Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron 63 (2007) 510–513
Tetrahedron

Enantioselective formal synthesis of (+)-precapnelladiene by chiral copper-catalyzed asymmetric [2+2]-cycloaddition reaction

Yosuke Takenaka, Hisanaka Ito* and Kazuo Iguchi*

School of Life Sciences, Tokyo University of Pharmacy and Life Sciences, 1432-1 Horinouchi, Hachioji, Tokyo 192-0392, Japan

Received 4 September 2006; accepted 2 October 2006
Available online 15 November 2006

Abstract—Enantioselective short formal synthesis of (+)-precapnelladiene (**1**) was achieved from a bicyclo[3.2.0]heptane derivative, which was prepared enantioselectively by chiral copper-catalyzed [2+2]-cycloaddition reaction of 2-methoxycarbonyl-2-cyclopenten-1-one with phenylthioacetylene developed by us.

1. Introduction

Precapnelladiene (**1**), isolated by Djerassi et al. from the soft coral, *Capnella imbricata*, is a sesquiterpene having a unique bicyclo[6.3.0]dodecane skeleton (Fig. 1).[1] Djerassi also proposed that precapnelladiene (**1**) was a precursor for the biosynthesis of tricyclic $\Delta^{9(12)}$-capnellene. Its unique structural character has attracted the attention of synthetic organic chemists and some synthetic studies have been reported.[2–6] Most of them were, however, synthesis of **1** as a racemic form. One reason was that the $[\alpha]_D$ value was not reported in the original paper. Only one example of the total synthesis of (8*R*,11*R*)-(−)-precapnelladiene was reported as an optically active form by Inouye et al.[5]

Moore et al. also reported the total synthesis of (±)-precapnelladiene through oxy-Cope rearrangement from the key intermediate **2**, which has a bicyclo[3.2.0]heptane skeleton, and the following palladium-catalyzed coupling reaction of the methyl group is shown in Scheme 1.[6] We recently reported a catalytic enantioselective [2+2]-cycloaddition reaction using a chiral copper catalyst (Scheme 1).[7,8] This reaction is useful for the construction of the bicyclo[3.2.0]-heptane skeleton as an optically active form. To demonstrate the utility of our enantioselective [2+2]-cycloaddition reaction, the preparation of the key intermediate **2** for the synthesis of (+)-precapnelladiene (**1**) was examined.

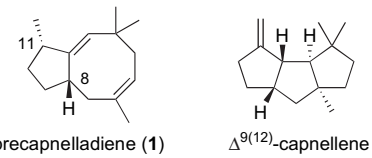
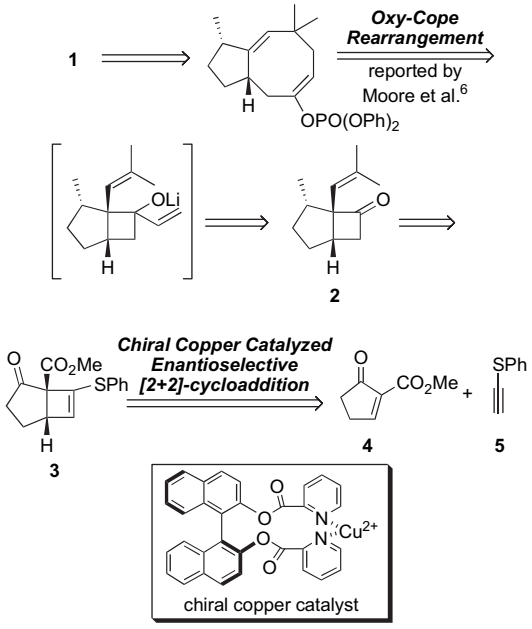


Figure 1.



Scheme 1. Our synthetic plan for compound **1**.

2. Results and discussion

2.1. Retrosynthetic analysis

Our retrosynthetic analysis of (+)-precapnelladiene (**1**) is shown in Scheme 1. Compound **1** can be synthesized from

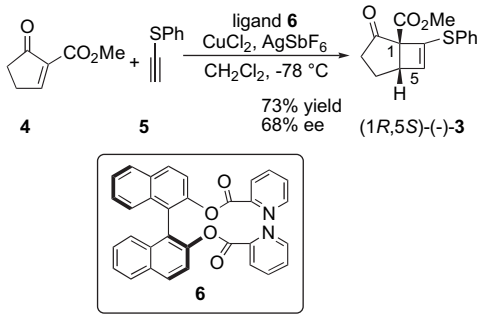
* Corresponding authors. Tel.: +81 42 676 5473; fax: +81 42 676 7282 (H.I.); tel.: +81 42 676 7273; fax: +81 42 676 7282 (K.I.); e-mail addresses: itohisa@ls.toyaku.ac.jp; onocerin@ls.toyaku.ac.jp

0040–4020/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2006.10.072

2 by Moore's reported procedure.[6] Compound **2** would be prepared from **3** through stereoselective introduction of a methyl group on the cyclopentane ring, conversion of the angular ester group to an isopropenyl group, and hydrolysis of vinyl sulfide to a carbonyl group. Compound **3** was already synthesized by our group as a key intermediate for an enantioselective total synthesis of tricycloclavulone.[7,8]

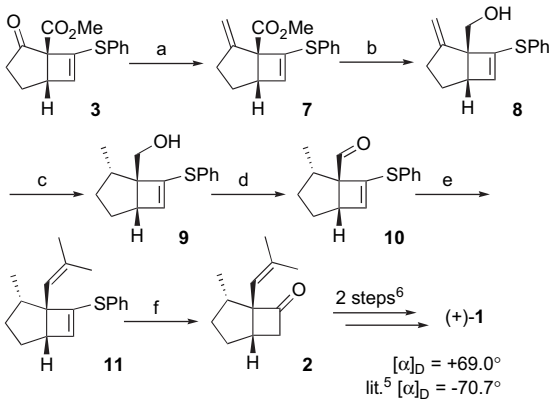
2.2. Synthesis of (+)-precapnelladiene (1)

Compound **3** was prepared by chiral copper complex-catalyzed enantioselective [2+2]-cycloaddition reaction (Scheme 2).[7,8] In the presence of 10 mol % of a chiral copper catalyst, which can be prepared from copper(II) chloride, silver hexafluoroantimonate, and chiral ligand **6**, the [2+2]-cycloaddition reaction of **4** with **5** proceeded at −78 °C and compound (1*R*,5*S*)-**3** was obtained in 73% yield (68% ee).



Scheme 2. Enantioselective [2+2]-cycloaddition reaction.

Stereoselective introduction of the methyl group on the cyclopentane ring was achieved by the following procedure (Scheme 3). The ketone moiety of compound **3** was converted to an *exo*-methylene group by Wittig reaction and **7** was obtained in 76% yield. For the diastereoselective reduction of the *exo*-methylene group, the angular ester group of **7** was reduced to a hydroxyl group to afford **8**. Coordination of the hydroxyl group at the angular position with the catalyst for the hydrogenation would result in the more favored approach of the catalyst to the *exo*-methylene from the convex face. The Crabtree catalyst (Ir(cod)py(PCy_3)PF_6) was employed for the reduction of the *exo*-methylene group; however, a complex mixture was obtained due to the reduction of the carbon–carbon double bond in the cyclobutene ring. Reduction of the *exo*-methylene group of **8** proceeded by the use of Wilkinson catalyst ($Rh(PPh_3)_3Cl$) in a highly diastereoselective manner and compound **9** was obtained in 66% yield (diastereomeric ratio was 11:1). The stereochemistry of compound **9** was determined by comparison with the reported data[6] after converting **9** to the known compound **2**. To increase the optical purity of **9**, recrystallization was examined; however, the crystals of **9** were obtained as a racemic form and enantiomeric excess of compound **9** in solution was increased up to 84% ee. With the increase of optical purity, compound **9** did not crystallize. Therefore, semi-preparative chiral HPLC (Chiralcel OD-H) was employed to increase the optical purity of **9** and the separation of both enantiomers was easily achieved to afford compound **9** in 99% ee (hexane/IPA=99:1; flow rate, 4.0 mL/min; (−)-**9** (major enantiomer), t_R=17.0 min; (+)-**9** (minor enantiomer), t_R=21.5 min). Oxidation of the hydroxyl group of **9** with Dess–Martin periodinane followed by the Wittig reaction of the resulting aldehyde **10** gave compound **11**. Hydrolysis of the vinyl sulfide moiety of **11** was examined by treating with $HgCl_2$. Although, the $HgCl_2$-mediated hydrolysis of the vinyl sulfide moiety of compound **9** smoothly proceeded to give the ketone compound in excellent yield (99% yield), similar hydrolysis of **11** gave compound **2** in 20% yield. We also examined other Hg salts; however, compound **2** was not obtained. Conversion of **2** to precapnelladiene (**1**) was achieved in two steps through vinylation of the carbonyl moiety of **2** and subsequent oxy-Cope rearrangement followed by palladium-catalyzed coupling reaction of the methyl group according to the reported procedure.[6] The spectral data of compound **2**,[6] precapnelladiene (**1**),[1] and the absolute value of optical rotation[5] were identical with those of the literature.



Scheme 3. (a) Methyltriphenylphosphonium bromide, *n*-BuLi, ether, 0 °C, 76%; (b) $LiAlH_4$, ether, 0 °C, 98%; (c) $Rh(PPh_3)_3Cl$, H_2, CH_2Cl_2, rt, 66% (11:1); (d) Dess–Martin periodinane, $NaHCO_3$, CH_2Cl_2, rt, 88%; (e) isopropyltriphenylphosphonium iodide, *n*-BuLi, THF, −78 °C, 86%; (f) $HgCl_2$, CH_3CN, H_2O, 70 °C, 20%.

3. Conclusion

Enantioselective formal synthesis of (+)-precapnelladiene (**1**) was achieved through an enantioselective [2+2]-cycloaddition reaction developed by us. The key intermediate **2** was synthesized from 2-methoxycarbonyl-2-cyclopenten-1-one (**4**) in seven steps.

4. Experimental

4.1. General

All reactions were carried out under an argon atmosphere. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. ^1H and ^{13}C NMR spectra were measured on a Bruker AV-300 and the chemical shifts are given in parts per million using $CHCl_3$ (7.26 ppm) in $CDCl_3$ for ^1H NMR and $CDCl_3$ (77.0 ppm) for ^{13}C NMR as an internal standard. IR spectra were taken with a Perkin–Elmer PARAGON 1000 FT-IR and only noteworthy absorptions were listed. Mass spectra were measured on a Micromass LCT.

4.2. (1*R*,5*S*)-1-Methoxycarbonyl-2-oxo-7-(phenylthio)-bicyclo[3.2.0]hept-6-ene (3)

A suspension of copper(II) chloride (960 mg, 7.14 mmol) and ligand **6** (4.25 g, 8.57 mmol) in CH_2Cl_2 (100 mL) was stirred at ambient temperature for 1.5 h and silver hexafluoroantimonate (5.15 g, 15.0 mmol) was added to the resulting mixture in the dark. After the mixture was stirred for 3 h at ambient temperature, a solution of 2-methoxycarbonyl-2-cyclohexen-1-one (**4**) (5.0 g, 35.9 mmol) and phenylthioacetylene (**5**) (5.7 g, 42.8 mmol) in CH_2Cl_2 (100 mL) was added to the mixture at −78 °C. After stirring the mixture for 1.5 h at the same temperature, phosphate buffer (pH 6.86, 150 mL) was added to the mixture and the mixture was extracted with AcOEt. The organic layer was washed with brine and dried over $MgSO_4$. Filtration and concentration of the mixture under reduced pressure gave a crude material, which was purified by silica gel column chromatography (hexane/AcOEt, 7:1) to afford compound **3** (7.18 g, 26.2 mmol) in 73% yield, 68% ee (Chiralcel OD-H, hexane/IPA=99:1). Pale yellow oil. $[\alpha]_D^{22}$ −451 (*c* 0.775, $CHCl_3$). IR (neat) ν, cm^{-1}: 1746, 1731, 1294, 747. ^1H NMR (300 MHz, $CDCl_3$) δ: 1.89 (1H, br dd, *J*=9.1, 13.5 Hz), 2.13 (1H, dddd, *J*=6.9, 8.7, 11.9, 13.5 Hz), 2.39 (1H, ddd, *J*=1.0, 8.7, 18.3 Hz), 3.02 (1H, ddd, *J*=9.1, 11.9, 18.3 Hz), 3.67 (1H, d, *J*=6.9 Hz), 3.75 (3H, s), 5.88 (1H, s), 7.26–7.38 (3H, m), 7.49–7.53 (2H, m). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 22.4 (CH_2), 34.9 (CH_2), 48.3 (CH), 52.3 (CH_3), 66.2 (C), 128.8 (CH), 129.4 (CH), 129.7 (C), 133.0 (CH), 133.8 (CH), 140.5 (C), 167.6 (C), 208.4 (C). EIMS *m/z*: 274 (M^+). Anal. Calcd for $C_{15}H_{14}O_3S$: C, 65.67; H, 5.14. Found: C, 65.55; H, 5.11.

4.3. (1*R*,5*S*)-1-Methoxycarbonyl-2-methylene-7-phenylsulfanylbicyclo[3.2.0]hept-6-ene (7)

A solution of *n*-BuLi (1.22 M in hexane, 3.6 mL, 4.37 mmol) was added to a suspension of methyltriphenylphosphonium bromide (1.69 g, 4.73 mmol) in ether (10 mL) at 0 °C and the resulting mixture was stirred at ambient temperature for 3 h. A solution of **3** (500 mg, 1.82 mmol) in ether (5 mL) was added to the mixture at 0 °C and the mixture was stirred at ambient temperature for 3 h. The mixture was diluted with ether and then water was added. The mixture was extracted with ether and the organic layer was washed with brine and dried over $MgSO_4$. Filtration and concentration of the mixture under reduced pressure gave a crude material, which was purified by silica gel column chromatography (hexane/AcOEt, 20:1) to afford compound **7** (376 mg, 1.38 mmol) as a pale yellow oil in 76% yield, 68% ee. $[\alpha]_D^{27}$ −320.0 (*c* 0.80, $CHCl_3$). IR (neat) ν, cm^{-1}: 1728, 1652, 1558. ^1H NMR (300 MHz, $CDCl_3$) δ: 1.56 (1H, dd, *J*=7.6, 12.7 Hz), 1.61–1.76 (1H, m), 2.23 (1H, dd, *J*=7.2, 15.3 Hz), 2.64–2.79 (1H, m), 3.57 (1H, d, *J*=6.7 Hz), 3.72 (3H, s), 5.06 (1H, br d, *J*=2.6 Hz), 5.10 (1H, br d, *J*=2.3 Hz), 5.64 (1H, s), 7.27–7.37 (3H, m), 7.46–7.53 (2H, m). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 25.7, 31.5, 51.8, 52.2, 65.4, 109.7, 128.0, 129.0, 130.3, 130.7, 133.3, 140.3, 146.7, 171.1. HRESIMS calcd for $C_{16}H_{17}O_2S$: 273.0949 $(M+H)^+$; found: 273.0935.

4.4. (1*R*,5*S*)-1-Hydroxymethyl-2-methylene-7-phenylsulfanylbicyclo[3.2.0]hept-6-ene (8)

To a solution of **7** (378 mg, 1.39 mmol) in ether (10 mL) was added $LiAlH_4$ (53 mg, 1.39 mmol) at 0 °C and the mixture was stirred at the same temperature for 1 h. Saturated aqueous Rochelle salt was added to the mixture and the mixture was stirred at ambient temperature for 30 min. The mixture was extracted with AcOEt and the organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/AcOEt, 5:1) to afford **8** (332 mg, 1.36 mmol) as a pale yellow oil in 98% yield, 68% ee. $[\alpha]_D^{27}$ −266.5 (*c* 0.89, $CHCl_3$). IR (neat) ν, cm^{-1}: 3402, 1652, 1558. ^1H NMR (300 MHz, $CDCl_3$) δ: 1.42–1.62 (2H, m), 2.36 (1H, dd, *J*=6.8, 15.2 Hz), 2.69–2.84 (1H, m), 3.22 (1H, d, *J*=6.7 Hz), 3.76 (1H, d, *J*=11.5 Hz), 3.82 (1H, d, *J*=11.5 Hz), 4.82 (1H, d, *J*=2.4 Hz), 5.04 (1H, d, *J*=2.4 Hz), 5.81 (1H, d, *J*=0.7 Hz), 7.28–7.37 (3H, m), 7.47–7.53 (2H, m). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 25.2, 32.5, 49.7, 62.4, 64.0, 107.1, 128.2, 129.1, 130.8, 131.4, 133.2, 140.7, 149.0. HRESIMS calcd for $C_{15}H_{17}OS$: 245.1000 $(M+H)^+$; found: 245.1006.

4.5. (1*S*,2*S*,5*S*)-1-Hydroxymethyl-2-methyl-7-phenylsulfanylbicyclo[3.2.0]hept-6-ene (9)

A mixture of **8** (125 mg, 0.512 mmol) and tris(triphenylphosphine)rhodium chloride (47 mg, 0.051 mmol) in CH_2Cl_2 (4 mL) was stirred under a hydrogen atmosphere at ambient temperature for 4 h. The mixture was concentrated under reduced pressure and the residue was purified by silica gel column chromatography (hexane/AcOEt, 8:1) to afford a mixture of **9** and diastereomer **9′** (diastereomeric ratio=11:1, 83.8 mg, 0.34 mmol) as a pale yellow oil in 98% yield. After separation of diastereomers **9** and **9′**, enantiomers of compound **9** were separated by the semi-preparative chiralcel OD-H column (hexane/IPA=99:1, flow rate, 4.0 mL/min; (−)-**9** (major), t_R=17.0 min; (+)-**9** (minor), t_R=21.5 min) to afford almost optically pure **9** (99% ee). Compound **9**: pale yellow oil (99% ee). $[\alpha]_D^{25}$ −67.8 (*c* 1.75, $CHCl_3$). IR (neat) ν, cm^{-1}: 3370, 2931, 2858, 1582, 1558. ^1H NMR (300 MHz, $CDCl_3$) δ: 1.14 (3H, d, *J*=6.2 Hz), 1.26–1.40 (1H, m), 1.43 (1H, dd, *J*=5.2, 13.0 Hz), 1.56–1.82 (3H, m), 2.89 (1H, d, *J*=6.6 Hz), 3.68 (1H, d, *J*=11.4 Hz), 3.89 (1H, d, *J*=11.4 Hz), 5.62 (1H, d, *J*=0.8 Hz), 7.27–7.38 (3H, m), 7.49–7.55 (2H, m). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 15.1, 26.0, 32.8, 35.8, 48.1, 64.6, 65.4, 128.0, 129.05, 129.1, 131.5, 132.9, 138.1. HRESIMS calcd for $C_{15}H_{19}OS$: 247.1157 $(M+H)^+$; found: 247.1149. Compound **9′**: pale yellow oil (68% ee). $[\alpha]_D^{22}$ −46.6 (*c* 0.58, $CHCl_3$). IR (neat) ν, cm^{-1}: 3402, 2945, 2873, 1584, 1558. ^1H NMR (300 MHz, $CDCl_3$) δ: 0.86 (3H, d, *J*=7.7 Hz), 1.33–1.61 (4H, m), 2.03–2.21 (2H, m), 2.86 (1H, d, *J*=6.6 Hz), 3.74 (1H, dd, *J*=6.4, 11.3 Hz), 3.86 (1H, dd, *J*=5.3, 11.3 Hz), 5.69 (1H, d, *J*=0.6 Hz), 7.29–7.38 (3H, m), 7.49–7.55 (2H, m). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 14.5, 23.9, 31.5, 32.1, 47.5, 63.5, 65.7, 128.1, 128.7, 129.2, 131.1, 133.1, 141.5. HRESIMS calcd for $C_{15}H_{19}OS$: 247.1157 $(M+H)^+$; found: 247.1142.

4.6. (1*S*,2*S*,5*S*)-1-Formyl-2-methyl-7-phenylsulfanyl-bicyclo[3.2.0]hept-6-ene (10)

To a solution of **9** (46 mg, 0.187 mmol) in CH_2Cl_2 (1 mL) were added $NaHCO_3$ (31 mg, 0.187 mmol) and Dess–Martin periodinane (95 mg, 0.224 mmol) at ambient temperature and the mixture was stirred at the same temperature for 1 h. A solution of sodium thiosulfate was added to the mixture and the mixture was extracted with AcOEt. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/AcOEt, 8:1) to afford **10** (40 mg, 1.64 mmol) as a pale yellow oil in 88% yield. $[\alpha]_D^{22}$ +0.84 (*c* 0.95, $CHCl_3$). IR (neat) ν, cm^{-1}: 2928, 1710, 1558. ^1H NMR (300 MHz, $CDCl_3$) δ: 1.17 (3H, d, *J*=6.8 Hz), 1.31–1.46 (1H, m), 1.50 (1H, dd, *J*=6.1, 12.9 Hz), 1.60–1.75 (1H, m), 1.82–1.90 (1H, m), 2.17–2.30 (1H, m), 3.17 (1H, d, *J*=6.8 Hz), 5.83 (1H, s), 7.30–7.41 (3H, m), 7.50–7.56 (2H, m), 9.71 (1H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 15.0, 26.6, 32.5, 33.5, 49.4, 73.3, 128.5, 129.3, 131.1, 131.5, 133.4, 137.5, 201.6. HRESIMS calcd for $C_{15}H_{17}OS$: 245.1000 $(M+H)^+$; found: 245.0999.

4.7. (1*S*,2*S*,5*S*)-2-Methyl-1-(2-methyl-1-propenyl)-7-phenylsulfanylbicyclo[3.2.0]hept-6-ene (11)

A solution of *n*-BuLi (1.2 M in hexane, 0.16 mL, 0.197 mmol) was added to a suspension of isopropyltriphenylphosphonium iodide (93 mg, 0.213 mmol) in THF (0.5 mL) at −78 °C and the mixture was stirred at ambient temperature for 30 min. A solution of **10** (40 mg, 0.164 mmol) in THF (1 mL) was added to the mixture at −78 °C and the mixture was stirred at the same temperature for 2 h. The mixture was diluted with ether and then water was added. The mixture was extracted with AcOEt and the organic layer was washed with brine and dried over $MgSO_4$. Filtration and concentration of the mixture under reduced pressure gave a crude material, which was purified by silica gel column chromatography (hexane) to afford compound **11** (38 mg, 0.141 mmol) as a pale yellow oil in 86% yield. $[\alpha]_D^{28}$ −75.0 (*c* 1.01, $CHCl_3$). IR (neat) ν, cm^{-1}: 2931, 2856, 1560. ^1H NMR (300 MHz, $CDCl_3$) δ: 1.10 (3H, d, *J*=6.3 Hz), 1.41–1.60 (3H, m), 1.66–1.78 (2H, m), 1.73 (3H, d, *J*=1.0 Hz), 1.77 (3H, d, *J*=1.3 Hz), 3.05 (1H, d, *J*=5.4 Hz), 5.48 (1H, s), 5.50 (1H, d, *J*=1.0 Hz), 7.27–7.37 (3H, m), 7.50–7.57 (2H, m). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 14.9, 19.0, 26.6, 26.7, 32.1, 41.6, 52.7, 63.4, 125.2, 127.1, 127.7, 129.0, 132.1, 133.0, 133.9, 140.9. HRESIMS calcd for $C_{18}H_{23}S$: 271.1520 $(M+H)^+$; found: 271.1538.

4.8. (1*S*,2*S*,5*S*)-2-Methyl-1-(2-methyl-1-propenyl)-bicyclo[3.2.0]heptan-7-one (2)

To a solution of **11** (38 mg, 0.141 mmol) in CH_3CN (0.75 mL) and water (0.25 mL) was added $HgCl_2$ (77 mg, 0.282 mmol) at ambient temperature and the mixture was stirred at 70 °C for 3 h. Water was added to the mixture and the resulting mixture was extracted with ether. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/$CHCl_3$, 1:2) to afford **2** (5.0 mg, 0.028 mmol) as a colorless oil in 20% yield. $[\alpha]_D^{28}$ +26.7 (*c* 0.43, $CHCl_3$). IR (neat) ν, cm^{-1}: 2925, 1771. ^1H NMR (300 MHz, $CDCl_3$) δ: 1.04 (3H, d, *J*=6.6 Hz), 1.39–1.47 (1H, m), 1.64 (3H, d, *J*=1.0 Hz), 1.71 (3H, d, *J*=1.3 Hz), 1.82 (1H, dd, *J*=6.2, 12.8 Hz), 1.90–2.08 (3H, m), 2.43 (1H, dd, *J*=4.5, 18.5 Hz), 2.82–2.91 (1H, m), 3.15 (1H, dd, *J*=9.2, 18.5 Hz), 5.27 (1H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 14.5, 19.4, 26.4, 32.3, 33.1, 37.5, 47.5, 49.5, 78.9, 123.5, 135.0, 214.4. HRESIMS calcd for $C_{12}H_{19}O$: 179.1436 $(M+H)^+$; found: 179.1422.

4.9. Data of synthetic (+)-precapnelladiene (1)[1,5,6]

Colorless oil. $[\alpha]_D^{22}$ +69.0 (*c* 0.113, $CHCl_3$). IR (neat) ν, cm^{-1}: 2952, 2866, 1458, 1374, 1358. ^1H NMR (300 MHz, $CDCl_3$) δ: 0.97 (3H, s), 0.99 (3H, s), 1.04 (3H, d, *J*=6.8 Hz), 1.17–1.28 (1H, m), 1.36–1.47 (1H, m), 1.63 (3H, s), 1.50–1.81 (4H, m), 2.29–2.44 (2H, m), 2.90 (1H, dd, *J*=9.5, 13.5 Hz), 3.44–3.57 (1H, m), 5.02 (1H, d, *J*=1.6 Hz), 5.33 (1H, t, *J*=8.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 22.0, 26.7, 29.8, 31.3, 31.4, 33.6, 38.7, 38.8, 39.6, 40.4, 42.3, 121.8, 130.3, 136.3, 145.5.

References and notes

1. Ayanoglu, E.; Gebreyesus, T.; Beechan, C. M.; Djerassi, C. *Tetrahedron* **1979**, *35*, 1035–1039.
2. (a) Mehta, G.; Murthy, A. N. *J. Chem. Soc., Chem. Commun.* **1984**, 1058–1060; (b) Mehta, G.; Murthy, A. N. *J. Org. Chem.* **1987**, *52*, 2875–2881.
3. (a) Kinney, W. A.; Coghlan, M. J.; Paquette, L. A. *J. Am. Chem. Soc.* **1984**, *106*, 6868–6870; (b) Kinney, W. A.; Coghlan, M. J.; Paquette, L. A. *J. Am. Chem. Soc.* **1985**, *107*, 7352–7360.
4. Petasis, N. A.; Patane, M. A. *Tetrahedron Lett.* **1990**, *31*, 6799–6802.
5. (a) Inouye, Y.; Shirai, M.; Michino, T.; Kakisawa, H. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 324–326; (b) Maeda, K.; Inouye, Y. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 2880–2882.
6. (a) MacDougall, J. M.; Turnbull, P.; Verma, S. K.; Moore, H. W. *J. Org. Chem.* **1997**, *62*, 3792–3793; (b) MacDougall, J. M.; Santora, V. J.; Verma, S. K.; Turnbull, P.; Hernandes, C. R.; Moore, H. W. *J. Org. Chem.* **1998**, *63*, 6905–6913.
7. Ito, H.; Hasegawa, M.; Takenaka, Y.; Kobayashi, T.; Iguchi, K. *J. Am. Chem. Soc.* **2004**, *126*, 4520–4521.
8. Takenaka, Y.; Ito, H.; Hasegawa, M.; Iguchi, K. *Tetrahedron* **2006**, *62*, 3380–3388.