Synthetic Studies on Cyathins: Enantioselective Total Synthesis of (+)-Allocyathin B₂

Masashi Takano, Akinori Umino, and Masahisa Nakada*

Department of Chemistry, School of Science and Engineering, Waseda University

3-4-1 Ohkubo, Shinjuku-ku, Tokyo 169-8555, Japan

General Information. ¹H and ¹³C NMR spectra were recorded on a JEOL AL-400 spectrometer. ¹H and ¹³C chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ scale) with the solvent resonances as internal standards. The following abbreviations were used to explain the multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; sept, septet; m, multiplet; band, several overlapping signals; br, broad. IR spectra were recorded on a JASCO FT/IR-8300. Melting points (mp) are uncorrected, recorded on a Yamato capillary melting point apparatus. Optical rotations were measured using a 2 ml cell with a 1 dm path length on a JASCO DIP-1000. Mass spectra and elemental analyses were provided at the Materials Characterization Central Laboratory, Waseda University. All reactions were carried out under an argon atmosphere with dry, freshly distilled solvents under anhydrous conditions, unless otherwise noted. All reactions were monitored by thin-layer chromatography carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as visualizing agent and phosphomolybdic acid and heat as developing agents. E. Merck silica gel (60, particle size 0.040-0.063 mm) was used for flash column chromatography. Preparative thin-layer chromatography (PTLC) separations were carried out on self-made 0.3 mm E. Merck silica gel plates (60F-254).

Materials. THF was distilled from sodium/benzophenone ketyl, and methylene chloride (CH₂Cl₂), and acetonitrile from calcium hydride. Toluene was distilled from sodium. DMF was distilled from CaH₂ under reduced pressure.

(*R*)-2-(Mesitylsulfonyl)-3-methyl-3-((phenylthio)methyl)cyclopentanone

a mixture of diastereomers (1:6)

R_f =0.33 (hexane/ethyl acetate= 4/1); a white solid; ¹H NMR (400 MHz, CDCl₃) δ major: 7.38 (2H, d, J = 8.2 Hz), 7.29 (2H, dd, J = 8.2, 7.3 Hz), 7.20 (1H, t, J = 7.3 Hz), 6.96 (2H, s), 4.18 (1H, s), 3.60 (1H, d, J = 13.1 Hz), 3.34 (1H, d, J = 13.1 Hz), 2.65 (6H, s), 2.68-2.45 (2H, m), 2.30 (3H, s), 2.04-1.89 (2H, m), 1.66 (3H, s); minor: 7.45 (2H, d, J = 8.2 Hz), 7.29 (2H, dd, J = 8.2, 7.3 Hz), 7.20

(1H, t, J = 7.3 Hz), 6.96 (2H, s), 4.18 (1H, s), 3.82 (1H, d, J = 13.3 Hz), 3.58 (1H, d, J = 13.3 Hz), 2.63 (6H, s), 2.68-2.45 (2H, m), 2.30 (3H, s), 2.04-1.89 (2H, m), 1.66 (3H, s); IR (KBr) $\nu_{\max}$ 1752, 1306, 1138, 740, 693 cm^{-1} ; FAB-MASS $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{22}\text{H}_{27}\text{O}_3\text{S}_2$: 403.1402, found: 403.1382.

(S)-3-Methyl-3-((phenylthio)methyl)cyclopentanone (8)

R_f =0.35 (hexane/ethyl acetate = 4/1); a colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.36 (2H, d, J = 7.9 Hz), 7.27 (2H, dd, J = 7.9, 7.3 Hz), 7.18 (1H, t, J = 7.3 Hz), 3.07 (2H, s), 2.32 (1H, d, J = 18.1 Hz), 2.33-2.29 (2H, m), 2.08 (1H, d, J = 18.1 Hz), 2.03-1.98 (1H, m), 1.85-1.78 (1H, m), 1.20 (3H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 218.2, 137.1, 129.5, 128.9, 126.2, 51.2, 46.2, 41.1, 36.8, 34.4, 25.6; IR (neat) $\nu_{\max}$ 1742, 740, 692 cm^{-1} ; FAB-MASS $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{13}\text{H}_{17}\text{OS}$: 221.1000, found: 221.1003; $[\alpha]_D^{23}$ -9.2 (c 1.87, CHCl_3).

(S)-7-Methyl-7-phenylsulfanylmethyl-1,4-dioxaspiro[4.4]nonane

R_f =0.45 (hexane/ethyl acetate = 4/1); a colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.35 (2H, dt, J = 7.8, 1.2 Hz), 7.25 (2H, dd, J = 7.8, 7.4 Hz), 7.14 (1H, tt, J = 7.4, 1.2 Hz), 3.89-3.82 (4H, m), 3.05 (2H, s), 1.99-1.87 (2H, m), 1.97 (1H, d, J = 13.9 Hz), 1.81-1.74 (1H, m), 1.73 (1H, d, J = 13.9 Hz), 1.61-1.55 (1H, m), 1.19 (3H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 137.9, 129.0, 128.7, 125.5, 117.7, 64.2, 64.0, 48.7, 46.8, 41.7, 36.7, 35.7, 26.7; IR (neat) $\nu_{\max}$ 1338, 1112, 1026, 738, 690 cm^{-1} ; FAB-MASS $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{15}\text{H}_{21}\text{O}_2\text{S}$: 265.1262, found: 265.1260; $[\alpha]_D^{33}$ +21.5 (c 1.49, CHCl_3).

(S)-7-Benzenesulfinylmethyl-7-methyl-1,4-dioxaspiro[4.4]nonane

a mixture of diastereomers (1:1.1)

R_f =0.09 (hexane/ethyl acetate = 4/1); a pale yellow oil; ^1H NMR (400 MHz, CDCl_3) δ major:

7.65-7.62 (2H, m), 7.54-7.45 (3H, m), 3.92-3.87 (4H, m), 2.93 (1H, d, $J=12.3$ Hz), 2.78 (1H, d, $J=12.3$ Hz), 2.14-1.69 (6H, m), 1.42 (3H, s); minor 7.65-7.62 (2H, m), 7.54-7.45 (3H, m), 3.92-3.87 (4H, m), 2.96 (1H, d, $J=12.3$ Hz), 2.70 (1H, d, $J=12.3$ Hz), 2.14-1.69 (6H, m), 1.42 (3H, s); IR (neat) $\nu_{\max}$ 1340, 1152, 1090, 1038, 754, 692 cm^{-1} ; FAB-MASS $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{15}\text{H}_{21}\text{O}_3\text{S}$: 281.1211, found: 281.1208.

(S)-7-Methyl-1,4-dioxaspiro[4.4]nonane-7-carbaldehyde (5)

$R_f=0.45$ (hexane/ethyl acetate= 2/1); a pale yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 9.50 (1H, s), 3.94-3.87 (4H, m), 2.31 (1H, d, $J=14.2$ Hz), 2.17-2.08 (1H, m), 1.95 (1H, ddd, $J=13.4, 6.8, 6.8$ Hz), 1.83 (1H, ddd, $J=13.4, 6.8, 6.8$ Hz), 1.67 (1H, d, $J=14.2$ Hz), 1.58-1.51 (1H, m), 1.2 (3H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 203.2, 117.1, 64.2, 64.1, 51.1, 43.3, 35.1, 31.4, 21.3; IR (neat) $\nu_{\max}$ 1728, 1338, 1106, 1022 cm^{-1} ; FAB-MASS $[\text{M}+\text{H}]^+$ calculated for $\text{C}_9\text{H}_{15}\text{O}_3$: 171.1021, found: 171.1023; $[\alpha]_D^{22} +9.97$ (c 0.93, CHCl_3).

(2R,4aR,5S,8aS)-Hexahydro-2-(4-methoxyphenyl)-4a-methyl-4H-benzo[d][1,3]dioxin-5-ol (10)

$R_f=0.24$ (hexane/ethyl acetate= 2/1); a white solid mp 91.8-92.3 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.42 (2H, d, $J=8.8$ Hz), 6.89 (2H, d, $J=8.8$ Hz), 5.47 (1H, s), 4.47-4.43 (1H, m), 4.26 (1H, d, $J=11.5$ Hz), 3.80 (3H, s), 3.80 (1H, s), 3.40 (1H, d, $J=11.5$ Hz), 1.83-1.68 (4H, m), 1.58-1.50 (2H, m), 0.79 (3H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 159.9, 131.3, 127.4, 113.6, 101.7, 81.9, 72.9, 67.7, 55.3, 37.4, 30.4, 26.9, 20.0, 13.3; IR (KBr) $\nu_{\max}$ 3375, 1615, 1588, 1518, 1250, 1226, 1052, 825, 783 cm^{-1} ; FAB-MASS $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{16}\text{H}_{23}\text{O}_4$: 279.1596, found: 279.1594; $[\alpha]_D^{21} +52.8$ (c 1.04, CHCl_3).

((2R,4aS,5S,8aS)-Hexahydro-2-(4-methoxyphenyl)-4a-methyl-4H-benzo[d][1,3]dioxin-5-yloxy)(tert-butyl)dimethylsilane

R_f = 0.70 (hexane/ethyl acetate = 2/1); a white solid; mp 95.2-96.2 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.41 (2H, d, J = 8.7 Hz), 6.89 (2H, J = 8.7 Hz), 4.41 (1H, dd, J = 11.2, 4.4 Hz), 4.15 (1H, d, J = 11.2 Hz), 3.80 (3H, s), 3.80 (1H, s), 3.31 (1H, d, J = 11.2 Hz), 1.79-1.66 (4H, m), 1.58-1.48 (2H, m), 0.89 (9H, s), 0.75 (3H, s), 0.10 (3H, s), 0.09 (3H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 159.9, 131.6, 127.5, 113.6, 101.8, 82.1, 73.1, 68.3, 55.3, 38.0, 30.6, 26.9, 26.0, 19.9, 18.1, 13.7, -3.9, -4.9; IR (KBr) ν_{max} 1616, 1519, 1249, 1224, 1033, 774 cm^{-1} ; FAB-MASS $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{22}\text{H}_{37}\text{O}_4\text{Si}$: 393.2461, found: 393.2460; $[\alpha]_{\text{D}}^{22}$ +48.9 (c 1.01, CHCl_3).

[(1*S*,2*S*,6*S*)-2-(*tert*-Butyl-dimethyl-silanyloxy)-6-(4-methoxy-benzyloxy)-1-methyl-cyclohexyl]-methanol (11)

R_f = 0.62 (hexane/ethyl acetate = 2/1); a colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.25 (2H, d, J = 8.4 Hz), 6.88 (2H, d, J = 8.4 Hz), 4.53 (1H, d, J = 11.1 Hz), 4.25 (1H, d, J = 11.1 Hz), 4.02 (1H, dd, J = 9.5, 3.7 Hz), 3.79 (3H, s), 3.68 (1H, dd, J = 10.4, 8.1 Hz), 3.57 (1H, s), 3.39 (1H, d, J = 10.4 Hz), 3.20 (1H, br), 1.78-1.73 (1H, m), 1.64-1.43 (5H, m), 0.88 (9H, s), 0.84 (3H, s), 0.07 (3H, s), 0.04 (3H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 159.1, 130.0, 129.3, 113.8, 83.8, 70.4, 69.6, 68.9, 55.2, 44.0, 30.4, 25.8, 24.1, 18.8, 18.0, 15.5, -4.1, -5.0; IR (neat) ν_{max} 3516, 1614, 1516, 1252, 1038, 776 cm^{-1} ; FAB-MASS $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{22}\text{H}_{39}\text{O}_4\text{Si}$: 395.2618, found: 395.2615; $[\alpha]_{\text{D}}^{28}$ +68.6 (c 1.04, CHCl_3).

((1*S*,2*S*,3*S*)-3-(4-Methoxybenzyloxy)-2-(iodomethyl)-2-methylcyclohexyloxy)(*tert*-butyl)dimethylsilane (6)

R_f = 0.65 (hexane/ethyl acetate = 4/1); a white solid mp 53.3-54.1 °C; ^1H NMR (400 MHz, CDCl_3) δ

7.32 (2H, d, $J = 8.7$ Hz), 6.89 (2H, d, $J = 8.7$ Hz), 4.47 (1H, d, $J = 10.5$ Hz), 4.36 (1H, d, $J = 10.5$ Hz), 3.85-3.82 (1H, m), 3.82 (3H, s), 3.66 (1H, d, $J = 9.0$ Hz), 3.52- 3.51 (1H, m), 3.45 (1H, d, $J = 9.0$ Hz), 1.78-1.70 (1H, m), 1.62-1.41 (5H, m), 0.98 (3H, s), 0.87 (9H, s), 0.02 (3H, s), 0.01 (3H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 159.0, 131.1, 129.3, 113.6, 80.7, 72.5, 71.1, 55.3, 43.5, 31.4, 25.9, 23.7, 22.1, 19.0, 18.0, -3.8, -4.8 ; IR (KBr) ν_{max} 1613, 1515, 1251, 1093, 771, 560 cm^{-1} ; FAB-MASS $[\text{M}-\text{H}]^+$ calculated for $\text{C}_{22}\text{H}_{36}\text{IO}_3\text{Si}$: 503.1478, found: 503.1484; $[\alpha]_{\text{D}}^{22} +76.6$ (c 1.05, CHCl_3).

2-[(1*S*,2*S*,6*S*)-2-(*tert*-Butyl-dimethyl-silanyloxy)-6-(4-methoxy-benzyloxy)-1-methyl-cyclohexyl]-1-[(7*S*)-7-methyl-1,4-dioxo-spiro[4.4]non-7-yl]-ethanol (12)

a mixture of diastereomers (2:1)

$R_f = 0.21$ (hexane/ethyl acetate = 4/1); a colorless oil; ^1H NMR (400 MHz, CDCl_3) δ major: 7.23 (2H, d, $J = 8.5$ Hz), 6.86 (2H, d, $J = 8.5$ Hz), 4.57 (1H, d, $J = 11.4$ Hz), 4.41 (1H, br), 4.33 (1H, d, $J = 11.4$ Hz), 3.93-3.85 (4H, m), 3.81 (3H, s), 3.61-3.56 (1H, m), 3.50-3.48 (1H, m), 3.43-3.42 (1H, m), 1.98-1.37 (14H, m), 1.03 (3H, s), 0.96 (3H, s), 0.86 (9H, s), 0.01 (6H, s); minor: 7.23 (2H, d, $J = 8.5$ Hz), 6.86 (2H, d, $J = 8.5$ Hz), 4.52 (1H, d, $J = 11.2$ Hz), 4.26 (1H, d, $J = 11.2$ Hz), 3.93-3.85 (5H, m), 3.81 (3H, s), 3.61-3.56 (1H, m), 3.50-3.48 (1H, m), 1.98-1.37 (14H, m), 1.01 (3H, s), 1.00 (3H, s), 0.88 (9H, s), 0.04 (3H, s), 0.03 (3H, s); IR (neat) ν_{max} 3432, 1516, 1336, 1252, 1034, 776 cm^{-1} ; FAB-MASS $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{31}\text{H}_{53}\text{O}_6\text{Si}$: 549.3611, found: 549.3633.

Dithiocarbonic Acid *O*-[2-[(1*S*,2*S*,6*S*)-2-(*tert*-Butyl-dimethyl-silanyloxy)-6-(4-methoxy-benzyloxy)-1-methyl-cyclohexyl]-1-((7*S*)-7-methyl-1,4-dioxo-spiro[4.4]non-7-yl)-ethyl] Ester *S*-Methyl Ester (13)

a mixture of diastereomers (1:1.5)

$R_f = 0.48$ (hexane/ethyl acetate = 4/1); an yellow oil; ^1H NMR (400 MHz, CDCl_3) δ major: 7.33 (2H, d, $J = 8.5$ Hz), 6.89 (2H, d, $J = 8.5$ Hz), 6.05 (1H, d, $J = 9.8$ Hz), 4.41 (1H, d, $J = 11.0$ Hz), 4.27 (1H, d,

$J=11.0$ Hz), 3.94-3.82 (5H, m), 3.83 (3H, s), 3.49-3.47 (1H, m), 2.48 (3H, s), 2.31-1.39 (14H, m), 1.18 (3H, s), 1.02 (3H, s), 0.88 (9H, s), 0.03 (6H, s); minor: 7.27 (2H, d, $J=8.5$ Hz), 6.88 (2H, d, $J=8.5$ Hz), 6.05 (1H, d, $J=9.8$ Hz), 4.52 (1H, d, $J=11.0$ Hz), 4.33 (1H, d, $J=11.0$ Hz), 3.94-3.82 (4H, m), 3.82 (3H, s), 3.72-3.70 (2H, m), 2.55 (3H, s), 2.31-1.39 (14H, m), 1.11 (3H, s), 0.94 (3H, s), 0.88 (9H, s), 0.03 (3H, s), 0.01 (3H, s); IR (neat) $\nu_{\max}$ 1616, 1516, 1338, 1250, 1042, 776 cm^{-1} ; FAB-MASS $[M-H]^+$ calculated for $\text{C}_{33}\text{H}_{55}\text{O}_6\text{S}_2\text{Si}$: 637.3053, found: 637.3067.

(+)-*tert*-Butyl-((1*S*,2*S*,3*S*)-3-(4-methoxy-benzyloxy)-2-methyl-2-((*S*)-2-(7-methyl-1,4-dioxaspiro [4.4]non-7-yl)-ethyl)-cyclohexyloxy)-dimethyl-silane (14)

$R_f=0.31$ (hexane/ethyl acetate=10/1); colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.25 (2H, d, $J=8.5$ Hz), 6.86 (2H, d, $J=8.5$ Hz), 4.48 (1H, d, $J=11.2$ Hz), 4.23 (1H, d, $J=11.2$ Hz), 3.89-3.81 (4H, m), 3.80 (3H, s), 3.69 (1H, dd, $J=8.8, 3.6$ Hz), 3.40 (1H, dd, $J=5.6, 1.7$ Hz), 1.93-1.80 (2H, m), 1.73-1.40 (11H, m), 1.38 (1H, ddd, $J=12.7, 12.5, 3.6$ Hz), 1.28 (1H, ddd, $J=12.7, 12.5, 4.6$ Hz), 1.18 (1H, ddd, $J=12.7, 12.5, 3.6$ Hz), 0.99 (3H, s), 0.87 (9H, s), 0.84 (3H, s), 0.02 (3H, s), 0.01 (3H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 158.8, 131.4, 128.9(2C), 118.2, 113.5(2C), 79.8, 74.4, 70.3, 64.1, 63.9, 55.3, 49.4, 42.5, 40.3, 37.4, 35.6, 35.2, 30.2, 29.7, 26.1, 25.9(2C), 23.7, 18.8, 18.1, 17.6, -3.9, -4.7; IR (neat) $\nu_{\max}$ 1616, 1516, 1250, 1040, 774 cm^{-1} ; FAB-MS $[M+H]^+$ calculated for $\text{C}_{31}\text{H}_{52}\text{O}_5\text{Si}$: 533.3662, found : 533.3653; $[\alpha]_D^{21.9} +59.3$ (c 1.04, CHCl_3).

(+)-(*S*)-3-(2-((1*R*,2*S*,6*S*)-2-(4-Methoxybenzyloxy)-6-hydroxy-1-methylcyclohexyl)ethyl)-3-methylcyclopentanone

$R_f=0.17$ (hexane/ethyl acetate=2/1); a white solid; mp 79.7-80.7 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.23 (2H, d, $J=8.5$ Hz), 6.86 (2H, d, $J=8.5$ Hz), 4.51 (1H, d, $J=11.2$ Hz), 4.17 (1H, d, $J=11.2$ Hz), 3.80 (3H, s), 3.77 (1H, dd, $J=10.3, 4.4$ Hz), 3.41 (1H, dd, $J=3.7, 1.5$ Hz), 2.29-2.13 (2H, m), 2.04 (1H, d, $J=18.1$ Hz), 1.99 (1H, d, $J=18.1$ Hz), 1.83-1.51 (10H, m), 1.45 (1H, ddd, $J=12.5, 12.0, 4.4$ Hz).

Hz), 1.33 (1H, ddd, $J=12.7, 11.0, 4.6$ Hz), 1.27 (1H, ddd, $J=12.7, 12.0, 4.4$ Hz), 1.01 (3H, s), 0.88 (3H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 220.0, 158.9, 131.0, 128.8(2C), 113.6(2C), 79.6, 73.9, 70.0, 55.3, 52.5, 42.0, 39.4, 36.8, 34.9, 34.3, 30.2, 29.9, 25.1, 23.2, 18.7, 16.3; IR (KBr) ν_{max} 3309, 1742, 1615, 1512, 1244, 1047, 814 cm^{-1} ; FAB-MS $[\text{M}]^+$ calculated for $\text{C}_{23}\text{H}_{34}\text{O}_4$: 374.2457, found : 374.2455; $[\alpha]_{\text{D}}^{24.9} +59.4$ (c 0.97, CHCl_3).

(+)-(2*S*,3*S*)-3-(4-Methoxybenzyloxy)-2-methyl-2-(2-((*S*)-1-methyl-3-oxocyclopentyl)ethyl)cyclohexanone (4)

$R_f=0.36$ (hexane/ethyl acetate=2/1); a colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.22 (2H, d, $J=8.5$ Hz), 6.86 (2H, d, $J=8.5$ Hz), 4.56 (1H, d, $J=11.5$ Hz), 4.31 (1H, d, $J=11.5$ Hz), 3.80 (3H, s), 3.40 (1H, dd, $J=6.8, 3.4$ Hz), 2.43-2.20 (4H, m), 2.02 (1H, d, $J=10.5$ Hz), 2.00 (1H, d, $J=10.5$ Hz), 2.05-1.91 (2H, m), 1.78-1.70 (3H, m), 1.65 (1H, ddd, $J=13.4, 12.9, 4.4$ Hz), 1.60-1.52 (2H, m), 1.26 (1H, ddd, $J=12.9, 12.9, 5.1$ Hz), 1.12 (3H, s), 1.06 (1H, ddd, $J=13.4, 13.2, 4.4$ Hz), 1.02 (3H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 219.5, 213.5, 159.0, 130.2, 129.1(2C), 113.6(2C), 83.0, 70.9, 55.2, 53.8, 52.3, 39.3, 37.8, 36.7, 34.9, 34.7, 26.9, 24.8, 24.1, 20.4, 19.7; IR (neat) ν_{max} 1738, 1708, 1614, 1516, 1250, 1036, 822 cm^{-1} ; FAB-MS $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{23}\text{H}_{33}\text{O}_4$: 373.2379, found : 373.2380; $[\alpha]_{\text{D}}^{22.5} +24.7$ (c 0.99, CHCl_3).

(+)-(3*aS*,5*aS*,6*S*,9*aR*,9*bR*)-6-(4-Methoxybenzyloxy)-decahydro-9*a*-hydroxy-3*a*,5*a*-dimethyl-2*H*-cyclopenta[*a*]naphthalen-1(9*bH*)-one (15)

$R_f=0.28$ (hexane/ethyl acetate=4/1); colorless crystal; mp 134.6-136.8 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.24 (2H, d, $J=8.5$ Hz), 6.85 (2H, d, $J=8.5$ Hz), 5.77 (1H, br), 4.54 (1H, d, $J=11.2$ Hz), 4.33 (1H, d, $J=11.2$ Hz), 3.79 (3H, s), 3.52 (1H, dd, $J=11.7, 4.4$ Hz), 2.55 (1H, ddd, $J=19.5, 12.0, 9.5$ Hz), 2.32 (1H, dd, $J=19.5, 8.8$ Hz), 2.02-1.94 (1H, m), 1.90-1.86 (1H, m), 1.82-1.48 (8H, m), 1.46-1.35 (2H, m), 1.28 (3H, s), 1.26 (1H, s), 0.91 (3H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 225.5, 158.7, 131.3, 128.9(2C), 113.5(2C), 81.9, 77.1, 71.6, 62.5, 55.2, 44.2, 40.6, 37.1, 36.3, 35.6, 29.5,

28.8, 25.6, 23.7, 19.2, 18.7; IR (KBr) $\nu_{\max}$ 3405, 1707, 1615, 1514, 1253, 1078, 819 cm^{-1} ; FAB-MS $[\text{M}]^+$ calculated for $\text{C}_{23}\text{H}_{32}\text{O}_4$: 372.2301, found : 372.2309; $[\alpha]_{\text{D}}^{21.1} +138.6$ (c 0.97, CHCl_3).

(+)-(3a*S*,5a*R*,6*S*,9b*R*)-6-(4-Methoxybenzyloxy)-3,3a,4,5,5a,6,7,8-octahydro-3a,5a-dimethyl-2H-cyclopenta[*a*]naphthalen-1(9bH)-one (16)

$R_f=0.36$ (hexane/ethyl acetate=4/1); pale yellow crystal; mp 134.2-135.9 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.26 (2H, d, $J=8.5$ Hz), 6.86 (2H, d, $J=8.5$ Hz), 5.42 (1H, dd, $J=4.2$, 3.2 Hz), 4.58 (1H, d, $J=11.7$ Hz), 4.38 (1H, d, $J=11.7$ Hz), 3.80 (3H, s), 3.17 (1H, dd, $J=4.2$, 1.7 Hz), 2.45 (1H, ddd, $J=19.5$, 11.7, 9.0 Hz), 2.36 (1H, ddd, $J=9.3$, 1.7, 1.7 Hz), 2.32-2.20 (3H, m), 2.09-2.01 (1H, m), 1.92-1.79 (3H, m), 1.70-1.61 (2H, m), 1.31 (1H, ddd, $J=13.9$, 6.3, 2.9 Hz), 1.15 (3H, m), 0.96 (1H, ddd, $J=13.7$, 3.4, 3.4 Hz), 0.84 (3H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 219.5, 158.7, 133.9, 131.3, 128.8(2C), 127.5, 113.5(2C), 80.6, 70.6, 65.4, 55.2, 40.4, 38.9, 35.6, 35.1, 29.1, 28.4, 26.0, 26.0, 21.6, 21.0; IR (KBr) $\nu_{\max}$ 1739, 1613, 1511, 1246, 1079, 826 cm^{-1} ; FAB-MS $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{23}\text{H}_{31}\text{O}_3$: 355.2273, found : 355.2291; $[\alpha]_{\text{D}}^{25.8} +126.9$ (c 1.03, CHCl_3).

(-)-(3a*S*,5a*R*,6*S*)-6-(4-Methoxybenzyloxy)-2,3,3a,4,5,5a,6,7,8,9-decahydro-3a,5a-dimethyl-cyclopenta[*a*]naphthalen-1-one (17)

$R_f=0.45$ (hexane/ethyl acetate=4/1); a colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.23 (2H, d, $J=8.6$ Hz), 6.85 (2H, d, $J=8.6$ Hz), 4.51 (1H, d, $J=11.4$ Hz), 4.27 (1H, d, $J=11.4$ Hz), 3.99 (1H, ddd, $J=13.2$, 1.2, 1.2 Hz), 3.80 (3H, s), 3.33 (1H, s), 2.52 (1H, ddd, $J=14.1$, 14.1, 2.9 Hz), 2.42 (1H, ddd, $J=18.9$, 12.1, 8.6 Hz), 2.20 (1H, dd, $J=18.9$, 8.6 Hz), 1.90-1.71 (5H, m), 1.70-1.61 (2H, m), 1.52-1.44 (2H, m), 1.13 (3H, s), 1.07 (3H, m), 1.03 (1H, ddd, $J=13.5$, 3.3, 3.3 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 208.4, 158.6, 153.0, 137.6, 130.9, 128.7(2C), 113.4(2C), 83.4, 70.4, 55.3, 42.5, 40.6, 36.9, 35.3, 33.4, 29.2, 25.9, 25.2, 23.6, 22.8, 21.6; IR (neat) $\nu_{\max}$ 1704, 1626, 1516, 1250, 1072, 822 cm^{-1} ; FAB-MS $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{23}\text{H}_{31}\text{O}_3$: 355.2273, found : 355.2273; $[\alpha]_{\text{D}}^{25.0} -139.8$ (c 1.03, CHCl_3).

(+)-(1R,3aS,5aR,6S,9bR)-6-(4-Methoxybenzyloxy)-2,3,3a,4,5,5a,6,7,8,9b-decahydro-3a,5a-dimethyl-1-(prop-1-en-2-yl)-1H-cyclopenta[a]naphthalen-1-ol (18)

$R_f=0.38$ (hexane/ethyl acetate=10/1); a colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.26 (2H, d, $J=8.8$ Hz), 6.86 (2H, d, $J=8.8$ Hz), 5.25 (1H, dd, $J=3.4$, 3.2 Hz), 4.89 (1H, d, $J=1.0$ Hz), 4.79 (1H, dd, $J=1.5$, 1.2 Hz), 4.57 (1H, d, $J=12.0$ Hz), 4.40 (1H, d, $J=12.0$ Hz), 3.79 (3H, s), 3.18 (1H, dd, $J=2.9$, 2.4 Hz), 2.40 (1H, s), 2.28-2.18 (1H, m), 2.20 (1H, ddd, $J=13.9$, 13.9, 3.4 Hz), 2.04-1.62 (7H, m), 1.78 (3H, d, $J=0.7$ Hz), 1.59-1.51 (2H, m), 1.32 (1H, dddd, $J=13.4$, 3.4, 3.4, 1.2 Hz), 1.10 (3H, s), 1.08 (3H, s), 0.88 (1H, ddd, $J=13.4$, 3.4, 3.4 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 158.8, 150.7, 136.1, 131.4, 129.0(2C), 127.5, 113.5(2C), 109.1, 85.6, 81.4, 70.7, 58.6, 55.2, 41.0, 40.8, 37.7, 37.0, 32.2, 29.0, 28.7, 27.8, 21.8, 20.5, 20.0; IR (neat) ν_{max} 3564, 1614, 1516, 1248, 1082, 820 cm^{-1} ; FAB-MS $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{26}\text{H}_{37}\text{O}_3$: 397.2743, found : 397.2751; $[\alpha]_{\text{D}}^{23.5} +11.6$ (c 1.02, CHCl_3).

(+)-(1S,3aS,5aR,6S,9bR)-2,3,3a,4,5,5a,6,7,8,9b-Decahydro-1-isopropyl-3a,5a-dimethyl-1H-cyclopenta[a]naphthalene-1,6-diol

$R_f=0.29$ (hexane/ethyl acetate=4/1); a white solid; mp 45.2-46.8°C; ^1H NMR (400 MHz, CDCl_3) δ 5.49 (1H, dd, $J=3.7$, 2.9 Hz), 3.47 (1H, br), 2.34-2.23 (1H, m), 2.28 (1H, s), 2.17-2.00 (3H, m), 1.95 (1H, ddd, $J=14.2$, 13.4, 3.2 Hz), 1.86 (1H, ddd, $J=12.5$, 9.5, 3.7 Hz), 1.78 (1H, ddd, $J=13.9$, 7.8, 3.7 Hz), 1.70-1.55 (4H, m), 1.35 (1H, ddd, $J=11.2$, 8.5, 8.5 Hz), 1.28-1.23 (1H, m), 1.13 (1H, s), 1.12 (3H, s), 1.03 (1H, ddd, $J=13.4$, 3.4, 3.4 Hz), 1.01 (3H, s), 0.97 (3H, d, $J=6.8$ Hz), 0.93 (3H, d, $J=6.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 138.0, 127.3, 85.5, 74.7, 58.4, 41.1, 40.0, 38.2, 37.0, 31.6, 31.1, 28.9, 27.7, 27.7, 24.4, 20.9, 18.9, 17.5; IR (KBr) ν_{max} 3415, 1295, 1062 cm^{-1} ; FAB-MS $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{18}\text{H}_{31}\text{O}_2$: 279.2324, found : 279.2321; $[\alpha]_{\text{D}}^{22.5} +53.4$ (c 1.01, CHCl_3).

(-)-(1*S*,3*aS*,5*aR*,9*bR*)-2,3,3*a*,4,5,5*a*,7,8-Octahydro-1-hydroxy-1-isopropyl-3*a*,5*a*-dimethyl-1*H*-cyclopenta[*a*]naphthalen-6(9*bH*)-one (19)

R_f =0.38 (hexane/ethyl acetate=4/1); a white solid; mp 74.8-76.2°C; ^1H NMR (400 MHz, CDCl_3) δ 5.70 (1H, dd, J =6.1, 2.9 Hz), 2.71 (1H, ddd, J =16.4, 7.8, 4.2 Hz), 2.64-2.55 (1H, m), 2.43-2.34 (1H, m), 2.33 (1H, s), 2.31-2.23 (1H, m), 1.96-1.88 (1H, m), 1.84-1.73 (3H, m), 1.67-1.51 (3H, m), 1.38-1.32 (1H, m), 1.31 (3H, s), 1.28-1.03 (2H, m), 1.00 (3H, d, J =6.8 Hz), 0.96 (3H, d, J =6.8 Hz), 0.94 (3H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 215.3, 140.6, 127.8, 86.2, 59.0, 48.2, 40.8, 37.9, 35.9, 34.4, 32.7, 32.3, 29.3, 27.6, 23.4, 23.3, 18.9, 17.5; IR (KBr) ν_{max} 3527, 1702, 1201 cm^{-1} ; FAB-MS $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{18}\text{H}_{29}\text{O}_2$: 277.2168, found : 277.2177; $[\alpha]_{\text{D}}^{21.1}$ -113.7 (c 1.01, CHCl_3).

(+)-(3*aR*,5*aR*)-2,3,3*a*,4,5,5*a*,7,8-Octahydro-1-isopropyl-3*a*,5*a*-dimethylcyclopenta[*a*]naphthalen-6-one (3)

R_f =0.36 (hexane/ethyl acetate=20/1); a colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 5.48 (1H, dd, J =4.2, 3.9 Hz), 2.87 (1H, sept, J =6.8 Hz), 2.71 (1H, ddd, J =13.9, 7.1, 4.9 Hz), 2.51-2.40 (3H, m), 2.33 (1H, dd, J =9.5, 6.1 Hz), 2.32 (1H, dd, J =9.5, 3.7 Hz), 1.80-1.51 (6H, m), 1.15 (3H, s), 1.00 (3H, d, J =6.8 Hz), 0.97 (3H, d, J =6.8 Hz), 0.91 (3H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 215.6, 142.0, 139.4, 137.7, 120.9, 48.6, 48.3, 39.4, 36.3, 35.8, 31.4, 28.3, 26.5, 25.5, 23.0, 22.9, 21.6, 21.6; IR (neat) ν_{max} 1716 cm^{-1} ; FAB-MS $[\text{M}-\text{H}]^+$ calculated for $\text{C}_{18}\text{H}_{25}\text{O}$: 257.1905, found : 257.1895; $[\alpha]_{\text{D}}^{21.5}$ +270.8 (c 0.98, CHCl_3).

(+)-(3*aR*,5*aR*)-Methyl

3,3*a*,4,5,5*a*,8-hexahydro-6-hydroxy-1-isopropyl-3*a*,5*a*-dimethyl-2*H*-cyclopenta[*a*]naphthalene-7-carboxylate

$R_f=0.51$ (hexane/ethyl acetate=20/1); a colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 12.38 (1H, s), 5.33 (1H, dd, $J=3.9, 3.4$ Hz), 3.78 (3H, s), 3.00 (1H, dd, $J=21.5, 4.4$ Hz), 2.93 (1H, dd, $J=21.5, 3.2$ Hz), 2.83 (1H, sept, $J=6.8$ Hz), 2.32 (1H, dd, $J=9.5, 6.6$ Hz), 2.31 (1H, dd, $J=9.5, 3.4$ Hz), 1.96 (1H, ddd, $J=13.4, 3.7, 3.4$ Hz), 1.84-1.76 (1H, m), 1.74 (1H, ddd, $J=12.2, 6.1, 3.7$ Hz), 1.64 (1H, dd, $J=8.5, 3.4$ Hz), 1.57-1.51 (1H, m), 1.22 (3H, s), 0.99 (3H, d, $J=6.8$ Hz), 0.96 (3H, d, $J=6.8$ Hz), 0.92 (3H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 176.1, 173.0, 141.4, 138.2, 135.9, 118.0, 92.9, 51.5, 48.0, 40.5, 39.5, 36.7, 32.4, 28.4, 26.5, 25.1, 23.2, 23.0, 21.7, 21.5; IR (neat) ν_{max} 1678, 1658, 1616, 1248 cm^{-1} ; FAB-MS $[\text{M}]^+$ calculated for $\text{C}_{20}\text{H}_{28}\text{O}_3$: 316.2038, found : 316.2042; $[\alpha]_{\text{D}}^{20.1} +116.3$ (c 0.90, CHCl_3).

(+)-(3a*R*,5a*R*,7*R*)-Methyl

3,3a,4,5,5a,6,7,8-octahydro-7-(iodomethyl)-1-isopropyl-3a,5a-dimethyl-6-oxo-2H-cyclopenta[*a*]naphthalene-7-carboxylate (20)

$R_f=0.36$ (hexane/ethyl acetate=20/1); white solid; mp 78.8-81.6°C; ^1H NMR (400 MHz, CDCl_3) δ 5.50 (1H, dd, $J=4.4, 4.2$ Hz), 3.81 (1H, d, $J=9.8$ Hz), 3.76 (3H, s), 3.52 (1H, d, $J=9.8$ Hz), 3.25 (1H, dd, $J=17.6, 4.2$ Hz), 2.88 (1H, sept, $J=6.8$ Hz), 2.39 (1H, dd, $J=17.6, 4.4$ Hz), 2.34-2.32 (2H, m), 1.77-1.51 (6H, m), 1.07 (3H, s), 1.02 (3H, d, $J=6.8$ Hz), 0.96 (3H, d, $J=6.8$ Hz), 0.91 (3H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 208.2, 169.1, 143.2, 138.0, 136.7, 118.1, 59.4, 52.7, 49.0, 48.0, 39.2, 36.1, 33.6, 32.0, 28.5, 26.5, 23.2, 22.4, 21.6, 21.6, 9.0; IR (KBr) ν_{max} 1743, 1700, 562 cm^{-1} ; FAB-MS $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{21}\text{H}_{30}\text{IO}_3$: 457.1240, found : 457.1251; $[\alpha]_{\text{D}}^{21.1} +195.3$ (c 1.04, CHCl_3).

(+)-(3a*R*,5a*R*,8*S*(or8*R*),10*Z*)-Methyl

2,3,3a,4,5,5a,6,7,8,9-decahydro-1-isopropyl-3a,5a-dimethyl-6-oxocyclohepta[e]indene-8-carboxylate (21)

major : $R_f=0.17$ (hexane/ethyl acetate=10/1); a colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 5.47 (1H, dd, $J=7.7, 7.5$ Hz), 3.73 (3H, s), 3.38 (1H, dd, $J=11.2, 9.7$ Hz), 2.99 (1H, ddd, $J=18.5, 9.7, 1.3$ Hz), 2.83 (1H, sept, $J=6.8$ Hz), 2.71 (1H, dd, $J=11.2, 1.1$ Hz), 2.38-2.29 (4H, m), 1.97 (1H, ddd, $J=13.0, 13.0, 5.5$ Hz), 1.73 (1H, ddd, $J=12.5, 6.6, 4.8$ Hz), 1.69-1.53 (3H, m), 1.19 (1H, ddd, $J=13.6, 3.5, 3.5$ Hz), 1.10 (3H, s), 1.02 (3H, s), 1.00 (3H, d, $J=6.8$ Hz), 0.95 (3H, d, $J=6.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 213.7, 173.8, 143.6, 140.6, 137.3, 120.8, 55.2, 52.1, 48.0, 42.2, 38.5, 37.9, 36.4, 32.6, 28.3, 26.6, 26.1, 23.6, 21.7, 21.5, 18.5; IR (neat) ν_{max} 1738, 1712 cm^{-1} ; FAB-MS $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{21}\text{H}_{31}\text{O}_3$: 331.2273, found : 331.2267; $[\alpha]_{\text{D}}^{26.0} +270.5$ (c 0.89, CHCl_3).

minor : $R_f=0.24$ (hexane/ethyl acetate=10/1); a white solid; mp 79.8-82.3°C; ^1H NMR (400 MHz, CDCl_3) δ 5.41 (1H, dd, $J=7.9, 7.2$ Hz), 3.71 (3H, s), 3.47 (1H, dd, $J=10.8, 10.8$ Hz), 3.07 (1H, dddd, $J=10.8, 6.8, 6.8, 1.8$ Hz), 2.81 (1H, sept, $J=6.8$ Hz), 2.50-2.42 (2H, m), 2.38-2.22 (3H, m), 2.05 (1H, ddd, $J=13.2, 13.2, 5.3$ Hz), 1.74 (1H, ddd, $J=12.5, 6.6, 4.8$ Hz), 1.66-1.58 (3H, m), 1.16 (1H, ddd, $J=13.6, 3.5, 3.5$ Hz), 1.10 (3H, s), 1.05 (3H, s), 0.99 (1H, d, $J=6.8$ Hz), 0.93 (1H, d, $J=6.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 214.3, 173.9, 143.7, 140.3, 137.2, 119.7, 55.4, 52.1, 48.0, 42.4, 38.4, 38.1, 36.5, 32.7, 28.3, 26.6, 26.0, 23.6, 21.6, 21.6, 18.5; IR (KBr) ν_{max} 1745, 1703 cm^{-1} ; FAB-MS $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{21}\text{H}_{31}\text{O}_3$: 331.2273, found : 331.2267; $[\alpha]_{\text{D}}^{24.9} +241.1$ (c 1.06, CHCl_3).

(+)-(3a*R*,5a*R*,8*E*,10*Z*)-Methyl

2,3,3a,4,5,5a,6,7-octahydro-1-isopropyl-3a,5a-dimethyl-6-oxocyclohepta[e]indene-8-carboxylate (2)

$R_f=0.24$ (hexane/ethyl acetate=10/1); a pale yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.27 (1H, dd, $J=6.1, 2.0$ Hz), 5.95 (1H, d, $J=6.1$ Hz), 3.86 (1H, dd, $J=11.0, 0.5$ Hz), 3.79 (3H, s), 3.39 (1H, ddd, $J=11.0, 2.0, 1.0$ Hz), 2.87 (1H, sept, $J=6.8$ Hz), 2.40 (2H, dd, $J=9.0, 5.6$ Hz), 2.02 (1H, ddd, $J=13.0, 13.0, 4.2$ Hz), 1.80-1.55 (4H, m), 1.44 (1H, ddd, $J=13.4, 4.2, 4.2$ Hz), 1.17 (3H, s), 1.05 (3H, d,

$J=6.8$ Hz), 1.02 (3H, s), 1.00 (3H, d, $J=6.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 205.2, 166.3, 148.7, 144.2, 139.6, 135.8, 123.7, 121.9, 56.9, 52.5, 49.3, 40.8, 38.6, 36.0, 34.2, 28.6, 26.8, 23.8, 22.4, 21.6, 21.6; IR (neat) ν_{max} 1716, 1590 cm^{-1} ; FAB-MS $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{21}\text{H}_{29}\text{O}_3$: 329.2117, found : 329.2113; $[\alpha]_{\text{D}}^{26.1} +53.1$ (c 0.92, CHCl_3).

(+)-(3a*R*,5a*R*,6*S*,8*E*,10*Z*)-2,3,3a,4,5,5a,6,7-Octahydro-8-(hydroxymethyl)-1-isopropyl-3a,5a-dimethylcyclohepta[e]inden-6-ol

$R_f=0.14$ (hexane/ethyl acetate=2/1); a colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 6.04 (1H, m), 5.60 (1H, d, $J=8.3$ Hz), 4.11 (1H, s), 3.59 (1H, m), 2.83 (1H, sept, $J=6.8$ Hz), 2.73 (1H, d, $J=17.6$ Hz), 2.59 (1H, dd, $J=17.6, 5.9$ Hz), 2.46 (1H, ddd, $J=13.9, 9.3, 9.3$ Hz), 2.37-2.32 (2H, m), 1.74-1.54 (4H, m), 1.24 (1H, ddd, $J=12.6, 3.5, 3.5$ Hz), 1.00 (3H, d, $J=6.8$ Hz), 0.95 (3H, s), 0.94 (3H, d, $J=6.8$ Hz), 0.93 (3H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 143.8, 143.2, 141.9, 138.0, 121.7, 119.3, 74.6, 68.8, 48.3, 47.2, 38.6, 36.8, 34.1, 32.9, 28.6, 26.9, 26.2, 23.8, 21.6, 21.6; IR (neat) ν_{max} 3364, 1596 cm^{-1} ; FAB-MS $[\text{M}]^+$ calculated for $\text{C}_{20}\text{H}_{30}\text{O}_2$: 302.2246, found : 302.2248; $[\alpha]_{\text{D}}^{28.8} +110.0$ (c 0.95, CHCl_3).

(+)-(3a*R*,5a*R*,6*S*,8*E*,10*Z*)-2,3,3a,4,5,5a,6,7-Octahydro-6-hydroxy-1-isopropyl-3a,5a-dimethylcyclohepta[e]indene-8-carbaldehyde (allocyathin B₂) (1)

$R_f=0.28$ (hexane/ethyl acetate=4/1); a pale yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 9.45 (1H, s), 6.81 (1H, dd, $J=8.1, 2.4$ Hz), 5.94 (1H, d, $J=8.1$ Hz), 3.72 (1H, dd, $J=8.5, 6.1$), 3.16 (1H, dd, $J=18.3, 5.9$ Hz), 2.83 (1H, sept, $J=6.8$ Hz), 2.55 (1H, d, $J=18.6$ Hz), 2.57-2.48 (1H, m), 2.45-2.37 (2H, m), 1.77-1.63 (4H, m), 1.34 (1H, ddd, $J=13.9, 3.7, 3.4$ Hz), 1.05 (3H, d, $J=6.8$ Hz), 1.00 (3H, s), 0.97 (3H, d, $J=6.8$ Hz), 0.96 (3H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 194.2, 155.1, 146.2, 144.3, 141.9, 137.9, 119.3, 74.2, 49.1, 48.3, 38.5, 36.5, 33.8, 29.2, 29.0, 26.9, 26.4, 23.8, 21.6, 21.6; IR (neat) ν_{max} 3586, 1684, 1570 cm^{-1} ; FAB-MS $[\text{M}]^+$ calculated for $\text{C}_{20}\text{H}_{28}\text{O}_2$: 300.2089, found : 300.2086; $[\alpha]_{\text{D}}^{29.6} +85.3$ (c 0.97, CH_3OH).

ORTEP Drawing of **15**