SUPPORTING INFORMATION

Unnatural Natural Products from the Transannular Cyclization of Lathyrane Diterpenes

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General. All new compounds were fully characterized by NMR, IR and HR-MS data. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) were recorded at room temperature with a Bruker ARX500 spectrometer with an inverse multinuclear 5 mm probehead equipped with a shielded gradient coil. The spectra were recorded in $CDCl_3$, and the solvent signals for $C\underline{H}Cl_3/\underline{C}DCl_3$ (7.26 and 77.0 ppm, respectively) were used as reference. The chemical shifts (δ) are given in ppm, and the coupling constants (*J*) in Hz. Assignments are based on COSY, HMQC and HMBC experiments, recorded with gradient enhancements using sine shaped gradient pulses. For the 2D heteronuclear correlation spectroscopy the refocusing delays were optimized for $^{1}J_{CH}$=145 Hz and $^{n}J_{CH}$=10 Hz. The raw data were transformed and the spectra were evaluated with the standard Bruker UXNMR software (rev. 941001). The known compounds **2** and **3** were identified by comparison of their physical- (mp) and spectroscopic data (IR, ^{1}H NMR) with those reported in the literature (references 6 and 11).

General Strategy for the Structure Elucidation. High resolution MS experiments suggested an elemental composition for each compound, and 1D NMR data confirmed the number of carbons and hydrogens. The scalar-coupled proton spin network was analyzed using the COSY correlations, and the positions of the individual protons on the carbons were obtained from the HMQC

experiments. HMBC correlations were then employed to establish the carbon-carbon connectivity via long-range ^{1}H-^{13}C heterocorrelations. Inspection of the correlations in the NOESY spectra was next employed to assign the configuration of the stereogenic centers. The determination of the structure of compound **12** is described as exemplificative: The HRMS data suggested the elemental composition $C_{29}H_{36}O_5$, indicating that compound **12** has an unsaturation index of twelve. The 1D NMR data suggested the presence of one benzene ring, two carbon-carbon double bonds and two carbonyl groups, and the compound should consequently be tetracyclic. The ^{1}H-^{1}H coupling between 2-H and 16-H_3 as well as the long-range ^{1}H-^{13}C coupling between 16-H_3 and C-1, C-2 and C-3, the ^{1}H-^{1}H couplings between 1-H and 2-H as well as 4-H, and between 3-H and 4-H, and the long-range ^{1}H-^{13}C couplings between both 2-H and 3-H and C-1 and C-15, established a cyclopentene ring substituted by a methyl and a phenylcarbonyloxy group. The latter was established by the HMBC correlations between both 3-H and Ar2'-H_2 and the benzoic acid ester carbon. 4-H couples with 5-H with a large coupling constant, indicating that the dihedral angle in this system is close to 0° or 180°. C-5 is acetylated, as shown by the HMBC correlations from the protons of both C-5 and the acetoxy group to the same carbonyl carbon. Besides to the carbons in the cyclopentene ring, 1-H also gives a HMBC correlation to C-14 which together with the HMBC correlation between 14-H and C-15 and the weak ^{1}H-^{1}H coupling between 1-H and 14-H (not resolved, only observed in the COSY spectrum) shows that C-14 is attached to C-15. The protons of C-20, appearing as a singlet in the 1H NMR spectrum, give HMBC correlations to C-12, C-13 and C-14, C-20 is obviously attached to C-13 which in turn must be attached to C-14. The ^{1}H-^{1}H couplings between 14-H and 17-H_2 together with the HMBC correlations from 17-H_2 to C-13, C-14 and C-15 positions C-17 adjacent to C-14. 17-H_2 also give HMBC correlations to C-5, C-6, C-7 and C-11, and the lack of further ^{1}H-^{1}H couplings show that C-17 must be attached to C-6, which is attached to C-5 as shown by the HMBC correlation from 5-H to C-6. 7-H_2 give HMBC correlations to C-5, C-6, C-9, C-11 and C-17, showing that C-7 as well as C-11 are attached to C-6,

and the ^{1}H-^{1}H couplings between 7-H2 and 8-H_2 as well as between 8-H_2 and 9-H and between 9-H and 11-H (together with the corresponding HMBC correlations) establish the second five-membered ring. The 2-(2-methoxypropyl) substituent on C-9 is shown by the HMBC correlations between 18-H_3 as well as 19-H_3 to C-9 and to C-10, and the HMBC correlations between 18-H_3 and C-19 as well as between 19-H_3 and C-18. The final connection in the structure, closing the fourth ring, is between C-11 and C-12, and this was readily made from the ^{1}H-^{1}H coupling between the two protons as well as from the HMBC correlations between 11-H and C-12 and C-13, and between 12-H and C-11.

As expected, the configuration of the stereogenic center at C-2, C-3, C-4 and C-5 is the same as in the starting material, as shown for example by the NOESY correlations between 3-H and 2-H as well as 4-H. 5-H gives a strong NOESY correlation to 11-H, but not to any of the two protons on C-17, which determines the configuration of C-6 and shows that 11-H is β. 9-H is on the other side of the cyclopentane ring, as demonstrated by the NOESY correlation between 9-H and 17-Ha, and between 11-H and 18-H3 as well as 19-H3, while 17-Hb is close in space to 4-H according to the NOESY correlation between the two. This also determines the configuration of C-14, which must be as shown in Scheme 5.

Starting Materials. The *Euphorbia* Factors L_1 and L_3 were isolated from commercial seeds of the caper spurge as described in ref. 7.

Cyclizations with formic acid. Reaction with **1a** as representative: A sample of the *Euphorbia* Factor L_1 (**1a**) (3.0 g, 5.43 mMol) was dissolved in 98% formic acid (50 mL). After stirring at room temp. for 24 h, the reaction was diluted with water (*ca.* 100 mL) and ice (*ca.* 100 mL). Solid $NaHCO_3$ was then carefully added until gas evolution ceased and neutrality was reached. The reaction mixture was then extracted with EtOAc (2 x 100 mL, 1 x 80 mL). The pooled organic phases were washed with brine, dried ($MgSO_4$) and evaporated, affording a semi-solid residue. The

latter was purified by CC (50 mL silica gel, hexane-EtOAc gradient, from 8:2 to 6:4), affording, in order of elution, 310 mg (6%) **4**, 1.52 g **3** (33%), and 2.10 g **2** (42%).

Reductions with $NaBH_4$-dioxane. Reaction with **1a** as representative: A sample of the *Euphorbia* Factor L_1 (5.0 g, 90.6 mMol) was suspended in dioxane (200 mL), and a large excess $NaBH_4$ (10.0 g) was added portionwise over 6 h. After stirring the milky suspension at room temp. for 72 h, the reaction was worked up by careful addition of ice and 2N H_2SO_4 to reach neutrality, and extraction with EtOAc (4 x 70 mL). The pooled organic phases were washed with brine, dried (Na_2SO_4) and evaporated. The alcohol **7a** was obtained as a white fluffy solid (4.90 g, 98%), which was directly used for the cyclization studies.

Cyclizations with Ytterbium Triflate. Reaction with **7b** as representative: To a suspension of **7b** (1.8 g, 3.4 mmol) in MeOH (50 mL), $Yb(OTf)_3$ (2.13 g, 3.4 mmol, 1 mol. Equiv.) was added portionwise over 5 min. After stirring at room temp. for 72 h, the reaction was worked up by dilution with brine (200 mL) and extraction with EtOAc (3 x 80 mL). After drying (Na_2SO_4) and evaporation, the residue was purified by CC (50 g silica gel, hexane-EtOAc gradient, from 9:1 to 5:5) to give 704 mg **12** (22%), 481 mg **11** (15%), and 320 mg recovered starting material.

Compound **4**: Amorphous powder, mp 76 °C; IR ν_{max} cm^{-1}: 1751, 1717, 1704, 1502, 1379, 1225, 1187, 1130; ^1H (δ, mult., *J*, assignment): 8.00, s, -OOCH; 7.32-7.24, m, Ar-H_5; 5.82, d, *J* = 5.8, 5-H; 5.53, dd, *J* = 3.1 and 3.4, 3-H; 5.10, dq, *J* = 7.8 and 1.7, 12-H; 4.06, s, 17-H_2; 3.04, d, *J* = 7.6, 11-H; 2.84, dd, *J* = 3.4 and 5.8, 4-H; 2.40, m, 8-Ha; 2.29, m, 8-Hb; 2.22, s, 15-$OCOCH_3$; 2.07, m, 2-H; 1.88, s, 5-$OCOCH_3$; 1.80, s, 20-H_3; 1.71, m, 7-Ha; 1.56, s, 18-H_3; 1.52, s, 19-H_3; 1.51, m, 1-H_2; 1.45, m, 7-Hb; 0.65, d, *J* = 6.8, 16-H_3; . ^{13}C (δ, assignment): 206.5 C-14, 170.8 15-O<u>C</u>OCH_3, 170.5 PhAc<u>C</u>O, 169.2 5-O<u>C</u>OCH_3, 160.2 -OOCH, 140.7 C-13, 134.5 C-9, 133.5 1-<u>Ph</u>Ac, 129.2 2-<u>Ph</u>Ac, 128.6 3-<u>Ph</u>Ac, 127.3 4-<u>Ph</u>Ac, 126.5 C-10, 126.4 C-12, 91.4 C-15, 79.6 C-3, 71.3 C-5, 64.0

C-17, 54.7 C-6, 52.8 C-4, 44.6 C-11, 41.8 PhAc, 41.5 C-1, 38.0 C-2, 30.6 C-7, 26.6 C-8, 21.5 C-20, 21.4 15-OCOCH$_3$, 20.8 C-19, 20.7 C-18, 20.7 5-OCOCH$_3$, 13.7 C-16. HRMS m/z 580.2667 (calculated for $C_{33}H_{40}O_9$, 580.2672)

Compound **5**: Colorless oil; IR ν_{max} cm^{-1}: 1740, 1710, 1670, 1650, 1340, 1255, 1190, 1145; ^{1}H (δ, mult., *J*, assignment): 8.46, d, *J* = 7.0, Ar-H$_2$; 7.97, s, H-COO-; 7.59, m, Ar-H; 7.54, m, Ar-H$_2$; 6.99, m, 12-H; 5.68, d, *J* = 10, 5-H; 5.48, dd, J = 3.4 and 4.1, 3-H; 4.38, s, 17-H$_2$; 4.01, brs, 11-H; 3.03, dd, *J* = 4.3 and 9.7, 4-H; 2.52, dd, *J* = 7.7 and 14.1, 8-Ha; 2.30, m, 2-H; 2.29, m, 1-Ha; 2.11, m, 7-Ha; 2.06, m, 7-Hb; 1.90, m, 1-Hb; 1.88, s, 19-H$_3$; 1.84, s, 18-H$_3$; 1.79, s, 20-H$_3$; 1.41, dd, *J* = 10.3 and 14.1, 8-Hb; 1.01, d, *J* = 6.7, 16-H$_3$. ^{13}C (δ, assignment): 211.8 C-14, 166.7 BzCO, 160.8 HCOO-, 159.6 C-12, 140.8 C-13, 136.8 C-6, 133.5 C-9, 132.9 Ar, 132.6 C-10, 130.2 Ar, 130.2 Ar, 128.6 Ar, 126.9 C-5, 79.7 C-3, 69.0 C-17, 61.7 C-15, 57.1 C-11, 48.8 C-4, 47.8 C-1, 40.0 C-2, 29.8 C-7, 29.7 C-8, 21.1 C-19, 21.0 C-18, 13.7 C-16, 10.4 C-20. HRMS m/z 448.2256 (calculated for $C_{28}H_{32}O_5$, 448.2250).

Compound **6**: Colorless oil; IR ν_{max} cm^{-1}: 1740, 1705, 1665, 1650, 1355, 1285, 1195, 1130; ^{1}H (δ, mult., *J*, assignment): 8.40, d, *J* = 7.0, Ar-H$_2$; 7.80, s, H-COO-; 7.54, m, Ar-H; 7.52, m, Ar-H$_2$; 6.97, m, 12-H; 5.78, d, *J* = 11, 5-H; 5.68, dd, J = 3.4 and 4.1, 3-H; 5.06 and 4.96, s, 17-H$_2$; 3.94, brs, 11-H; 2.73, dd, *J* = 4.3 and 11.3, 4-H; 2.68, dd, *J* = 6.6 and 13.7, 8-Ha; 2.27, m, 2-H; 2.26, m, 1-Ha; 2.17, m, 7-Ha; 1.89, m, 7-Hb; 1.87, s, 18-H$_3$; 1.87, s, 19-H$_3$; 1.82, m, 1-Hb; 1.78, s, 20-H$_3$; 1.59, m, 8-Hb; 0.97, d, *J* = 6.7, 16-H$_3$. ^{13}C (δ, assignment): 211.7 C-14, 166.4 BzCO, 159.6 HCOO-, 159.0 C-12, 144.5 C-6, 140.9 C-13, 132.9 C-9, 132.6 Ar, 132.4 C-10, 130.1 Ar, 130.1 Ar, 128.5 Ar, 122.2 C-17, 78.2 C-3, 73.6 C-5, 57.0 C-11, 56.2 C-15, 50.9 C-1, 50.3 C-4, 39.0 C-2, 31.8 C-8, 30.1 C-7, 21.6 C-18, 20.9 C-19, 13.5 C-16, 10.4 C-20. HRMS m/z 448.2259 (calculated for $C_{28}H_{32}O_5$, 448.2250).

Compound **7a**: White powder, mp 146-148 °C; IR ν_{max} cm^{-1}: 3588, 1750, 1745, 1561, 1458, 1375, 1238, 1163, 1060;^{1}H (δ, mult., *J*, assignment): 7.32, m, Ar-2'-H$_2$; 7.28, m, Ar-3'-H$_2$; 7.26, m, Ar-

4'-H; 5.81, brs, 5-H; 5.71, d, *J* =11.0, 12-H; 5.57, dd, *J* = 3.5 and 3.5, 3-H; 5.28, s, 14-H; 3.64 and 3.62, d, *J* = 15.0, PhAc-CH_2-; 2.77, d, *J* = 4.8, 17-Ha; 2.51, d, *J* = 4.8, 17-Ha; 2.32, dd, *J* = 9.4 and 14.6, 1-Ha; 2.15, m, 4-H; 2.15, s, 5-Ac, 2.01, m, 2-H; 1.93, s, 14-Ac; 1.82, m, 8-Ha; 1.79, s, 20-H_3; 1.65, dd, *J* = 10.6 and 14.6, 1-Hb; 1.60, m, 7-Ha; 1.49, dd, *J* = 7.6 and 13.2, 7-Hb; 1.31, m, 8-Hb; 1.29, dd, *J* = 8.9 and 10.7, 11-H; 1.16, s, 18-H_3; 1.08, s, 19-H_3; 0.90, ddd, *J* = 3.8, 8.9 and 12.7, 9-H; 0.75, d, *J* = 6.7, 16-H_3. ^{13}C (δ, assignment): 170.7 PhAcCO-, 170.0 5-AcCO-, 170.0 14-AcCO-, 133.6 Ar-1', 130.1 C-13, 129.3 Ar-2', 128.7 Ar-3', 127.3 Ar-4', 125.5 C-12, 82.6 C-15, 79.5 C-14, 77.8 C-3, 66.4 C-5, 58.7 C-6, 50.9 C-17, 47.7 C-4, 47.6 C-1, 41.7 PhAc-CH_2-, 36.8 C-2, 32.3 C-9, 31.8 C-7, 28.8 C-18, 24.8 C-11, 22.5 C-10, 20.9 5-Ac-CH_3, 20.9 14-Ac-CH_3, 18.8 C-8, 16.5 C-20, 15.2 C-19, 14.0 C-16. HRMS m/z 554.2883 (calculated for $C_{32}H_{42}O_8$, 554.2880).

Compound **7b**: Amorphous powder, mp 51 °C; IR ν_{max} cm^{-1}: 3600, 1750, 1737, 1512, 1385, 1245, 1128, 1110; ^{1}H (δ, mult., *J*, assignment): 8.00, d, *J* = 7.8, Ar-2'-H_2; 7.45, t, *J* = 8, Ar-4'-H; 7.33, t, *J* = 8, Ar-3'-H_2; 6.19, d, *J* = 10.8, 12-H; 5.70, d, *J* = 10.5, 5-H; 5.59, m, 3-H; 5.00, s, 14-H; 4.90 and 4.91, s, 17-H_2; 2.46, dd, *J* = 4.3 and 10.9, 4-H; 2.33, m, 7-Ha; 2.25, dd, *J* = 8.8 and 13.3, 1-Ha; 2.15, m, 2-H; 11.95, m, 7-Hb; 1.95, s, 12-Ac; 1.77, m, 1-Hb; 1.75, s, 5-Ac; 1.68, m, 8-Ha; 1.64, s, 20-H_3; 1.50, m, 8-Hb; 0.99, s, 18-H_3; 0.87, m, 11-H; 0.84, s, 19-H_3; 0.83, d, *J* = 6.5, 16-H_3; 0.41, m, 9-H. ^{13}C (δ, assignment): 172.2 12-Ac, 170.2 5-Ac, 166.7 BzCO-, 145.2 C-6, 136.1 C-14, 132.6 Ar-4', 130.3 Ar-1', 129.7 Ar-2', 128.3 C-13, 128.0 Ar-3', 114.5 C-17, 81.5 C-15, 79.1 C-3, 71.9 C-12, 69.7 C-5, 54.6 C-4, 52.9 C-1, 37.4 C-7, 36.9 C-2, 29.6 C-9, 28.6 C-18, 26.8 C-11, 22.4 C-8, 21.1 5-Ac, 20.8 12-Ac, 18.4 C-20, 18.1 C-10, 15.2 C-19, 14.2 C-16. HRMS m/z 524.2768 (calculated for $C_{31}H_{40}O_7$, 524.2774).

Compound **8**: Amorphous; IR ν_{max} cm^{-1}: 1745, 1740, 1555, 1492, 1371, 1235, 1220, 1137; ^{1}H (δ, mult., *J*, assignment): 7.30-7.28, m, PhAc-H_5; 5.53, dd, *J* =5.7 and 7.4, 3-H; 5.24, d, *J* = 11.1, 5-H; 4.70, s, 14-H; 3.96, d, *J* = 9.7, 17-Ha; 3.66 and 3.62, d, *J* = 15.6, PhAc-CH_2-; 3.31, d, *J* = 9.7,

17-Hb; 3.19, s, 10-OMe; 2.70, dd, *J* = 5.6 and 11.2, 4-H; 2.53, dd, *J* = 5.2 and 14.7, 11-Ha; 2.51, m, 2-H; 2.38, dd, *J* = 2 and 14.5, 1-Ha; 2.15, dd, *J* = 10.8 and 14.5, 1-Hb; 2.04, s, 5-Ac; 1.96, dd, *J* = 12.8 and 14.7, 11-Hb; 1.81, s, 9-Ac; 1.70, m, 9-H; 1.68, s, 20-H_3; 1.61, m, 7-Ha; 1.42, m, 8-H_2; 1.16, s, 18-H_3; 1.15, s, 19-H_3; 1.04, m, 7-Hb; 0.71, d, *J* = 7.5, 16-H_3. ^{13}C (δ, assignment): 171.9 PhAc-CO-, 170.7 15-Ac, 170.4 5-Ac, 134.4 C-12, 134.3 Ar-1', 129.6 C-13, 129.5 Ar-2', 128.4 Ar-3', 126.9 Ar-4', 92.2 C-15, 77.0 C-10, 76.4 C-14, 73.7 C-3, 68.4 C-5, 67.8 C-17, 53.8 C-4, 48.8 10-OMe, 41.8 C-9, 41.7 C-6, 41.4 PhAc-CH_2-, 40.0 C-1, 33.4 C-2, 26.7 C-7, 24.4 C-11, 22.1 15-Ac, 21.8 C-18, 21.8 C-19, 20.9 5-Ac, 20.4 C-8, 18.3 C-20, 16.0 C-16. HRMS m/z 568.3039 (calculated for $C_{33}H_{44}O_8$, 568.3036).

Compound **9**: White powder, mp 89-90 °C; IR ν_{max} cm^{-1}: 1740, 1735, 1560, 1508, 1319, 1245, 1181, 1133; ^{1}H (δ, mult., *J*, assignment): 7.35-7.25, m, PhAc-H_5; 5.79, s, 14-H; 5.05, dd, *J* = 4 and 4, 3-H; 3.89, d, *J* = 12, 17-Ha; 3.75 and 3.70, d, *J* = 15, PhAc-CH_2-; 3.48, d, *J* = 12, 17-Hb; 3.39, d, *J* = 11, 5-H; 3.17, s, 10-OMe; 2.15, dd, *J* = 6 and 11, 4-H; 1.99, m, 1-Ha; 1.99, m, 2-H; 1.96, m, 7-Ha; 1.93, m, 9-H; 1.81, s, 20-H_3; 1.79, m, 8-Ha; 1.77, m, 1-Hb; 1.61, m, 8-Hb; 1.60, m, 11-Ha; 1.36, m, 11-Hb; 1.26, m, 7-Hb; 1.10, s, 18-H_3; 1.10, s, 19-H_3; 0.98, d, *J* = 6.5, 16-H_3. ^{13}C (δ, assignment): 174.0 PhAc-CO-, 145.7 C-13, 135.8 C-14, 133.7 Ar-1', 129.2 Ar-2', 128.7 Ar-3', 127.3 Ar-4', 87.7 C-15, 87.6 C-12, 79.9 C-3, 77.1 C-10, 77.0 C-5, 63.7 C-17, 51.6 C-4, 48.9 10-OMe, 41.6 PhAc-CH_2-, 40.9 C-6, 40.4 C-1, 37.4 C-9, 37.0 C-2, 29.9 C-8, 27.4 C-7, 22.0 C-18, 21.1 C-19, 19.2 C-11, 15.0 C-20, 13.2 C-16. HRMS m/z 470.2674 (calculated for M – MeOH ($C_{28}H_{38}O_6$), 470.2668).

Compound **10**: Amorphous; IR ν_{max} cm^{-1}: 1740, 1562, 1503, 1325, 1248, 1182, 1130; ^{1}H (δ, mult., *J*, assignment): 7.32-7.25, m, PhAc-H_5; 5.74, brs, 14-H; 5.58, d, *J* = 2.9, 11-H; 5.37, dd, *J* = 4 and 4, 3-H; 5.15, dd, *J* = 1.0 and 10.5, 5-H; 4.30, d, *J* = 8.2, 17-Ha; 3.60, s, PhAc-CH_2-; 3.45, m, 4-H; 3.32, dd, *J* = 1.3 and 8.3, 17-Hb; 3.26, s, 10-OMe; 2.50, ddd, *J* = 2.8, 6.8 and 10.7, 9-H; 2.25, m, 1-Ha; 2.05, s, 5-Ac; 1.96, m, 1-Hb; 1.95, m, 2-H; 1.75, m, 8-Ha; 1.70, m, 7-Ha; 1.60, m, 8-Hb;

1.41, s, 20-H_3; 1.21, s, 18-H_3; 1.16, s, 19-H_3; 1.14, m, 7-Hb; 0.64, d, *J* = 6.7, 16-H_3. ^{13}C (δ, assignment): 171.4 PhAc-CO-, 170.5 5-Ac, 147.5 C-12, 142.0 C-15, 134.3 Ar-1', 131.5 C-14, 129.6 Ar-2', 128.3 Ar-3', 126.8 Ar-4', 117.6 C-11, 80.4 C-13, 78.5 C-3, 77.7 C-10, 73.6 C-17, 71.1 C-5, 50.2 C-4, 49.8 C-6, 48.9 10-OMe, 43.3 C-9, 41.7 PhAc-CH_2-, 39.5 C-1, 37.1 C-2, 28.4 C-7, 24.8 C-20, 22.4 C-18, 21.5 C-19, 21.0 5-Ac, 20.0 C-8, 13.1 C-16. HRMS m/z 508.2820 (calculated for $C_{31}H_{40}O_6$, 508.2825).

Compound **11**: Amorphous; IR ν_{max} cm^{-1}: 3300, 1740, 1722, 1562, 1509, 1379, 1245, 1231, 1130; ^{1}H (δ, mult., *J*, assignment): 8.00, d, *J* = 8.5, Ar-2'-H_2; 7.56, t, *J* = 8, Ar-4'-H; 7.45, t, *J* = 8, Ar-3'-H_2; 5.72, dd, *J* = 4.3 and 5.9, 3-H; 5.64, d, *J* = 1.4, 14-H; 5.04, d, *J* = 11.0, 5-H; 3.20, s, 10-OMe; 2.50, m, 2-H; 2.34, m, 11-H; 2.33, m, 12-H; 2.32, m, 17-Ha; 2.24, dd, *J* = 4 and 10, 4-H; 2.18, m 1-Ha; 2.16, m, 7-Ha; 2.02, s, 5-Ac; 1.84, m, 8-Ha; 1.82, s, 20-H_3; 1.65, m, 8-Hb; 1.62, m, 9-H; 1.56, m, 7-Hb; 1.47, 17-Hb; 1.24, 1-Hb; 1.15, s, 18-H_3; 1.15, s, 19-H_3; 1.00, d, *J* = 6.5, 16-H_3. ^{13}C (δ, assignment): 172.1 5-Ac, 166.4 Bz<u>C</u>O, 145.9 C-13, 132.7 Ar-4', 132.2 C-14, 130.4 Ar-1', 129.5 Ar-2', 128.4 Ar-3', 78.2 C-3, 77.8 C-10, 76.6 C-6, 75.8 C-5, 56.7 C-15, 50.4 C-4, 49.0 10-OMe, 48.7 C-11, 44.5 C-12, 43.7 C-9, 41.2 C-1, 39.5 C-17, 35.7 C-2, 33.3 C-7, 22.9 C-8, 22.5 C-18, 21.4 C-19, 21.1 5-Ac, 16.0 C-16, 15.1 C-20. HRMS m/z 478.2710 (calculated for M – H_2O, $C_{30}H_{38}O_5$, 478.2719).

Compound **12**: Amorphous, IR ν_{max} cm^{-1}: 1740, 1720, 1562, 1503, 1309, 1245, 1141, 1095; ^{1}H (δ, mult., *J*, assignment): 7.92, d, *J* = 8.5, Ar-2'-H_2; 7.55, t, *J* = 8, Ar-4'-H; 7.42, t, *J* = 8, Ar-3'-H_2; 5.71, dd, *J* = 3 and 3, 3-H; 5.50, d, *J* = 3, 12-H, 5.35, brs, 1-H; 4.99, d, *J* = 11, 5-H; 3.17, 10-OMe; 3.16, m, 4-H; 3.05, m, 2-H; 2.82, m, 14-H, 2.34, m, 11-H; 2.02, m, 9-H; 1.95, s, 5-Ac; 1.79, s, 20-H_3; 1.79, m, 8-Ha; 1.70, m, 17-Ha; 1.60, m, 17-Hb; 1.55, m, 8.Hb; 1.38, m, 7-H_2; 1.10, s, 18-H_3; 1.07, s, 19-H_3; 1.01, d, *J* = 6.5, 16-H_3. ^{13}C (δ, assignment): 170.5 5-Ac, 166.1 Bz<u>C</u>O, 141.5 C-15, 134.9 C-13, 132.7 Ar-4', 130.2 Ar-1', 129.5 Ar-2', 128.3 Ar-3', 125.3 C-1, 124.8 C-12, 77.6 C-10, 75.5 C-3, 75.1 C-5, 51.8 C-9, 50.9 C-4, 49.8 C-11, 48.9 10-OMe, 44.8 C-6, 44.3 C-2, 36.6

C-14, 33.0 C-7, 30.3 C-17, 25.7 C-8, 22.6 C-18, 21.8 C-20, 21.8 C-19, 20.7, 5-Ac, 13.4 C-16. HRMS m/z 464.2571 (calculated for $C_{29}H_{36}O_5$, 464.2563).