An Unexpected Double-Bond Isomerization Catalyzed by Crabtree's Iridium(I) Catalyst

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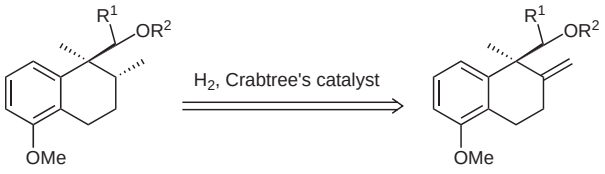
Abstract: The first iridium-catalyzed isomerization of an exocyclic into an endocyclic double bond is described. A mechanism is proposed for this reaction. Crabtree's catalyst thus allows the migration of a double bond that does not occur under classical conditions.

Key words: iridium, catalysis, isomerization, olefination, aldol-like reaction

Heteroatom-directed homogeneous hydrogenation of olefins in the presence of a transition metal catalyst provides a powerful method for regio- and stereochemical control in organic synthesis.[1] The directing effects arise when the heteroatom, hydrogen and the alkene bind simultaneously to the transition metal, permitting exclusive *syn* delivery of hydrogen to the unsaturated site. For this reaction, Crabtree's catalyst[2] $[Ir(cod)py(PCy_3)]PF_6$ is effective with a variety of directing groups such as hydroxyl, methoxy, ester, carboxamide and carbalkoxy.[3]

In a project aimed at the synthesis of natural products, we planned to synthesize compounds **1** and **2** as useful synthetic intermediates. The secondary methyl group of compounds **1** and **2** could ideally be obtained by reduction of the corresponding exo-double bond present in compounds **3** and **4** (Scheme 1).



1: $R^1 = CH_3$; $R^2 = H$ **3**: $R^1 = CH_3$; $R^2 = H$
2: $R^1 = OMe$; $R^2 = (CH_2)_3OMe$ **4**: $R^1 = OMe$; $R^2 = (CH_2)_3OMe$

Scheme 1

Contrary to expectation, the double bond of compound **4** was resistant to hydrogenation in the presence of Crabtree's catalyst. Only the migration of the double bond into the six-membered ring was observed. In this letter we wish to describe the influence of the environment around the hydroxyl or the methoxy group in directed stereoselective hydrogenation of exocyclic olefins with Crabtree's catalyst.

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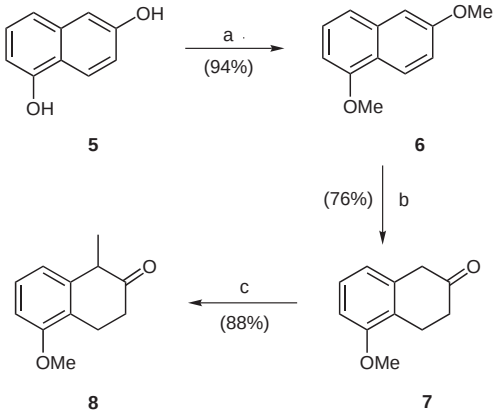
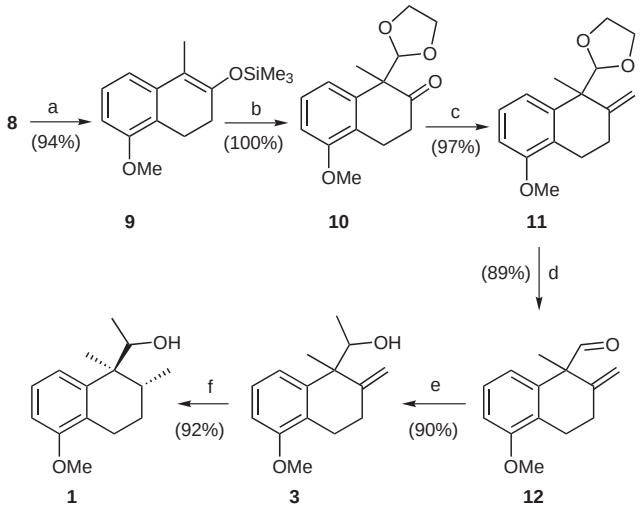
Olefinic substrates **3** and **4** were readily obtained from the appropriate ketones **10** and **13** via a Wittig reaction. These ketones were prepared from of 1-methyl-5-methoxy-2-tetralone (**8**).[4] Bis-O-methylation (Me_2SO_4, NaOH, acetone)[5] of 1,6-dihydroxynaphthalene (**5**) gave dimethyl ether **6** in 94% yield, which was then subjected to Bouvier reduction under the conditions described by Cornforth (Na, EtOH, concd HCl)[6] to afford ketone **7** in 76% yield. The desired 1-methyl derivative of the naphthalen-2-one **7** was then obtained by the use of an enamine alkylation reaction: ketone **7** was converted into its pyrrolidine enamine, which without isolation, was alkylated by refluxing with methyl iodide in dry dioxane solution (Scheme 2).



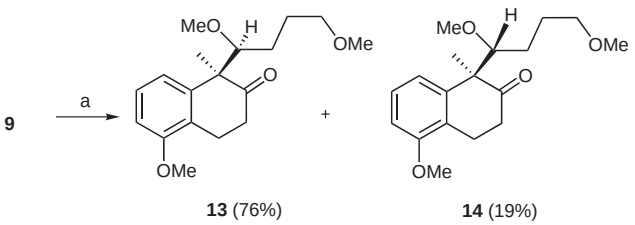
Scheme 2 *Reagents and conditions*: (a) Me_2SO_4, NaOH, acetone, reflux; (b) i) Na, EtOH reflux; ii) aq HCl reflux; (c) i) pyrrolidine, toluene, reflux; ii) CH_3I, dioxane.

Our strategy to form the critical quaternary center of the target molecules **1** and **2** was based on an aldol-like alkylation reaction with acetals.[7] A short synthesis of **1** is summarized in Scheme 3. Ketone **8** was first converted into the corresponding silyl enol ether **9**. Reaction of **9** with 2-methoxy-1,3-dioxolane in the presence of $BF_3{\cdot}OEt_2$ afforded **10** in quantitative yield. Wittig olefination gave an almost quantitative yield of exocyclic olefin **11**. The dioxolane group of **11** was removed with pyridinium *para*-toluenesulfonate to give the aldehyde **12** in 89% yield. Reaction of **12** with methyllithium afforded alcohol **3** as a 85:15 mixture of C13 epimers.[8] Directed stereoselective hydrogenation of the exocyclic double bond of **3** with Crabtree's catalyst furnished compound **1** in >90% de.[8,9]



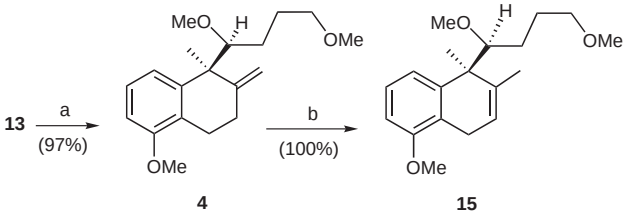
Scheme 3 *Reagents and conditions*: (a) $ClSiMe_3$, Et_3N, CH_2Cl_2, r.t.; (b) 2-methoxy-1,3-dioxolane, $BF_3{\cdot}OEt_2$, CH_2Cl_2, –78 °C; (c) $CH_2{=}PPh_3$, THF, r.t.; (d) PPTS, acetone, reflux; (e) MeLi, THF, –78 °C; (f) $[Ir(cod)py(PCy_3)]PF_6$, H_2, CH_2Cl_2, r.t.

Compound **13**, which possesses a longer side chain, was synthesized by reaction of **9** with 1,1,4-trimethoxybutane. A diastereoisomeric mixture of ketones **13**[10] and **14**[10] was obtained, which was separated chromatographically. The stereochemistry of **13** was determined by single-crystal X-ray crystallography (Scheme 4).



Scheme 4 *Reagents and conditions*: (a) 1,1,4-trimethoxybutane, $BF_3{\cdot}OEt_2$, CH_2Cl_2, –78 °C.

The exocyclic olefin **4**[10] was synthesized in near quantitative yield by Wittig olefination of the ketone **13**.[10] Attempts to hydrogenate **4** in the presence of Crabtree's catalyst were unsuccessful. Contrary to expectation, the migration of the exo-double bond into the six-membered ring occurred in quantitative yield (Scheme 5).[10]



Scheme 5 *Reagents and conditions*: (a) $CH_2{=}PPh_3$, THF, r.t.; (b) $[Ir(cod)py(PCy_3)]PF_6$, H_2, CH_2Cl_2, r.t.

It should be noted that the migration of the double bond under classical conditions failed (acidic or basic conditions, Wilkinson catalyst, microwaves); the starting material was transformed into 5-methoxy-1,2-dimethylnaphthalene. Moreover, hydrogenation of **4** in the presence of palladium on charcoal afforded one diastereoisomer of **2** in quantitative yield.

These results led us to investigate more closely the reaction of **4** with Crabtree's catalyst. No deuterium incorporation was observed after exposure of **4** to deuterium in the presence of iridium(I) catalyst. Only the double-bond migration took place under these conditions. No double-bond migration occurred when **4** was mixed with Crabtree's catalyst in the absence of hydrogen. The following mechanisms are proposed to rationalize these results. Upon treatment with hydrogen, the cyclooctadiene is reduced, and the 12-electron 'IrR_2' system is formed. The OMe group and the neighboring exocyclic alkene bind to the coordinatively unsaturated metal complex. The steric hindrance of the side chain or another interaction with the second OMe group prevents the oxidative addition of hydrogen to the iridium complex (Scheme 6). No directed hydrogenation can occur under these conditions. Instead, an insertion of the metal complex into the CH bond α to the double bond is favored leading to the formation of an η^3-allyl hydride complex.[11,12] Subsequent reductive elimination affords the endocyclic alkene **15** under neutral conditions. When the side chain is shorter the oxidative addition of hydrogen to the iridium complex is possible leading to the directed hydrogenation of the exo-double bond present in compound **3**.

In summary, we describe here the first example of an efficient iridium(I)-catalyzed isomerization of an exo- to an endocyclic double bond. In addition, this method could also be very useful when classical methods for isomerization of double bonds fail. The general applicability of this method is currently being investigated.

Acknowledgment

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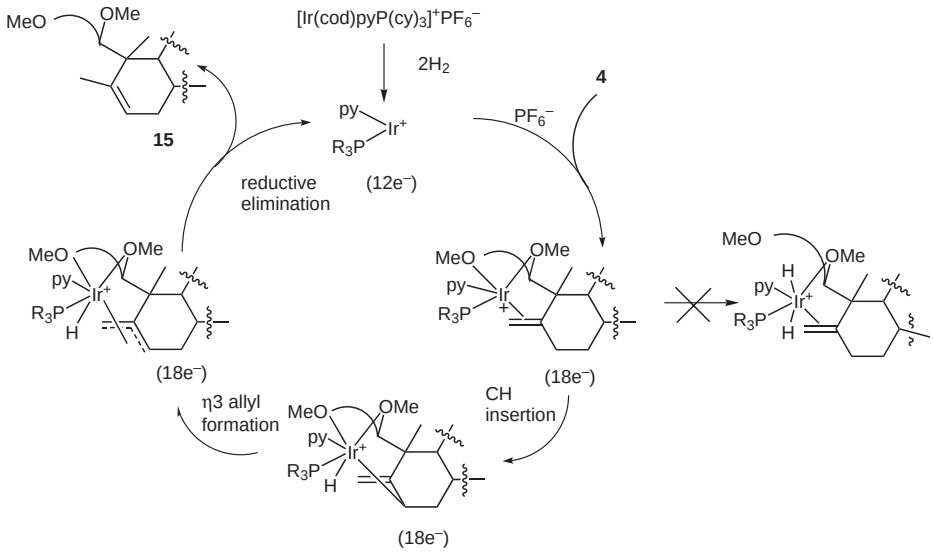

Scheme 6

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(8) **Representative Procedures for the Synthesis of 3 and 1.**
1-(5-Methoxy-1-methyl-2-methylene-1,2,3,4-tetrahydronaphthalen-1-yl)ethanol (3).
To a solution of aldehyde **12** (83 mg, 0.38 mmol) in THF was added methyllithium (1.6 N solution in hexane, 0.53 mL, 0.85 mmol) at –78 °C. The solution was stirred at –78 °C for 2 h. The reaction mixture was quenched with aq sat. $NaHCO_3$ at –78 °C and extracted with CH_2Cl_2. The combined organic layers were washed with H_2O, brine, and dried (Na_2SO_4), and the solvent was evaporated. Chromatography on preparative TLC (elution with heptane–EtOAc, 85:15) of the residue afforded **3** (77 mg, 87%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.19 (t, *J* = 7.9 Hz, 1 H, H7), 6.98 (d, *J* = 8,0 Hz, 1 H, H6), 6.73 (d, *J* = 8,0 Hz, 1 H, H8), 5.13 (s, 1 H, 15%, H14α), 5.11 (s, 1 H, 85%, H14α), 5.00 (s, 1 H, 85%, H14β), 4.91 (s, 1 H, 15%, H14β), 4.13 (q, *J* = 7.1 Hz, 1 H, 15%, H13), 4.06 (quad, *J* = 6.5 Hz, 1 H, 85%, H13), 3.83 (s, 3 H, H11), 3.10–2.95 (m, 1 H, H4α), 2.69–2.36 (m, 3 H, H4β-H3), 1.48 (s, 3 H, H12), 1.69 (d, *J* = 6.3 Hz, 3 H, 15%, H15), 1.02 (d, *J* = 6.4 Hz, 3 H, 85%, H15) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.5 (C5), 151.0 (C2), 144.5 (C9), 127.2 (C7), 126.9 (C10), 119.6 (C8), 111.2 (C15), 108.1 (C6), 74.1 (C13), 56.1 (C11), 48.9 (C1), 32.7 (C3), 23.1 (C12), 19.5 (C14) ppm. IR ($CHCl_3$): ν = 1577, 1461, 1251, 1047 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{15}H_{20}O_2$: 232.1463; found: 255.1374 [M + Na].
1-(5-Methoxy-1,2-dimethyl-1,2,3,4-tetrahydronaphthalen-1-yl)ethanol (1).
A solution of alcohol **3** (28 mg, 0.12 mmol) in 2 mL of CH_2Cl_2 in a Schlenk apparatus was cooled at –180 °C and degassed under vacuum then filled with argon. Crabtree's catalyst (10 mg, 0.012 mmol) was added and the solution degassed again under vacuum and filled with argon. The mixture was allowed to warm to r.t. and the Schlenk tube was linked to an hydrogenation apparatus. The system was flushed ten times with hydrogen and stirred 12 h at r.t. under an atmospheric pressure of hydrogen. The solvent was then removed under vacuum and the resulting slurry dissolved in Et_2O and filtered on a short silica pad. Chromatography on preparative TLC (elution with heptane–EtOAc, 85:15) of the residue afforded **1** (26 mg, 92%) as a colorless oil. H NMR (300 MHz, $CDCl_3$): δ = 7.19 (t, *J* = 7.9 Hz, 1 H, H7), 6.98 (d, *J* = 8.0 Hz, 1 H, H6), 6.73 (d, *J* = 8.0 Hz, 1 H, H8), 5.13 (s, 1 H, 15%, H14α), 5.11 (s, 1 H, 85%, H14α), 5.00 (s, 1 H, 85%, H14β), 4.91 (s, 1 H, 15%, H14β), 4.13 (quad, *J* = 7.1 Hz, 1 H, 15%, H13), 4.06 (quad, *J* = 6.5 Hz, 1 H, 85%, H13), 3.83 (s, 3 H, H11), 3.10–2.95 (m, 1 H, H4α), 2.69–2.36 (m, 3 H, H4β-H3), 1.48 (s, 3 H, H12), 1.69 (d, *J* = 6.3 Hz, 3 H, 15%, H15), 1.02 (d, *J* = 6.4 Hz, 3 H, 85%, H15) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.5 (C5), 151.0 (C2), 144.5 (C9), 127.2 (C7), 16.9 (C10), 119.6 (C8), 111.2 (C15), 108.1 (C6), 74.1 (C13), 56.1 (C11), 48.9 (C1), 32.7 (C3), 25.1 (C4), 23.1 (C12), 19.5 (C14) ppm. IR ($CHCl_3$): ν = 3453, 1579, 1459, 1254, 1062 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{15}H_{22}O_2$: 234.1620; found: 257.1492 [M + Na].
(9) When this reaction was conducted in the same conditions with shorter time (1 h) no isomerization of **3** was observed.
(10) **Representative Procedures for the Synthesis of 13, 14, 4 and 15.**
1-(1,4-Dimethoxybutyl)-5-methoxy-1-methyl-3,4-dihydro-1*H*-naphthalen-2-one (13).
To a solution of **9** (68 mg, 0.26 mmol) in CH_2Cl_2 580 mL was added 1,1,4-trimethoxybutane (3.8 g, 26.2 mmol) at –78 °C. The solution was stirred at –78 °C for 10 min then $BF_3{\cdot}OEt_2$ (2.94 mL, 23.2 mmol) was added. The reaction mixture was stirred for 6 h at –78 °C. The residue was diluted with CH_2Cl_2 and washed with sat. aq $NaHCO_3$. The combined organic layers were washed with H_2O, brine, and dried (Na_2SO_4), and the solvent was evaporated. Flash chromatography on silica gel (elution with heptane–EtOAc, 90:10) of the residue afforded **13** (3.63 g, 76%) and **14** (907 mg, 19%) as white solids.
Compound **13**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.21 (t, *J* = 8.0 Hz, 1 H, H7), 6.91 (d, *J* = 8.0 Hz, 1 H, H8), 6.80 (d,

J = 8.1 Hz, 1 H, H6), 3.85 (s, 3 H, H11), 3.66 (dd, *J* = 10.4, 2.2 Hz, 1 H, H13), 3.33–3.15 (m, 3 H, H16-H4α), 3.31 (s, 3 H, H17), 3.17 (s, 3 H, H18), 2.94 (ddd, *J* = 16.1, 11.8, 5.5 Hz, 1 H, H4β), 2.73 (ddd, *J* = 16.2, 5.3, 3.3 Hz, 1 H, H3α), 2.44 (ddd, *J* = 16.2, 11.7, 6.9 Hz, 1 H, H3β), 1.70–1.45 (m, 2 H, H14), 1.43 (s, 3 H, H12), 1.35–1.20 (m, 2 H, H15) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 213.9 (C2), 156.0 (C5), 142.2 (C9), 127.1 (C7), 125.1 (C10), 120.1 (C8), 107.8 (C6), 88.4 (C13), 72.7 (C16), 61.7 (C18), 58.5 (C17), 56.2 (C1), 55.4 (C11), 37.9 (C3), 29.5 (C14), 27.0 (C15), 23.4 (C12), 21.6 (C12) ppm. IR ($CHCl_3$): ν = 3155, 2985, 2255, 1805, 1794, 1643, 1470, 1382, 1167, 1096, 926 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{18}H_{26}O_4$: 306.3966; found: 329.1734 [M + Na]. Anal. Calcd for $C_{18}H_{26}O_4$ (%): C, 69.54; H, 7.30; O, 23.16. Found: C, 69.48; H, 7.37; O, 23.15.

Compound **14**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.21 (t, *J* = 8.0 Hz, 1 H, H7), 6.91 (d, *J* = 8.0 Hz, 1 H, H8), 6.80 (d, *J* = 8.1 Hz, 1 H, H6), 3.85 (s, 3 H, H11), 3.66 (dd, *J* = 10.4, 2.2 Hz, 1 H, H13), 3.33–3.15 (m, 3 H, H16, H4α), 3.31 (s, 3 H, H17), 3.17 (s, 3 H, H18), 2.94 (ddd, *J* = 16.1, 11.8, 5.5 Hz, 1 H, H4β), 2.73 (ddd, *J* = 16.2, 5.3, 3.3 Hz, 1 H, H3α), 2.44 (ddd, *J* = 16.2, 11.7, 6.9 Hz, 1 H, H3β), 1.70–1.45 (m, 2 H, H14), 1.43 (s, 3 H, H12), 1.35–1.20 (m, 2 H, H15) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 215.2 (C2), 156.1 (C5), 140.4 (C9), 126.6 (C7), 125.5 (C10), 120.6 (C8), 108.3 (C6), 88.5 (C13), 72.7 (C16), 61.2 (C18), 58.6 (C17), 56.3 (C1), 55.4 (C11), 37.8 (C3), 28.4 (C14), 26.9 (C15), 20.3 (C4), 20.2 (C12) ppm. IR ($CHCl_3$): ν = 3155, 2984, 2254, 1794, 1706, 1642, 1469, 1382, 1261, 1167, 1096 cm^{-1}.

1-(1,4-Dimethoxybutyl)-5-methoxy-1-methyl-2-methylene-1,2,3,4-tetrahydronaphthalene (4).

To a solution of ketone **12** (3.3 g, 10.7 mmol) in THF were successively added at r.t. methyltriphenylphosphonium bromide (19.1g, 54 mmol) and potassium *tert*-butoxide (6 g, 54 mmol). The reaction mixture was stirred at r.t. for 48 h. The reaction mixture was diluted with Et_2O and washed with sat. aq $NaHCO_3$. The combined organic layers were washed with H_2O, brine, and dried (Na_2SO_4), and the solvent was evaporated. Flash chromatography on silica gel (elution with heptane–EtOAc, 90:10) of the residue afforded **4** (3.17g, 97%) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.22–7.15 (m, 2 H, H7, H8), 6.69 (dd, *J* = 7.3, 1.8 Hz, 1 H, H6), 5.03 (q, *J* = 1.3 Hz, 1 H, H19α), 4.85 (d, *J* = 1.3 Hz, 1 H, H19β), 3.82 (s, 3 H, H11), 3.39 (dd, *J* = 10.2, 2.0 Hz, 1 H, H13), 3.34 (t, *J* = 6.7 Hz, 2 H, H16), 3.31 (s, 3 H, H18), 3.17 (s, 3 H, H18), 2.95–2.80 (m, 1 H, H4α), 2.80–2.55 (m, 2 H, H3α, H4β), 2.50–2.40 (m, 1 H, H3β), 1.85–1.70 (m, 2 H, H15), 1.44 (s, 3 H, H12), 1.35–1.15 (m, 2 H, H14) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.3 (C5), 151.8 (C2), 143.6 (C9), 127.2 (C10), 125.9 (C7), 119.9 (C8), 109.1 (C9), 107.0 (C6), 90.8 (C13), 73.0 (C16), 61.5 (C18), 58.5 (C17), 55.4 (C11), 48.1 (C1), 32.7 (C3), 28.2 (C14), 27.2 (C15), 26.2 (C12), 24.6 (C4) ppm. Anal. Calcd for $C_{19}H_{28}O_3$ (%): C, 74.96; H, 9.27; O, 15.77. Found: C, 74.75; H, 9.09; O, 16.01. IR ($CHCl_3$): ν = 1577, 1461, 1433, 1367, 1254, 1047 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{19}H_{28}O_3$: 304.2038; found: 327.1894 [M + Na].

1-(1,4-Dimethoxybutyl)-5-methoxy-1,2-dimethyl-1,4-dihydronaphthalene (15).

A solution of alkene **4** (98 mg, 0.32 mmol) in 3 mL of CH_2Cl_2 in a Schlenk apparatus was cooled at –180 °C and degassed under vacuum then filled with argon. Crabtree's catalyst (11 mg, 0.012 mmol) was added and the solution degassed again under vacuum and filled with argon. The mixture was allowed to warm to r.t. and the Schlenk tube was linked to an hydrogenation apparatus. The system was flushed ten times with hydrogen and stirred 12 h at r.t. under an atmospheric pressure of hydrogen. The solvent was then removed under vacuum and the resulting slurry dissolved in Et_2O and filtered on a short silica pad. Chromatography on preparative TLC (elution with heptane–EtOAc, 85:15) of the residue afforded **1** (90 mg, 92%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.27 (dd, *J* = 8.0, 1.1 Hz, 1 H, H8), 7.17 (t, *J* = 8.0 Hz, 1 H, H7), 6.71 (dd, *J* = 7.9, 1.0 Hz, 1 H, H6), 5.59 (dqd, *J* = 2.7, 1.7, 0.6 Hz, 1 H, H3), 3.83 (s, 3 H, H11), 3.51 (s, 3 H, H18), 3.26 (s, 3 H, H18), 3.30–3.20 (m, 4 H, H4α, H13, H16), 3.08 (dq, *J* = 22.4, 2.6 Hz, 1 H, H4β), 1.88 (dd, *J* = 2.6, 1.7 Hz, 3 H, H19), 1.65–1.60 (m, 2 H, H14), 1.55 (s, 3 H, H12), 1.45–1.38 (m, 1 H, H15), 1.00–0.90 (m, 1 H, H15) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.9 (C5), 141.3 (C9), 136.2 (C2), 125.9 (C7), 124.0 (C10), 122.6 (C3), 120.5 (C8), 106.9 (C6), 88.4 (C13), 73.1 (C16), 61.8 (C18), 58.5 (C17), 55.2 (C11), 47.1 (C1), 28.9 (C15), 27.2 (C14), 25.1 (C4), 23.3 (C12), 20.5 (C19). IR ($CHCl_3$): ν = 1582, 1462, 1423. HRMS (ESI): *m/z* calcd for $C_{19}H_{28}O_3$: 304.2038; found: 327.1950 [M + Na].

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(12) For the isomerization of allyl ethers see: (a) Nelson, S. G.; Bungard, C. J.; Wang, K. *J. Am. Chem. Soc.* **2003**, *125*, 13000. (b) Ohmura, T.; Yamamoto, Y. Y.; Miyaura, N. *Organometallics* **1999**, *18*, 413; and references therein.