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Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Stereoselective Isomerization of Unsymmetrical Diallyl Ethers to Allyl (E)-Vinyl Ethers by a Cationic Iridium Catalyst

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Published online: 04 Dec 2007.

To cite this article: Yasunori Yamamoto , Ryou Fujikawa & Norio Miyaura (2000) Stereoselective Isomerization of Unsymmetrical Diallyl Ethers to Allyl (E)-Vinyl Ethers by a Cationic Iridium Catalyst, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 30:13, 2383-2391, DOI: 10.1080/00397910008086880

To link to this article: http://dx.doi.org/10.1080/00397910008086880

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SYNTHETIC COMMUNICATIONS, 30(13), 2383–2391 (2000)

STEREOSELECTIVE ISOMERIZATION OF UNSYMMETRICAL DIALLYL ETHERS TO ALLYL (*E*)-VINYL ETHERS BY A CATIONIC IRIDIUM CATALYST

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Abstract: *The stereoselective isomerization of unsymmetrical diallyl ethers to allyl (E)-vinyl ethers was carried out in the presence of a cationic iridium(I) catalyst. The catalyst prepared in situ by treating* $[Ir(cod)(PPh_2Me)_2]PF_6$ *with hydrogen was found to be an excellent catalyst to selectively isomerize the less substituted allyl group to an (E)-vinyl ether.*

The positional double-bond migration (isomerization)[1] of allyl ethers[2], allyl acetals[3], or allyl alcohols[4] has found various applications in organic synthesis. Among them, the catalytic isomerization of allyl ethers to vinyl ethers has been studied extensively[2], though their stereoselective transformation has not received much attention. For example, a novel and valuable route for the synthesis of a range of γ,δ-unsaturated aldehydes or ketones from diallyl ethers makes use of the double-bond migration catalyzed by $RuCl_2(PPh_3)_3$ to give an intermediate allyl vinyl ether and its *in situ* Claisen rearrangement.[5] However, the *E/Z*-selective transformation can be of interest when the vinyl ethers are used for the stereoselective reactions. The isomerization of allyl ethers, including diallyl ethers, with $NiCl_2$•dppb/$LiHBEt_3$ or a base (e.g., ^tBuOK, $LiNR_2$) provides (*Z*)-vinyl ethers.[6] On the other hand, various cationic iridium complexes stereoselectively isomerize allyl silyl ethers to the corresponding (*E*)-vinyl silyl ethers (*E*> 88~99%).[7]

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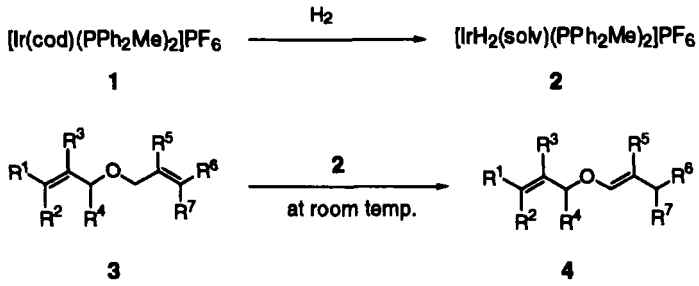
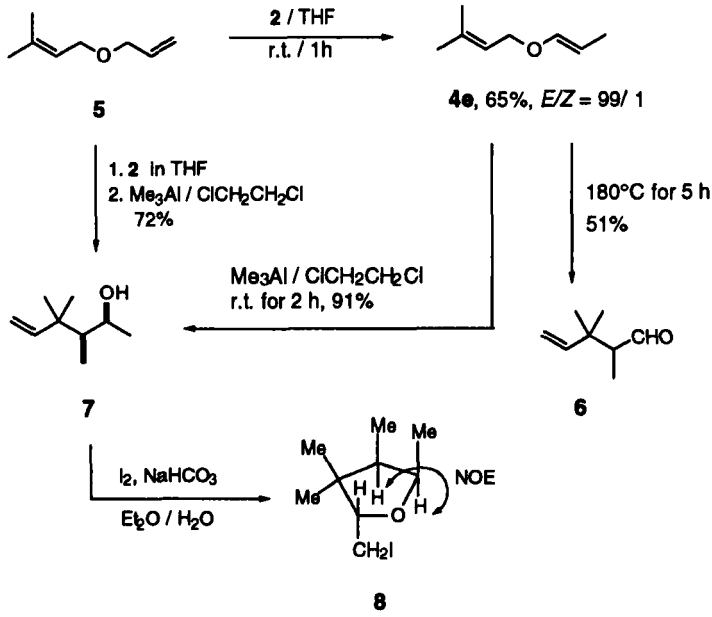


a. R^1 = Ph; R^2, R^3, R^4, R^5, R^6, R^7 = H
b. R^1 = Ph; R^2, R^3, R^4, R^5, R^7 = H; R^6 = Me
c. R^1 = Ph; R^2, R^3, R^4, R^6, R^7 = H; R^5 = Me
d. R^1, R^2 = Me; R^4, R^5 = H; R^6 = Ph; R^7 = H
e. R^1, R^2 = Me; R^3, R^4, R^5, R^6, R^7 = H
f. R^1, R^2 = Me; R^3, R^4, R^5, R^7 = H; R^6 = Me
g. R^1, R^2 = Me; R^3, R^4, R^6, R^7 = H; R^5 = Me
h. R^1, R^3 = H; R^2, R^4 = -$(CH_2)_3$-; R^5, R^6, R^7 = H
i. R^1, R^3 = H; R^2, R^4 = -$(CH_2)_3$-; R^5, R^7 = H; R^6 = Me
j. R^1, R^3 = H; R^2, R^4 = -$(CH_2)_3$-; R^5 = Me; R^6, R^7 = H

Scheme 1. Isomerization of Unsymmetrical Diallyl Ethers



Scheme 2. A Sequence of Isomerization and [3,3] Rearrangement for the Syntheses of Claisen Products

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Table 1. Effect of Catalysts on the Isomerization of Cinnamyl Prenyl Ether[a]

entry	catalyst	solvent	yield/%[b]	E/Z[c]
1	$[Ir(cod)(PPh_2Me)_2]PF_6$	THF	51	99/ 1
2		dioxane	42	99/ 1
3		DMI[d]	8	99/ 1
4		CH_2Cl_2	trace	
5		benzene	trace	
6	$[Ir(cod)(PPh_3)_2]PF_6$	THF	45	98/ 2
7	$[Ir(cod)(PMe_3)_2]PF_6$	THF	trace	

[a]The catalysts were *in situ* prepared by bubbling hydrogen into a solution of $[Ir(cod)(PR_3)_2]PF_6$ (3 mol%). The diallyl ether (1 mmol) was added, and the resulting solution was then stirred for 1 h at room temperatuture.
[b]Isolated yields by chromatography over silica gel.
[c]The ratio obtained by ^1H NMR.
[d]1,3-Dimethyl-2-imidazolidinone.

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In this paper, we wish to report the iridium-catalyzed isomerization of unsymmetrical diallyl ethers to (*E*)-allyl vinyl ethers which are a useful intermediate for the preparation of γ,δ-unsaturated carbonyl compounds or alcohols *via* the stereoselective Claisen rearrangement (Schemes 1 and 2).

To optimize the reaction conditions, the isomerization of cinnamyl prenyl ether (**3d**) was carried out at room temperature for 1 h by the use of various solvents and cationic iridium catalysts[8,9] (Table 1). The catalyst (**2**) active for the isomerization was prepared *in situ* by bubbling hydrogen into a red solution of $[Ir(cod)(PR_3)_2]PF_6$ (**1**) by the method reported by Felkin.[7a]

In all reactions, the prenyl group remained intact during the isomerization of the cinnamyl group to the (*E*)-2-benzylethenyl ether. The yields were highly dependent on the solvents. Thus, the diallyl ether was recovered without isomerization in DMI, DMF, dichloromethane and benzene, but 51% of **4d** was obtained in THF which has medium coordination ability to the iridium metal center. Both the PPh_2Me complex (entry 1) and the PPh_3 complex (entry 6) revealed similar catalyst activity, but the trimethylphosphine complex did not catalyze the reaction (entry 7). The (*E*)-stereoselectivity exceeded 99%.

The results of the isomerization of various unsymmetrical diallyl ethers are shown in Table 2. A series of cinnamyl ethers was treated with an iridium catalyst (**2**) for 1 h at room temperature. Allyl, crotyl, and methallyl ethers were readily converted into the vinyl ethers with some accompanying isomeric products derived

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Table 2. Isomerization of Diallyl Ethers **3** to Allyl Vinyl Ethers **4**

entry	diallyl ether	product	yield (%)[a]	E/Z[b]
1	$PhCH{=}CHCH_2OCH_2CH{=}CH_2$ (**3a**)	$PhCH{=}CHCH_2OCH{=}CHCH_3$ (**4a**)	78[c]	96/4
2	$PhCH{=}CHCH_2OCH_2CH{=}CHCH_3$ (**3b**)	$PhCH{=}CHCH_2OCH{=}CHCH_2CH_3$ (**4b**)	60[d]	99/1
3	$PhCH{=}CHCH_2OCH_2C(CH_3){=}CH_2$ (**3c**)	$PhCH{=}CHCH_2OCH{=}C(CH_3)_2$ (**4c**)	56	-
4	$PhCH{=}CHCH_2OCH_2CH{=}C(CH_3)_2$ (**3d**)	$PhCH_2CH{=}CHOCH_2CH{=}C(CH_3)_2$ (**4d**)	51	99/1
5	$(CH_3)_2C{=}CHCH_2OCH_2CH{=}CH_2$ (**3e**)	$(CH_3)_2C{=}CHCH_2OCH{=}CHCH_3$ (**4e**)	65	99/1
6	$(CH_3)_2C{=}CHCH_2OCH_2CH{=}CHCH_3$ (**3f**)	$(CH_3)_2C{=}CHCH_2OCH{=}CHCH_2CH_3$ (**4f**)	25	E>99
7	$(CH_3)_2C{=}CHCH_2OCH_2C(CH_3){=}CH_2$ (**3g**)	$(CH_3)_2C{=}CHCH_2OCH{=}C(CH_3)_2$ (**4g**)	66	-
8	 $OCH_2CH{=}CH_2$ (**3h**)	 $OCH{=}CHCH_3$ (**4h**)	78	97/3
9	 $OCH_2CH{=}CHCH_3$ (**3i**)	 $OCH{=}CHCH_2CH_3$ (**4i**)	74	E>99
10	 $OCH_2C(CH_3){=}CH_2$ (**3j**)	 $OCH{=}C(CH_3)_2$ (**4j**)	68	-

[a]Isolated yields. [b]The ratio of (*E*)- and (*Z*)-vinylic protones in ^1H NMR. [c]$PhCH_2CH{=}CHOCH{=}CHCH_3$ (10%) was also produced. [d]The reaction accompanied with $PhCH_2CH{=}CHOCH{=}CHCH_2CH_3$ (16%) and $PhCH_2CH{=}CHOCH_2CH{=}CHCH_3$ (10%).

from the isomerization of cinnamyl group (entries 1-3), but the prenyl group was strongly resistant to the isomerization (entries 4-7). The 2-cyclohexenyl group was the most strongly resistant (entries 8-10) because its isomerization was not observed in the reaction of 2-cyclohexenyl prenyl ether. A series of acyclic and cyclic allyl ethers revealed an order of reactivity which favored the isomerization at the less substituted allyl group. The order of reactivity thus obtained was CH_2=$CHCH_2$ > CH_2=$C(CH_3)CH_2$ ~ CH_3CH=$CHCH_2$ > PhCH=$CHCH_2$ >> $(CH_3)_2C$=$CHCH_2$ > 2-cyclohexenyl.

The utility of the present process was demonstrated in the stereoselective synthesis of Claisen substrates (Scheme 2). 2,3,3-Trimethyl-4-pentenal (**6**) was obtained in a yield of 51% when the isomerization of **5** to give **4e** was followed by the aliphatic Claisen rearrangement at 180 ℃.

Nozaki's procedure for the alkylative Claisen rearrangement of **4e** afforded **7** with high diastereoselectivity (*syn/anti*=95/5).[10] The stereochemistry was further confirmed by its iodocyclization into **8**, which revealed NOE between two hydrogens shown in **8**. The synthesis of various olefinic alcohols which are produced by the rearrangement and successive alkylation with methyl-, 1-alkenyl, 1-alkynylaluminums has been reported. The mild conditions of the rearrangement and alkylation occurring at room temperature allow the one-pot synthesis of Claisen products in the same flask. The *in situ* operation of the two steps, thus, the isomerization of **5** followed by the [3,3] rearrangement of the crude **4e** with trimethylaluminum afforded **7** in 72% yield.

Experimental Section

Reagents. The diallyl ethers were synthesized by a general procedure for the Williamson ether synthesis. The reported procedure gave a red crystal of $[Ir(cod)(PPh_2Me)_2]PF_6$ (**1**). THF was distilled from benzophenone ketyl.

Isomerization of Diallyl Ether (Tables 1 and 2). A typical procedure for the isomerization of cinnamyl prenyl ether with $[Ir(cod)(PPh_2Me)_2]PF_6$ is described. $[Ir(cod)(PPh_2Me)_2]PF_6$] (25 mg, 0.03 mmol) and THF (5 ml) were charged in a flask, and flushed with argon. Hydrogen was bubbled into the solution to give a yellow catalyst solution of $[IrH_2(thf)_2(PPh_2Me)_2]PF_6$. The excess hydrogen was then removed by bubbling argon into the solution. Cinnamyl prenyl ether (0.202 g, 1 mmol) was added and the resulting mixture was then stirred at room temperature. After being stirred for 1h, the mixture was quenched with a buffer solution (pH 7). The product was extracted with diethyl ether and dried over $MgSO_4$. The allyl vinyl ether (**4d**) was isolated by thin-layer chromatography on silica gel with hexane/ethyl acetate = 15/1 (0.096 g, 51%). **4d**: IR (neat) 1255 and 1030 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.67 (s, 3H), 1.76 (s, 3H), 3.25 (d, 2H, *J*= 7.3 Hz), 4.19 (d, 2H, *J*= 6.4 Hz), 4.95 (dt, 1H,

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J= 12.7 and 7.3), 5.36-5.40 (m, 1H), 6.35 (d, 1H, *J*= 12.4 Hz), 7.16-7.40 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.07, 25.75, 34.09, 65.79, 103.1, 119.8, 125.9, 128.2, 128.3, 137.9, 141.7, 147.0; MS *m/z* 41 (65), 69 (100), 92 (38), 134 (43), 184 (1), 187 (0.9), 202 (1, M^+); HRMS *m/z* $C_{14}H_{18}O$ calcd for 202.1358, found 202.1368.

The following compounds were prepared by the above general procedure.

4a: IR (neat) 1260 and 1030 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.56 (dd, 3H, *J*= 6.7 and 1.5 Hz), 4.33 (dd, 2H, *J*= 5.9 and 1.5 Hz), 4.86 (dq, 1H, *J*= 12.4 and 6.8 Hz), 6.24-6.32 (m, 2H), 6.62 (d, 1H, *J*= 15.9 Hz), 7.18-7.40 (m, 5H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 12.56, 69.83, 99.51, 125.0, 126.5, 127.8, 128.5, 132.7, 136.5, 146.0; MS *m/z* 51 (4), 65 (4), 77 (4), 91 (14), 105 (4), 117 (100), 131 (2), 174 (2, M^+); HRMS *m/z* $C_{12}H_{14}O$ calcd for 174.1044, found 174.1050.

4b: IR (neat) 1255 and 1020 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 (t, 3H, *J*= 7.4 Hz), 1.95 (dq, 2H, *J*= 7.4 and 7.2 Hz), 4.34 (dd, 2H, *J*= 5.9 and 1.5 Hz), 4.87-4.94 (m, 1H), 6.26-6.34 (m, 2H), 6.63 (d, 1H, *J*= 16.1 Hz), 7.19-7.40 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.26, 21.08, 69.80, 107.0, 124.9, 126.5, 127.8, 128.6, 132.7, 136.5, 145.1; MS *m/z* 55 (14), 77 (5), 91 (19), 105 (4), 117 (100), 134 (6), 188 (5, M^+); HRMS *m/z* $C_{13}H_{16}O$ calcd for 188.1201, found 188.1217.

4c: IR (neat) 1250 and 1030 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.55 (s, 3H), 1.65 (s, 3H), 4.13 (dd, 2H, *J*= 5.9 and 1.5 Hz), 5.87-5.88 (m, 1H), 6.31 (dt, 1H, *J*= 15.6 and 6.0 Hz), 6.61 (d, 1H, *J*= 16.1 Hz), 7.15-7.40 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.56, 33.98, 70.46, 112.5, 126.5, 127.6, 128.3, 128.5, 132.4, 136.8,139.5; MS *m/z* 55 (30), 77 (13), 91 (29), 105 (48), 117 (100), 132 (18), 188 (10, M^+); HRMS *m/z* $C_{13}H_{16}O$ calcd for 188.1201, found 188.1216.

4e: IR (neat) 1270 and 980 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.58 (dd, 3H, *J*= 6.8 and 1.7 Hz), 1.65 (s, 3H), 1.73 (s, 3H), 4.24 (d, 2H, *J*= 6.8 Hz), 4.79 (dq, 1H, *J*= 26.4 and 6.8 Hz), 5.37 (t, 1H, *J*= 6.8 Hz), 6.22 (dq, 1H, *J*= 12.6 and 1.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.62, 18.02, 25.74, 65.75, 98.67, 120.0, 137.7, 146.3; MS *m/z* 41 (100), 53 (9), 58 (11), 69 (92), 84 (13), 93 (5),108 (9), 126 (4, M^+); HRMS *m/z* $C_8H_{14}O$ calcd for 126.1044, found 126.1051.

4f: IR (neat) 1250 and 1020 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97 (t, 3H, *J*= 7.4 Hz), 1.69 (s, 3H), 1.76 (s, 3H) 1.94 (dq, 2H, *J*= 7.4 and 7.3 Hz), 4.15 (d, 2H, *J*= 6.8 Hz), 4.83 (dt, 1H, *J*= 12.7 and 5.6 Hz), 5.38 (t, 1H, *J*= 6.8 Hz), 6.24 (dt, 1H, *J*= 12.4 and 1.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.31, 18.04, 21.15, 25.75, 29.69, 65.74, 106.3, 120.0, 145.3; MS *m/z* 41 (90), 58 (20), 69 (100), 85 (8), 93 (7), 112 (3), 140 (2, M^+); HRMS *m/z* $C_9H_{16}O$ calcd for 140.1201, found 140.1214.

4g: IR (neat) 1280 and 1050 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.55 (s, 3H), 1.61 (s, 3H), 1.68 (s, 3H), 1.75 (s, 3H), 4.18 (d, 2H, *J*= 6.8 Hz), 5.37 (t, 1H, *J*= 6.8 Hz), 5.8-5.8 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.02, 18.05, 19.62, 25.79, 68.05, 110.4, 120.8, 137.1, 139.7; MS *m/z* 69 (16), 72 (100), 84 (6), 107 (5), 122 (31), 140 (19, M^+); HRMS *m/z* $C_9H_{16}O$ calcd for 140.1201, found 140.1192.

4h: IR (neat) 1270 and 1020 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.55 (dd, 3H, *J*= 6.7 and 1.5 Hz), 1.70-1.87 (m, 4H), 1.92-2.16 (m, 2H), 4.17-4.21 (m, 1H), 4.90 (dq, 1H, *J*= 12.8 and 6.8 Hz), 5.76 (dd, 1H, *J*= 10.1 and 5.1 Hz), 5.90 (dt, 1H, *J*= 10.1 and 3.7 Hz), 6.13 (dq, 1H, *J*= 12.3 and 1.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.54, 18.95, 25.01, 28.50, 73.13, 100.8, 126.7, 131.7, 145.0; MS *m/z* 41 (18), 53 (15), 65 (3), 80 (59), 81 (100), 138 (5, M^+); HRMS *m/z* $C_9H_{14}O$ calcd for 138.1045, found 138.1036.

4i: IR (neat) 1200, 1020 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.97 (t, 3H, *J*=7.3 Hz) 1.49-1.86 (m, 4H), 1.90-2.11 (m, 2H), 1.93 (dq, 2H, *J*=7.4 and 7.3 Hz), 4.17-4.21 (m, 1H), 4.95 (dt, 1H, *J*= 12.4 and 7.1 Hz), 5.77 (dd, 1H, *J*= 10.1 and 5.0 Hz), 5.90 (dt, 1H, *J*= 10.1 and 3.7 Hz), 6.15 (dt, 1H, *J*= 12.4 and 1.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.19, 18.97, 21.07, 25.02, 28.49, 73.10, 108.3, 126.7, 131.7, 144.0; MS *m/z* 72 (1), 80 (100), 81 (28), 123 (1), 134 (1), 152 (19, M^+); HRMS *m/z* $C_{10}H_{16}O$ calcd for 152.1201, found 152.1209.

4j: IR (neat) 1200, 1020 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.55 (s, 3H), 1.61 (s, 3H), 1.51-1.85 (m, 4H), 1.91-2.11 (m, 2H), 4.07-4.11 (m, 1H), 5.75 (dd, 1H, *J*= 10.1 and 5.1 Hz), 5.86-5.91 (m, 1H), 5.87-5.88 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.18, 19.07, 19.62, 25.09, 28.78, 74.10, 111.1, 127.3, 131.3, 138.6; MS *m/z* 72 (44), 78 (3), 80 (100), 81 (27), 152 (52, M^+); HRMS *m/z* $C_{10}H_{16}O$ calcd for 152.1201, found 152.1215.

Aliphatic Claisen Rearrangement (Scheme 2). Prenyl 1-propenyl ether (**4e**) (1 mmol) was sealed in a Pyrex tube under reduced pressure and then heated for 5 h at 180 ℃. The column chromatography on silica gel with hexane/diethyl ether = 20/1 gave 51% of **6**.

6: IR (neat) 1720 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.03 (d, 3H, *J*= 7.1 Hz), 1.08 (s, 3H), 1.11 (s, 3H), 2.24 (dq, 1H, *J*= 7.0 and 2.7 Hz), 5.02 (dd, 1H, *J*= 17.6 and 1.0 Hz), 5.07 (dd, 1H, *J*= 10.7 and 1.0 Hz), 5.87 (dd, 1H, *J*= 17.3 and 10.7 Hz), 9.72 (d, 1H, *J*= 2.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.12, 24.36, 24.86, 38.60, 54.56, 112.6, 145.3, 205.8; MS *m/z* 69 (53), 85 (11), 97 (19), 103 (100), 111 (12), 126 (27, M^+); HRMS *m/z* $C_8H_{14}O$ calcd for 126.1044, found 126.1054.

To a solution of **4e** (1 mmol) in dichloroethane (7.5 ml) was added Me_3Al (1 M in hexane, 2 ml, 2 mmol). After being stirred for 2 h, the mixture was poured into 1N HCl (7.5 ml). The product was extracted with CH_2Cl_2, successively washed with brine and aqueous Na_2CO_3, and dried over $MgSO_4$. The chromatography over silica gel with hexane/diethyl ether = 1/1 gave 91% of **7**.

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7: IR (neat) 3450 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.91 (d, 3H, J= 7.3 Hz), 1.03 (s, 3H), 1.07 (s, 3H), 1.12 (d, 3H, J= 6.3 Hz), 1.28 (q, 1H, J= 7.1 Hz), 1.37 (d, 1H, J= 3.7 Hz), 4.14-4.23 (m, 1H), 5.00-5.06 (m, 2H), 5.97 (dd, 1H, J= 18.1 and 10.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 6.89, 22.73, 25.42, 25.56, 39.49, 48.34, 67.09, 111.7, 147.5; MS *m/z* 41 (84), 45 (43), 55 (87), 69 (100), 83 (44), 98 (21), 109 (27), 124 (10), 142 (0.8, M^+); HRMS *m/z* $C_9H_{18}O$ calcd for 142.1358, found 142.1360.

To a solution of **7** (0.142 g, 1 mmol) and $NaHCO_3$ (0.168 g, 2 mmol) in Et_2O/H_2O (5 ml/2 ml) was added I_2 (0.305 g, 1.2 mmol) at 0℃. After being stirred for 3 h, the mixture was treated with aqueous sodium thiosulfate. The product was extracted with diethyl ether and dried over anhydrous $MgSO_4$. The chromatography on silica gel with CH_2Cl_2 gave **8** (0.107 g, 40%).

8: IR (neat) 1200 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.86 (d, 3H, J= 7.3 Hz), 1.00 (s, 3H), 1.03 (s, 3H), 1.12 (d, 3H, J= 6.6 Hz), 1.92 (dq, 1H, J= 7.3 and 7.0 Hz), 3.15-3.19 (m, 2H), 3.91 (dd, 1H, J= 8.9 and 4.2 Hz), 4.36 (dq, 1H, J= 6.6 and 6.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 5.81, 10.07, 17.06, 22.87, 22.99, 44.73, 47.21, 75.53, 85.23; MS *m/z* 43 (69), 55 (76), 71 (57), 83 (65), 98 (30), 127 (100), 141 (8), 268 (6, M^+); HRMS *m/z* $C_9H_{17}IO$ calcd for 268.0324, found 268.0302.

One-pot Procedure for the Synthesis of 7. Hydrogen was bubbled into a red solution of $[Ir(cod)(PPh_2Me)_2]PF_6$ (25 mg, 0.03 mmol) in THF (5 ml) to give the catalyst, $[IrH_2(thf)_2(PPh_2Me)_2]PF_6$. The excess hydrogen was then removed by bubbling argon into the solution. Allyl prenyl ether **5** (1 mmol) was added and the resulting mixture was then stirred at room temperature for 1 h to synthesize **4e**. The mixture was quenched with ethylenediamine (0.0013 ml, 0.06 mmol) to inactivate the catalyst. The solvent was then evaporated in vacuo at room temperature. 1,2-Dichloroethane (7.5 ml) and Me_3Al in hexane (1.0 M, 2 ml, 2 mmol) were successively added to the oily residue, and the mixture was stirred for 2 h, diluted with CH_2Cl_2 (15 ml), and poured into 1N HCl (7.5 ml). The separated organic layer was washed with brine and aqueous Na_2CO_3, and dried over $MgSO_4$. The column chromatography on silica gel (hexane-diethyl ether = 1:1) gave 72% of **7**.

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Received in Japan 7/28/99

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