Supporting Information to Accompany:

Asymmetric Total Synthesis of (+)-Aphanamol I via The Transition Metal Catalyzed Intramolecular [5+2] Cycloaddition of Allenes and Vinylcyclopropanes

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General methods. Air- and moisture-sensitive reactions were carried out in oven-dried glassware sealed with rubber septa under a positive pressure of dry nitrogen or argon from a manifold or balloon, unless otherwise indicated. Similarly sensitive liquids and solutions were transferred via syringe or stainless steel cannula. Reactions were stirred using Teflon-coated magnetic stir bars. Elevated temperatures were maintained using Thermowatch-controlled silicone oil baths. Organic solutions were concentrated using a Buchi rotary evaporator with a water aspirator or recirculating aspirator pump. Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone prior to use. Toluene was distilled from sodium prior to use. Wilkinson's catalyst ($RhCl(PPh_3)_3$) and silver triflate (AgOTf) were purchased through Aldrich and $[Rh(CO)_2Cl]_2$ was purchased through Pressure Chemicals. Analytical TLC was performed with 0.25 mm silica gel 60F plates with 254 nm fluorescent indicator from Merck. Plates were visualized by ultraviolet light and treatment with acidic *p*-anisaldehyde stain followed by gentle heating. Chromatographic purification of products was accomplished by flash chromatography, as described by Still and co-workers. Silica gel 60, 230-400 mesh was purchased from EM.

NMR spectra were measured on a Varian INOVA 500 (^1H at 500 MHz, ^{13}C at 125 MHz), Varian XL-400 (^1H at 400 MHz, ^{13}C at 100 MHz), Varian Gem-300 (^1H at 300 MHz, ^{13}C at 75 MHz), or Varian Gem-200 (^1H at 200 MHz, ^{13}C at 50 MHz) magnetic resonance spectrometer. Data for ^1H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, dddd = doublet of doublet of doublet of doublets, ddt = doublet of doublet of triplets, m = multiplet), coupling constant (Hz), and integration. Data for ^{13}C are reported in terms

of chemical shift relative to residual solvent peak. Infrared spectra were recorded on a Perkin-Elmer 1600 Series Fourier transform spectrometer (FTIR) and are reported in wavenumbers (cm^{-1}). High-resolution mass spectra (HRMS) were recorded at the NIH regional mass spectrometry facility at the University of California, San Francisco. Reported mass values are with error limits of ±13 millimass units. Elemental analyses (%C, %H) were determined by Desert Analytics, Tucson, Arizona. Reported atomic percentages are within error limits of ±0.4%.

Propargyl alcohol from methyl ester 2: To a cold (-78ºC), stirred solution of (Z/E)-1-bromopropene (0.19 ml, 2.25 mmol) in 8 ml dry THF was added *n*-BuLi (1.65M in hexane, 2.0 ml, 3.20 mmol) dropwise. The reaction mixture was stirred for 2 hours, then the methyl ester **2** (290 mg, 1.45 mmol) in 4 ml dry THF was added. The reaction mixture was stirred for additional 1.5 hours at -78^0C, then was warmed up to room temperature and quenched with saturated NH_4Cl aqueous solution. The aqueous layer was extracted with EtOAc twice and the combined organic extracts were washed with H_2O, brine and dried over $MgSO_4$. The solvent was removed by *vacuo* and the residue was directly used in the next step without further purification. ^{1}H-NMR (300MHz, $CDCl_3$/TMS): δ = 3.65 (s, 1H), 2.24 (ddd, J = 49 Hz, J = 15 Hz, J = 6 Hz, 2H), 2.05 (d, J = 11.5 Hz, 1H), 1.51-1.84 (m, 4H),1.41-1.50 (m, 1H), 1.43 (s, 3H), 0.86 (dd, J = 12 Hz, J = 7 Hz, 6H) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 174.46, 82.99, 79.20, 68.23, 68.20, 51.47, 41.28, 40.81, 40.74, 35.81, 30.02, 29.79, 25.97, 19.42, 18.48, 18.45, 3.42 ppm. IR (FT-IR, film): ν = 3456.0 (br), 2953.0 (m), 2869.2 (w), 2241.0 (w), 1733.1 (s), 1434.7 (m), 1366.7 (m), 1256.7 (m), 1162.5 (m), 1101.1 (m), 1010.7 (w), 937.4 (w), 879.8 (w) cm^{-1}. HRMS calcd. for $C_{14}H_{24}O_3$: 223.1698 (loss of OH). Found: 223.1704. Anal. calcd. for $C_{14}H_{24}O_3$: C: 69.96, H: 10.06. Found: C: 70.24, H: 10.07.

Propargyl acetate from methyl ester 2: To a stirred solution of the propargyl alcohol (from the previous procedure) in 10 ml dry CH_2Cl_2 was added DMAP (23 mg, 0.19 mmol), NEt_3 (0.26 ml, 1.90 mmol) and Ac_2O (0.18 ml, 1.90 mmol). The reaction mixture was stirred under N_2 at room temperature for 12 hours, then was diluted with EtOAc and the mixture was washed with H_2O, brine and dried over $MgSO_4$. The solvent was removed by *vacuo* and the residue was directly used in the

next step without further purification. ^{1}H-NMR (300MHz, $CDCl_3$/TMS): δ = 3.67 (s, 3H), 2.25 (ddd, *J* = 51.5 Hz, *J* = 15 Hz, *J* = 6 Hz, 2H), 2.00 (s, 3H), 1.69-1.96 (m, 4H), 1.62 (s, 3H), 1.34-1.58 (m, 2H), 0.87 (dd, *J* = 10 Hz, *J* = 6.5 Hz, 6H) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 174.20, 169.37, 81.13, 81.09, 79.35, 75.74, 75.67, 51.37, 40.68, 39.19, 35.73, 29.66, 29.60, 26.52, 25.36, 21.99, 19.40, 19.35, 18.43, 18.35, 3.58 ppm. IR (FT-IR, film): ν = 2953.0 (m), 2879.7 (w), 2241.0 (w), 1738.4 (s), 1460.9 (m), 1434.7 (m), 1366.7 (m), 1241.0 (s), 1162.5 (m), 1110.1 (w), 1052.6 (w), 1015.6 (m), 942.6 (w), 885.0 (w), 832.7 (w) cm^{-1}. HRMS calcd. for $C_{16}H_{26}O_4$: 223.1698 (loss of C_2H_3O). Found: 223.1690. Anal. calcd. for $C_{16}H_{26}O_4$: C: 68.06. H: 9.28. Found: C: 68.01. H: 9.35.

Allene Ester 3: To a cold (-30°C), stirred suspension of CuI (830 mg, 4.35 mmol) in 6 ml dry Et_2O was added MeLi (1.4M in Et_2O, 8.70 mmol) dropwise. The resultant colorless solution was stirred at -30°C for 1 hour then was cooled down to -78°C. The solution of the propargyl acetate (from the previous procedure) in 3 ml Et_2O was added and the reaction mixture was stirred for additional 20 min before being warmed up to room temperature. The reaction was quenched with sat. NH_4Cl aqueous solution and air was bubbled through the solution until the yellowish precipitates disappeared. The resultant blue solution was extracted with Et_2O (2 x 20 ml) and the combined organic extracts were washed by sat. $NaHCO_3$ aqueous solution, brine and dried over $MgSO_4$. The solvent was removed by *vacuo* and the residue was purified by flash chromatography (Et_2O: hexane 1:15) to give 236 mg (69%) of the allene ester **3** as a colorless oil over three steps.

Alternative one-step procedure of methyl ester **2** to allene ester **3**: To a stirred solution of titanocene dichloride (159 mg, 0.64 mmol) in 6 ml dry THF at –40°C under N_2 was added 0.5 M THF solution of 2-methyl propenyl magnesium bromide (2.56 ml, 1.28 mmol) dropwise. The resultant dark red solution was slowly warmed up to 0°C over 3 hours. The solution of the methyl ester **2** (64 mg, 0.32 mmol) in 2ml THF was added and the reaction mixture was stirred at room temperature overnight. 50 ml hexane and 30 ml 0.5N HCl aqueous solution were added and the reaction mixture was further stirred for 10 min. The mixture then was filtered through a pad of celite to remove the resultant yellow precipitates. The filtrate was washed with H_2O, brine and dried over $MgSO_4$. The solvent was removed by *vacuo* and the residue was purified by flash chromatography (Et_2O: hexane 1:15) to give

38 mg (51%) of the allene ester **3** as a colorless oil ^{1}H-NMR (300MHz, $CDCl_3$/TMS): δ = 3.66 (s, 3H), 2.23 (ddd, *J* = 36 Hz, *J* = 15 Hz, *J* = 7 Hz, 2H), 1.82-1.92 (m, 3H), 1.67-1.79 (m, 1H), 1.64 (s, 6H), 1.62 (s, 3H),1.40-1.50 (septet, *J* = 7 Hz, 1H), 1.24-1.38 (septet, *J* = 7 Hz, 1H), 0.85 (t, *J* = 7.5 Hz, 6H) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 198.89, 174.46, 96.43, 93.89, 51.31, 40.13, 39.90, 39.85, 35.65, 31.87, 29.48, 28.61, 20.94, 20.91, 19.27, 18.33, 18.27 ppm. IR (FT-IR, film): ν = 2956.4 (s), 2929.8 (s), 1740.2 (s), 1440.5 (m), 1367.2 (m), 1330.4 (w), 1251.5 (m) 1192.3 (m), 1156.6 (m), 1103.5 (w), 1019.6 (w), 881.5 (w), 842.1 (w) cm^{-1}. HRMS calcd. for $C_{15}H_{26}O_2$: 238.1933. Found: 238.1933.

Diol 5: To a cold (0ºC), stirred suspension of $LiAlH_4$ (8.61 g, 226.8 mmol) in 200 ml dry THF was added the solution of diethyl 1,1-cyclopropanedicarboxylate **4** (18.0 g, 113.4 mmol) in 30 ml dry THF dropwise. The reaction mixture was heated to reflux for 16 hours then was cooled down to 0ºC. 8.6 ml H_2O, 8.6 ml 15% NaOH aqueous solution and 25 ml H_2O were added consequently. The mixture was stirred for additional 3 hours, then was filtered and eluted with THF. The filtrate was dried over Na_2SO_4 and the solvent was removed by *vacuo* to give 11.4 g (99%) of the diol **5** as a colorless oil. Spectral data obtained are identical to the previously reported values.[11]

Benzyl mono-protected diol 6: To a stirred suspension of NaH (116 mg of 60% dispersion in mineral oil, 2.89 mmol) in 40 ml DMF was added the solution of the diol **5** (295 mg, 2.89 mmol) in 10 ml DMF dropwise at -10 ºC. The reaction mixture was stirred for 10 min, then the solution of BnBr (0.50 ml, 4.34 mmol) in 10 ml DMF was added. The reaction mixture was slowly warmed up to room temperature over 3 hours, then was partitioned between 70 ml EtOAc and 70 ml H_2O. The aqueous layer was further extracted with EtOAc (2 x 15 ml). The combined organic extracts were washed with H_2O, brine and dried over $MgSO_4$. The solvent was removed by *vacuo* and the residue was purified by flash chromatography (EtOAc: hexane 1:2) to give 438 mg (79%) of the benzyl-monoprotected diol **6** as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$/TMS): δ = 7.30-7.36 (m, 5H), 4.55 (s, 2H), 3.56 (d, *J* = 5.5 Hz, 2H), 3.46 (s, 2H), 2.48 (t, *J* = 5.5 Hz, 1H), 0.47-0.57 (dm, 4H) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 138.00, 128.45, 127.70, 73.10, 69.15, 22.49, 8.85 ppm. IR

(FT-IR, film): ν = 3389.3 (br), 3072.0 (w), 3001.5 (w), 2919.2 (w), 2860.5 (m), 1490.1(w), 1454.8 (w), 1413.7 (w), 1360.8 (w), 1202.1 (w), 1090.5 (s), 1067.0 (s), 1025.9 (s), 732.1 (m), 696.8 (m) cm^{-1}. Anal. calcd. for $C_{12}H_{16}O_2$: C: 74.96. H: 8.38. Found: C: 74.65. H: 8.39.

Aldehyde 7: To a cold (-78°C), stirred solution of oxalyl chloride (0.27 ml, 3.10 mmol) in 15 ml CH_2Cl_2 was added the solution of DMSO (0.44 ml, 6.20 mmol) in 2 ml CH_2Cl_2 dropwise. The reaction mixture was stirred for 10min, then the solution of the benzyl-monoprotected diol **6** (0.40 g, 2.1 mmol) in 5 ml CH_2Cl_2 was added. The reaction mixture was stirred for 30min at –78°C, then NEt_3 (1.44 ml, 10.3 mmol) was added. The resultant yellowish solution was warmed up to room temperature and diluted with 150ml 1:1 hexane: Et_2O. The organic layer was washed with H_2O, 1N HCl, sat. $NaHCO_3$ aqueous solution, brine and dried over $MgSO_4$. The solvent was removed by *vacuo* and the residue was purified by flash chromatography (Et_2O: hexane 1:4) to give 0.35 g (90%) of the aldehyde **7** as a colorless oil. ^{1}H-NMR (300MHz, $CDCl_3$/TMS): δ = 9.04 (s, 1H), 7.25-7.35 (m, 5H), 4.55 (s, 2H), 3.70 (s, 2H), 1.10-1.26 (dm, 4H) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 201.03, 138.04, 128.38, 127.67, 73.08, 69.46, 32.36, 12.77 ppm. IR (FT-IR, film): ν = 3064.0 (w), 3033.0 (w), 2857.0 (m), 2743.1 (w), 2712.0 (w), 1708.8 (s), 1491.4 (w), 1450.0 (w), 1362.0 (w), 1325.7 (w), 1242.9 (w), 1201.5 (w), 1097.9 (s), 1025.4 (m), 901.2 (m), 740.7 (m), 699.3 (m) cm^{-1}. Anal. calcd. for $C_{12}H_{14}O_2$: C: 75.76. H: 7.41. Found: C: 75.37. H: 7.40.

Aldol adduct 8: To a cold (-78°C), stirred solution of LDA (0.52 mmol) in 5 ml dry THF was added the solution of the allene ester **3** (70 mg, 0.29 mmol) in 3 ml THF. The solution was stirred for 2 hours then the solution of the aldehyde **7** (51 mg, 0.26 mmol) in 2 ml THF was added. The reaction mixture was further stirred for 10min then was quenched with sat. NH_4Cl aqueous solution at -78°C. The aqueous layer was extracted with Et_2O (2 x 10 ml) and the combined organic extracts were washed with H_2O, brine and dried over $MgSO_4$. The solvent was removed by *vacuo* and the residue was purified by flash chromatography (Et_2O: hexane 1:4) to give 91 mg (81%) of the aldol product **8** as a colorless oil. The major diastereomer was characterized. ^{1}H-NMR (300MHz, $CDCl_3$/TMS): δ = 7.26-7.38 (m, 5H), 4.51 (dd, *J* = 14.5 Hz, *J* = 12 Hz, 2H), 4.31 (dd, *J* = 10 Hz, *J* = 1.5 Hz, 1H), 3.58

(s, 3H), 3.44 (d, *J* = 8 Hz, 1H), 2.94-3.06 (m, 2H), 2.72 (d, *J* = 10 Hz, 1H), 1.88-2.05 (m, 3H), 1.70-1.86 (m, 2H), 1.64 (s, 6H), 1.62 (s, 3H), 1.32-1.52 (m, 1H), 0.90 (dd, *J* = 70 Hz, *J* = 7 Hz, 6H), 0.26-0.78 (qm, 4H) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 198.98, 174.20, 137.49, 128.51, 127.88, 127.72, 96.93, 93.37, 77.08, 75.51, 73.49, 50.82, 49.84, 41.91, 33.85, 29.61, 25.02, 23.20, 21.08, 21.00, 20.84, 19.10, 18.33, 11.56, 9.24 ppm. IR (FT-IR, film): ν = 3514.4 (m), 3072.0 (w), 2952.4 (s), 2872.2 (m), 1731.5 (s), 1439.3 (m), 1366.0 (m), 1245.8 (m), 1191.0 (m), 1151.4 (m), 1071.7 (s), 741.4 (m), 698.3 (m) cm^{-1}. HRMS calcd. for $C_{27}H_{40}O_4$: 428.2927. Found: 428.2920.

Acetate 9: To a stirred solution of the aldol product **8** (551 mg, 1.29 mmol) in 20 ml dry CH_2Cl_2 was added DMAP (32 mg, 0.26 mmol), NEt_3 (0.37 ml, 2.60 mmol) and Ac_2O (0.25 ml, 2.60 mmol). The reaction mixture was stirred under N_2 at room temperature for 24 hours, then was diluted with 150 ml Et_2O: hexane (1:1). The organic layer was washed with H_2O, brine and dried over $MgSO_4$. The solvent was removed by *vacuo* and the residue was directly used in the next step without further purification. The major diastereomer of **9** was characterized. ^{1}H-NMR (300MHz, $CDCl_3$/TMS): δ = 7.26-7.38 (m, 5H), 4.73 (d, *J* = 11 Hz, 1H), 4.49 (dd, *J* = 16.5 Hz, *J* = 12 Hz, 2H), 3.58 (s, 3H), 3.48 (dd, *J* = 24.5 Hz, *J* = 10.5 Hz, 2H), 3.31 (dd, *J* = 11 Hz, *J* = 2.5 Hz, 1H), 2.04 (s, 3H), 1.73-1.88 (m, 4H), 1.64 (s, 6H), 1.58 (s, 3H), 1.30-1.44 (m, 2H), 0.89 (dd, *J* = 34.5 Hz, *J* = 7 Hz, 6H), 0.47-0.79 (qm, 4H) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 199.06, 173.27, 170.37, 138.72, 128.27, 127.39, 96.54, 93.54, 77.14, 72.66, 72.48, 50.96, 47.19, 42.48, 33.77, 29.60, 25.38, 22.88, 21.07, 20.98, 20.91, 20.74, 18.86, 18.37, 10.14, 9.98 ppm. IR (FT-IR, film): ν = 2953.8 (m), 2902.9 (m), 2862.2 (m), 1739.5 (s), 1444.6 (m), 1363.3 (m), 1231.0 (s), 1154.8 (m), 1095.7 (m), 1023.2 (m), 981.9 (w), 737.3 (w), 697.1 (w) cm^{-1}. HRMS calcd. for $C_{29}H_{42}O_5$: 427.2484 (loss of C_3H_7). Found: 427.2489.

Allenyl Vinylcyclpropane 10:

To a stirred solution of the acetate **9** (from the previous procedure) in 60ml dry DMSO was added NaCN (632 mg, 13.0 mmol). The reaction mixture was heated to 130^{o}C for 72 hours, then was cooled down to room temperature. The reaction mixture was diluted with 150 ml Et_2O. The organic layer was washed with H_2O, brine and dried over $MgSO_4$. The solvent was removed by *vacuo* and

the residue was purified by flash chromatography (Et_2O: hexane 1:10) to give 230 mg (51%) of the allenyl vinylcyclopropane **10** as a colorless oil. ^{1}H-NMR (300MHz, $CDCl_3$/TMS): δ = 7.25-7.34 (m, 5H), 5.30 (d, *J* = 15.5 Hz, 1H), 5.18 (dd, *J* = 15.5 Hz, *J* = 9 Hz, 1H), 4.53 (s, 2H), 1.81-1.92 (m, 1H), 1.71-1.78 (m, 2H), 1.64 (s, 6H), 1.60 (m, 3H), 1.43-1.57 (m, 2H), 1.23-1.32 (s, 1H), 0.81 (dd, *J* = 14.5 Hz, *J* = 7 Hz, 6H), 0.59-0.67 (m, 4H) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 198.83, 138.61, 133.89, 129.78, 129.71, 128.27, 127.67, 127.41, 97.05, 93.68, 75.88, 72.54, 48.57, 48.43, 32.14, 31.91, 30.26, 30.14, 21.75, 21.08, 20.83, 19.63, 19.06, 18.97, 12.22, 12.12 ppm. IR (FT-IR, film): ν = 3066.2 (w), 2959.8 (s), 2921.2 (s), 2863.1 (s), 1957.7 (w), 1870.8 (w), 1662.7 (w), 1595.0 (w), 1445.1 (m), 1362.9 (m), 1309.7 (w), 1246.9 (w), 1203.4 (w), 1159.8 (w), 1097.0 (s), 1019.6 (w), 966.4 (w), 734.3 (m), 695.6 (m) cm^{-1}. HRMS: calcd. for $C_{25}H_{36}O$: 352.2766. Found: 352.2767. Anal. calcd. for $C_{25}H_{36}O$: C: 85.17. H: 10.29. Found: C: 84.90. H: 10.53.

Cycloadduct 13

To a base-washed, oven-dried, argon flushed schlenck glassware was added $[Rh(CO)_2Cl]_2$ (2.4 mg, 0.006 mmol), which was then dissolved in 6 ml anhydrous toluene under argon. The solution of allenyl vinylcyclopropane **10** (44 mg, 0.126 mmol) was added to the resultant yellowish solution and argon was bubbled through the solution for 15 min before being heated up to 110^{o}C. The reaction mixture was stirred at 110^{o}C for 30 min, then was cooled down to room temperature. The reaction mixture was filtered through a pad of neutral aluminum oxide with Et_2O as effluent. The solvent was removed by *vacuo* and the residue was purified by flash chromatography (Et_2O: hexane 1:10) to give 41mg (93%) cycloadduct **13** as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$/TMS): δ = 7.25-7.34 (m, 5H), 5.27 (br, 1H), 4.36 (dd, *J* = 23 Hz, , *J* = 11.5Hz, 2H), 3.83 (dd, *J* = 33 Hz, *J* = 11.5 Hz, 2H), 2.31-2.56 (m, 5H), 1.82-1.92 (m, 3H), 1.72 (s, 3H), 1.66 (s, 3H), 1.44-1.57 (m, 3H), 1.09 (s, 3H), 0.91 (dd, *J* = 18 Hz, *J* = 6 Hz, 6H) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 138.98, 138.68, 136.77, 135.10, 128.27, 127.80, 127.38, 123.39, 76.68, 70.38, 56.76, 56.21, 51.92, 38.66, 35.14, 30.29, 29.84, 28.12, 26.05, 23.11, 22.52, 22.10, 21.08 ppm. IR (FT-IR, film): ν = 3067.9 (w), 3026.4 (w), 2949.5 (s), 2870.6 (m), 1453.7 (m), 1364.9 (m), 1310.7 (w), 1251.5 (w), 1202.1 (w), 1167.6 (w), 1088.7 (m), 1069.0 (m), 1029.5 (w), 955.5 (w), 901.2 (w), 812.5 (w), 733.5 (m), 694.1 (m) cm^{-1}

HRMS calcd. for $C_{25}H_{36}O$: 352. 2766. Found: 352.2765. Anal. calcd. for $C_{25}H_{36}O$: C: 85.17. H: 10.29. Found: C: 84.93. H: 10.25.

Aldehyde 15: To a stirred solution of the cycloadduct **13** (100 mg, 0.284 mmol) in 14 ml CH_2Cl_2:H_2O (10:1) was added DDQ (327 mg, 1.42 mmol) at room temperature. The resultant suspension was stirred under N_2 at room temperature for 72 hours, then was partitioned between 100ml Et_2O and 50ml H_2O. The aqueous layer was further extracted with Et_2O (2 x 10 ml). The combined organic extracts were washed with H_2O, $NaHCO_3$ saturated aqueous solution, 10% $NaHSO_3$ aqueous solution, brine and dried over $MgSO_4$. The organic solvent was removed by *vacuo* and the residue was purified by flash chromatography (Et_2O: hexane 1:12) to give 64 mg (87%) of the aldeheyde **15** as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$/TMS): δ = 9.29 (s, 1H), 6.31 (d, *J* = 4 Hz, 3H), 2.26-2.80 (m, 4H), 1.94-2.00 (m, 1H), 1.73-1.85 (m, 2H), 1.70 (s, 3H), 1.65 (s, 3H), 1.47-1.63 (m, 4H), 1.15 (s, 3H), 0.94 (dd, *J* = 10.5 Hz, *J* = 6 Hz, 6H) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 196.16, 162.69, 141.91, 137.14, 125.07, 57.57, 56.18, 39.16, 35.05, 29.82, 29.69, 27.33, 26.39, 25.82, 23.22, 22.43, 22.14, 20.99 ppm. IR (FT-IR, film): ν = 29.45 (s), 2871.19 (m), 2703.4 (w), 1682.8 (s), 1640.7 (m), 1461.6 (m), 1372.0 (m), 1308.8 (w), 1240.4 (w), 1177.2 (m), 1077.1 (w), 1024.4 (w), 898.0 (w), 808.5 (w) cm^{-1}. HRMS calcd. for $C_{18}H_{28}O$: 260.2140. Found: 260.2148. Anal. calcd. for $C_{25}H_{36}O$: C: 83.02. H: 10.84. Found: C: 82.80. H: 11.15.

Keto-aldehyde 16:

To a cold (-78 ^{o}C), stirred solution of the aldehyde **15** (61 mg, 0.235 mmol) in 10 ml CH_2Cl_2 was added ozone-saturated CH_2Cl_2. The reaction was monitored closely by TLC. Right after the starting material spot dissappeared, dimethylsulfide (0.05 ml, 0.68 mmol) were added. After being warmed up to the room temperature, the reaction mixture was partitioned between 30 ml Et_2O and 30 ml H_2O. The aqueous layer was further extracted with 10 ml Et_2O. The combined organic extracts were washed with H_2O, brine and dried over $MgSO_4$. The solvent was removed by *vacuo* and the residue was purified by flash chromatography (EtOAc: hexane 1:10) to give 34 mg (61%) of the ketone **16** as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$/TMS): δ = 9.35 (s, 1H), 6.63 (d, *J* = 5.5 Hz, 1H),

2.69-2.82 (m, 2H), 2.38-2.56 (m, 2H), 2.16-2.24 (m, 1H), 1.78-1.94 (m, 2H), 1.60-1.71 (m, 1H), 1.38-1.48 (m, 3H), 1.33 (s, 3H), 0.94 (d, *J* = 6.5 Hz, 6H) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 192.73, 158.74, 143.77, 77.21, 59.62, 55.37, 53.15, 38.91, 35.11, 32.39, 26.81, 24.98, 21.98, 19.64, 19.48 ppm. IR (FT-IR, film): ν = 2953.0 (s), 2869.3 (m), 2816.9 (w), 2712.2 (w), 1686.0 (s), 1633.7 (m), 1455.7 (m), 1419.0 (w), 1371.9 (w), 1314.3 (w), 1251.5 (w), 1178.2 (w), 1068.3 (w), 942.6 (w), 911.2 (w), 790.8 (w) cm^{-1}. HRMS calcd. for $C_{15}H_{22}O_2$: 234.1620. Found: 234.1620.

(+)-Aphanamol I: To a cold (-78°C), stirred solution of the keto-aldehyde **16** (10 mg, 0.043 mmol) with $CeCl_3 \cdot 7H_2O$ (0.047 mmol) in 5 ml dry methanol was added the solution of $NaBH_4$ (1.78 mg, 0.047 mmol) in methanol dropwise. The reaction was followed by TLC. After the starting material was completely consumed, the reaction was quenched with 1 drop acetone and 20 ml Et_2O was added. The mixture was washed with H_2O, brine and dried over $MgSO_4$. The solvent was removed by *vacuo* and the residue was purified by flash chromatography (EtOAc: hexane 1:3) to give 9.8 mg (97%) of (+)-aphanamol I as a colorless oil. The spectra data obtained are identical to the reported values.[4, 5] (+)-Aphanamol I (**1**): reported: $[\alpha]_D$= +23°. Observed: $[\alpha]_D^{20}$ = +23° (C=0.4, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$/TMS): δ = 5.52 (d, *J* = 4.1 Hz, 1H), 4.03 (s, 2H), 2.79-2.86 (m, 1H), 2.37-2.61 (m, 2H), 2.27-2.35 (m, 2H), 2.02-2.18 (m, 1H), 1.71-1.84 (m, 1H), 1.40-1.69 (m, 4H), 1.31-1.38 (m, 2H), 1.27 (s, 3H), 0.91 (dd, *J* = 6.5 Hz, *J* = 3.7 Hz, 6H) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 213.67, 141.65, 132.96, 67.13, 58.91, 56.03, 51.44, 39.92, 34.51, 33.02, 27.07, 24.92, 24.68, 22.07, 19.94 ppm. IR (FT-IR, film): ν = 3396.2 (br), 2955.9 (s), 2870.3 (m), 1697.0 (s), 1460.6 (m), 1418.3 (w), 1381.2 (w), 1365.4 (w), 1254.3 (w), 1175.0 (w), 1074.5 (m), 1022.7 (m) cm^{-1}. HRMS calcd. for $C_{15}H_{24}O_2$: 236.1776. Found: 236.1776.