**).

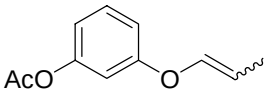
Benzyl 2-methyl-1-propenyl ether (3d).[12] ^{1}H NMR (396 MHz, $CDCl_3$) δ 1.54 (s, 3H), 1.65 (s, 3H),  4.74 (s, 2H), 5.88 (bs, 1H), 7.26-7.39 (m, 5H).

Benzyl 3-phenyl-1-propenyl ether (3e). *E*-3e: ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.28 (bd, *J* = 7.4 Hz,  2H), 4.76 (s, 2H), 5.06 (dt, *J* = 12.6, 7.4 Hz, 1H), 6.45 (dm, *J* = 12.6 Hz, 1H), 7.16-7.43 (m, 10H). ***Z*-3e:** ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.49 (bd, *J* = 7.4 Hz, 2H), 4.63 (td, *J* = 7.4, 6.3 Hz, 1H), 4.86 (s, 2H), 6.15 (dt, *J* = 6.3, 1.5 Hz, 1H), 7.16-7.43 (m, 10H); GLC [TC-17 (30 m), column temperature 230 °C, detection FID] t_R = 11.5 min (*Z*-**3e**), 12.5 min (*E*-**3e**), 15.1 min (**2e**).

1-Phenylethyl 1-propenyl ether (3h).[13] ***E*-3h:** ^{1}H NMR (396 MHz, $CDCl_3$) δ 1.47 (dd, *J* = 6.8, 1.5 Hz,  3H), 1.50 (d, *J* = 6.3 Hz, 3H), 4.77 (q, *J* = 6.3 Hz, 1H), 4.88 (dq, *J* = 12.6, 6.8 Hz, 1H), 6.07 (dq, *J* = 12.6, 1.5 Hz, 1H), 7.24-7.39 (m, 5H); ^{13}C NMR (99.5 MHz, $CDCl_3$) δ 12.6, 23.81, 78.0, 101.5, 126.0, 127.5, 128.53, 143.4, 145.2. ***Z*-3h:** ^{1}H NMR (396 MHz, $CDCl_3$) δ 1.53 (d, *J* = 6.3 Hz, 3H), 1.64 (dd, *J* = 6.8, 1.9 Hz, 3H), 4.39 (dq, *J* = 6.3, 6.3 Hz, 1H), 4.75 (q, *J* = 6.3 Hz, 1H), 5.93 (dq, *J* = 6.3, 1.9 Hz, 1H), 7.24-7.39 (m, 5H); ^{13}C NMR (99.5 MHz, $CDCl_3$) δ 9.5, 23.78, 79.3, 101.8, 126.0, 127.6, 128.50, 143.5, 144.3; GLC [TC-17 (30 m), column temperature 120 °C, detection

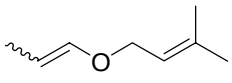
FID] t_R = 10.8 min (**2h**), 12.1 min (*Z*-**3h**), 13.4 min (*E*-**3h**).

3-Acetoxyphenyl 1-propenyl ether (3i). ***E*-3i:** ^{1}H NMR (396 MHz, $CDCl_3$) δ 1.67 (dd, *J* = 6.8, 1.5 Hz, 3H), 2.29 (s, 3H), 5.41 (dq, *J* = 12.1, 6.8 Hz, 1H), 6.39 (dq, *J* = 12.1, 1.5 Hz, 1H), 6.71-6.80 (m, 2H), 6.87 (dm, *J* = 8.2 Hz, 1H), 7.30 (t, *J* = 8.2 Hz, 1H); ***Z*-3i:** ^{1}H NMR (396 MHz, $CDCl_3$) δ 1.70 (dd, *J* = 6.8, 1.9 Hz, 3H), 2.29 (s, 3H), 4.92 (qd, *J* = 6.8, 6.3 Hz, 1H), 6.35 (dq, *J* = 6.3, 1.9 Hz, 1H), 6.71-6.80 (m, 2H), 6.85 (dm, *J* = 8.2 Hz, 1H), 7.29 (t, *J* = 8.2 Hz, 1H); GLC [TC-17 (30 m), column temperature 180 °C, detection FID] t_R = 9.1 min (*Z*-**3i**), 9.8 min (*E*-**3i**), 10.5 min (**2i**). HRMS (EI) calcd for $C_{11}H_{12}O_3$ 192.0786, found 192.0784.



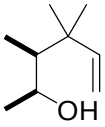
1-Phenylethylalcohol (4h). GLC [SUPELCO β-DEX 120 (30 m), column temperature 120 °C, detection FID] t_R = 19.8 min (*R*-**4h**), 20.5 min (*S*-**4h**).

3-Methyl-2-butenyl 1-propenyl ether (6). ***E*-6:**[13] ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.58 (dd, *J* = 6.6, 1.8 Hz, 3H), 1.69 (bs, 3H), 1.76 (bs, 3H), 4.15 (d, *J* = 6.9 Hz, 2H), 4.80 (dq, *J* = 12.4, 6.6 Hz, 1H), 5.37 (t, *J* = 6.9 Hz, 1H), 6.23 (dq, *J* = 12.4, 1.8 Hz, 1H). ***Z*-6:** ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.55 (dd, *J* = 6.6, 1.7 Hz, 3H), 1.69 (bs, 3H), 1.76 (bs, 3H), 4.24 (d, *J* = 6.9 Hz, 2H), 4.38 (qd, *J* = 6.6, 6.1 Hz, 1H), 5.37 (t, *J* = 6.9 Hz, 1H), 5.97(dq, *J* = 6.1, 1.7 Hz, 1H); GLC [TC-17 (30 m), column temperature 80 °C, detection FID] t_R = 8.2 min (**5**), 8.6 min (*Z*-**6**), 9.6 min (*E*-**6**).



Alkylative Claisen Rearrangement of 6.

3,3,4-Trimethyl-1-hexen-5-ol (7).[14] To a solution of prenyl 1-propenyl ether **6** obtained as above (0.5 mmol) in dichloroethane (3.8 mL) was added Me_3Al (1 mol/L hexane solution, 1 mL, 1 mmol) at ambient temperature. After it was stirred for 2 h, the reaction mixture was poured into 1*N* HCl (4 mL) and the product was extracted with dichloromethane. The combined organic layers were washed with brine and dried over $MgSO_4$. Purification by silica gel chromatography (hexane/ether = 1:1) gave **7** in 72% yield (*syn/anti* = 95:5). ***syn*-7:** ^{1}H NMR (396 MHz, $CDCl_3$) δ 0.91 (d, *J* = 7.2 Hz, 3H), 1.03 (s, 3H), 1.08 (s, 3H), 1.12 (d, *J* = 6.3 Hz, 3H), 1.27 (qd, *J* = 7.2, 1.0 Hz, 1H), 1.35 (bs, 1H), 4.17 (bq, *J* = 6.3 Hz, 1H), 5.01 (dd, *J* = 10.1, 1.5 Hz, 1H), 5.03 (dd, *J* = 17.9, 1.5 Hz, 1H), 5.97 (dd, *J* = 17.9, 10.1 Hz, 1H); ^{13}C NMR (99.4 MHz, $CDCl_3$) δ 7.0, 22.9, 25.5, 25.6, 39.6, 48.5, 67.2, 111.8, 147.6. ***anti*-7:** ^{1}H NMR (396 MHz, $CDCl_3$) δ 0.85 (d, *J* = 7.2 Hz, 3H), 1.00 (s, 3H), 1.01 (s, 3H), 1.11 (d, *J* = 6.3 Hz, 3H), 1.22-1.33 (m, 2H), 3.86 (m, 1H), 4.95-5.06 (m, 2H), 5.97 (m, 1H).



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