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Total Syntheses of (±)-Cyclolaurene, (±)-Epicyclolaurene and (±)-β-Cuparenones

Adusumilli Srikrishna* and Kathiresan Krishnan

Department of Organic Chemistry, Indian Institute of Science Bangalore - 560 012, INDIA.

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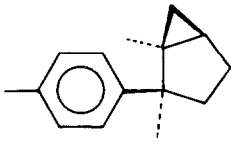
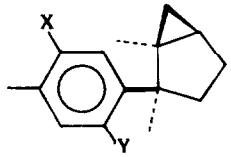
***ABSTRACT**: The first total synthesis of (±)-cyclolaurene (1) and (±)-epicyclolaurene (5), and a new route to (±)-β-cuparenone (4) are reported. Thus, orthoester Claisen rearrangement of the cinnamyl alcohol 8 furnished the ene-ester 10. Anhydrous $CuSO_4$ catalysed intramolecular cyclopropanation of the diazoketone derived from the ene-acid 7, generated a diastereoisomeric mixture of cyclopropyl ketone 6. The Huang-Minlon reduction of the ketones 6a and 6b furnished the cyclolaurene (1) and epicyclolaurene (5), whereas regiospecific ring cleavage using lithium in liquid ammonia furnished the β-cuparenone (4).*

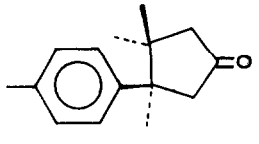
Recently, Higa and Ichiba have reported[1] the isolation of cyclolaurene 1, the parent hydrocarbon of tricyclic aromatic sesquiterpenes[2] laurinterols 2, from the sea hare, *Aplysia dactylomela* along with cyclolaurenols 3 and cupalaurenols. The structure and the absolute configuration of cyclolaurene was established from the spectral data and chemical correlation with cyclolaurenol. The bicyclic sesquiterpene, β-cuparenone 4, was first isolated[3] from the ketonic fraction of *Thuja orientalis*, and later on its presence was detected in various essential oils. The cuparenoids, aplysins and their analogues, present an interesting synthetic challenge[4] owing to the presence of two vicinal quaternary carbon atoms on the cyclopentane ring. In continuation[5] of our interest in the synthesis of natural products containing multiple quaternary carbon atoms, using Claisen rearrangement and intramolecular diazoketone cyclopropanation as key reactions, herein we describe the first total synthesis of (±)-cyclolaurene (1) and its epimer 5, and a new route to (±)-β-cuparenone (4).



1



2. X = Br or H; Y = OH
3. X = OH or OAc; Y = Br



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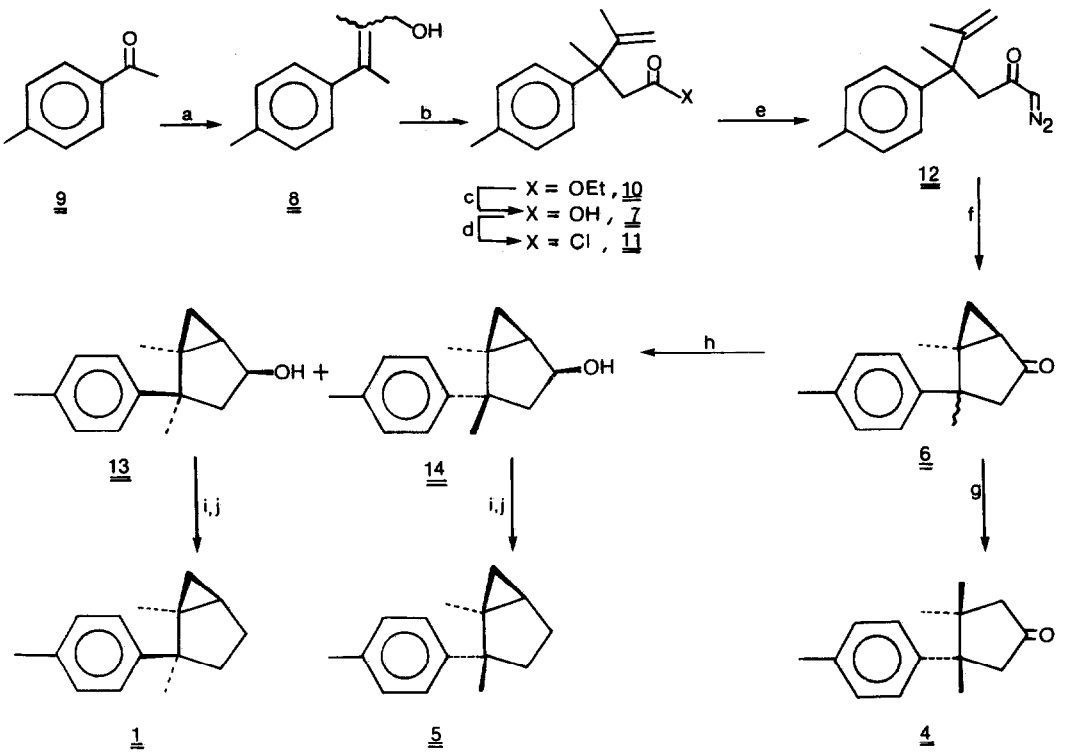
The retrosynthetic sequence based on intramolecular diazoketone cyclopropanation and orthoester Claisen rearrangement, readily identified the cyclopropyl ketone **6**, and the olefin acid **7** as common intermediates for cyclolaurenes **1**, **5** and β-cuparenone (**4**). The synthetic sequence is depicted in the Scheme 1. The starting material required for the orthoester Claisen rearrangement, the cinnamyl alcohol **8** was readily obtained[6] from p-methylacetophenone (**9**) via Wittig-Horner-Emmons reaction (NaOEt, EtOH, triethyl phosphonopropionate), followed by LAH reduction of the resultant ester. The orthoester Claisen rearrangement[7] of the allyl alcohol **8** with triethyl orthoacetate in the presence of a catalytic amount of propionic acid in

SCHEME 1



REAGENTS: (a) Ref. 6; (b) $MeC(OEt)_3$, EtCOOH, Sealed tube, 160°C, 36 hrs; (c) MeOH, 10% aq. NaOH, reflux, 8 hrs; (d) C_6H_6, $(COCl)_2$, RT, 5 hrs; (e) Et_2O, CH_2N_2, RT, 3 hrs; (f) Anhydrous $CuSO_4$, C_6H_{12}, 5.5 hrs; (g) Li, liq. NH_3, 15 min; (h) $NaBH_4$, MeOH, 10 hrs (i) PCC, NaOAc, CH_2Cl_2, 3 hrs; (j) NH_2NH_2, Digol, $(CH_2OH)_2$, reflux, 0.5 hrs; Na in digol, reflux, 5 hrs.

toluene (160°C, 36 hrs) furnished, in 68% yield, the ene-ester 10, generating the first quaternary carbon. Base catalysed hydrolysis of the ester 7 produced the first key intermediate, the ene-acid 7. The second quaternary carbon was created using an intramolecular diazoketone cyclopropanation reaction.[8] Thus, treatment of the acid chloride 11, obtained from the acid 10 and oxalyl chloride, with an excess of ethereal diazomethane furnished the diazoketone 12. Anhydrous copper sulphate catalysed decomposition of the diazoketone 12 in refluxing (using a 100W tungsten lamp) cyclohexane, and intramolecular insertion of the resultant ketocarbene into the olefin, furnished, an inseparable 1:2 diastereoisomeric mixture of the cyclopropyl ketone 6. The structure and the ratio of the epimers of 6 was delineated from the ^{1}H and ^{13}C NMR spectra. But more conclusive evidence came from its conversion to β-cuparenone (4). Thus, regiospecific cyclopropane ring cleavage[9] of the diastereoisomeric mixture of the cyclopropyl ketone 6 with lithium in liquid ammonia furnished the β-cuparenone (4), which exhibited the spectral data (IR & ^{1}H NMR) identical with that reported[3] in the literature. To resolve the diastereoisomers of 6 we have resorted to the chemical modification, to the corresponding alcohols. Thus, stereospecific sodium borohydride reduction of the diastereoisomeric mixture of 6 in methanol, furnished a separable mixture of the *endo* alcohols 13 and 14. Oxidation of the alcohols 13 and 14 with buffered (NaOAc) pyridinium chlorochromate (PCC) generated the cyclopropyl ketones 6a and 6b. The stereochemical assignments for 6a and 6b were arrived on the basis of the ^{1}H NMR signals, in particular the upfield methyl signal for 6b at δ 0.88 ppm, typical in the cuparenoids[3] for the vicinal methyl *cis* to aromatic group. Finally, Huang-Minlon modified Wolff-Kishner reduction of the cyclopropyl ketones 6a and 6b, furnished the cyclolaurene (1) and epicyclolaurene (5).

In conclusion, we have reported here the first total synthesis of cyclolaurene and epicyclolaurenes, and a new route to β-cuparenone, using orthoester Claisen rearrangement and intramolecular diazoketone cyclopropanation reactions for the construction of the two quaternary centres.

EXPERIMENTAL SECTION

IR spectra were recorded on a Hitachi 270-50 spectrophotometer. ^{1}H (90, 200, 270 MHz) and ^{13}C NMR (22.5 MHz) spectra were recorded on Jeol FX-90Q, Brucker ACF-200 and WH-270 spectrometers, and the chemical shift (δ ppm) and coupling constants (Hz) are reported in standard fashion with reference to either internal tetramethylsilane (for ^{1}H) or the central line (77.1 ppm) of $CDCl_3$ (for ^{13}C). High and low resolution mass measurements were carried out on a Jeol JMS-DX 303 GC-MS instrument using a direct inlet mode. Acme's silica gel (100-200 mesh) was used for column chromatography. Cinnamyl alcohol 8 was prepared according to the literature procedure.[6]

Ethyl 3,4-dimethyl-3-(4-methylphenyl)-pent-4-enoate (10):

A mixture of the cinnamyl alcohol **8** (1.232 g, 7 mmol), triethyl orthoacetate (2.285 g, 14 mmol) and a catalytic amount of propionic acid in 2 ml toluene was placed in a Carius tube under nitrogen atmosphere and heated to 160°C for 36 hrs. The reaction mixture was cooled, poured into water and extracted with benzene (40 ml x 3). The benzene extract was washed with 10% aq. HCl (20 ml x 2) followed by saturated aqueous $NaHCO_3$ solution (10 ml) and dried over anhydrous Na_2SO_4. Evaporation of the solvent and purification of the residue on a silica gel (8 g) column using ethyl acetate - hexane (1:20) as eluent furnished the ester **10** (1.17 g, 68%) as a colourless oil. IR (neat): ν_{max} 1740, 1641, 1515, 1446, 1374, 1320, 1179, 1092,1071, 1032, 894, 816 cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$): δ 7.1 (4 H, br s, aromatic), 4.96 (2 H, s, olefinic), 4.0 (2 H, q, J = 7.2 Hz, $OC\underline{H}_2CH_3$), 2.84 (2 H, s, CH_2CO), 2.32 (3 H, s, Ar–Me), 1.6 (3 H, s, C_3–Me), 1.56 (3 H, s, olefinic Me), 1.12 (3 H, t, J = 7.2 Hz, $OCH_2C\underline{H}_3$). ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 171.5 (s, O–C=O), 150.3 (s, $\underline{C}=CH_2$), 142.9 (s), 135.4 (s), 128.8 (2 C, d) and 126.1 (2 C, d) (aromatic), 110.7 (t, $C=\underline{C}H_2$), 59.8 (t, $O\underline{C}H_2CH_3$), 46.0 (s, benzylic), 44.3 (t, $\underline{C}H_2COO$), 25.6 (q, C_3–Me), 20.8 (q, olefinic Me), 20.2 (q, Ar–Me), 14.0 (q, $OCH_2\underline{C}H_3$). Mass: m/e 246 (M^+,10%), 159 (100), 158 (80), 143 (23), 131 (15), 105 (11). HRMS: m/e Calcd. for $C_{16}H_{22}O_2$, 246.1620; found, 246.1613.

3,4-Dimethyl-3-(4-methylphenyl)-pent-4-enoicacid (7):

To a magnetically stirred solution of the ester **10** (1.1 g, 4.5 mmol) in methanol (15 ml) was added 10% aqueous NaOH (15 ml) and refluxed for 8 hrs. The methanol was removed under reduced pressure, the residue was taken in water (15 ml) and washed with methylene chloride (25 ml x 2). The aqueous layer was acidified with 10% aq.HCl and extracted with methylene chloride (40 ml x 3). The organic phase was washed with water and dried over anhydrous Na_2SO_4. Evaporation of the solvent furnished the acid **7** (843 mg, 86%) as a colourless oil. IR (neat): ν_{max} 3650 – 2300 (COOH), 1713, 1641, 1515, 1443, 1410, 1380, 1317, 1263, 1194, 897, 816 cm^{-1}. ^1H NMR (90 MHz $CDCl_3$): δ 7.1 (4 H, s, aromatic), 4.98 (2 H, s, olefinic), 2.88 (2 H, s, $C\underline{H}_2CO$), 2.32 (3 H, s, Ar–Me), 1.6 (3 H, s, C_3–Me), 1.55 (3 H, s, olefinic Me). ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 178.3 (s, O–C=O), 150.1 ($\underline{C}=CH_2$), 143.0, 135.8, 129.2 (2 C) and 126.2 (2 C) (aromatic), 111.4 ($C=\underline{C}H_2$), 46.1 (benzylic), 44.4 ($\underline{C}H_2CO$), 25.7 (C_3–Me), 21.0 (olefinic Me), 20.3 (Ar–Me). Mass: m/e 218 (15%, M^+), 159 (100), 158 (80), 143 (33), 131 (17), 105 (14), 91 (12). HRMS: m/e Calcd. for $C_{14}H_{18}O_2$, 218.1307; found, 218.1306.

4,5-Dimethyl-4-(4-methylphenyl)-bicyclo[3.1.0]hexan-2-one (6):

To a magnetically stirred solution of the acid **7** (218 mg, 1 mmol) in benzene (2 ml) was added oxalyl chloride (0.18 ml, 2 mmol) and the solution was stirred at room temperature for 5 hrs. Evaporation of the solvent and

excess oxalyl chloride under reduced pressure afforded the acid chloride 11 which was immediately used for the preparation of the diazo ketone 12.

A solution of the acid chloride 11 in anhydrous ether (5 ml) was added dropwise with stirring to a cold ethereal solution of diazomethane (excess, freshly prepared from N-nitroso-N-methylurea). The reaction mixture was stirred for 3 hrs at room temperature. The excess diazomethane and ether were removed by careful evaporation on a hot water bath and the residue was filtered through a silica gel (4 g) column using ethyl acetate - hexane (1:5) as eluent to furnish the diazo ketone 12 [IR (neat): ν_{max} 3088, 2098, 1641, 1515, 1443, 1356, 1191, 1146, 1116, 1053, 894, 816 cm^{-1}].

A solution of the diazo ketone 12 in cyclohexane (5 ml) was added dropwise, over a period of 0.5 hr, to a refluxing (using a 100 W tungsten lamp), magnetically stirred suspension of anhydrous $CuSO_4$ (0.4 g) in cyclohexane (30 ml), and stirred at reflux for 5 hrs. The reaction mixture was cooled and $CuSO_4$ was filtered off using a sintered funnel. Evaporation of the solvent and purification of residue on a silica gel (8 g) column using ethyl acetate hexane (1:20) as eluent furnished a diastereoisomeric mixture (1:2) of the cyclopropyl ketone 6 (103 mg, 48%) as a colourless oil.

3-(4-Methylphenyl)-3,4,4-trimethylcyclopentanone (β-cuparenone) (4):

To a magnetically stirred, freshly distilled ammonia (20 ml) in a three necked flask equipped with a Dewar condenser, was added a solution of the diastereoisomeric cyclopropyl ketone 6 (54 mg, 0.25 mmol) in 0.5 ml of dry ether, followed by freshly cut lithium (7 mg, 1 mmol), and the reaction mixture was stirred at −33°C for 15 minutes. The reaction was quenched with solid NH_4Cl and ammonia was slowly evaporated. The residue was taken in water (10 ml) and extracted with ether (20 ml x 3). The ether extract was washed with brine (10 ml) and dried over anhydrous Na_2SO_4. Evaporation of solvent and purification of the residue on a silica gel (3 g) column using ethyl acetate - hexane (1:20) as eluent furnished the β-cuparenone (4, 44 mg, 81%) as a colourless oil. **IR (neat):** ν_{max} 1746, 1518, 1455, 1407, 1383, 1290, 1203, 1020, 816 cm^{-1}. **^{1}H NMR (90 MHz, $CDCl_3$):** δ 7.16 (4 H, s, aromatic), 3.13 and 2.32 (2 H, AB q, J = 18 Hz, H-2), 2.35 (3 H, s, Ar-Me), 2.28 (2 H, s, H-4), 1.42 (3 H, s, C_3-Me), 1.26 (3 H, s, C_4-Me trans to tolyl), 0.74 (3 H, s, C_4-Me cis to tolyl).

2-endo,4-endo,4,5-Dimethyl-4-(4-methylphenyl)-bicyclo[3.1.0]hexan-2-ol (13)
2-endo,4-exo,4,5-dimethyl-4-(4-methylphenyl)-bicyclo[3.1.0]hexan-2-ol (14):

To a magnetically stirred, ice cold solution of the diastereoisomeric mixture of the cyclopropyl ketone 6 (1:2, 300 mg, 1.4 mmol) in dry methanol (5 ml) was added sodium borohydride (50 mg, 1.4 mmol), and the reaction mixture was stirred at room temperature for 10 hrs. The solvent was removed under reduced pressure, residue was taken in water (10 ml) and extracted

with methylene chloride (15 ml x 3). The organic extract was washed with brine (10 ml) and dried over anhydrous Na_2SO_4. Evaporation of the solvent and purification of the residue on a silica gel (10 g) column using ethyl acetate - hexane (1:20) as eluent, first furnished the alcohol **14** (140 mg, 46%) as a colourless oil. IR (neat): ν_{max} 3358, 1515, 1452, 1413, 1389, 1305, 1284, 1170, 1089, 1023, 1002, 972, 951, 912, 855, 816, 738 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.55 and 7.14 (4 H, AB q, J = 8.2 Hz), 4.25 (1 H, br s, C<u>H</u>OH), 2.33 (3 H, s, Ar–Me), 1.78 (2 H, m, C<u>H</u>$_2$CHOH), 1.6 – 1.66 (2 H, m, bridgehead CH and OH) 1.43 (3 H, s), 1.05 (3 H, s), 0.39 (1 H, dd, J = 8.4, 5 Hz) and 0.28 (1 H, t, J = 3.7 Hz) (cyclopropane CH_2). Mass: m/e 216 (M^+, 24%), 160 (26), 159 (66), 157 (17), 149 (16), 133 (100), 132 (48), 119 (21), 105 (37). HRMS: m/e Calcd. for $C_{15}H_{20}O$, 216.1514; found, 216.1505.

Further elution of the column using the same solvent gave the alcohol **13** (68 mg, 22.5%) as a colourless solid, mp: 99 - 101°C. IR ($CHCl_3$): ν_{max} 3604, 1602, 1443, 1386, 1275, 1110, 1068, 1017, 993, 924, 654 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.31 and 7.12 (4 H, AB q, J = 8.2 Hz, aromatic), 4.25 (1 H, d, J = 5.2 Hz, C<u>H</u>OH), 2.33 (3 H, s, Ar–Me), 1.92 (1 H, d of ½ AB q, J = 14.6, 1.3 Hz) and 1.7 (1 H, d of ½ AB q, J = 14.6, 5.3 Hz) (C<u>H</u>$_2$CHOH), 1.61 (1 H, s, OH), 1.58 (3 H, s, cyclopropyl Me), 1.37 (3 H, s, benzylic Me), 1.3 – 1.34 (1 H, m, H–1), 0.63 (1 H, dd, J = 8.5, 5.4 Hz) and 0.38 (1 H, t, J = 5 Hz) (cyclopropane CH_2). Mass: m/e 216 (M^+, 18%), 160 (36), 159 (100), 149 (19), 133 (40), 119 (25), 105 (26), 91 (13). HRMS: m/e Calcd. for $C_{15}H_{20}O$, 216.1514; found, 216.1499.

*4-endo,4,5-Dimethyl-4-(4-methylphenyl)-bicyclo[3.1.0]hexan-2-one (**6a**):*

To a magnetically stirred suspension of PCC (102 mg, 0.48 mmol) and sodium acetate (82 mg, 1 mmol) in dry methylene chloride (2 ml) was added a methylene chloride solution of the alcohol **13** (68 mg, 0.32 mmol) in one portion. The reaction mixture was stirred at room temperature for 3 hrs and filtered through a silica gel (5 g) column using methylene chloride as eluent. Evaporation of the solvent furnished the ketone **6a** (63 mg, 94%) as a colourless oil. IR (neat): ν_{max} 1728, 1515, 1455, 1419, 1392, 1380, 1275, 1236, 1197, 1116, 1080, 1023, 951, 903, 816, 786 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.31 and 7.17 (4 H, AB q, J = 8.0 Hz, aromatic), 2.46 (1 H, ½ AB q, J = 17.2 Hz) and 2.18 (1 H, d of ½ AB q, J = 17.2, 1.3 Hz) (C<u>H</u>$_2$CO), 2.35 (3 H, s, Ar–Me), 1.76 (1 H, dd, J = 8.7, 3.2 Hz, COCH), 1.49 (3 H, s), 1.44 (3 H, s), 1.35 – 1.5 (2 H, m, cyclopropane CH_2). ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 211.5 (s, C=O), 142.8 (s), 135.7 (s), 129.1 (2 C, d) and 126.1 (2 C, d) (aromatic), 49.3 (t, CO<u>C</u>H_2), 44.6 (s, benzylic), 36.1 (s, bridgeheead C), 35.2 (d, CO<u>C</u>H), 28.3 (q, benzylic Me), 23.4 (t, cyclopropane CH_2), 20.8 (q, Ar–Me), 17.5 (q, cyclopropyl Me). Mass: m/e 214 (M^+, 36%), 171 (19), 159 (100), 157 (31), 149 (35), 105 (23), 91 (17). HRMS: m/e Calcd. for $C_{15}H_{18}O$,

214.1358, found, 214.1358.

4-exo,4,5-Dimethyl-4-(4-methylphenyl)-bicyclo[3.1.0]hexan-2-one (6b):

Oxidation of the alcohol 14 (138 mg, 0.64 mmol) with PCC (207 mg, 0.96 mmol) and sodium acetate (157 mg, 1.92 mmol) in dry methylene chloride (2 ml) as described above, furnished the ketone 6b (130 mg, 95%) as a colourless oil. IR (neat): ν_{max} 1725, 1515, 1458, 1416, 1392, 1281, 1242, 1194, 1074, 1032, 900, 819, 780 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.14 (4 H, close AB q, J = 8.8 Hz, aromatic), 2.32 (3 H, s, Ar–Me), 2.28 (2 H, close AB q, J = 18.2 Hz, $COCH_2$), 1.9 (1 H, dd, J = 8.9, 2.8 Hz, COCH), 1.56 (3 H, s, benzylic Me), 1.33 (1 H, dd, J = 4.9, 3.0 Hz) and 1.14 (1 H, dd, J = 8.6, 5 Hz) (cyclopropane CH_2), 0.88 (3 H, s, cyclopropyl Me). ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 213.5 (s, C=O), 144 (s), 135.6 (s), 128.9 (2 C, d) and 125.6 (2 C, d) (aromatic), 49.8 (t, $CO\underline{C}H_2$), 43.6 (s, benzylic), 38.9 (s, bridgehead C), 37.0 (d, $CO\underline{C}H$), 21.3 (q, benzylic Me), 20.7 (q, Ar–Me), 20.0 (t, cyclopropane CH_2), 16.7 (q, cyclopropyl Me). Mass: m/e 214 (M^+, 49%), 172 (20), 171 (22), 159 (100), 157 (52), 149 (40), 132 (22), 105 (23), 91 (16). HRMS: m/e Calcd. for $C_{15}H_{18}O$, 214.1358; found, 214.1357.

2-endo,1,2-Dimethyl-2-(4-methylphenyl)-bicyclo[3.1.0]hexane (cyclolaurene) (1):

Hydrazine hydrate (99%, 0.1 ml, 2 mmol) was added to a solution of the ketone 6a (32 mg, 0.15 mmol) in digol (1 ml) and ethylene glycol (0.25 ml). The mixture was heated to 184°C for 90 minutes, cooled to 70°C and sodium (40 mg, 1.75 mmol) in digol (0.82 ml) was added. The reaction mixture was heated under reflux for 4 hrs, poured into ice water (10 ml) and extracted with petroleum ether (10 ml x 2). The organic extract was washed with brine and dried over anhydrous Na_2SO_4. Evaporation of the solvent and purification of the residue through a silica gel (2 g) column using petroleum ether as eluent furnished the cyclolaurene (1, 24 mg, 80%) as a colourless oil. IR (neat): ν_{max} 1515, 1455, 1374, 1278, 1113, 1074, 1023, 945, 819 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.32 and 7.08 (4 H, AB q, J = 8.2 Hz, aromatic), 2.32 (3 H, s, Ar–Me), 1.94 (1 H, m), 1.64 (2 H, m), 1.39 (1 H, m), 1.34 (3 H, s, benzylic Me), 1.24 (3 H, s, cycloprpyl Me), 1.07 (1 H, t of d, J = 8, 4 Hz, bridgehead CH), 0.61 (1 H, t, J = 4.5 Hz) and 0.42 (1 H, dd, J = 7.9, 4.9 Hz) (cyclopropane CH_2). ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 134.9, 128.9 (3 C), 126.6 (2 C), 38.4, 29.9, 29.4, 26.5, 25.8, 23.9, 21.1, 18.5, 16.0. Mass: m/e 200 (M^+, 34%), 185 (16), 159 (59), 132 (100), 105 (27).

2-exo,1,2-Dimethyl-2-(4-methylphenyl)bicyclo[3.1.0]hexane (epicyclolaurene) (5):

Huang-Minlon modified Wolff-Kishner reduction of the cyclopropyl ketone 6b (32 mg, 0.15 mmol) as described above furnished the epicyclolaurene (5, 23 mg, 78%) as a colourless oil. IR (neat): ν_{max} 1515, 1458, 1377, 1278, 1197,

1122, 1086, 1041, 1017, 945, 813 cm-1. **1H NMR (200 MHz, $CDCl_3$):** δ 7.24 and 7.1 (4 H, AB q, J = 8.5 Hz, aromatic), 2.32 (3 H, s, Ar–Me), 2.02 (1 H, m), 1.65 (1 H, dd, J = 12.5, 7.1 Hz), 1.3 – 1.5 (3 H, m), 1.41 (3 H, s, benzylic Me), 0.91 (3 H, s, cyclopropyl Me), 0.47 (1 H, J = 4.3 Hz) and 0.25 (1 H, ddd, J = 7.8, 4.8, 0.8 Hz) (cyclopropane CH_2). **^{13}C NMR (22.5 MHz, $CDCl_3$):** δ 134.8, 130.0, 128.8 (2 C), 126.7 (2 C), 39.3, 29.9, 27.1 (2 C), 22.3, 21.1, 18.0, 14.5. **Mass: m/e** 200 (M^+, 30%), 185 (16), 159 (42), 132 (100), 105 (25).

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