# Short Total Synthesis of (±)-Galbulin and (±)-Isogalbulin Using Zirconium Chemistry

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## Introduction

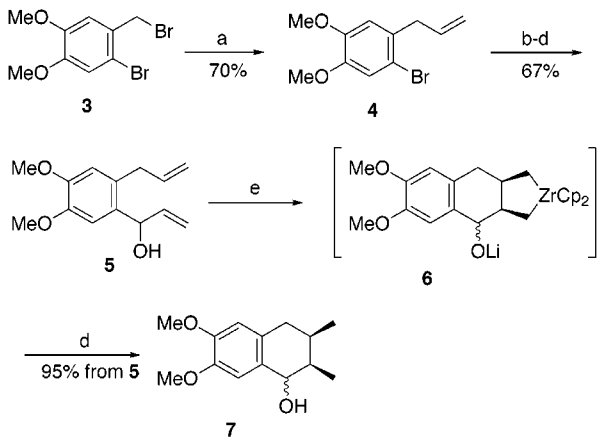
Galbulin (**1**) and isogalbulin (**2**) are natural lignans first isolated from *Himantandra baccata* and *Himantandra belgraveana*.[1] Excluding the synthesis of **1** and **2** by interconversion of other natural compounds (mostly lignans),[2−7] they have been previously prepared by cationic cyclization of 4,4-diveratryl-2,3-dimethylbutanoic acid[8] or 1,4-diveratryl-2,3-dimethyl-1-butanol,[9] and by oxidative coupling of 1,4-diveratryl-2,3-dimethylbutane.[10,11] However, all these methods suffered from low total yield and were accompanied by formation of complex mixtures of stereoisomers. We describe here a short, stereoselective, and experimentally simple route to both (±)-galbulin and (±)-isogalbulin using zirconium-promoted cyclization of 1,7-dienes[12] as a key step.


**1** Ar = 2,3-$(MeO)_2C_6H_3$ **2**

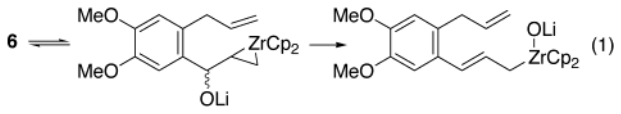
## Results

Copper-catalyzed reaction of the readily available dibromide **3**[13] with vinylmagnesium bromide[14] afforded the unsaturated monobromide **4** in high yield (Scheme 1). Lithium−bromine exchange by treatment of **4** with 2.2 equiv of *t*-BuLi followed by reaction of the resulting aryllithium with acrolein and hydrolysis gave the alcohol **5** containing a 1,7-dienic system. The reaction between the lithium alcoholate of **5** and dibutylzirconocene (Negishi reagent, prepared in situ from $Cp_2ZrCl_2$ and 2 equiv of BuLi)[15] at 20 °C for 1.5 h led to the *cis*-fused zirconacycle **6**. Hydrolysis of **6** furnished the substituted tetrahydronaphthol **7**[16] as ∼1:1 mixture of diastereoisomers, both having the *cis*-stereochemistry of the *β*- and *γ*-methyl groups. The exclusive formation of the *cis*-fused zirconacycle is in accord with Takahashi's observations on cocyclizations of 1,4,7-octatrienes.[17] Our attempts to isomerize **6** to the corresponding *trans*-fused zirconacycle by heating in THF (50 °C, 6 h)[18] failed, probably because of elimination of the alcoholate group from an intermediate zirconocene−alkene complex (eq 1).[19] The poor relative diastereocontrol between the alcoholate group and the adjacent ring junction stereocenter in the zirconacycle **6** is surprising. Cyclization of the lithium alkoxide of 1,7-octadien-3-ol is reported to give >94% diastereoisomeric excess between the analogous centers.[20]

**Scheme 1**[a]




[a] Reagents and conditions: (a) $CH_2$=CHMgBr, CuI/2,2′-bipyridyl (10 mol %), THF/benzene, 20 °C, 3 h; (b) tert-BuLi (2.2 equiv), THF, −78 °C, 30 min; (c) acrolein, −78 to −50 °C, 1 h; (d) $H_2O$; (e) $Cp_2ZrBu_2$, BuLi (1.3 equiv), −78 to 20 °C, then 20 °C, 1.5 h.




The *trans*-*β*,*γ*-substituted tetrahydronaphthol **8** was synthesized as shown in Scheme 2. Oxidation of **7** with PCC gave the isomerically pure *cis*-ketone **9** in high yield.

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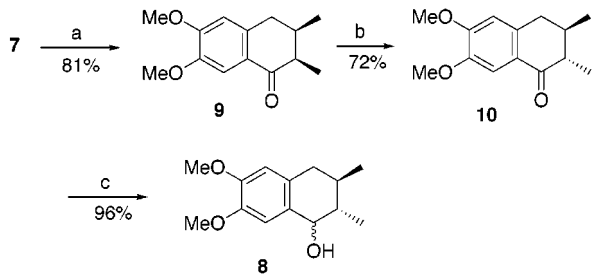
**Scheme 2**[a]




[a] Reagents and conditions: (a) PCC, $CH_2Cl_2$, 20 °C, 1 h; (b) KOH, EtOH, 20 °C, 1.5 h; (c) $NaBH_4$, MeOH, 20 °C, 1 h.

Epimerization of **9** with potassium hydroxide in ethanol at room-temperature resulted in the precipitation of the *trans*-ketone **10** with >98% isomeric purity (72% yield). Workup of the mother liquor gave a 71:29 (HPLC) mixture of **10**:**9** (28% yield). Reduction of **10** with sodium borohydride in methanol led to **8**[16] as 60:40 mixture of diastereoisomers.

The relative configuration of the *cis*- and *trans*-ketones **9**, **10** was proven by NMR-spectroscopy. In the carbon-13 NMR spectrum of the *cis*-isomer **9** the signals of the $\beta$- and $\gamma$-methyl groups are 1.7 and 4.6 ppm higher field than those in the spectrum of the *trans*-isomer **10** ($\gamma$-gauche effect[21]). $^1$H NMR data of **9** and **10** are also in good agreement with the data of *cis*- and *trans*-2,3-dimethyl-1-tetralones (demethoxy-analogues of **9**, **10**), respectively.[22] Noteworthy that in contrast to **9** which is a viscous oil at 20 °C, the *trans*-isomer **10** is a light yellow solid with mp 135 °C.

The reaction of **7** with 5 equiv of veratrole in the presence of aluminum chloride under Friedel−Crafts conditions described for similar systems[23] led to (±)-isogalbulin (**2**) in low yield contaminated with (±)-galbulin (**1**) (Table 1, entry 1). Simultaneously a large amount of polymeric material was formed. The presence of **1** can be explained by isomerization of the initially formed *cis*-carbocation **11** to the *trans*-carbocation **12** through a $\beta$-elimination−protonation mechanism followed by the attack of veratrole to the less-hindered side of **12** (Scheme 3). The use of a larger excess of veratrole (cosolvent) increased the yield but did not change the **9**/**10** ratio (Table 1, entry 2). However, decreasing the temperature from 20 to −30 °C led to almost exclusive formation of (±)-isogalbulin (**2**) (entry 3). The reaction of **8** with veratrole under the same optimized conditions afforded (±)-galbulin (**1**) in high yield containing only 6% of **2** probably due to isomerization of the *trans*-carbocation **12** as shown in Scheme 3 (entry 4). The spectral data of both isomers **1**[10,24] and **2**[6,9,25] were in good agreement with those described in the literature.

**Scheme 3**

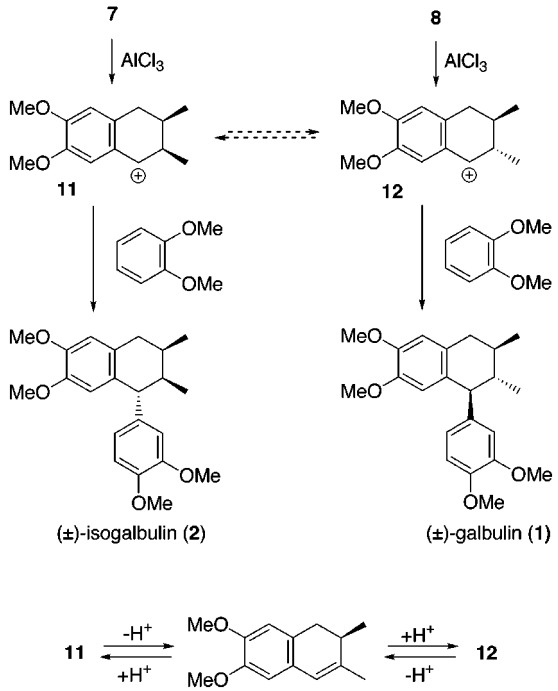



**Table 1. Friedel−Crafts Reaction of 7 and 8 with Veratrole**[a]

| entry | alcohol | excess of veratrole | *T*, °C | **2**:**1**[c] | yield of **2**+**1**, % |
|---|---|---|---|---|---|
| 1 | 7 | 5 equiv | 20 | 89:11 | 26 |
| 2 | 7 | cosolvent[b] | 20 | 89:11 | 57 |
| 3 | 7 | cosolvent[b] | −30 | 97:3 | 47 |
| 4 | 8 | cosolvent[b] | −30 | 6:94 | 76 |

[a] Slow addition of an alcohol to a solution of veratrole and $AlCl_3$ in dichloroethane was used in all cases. [b] 1:1 mixture of veratrole and dichloroethane. [c] According to $^1$H NMR spectroscopy.

## Experimental Section

**General Methods and Materials.** $Cp_2ZrCl_2$ and anhydrous $AlCl_3$ were purchased from Aldrich. 1-Bromo-2-(bromomethyl)-4,5-dimethoxybenzene (**3**) was prepared by bromination of commercial (3,4-dimethoxyphenyl)methanol.[13] THF and 1,2-dichloroethane were dried by refluxing over benzophenone ketyl and calcium hydride, respectively, followed by distillation. Air and moisture sensitive reactions were run in oven dried glassware under a positive pressure of argon. Chromatography was carried out on silica gel (230−400 mesh). NMR spectra (300 MHz proton, 75 MHz carbon) were recorded as solutions in $CDCl_3$. Proton spectra were referenced to $CHCl_3$, and carbon spectra to $CDCl_3$. IR spectra were recorded as films (oils) or solutions in chloroform.

**1-Allyl-2-bromo-4,5-dimethoxybenzene (4).** The title compound was prepared according to the procedure described for 1-allyl-2-bromobenzene.[14] To a stirred mixture of **3** (3.00 g, 9.68 mmol), CuI (0.184 g, 0.97 mmol), 2,2′-bipyridyl (0.151 g, 0.97 mmol), and benzene (3.5 mL) was rapidly added vinylmagnesium bromide (19.20 mL, 0.78 M in THF, 14.98 mmol) at 5 °C. After the exothermic reaction was complete, the cooling bath was removed and the reaction mixture was stirred at 20 °C for 3 h. Saturated aq $NH_4Cl$ (40 mL) and 35% aq $NH_3$ (10 mL) were added, and the mixture was stirred for 30 min and extracted with ether. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (40−60 petroleum ether−EtOAc, 4:1) followed by Kugelrohr distillation (bp 105−108 °C/0.5 mmHg) to afford the title compound (1.741 g, 70% yield). $^1$H NMR $\delta$ 3.35 (d, $J$ = 6.0 Hz, 2 H), 3.76 (s, 6 H), 4.95−5.05 (m, 2 H), 5.80−5.95 (m, 1 H), 6.65 (s, 1 H), 6.95 (s, 1 H). $^{13}$C NMR $\delta$ 38.20, 54.34, 54.57, 111.44, 112.57, 113.94, 114.67, 129.68, 134.30, 146.44, 146.86. IR 1637, 1602 cm$^{-1}$. Anal. Calcd for $C_{11}H_{13}BrO_2$: C, 51.38; H, 5.09; Br, 31.07. Found: C, 51.77; H, 5.24; Br, 31.21.

**1-(2-Allyl-4,5-dimethoxyphenyl)-2-propen-1-ol (5).** To a solution of **4** (2.99 g, 11.62 mmol) in THF (60 mL) was added

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*t*-BuLi (15.0 mL, 1.7 M in pentane, 25.6 mmol) at −78 °C. The reaction mixture was stirred at −78 °C for 30 min, and then freshly distilled acrolein (0.847 g, 15.1 mmol) was added. The resulting solution was slowly warmed to −50 °C over 1 h and hydrolyzed by addition of water (40 mL). After extraction with ether the organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (40−60 petroleum ether−EtOAc, 2:1) to give the title alcohol (1.822 g, 67% yield). $^1$H NMR $\delta$ 2.04 (d, $J$ = 3.3 Hz, OH), 3.42 (d, $J$ = 5.9 Hz, 2 H), 3.88 (s, 6 H), 5.00 (d, $J$ = 16.9 Hz, 1 H), 5.07 (d, $J$ = 9.9 Hz, 1 H), 5.19 (d, $J$ = 9.9 Hz, 1 H), 5.32 (d, $J$ = 16.9 Hz, 1 H), 5.41 (m, 1 H), 5.90−6.10 (m, 2 H), 6.67 (s, 1 H), 6.99 (s, 1 H). $^{13}$C NMR $\delta$ 36.48, 56.03, 71.11, 109.90, 113.04, 114.88, 115.95, 129.43, 132.70, 137.80, 140.02, 147.81, 148.45. IR 3500, 1637, 1608 cm$^{-1}$. Anal. Calc. for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.50; H, 7.66.

***rac*-(1*RS*,2*R*,3*R*)-6,7-Dimethoxy-2,3-dimethyl-1,2,3,4-tetrahydro-1-naphthalenol (7).** To a solution of $Cp_2ZrCl_2$ (2.035 g, 6.97 mmol) in THF (60 mL) was added BuLi (9.20 mL, 2.5 M in hexanes, 23.0 mmol) at −78 °C. The reaction mixture was stirred at −78 °C for 1 h, and then a solution of **5** (1.631 g, 6.97 mmol) in THF (10 mL) was added and the cooling bath was removed. After stirring at room temperature for 1.5 h, saturated aq $NaHCO_3$ (50 mL) was added, and the mixture was stirred for 1 h and extracted with ether. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product (1.563 g, 95% yield, ∼1:1 mixture of two diastereoisomers) had satisfactory NMR data and was used further without purification. $^1$H NMR $\delta$ 0.75 (d, $J$ = 7.0 Hz, 3 H), 0.78 (d, $J$ = 7.4 Hz, 3 H), 0.96 (d, $J$ = 6.6 Hz, 3 H), 1.00 (d, $J$ = 7.0 Hz, 3 H), 1.58 (d, $J$ = 6.3 Hz, 1 H), 1.62 (d, $J$ = 8.5 Hz, 1 H), 1.82−2.10 (m, 2 H + 1 H), 2.23 (m, 1 H), 2.26−2.47 (m, 1 H + 1 H), 2.52 (dd, $J_1$ = 16.5 Hz, $J_2$ = 5.5 Hz, 1 H), 2.61 (dd, $J_1$ = 16.2 Hz, $J_2$ = 4.8 Hz, 1 H), 3.80 and 3.83 (two s, 6 H + 6 H), 4.33 (m, 1 H), 4.74 (m, 1 H), 6.47 (s, 1 H), 6.50 (s, 1 H), 6.80 (s, 1 H), 7.03 (s, 1 H). $^{13}$C NMR $\delta$ 5.90, 11.18, 17.78, 19.14, 27.54, 31.55, 33.28, 33.39, 39.10, 40.17, 55.48, 55.51, 55.54, 72.84, 74.25, 109.74, 111.03, 111.41, 112.65, 128.07, 128.86, 129.02, 130.18, 147.74, 148.78.

***rac*-(2*R*,3*R*)-6,7-Dimethoxy-2,3-dimethyl-3,4-dihydro-2*H*-naphthalen-1-one (9).** To a suspension of pyridinium chlorochromate (1.569 g, 7.28 mmol) in dichloromethane (100 mL) was added a solution of **7** (1.321 g, 5.60 mmol) in dichloromethane (10 mL). The reaction mixture was stirred at 20 °C for 1 h, diluted with ether (120 mL), and filtered through a short silica gel column. After concentration under reduced pressure, the crude product was purified by column chromatography on silica gel (40−60 petroleum ether−EtOAc, 3:1) to give the title *cis*-ketone (1.061 g, 81% yield) of more than 98% isomeric purity. $^1$H NMR $\delta$ 0.98 (d, $J$ = 7.0 Hz, 3 H), 1.16 (d, $J$ = 7.0 Hz, 3 H), 2.43 (m, 1 H), 2.67 (m, 1 H), 2.73 (dd, $J_1$ = 16.6 Hz, $J_2$ = 7.0 Hz, 1 H), 2.98 (dd, $J_1$ = 16.6 Hz, $J_2$ = 4.8 Hz, 1 H), 3.89 (s, 3 H), 3.93 (s, 3 H), 6.63 (s, 1 H), 7.50 (s, 1 H). $^{13}$C NMR $\delta$ 11.38, 15.81, 34.20, 35.07, 46.39, 56.12, 56.16, 108.65, 110.62, 125.02, 137.39, 147.97, 153.58, 200.60. IR 1667, 1599 cm$^{-1}$. Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.56; H, 7.71.

***rac*-(2*S*,3*R*)-6,7-Dimethoxy-2,3-dimethyl-3,4-dihydro-2*H*-naphthalen-1-one (10)**. A solution of **9** (1.061 g, 4.53 mmol) and KOH (0.254 g, 4.53 mmol) in ethanol (18.0 mL) was stirred at 20 °C for 1.5 h. The resulting light yellow solid was filtered, washed with cooled ethanol (2 × 5.0 mL), and dried at 0.5 mmHg for 1 h to afford the title *trans*-ketone (0.763 g, 72% yield) of more than 98% isomeric purity. Mp 135 °C (ethanol). $^1$H NMR $\delta$ 1.13 (d, $J$ = 6.3 Hz, 3 H), 1.27 (d, $J$ = 7.0 Hz, 3 H), 1.99 (m, 1 H), 2.20 (m, 1 H), 2.68 (dd, $J_1$ = 16.5 Hz, $J_2$ = 10.3 Hz, 1 H), 2.91 (dd, $J_1$ = 16.5 Hz, $J_2$ = 4.0 Hz, 1 H), 3.90 (s, 3 H), 3.93 (s, 3 H), 6.65 (s, 1 H), 7.50 (s, 1 H). $^{13}$C NMR $\delta$ 13.05, 20.43, 36.80, 37.32, 48.89, 56.13, 56.17, 108.83, 110.14, 125.21, 137.91, 148.02, 153.50, 199.58. IR 1655, 1601 cm$^{-1}$. Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.60; H, 7.68.

***rac*-(1*RS*,2*S*,3*R*)-6,7-Dimethoxy-2,3-dimethyl-1,2,3,4-tetrahydro-1-naphthalenol (8).** To a solution of **10** (0.763 g, 3.26 mmol) in methanol (25 mL) was added sodium borohydride (0.223 g, 5.87 mmol) at 20 °C. The reaction mixture was stirred for 1 h at room temperature, methanol was removed under reduced pressure, and saturated aq $NaHCO_3$ (5 mL) was added. After extraction with ether, the organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product (0.739 g, 96% yield, ∼60:40 mixture of two diastereoisomers) had satisfactory NMR data and was used further without purification. $^1$H NMR $\delta$ 0.90 (d, $J$ = 7.0 Hz, 3 H major), 0.97 (d, $J$ = 6.6 Hz, 6 H minor), 1.09 (d, $J$ = 6.3 Hz, 3 H major), 1.22 (m, 1 H major + 1 H minor), 1.51 (m, 1 H major), 1.80 (br. s, 1 H major + 1 H minor), 2.20 (m, 1 H minor), 2.30−2.43 (m, 1 H major + 1 H minor), 2.61 (dd, $J_1$ = 16.2 Hz, $J_2$ = 4.8 Hz, 1 H major), 2.88 (dd, $J_1$ = 15.1 Hz, $J_2$ = 7.0 Hz, 1 H minor), 3.77 and 3.80 (two s, 6 H major + 6 H minor), 4.16 (d, $J$ = 9.2 Hz, 1 H major), 6.45 (s, 1 H major + 1 H minor), 6.57 (s, 1 H minor), 6.98 (s, 1 H major). $^{13}$C NMR $\delta$ 15.87, 17.36, 19.69, 21.73, 33.29, 34.24, 35.82, 38.35, 45.15, 56.00, 56.06, 56.13, 75.72, 76.79, 109.03, 109.93, 110.65, 112.01, 125.42, 127.44, 128.93, 131.51, 147.25, 147.31, 147.63, 148.21.

**(±)-Isogalbulin (2)** (Table 1, entry 3). To a mixture of veratrole (4.0 mL), 1,2-dichloroethane (4.0 mL), and aluminum chloride (0.100 g, 0.75 mmol) was added dropwise during 30 min a solution of **7** (0.146 g, 0.62 mmol) in 1,2-dichloroethane (4.0 mL) at −30 °C. After addition was complete, the mixture was stirred at −30 °C for 30 min and hydrolyzed with 2 M aq HCl (10 mL). The organic layer was separated, washed with saturated aq $NaHCO_3$ and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The excess of veratrole was removed by Kugelrohr distillation (50−60 °C, 5 mmHg). The residue was purified by column chromatography on silica gel (40−60 petroleum ether−EtOAc, 3:1) to give the title compound (0.104 g, 47% yield). $^{13}$C NMR $\delta$ 15.53, 16.70, 28.72, 34.88, 40.95, 51.03, 55.87, 55.91, 55.95, 56.00, 110.69, 111.28, 112.29, 113.35, 121.45, 128.58, 129.64, 139.95, 147.22, 147.37, 148.70. $^1$H NMR and IR spectral data were in good agreement with those described in the literature.[6,9,25]

**(±)-Galbulin (1)** (Table 1, entry 4). The title compound was prepared from **8** in 76% yield as described above. $^{13}$C NMR $\delta$ 17.33, 20.17, 35.71, 39.17, 43.95, 54.44, 55.94, 56.04, 110.71, 110.79, 112.15, 112.91, 122.09, 129.24, 132.59, 139.17, 147.01, 147.13, 147.42, 148.96. $^1$H NMR and IR spectral data were in good agreement with those described in the literature.[10,24]

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