Stereoselective Construction of Copaborneol and Longiborneol Frameworks by Intramolecular Double Michael Reaction

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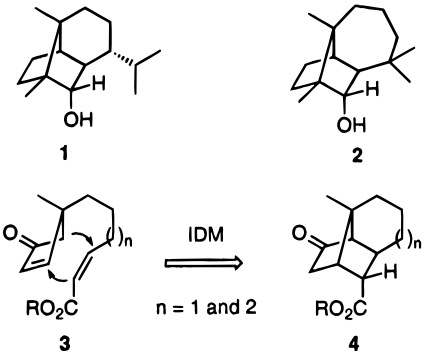
Stereoselective syntheses of tricyclo[5.3.0.0^{3,8}]decane **22** and tricyclo[6.3.0.0^{3,9}]undecane **26**, the basic skeletons of copaborneol and longiborneol, were achieved by the intramolecular double Michael reactions of 2-cyclopenten-1-ones **15**−**17**. The substrates were prepared starting with tricyclo-[5.2.1.0^{2,6}]deca-4,8-dien-3-one (**6**). The intramolecular double Michael reactions were carried out under three different conditions: TMSCl−Et_3N−$ZnCl_2$, TMSI−$(TMS)_2NH$, and Bu_2BOTf−$(TMS)_2NH$. The framework **26** of longiborneol was constructed in good yields using the latter two reagent systems.

Introduction

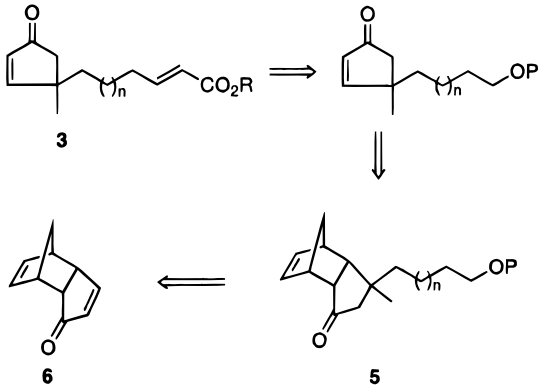
There are many sesquiterpenes characterized by the presence of a bicyclo[2.2.1]heptane system with an additional three or four carbon bridge, e.g., (+)-copaborneol (the antipode of **1**)[1] or (+)-logiborneol (**2**).[2] Although most synthetic approaches to these natural products are composed of the stepwise constructions of three rings,[3] the routes utilizing the intramolecular Diels−Alder reaction (IDA) seem to be attractive since two rings are assembled in one step. Fallis achieved the short synthesis of (+)-longifolene using this strategy.[4] Snowden reported the IDA approach to the tricyclo[4.3.0.0^{3,7}]-nonane, which is convertible to (±)-sativene.[5] The intramolecular double Michael reaction (IDM) is similar to the IDA and has several advantages over the IDA: high stereoselectivity, complete regioselectivity, milder reaction conditions, and so forth.[6] As an extension of the IDM strategy, the construction of tricyclo[5.3.0.0^{3,8}]-decane and tricyclo[6.3.0.0^{3,9}]undecane systems **4** was investigated starting with 2-cyclopenten-1-ones **3**. The desired transformation was performed under three conditions using (A) TMSCl−Et_3N−$ZnCl_2$,[5,7] (B) TMSI−$(TMS)_2$-NH,[8,9] and (C) Bu_2BOTf−$(TMS)_2NH$.[10] The latter two conditions B and C were applied to the IDM for the first time and were extremely useful for the synthesis of the tricyclo[6.3.0.0^{3,9}]undecane ring system. Several results supporting the stepwise mechanism have been obtained during this study.



Results and Discussion

Preparation of Substrates. It is expected that 2-cyclopenten-1-ones **3** possessing an α,β-unsaturated ester side chain could be readily derived from **5**, which would be prepared by the introduction of two appropriate alkyl groups to the enone **6**[11] (Scheme 1).

Scheme 1



According to the above considerations, the conjugate addition of the Grignard reagents of four carbon units to **6**[11] was first examined under various conditions but poor results were obtained. The introduction of four carbon

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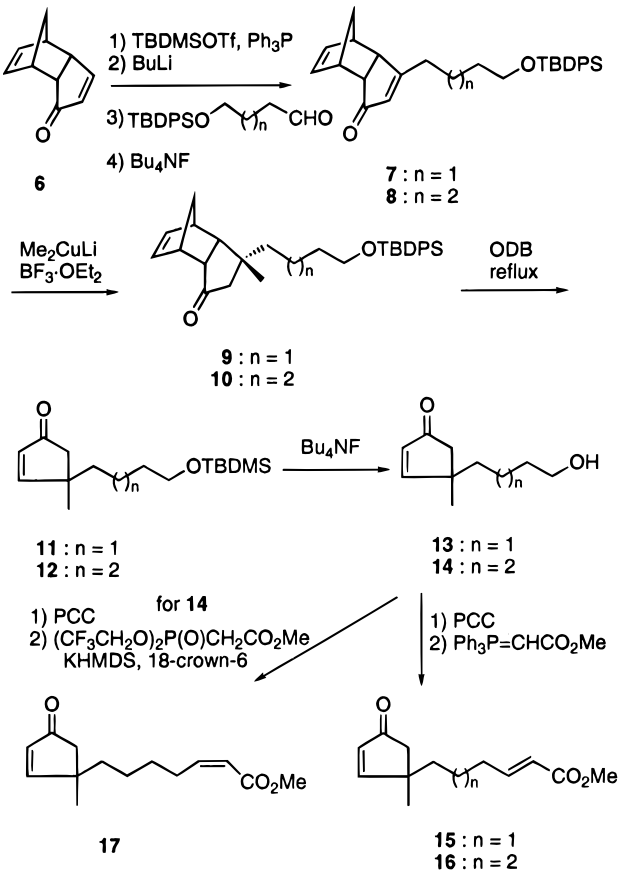
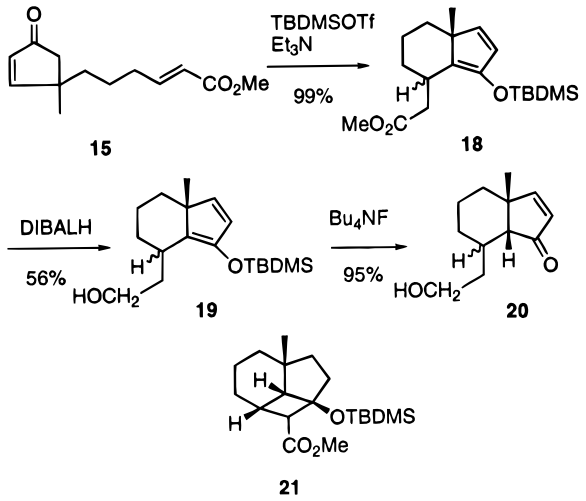
Scheme 2



Scheme 3



units retaining the olefin function was achieved by the application of Kozikowski's method.[12] Namely, the 1,4-addition of triphenylphosphine to **6** in the presence of *tert*-butyldimethylsilyl trifluoromethanesulfonate (TBDMSOTf), followed by treatment with butyllithium, produced an ylide, which was subjected to the Wittig reaction. The resulting silyl enol ether was treated with tetrabutylammonium fluoride to afford **7** in 78% overall yield from **6** (Scheme 2). Introduction of a methyl group to **7** was also difficult, and the conversion was carried out in a reasonable yield with Gilman reagent in the presence of boron trifluoride etherate.[13] When the hydroxyl group was protected with a tetrahydropyranyl group, unsatisfactory results were observed due to the deprotection during the reaction. Therefore, the protection of the hydroxyl group with the *tert*-butyldiphenylsilyl (TBDPS) group was crucial.

The retro Diels−Alder reaction of **9**, obtained in 72% yield, was carried out in refluxing *o*-dichlorobenzene (ODB), and provided **11** in 97% yield. After deprotection of the TBDPS group, the resulting **13**, produced in 88% yield, was oxidized with pyridinium chlorochromate (PCC) in the presence of 4 Å molecular sieves and then subjected to the Wittig reaction utilizing a stable ylide to give **15** in 68% overall yield from **13**.

According to the same procedure as above, the five-carbon unit was introduced to **6** to afford **8** in 72% overall yield, which was methylated giving **10** in 76% yield. After the retro Diels−Alder reaction (94% yield), the deprotection (94%), followed by oxidation and the subsequent Wittig reaction, produced **16** in 68% overall yield from **14**. When the final reaction was carried out using Still's reagent[14] in the presence of potassium hexamethyldisilazide (KHMDS) and 18-crown-6, the (*Z*)-isomer **17** was obtained in 55% overall yield from **14** together with the (*E*)-isomer **16** (3% yield). Both isomers **16** and **17** were easily separated by column chromatography on silica gel.

Intramolecular Double Michael Reaction (IDM). The IDM has so far been carried out under three different conditions: lithium hexamethyldisilazide (LHMDS), TBDMSOTf−Et_3N, and TMSCl−Et_3N−$ZnCl_2$.[6] The reaction of **15** with LHMDS gave an intractable mixture, while bicyclic **18** was formed in 99% yield as a 1:1.8 diastereoisomeric mixture by treatment with TBDMSOTf in the presence of Et_3N in CH_2Cl_2. Since the product was converted into enone **20** in two steps (Scheme 3), the tricyclic structure **21**, formed by the intramolecular Michael−aldol reaction, was excluded.

Upon treatment of **15** with TMSCl, Et_3N, and $ZnCl_2$ in toluene in a sealed tube at 180 °C for 72 h, the desired tricyclic compounds **22** and **23** were produced in 31% and 9% yields, respectively (Scheme 4 and Table 1, entry 1). In the IR spectra ($CHCl_3$) of products, absorptions due to carbonyl groups were observed at 1730 and 1740 cm^{-1} while the ^1H NMR spectra showed no olefinic resonance. The long-range coupling (J = 2.2 Hz) due to the W-configuration was observed between hydrogens neighboring on the ester group (3.05 ppm) and the keto carbonyl group (2.32 ppm) in the ^1H NMR spectrum of the major isomer **22**; the observations supported the stereostructure.

The IDM was further performed under two other reaction conditions, which had been useful for the intramolecular Michael−aldol reaction.[9,10] Namely, the tricyclic compound **22** was obtained in 10% yield as a single isomer upon treatment of **15** with TMSI in the presence of (TMS)NH[8,9] in $ClCH_2CH_2Cl$ at ambient temperature for 1 h. At the same time, bicyclic products **24** and **25** were produced, respectively, in 37% yield as a single isomer and in 10% yield as a separable 1:1 mixture of two stereoisomers, although their stereochemistries were obscure (Table 1, entry 2). On the other hand, treatment of **15** with Bu_2BOTf in the presence of

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Scheme 4

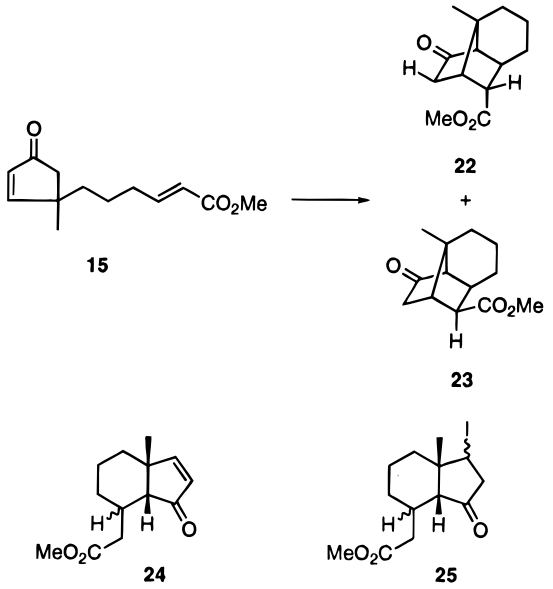


Table 1. The IDM of 15

		yield (%) of products	
entry	conditions	**22**	**23**
1	TMSCl, Et_3N, $ZnCl_2$, 180 °C	31	9
2[a]	TMSI, $(TMS)_2NH$, rt	10	0
3	Bu_2BOTf, $(TMS)_2NH$	28	0

[a] Bicyclic compounds **24** and **25** were also obtained in 37% and 10% yields.

Scheme 5

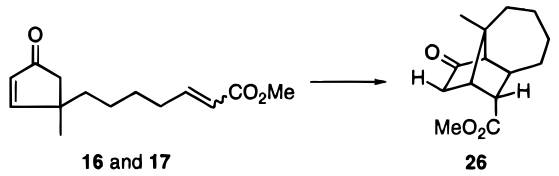


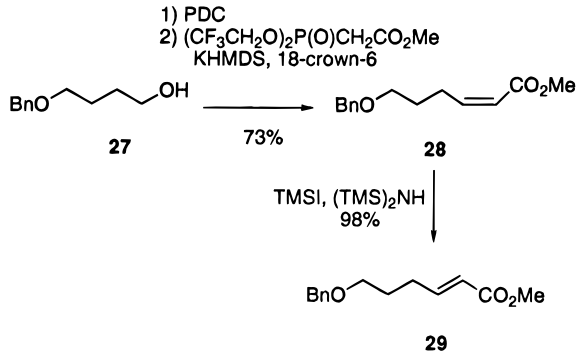
Table 2. The IDM of 16 and 17

entry	substrate	conditions	yield (%) of **26**
1	**16**	TMSCl, Et_3N, $ZnCl_2$, 180 °C	29
2	**16**	TMSI, $(TMS)_2NH$, rt	69
3	**16**	Bu_2BOTf, $(TMS)_2NH$, rt	71
4	**17**	TMSCl, Et_3N, $ZnCl_2$, 180 °C	0
5	**17**	TMSI, $(TMS)_2NH$, rt	67
6	**17**	Bu_2BOTf, $(TMS)_2NH$, rt	7

$(TMS)_2NH$ in $ClCH_2CH_2Cl$ at ambient temperature for 3 h provided **22** in 28% yield. No formations of **23** and **24** were detected by this reaction.

Reactions of **16** with LHMDS and TBDMSOTf−Et_3N gave no tricyclic product. The objective compound **26** was obtained in 29% yield by heating **16** together with TMSCl, Et_3N, and $ZnCl_2$ in toluene in the sealed tube at 180 °C for 72 h (Scheme 5 and Table 2, entry 1). The stereochemistry of **26**, produced as a single stereoisomer, was determined by the W-type long range coupling in the ^1H NMR spectra. Furthermore, the tricyclic compound **26** was provided in 69% yield upon treatment of **16** with TMSI in the presence of $(TMS)_2NH$ in $ClCH_2CH_2Cl$ at ambient temperature for 1 h (Table 2, entry 2) and in 71% yield upon the reaction of **16** with Bu_2BOTf in the presence of $(TMS)_2NH$ in $ClCH_2CH_2Cl$ at ambient temperature for 3 h (Table 2, entry 3).

Scheme 6



It is noteworthy that the (*Z*)-unsaturated ester (**17**) showed considerably different behaviors under the above three conditions. No tricyclic compound **26** was obtained by heating **17** with TMSCl, Et_3N, and $ZnCl_2$ in toluene (Table 2, entry 4). The treatment of **17** with TMSI and $(TMS)_2NH$ gave **26** in 67% yield (Table 2, entry 5), while **26** was produced in 7% yield by the reaction with Bu_2-BOTf and $(TMS)_2NH$ (Table 2, entry 6). No formation of the corresponding stereoisomer was observed during the three reactions.

Consideration of Reaction Mechanism. Although it is difficult to determine that the above annulations proceed *via* a stepwise mechanism or *via* a concerted mechanism, the former one seems to be likely based on the following reasons. The significant amount of stereoisomer **23** formed upon the treatment of **15** with TMSCl−Et_3N−$ZnCl_2$ (Table 1, entry 1). Mono Michael adducts **24** and **25** were obtained by the reaction of **15** with TMSI−$(TMS)_2NH$ (Table 1, entry 2). The same stereoisomer **26** was produced from both the (*E*)- and (*Z*)-unsaturated esters **16** and **17** (Table 2, entries 2, 3, 5, and 6). However, the (*Z*)-unsaturated ester **28**, prepared from **27**, was readily isomerized to the (*E*)-unsaturated ester **29** upon treatment with TMSI and $(TMS)_2NH$ in $ClCH_2CH_2Cl$ (Scheme 6). Therefore, there is a possibility of concerted ring formation after the isomerization of the double bond under the reaction conditions. But no isomerization was observed when the reaction conditions using Bu_2BOTf−$(TMS)_2NH$ were applied to **28**. Although it is obvious that each reaction takes place through different intermediates, the tandem mechanism is more reasonable than the concerted one for the annulation under the stated conditions on the basis of these results.

Conclusions

The skeletons of copaborneol (**1**) and longiborneol (**2**) were stereoselectively constructed by the IDM of 2-cyclopenten-1-one derivatives **15**−**17**. The reactions were conducted under three different conditions: TMSCl−Et_3N−$ZnCl_2$, TMSI−$(TMS)_2NH$, and Bu_2BOTf−$(TMS)_2$-NH. It is notable that the seven-membered ring was effectively built by the IDM, and the reaction was carried out by TMSI−$(TMS)_2NH$ and Bu_2BOTf−$(TMS)_2NH$. Determination of the reaction mechanism details under each reaction conditions is an interesting problem for future studies.

Experimental Section

General Procedure. All reactions were carried out under a positive atmosphere of N_2 or Ar unless otherwise indicated. Solvents were distilled prior to use. THF, Et_2O, benzene, and

toluene were distilled from sodium benzophenone while CH_2Cl_2, $ClCH_2CH_2Cl$, and ODB were distilled from CaH_2 and stored over 4 Å MS. All new compounds are homogeneous on TLC, and their purities were verified on the basis of their 300 MHz ^1H NMR spectra.

(±)-(1*S,2*R**,6*S**,7*R**)-5-[4-(*tert*-Butyldiphenylsiloxy)butyl]tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-one (7).** A mixture of 4-(*tert*-butyldiphenylsiloxy)butan-1-ol[15] (7.0 g, 21.3 mmol), 4 Å molecular sieves (17.6 g), and PDC (8.83 g, 23.5 mmol) in dry CH_2Cl_2 (50 mL) was stirred for 2.5 h at rt. After dilution with Et_2O, the mixture was filtered through Celite and then evaporated. Chromatography on silica gel with AcOEt−hexane (1:4 v/v) as the eluent gave the corresponding aldehyde (4.74 g, 68%) as a pale yellowish oil.

To a stirred solution of **6** (1.93 g, 13.2 mmol) and Ph_3P (3.81 g, 14.5 mmol) in dry THF (30 mL) at rt was added TBDMSOTf (3.03 mL, 13.2 mmol). The mixture was then stirred for 30 min at rt. After the addition of 1.56 M BuLi in hexane (8.46 mL, 13.2 mmol) at −78 °C, followed by 30 min of stirring at −78 °C, to the resulting mixture was added at the same temperature a solution of the above aldehyde (4.74 g, 14.5 mmol) in dry THF (10 mL). The mixture was stirred for 30 min at rt. After the addition of 1.0 M Bu_4NF in THF (15.8 mL, 15.8 mmol) at 0 °C, the mixture was stirred for 30 min at rt and then diluted with Et_2O. The mixture was washed with brine, dried (Na_2SO_4), and evaporated to give a residue that was subjected to column chromatography on silica gel. Elution with AcOEt−hexane (3:17 v/v) yielded **7** (4.61 g, 78%) as a colorless oil: IR (neat) 1700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.69−7.62 (m, 4H), 7.47−7.34 (m, 6H), 5.98 (dd, 1H, J = 5.5, 2.9 Hz), 5.73 (dd, 1H, J = 5.5, 2.9 Hz), 5.68 (s, 1H), 3.69 (t, 2H, J = 5.7 Hz), 3.26−3.20 (m, 1H), 3.17 (br s, 1H), 2.96 (br s, 1H), 2.83 (t, 1H, J = 5.1 Hz), 2.28−2.19 (m, 2H), 1.79−1.52 (m, 6H), 1.06 (s, 9H); HRMS calcd for $C_{30}H_{36}O_2Si$ (M^+) 456.2482, found 456.2516.

(±)-(1*S,2*R**,6*S**,7*R**)-5-[4-(*tert*-Butyldiphenylsiloxy)pentyl]tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-one (8).** Using the same procedure as above, **8** (4.49 g, 72%) was prepared from **6** (2.0 g, 13.4 mmol) as a colorless oil: IR (neat) 1700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.71−7.63 (m, 4H), 7.46−7.34 (m, 6H), 5.98 (dd, 1H, J = 5.8, 2.7 Hz), 5.75 (dd, 1H, J = 5.8, 2.7 Hz), 5.68 (br s, 1H), 3.67 (t, 1H, J = 6.3 Hz), 3.28−3.21 (m, 1H), 3.18 (br s, 1H), 3.01−2.94 (m, 1H), 2.87−2.77 (m, 1H), 2.30−2.18 (m, 2H), 1.79−1.71 (m, 1H), 1.65−1.35 (m, 8H), 1.05 (s, 9H); HRMS calcd for $C_{27}H_{29}O_2Si$ (M^+ − ^{t}Bu) 413.1935, found 413.1911.

(±)-(1*S,2*R**,5*R**,6*S**,7*R**)-5-[4-(*tert*-Butyldiphenylsiloxy)butyl]-5-methyltricyclo[5.2.1.0^{2,6}]dec-8-en-3-one (9).** To a stirred mixture of CuI (2.5 g, 13.13 mmol) in dry Et_2O (15 mL) at 0 °C was added 1.04 M MeLi in Et_2O (25.28 mL, 26.30 mmol). The mixture was then stirred for 30 min at the same temperature. After the addition of $BF_3{\cdot}OEt_2$ (0.6 mL, 0.59 mmol) at −78 °C, followed by 20 min of stirring at −78 °C, to the stirred mixture at −78 °C was added a solution of **7** (2.0 g, 4.38 mmol) in dry Et_2O (10 mL). The mixture was then stirred for 30 min at the same temperature. After the addition of $BF_3{\cdot}OEt_2$ (0.6 mL, 0.59 mmol), the mixture was further stirred for 1 h at rt. After the addition of saturated NH_4Cl, the mixture was thoroughly extracted with Et_2O. The combined extracts were washed with brine, dried (Na_2SO_4), and evaporated. The residue was purified by column chromatography on silica gel. Elution with AcOEt−hexane (1:9 v/v) afforded **9** (1.50 g, 72%) as a colorless oil: IR (neat) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.70−7.65 (m, 4H), 7.45−7.35 (m, 6H), 6.16 (dd, 1H, J = 5.5, 2.6 Hz), 6.02 (dd, 1H, J = 5.5, 2.6 Hz), 3.70 (t, 2H, J = 6.0 Hz), 3.20−3.13 (m, 1H), 3.04−2.95 (m, 2H), 2.55−2.49 (m, 1H), 1.88 (d, 1H, J = 18.1 Hz), 1.75 (d, 1H, J = 18.1 Hz), 1.90−1.18 (m, 8H), 1.06 (s, 9H), 0.94 (s, 3H); HRMS calcd for $C_{27}H_{31}O_2Si$ (M^+ − ^{t}Bu) 415.2092, found 415.2076.

(±)-(1*S,2*R**,5*R**,6*S**,7*R**)-5-[4-(*tert*-Butyldiphenylsiloxy)pentyl]-5-methyltricyclo[5.2.1.0^{2,6}]dec-8-en-3-one (10).** Using the same procedure as above, **8** (4.47 g, 9.5 mmol) was converted into **10** (3.5 g, 76%) as a colorless oil: IR (neat) 1740 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.70−7.66 (m, 4H), 7.46−7.34 (m, 6H), 6.20 (dd, 1H, J = 5.5, 2.7 Hz), 6.03 (dd, 1H, J = 5.5, 2.7 Hz), 3.67 (t, 2H, J = 6.5 Hz), 3.19−3.14 (m, 1H), 3.05−2.95 (m, 2H), 2.52 (dd, 1H, J = 8.4, 3.8 Hz), 1.88 (d, 1H, J = 18.0 Hz), 1.75 (d, 1H, J = 18.0 Hz), 1.64−1.12 (m, 10H), 1.06 (s, 9H), 0.95 (s, 3H); HRMS calcd for $C_{28}H_{34}O_2Si$ (M^+ − ^{t}Bu) 429.2248, found 429.2278.

4-[4-(*tert*-Butyldiphenylsiloxy)butyl]-4-methyl-2-cyclopenten-1-one (11). A solution of **9** (1.38 g, 2.92 mmol) in dry ODB (30 mL) was heated for 48 h under reflux. The reaction mixture was directly subjected to column chromatography on silica gel with AcOEt−hexane (3:17 v/v) as the eluent to provide **11** (1.15 g, 97%) as a pale yellowish oil: IR (neat) 1720 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.66−7.63 (m, 4H), 7.43−7.34 (m, 7H), 6.02 (d, 1H, J = 5.8 Hz), 3.65 (t, 2H, J = 6.2 Hz), 2.28 (d, 1H, J = 18.5 Hz), 2.10 (d, 1H, J = 18.5 Hz), 1.60−1.20 (m, 6H), 1.18 (s, 3H), 1.04 (s, 9H); MS m/z 349 (M^+ − ^{t}Bu). Anal. Calcd for $C_{26}H_{34}O_2Si$: C, 76.80; H, 8.43. Found: C, 76.57; 8.47.

4-[5-(*tert*-Butyldiphenylsiloxy)pentyl]-4-methyl-2-cyclopenten-1-one (12). Similarly, **10** (1.0 g, 2.06 mmol) was transformed into **12** (810 mg, 94%) as a pale yellowish oil: IR (neat) 1720 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.69−7.64 (m, 4H), 7.64−7.34 (m, 7H), 6.02 (d, 1H, J = 5.5 Hz), 3.64 (t, 2H, J = 6.3 Hz), 2.27 (d, 1H, J = 18.7 Hz), 2.09 (d, 1H, J = 18.7 Hz), 1.61−1.20 (m, 8H), 1.19 (s, 3H), 1.04 (s, 9H); MS m/z 363 (M^+ − ^{t}Bu). Anal. Calcd for $C_{27}H_{36}O_2Si$: C, 77.09; H, 8.63. Found: C, 77.06; H, 8.63.

4-(4-Hydroxybutyl)-4-methyl-2-cyclopenten-1-one (13). A mixture of **11** (1.23 g, 3.02 mmol) and 1.0 M Bu_4NF in THF (4.54 mL, 4.54 mmol) in dry THF (20 mL) was stirred for 2 h at rt. After dilution with Et_2O, the mixture was washed with brine, dried (Na_2SO_4), and evaporated to give a residue, which was purified by column chromatography on silica gel. Elution with AcOEt−hexane (3:7 v/v) provided **13** (422 mg, 88%) as a colorless oil: IR (neat) 3400, 1710 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.44 (d, 1H, J = 5.5 Hz), 6.04 (d, 1H, J = 5.5 Hz), 3.65 (t, 2H, J = 6.5 Hz), 2.32 (d, 1H, J = 18.7 Hz), 2.13 (d, 1H, J = 18.7 Hz), 1.86−1.24 (m, 7H), 1.22 (s, 3H); MS m/z 168 (M^+). Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.62; H, 9.69.

4-(5-Hydroxypentyl)-4-methyl-2-cyclopenten-1-one (14). Using the same method as above, **12** (1.24 g, 2.95 mmol) was transformed into **14** (506 mg, 94%) as a colorless oil: IR (neat) 3400, 1710 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.44 (d, 1H, J = 5.5 Hz), 6.03 (d, 1H, J = 5.5 Hz), 3.62 (t, 2H, J = 6.6 Hz), 2.30 (d, 1H, J = 18.7 Hz), 2.21 (d, 1H, J = 18.7 Hz), 1.79 (br s, 1H), 1.60−1.23 (m, 8H), 1.21 (s, 3H); MS m/z 182 (M^+). Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.65; H, 9.74.

4-[(4*E*)-5-(Methoxycarbonyl)-4-pentenyl]-4-methyl-2-cyclopenten-1-one (15). To a stirred solution of **13** (285 mg, 1.70 mmol) in dry CH_2Cl_2 (40 mL) at 0 °C were added 4 Å molecular sieves (601 mg) and PCC (401 mg, 1.87 mmol). The mixture was then stirred for 2 h at rt. After dilution with Et_2O, followed by filtration through Celite, evaporation of the solvents gave the corresponding aldehyde, which was used in the following reaction without purification.

A solution of the above product and $Ph_3P{=}CHCO_2Me$ (737 mg, 2.20 mmol) in dry CH_2Cl_2 (15 mL) was stirred for 5 h at rt. Evaporation of the solvent afforded a residue, which was chromatographed on silica gel. Elution with AcOEt−hexane (1:4 v/v) provided **15** (256 mg, 68%) as a colorless oil: IR (neat) 1710, 1660 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, 1H, J = 5.7 Hz), 6.92 (dt, 1H, J = 15.7, 6.9 Hz), 6.05 (d, 1H, J = 5.7 Hz), 5.82 (dt, 1H, J = 15.7, 1.6 Hz), 3.73 (s, 3H), 2.30 (d, 1H, J = 18.4 Hz), 2.25−2.17 (m, 2H), 2.13 (d, 1H, J = 18.4 Hz), 1.57−1.33 (m, 4H), 1.22 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.7, 172.6, 167.0, 148.5, 132.0, 121.6, 51.3, 47.6, 44.7, 39.7, 32.2, 26.0, 23.4; MS m/z 222 (M^+). Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.25; H, 8.16. Found: C, 70.32; H, 8.33.

4-[(5*E*)-6-(Methoxycarbonyl)-5-hexenyl]-4-methyl-2-cyclopenten-1-one (16). Using the same procedure as above, **14** (170 mg, 0.93 mmol) was converted into **16** (150 mg, 68%) as a colorless oil: IR (neat) 1710, 1660 cm^{-1}; ^1H NMR (300

(15) Genard, S.; Patin, H. *Bull. Soc. Chim. Fr.* **1991**, 397−406.

MHz, $CDCl_3$) δ 7.43 (d, 1H, J = 5.5 Hz), 6.94 (dt, 1H, J = 15.7, 6.9 Hz), 6.03 (d, 1H, J = 5.5 Hz), 5.67 (dt, 1H, J = 15.7, 1.4 Hz), 3.73 (s, 3H), 2.29 (d, 1H, J = 18.4 Hz), 2.25−2.14 (m, 2H), 2.12 (d, 1H, J = 18.4 Hz), 1.59−1.23 (m, 6H), 1.21 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.9, 172.9, 167.1, 149.1, 131.9, 121.2, 51.3, 47.6, 44.7, 40.1, 31.8, 28.3, 26.1, 24.1; MS m/z 236 (M^+). Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 70.99; H, 8.57.

4-[(5*Z*)-6-(Methoxycarbonyl)-5-hexenyl]-4-methyl-2-cyclopenten-1-one (17). Oxidation of **14** (100 mg, 0.55 mmol) with PCC (3.90 mg, 1.81 mmol) in the presence of 4 Å molecular sieves (585 mg) in dry CH_2Cl_2 (50 mL) as above gave the aldehyde, which was used in the following reaction without purification.

To a stirred solution of $(CF_3CH_2O)_2P(O)CH_2CO_2Me$[14] (0.17 mL, 0.82 mmol) and 18-crown-6 (725 mg, 2.75 mmol) in dry THF (15 mL) at −78 °C was added 0.5 M KHMDS in toluene (1.43 mL, 0.72 mmol). After the addition of the above aldehyde in dry THF (10 mL), the mixture was stirred for 30 min at the same temperature. After the addition with saturated NH_4Cl, the mixture was thoroughly extracted with Et_2O. The extract was washed with brine, dried (Na_2SO_4), and evaporated to afford a residue which was subjected to column chromatography on silica gel. Elution with AcOEt−hexane (1:4 v/v) provided **17** (71 mg, 55%) as a pale yellowish oil: IR (neat) 1720, 1650 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, 1H, J = 5.5 Hz), 6.20 (dt, 1H, J = 11.4, 7.7 Hz), 6.03 (d, 1H, J = 5.5 Hz), 5.78 (dd, 1H, J = 11.4, 1.9 Hz), 3.71 (s, 3H), 2.69−2.61 (m, 2H), 2.29 (d, 1H, J = 18.7 Hz), 2.11 (d, 1H, J = 18.7 Hz), 1.65−1.24 (m, 6H), 1.20 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210, 173.1, 167.0, 150.3, 131.8, 119.6, 50.9, 47.7, 44.8, 40.1, 29.2, 28.6, 26.1, 24.5; HRMS calcd for $C_{14}H_{20}O_3$ (M^+) 236.1411, found 236.1396.

Further elution gave **16** (4 mg, 3%) as a colorless oil, which was identical with the authentic compound in all respects.

1-Methyl-5-[2-(methoxycarbonyl)methyl]-2-(*tert*-butyldimethylsiloxy)bicyclo[4.3.0]nona-6,8-diene (18). To a stirred solution of **15** (30 mg, 0.14 mmol) and Et_3N (0.094 mL, 0.86 mmol) in dry CH_2Cl_2 (3 mL) at 0 °C was added TBDPSOTf (0.078 mmol, 0.34 mmol), and the mixture was stirred for 2.5 h at rt. After dilution with CH_2Cl_2, the mixture was washed with 10% $KHSO_4$ and brine, dried (Na_2SO_4), and evaporated to give a residue, which was purified by column chromatography on silica gel. Elution with AcOEt−hexane (1:19 v/v) afforded a 1:1.8 mixture of **18** (46 mg, 99%) as a colorless oil: IR (neat) 1735, 1740 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.25 (d, 0.36H, J = 5.5 Hz), 6.17 (d, 0.64H, J = 5.5 Hz), 6.07 (d, 0.36H, J = 5.5 Hz), 6.02 (d, 0.64H, J = 5.5 Hz), 3.68 (s, 1.08 H), 3.66 (s, 1.92H), 3.54−3.45 (m, 0.64H), 3.26−3.18 (m, 0.36H), 2.69−2.33 (m, 2H), 1.93−1.44 (m, 6H), 1.11 (s, 1.92H), 1.01 (s, 1.08H), 0.97 (s, 5.76H), 0.94 (s, 3.24H), 0.18 (s, 1.08H), 0.17 (s, 1.08H), 0.15 (s, 1.92H), 0.13 (s, 1.92H); HRMS calcd for $C_{19}H_{32}O_3Si$ (M^+) 336.2119, found 336.2013.

1-Methyl-5-(2-hydroxyethyl)bicyclo[4.3.0]non-8-en-7-one (20). To a stirred solution of **18** (18.6 mg, 0.056 mmol) in dry CH_2Cl_2 (10 mL) at −78 °C was added 0.98 M DIBALH in hexane (0.21 mL, 0.20 mmol). The mixture was then stirred for 1 h at −78 °C. After dilution with Et_2O, followed by the addition of H_2O (0.21 mL), the mixture was stirred for 1.5 h at rt. Filtration thorough Celite, followed by evaporation of the solvents, gave a residue that was chromatographed on silica gel. Elution with AcOEt−hexane (3:17 v/v) yielded **19** (9.5 mg, 56%) as a colorless oil.

A mixture of **19** (9.5 mg, 0.029 mmol) and 1 M Bu_4NF in THF (0.046 mL, 0.046 mmol) in dry THF (10 mL) was stirred for 2 h at rt. After dilution with Et_2O, the mixture was washed with brine, dried (Na_2SO_4), and evaporated. Column chromatography of the residue on silica gel with AcOEt−hexane (2:3 v/v) as the eluent provided a 1:1.8 mixture of **20** (5.6 mg, 95%) as a colorless oil: IR (neat) 3400, 1700 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (d, 0.64H, J = 5.8 Hz), 7.36 (d, 0.36H, J = 5.8 Hz), 6.08 (d, 0.36H, J = 5.8 Hz), 6.02 (d, 0.64H, J = 5.8 Hz), 3.87−3.62 (m, 2H), 2.36−1.32 (m, 11H), 1.25 (s, 1.08H), 1.23 (s, 1.92H); HRMS calcd for $C_{12}H_{18}O_2$ (M^+) 194.1306, found 194.1309.

(±)-(1*S,2*S**,3*R**,7*R**,8*R**)-(22) and (±)-(1*S**,2*R**,3*R**,7*R**,8*R**)-2-(Methoxycarbonyl)-7-methyltricyclo[5.3.0.0^{3,8}]decan-9-one (23).** (A) To a mixture of **15** (153 mg, 0.69 mmol), $ZnCl_2$ (939 mg, 6.89 mmol), and Et_3N (1.44 mL, 10.3 mmol) in dry toluene (7 mL) in a sealed tube was added TMSCl (0.93 mL, 6.89 mmol). The mixture was then heated for 72 h at 180 °C. After dilution with benzene, the resulting mixture was washed with 10% HCl and brine, dried (Na_2SO_4), and evaporated. Column chromatography of the residue on silica gel with AcOEt−hexane (1:4 v/v) as the eluent gave a 3.6:1 mixture of **22** and **23** (61.6 mg, 40%) as a colorless oil, which was separated by HPLC using Dynamax Microsorb silica (5 nm; 4 × 250 mm) with AcOEt−hexane (1:9 v/v; 1 mL·min^{-1}).

22: IR 1740, 1730 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.68 (s, 3H), 3.09−3.03 (m, 1H), 3.05 (ddd, 1H, J = 5.0, 2.7, 2.2 Hz), 2.68−2.62 (m, 1H), 2.51 (dt, 1H, J = 4.7, 1.7 Hz), 2.32 (ddd, 1H, J = 19.0, 4.7, 2.2 Hz), 2.04 (s, 1H), 1.82−1.46 (m, 7H), 1.07 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 216.8, 174.3, 61.1, 51.9, 49.5, 47.5, 47.2, 39.9, 36.5, 32.2, 28.1, 21.9, 18.0; HRMS calcd for $C_{13}H_{18}O_3$ (M^+) 222.1255, found 222.1263.

23: IR (neat) 1740, 1730 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.64 (s, 3H), 3.22−3.15 (m, 1H), 2.61 (br s, 1H), 2.51 (d, 1H, J = 5.5 Hz), 2.34 (t, 1H, J = 18.4 Hz), 1.99 (d, 1H, J = 18.4 Hz), 1.90 (d, 1H, J = 4.3 Hz), 1.87−1.54 (m, 6H), 0.98 (s, 3H); HRMS calcd for $C_{13}H_{18}O_3$ (M^+) 222.1255, found 222.1263.

(B) To a stirred solution of **15** (60 mg, 0.27 mmol) in dry $ClCH_2CH_2Cl$ (10 mL) were added at 0 °C $(TMS)_2NH$ (0.086 mL, 0.41 mmol) and TMSI (0.046 mL, 0.32 mmol), and the mixture was stirred for 1 h at rt. After dilution with Et_2O, the mixture was washed with saturated NH_4Cl and brine, dried (Na_2SO_4), and evaporated. The residue was purified by column chromatography on silica gel with AcOEt−hexane (3:7 v/v) as the eluent, followed by HPLC using Dynamax Microsorb silica (5 nm, 4 × 250 mm) with AcOEt−hexane (1:8 v/v; 1 mL·min^{-1}). The first fraction afforded one isomer of **25** (4.9 mg, 5%) as a colorless oil: IR (neat) 1735 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.72 (dd, 1H, J = 10.2, 9.1 Hz), 3.65 (s, 3H), 3.01 (dd, 1H, J = 19.8, 8.8 Hz), 2.78−2.68 (m, 2H), 2.09 (dd, 1H, J = 15.9, 9.1 Hz), 1.96−1.77 (m, 3H), 1.72−1.14 (m, 5H), 1.09 (s, 3H); HRMS calcd for $C_{13}H_{19}IO_3$ (M^+) 350.0377, found 350.0367.

The second fraction gave the other isomer of **25** (4.9 mg, 5%) as a colorless oil: IR (neat) 1735 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.13 (dd, 1H, J = 11.5, 8.5 Hz), 3.68 (s, 3H), 2.98−2.82 (m, 2H), 2.69 (dd, J = 19.5, 11.5 Hz), 2.49 (dd, 2H, J = 8.2, 4.1 Hz), 2.03 (br s, 1H), 1.56−1.27 (m, 6H), 1.23; HRMS calcd for $C_{13}H_{19}IO_3$ (M^+) 350.0377, found 350.0356.

The third fraction provided **22** (6.3 mg, 10%) as a colorless oil, whose ^{1}H NMR (300 MHz, $CDCl_3$) spectrum was identical with that of the above compound, prepared by method A.

The fourth fraction yielded **24** (22.2 mg, 37%) as a colorless oil: IR (neat) 1740, 1700 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, 1H, J = 5.8 Hz), 6.01 (d, 1H, J = 5.8 Hz), 3.67 (s, 3H), 2.95 (t, 1H, J = 15.1 Hz), 2.30 (dd, 1H, J = 15.1, 9.3 Hz), 2.25−2.11 (m, 1H), 1.82−1.71 (m, 7H), 1.21 (s, 3H); HRMS calcd for $C_{13}H_{18}O_3$ (M^+) 222.1255, found 222.1256.

(C) To a stirred solution of **15** (29 mg, 0.13 mmol) in dry $ClCH_2CH_2Cl$ (15 mL) at 0 °C were added $(TMS)_2NH$ (0.14 mL, 0.65 mmol) and 1 M Bu_2BOTf in CH_2Cl_2 (0.39 mL, 0.39 mmol). The mixture was then stirred for 3 h at rt. After dilution with Et_2O, the mixture was washed with saturated NH_4Cl and brine, dried (Na_2SO_4), and evaporated. Column chromatography on silica gel with AcOEt−hexane (1:4 v/v) as the eluent gave **22** (8.0 mg, 28%) as a colorless oil, which was identical with the authentic sample in all respects.

(±)-(1*S,2*S**,3*R**,8*R**,9*R**)-2-(Methoxycarbonyl)-8-methyltricyclo[6.3.0.0^{3,9}]undecan-10-one (26).** (A) A mixture of **16** (45 mg, 0.19 mmol), Et_3N (0.40 mL, 2.85 mmol), $ZnCl_2$ (260 mg, 1.90 mmol), and TMSCl (0.24 mL, 1.90 mmol) in dry toluene (3 mL) was heated for 72 h at 180 °C in a sealed tube. After dilution with benzene, the mixture was washed with 10% HCl and brine, dried (Na_2SO_4), and evaporated to afford a residue, which was subjected to column chromatography on silica gel. Elution with AcOEt−hexane (1:4 v/v) provided **26** (13 mg, 29%) as a colorless oil: IR (neat) 1740, 1735 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.70 (s, 3H), 3.17 (ddd,

1H, J = 6.3, 4.1, 2.2 Hz), 2.56−2.49 (m, 1H), 2.44 (dt, 1H, J = 4.9, 1.9 Hz), 2.29 (dddd, 1H, J = 18.7, 4.7, 2.2, 0.8 Hz), 2.44−2.22 (m, 1H), 2.00 (d, 1H, J = 18.7 Hz), 1.90−1.78 (m, 2H), 1.72−1.17 (m, 6H), 1.06 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.6, 174.7, 63.5, 51.9, 50.7, 49.2, 47.0, 39.3, 39.0, 38.4, 29.7, 26.5, 25.2, 24.0; HRMS calcd for $C_{14}H_{20}O_3$ (M^+) 236.1411, found 236.1426.

(B) Treatment of **16** (30 mg, 0.12 mmol) with $(TMS)_2NH$ (0.046 mL, 0.21 mmol) and TMSI (0.027 mL, 0.19 mmol) in $ClCH_2CH_2Cl$ (5 mL) for 1 h at rt, followed by the similar workup and purification as above, gave **26** (21 mg, 69%) as a colorless oil, which was identical with the authentic compound, prepared by method A, in all respects.

(C) Reaction of **16** (31 mg, 0.13 mmol) with $(TMS)_2NH$ (0.14 mL, 0.65 mmol) and 1.0 M Bu_2BOTf in CH_2Cl_2 (0.39 mL, 0.39 mmol) in $ClCH_2CH_2Cl$ (10 mL) for 3 h at rt, followed by the similar workup and purification as the case of A, provided **26** (22 mg, 71%) as a colorless oil, which was identical with the authentic compound in all respects.

(D) Treatment of **17** (20 mg, 0.085 mmol) with $(TMS)_2NH$ (0.03 mL, 0.14 mmol) and TMSI (0.018 mL, 0.13 mmol) in dry $ClCH_2CH_2$ (5 mL) for 1 h at rt, followed by the same workup and purification procedure as above, yielded **26** (13 mg, 67%) as a colorless oil, which was identical with the authentic compound in all respects.

(E) Reaction of **17** (23 mg, 0.097 mmol) with $(TMS)_2NH$ (0.10 mL, 0.48 mmol) and 1.0 M Bu_2BOTf in CH_2Cl_2 (0.29 mL, 0.29 mmol) in dry $ClCH_2CH_2Cl$ (10 mL) for 3 h at rt, followed by the same workup and purification as above, gave **26** (1.6 mg, 7%) as a colorless oil, which was identical with the authentic compound in all respects.

Methyl (2*Z*)- (28) and (2*E*)-6-(Benzyloxy)-2-hexenates (29). A mixture of 4-(benzyloxy)butan-1-ol[16] (500 mg, 2.77 mmol), 4 Å molecular sieves (1 g), and PDC (1.25 g, 3.32 mmol) in dry CH_2Cl_2 (15 mL) was stirred for 2 h at rt. After dilution with Et_2O, followed by filtration through Celite, evaporation of the solvents gave the corresponding aldehyde, which was used in the following reaction without purification.

After treatment of $(CF_3CH_2O)_2P(O)CH_2CO_2Me$[14] (0.76 mL, 3.59 mmol) with 0.5 M KHMDS in toluene (6.66 mL, 3.33 mmol) in the presence of 18-crown-6 (2.2 g, 8.32 mmol) in dry THF (20 mL) for 30 min at −78 °C, to the resulting mixture at −78 °C was added a solution of the above aldehyde in dry THF (8 mL). After being stirred for 1.5 h at −78 °C, the mixture was diluted with Et_2O. The mixture was washed with brine, dried ($MgSO_4$), and evaporated. Column chromatography on silica gel with AcOEt−hexane (15:85 v/v) as the eluent gave **28** (473 mg, 73%) as a colorless oil: IR (neat) 1720, 1645 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36−7.27 (m, 5H), 6.25 (dt, 1H, J = 11.5, 7.4 Hz), 5.79 (dt, 1H, J = 11.5, 1.6 Hz), 4.50 (s, 2H), 3.70 (s, 3H), 3.51 (t, 2H, J = 6.6 Hz), 2.80−2.71 (m, 2H), 1.83−1.73 (m, 2H); HRMS calcd for $C_{14}H_{19}O_3$ (M^+ + H) 235.1335, found 235.1286.

Further elution gave the (*E*)-isomer **29** (41 mg, 6.3%) as a colorless oil: IR (neat) 1720, 1655 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37−7.27 (m, 5H), 6.98 (dt, 1H, J = 15.7, 7.0 Hz), 5.83 (dt, 1H, J = 15.7, 1.6 Hz), 4.50 (s, 2H), 3.73 (s, 3H), 3.49 (t, 2H, J = 6.3 Hz), 2.37−2.27 (m, 2H), 1.83−1.73 (m, 2H); HRMS calcd for $C_{14}H_{19}O_3$ (M^+ + H) 235.1335, found 235.1361.

Isomerization of 28. To a stirred solution of **28** (40 mg, 0.17 mmol) in dry $ClCH_2CH_2Cl$ (5 mL) at 0 °C were added $(TMS)_2NH$ (0.055 mL, 0.26 mmol) and TMSI (0.032 mL, 0.22 mmol), and the mixture was stirred for 1 h at rt. After dilution with Et_2O, the mixture was washed with saturated NH_4Cl, 5% $Na_2S_2O_3$, and brine, dried ($MgSO_4$), and evaporated. Column chromatography on silica gel with AcOEt−hexane (1:4 v/v) provided the (*E*)-isomer **29**, whose ^{1}H NMR (300 MHz, $CDCl_3$) spectrum was identical with that of the authentic sample. No (*Z*)-isomer **28** was detected on the ^{1}H NMR spectrum.

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Supporting Information Available: ^{1}H NMR spectra of compounds **7**−**10**, **17**, **18**, **20**, **22**, **23**, **26**, **28**, and **29** (12 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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