Model Studies Toward the Synthesis of Natural Indans Utilizing a Thallium(III)-Mediated Ring-Contraction Reaction

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Abstract: 6-Methoxy-1-tetralone was transformed in six steps into an indan derivative related to the sesquiterpenes mutisianthol and jungianol. Key steps involve a thallium(III)-promoted ring-contraction (to assemble the indan unit) and a Wittig olefination (to attach the side chain).

Key words: indan, jungianol, mutisianthol, ring contraction, thallium trinitrate

The synthesis of sesquiterpenes possessing a fused bicyclic system has been an important theme in organic chemistry for decades.[1] Synthetic targets include the indan ring system, which is present in phenolic sesquiterpenes such as mutisianthol[2–4] and jungianol[4,5] (Figure 1).

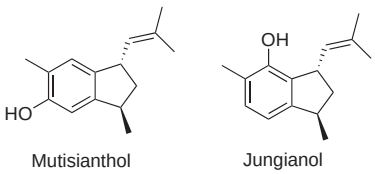
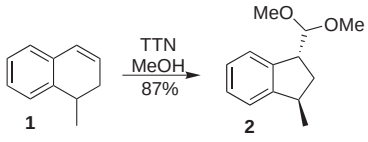


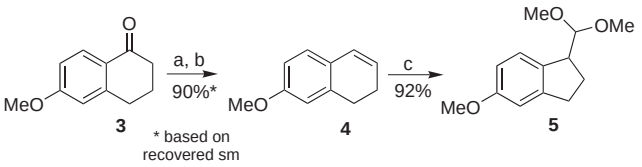
Figure 1 Structures of sesquiterpenes mutisianthol and jungianol

Recently, we found that the ring contraction of 1-methyl-1,2-dihydronaphthalene (**1**), promoted by thallium trinitrate (TTN), led to the indan **2**, as outlined in Scheme 1.[6] Such an indan shows the same relative configuration of mutisianthol and jungianol, as well as a protected aldehyde group, which could be used to introduce the olefin moiety present in the side chain. Thus, we consider the possibility of applying this ring contraction to the total syntheses of mutisianthol and of jungianol. A model study for these syntheses, namely the construction of the indan **15**, closely related to the target molecules, is presented here.



Scheme 1

The starting material for this study was the commercially available 6-methoxy-1-tetralone (**3**), which was transformed into the corresponding 1,2-dihydronaphthalene **4** by reduction followed by dehydration. The next step was the thallium(III)-promoted oxidative rearrangement of **4**, which gave the desired ring-contracted product **5** in excellent yield (Scheme 2).



Scheme 2 *Reagents and Conditions*: a) $NaBH_4$, MeOH, r.t.; b) *p*-TsOH, benzene, reflux; c) TTN, trimethyl orthoformate (TMOF), 0 °C

During the oxidation of **4**, the formation of non-rearranged products, such as dimethoxylated diols did not occur, in contrast to the results observed with other methoxy-substituted 1,2-dihydronaphthalenes previously investigated (**6** and **7**, Figure 2).[6] This different behavior can be attributed to the position of the methoxy group in the aromatic ring of **4**, which is prone to donate electrons to the migrating carbon, facilitating the rearrangement. The same effect is not possible for olefins **6** and **7**.

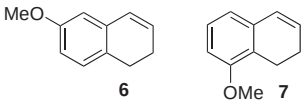
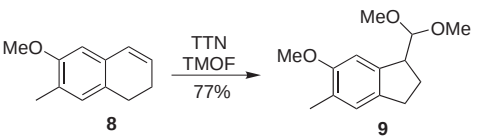


Figure 2 Structures of 6-methoxy-1,2-dihydronaphthalene (**6**) and 8-methoxy-1,2-dihydronaphthalene (**7**)

Similar to the olefin **4**, the 1,2-dihydronaphthalene **8**, when treated with TTN, afforded the indan derivative **9**, as the only product (Scheme 3).

Therefore, these results show that the presence of an electron-donating group at the *p*-position of the migrating car-



Scheme 3

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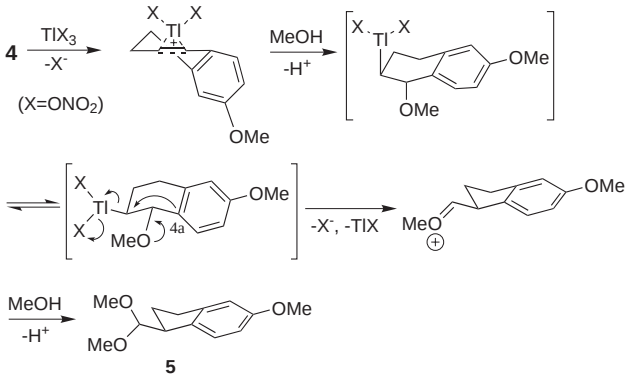
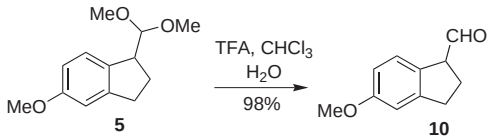
bon 4a plays an important role in the ring contraction of 1,2-dihydronaphthalenes. A plausible mechanism for such a rearrangement is exemplified for the olefin **4** in Scheme 4.[7]



Scheme 4

The next step in the synthetic sequence toward the target molecule **15** is the deprotection of the acetal group in **5**, which was done by treatment with trifluoroacetic acid affording the aldehyde **10** in 98% yield (Scheme 5). This reaction was also performed utilizing AcOH, however, a slightly lower yield (94%) was observed.

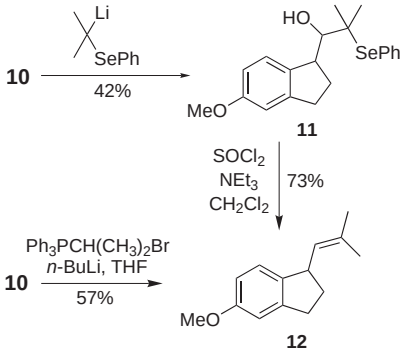


Scheme 5

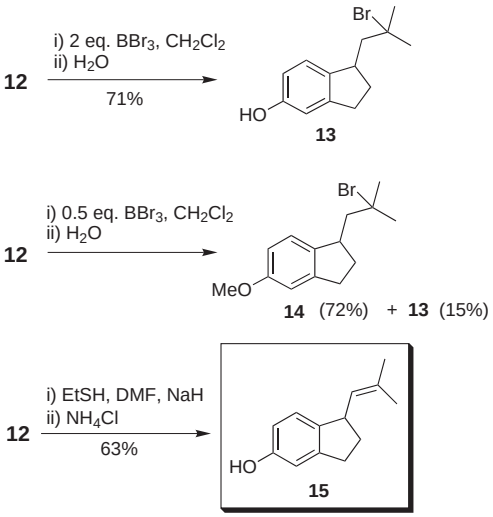
With the desired aldehyde **10** in hand, our attention turned toward the introduction of the olefin moiety, which proved to be the most difficult step in the synthetic sequence. Our first choice for the transformation of the aldehyde **10** into the olefin **12** was a Wittig reaction, which indeed gave the best result. However, good yields for this reaction were obtained only after significant experimentation of the reaction conditions, and during this time other approaches, such as Peterson olefination[8] and elimination of β-hydroxyselenides,[9,10] were also tested. Scheme 6 summarizes the two best conditions to prepare indan **12** from aldehyde **10**.

The last step to obtain the indan **15** was the cleavage of the methyl ether of **12** to the phenolic hydroxyl group. One of the most used reagents to achieve such a transformation is the Lewis acid, boron tribromide.[11] The desired deprotection did take place utilizing 2 equivalents of BBr_3 in CH_2Cl_2. However, addition of HBr to the double bond was also observed, and the bromide **13** was the only isolated product.

BBr_3 has already been used in the deprotection of phenolic ethers bearing an alkenyl moieties.[12,13] Even by decreasing the amount of BBr_3, addition to the double bond continued to be the predominant pathway giving the bromide **14** as the main product, together with minor amounts of **13**. Eventually, we succeeded in deprotecting **12** under basic conditions. Thus, treatment of **12** with sodium ethanethiolate gave the required indan derivative **15** in an acceptable yield (Scheme 7).



Scheme 6



Scheme 7

In summary, an efficient six-step sequence was developed to transform a commercially available tetralone into an indan possessing structural features of the natural sesquiterpenes mutisianthol and jungianol. The application of the present sequence, in conjunction with our previous studies for the construction of *trans*-1,3-disubstituted indans (see Scheme 1), should lead to an efficient approach to the mentioned target molecules.

Information concerning general experimental methods was recently published.[7a] **Warning!** Thallium salts are toxic and must be handled with care.

7-Methoxy-1,2-dihydronaphthalene (4)

To a stirred solution of the commercially available 6-methoxy-1-tetralone (0.503 g, 2.86 mmol) in anhyd EtOH (7 mL), was added $NaBH_4$ (54.7 mg, 1.45 mmol) in portions at r.t. The mixture was heated at the reflux temperature for 15 min. After cooling, the reaction was quenched with H_2O (7 mL) and the solvent was removed under reduced pressure. The remaining solution was extracted with

benzene (2 × 11 mL) and dried (Na_2SO_4). After filtration, a few crystals of *p*-TsOH were added to the filtrate and the mixture was heated for 3 h using a Dean–Stark apparatus. The organic phase was washed with 5% aq $NaHCO_3$ (2 ×), brine, and dried (Na_2SO_4). The solvent was removed under reduced pressure and the yellow oil obtained was chromatographed on silica gel (80–230 mesh, 20% EtOAc in hexanes) to afford **4**[14] (0.320 g, 71%) as a colorless oil, and 6-methoxy-1-tetralone (0.106 g, 21%).

1-Dimethoxymethyl-5-methoxyindan (5); Typical Procedure

To a stirred solution of **4** (2.26 g, 14.1 mmol) in TMOF (70 mL), was added TTN (6.90 g, 15.5 mmol) at 0 °C, which promptly dissolved. The mixture was stirred for 1 min at r.t. leading to an abundant precipitation. The resulting suspension was filtered through a silica gel pad (70–230 mesh, ca. 10 cm) using CH_2Cl_2 as eluent. The filtrate was washed with H_2O (2 ×), brine, and dried ($MgSO_4$). The solution was concentrated under reduced pressure to give a yellow oil which was purified by flash chromatography [silica gel 200–400 mesh, eluent: hexanes (80%), CH_2Cl_2 (10%) and EtOAc (10%)] to afford **5** (2.87 g, 92%) as a colorless oil.

IR (film): 1254, 2831 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.93–2.00 (m, 1 H), 2.17–2.24 (m, 1 H), 2.78–2.84 (m, 1 H), 2.88–2.94 (m, 1 H), 3.36 (s, 3 H), 3.37–3.40 (m, 1 H), 3.42 (s, 3 H), 3.77 (s, 3 H), 4.27 (d, *J* = 4.5 Hz, 1 H), 6.71 (dd, *J* = 5.0, 1.5 Hz, 1 H), 6.75 (d, *J* = 1.5 Hz, 1 H), 7.30 (d, *J* = 5.0 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.8, 31.6, 46.6, 52.9, 54.1, 55.3, 107.5, 109.7, 112.1, 126.0, 134.9, 146.3, 159.2.

MS: *m*/*z* (%) = 222 (M^+, 3), 75 (100).

Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.11; H, 7.85.

6-Methoxy-7-methyl-1,2-dihydronaphthalene (8)

To a stirred solution of 7-methoxy-6-methyl-3,4-dihydro-2*H*-naphthalen-1-one[15] (0.176 g, 0.927 mmol) in anhyd EtOH (2 mL) under N_2, was added $NaBH_4$ (0.0442 g, 1.17 mmol) in portions at 0 °C. The mixture was stirred for 26 h at r.t. and then the reaction was quenched with H_2O (3 mL) at 0 °C. Aq 10% HCl was added until pH 5. The organic phase was extracted with Et_2O (3 × 20 mL), and the combined organic layers were washed with sat. aq solution of $NaHCO_3$ (2 ×), brine and dried ($MgSO_4$). The crude product obtained by removal of the solvent under reduced pressure was purified by flash chromatography [silica gel 200–400 mesh, eluent: hexanes (80%) and EtOAc (20%)] to afford 7-methoxy-6-methyl-1,2,3,4-tetrahydronaphthalen-1-ol (0.142 g, 80%) as a white solid; mp 66.8–67.6 °C.

7-Methoxy-6-methyl-1,2,3,4-tetrahydronaphthalen-1-ol

^1H NMR (300 MHz, $CDCl_3$): δ = 1.68–2.01 (m, 5 H,), 2.17 (s, 3 H), 2.55–2.75 (m, 2 H), 3.80 (s, 3 H), 4.70 (t, *J* = 4.9 Hz, 1 H), 6.85 (s, 1 H), 6.88 (s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.8, 19.1, 28.3, 32.6, 55.4, 68.4, 109.6, 126.3, 128.5, 131.0, 137.0, 156.2.

To a stirred solution of 7-methoxy-6-methyl-1,2,3,4-tetrahydronaphthalen-1-ol (0.117 g, 0.610 mmol) in benzene (3 mL) were added a few crystals of *p*-TsOH. The mixture was stirred at r.t. for 4 h and then diluted with hexanes. The mixture was washed with an 5% aq solution of $NaHCO_3$ (2 ×), brine and dried ($MgSO_4$). Removal of the solvent under reduced pressure gave a colorless crude product which was purified by flash chromatography [silica gel 200–400 mesh, eluent: hexanes (95%) and EtOAc (5%)] to give **8** (0.0784 g, 74%) as a white solid; mp 49.6–50.4 °C.

8

IR (film): 1609, 1460, 707 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.18 (s, 3 H), 2.23–2.31 (m, 2 H), 2.66–2.71 (m, 2 H), 3.80 (s, 3 H), 5.97 (dt, 1 H, *J* = 9.6, 4.4 Hz), 6.41 (dt, 1 H, *J* = 9.6, 1.8 Hz), 6.53 (s, 1 H), 6.86 (s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.9, 23.6, 26.6, 55.5, 108.3, 124.8, 127.1, 127.8, 128.0, 129.9, 132.6, 156.3.

MS: *m*/*z* (%) = 174 (M^+, 100).

Anal. Calcd for $C_{12}H_{14}O$: C, 82.72, H, 8.10. Found: C, 82.51, H, 7.91.

1-Dimethoxymethyl-6-methoxy-5-methylindan (9)

The reaction was performed following the procedure above described for **5**, but using **8** (0.0510 g, 0.293 mmol), TMOF (1.5 mL), TTN·$3H_2O$ (0.143 g, 0.322 mmol) with a reaction time of 1 min. The crude product was purified by flash chromatography [silica gel 200–400 mesh, eluent: hexanes (80%), CH_2Cl_2 (10%) and EtOAc (10%)] to give the indan **9** (0.0533 g, 77%) as a colorless oil.

IR (film): 1121, 2830 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.90–2.02 (m, 1 H), 2.14–2.26 (m, 1 H), 2.18 (s, 3 H), 2.70–2.90 (m, 2 H), 3.38 (s, 3 H), 3.41–3.44 (m, 1 H), 3.44 (s, 3 H), 3.82 (s, 3 H), 4.30 (d, *J* = 7.7 Hz, 1 H), 6.95 (s, 1 H), 6.97 (s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.3, 27.9, 30.6, 47.6, 52.6, 54.3, 55.5, 107.4, 107.6, 125.3, 126.1, 136.1, 141.2, 156.6.

MS: *m*/*z* (%) = 236 (M^+, 8), 75 (100).

Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16, H, 8.53. Found: C, 71.22, H, 8.55.

5-Methoxyindan-1-carbaldehyde (10)

To a stirred solution of the acetal **5** (0.390 g, 1.76 mmol) in $CHCl_3$ (5 mL), was added an aq 50% solution of trifluoroacetic acid (2.5 mL) at 0 °C. The mixture was stirred for 20 min at 0 °C and for 2.5 h at r.t. A sat. aq solution of $NaHCO_3$ was added dropwise at 0 °C until pH 7 and the mixture was extracted with $CHCl_3$ (3 × 20 mL). The combined organic phases were washed with aq sat. solution of $NaHCO_3$, H_2O, and brine and dried (Na_2SO_4). The solution was concentrated under reduced pressure to give **10** (0.303 g, 98%) as a yellow oil.

IR (film): 1720 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.26–2.49 (m, 2 H), 2.89–3.07 (m, 2 H), 3.79 (s, 3 H,), 3.86 (ddd, *J* = 8.5, 5.8 , 3.0 Hz, 1 H), 6.77 (dd, *J* = 8.3, 2.5 Hz, 1 H), 6.83–6.84 (m, 1 H), 7.17 (d, *J* = 8.3 Hz, 1 H), 9.62 (d, *J* = 3.0 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.9, 32.0, 55.4, 57.1, 110.6, 112.7, 125.5, 130.4, 146.5, 160.1, 200.7.

MS: *m*/*z* (%) = 176 (M^+, 7), 147 (100).

HRMS: *m*/*z* Calcd for $C_{11}H_{12}O_2$: 176.0837. Found: 176.0816.

5-Methoxy-1-(2-methylpropenyl)indan (12)

Method A (via Wittig Reaction): To a stirred solution of Ph_3CHMe_2Br[16] (0.139 g, 0.362 mmol) in anhyd THF (2 mL) under N_2, was added dropwise BuLi (2.09 M in hexanes, 0.17 mL, 0.36 mmol) at 10 °C. The resulting red solution was stirred for 20 min at 10 °C. Then, a solution of the aldehyde **10** (0.0633 g, 0.360 mmol) in anhyd THF (2 mL) was added dropwise and the mixture was stirred for 30 min at 10 °C. The reaction was quenched with H_2O (3 mL) and extracted with Et_2O (3 × 20 mL). The combined organic phases were washed with brine and dried ($MgSO_4$). The solution was concentrated under reduced pressure to give a yellow solid. This was purified by flash chromatography [silica gel 200–400 mesh, eluent: hexanes (80%), CH_2Cl_2 (10%) and EtOAc (10%)] to

afford the starting material **10** (0.0048 g, 8%), and the product **12** (0.0411 g, 57%) as a colorless oil.

IR (film): 1606, 805 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.64–1.75 (m, 1 H), 1.76 (s, 3 H), 1.77 (s, 3 H), 2.26–2.36 (m, 1 H), 2.76–2.93 (m, 2 H), 3.78 (s, 3 H), 3.85–3.94 (m, 1 H), 5.12–5.17 (m, 1 H), 6.70 (dd, *J* = 8.2, 2.5 Hz, 1 H), 6.77–6.78 (m, 1 H), 6.95–6.98 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.2, 25.8, 32.0, 34.4, 43.5, 55.5, 109.9, 112.0, 124.5, 128.5, 132.0, 139.4, 145.4, 158.8.

MS: *m*/*z* (%) = 202 (M^+, 47), 187 (100).

HRMS: *m*/*z* Calcd for $C_{14}H_{18}O$: 202.1358. Found: 202.1370.

Method B (via Selenide Addition Followed by $SOCl_2$): To a stirred solution of 2,2-bis(phenylseleno)propane[17] (0.211 g, 0.595 mmol) in anhyd THF (1.0 mL) under N_2, was added dropwise BuLi (2.35 M in hexanes, 0.25 mL, 0.59 mmol) at –72 °C. The mixture was stirred for 7 min and a solution of the aldehyde **10** (0.105 g, 0.594 mmol) in anhyd THF (1.5 mL) was added. The mixture was stirred for 30 min at –72 °C. The reaction was quenched with an aq sat. solution NH_4Cl (3 mL) and allowed to warm to r.t. The aqueous phase was extracted with Et_2O (3 × 20 mL), washed with brine, and dried ($MgSO_4$). The solution was concentrated under reduced pressure to give a yellow oil, which was purified by flash chromatography (silica gel 200–400 Mesh, 20% EtOAc in hexanes) to afford **11** (0.0930 g, 42%) as a pale yellow oil.

11

IR (film): 1112, 3492 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.48 (s, 3 H), 1.49 (s, 3 H), 1.99–2.10 (m, 1 H), 2.30 (br, 1 H), 2.25–2.38 (m, 1 H), 2.76–2.87 (m, 1 H), 2.91–3.00 (m, 1 H), 3.44–3.49 (m, 1 H), 3.76 (s, 3 H), 3.97 (d, *J* = 1.4 Hz, 1 H), 6.69–6.76 (m, 2 H), 6.89–6.91 (m, 1 H), 7.30–7.44 (m, 3 H), 7.65–7.69 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.2, 25.9, 27.4, 32.5, 45.0, 54.6, 55.4, 77.5, 109.9, 112.6, 123.4, 127.2, 128.9, 128.9, 137.4, 138.3, 145.9, 159.1.

MS: *m*/*z* (%) = 376 (M^+, 0.5), 147 (100).

Anal. Calcd for $C_{20}H_{24}O_2Se$: C, 64.00; H, 6.44. Found: C, 64.17; H, 6.40.

To a stirred solution of the hydroxyselenide **11** (0.0894 g, 0.238 mmol) in anhyd CH_2Cl_2 (2 mL) under N_2, was added Et_3N (0.23 mL, 0.17 g, 1.7 mmol) at 20 °C. To this mixture was added a solution of $SOCl_2$ (0.03 mL, 0.06 g, 0.5 mmol) in CH_2Cl_2 (1 mL) and the mixture was stirred for 1 h at 20 °C. The reaction was quenched with aq sat. $NaHCO_3$ until pH 7. The solution was concentrated under reduced pressure and the resulting residue was diluted with Et_2O. The organic phase was washed with an aq sat. solution of $NaHCO_3$, brine and dried ($MgSO_4$). The solution was concentrated under reduced pressure to give a yellow oil which was purified by flash chromatography (silica gel 200–400 mesh, hexanes) to afford **12** (0.0353 g, 73%) as a colorless oil.

1-(2-Methylpropenyl)indan-5-ol (15)

To a stirred mixture of EtSH (0.40 mL, 5.4 mmol) and anhyd DMF (3 mL) under N_2 at 0 °C, was added NaH (0.204 g, 5.10 mmol, 60% in mineral oil). The mixture was stirred for 30 min at r.t. and was then added to a stirred solution of **12** (0.0461 g, 0.228 mmol) in DMF (1 mL). The resulting mixture was stirred for 3 h at 140 °C whereupon it became black in color. The mixture was cooled to r.t. and an aq sat. solution of NH_4Cl (4 mL) was added. EtOAc was added and the organic phase was washed with H_2O and brine, and dried ($MgSO_4$). The solution was concentrated under reduced pressure and the resulting black oil was purified by flash chromatography (30% EtOAc in hexanes) to give the impure starting material (0.026 g), and **15** (0.0270 g, 63%) as a yellow solid; mp 61.5–62.3 °C.

IR (film): 3786, 1222, 1671, 815 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.63–1.73 (m, 1 H), 1.76 (s, 3 H), 1.77 (s, 3 H), 2.25–2.35 (m, 1 H), 2.74–2.91 (m, 2 H), 3.87 (q, *J* = 8.7 Hz, 1 H), 4.56 (br, 1 H), 5.11–5,15 (m, 1 H), 6.61 (dd, *J* = 8.0, 2.4 Hz, 1 H), 6.69 (m, 1 H), 6.90 (d, *J* = 8.0 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.1, 25.8, 31.8, 34.3, 43.4, 111.3, 113.1, 124.7, 128.4, 132.0, 139.4, 145.7, 154.4.

MS: *m*/*z* (%) = 188 (M^+, 37), 173 (100).

HRMS: *m*/*z* Calcd for $C_{13}H_{16}O$: 188.1201. Found: 188.1243.

Acknowledgments

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References

(1) For examples, see: (a) Corey, E. J.; Cheng, X.-M. *The Logic of Chemical Synthesis*; Wiley: New York, **1989**. (b) Fraga, B. M. *Nat. Prod. Rep.* **2001**, *18*, 650.
(2) Bohlmann, F.; Zdero, C.; Le Van, N. *Phytochemistry* **1979**, *18*, 99.
(3) Ho, T.-L.; Lee, K.-Y.; Chen, C.-K. *J. Org. Chem.* **1997**, *62*, 3365.
(4) The relative configuration of mutisianthol and of jungianol was assigned by Bohlmann and co-workers[2,5] as *cis*. However, synthetic studies of Ho and his group[3] have shown that the correct configuration for mutisianthol is *trans*. Moreover, the same group proposed that jungianol might also have a *trans* relationship.
(5) Bohlmann, F.; Zdero, C. *Phytochemistry* **1977**, *16*, 239.
(6) Ferraz, H. M. C.; Silva, L. F. Jr.; Vieira, T. O. *Tetrahedron* **2001**, *57*, 1709.
(7) For additional aspects of the mechanism of thallium(III)-mediated ring contraction of 1,2-dihydronaphthalenes, see: (a) Ferraz, H. M. C.; Silva, L. F. Jr. *Tetrahedron* **2001**, *57*, 9939. (b) Ferraz, H. M. C.; Silva, L. F. Jr. *Synthesis* **2002**, 1033. (c) Silva, L. F. Jr. *Tetrahedron* **2002**, *58*, 9137.
(8) Cohen, T.; Sherbine, J. P.; Matz, J. R.; Hutchins, R. R.; McHenry, B. M.; Willey, P. R. *J. Am. Chem. Soc.* **1984**, *106*, 3245.
(9) Rémion, J.; Krief, A. *Tetrahedron Lett.* **1976**, 3743.
(10) Krief, A.; Dumart, W.; Clarembeau, M.; Bernard, G.; Badaoui, E. *Tetrahedron* **1989**, *45*, 2005.
(11) McOmie, J. F. W.; Watts, M. L.; West, D. E. *Tetrahedron* **1968**, *24*, 2289.
(12) Kopcho, J. J.; Schaeffer, J. C. *J. Org. Chem.* **1986**, *51*, 1620.
(13) Inoue, M.; Carson, M. W.; Frontier, A. J.; Danishefsky, S. J. *J. Am. Chem. Soc.* **2001**, *123*, 2289.
(14) Radcliffe, M. M.; Weber, W. P. *J. Org. Chem.* **1977**, *42*, 297.
(15) Zubaidha, P. K.; Chavan, S. P.; Racherle, U. S.; Ayyangar, N. R. *Tetrahedron* **1991**, *47*, 5759.
(16) Fagerlund, U. H. M.; Idler, D. R. *J. Am. Chem. Soc.* **1957**, *79*, 6473.
(17) Clarembeau, M.; Cravador, A.; Dumont, W.; Hevesi, L.; Krief, A.; Luchetti, J.; Van Ende, D. *Tetrahedron* **1985**, *41*, 4783.