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Regioselective Total Synthesis of (±) Neorautane, (±) Neorautanin and Their Analogs. Microwave Mediated Synthesis of 2*H*-Chromenes from Propargyl Phenyl Ethers.

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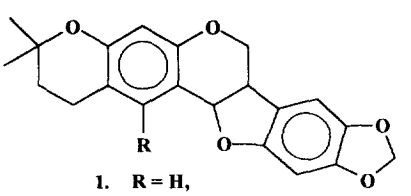
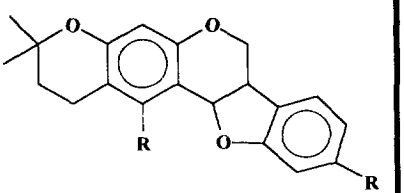
Abstract: Herein we describe the total synthesis of (±) Neorautane **1**, (±) Neorautanin **2** and their analogs **15-18**. The key intermediates Chromenes **10-13** were synthesised by microwave irradiation of propargyl phenyl ethers **8** and **9** in DMF under pressure. © 1997 Published by Elsevier Science Ltd.

A large number of pterocarpans isolated from plant sources are reported to possess antifungal and antitumour activity.[1] These biologically active compounds, like Carbenegrin A-I, Carbenegrin A-II (antidote against snake venom), Neorautenane and Neorautane were synthesised by chemoselective coupling of 2-chloromercuriophenol with the corresponding 2*H*-chromenes using Li_2PdCl_4.[2] Breytenbach et al[3] reported the synthesis of 6,12-Methano-12*H*-dibenzo[d,g][1,3]dioxocins along with the pterocarpans by extension of the Li_2PdCl_4 method. Engler et al[4] have reported the synthesis of natural as well as substituted pterocarpans by Ti (IV) promoted formal (3+2) cycloaddition reactions of 2-alkoxy-1,4-benzoquinones with 2*H*-chromenes. The substituted pterocarpans were found to be anti-**HIV** agents.[5] We have also reported Ti (IV) and $ZnCl_2$ promoted synthesis of substituted pterocarpans having a 2,2-dimethyldihydropyrano moiety as part of their structure.[6]

CHART - 1.



1. R = H,
2. R = OCH_3.



3. R = OCH_3.

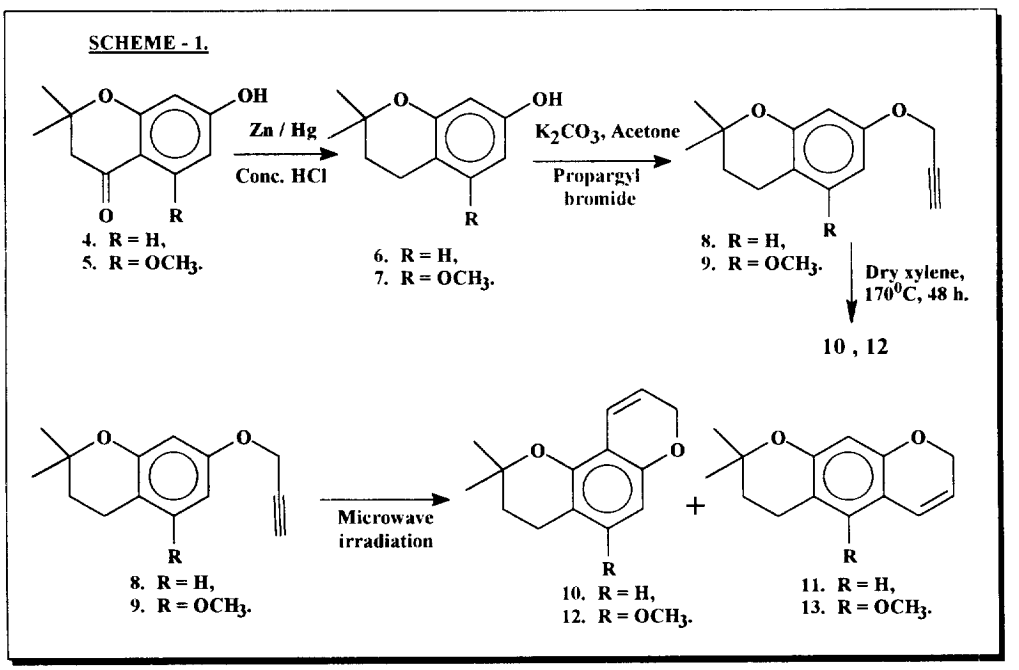
Literature shows that the construction of benzopyran and 2*H*-chromene ring systems can be achieved by different routes. Thermal cyclisation of aryl propargyl ethers in solvents such as N,N-diethyl aniline and xylene gave benzopyrans in good yields but it requires prolonged heating.[2a,7] Costa et al[2c] have reported the synthesis of intermediate chromene for Neorautenane, by acid catalysed cyclisation of the corresponding acetal. We have recently communicated the total synthesis of Edulane **3** (Chart-1) by $ZnCl_2$ promoted cycloaddition of

2-methoxy-1,4-benzoquinone with 2*H*-chromene **13**, synthesised by acid catalysed cyclisation of the corresponding acetal.[8]

Microwave irradiation has become a powerful tool in organic synthesis in recent years[9] and has hence attracted many organic chemists. Unlike thermal reactions, these reactions take place in short time and result in higher yields of the products.[10] Saidi et al[11] have reported the synthesis of naphthopyrans and naphthofurans from propargyl naphthyl ethers by microwave irradiation. Our strategy involves microwave irradiation of propargyl phenyl ethers **8** and **9** to get the key chromenes **10-13**. In continuation of our work on regioselective[6,8] and enantioselective[12] synthesis of pterocarpans, the total synthesis of Neorautane **1**, Neorautanin **2**, isolated from the root bark of *Neorautania edulis*[13] (Chart-1), and their analogs **15-18** has been carried out.

RESULTS AND DISCUSSION:

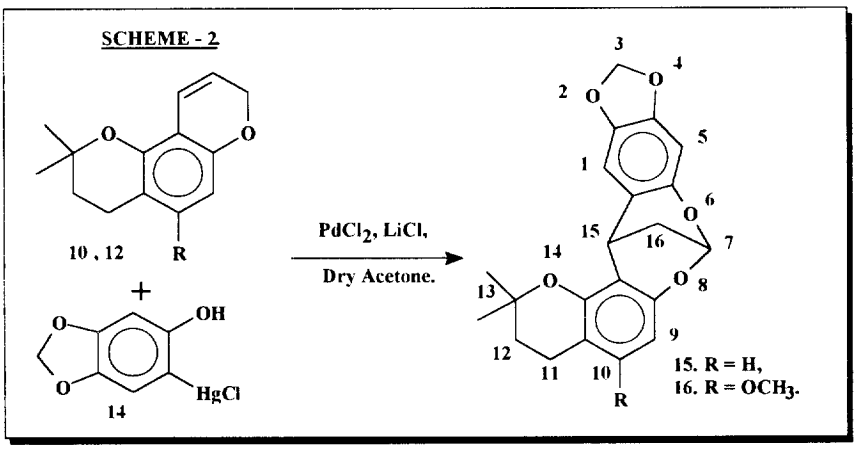
The synthesis of chromenes **10-13** is shown in scheme-I. Chromans **6** and **7**, prepared by Clemmenson reduction of corresponding chromanones **4** and **5**, were transformed to ethers **8** and **9** by heating to reflux in dry acetone with a mixture of propargyl bromide and K_2CO_3. These ethers were subjected to thermal cyclisation reactions in dry xylene at 170^{0}C and in dry N,N-diethyl aniline at 140^{0}C for 48 h. Formation of angular chromenes **10** and **12** was observed only in dry xylene. Microwave irradiation of ethers **8** and **9** in DMF under pressure, lead to both linear and angular fusion, resulting in the formation of chromenes **10 - 13** in moderate yields in 25 to 30 min (scheme-I). Hence the synthesis of chromene **11**, synthesised in five steps by Narkhede et al[2b] has now been achieved in only three steps.

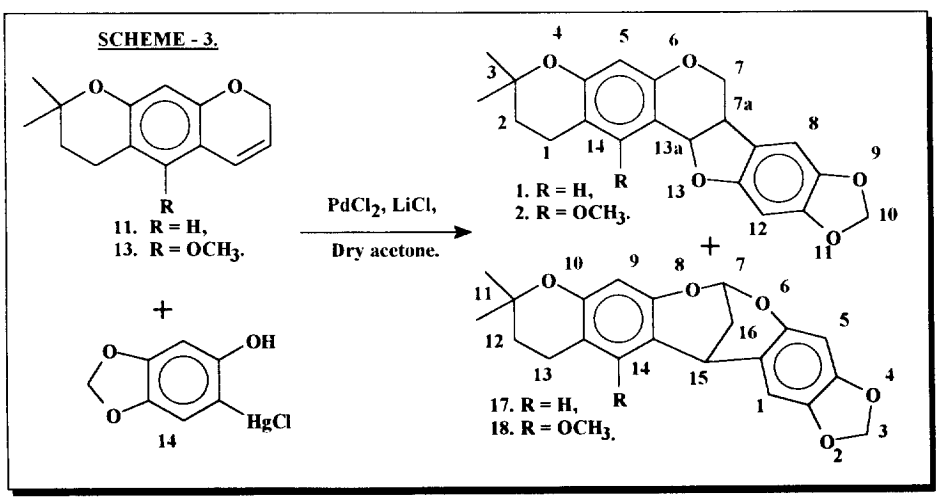


The formation of chromenes **10** and **11** was confirmed by the disappearance of the acetylinic peak at 3288 cm^{-1} in the IR, an acetylinic proton triplet with J=2.58 Hz at δ 2.50 in ^{1}H NMR, the appearance of a

double bond peak at 1619 cm^{-1}, and of a one proton triplet of doublet at around δ 5.60 in ^1H NMR. The appearance of two aromatic protons as one proton singlets in the ^1H NMR spectrum at δ 6.25 and 6.66 for chromene **11** and two doublets with J=8.2 Hz at δ 6.32 and 6.79 for chromene **10** confirms the linear and angular fusion. The chromene **13** and its isomer **12** were identified by comparison with the reported values.[8] The ^1H NMR and IR spectra were found to be superposable with the reported one.

Reaction of the 2*H*-chromene **10** and **12** with 2-chloromercurio-4,5-methylenedioxyphenol **14** in the presence of Li_2PdCl_4 afforded only the 7,15-methano-15*H*-dibenzo[d,g][1,3]dioxocins **15** and **16** (Scheme-2). The presence of two proton doublet of doublets with J=2.19 & 3.3 Hz at δ 2.11 (C_{16}-H), a one proton doublet of doublets with J=2.9 and 4.6 Hz at δ 4.27 (C_{15}-H) and a one proton doublet of doublets with J=2.01 & 3.9 Hz at δ 6.06 (C_7-H) suggested the formation of compound **15**, while compound **16** was identified by the appearance of a two proton doublet of doublets with J=2.35 and 3.11 Hz at around δ 2.10 (C_{16}-H), a one proton doublet with J=1.46 Hz at δ 4.19 (C_{15}-H) and a one proton doublet of doublets with J=2.19 and 3.84 Hz at δ 6.06 (C_7-H) in the ^1H NMR spectrum.





The synthesis of Neorautane **1** and Neorautanin **2** are shown in scheme-3. Chromenes **11** and **13** were subjected to a Heck reaction with phenol **14** in the presence of Li_2PdCl_4 to obtain Neorautane **1**, Neorautanin **2** and 7,15-methano-15*H*-dibenzo[d,g][1,3]dioxocins **17** and **18**. The formation of **2** was confirmed by the presence of a single proton doublet with J=6.6 Hz at δ 5.64 (C_{13a}-H) and another single proton multiplet at δ 3.35 (C_{7a}-H) in the ^{1}H NMR spectrum of compound **2**, while the appearance of a one proton doublet with J=6.96 Hz at δ 5.46 and a one proton multiplet at δ 3.45 in the ^{1}H NMR spectrum confirms the formation of compound **1**.

EXPERIMENTALS:

Melting points are uncorrected. IR spectra were recorded on a Perkin Elmer 688 Spectrometer. NMR spectra were recorded on a Varian VXR 300S using $CDCl_3$ as the solvent containing TMS as the internal standard with chemical shifts (δ) expressed as ppm down field with respect to TMS. The J values are given in Hz. Elemental analyses were performed on a CEST 1106 elemental analyser. Mass spectra were recorded on a Hewlett Packard MS Engine 5989-A mass spectrometer. A commercial oven Microwin MX 1000 was used for microwave irradiation reactions.

7-(2'-Propynyloxy)-2,2-dimethyl-3,4-dihydrobenzo[*1,2-b*]pyran (8).

A 250 mL round bottom flask fitted with a stirrer, reflux condenser and guard tube was charged with K_2CO_3, (5.53 g, 40 mmol), dry acetone (50 mL) and chroman **6** (5.0 g, 28 mmol) under a nitrogen atmosphere. To this well stirred and cooled mixture (0-5^{0}C), propargyl bromide (3.0 mL, 34.0 mmol) was added dropwise for 5 min. The mixture was allowed to come to room temperature and then heated to reflux for 12 h. After completion of the reaction, solid material was filtered off and the filtrate was concentrated under vacuum. Water (50 mL) was added to the product and extracted with ethyl acetate (3×50 mL), washed with water, brine and then dried over anhydrous Na_2SO_4. After removal of the solvent, the product was chromatographed over silica gel using pet. ether / ethyl acetate (98:2) as eluant to afford ether **8** as a colourless liquid (4.9 g, 81%). IR (neat): ν max 3288, 2979, 2929, 1619, 1587, 1489, 1272 and 1159 cm^{-1}. ^{1}H NMR (300 MHz): δ 1.32 (s, 6H, $(CH_3)_2$), 1.77 (t, 2H, J=6.77 Hz, C_3-H), 2.50 (t, 1H, J=2.58, $C_{3'}$-H), 2.70 (t, 2H, J=6.70 Hz, C_4-H), 4.62 (d, 2H, J=2.5 Hz, $C_{1'}$-H), 6.41 (d, 1H, J=2.58 Hz, C_8-H), 6.48 (dd, 1H, J=2.55 & 8.3 Hz, C_6-H), and 6.95 (d, 1H, J=8.28 Hz, C_5-H). ^{13}C NMR (75 MHz): δ 21.82, 26.88, 32.91, 55.86, 74.41, 75.35, 78.84, 102.99, 107.42, 114.08, 129.97, 154.74 and 157.08.

7-(2'-Propynoloxy)-5-methoxy-2,2-dimethyl-3,4-dihydrobenzo[*1,2-b*]pyran (9).

Chroman **7** (8.32 g, 40 mmol), propargyl bromide (4.83 mL, 54 mmol) and K_2CO_3 (8.3 g, 60 mmol) gave ether **9** as a colourless liquid (8.26 g, 84%). IR (neat): ν max 3295, 2974, 2937, 1620, 1596, 1460, 1157 and 1107 cm^{-1}; ^{1}H NMR (300 MHz): δ 1.31 (s, 6H, -$(CH_3)_2$), 1.75 (t, 2H, J=6.77 Hz, C_3-H), 2.52 (t, 1H, J=2.4 Hz, $C_{3'}$-H), 2.57 (t, 2H, J=6.78 Hz, C_4-H), 3.78 (s, 3H, -OCH_3), 4.61 (d, 2H, J=2.4 Hz, $C_{1'}$-H), 6.06 (d, 1H, J=2.4 Hz, Ar-H) and 6.1 (d, 1H, J=2.4 Hz, Ar-H). MS m/e: M^+ 246 (59%), 215 (44%), 191 (100%) and 162 (70%).

Synthesis of chromenes (10) and (11):

Propargyl phenyl ether **8** (2.16 g, 10 mmol) in DMF was placed in a sealed glass tube and subjected to microwave irradiation for 30 min. Solvent was evaporated to dryness under reduced pressure and the residue obtained was extracted with dichloromethane, washed with water, brine and then dried over Na_2SO_4.

Purification of the crude product on silica gel column using pet. ether / ethyl acetate (99:1 and 98:2) as eluant gave the pure compounds **10** and **11**.

7,8-Dihydro-6,6-dimethyl-2*H*,6*H*-benzo[*1,2-b:3,4-b'*]pyran (10).

Colourless liquid (0.49 g, 23%). IR (neat): ν_{max} 3019, 2981, 1633, 1614, 1588, 1446 and 1220 cm^{-1}; ^1H NMR (300 MHz): δ 1.32 (s, 6H, -$(CH_3)_2$), 1.76 (t, 2H, J=6.6 Hz, C_7-H), 2.67 (t, 2H, J=6.5 Hz, C_8-H), 4.70 (q, 2H, J=1.8 Hz, C_2-H), 5.69 (td, 1H, J=3.6 & 10.1 Hz, C_3-H), 6.32 (d, 1H, J=8.1 Hz, Ar-H), 6.76 (d, 1H, J=10.1 Hz, C_4-H), 6.79 (d, 1H, J=8.2 Hz, Ar-H).

6,7-Dihydro-8,8-dimethyl-2*H*,8*H*-benzo[*1,2-b:5,4-b'*]pyran (11).

Colourless liquid (0.61 g, 28%). IR (neat): ν_{max} 1620, 1570, 1490, 1450 and 1380 cm^{-1}; ^1H NMR (300 MHz): δ 1.33 (s, 6H, -$(CH_3)_2$), 1.78 (t, 2H, J=6.7 Hz, C_7-H), 2.67 (t, 2H, J=6.7 Hz, C_6-H), 4.75 (dd, 2H, J=1.8 & 3.4 Hz, C_2-H), 5.61 (td, 1H, J=3.6 & 10.1 Hz, C_3-H), 6.25 (s, 1H, C_{10}-H), 6.34 (d, 1H, J=10.1 Hz, C_4-H), 6.66 (s, 1H, C_5-H).

Synthesis of Chromenes (12) and (13).

Propargyl phenyl ether **9** (2.46 g, 10 mmol) in DMF was placed in a sealed tube and subjected to microwave irradiation for 25 min. The solvent was evaporated to dryness under reduced pressure and residue was extracted with dichloromethane, washed with water, brine and then dried over Na_2SO_4. Purification of the crude product on silica gel column using pet. ether / ethyl acetate (99:1 and 98:2) as eluant gave the pure compounds **12** and **13**.

7,8-Dihydro-6,6-dimethyl-9-methoxy-2*H*,6*H*-benzo[*1,2-b:3,4-b'*]pyran (12).

Colourless liquid (0.54 g, 22%). IR (neat): ν_{max} 3019, 1979, 2940, 1621, 1453, 1216 and 755 cm^{-1}; ^1H NMR (300 MHz) δ 1.31 (s, 6H, -$(CH_3)_2$), 1.74 (t, 2H, J=6.95 Hz, C_7-H), 2.54 (t, 2H, J=6.96 Hz, C_8-H), 3.76 (s, 3H, -OMe), 4.69 (q, 2H, J=1.65 Hz, C_2-H), 5.55 (td, 1H, J=3.84 & 9.82 Hz, C_3-H), 5.97 (s, 1H, C_{10}-H), 6.70 (dtd, 1H, J=0.56, 1.61 & 9.79 Hz, C_4-H). ^{13}C NMR (125 MHz): δ 16.93, 26.93, 32.46, 55.62, 65.51, 74.5, 91.03, 102.85, 105.30, 116.15, 120.2, 150.38, 154.0 and 158.2. MS m/e: M^+ 246 (99%), 191 (80%) and 161 (100%).

6,7-Dihydro-8,8-dimethyl-5-methoxy-2*H*,8*H*-benzo[*1,2-b:5,4-b'*]pyran (13).

Colourless liquid (0.79 g, 32%), IR (neat): ν_{max} 3026, 2979, 2940, 1617, 1479, 1143 and 762 cm^{-1}; ^1H NMR (300 MHz): δ 1.31 (s, 6H, -$(CH_3)_2$), 1.75 (t, 2H, J=6.77 Hz, C_7-H), 2.65 (t, 2H, J=6.77 Hz, C_6-H), 3.74 (s, 3H, -OCH_3), 4.69 (q, 2H, J=1.83 Hz, C_2-H), 5.64 (td, 1H, J=3.84 & 9.88 Hz, C_3-H), 6.10 (s, 1H, C_{10}-H), 6.61 (dtd, 1H, J=0.74, 1.75 & 9.72 Hz, C_4-H). ^{13}C NMR (125 MHz): δ 17.08, 26.95, 32.61, 61.53, 65.38, 74.64, 100.8, 107.7, 108.8, 118.4, 119.9, 154.2, 154.69 and 155.43. MS m/e: M^+ 246 (86%), 191 (69%) and 83 (100%).

Thermal reactions: Synthesis of Chromene (10) and (12).

A 100 mL 3-necked flask equipped with a stirrer, reflux condenser and guard tube was charged with propargyl ether **8** (2.16 g, 10 mmol) in anhydrous xylene (10 mL) under N_2 atmosphere. The reaction mixture was heated to reflux at 170°C for 48h. After completion of the reaction, solvent was evaporated to dryness under reduced pressure. The oily mass was chromatographed over silica gel using pet. ether / ethyl acetate (99:1) as eluant to obtain the chromene **10** as a colourless oil in 76% yield. Chromene **12** was obtained in 83% yield from the ether **9** by the above procedure.

13,13-Dimethyl-11,12-dihydro-7,15-methano-15*H*-dibenzo[d,g][1,3]dioxocin (15).

Chromene **10** (0.09 g, 0.4 mmol), palladium dichloride (0.072 g, 0.4 mmol) and lithium chloride (0.017 g, 0.4 mmol) were mixed in dry acetone (15 mL). After stirring the reaction mixture for 15 min, 2-chloromercurio-4,5-methylenedioxyphenol **14** (0.150 g, 0.4 mmol) in dry acetone (7 mL) was added and stirring was continued for a further 15 min at room temperature. Usual work up, after completion of the reaction, afforded the crude solid which on being subjected to silica gel column chromatography to obtain compound **15** (0.081 g, 58%); m.p; 128^{0}C; IR ($CHCl_3$): ν max 3021, 2988, 1620, 1580, and 1446 cm^{-1}; ^{1}H NMR (300 MHz): δ 1.36 (s, 3H, -CH_3), 1.43 (s, 3H, -CH_3), 1.77 (t, 2H, J=6.78 Hz, C_{12}-H), 2.11 (dd, 2H, J=2.19 & 3.3 Hz, C_{16}-H), 2.67 (dt, 2H, J=4.8 & 6.78 Hz, C_{11}-H), 4.27 (dd, 1H, J=2.9 & 4.6 Hz, C_{15}-H), 5.80 & 5.85 (2 x d, 2H, J=1.28 Hz, C_3-H), 6.06 (dd, 1H, J=2.01 & 3.9 Hz, C_7-H), 6.42 (d, 1H, J=8.4 Hz, Ar-H), 6.43 (s, 1H, Ar-H), 6.77 (d, 1H, J=8.4 Hz, Ar-H), 6.83 (s, 1H, Ar-H). Anal. Calcd for $C_{21}H_{20}O_5$: C, 71.58; H, 5.72. Found: C, 71.61; H, 5.79. MS m/e: M^+ 352.3 (60 %), 296 (70), 279 (100), 175 (68.8) and 159 (50).

13,13-Dimethyl-11,12-dihydro-10-methoxy-7,15-methano-15*H*-dibenzo[d,g][1,3]dioxocin (16).

Chromene **12** (0.098 g, 0.4 mmol)), palladium dichloride (0.070 g, 0.4 mmol), lithium chloride (0.017 g, 0.4 mmol) and 2-chloromercurio-4,5-methylenedioxyphenol **14** (0.150 g, 0.4 mmol) in dry acetone (7 mL) gave compound **16** (0.075 g, 49%). m.p; 152^{0}C; IR ($CHCl_3$): ν max 3019, 2981, 1617, 1584, 1485, 1446, 1222, 1123 and 775 cm^{-1}; ^{1}H NMR (300 MHz): δ 1.34 (s, 3H, -CH_3), 1.41 (s, 3H, -CH_3), 1.74 (t, 2H, J=6.77 Hz, C_{12}-H), 2.10 (dd, 2H, J=2.35 & 3.11 Hz, C_{16}-H), 2.53 (m, 2H, C_{11}-H), 3.72 (s, 3H, -OMe), 4.19 (d, 1H, J=1.46 Hz, C_{15}-H), 5.80 & 5.85 (2 x d, 2H, J=1.47 Hz, C_3-H), 6.04 (s, 1H, C_9-H), 6.06 (dd, 1H, J=2.19 & 3.85 Hz, C_7-H), 6.43 (s, 1H, Ar-H), 6.80 (s, 1H, Ar-H). MS m/e: M^+ 382 (100%), 326 (86%), 309 (56%), 297 (17%) and 189 (32%). Anal. Calcd for $C_{22}H_{22}O_6$: C, 69.10; H, 5.80. Found: C, 69.16; H, 5.79.

Synthesis of Neorautane (1) and its analog (17).

Chromene **11** (0.040 g, 0.185 mmol), palladium dichloride (0.035 g, 0.2 mmol) and lithium chloride (0.008 g, 0.188 mmol) were mixed in dry acetone (10 mL). After stirring the reaction mixture for 15 min, 2-chloromercurio-4,5-methylenedioxyphenol **14** (0.074 g, 0.2 mmol) in dry acetone (5 mL) was added and the stirring was continued for further 20 min at room temperature. Usual work up afforded the crude product which was purified on a silica gel column using pet. ether / ethyl acetate (98:2 & 96:4) to get products **17** and **1** respectively.

11,11-Dimethyl-12,13-dihydro-7,15-methano-15*H*-dibenzo[d,g][1,3]dioxocin (17).

Colourless solid (0.017 g, 26%). m.p; 209^{0}C; IR ($CHCl_3$): ν max 3019, 2966, 1627, 1584, 1479, 1130 and 755 cm^{-1}, ^{1}H NMR (300 MHz): δ 1.24 (s, 3H, -CH_3), 1.29 (s, 3H, -CH_3), 1.73 (t, 2H, J=6.78 Hz, C_{12}-H), 2.17 (m, 2H, C_{16}-H), 2.66 (dt, 2H, J=2.38 & 6.69 Hz, C_{13}-H), 3.72 (br s, 1H, C_{15}-H), 5.81 & 5.87 (2 x d, 2H, J=1.28 Hz, C_3-H), 6.04 (dd, 1H, J=2.2 & 3.8 Hz, C_7-H), 6.34 (s, 1H, Ar-H), 6.44 (s, 1H, Ar-H), 6.62 (s, 1H, Ar-H), 6.80 (s, 1H, Ar-H). Anal. Calcd for $C_{21}H_{20}O_5$: C, 71.58; H, 5.72. Found: C, 71.66; H, 5.75. MS m/e: M^+ 352 (100%), 298.4 (33.5), 295 (47.7) and 175 (85).

Neorautane (1).

Colourless solid (0.024 g, 37 %). m.p; 207-209^{0}C; IR ($CHCl_3$): ν max 3019, 2927, 1624, 1587, 1479, 1347, 1222, 1137 and 764 cm^{-1}; ^{1}H NMR (300 MHz): δ 1.30 (s, 3H, -CH_3), 1.34 (s, 3H, -CH_3), 1.79 (t, 2H, J=6.9 Hz, C_2-H), 2.76 (t, 2H, J=6.77 Hz, C_1-H), 3.45 (m, 1H, C_{7a}-H), 3.60 (t, 1H, J=10.8 Hz, C_{7ax}-H), 4.18 (m, 1H, C_{7eq}-H), 5.46 (d, 1H, J=6.96 Hz, C_{13a}-H), 5.89 & 5.92 (2 x d, 2H, J=1.28 Hz, -OCH_2O), 6.37 (s, 1H,

Ar-H), 6.43 (s, 1H, Ar-H), 6.71 (s, 1H, Ar-H), 7.19 (s, 1H, Ar-H). Anal. Calcd for $C_{21}H_{20}O_5$: C, 71.58; H, 5.72. Found: C, 71.71; H, 5.69. MS m/e: M^+ 352.1 (100%), 297.2 (39), 279 (15.4) and 239 (13.5).

Synthesis of Neorautanin (2) and its analog (18).

Chromene **13** (0.040 g, 0.16 mmol), palladium dichloride (0.028 g, 0.16 mmol) and lithium chloride (0.007 g, 0.16 mmol) were mixed in dry acetone (10 mL). After stirring the reaction mixture for 15 min, 2-chloromercurio-4,5-methylenedioxyphenol **14** (0.060 mg, 0.16 mmol) in dry acetone (5 mL) was added and stirring was continued for further 20 min at room temperature. Usual work up afforded the crude product which was purified on a silica gel column using pet. ether / ethyl acetate (98:2 & 96:4) to get products **18** and **2** respectively.

11,11-Dimethyl-12,13-dihydro-14-methoxy-7,15-methano-15*H*-dibenzo[d,g][1,3]dioxcin (18).

Colourless solid (0.009 g, 15%). m.p; 209^{0}C; IR ($CHCl_3$): ν_{max} 3026, 2978, 1624, 1584, 1479, 1222 and 762 cm^{-1}; ^{1}H NMR (300 MHz): δ 1.27 (s, 3H, -CH_3), 1.30 (s, 3H, -CH_3), 1.71 (m, 2H, C_{12}-H), 2.14 (dd, 2H, J=2.38 & 5.4 Hz, C_{16}-H), 2.60 (m, 2H, C_{13}-H), 3.87 (s, 3H, -OMe), 4.14 (m, 1H, C_{15}-H), 5.83 (2 x d, 2H, J=1.46 Hz, C_3-H), 6.04 (dd, 1H, J=2.2 & 3.85 Hz, C_7-H), 6.19 (s, 1H, C_9-H), 6.42 (s, 1H, Ar-H), 6.79 (s, 1H, Ar-H). MS m/e: M^+ 382 (100%), 351 (32), 327 (37), 245 (45) and 175 (57). Anal. Calcd for $C_{22}H_{22}O_6$: C, 69.10; H, 5.80. Found: C, 69.13; H, 5.84.

Neorautanin (2).

Colourless solid (0.031 g, 51 %). m.p; 206^{0}C; IR ($CHCl_3$): ν_{max} 3019, 2927, 1624, 1587, 1479, 1347, 1222, 1137 and 764 cm^{-1}; ^{1}H NMR (300 MHz): δ 1.32 (s, 3H, -CH_3), 1.34 (s, 3H, -CH_3), 1.77 (t, 2H, J=6.7 Hz, C_2-H), 2.75 (dt, 2H, J=2.74 & 6.78 Hz, C_1-H), 3.35 (m, 1H, C_{7a}-H), 3.62 (t, 1H, J=10.8 Hz, C_{7ax}-H), 3.95 (s, 3H, -OMe), 4.14 (m, 1H, C_{7eq}-H), 5.64 (d, 1H, J=6.6 Hz, C_{13a}-H), 5.90 & 5.92 (2 x d, 2H, J=1.46 Hz, -OCH_2O), 6.22 (s, 1H, C_5-H), 6.45 (s, 1H, C_{12}-H), 6.72 (s, 1H, C_8-H). MS m/e: M^+ 382 (100%), 327 (57%), 311 (27%) and 176 (32%). Anal. Calcd for $C_{22}H_{22}O_6$: C, 69.10; H, 5.80. Found: C, 69.11; H, 5.81.

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