Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Design, synthesis and biological activity of new brassinosteroid analogues with phenyl group in the side chain

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Supplementary information

1) Preparation of **8a** with sodium hydride as a base and NMR study of products.
2) Experimental procedures and data for compounds of series b, d, e, and f.
3) Molecular docking into BRI1.
4) Biological activities

1) Preparation of 8b with sodium hydride as a base and NMR study of products:

To a suspension of sodium hydride (60%, 45 mg; 1.125 mmol) in dried THF (5 mL) was added a solution of diethyl phenylphosphonate (200 µL; 0.80 mmol) in dried THF (5 mL) at room temperature and reaction mixture was stirred for 1 h. To the resultant yellow solution was added a solution of aldehyde **7** (300 mg, 0.80 mmol) in THF (10 mL) and stirred for 8 h at 60 °C. The reaction mixture was quenched by water and extracted with Et_2O (2 × 10 mL). The combined organic fractions were washed with brine and dried over anhydrous magnesium sulfate. Evaporation of the volatiles under reduced pressure followed by column chromatography on silica gel (2 % of ethyl acetate in cyclohexane) afforded inseparable mixture of **8a** (20*S*) and **20*R*-8a** in ration 3:1. After hydrolysis of ketals according to general procedure and chromatography in the same mobile phase we obtained mixture of two inseparable isomers **8b** (20*S*) and **20*R*-8b** in the same ratio (Fig. S1). This mixture was then studied by NMR techniques (Fig. S2).

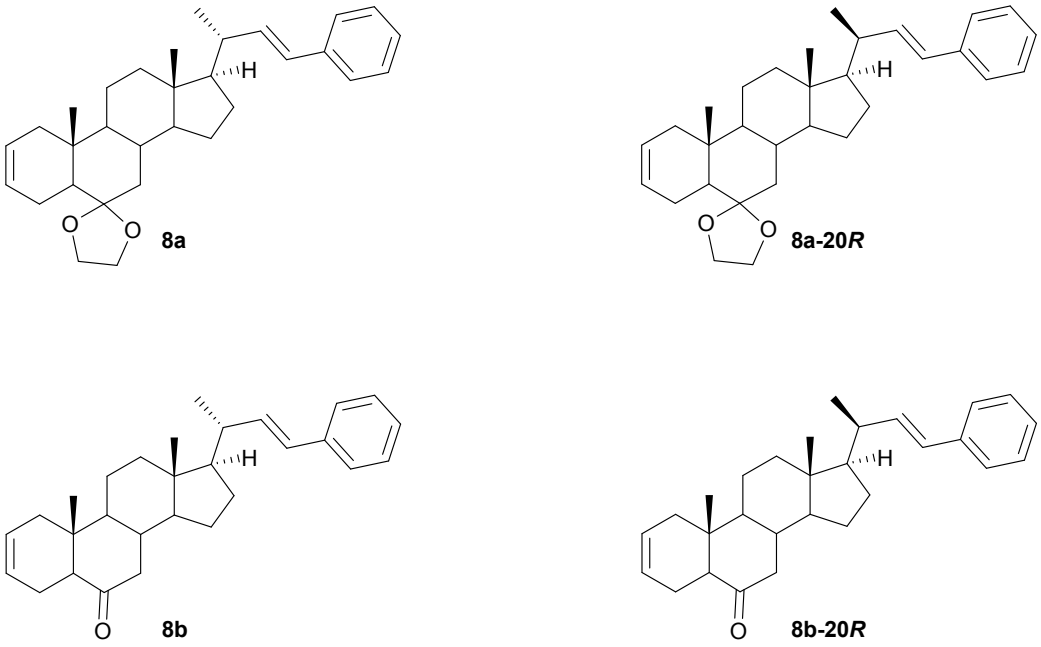


Fig. S1: Structures of both isomers

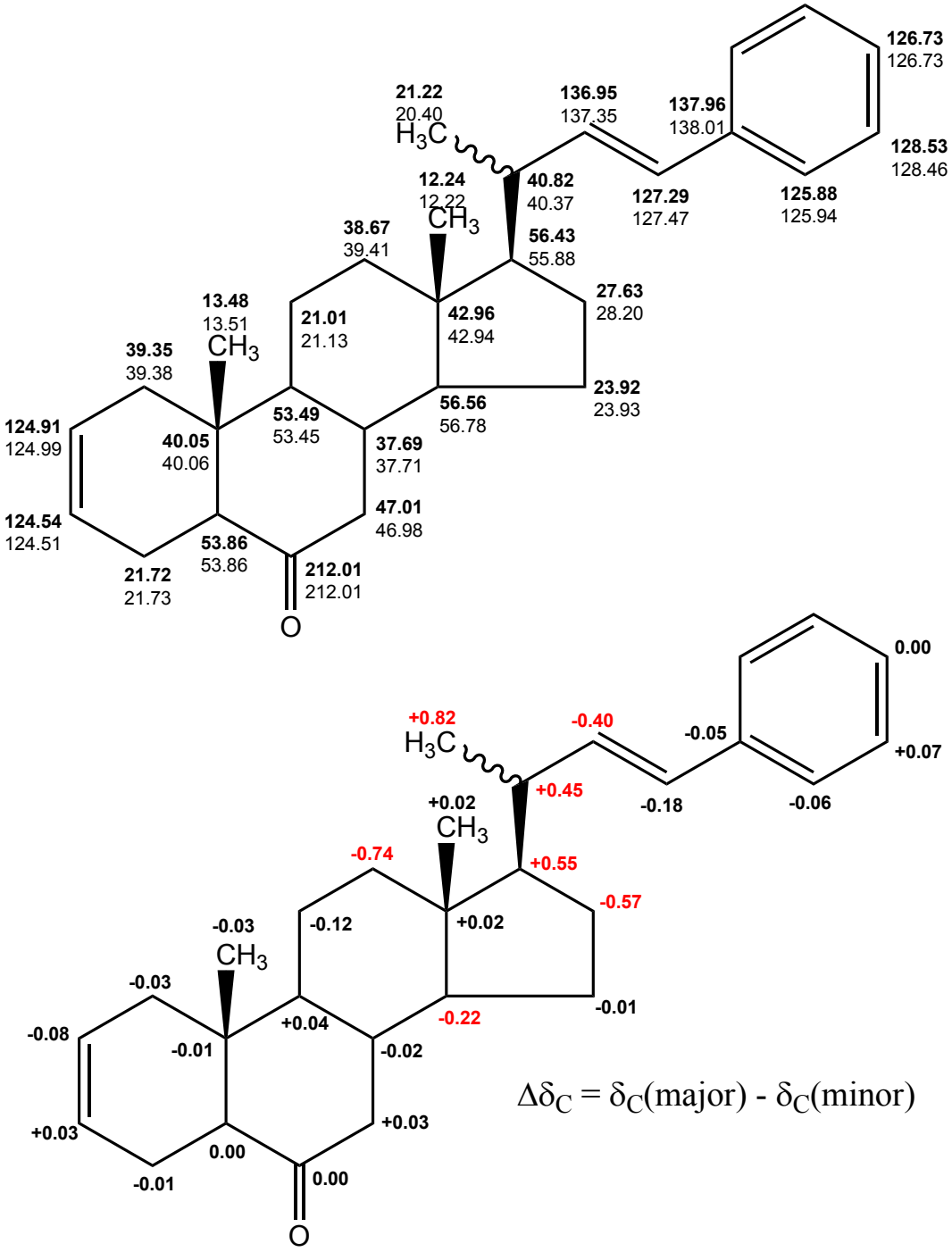


Fig. S2: Top - carbon assignment of compound **8b** and **8b-20*R*** (chemical shifts in bold) in the mixture after removal of large amount of **8b** as crystals in DMSO (due to traces of DMSO and mixture of both isomers the chemical shifts of **8b** is slightly different than when it was prepared and measured differently). Bottom - difference of carbon chemical shifts between **8b** (minor) and **8b-20R** (major); most significant differences in red.

2) Experimental procedures and data for compounds of series b, d, e, and f:

General procedure for hydrolysis of ketals

To a solution of ketal (190 mg) in THF (8 mL) was added 5% aqueous solution of hydrochloric acid (1 mL) and the reaction mixture was stirred at 60 °C for 5 h. This was then diluted with Et_2O (20 mL) and extracted with water (2 × 10 mL). The combined organic fractions were dried over anhydrous magnesium sulfate and evaporated under reduced pressure. Column chromatography on silica gel gave the desired product.

(*22E*)-23-phenyl-24-nor-5α-chola-2,22-diene-6-one (8b)

The general procedure for ketal hydrolysis of **8a** and chromatography on silica (Et_2O/cyclohexane - 1/19) afforded 168 mg (98 %) of the title compound **8b** as a colorless oil: IR ν (cm^{-1}) 2933, 1702, 1659, 1597. ^{1}H NMR ($CDCl_3$) δ 0.72, 0.74 (both s, 3H, CH_3), 1.14 (d, 3H, J = 6.4 Hz, CH_3), 1.69-1.80 (m, 2H), 1.96-2.04 (m, 4H), 2.07 (dt, 1H, J = 12.6, J´ = 3.3 Hz), 2.23-2.31 (m, 2H), 2.34-2.37, (m, 2H), 5.57 (m, 1H, H-3), 5.69 (m, 1H, H-2), 6.06 (dd, 1H, J = 15.9, J´ = 8.9 Hz, H-22), 6.30 (d, 1H, J = 15.9 Hz, H-23), 7.19 (m, 1H, Ar-H), 7.27-7.35 (m, 4H, 4×Ar-H). ^{13}C NMR δ 12.19 (CH_3), 13.50 (CH_3), 20.38 (CH_3), 21.10 (CH_2), 21.70 (CH_2), 23.92 (CH_2), 28.21 (CH_2), 37.68 (CH_2), 39.35 (CH_2), 39.37 (CH_2), 40.04 (C), 40.39 (CH), 42.92 (C), 46.96 (CH), 53.40 (CH), 53.83 (CH), 55.83 (CH), 56.75 (CH), 124.49 (CH), 124.95 (CH), 125.92 (2×CH), 126.72 (CH), 127.42 (CH), 128.45 (2×CH), 136.94 (CH), 137.98 (C), 211.98 (C). HRMS: (API+) calculated for $C_{29}H_{39}O$ ($[M+H]^+$) 403.3001, Found 403.3003.

(*22E*)-23-(4-fluorophenyl)-24-nor-5α-chola-2,22-diene-6-one (9b)

The general procedure for ketal hydrolysis of **9a** and chromatography on silica (Et_2O/cyclohexane - 1/19) afforded 171 mg (99 %) of the title compound **9b** as a colorless oil: IR ν (cm^{-1}) 2933, 1705, 1656, 1593. ^{1}H NMR ($CDCl_3$) δ 0.72, 0.73 (both s, 3H, CH_3), 1.13 (d, 3H, J = 6.7 Hz, CH_3), 1.71-1.80 (m, 2H), 1.96-2.04 (m, 4H), 2.08 (dt, 1H, J = 12.5, J´ = 3.2 Hz), 2.22-2.31 (m, 2H), 2.33-2.37, (m, 2H), 5.57 (m, 1H, H-3), 5.69 (m, 1H, H-2), 5.97 (dd, 1H, J = 15.7, J´ = 8.7 Hz, H-22), 6.26 (d, 1H, J = 15.7 Hz, H-23), 6.97 (m, 2H, 2×Ar-H), 7.27 (m, 2H, 2×Ar-H). ^{13}C NMR δ 12.17 (CH_3), 13.48 (CH_3), 20.35 (CH_3), 21.08 (CH_2), 21.69 (CH_2), 23.88 (CH_2), 28.21 (CH_2), 37.65 (CH_2), 39.32 (CH_2), 39.34 (CH_2), 40.01 (C), 40.33 (CH), 42.89 (C), 46.92 (CH), 53.36 (CH), 53.80 (CH), 55.79 (CH), 56.71 (CH), 115.25 (d, J = 20.4 Hz, 2×CH), 124.47 (CH), 124.93 (CH), 126.25 (CH), 127.28 (d, J = 8.4 Hz, 2×CH), 134.07 (d, J = 3.6 Hz, C), 136.65 (d, J = 2.4 Hz, CH), 161.79 (d, J = 244.7 Hz, C), 211.93 (C). ^{19}F NMR {^{1}H} δ -115.78 (s, 1F). HRMS: (API+) calculated for $C_{29}H_{38}FO$ ($[M+H]^+$) 421.2907, Found 421.2910.

(*22E*)-23-(4-chlorophenyl)-24-nor-5α-chola-2,22-diene-6-one (10b)

The general procedure for ketal hydrolysis of **10a** and chromatography on silica (Et_2O/cyclohexane - 1/19) afforded 171 mg (99 %) of the title compound **10b** as a colorless oil: IR ν (cm^{-1}) 2940, 1700, 1655, 1592. ^{1}H NMR ($CDCl_3$) δ 0.72, 0.73 (both s, 3H, CH_3), 1.13 (d, 3H, J = 6.7 Hz, CH_3), 1.70-1.80 (m, 2H), 1.96-2.04 (m, 4H), 2.07 (dt, 1H, J = 12.5, J´ = 3.4 Hz), 2.22-2.30 (m, 2H), 2.34-2.37, (m, 2H), 5.57 (m, 1H, H-3), 5.69 (m, 1H, H-2), 6.03 (dd, 1H, J = 15.9, J´ = 8.9 Hz, H-22), 6.27 (d, 1H, J = 15.9 Hz, H-23), 7.24 (s, 4H, 4×Ar-H). ^{13}C NMR δ 12.19

(CH_3), 13.50 (CH_3), 20.27 (CH_3), 21.09 (CH_2), 21.70 (CH_2), 23.91 (CH_2), 28.21 (CH_2), 37.66 (CH_2), 39.33 (CH_2), 39.36 (CH_2), 40.04 (C), 40.39 (CH), 42.93 (C), 46.94 (CH), 53.37 (CH), 53.82 (CH), 55.75 (CH), 56.72 (CH), 124.49 (CH), 124.96 (CH), 126.30 (CH), 127.12 (2×CH), 128.55 (2×CH), 132.22 (C), 136.45 (C), 137.64 (CH), 211.96 (C). HRMS: (API+) calculated for $C_{29}H_{38}ClO$ ($[M+H]^+$) 437.2611, Found 437.2615.

(*22E*)-23-(4-bromophenyl)-24-nor-5α-chola-2,22-diene-6-one (11b)

The general procedure for ketal hydrolysis of **11a** and chromatography on silica (Et_2O/cyclohexane - 1/19) afforded 169 mg (97 %) of the title compound **11b** as a colorless oil: IR ν (cm^{-1}) 2943, 1700, 1655, 1586. ^1H NMR ($CDCl_3$) δ 0.72, 0.73 (both s, 3H, CH_3), 1.13 (d, 3H, J = 6.7 Hz, CH_3), 1.70-1.79 (m, 2H), 1.96-2.04 (m, 4H), 2.07 (dt, 1H, J = 12.5, J´ = 3.3 Hz), 2.22-2.30 (m, 2H), 2.33-2.37, (m, 2H), 5.57 (m, 1H, H-3), 5.69 (m, 1H, H-2), 6.05 (dd, 1H, J = 15.7, J´ = 8.7 Hz, H-22), 6.24 (d, 1H, J = 15.7 Hz, H-23), 7.18 (m, 2H, 2×Ar-H), 7.39 (m, 2H, 2×Ar-H). ^{13}C NMR δ 12.19 (CH_3), 13.49 (CH_3), 20.24 (CH_3), 21.08 (CH_2), 21.70 (CH_2), 23.90 (CH_2), 28.19 (CH_2), 37.65 (CH_2), 39.32 (CH_2), 39.35 (CH_2), 40.02 (C), 40.40 (CH), 42.92 (C), 46.93 (CH), 53.36 (CH), 53.81 (CH), 55.71 (CH), 56.70 (CH), 120.30 (C), 124.47 (CH), 124.95 (CH), 126.33 (CH), 127.47 (2×CH), 131.48 (2×CH), 136.89 (C), 137.77 (CH), 211.92 (C). HRMS: (API+) calculated for $C_{29}H_{38}{}^{79}BrO$ ($[M+H]^+$) 481.2106, Found 481.2111.

(*22E*)-23-(4-iodophenyl)-24-nor-5α-chola-2,22-diene-6-one (12b)

The general procedure for ketal hydrolysis of **12a** and chromatography on silica (Et_2O/cyclohexane - 1/19) afforded 172 mg (98 %) of the title compound **12b** as a colorless oil: IR ν (cm^{-1}) 2939, 1701, 1656, 1582. ^1H NMR ($CDCl_3$) δ 0.72, 0.73 (both s, 3H, CH_3), 1.12 (d, 3H, J = 6.7 Hz, CH_3), 1.69-1.79 (m, 2H), 1.96-2.04 (m, 4H), 2.06 (dt, 1H, J = 12.5, J´ = 3.1 Hz), 2.22-2.30 (m, 2H), 2.33-2.37, (m, 2H), 5.57 (m, 1H, H-3), 5.69 (m, 1H, H-2), 6.06 (dd, 1H, J = 15.7, J´ = 8.7 Hz, H-22), 6.22 (d, 1H, J = 15.7 Hz, H-23), 7.06 (m, 2H, 2×Ar-H), 7.59 (m, 2H, 2×Ar-H). ^{13}C NMR δ 12.19 (CH_3), 13.50 (CH_3), 20.22 (CH_3), 21.08 (CH_2), 21.70 (CH_2), 23.90 (CH_2), 28.18 (CH_2), 37.65 (CH_2), 39.32 (CH_2), 39.35 (CH_2), 40.02 (C), 40.40 (CH), 42.92 (C), 46.93 (CH), 53.36 (CH), 53.81 (CH), 55.70 (CH), 56.69 (CH), 91.62 (C), 124.48 (CH), 124.95 (CH), 126.44 (CH), 127.76 (2×CH), 137.44 (2×CH), 137.48 (C), 137.90 (CH).211.92 (C). HRMS: (API+) calculated for $C_{29}H_{38}IO$ ($[M+H]^+$) 529.1967, Found 529.1970.

(*22E*)-23-(4-nitrophenyl)-24-nor-5α-chola-2,22-diene-6-one (13b)

The general procedure for ketal hydrolysis of **13a** and chromatography on silica (Et_2O/cyclohexane - 1/19) afforded 171 mg (99 %) of the title compound **13b** as a colorless oil: IR ν (cm^{-1}) 2929, 1697, 1651, 1595, 1518, 1342. ^1H NMR ($CDCl_3$) δ 0.72, 0.75 (both s, 3H, CH_3), 1.16 (d, 3H, J = 6.7 Hz, CH_3), 1.71-1.81 (m, 2H), 1.97-2.05 (m, 4H), 2.07 (dt, 1H, J = 12.6, J´ = 3.3 Hz), 2.22-2.31 (m, 2H), 2.32-2.37, (m, 2H), 5.58 (m, 1H, H-3), 5.69 (m, 1H, H-2), 6.27 (dd, 1H, J = 15.9, J´ = 8.6 Hz, H-22), 6.38 (d, 1H, J = 15.9 Hz, H-23), 7.44 (m, 2H, 2×Ar-H), 8.15 (m, 2H, 2×Ar-H). ^{13}C NMR δ 12.20 (CH_3), 13.49 (CH_3), 20.01 (CH_3), 21.08 (CH_2), 21.69 (CH_2), 23.91 (CH_2), 28.18 (CH_2), 37.63 (CH_2), 39.32 (CH_2), 39.34 (CH_2), 40.01 (C), 40.66 (CH), 43.03 (C), 46.91 (CH), 53.34 (CH), 53.81 (CH), 55.52 (CH), 56.64 (CH), 123.94 (2×CH), 124.45 (CH),

124.95 (CH), 125.90 (CH), 126.34 (2×CH), 142.10 (CH), 144.53 (C), 146.36 (C), 211.82 (C). HRMS: (API+) calculated for $C_{29}H_{38}NO_3$ ($[M+H]^+$) 448.2852, Found 448.2854.

(*22E*)-23-(4-methylphenyl)-24-nor-5α-chola-2,22-diene-6-one (14b)

The general procedure for ketal hydrolysis of **14a** and chromatography on silica (Et_2O/cyclohexane - 1/19) afforded 167 mg (97 %) of the title compound **14b** as a colorless oil: IR ν (cm^{-1}) 2936, 1701, 1652, 1591. ^1H NMR ($CDCl_3$) δ ^1H NMR ($CDCl_3$) δ 0.72, 0.73 (both s, 3H, CH_3), 1.12 (d, 3H, J = 6.7 Hz, CH_3), 1.70-1.79 (m, 2H), 1.96-2.04 (m, 4H), 2.07 (dt, 1H, J = 12.5, J´ = 3.4 Hz), 2.22-2.30 (m, 2H), 2.32 (s, 3H, CH_3), 2.33-2.37, (m, 2H), 5.57 (m, 1H, H-3), 5.69 (m, 1H, H-2), 6.00 (dd, 1H, J = 15.9, J´ = 8.9 Hz, H-22), 6.27 (d, 1H, J = 15.9 Hz, H-23), 7.09 (d, 2H, J = 7.9 Hz, 2×Ar-H), 7.22 (d, 2H, J = 7.9 Hz, 2×Ar-H). ^{13}C NMR δ 12.19 (CH_3), 13.49 (CH_3), 20.42 (CH_3), 21.09 (CH_2, CH_3), 21.70 (CH_2), 23.90 (CH_2), 28.19 (CH_2), 37.68 (CH_2), 39.34 (CH_2), 39.36 (CH_2), 40.04 (C), 40.34 (CH), 42.88 (C), 46.95 (CH), 53.39 (CH), 53.81 (CH), 55.89 (CH), 56.75 (CH), 124.50 (CH), 124.95 (CH), 125.80 (2×CH), 127.21 (CH), 129.13 (2×CH), 135.18 (C), 135.94 (CH), 136.40 (C), 212.00 (C). HRMS: (API+) calculated for $C_{30}H_{41}O$ ($[M+H]^+$) 417.3157, Found 417.3159.

(*22E*)-23-(4-methoxyphenyl)-24-nor-5α-chola-2,22-diene-6-one (15b)

The general procedure for ketal hydrolysis of **15a** and chromatography on silica (Et_2O/cyclohexane - 1/19) afforded 168 mg (97 %) of the title compound **15b** as a colorless oil: IR ν (cm^{-1}) 2937, 1702, 1650, 1605. ^1H NMR ($CDCl_3$) δ 0.72, 0.73 (both s, 3H, CH_3), 1.12 (d, 3H, J = 6.7 Hz, CH_3), 1.70-1.80 (m, 2H), 1.96-2.04 (m, 4H), 2.07 (dt, 1H, J = 12.5, J´ = 3.4 Hz), 2.21-2.30 (m, 2H), 2.33-2.37, (m, 2H), 3.80 (s, 3H, CH_3), 5.57 (m, 1H, H-3), 5.69 (m, 1H, H-2), 5.91 (dd, 1H, J = 15.9, J´ = 8.7 Hz, H-22), 6.25 (d, 1H, J = 15.9 Hz, H-23), 6.83 (m, 2H, 2×Ar-H), 7.26 (m, 2H, 2×Ar-H). ^{13}C NMR δ 12.19 (CH_3), 13.50 (CH_3), 20.49 (CH_3), 21.10 (CH_2), 21.70 (CH_2), 23.91 (CH_2), 28.23 (CH_2), 37.69 (CH_2), 39.34 (CH_2), 39.37 (CH_2), 40.05 (C), 40.34 (CH), 42.88 (C), 46.97 (CH), 53.40 (CH), 53.82 (CH), 55.29 (CH_3), 55.94 (CH), 56.77 (CH), 113.88 (2×CH), 124.51 (CH), 124.95 (CH), 126.72 (CH), 126.96 (2×CH), 130.80 (C), 134.90 (CH), 158.56 (C), 212.02 (C). HRMS: (API+) calculated for $C_{30}H_{41}O_2$ ($[M+H]^+$) 433.3107, Found 433.3109.

(*22E*)-23-(4-isopropylphenyl)-24-nor-5α-chola-2,22-diene-6-one (16b)

The general procedure for ketal hydrolysis of **16a** and chromatography on silica (Et_2O/cyclohexane - 1/19) afforded 168 mg (97 %) of the title compound **16b** as a colorless oil: IR ν (cm^{-1}) 2933, 1701, 1651, 1595. ^1H NMR ($CDCl_3$) δ 0.72, 0.73 (both s, 3H, CH_3), 1.12 (d, 3H, J = 6.7 Hz, CH_3), 1.24 (d, 6H, J = 7.0 Hz, 2×CH_3), 1.70-1.80 (m, 2H), 1.96-2.04 (m, 4H), 2.07 (dt, 1H, J = 12.8, J´ = 3.4 Hz), 2.22-2.30 (m, 2H), 2.33-2.37, (m, 2H), 2.87 (septet, 1H, J = 6.9 Hz, C*H*(CH_3)$_2$), 5.58 (m, 1H, H-3), 5.69 (m, 1H, H-2), 6.01 (dd, 1H, J = 15.9, J´ = 8.9 Hz, H-22), 6.27 (d, 1H, J = 15.9 Hz, H-23), 7.15 (d, 2H, J = 8.3 Hz, 2×Ar-H), 7.26 (d, 2H, J = 8.3 Hz, 2×Ar-H). ^{13}C NMR δ 12.19 (CH_3), 13.50 (CH_3), 20.46 (CH_3), 21.10 (CH_2), 21.70 (CH_2), 23.91 (CH_2), 23.97 (2×CH_3), 28.20 (CH_2), 33.79 (CH), 37.69 (CH_2), 39.34 (CH_2), 39.37 (CH_2), 40.05 (C), 40.40 (CH), 42.89 (C), 46.96 (CH), 53.40 (CH), 53.82 (CH), 55.86 (CH), 56.76 (CH), 124.51 (CH), 124.96

(CH), 125.88 (2×CH), 126.51 (2×CH), 127.21 (CH), 135.60 (C), 136.08 (CH), 147.53 (C), 212.04 (C). HRMS: (API+) calculated for $C_{32}H_{45}O$ ($[M+H]^+$) 445.3470, Found 445.3474.

(*22E*)-23-(4-cyanophenyl)-24-nor-5α-chola-2,22-diene-6-one (17b)

The general procedure for ketal hydrolysis of **17a** and chromatography on silica (Et_2O/cyclohexane - 1/19) afforded 165 mg (96 %) of the title compound **17b** as an amorphous solid: IR ν (cm^{-1}) 2941, 2223, 1701, 1647, 1602. ^1H NMR ($CDCl_3$) δ 0.72, 0.74 (both s, 3H, CH_3), 1.15 (d, 3H, J = 6.4 Hz, CH_3), 1.70-1.80 (m, 2H), 1.96-2.04 (m, 4H), 2.07 (dt, 1H, J = 12.5, J´ = 3.3 Hz), 2.22-2.32 (m, 2H), 2.34-2.37, (m, 2H), 5.57 (m, 1H, H-3), 5.69 (m, 1H, H-2), 6.21 (dd, 1H, J = 15.7, J´ = 8.6 Hz, H-22), 6.32 (d, 1H, J = 15.7 Hz, H-23), 7.39 (m, 2H, 2×Ar-H), 7.56 (m, 2H, 2×Ar-H). ^{13}C NMR δ 12.20 (CH_3), 13.50 (CH_3), 20.07 (CH_3), 21.08 (CH_2), 21.70 (CH_2), 23.91 (CH_2), 28.18 (CH_2), 37.64 (CH_2), 39.33 (CH_2), 39.35 (CH_2), 40.02 (C), 40.56 (CH), 43.01 (C), 46.92 (CH), 53.35 (CH), 53.82 (CH), 55.56 (CH), 56.66 (CH), 109.87 (C), 119.16 (C), 124.46 (CH), 125.96 (CH), 126.23 (CH), 126.39 (2×CH), 132.31 (2×CH), 141.07 (CH), 142.50 (C), 211.87 (C). HRMS: (API+) calculated for $C_{30}H_{38}NO$ ($[M+H]^+$) 428.2953, Found 428.2955.

General procedure for acetylation

To a solution of tetraol (100 mg) in pyridine (3 mL) was added acetic anhydride (1 mL) and the mixture was left to stand overnight (approx. 18 hours). It was then diluted with ethyl acetate (20 mL) and extracted with 5% aqueous solution of hydrochloric acid (20 mL) and then with water (2 × 10 mL). The combined organic fractions were dried over anhydrous magnesium sulfate and evaporated under reduced pressure. Column chromatography on silica gel gave the desired product.

(*22R*, *23R*)-2α,3α,22,23-tetraacetoxy-23-phenyl-24-nor-5α-cholan-6-one (8d)

The general procedure for acetylation of **8c** and chromatography on silica (EtOAc/cyclohexane - 1/2) afforded 119 mg (88 %) of the title compound **8d** as a colorless oil: IR ν (cm^{-1}) 2938, 1735, 1709, 1612, 1512, 1237. ^1H NMR ($CDCl_3$) δ 0.39, 0.78 (both s, 3H, CH_3), 1.02 (d, 3H, J = 6.7 Hz, CH_3), 1.79-1.84 (m, 2H), 1.90-1.96 (m, 2H), 1.98, 1.99 (both s, 3H, CH_3), 2.02-2.10 (m, 2H), 2.08, 2.11 (both s, 3H, CH_3), 2.27 (dd, 1H, J = 13.1, J´ = 4.6 Hz), 2.54 (dd, 1H, J = 11.9, J´ = 4.0 Hz), 4.92 (m, 1H, ΣJ = 20.2 Hz), 5.37 (m, 1H), 5.44 (d, 1H, J = 9.6 Hz), 5.87 (d, 1H, J = 9.6 Hz), 7.33-7.40 (m, 5H, 5×Ar-H). ^{13}C NMR δ 11.38 (CH_3), 12.89 (CH_3), 13.47 (CH_3), 20.92 (CH_3), 21.00 (CH_3), 21.03 (CH_3), 21.08 (CH_3), 21.09 (CH_2), 23.66 (CH_2), 24.74 (CH_2), 27.82 (CH_2), 29.67 (CH_2), 36.07 (CH), 37.41 (CH), 39.11 (C), 42.33 (C), 42.58 (CH_2), 46.34 (CH_2), 51.72 (CH), 52.25 (CH), 53.54 (CH), 56.46 (CH), 68.05 (CH), 69.03 (CH), 76.09 (CH), 76.28 (CH), 127.78 (2×CH), 128.79 (2×CH), 128.90 (CH), 136.66 (C), 169.94 (C), 170.05 (C), 170.24 (C), 170.60 (C), 210.51 (C). HRMS: (API+) calculated for $C_{37}H_{51}O_9$ ($[M+H]^+$) 639.3533, Found 639.3537.

(*22R*, *23R*)-2α,3α,22,23-tetraacetoxy-23-(4-fluorophenyl)-24-nor-5α-cholan-6-one (9d)

The general procedure for acetylation of **9c** and chromatography on silica (EtOAc/cyclohexane - 1/2) afforded 116 mg (86 %) of the title compound **9d** as a colorless oil: IR ν (cm^{-1}) 2930, 1732, 1712, 1610, 1510, 1235. ^{1}H NMR ($CDCl_3$) δ 0.42, 0.79 (both s, 3H, CH_3), 1.01 (d, 3H, J = 6.7 Hz, CH_3), 1.80-1.85 (m, 2H), 1.91-1.96 (m, 2H), 1.988, 1.991 (both s, 3H, CH_3), 2.02-2.11 (m, 2H), 2.08, 2.11 (both s, 3H, CH_3), 2.28 (dd, 1H, J = 13.4, J´ = 4.6 Hz), 2.54 (dd, 1H, J = 11.9, J´ = 4.3 Hz), 4.93 (m, 1H, ΣJ = 20.5 Hz), 5.37 (m, 1H), 5.40 (d, 1H, J = 9.8 Hz), 5.85 (d, 1H, J = 9.8 Hz), 7.07 (m, 2H), 7.37 (m, 2H). ^{13}C NMR δ 11.41 (CH_3), 12.81 (CH_3), 13.47 (CH_3), 20.87 (CH_3), 20.97 (2×CH_3), 21.07 (CH_3, CH_2), 23.63 (CH_2), 24.72 (CH_2), 27.88 (CH_2), 29.63 (CH_2), 36.10 (CH), 37.39 (CH), 39.10 (C), 42.31 (C), 42.58 (CH_2), 46.30 (CH_2), 51.71 (CH), 52.19 (CH), 53.53 (CH), 56.44 (CH), 68.04 (CH), 69.02 (CH), 75.31 (CH), 76.06 (CH), 115.85 (d, J = 21.6 Hz, 2×CH), 129.57 (d, J = 7.2 Hz, 2×CH), 132.61 (d, J = 3.6 Hz, C), 162.76 (d, J = 248.3 Hz, C), 169.94 (C), 170.01 (C), 170.24 (C), 170.55 (C), 210.48 (C). ^{19}F NMR {^{1}H} δ -112.07 (s, 1F). HRMS: (API+) calculated for $C_{37}H_{50}FO_9$ ($[M+H]^+$) 657.3439, Found 657.3438.

(*22R*, *23R*)-2α,3α,22,23-tetraacetoxy-23-(4-chlorophenyl)-24-nor-5α-cholan-6-one (10d)

The general procedure for acetylation of **10c** and chromatography on silica (EtOAc/cyclohexane - 1/2) afforded 116 mg (87 %) of the title compound **10d** as a colorless oil: IR ν (cm^{-1}) 2932, 1735, 1710, 1611, 1513, 1237. ^{1}H NMR ($CDCl_3$) δ 0.43, 0.79 (both s, 3H, CH_3), 1.02 (d, 3H, J = 6.7 Hz, CH_3), 1.80-1.85 (m, 2H), 1.91-1.96 (m, 2H), 1.988, 1.990 (both s, 3H, CH_3), 2.02-2.11 (m, 2H), 2.08, 2.11 (both s, 3H, CH_3), 2.28 (dd, 1H, J = 13.3, J´ = 4.4 Hz), 2.54 (dd, 1H, J = 11.6, J´ = 4.0 Hz), 4.93 (m, 1H, ΣJ = 19.6 Hz), 5.37 (m, 1H), 5.44 (d, 1H, J = 9.8 Hz), 5.83 (d, 1H, J = 9.8 Hz), 7.32-7.37 (m, 4H, 4×Ar-H). ^{13}C NMR δ 11.47 (CH_3), 12.84 (CH_3), 13.47 (CH_3), 20.87 (CH_3), 20.94 (CH_3), 20.98 (CH_3), 21.07 (CH_3), 21.08 (CH_2), 23.63 (CH_2), 24.72 (CH_2), 27.90 (CH_2), 29.63 (CH_2), 36.16 (CH), 37.38 (CH), 39.10 (C), 42.31 (C), 42.58 (CH_2), 46.30 (CH_2), 51.71 (CH), 52.18 (CH), 53.53 (CH), 56.45 (CH), 68.03 (CH), 69.02 (CH), 75.32 (CH), 75.88 (CH), 129.08 (2×CH), 129.14 (2×CH), 134.74 (C), 135.23 (C), 169.93 (C), 169.94 (C), 170.22 (C), 170.51 (C), 210.45 (C). HRMS: (API+) calculated for $C_{37}H_{50}ClO_9$ ($[M+H]^+$) 673.3143, Found 673.3142.

(*22R*, *23R*)-2α,3α,22,23-tetraacetoxy-23-(4-bromophenyl)-24-nor-5α-cholan-6-one (11d)

The general procedure for acetylation of **11c** and chromatography on silica (EtOAc/cyclohexane - 1/2) afforded 114 mg (87 %) of the title compound **11d** as a colorless oil: IR ν (cm^{-1}) 2932, 1734, 1711, 1612, 1512, 1237. ^{1}H NMR ($CDCl_3$) δ 0.43, 0.79 (both s, 3H, CH_3), 1.02 (d, 3H, J = 6.7 Hz, CH_3), 1.80-1.86 (m, 2H), 1.91-1.97 (m, 2H), 1.987, 1.989 (both s, 3H, CH_3), 2.02-2.10 (m, 2H), 2.08, 2.11 (both s, 3H, CH_3), 2.28 (dd, 1H, J = 13.4, J´ = 4.6 Hz), 2.54 (dd, 1H, J = 11.8, J´ = 4.1 Hz), 4.93 (m, 1H, ΣJ = 20.5 Hz), 5.37 (m, 1H), 5.40 (d, 1H, J = 9.6 Hz), 5.81 (d, 1H, J = 9.6 Hz), 7.27 (m, 2H), 7.52 (m, 2H). ^{13}C NMR δ 11.50 (CH_3), 12.85 (CH_3), 13.48 (CH_3), 20.87 (CH_3), 20.94 (CH_3), 20.99 (CH_3), 21.08 (CH_3, CH_2), 23.64 (CH_2), 24.74 (CH_2), 27.91 (CH_2), 29.64 (CH_2), 36.17 (CH), 37.40 (CH), 39.12 (C), 42.32 (C), 42.59 (CH_2), 46.31 (CH_2), 51.73 (CH), 52.19 (CH), 53.53 (CH), 56.46 (CH), 68.05 (CH), 69.04 (CH), 75.40 (CH), 75.84 (CH), 122.99 (C), 129.45 (2×CH), 132.05 (2×CH), 136.74 (C), 169.96 (2×C), 170.25 (C),

170.62 (C), 210.47 (C). HRMS: (API+) calculated for $C_{35}H_{46}{}^{79}BrO_7$ ([M-AcOH+H]$^+$) 657.2427, Found 657.2429.

(*22R*, *23R*)-2α,3α,22,23-tetraacetoxy-23-(4-iodophenyl)-24-nor-5α-cholan-6-one (12d)

The general procedure for acetylation of **12c** and chromatography on silica (EtOAc/cyclohexane - 1/2) afforded 109 mg (85 %) of the title compound **12d** as a colorless oil: IR ν (cm^{-1}) 2935, 1735, 1709, 1612, 1512, 1234. ^{1}H NMR ($CDCl_3$) δ 0.44, 0.79 (both s, 3H, CH_3), 1.01 (d, 3H, J = 6.7 Hz, CH_3), 1.80-1.87 (m, 2H), 1.91-1.97 (m, 2H), 1.985, 1.987 (both s, 3H, CH_3), 2.02-2.10 (m, 2H), 2.08, 2.11 (both s, 3H, CH_3), 2.28 (dd, 1H, J = 13.4, J´ = 4.6 Hz), 2.54 (dd, 1H, J = 11.8, J´ = 4.1 Hz), 4.93 (m, 1H, ΣJ = 20.2 Hz), 5.37 (m, 1H), 5.39 (d, 1H, J = 9.8 Hz), 5.79 (d, 1H, J = 9.8 Hz), 7.14 (m, 2H), 7.72 (m, 2H). ^{13}C NMR δ 11.54 (CH_3), 12.87 (CH_3), 13.50 (CH_3), 20.89 (CH_3), 20.96 (CH_3), 21.01 (CH_3), 21.09 (CH_3, CH_2), 23.66 (CH_2), 24.76 (CH_2), 27.93 (CH_2), 29.66 (CH_2), 36.22 (CH), 37.41 (CH), 39.14 (C), 42.34 (C), 42.61 (CH_2), 46.33 (CH_2), 51.74 (CH), 52.21 (CH), 53.55 (CH), 56.49 (CH), 68.06 (CH), 69.04 (CH), 75.53 (CH), 75.81 (CH), 94.86 (C), 129.64 (2×CH), 136.37 (C), 137.99 (2×CH), 169.97 (2×C), 170.26 (C), 170.54 (C), 210.49 (C). HRMS: (API+) calculated for $C_{37}H_{50}IO_9$ ([M+H]$^+$) 765.2500, Found 765.2499.

(*22R*, *23R*)-2α,3α,22,23-tetraacetoxy-23-(4-nitrophenyl)-24-nor-5α-cholan-6-one (13d)

The general procedure for acetylation of **13c** and chromatography on silica (EtOAc/cyclohexane - 1/2) afforded 114 mg (86 %) of the title compound **13d** as a colorless oil: IR ν (cm^{-1}) 2938, 1735, 1710, 1612, 1520, 1347, 1229. ^{1}H NMR ($CDCl_3$) δ 0.42, 0.79 (both s, 3H, CH_3), 1.05 (d, 3H, J = 6.1 Hz, CH_3), 1.79-1.85 (m, 2H), 1.91-1.96 (m, 2H), 1.99, 2.03 (both s, 3H, CH_3), 2.02-2.10 (m, 2H), 2.08, 2.12 (both s, 3H, CH_3), 2.27 (dd, 1H, J = 13.4, J´ = 4.6 Hz), 2.54 (dd, 1H, J = 11.8, J´ = 4.1 Hz), 4.93 (m, 1H, ΣJ = 20.2 Hz), 5.37 (m, 1H), 5.43 (d, 1H, J = 9.5 Hz), 5.91 (d, 1H, J = 9.5 Hz), 7.58 (m, 2H), 8.25 (m, 2H). ^{13}C NMR δ 11.50 (CH_3), 13.00 (CH_3), 13.49 (CH_3), 20.83 (CH_3), 20.86 (CH_3), 21.00 (CH_3), 21.08 (CH_3, CH_2), 23.62 (CH_2), 24.74 (CH_2), 28.01 (CH_2), 29.66 (CH_2), 36.39 (CH), 37.36 (CH), 39.11 (C), 42.31 (C), 42.62 (CH_2), 46.29 (CH_2), 51.73 (CH), 52.18 (CH), 53.53 (CH), 56.44 (CH), 68.05 (CH), 69.03 (CH), 75.06 (CH), 75.54 (CH), 124.09 (2×CH), 128.68 (2×CH), 143.90 (CH), 148.08 (C), 169.86 (C), 169.95 (C), 170.25 (C), 170.41 (C), 210.38 (C). HRMS: (API+) calculated for $C_{37}H_{50}NO_{11}$ ([M+H]$^+$) 684.3384, Found 684.3381.

(*22R*, *23R*)-2α,3α,22,23-tetraacetoxy-23-(4-methylphenyl)-24-nor-5α-cholan-6-one (14d)

The general procedure for acetylation of **14c** and chromatography on silica (EtOAc/cyclohexane - 1/2) afforded 116 mg (86 %) of the title compound **14d** as a colorless oil: IR ν (cm^{-1}) 2932, 1739, 1711, 1611, 1513, 1227. ^{1}H NMR ($CDCl_3$) δ 0.41, 0.79 (both s, 3H, CH_3), 1.01 (d, 3H, J = 6.7 Hz, CH_3), 1.80-1.86 (m, 2H), 1.91-1.97 (m, 2H), 1.98, 1.99 (both s, 3H, CH_3), 2.02-2.10 (m, 2H), 2.08, 2.10 (both s, 3H, CH_3), 2.27 (dd, 1H, J = 13.3, J´ = 4.7 Hz), 2.35 (s, 3H, CH_3), 2.54 (dd, 1H, J = 11.6, J´ = 4.0 Hz), 4.93 (m, 1H, ΣJ = 20.2 Hz), 5.37 (m, 1H), 5.43 (d, 1H, J = 9.8 Hz), 5.85 (d, 1H, J = 9.8 Hz), 7.17 (d, 2H, J = 7.9 Hz), 7.27 (d, 2H, J = 7.9 Hz). ^{13}C NMR δ 11.47 (CH_3), 12.85 (CH_3), 13.50 (CH_3), 20.96 (CH_3), 21.02 (CH_3), 21.08 (CH_3), 21.10

(CH_3, CH_2), 21.25 (CH_3), 23.69 (CH_2), 24.76 (CH_2), 27.86 (CH_2), 29.67 (CH_2), 36.14 (CH), 37.44 (CH), 39.14 (C), 42.36 (C), 42.59 (CH_2), 46.37 (CH_2), 51.74 (CH), 52.27 (CH), 53.56 (CH), 56.49 (CH), 68.06 (CH), 69.04 (CH), 75.98 (CH), 76.29 (CH), 127.74 (2×CH), 129.50 (2×CH), 133.60 (CH), 138.73 (C), 169.96 (C), 170.09 (C), 170.26 (C), 170.64 (C), 210.57 (C). HRMS: (API+) calculated for $C_{36}H_{49}O_7$ ($[M\text{-}AcOH+H]^+$) 593.3478, Found 593.3483.

(*22R*, *23R*)-2α,3α,22,23-tetraacetoxy-23-(4-methoxyphenyl)-24-nor-5α-cholan-6-one (15d)
General procedure for acetylation of **15c** and chromatography on silica (EtOAc/cyclohexane - 1/2) afforded 118 mg (88 %) of the title compound **15d** as a colorless oil: IR ν (cm^{-1}) 2938, 1737, 1711, 1614, 1513, 1230. ^{1}H NMR ($CDCl_3$) δ 0.42, 0.79 (both s, 3H, CH_3), 1.00 (d, 3H, J = 6.7 Hz, CH_3), 1.79-1.85 (m, 2H), 1.91-1.96 (m, 2H), 1.98, 1.99 (both s, 3H, CH_3), 2.02-2.10 (m, 2H), 2.08, 2.10 (both s, 3H, CH_3), 2.28 (dd, 1H, J = 13.4, J´ = 4.6 Hz), 2.54 (dd, 1H, J = 11.8, J´ = 4.1 Hz), 3.82 (s, 3H, CH_3), 4.93 (m, 1H, ΣJ = 20.2 Hz), 5.37 (m, 1H), 5.42 (d, 1H, J = 9.8 Hz), 5.84 (d, 1H, J = 9.8 Hz), 6.90 (m, 2H), 7.31 (m, 2H). ^{13}C NMR δ 11.48 (CH_3), 12.81 (CH_3), 13.50 (CH_3), 20.96 (CH_3), 21.02 (CH_3), 21.08 (CH_3), 21.10 (CH_3, CH_2), 23.69 (CH_2), 24.76 (CH_2), 27.89 (CH_2), 29.67 (CH_2), 36.15 (CH), 37.44 (CH), 39.14 (C), 42.36 (C), 42.59 (CH_2), 46.36 (CH_2), 51.74 (CH), 52.26 (CH), 53.56 (CH), 55.21 (CH_3), 56.50 (CH), 68.07 (CH), 69.04 (CH), 75.72 (CH), 76.27 (CH), 114.15 (2×CH), 128.71 (CH), 129.15 (2×CH), 159.81 (C), 169.96 (C), 170.14 (C), 170.26 (C), 170.65 (C), 210.55 (C). HRMS: (API+) calculated for $C_{36}H_{49}O_8$ ($[M\text{-}AcOH+H]^+$) 609.3427, Found 609.3427.

(*22R*, *23R*)-2α,3α,22,23-tetraacetoxy-23-(4-isopropylphenyl)-24-nor-5α-cholan-6-one (16d)
General procedure for acetylation of **16c** and chromatography on silica (EtOAc/cyclohexane - 1/2) afforded 114 mg (86 %) of the title compound **16d** as a colorless oil: IR ν (cm^{-1}) 2935, 1738, 1712, 1615, 1513, 1234. ^{1}H NMR ($CDCl_3$) δ 0.39, 0.78 (both s, 3H, CH_3), 1.01 (d, 3H, J = 6.7 Hz, CH_3), 1.24 (d, 6H, J = 6.7 Hz, 2×CH_3), 1.80-1.85 (m, 2H), 1.91-1.96 (m, 2H), 1.98, 1.99 (both s, 3H, CH_3), 2.02-2.11 (m, 2H), 2.08, 2.10 (both s, 3H, CH_3), 2.27 (dd, 1H, J = 13.4, J´ = 4.6 Hz), 2.54 (dd, 1H, J = 11.8, J´ = 4.1 Hz), 2.91 (septet, 1H, J = 6.7 Hz), 4.92 (m, 1H, ΣJ = 19.6 Hz), 5.37 (m, 1H), 5.43 (d, 1H, J = 9.7 Hz), 5.86 (d, 1H, J = 9.7 Hz), 7.22 (d, 2H, J = 7.9 Hz), 7.29 (d, 2H, J = 7.9 Hz). ^{13}C NMR δ 11.42 (CH_3), 12.90 (CH_3), 13.50 (CH_3), 20.98 (CH_3), 21.03 (CH_3), 21.09 (2×CH_3), 21.11 (CH_2), 23.69 (CH_2), 23.79 (CH_3), 23.86 (CH_3), 24.76 (CH_2), 26.88 (CH_2), 27.80 (CH_2), 33.82 (CH), 36.06 (CH), 37.45 (CH), 39.15 (C), 42.36 (C), 42.60 (CH_2), 46.38 (CH_2), 51.75 (CH), 52.30 (CH), 53.56 (CH), 56.48 (CH), 68.07 (CH), 69.05 (CH), 76.01 (CH), 76.38 (CH), 126.84 (2×CH), 127.79 (2×CH), 133.85 (C), 149.61 (C), 169.98 (C), 170.14 (C), 170.37 (C), 170.66 (C), 210.58 (C). HRMS: (API+) calculated for $C_{38}H_{53}O_7$ ($[M\text{-}AcOH+H]^+$) 621.3791, Found 621.3794.

(*22R*, *23R*)-2α,3α,22,23-tetraacetoxy-23-(4-cyanophenyl)-24-nor-5α-cholan-6-one (17d)
General procedure for acetylation of **17c** and chromatography on silica (EtOAc/cyclohexane - 1/2) afforded 117 mg (87 %) of the title compound **17d** as a colorless oil: IR ν (cm^{-1}) 2940, 2230, 1736, 1710, 1614, 1510, 1227. ^{1}H NMR ($CDCl_3$) δ 0.42, 0.79 (both s, 3H, CH_3), 1.03 (d, 3H, J = 6.7 Hz, CH_3), 1.80-1.85 (m, 2H), 1.91-1.96 (m, 2H), 1.99, 2.02 (both s, 3H, CH_3), 2.02-

2.10 (m, 2H), 2.08, 2.12 (both s, 3H, CH_3), 2.28 (dd, 1H, J = 13.1, J´ = 4.6 Hz), 2.54 (dd, 1H, J = 11.8, J´ = 4.1 Hz), 4.93 (m, 1H, ΣJ = 19.5 Hz), 5.37 (m, 1H), 5.40 (d, 1H, J = 9.5 Hz), 5.85 (d, 1H, J = 9.5 Hz), 7.51 (m, 2H), 7.69 (m, 2H). ^{13}C NMR δ 11.47 (CH_3), 13.00 (CH_3), 13.51 (CH_3), 20.85 (CH_3), 20.87 (CH_3), 21.02 (CH_3), 21.08 (CH_2), 21.09 (CH_3), 23.62 (CH_2), 24.75 (CH_2), 27.98 (CH_2), 36.32 (CH), 37.37 (CH), 37.43 (CH_2), 39.11 (C), 42.32 (C), 42.68 (CH_2), 46.30 (CH_2), 51.74 (CH), 52.18 (CH), 53.53 (CH), 56.44 (CH), 68.05 (CH), 69.03 (CH), 75.32 (CH), 75.55 (CH), 112.89 (C), 118.24 (C), 128.46 (2×CH), 132.68 (2×CH), 141.99 (C), 169.87 (C), 169.94 (C), 170.24 (C), 170.42 (C), 210.38 (C). HRMS: (API+) calculated for $C_{38}H_{50}NO_9$ ($[M+H]^+$) 664.3486, Found 664.3481.

General procedure for Baeyer-Villiger oxidation

To a solution of ketone (100 mg) in dichloromethane (5 mL) was added solution of trifluoroperoxyacetic acid* (2 mL) and mixture was stirred for 3 hours. The reaction mixture was then diluted with ethyl acetate (20 mL) and extracted with saturated solution of sodium sulfite (10 mL), saturated solution of sodium bicarbonate (10 mL), and with water (10 mL). The combined organic fractions were dried over anhydrous magnesium sulfate and evaporated under reduced pressure. Column chromatography on silica gel afforded desired product.

* Solution of trifluoroperoxyacetic acid was freshly prepared from dichloromethane (20 mL), trifluoroacetic anhydride (2.14 mL), and 30% solution of hydrogen peroxide (0.5 mL).

(*22R*, *23R*)-2α,3α,22,23-tetraacetoxy-7-oxa-7a-homo-23-phenyl-24-nor-5α-cholan-6-one (8e)

General procedure for Baeyer-Villiger of **8d** oxidation and chromatography on silica (EtOAc/cyclohexane - 2/3) afforded 90 mg (88 %) of the title compound **8e** as a colorless oil: IR ν (cm^{-1}) 2922, 1736, 1612, 1509, 1225. ^{1}H NMR ($CDCl_3$) δ 0.42, 0.94 (both s, 3H, CH_3), 1.01 (d, 3H, J = 6.7 Hz, CH_3), 1.86-1.93 (m, 3H), 1.99 (s, 6H, 2×CH_3), 2.00-2.12 (m, 2H), 2.100, 2.105 (both s, 3H, CH_3), 2.27 (m, 1H, ΣJ = 30.6 Hz), 2.97 (dd, 1H, J = 12.2, J´ = 4.6 Hz, H-5α), 4.01 (dd, 1H, J = 12.5, J´ = 9.2 Hz, H-7a_1), 4.07 (dd, 1H, J = 12.5, J´ = 1.2 Hz, H-7a_2), 4.85 (m, 1H, ΣJ = 19.9 Hz), 5.35 (m, 1H), 5.42 (d, 1H, J = 9.6 Hz), 5.87 (d, 1H, J = 9.6 Hz), 7.33-7.40 (m, 5H, 5×Ar-H). ^{13}C NMR δ 11.18 (CH_3), 12.63 (CH_3), 15.37 (CH_3), 20.91 (CH_3), 21.03 (2×CH_3), 21.11 (CH_3), 22.11 (CH_2), 24.54 (CH_2), 27.74 (CH_2), 29.20 (CH_2), 36.12 (CH), 38.29 (CH_2), 38.77 (C), 39.01 (CH), 39.28 (CH_2), 41.92 (CH), 42.26 (C), 51.19 (CH), 52.23 (CH), 58.23 (CH), 67.84 (CH), 68.86 (CH), 70.32 (CH_2), 76.05 (CH), 76.21 (CH), 127.75 (2×CH), 128.82 (2×CH), 128.96 (CH), 136.59 (C), 169.95 (C), 170.05 (C), 170.22 (C), 170.60 (C), 175.04 (C). HRMS: (API+) calculated for $C_{37}H_{51}O_{10}$ ($[M+H]^+$) 655.3482, Found 655.3483.

(*22R*, *23R*)-2α,3α,22,23-tetraacetoxy-7-oxa-7a-homo-23-(4-fluorophenyl)-24-nor-5α-cholan-6-one (9e)

General procedure for Baeyer-Villiger oxidation of **9d** and chromatography on silica (EtOAc/cyclohexane - 2/3) afforded 87 mg (85 %) of the title compound **9e** as a colorless oil: IR ν (cm^{-1}) 2931, 1738, 1608, 1510, 1233. ^{1}H NMR ($CDCl_3$) δ 0.45, 0.94 (both s, 3H, CH_3), 1.00

(d, 3H, J = 6.4 Hz, CH_3), 1.86-1.93 (m, 3H), 1.991, 1.994 (both s, 3H, CH_3), 2.00-2.12 (m, 2H), 2.099, 2.105 (both s, 3H, CH_3), 2.27 (m, 1H, ΣJ = 30.6 Hz), 2.97 (dd, 1H, J = 12.2, J´ = 4.6 Hz, H-5α), 4.01 (dd, 1H, J = 12.5, J´ = 9.2 Hz, H-7a_1), 4.07 (dd, 1H, J = 12.5, J´ = 1.2 Hz, H-7a_2), 4.85 (m, 1H, ΣJ = 19.9 Hz), 5.35 (m, 1H), 5.38 (d, 1H, J = 9.8 Hz), 5.84 (d, 1H, J = 9.8 Hz), 7.08 (m, 2H), 7.37 (m, 2H). ^{13}C NMR δ 11.23 (CH_3), 12.78 (CH_3), 15.39 (CH_3), 20.89 (CH_3), 21.00 (CH_3), 21.02 (CH_3), 21.12 (CH_3), 22.13 (CH_2), 24.54 (CH_2), 27.82 (CH_2), 29.21 (CH_2), 36.17 (CH), 38.31 (CH_2), 38.79 (C), 39.03 (CH), 39.30 (CH_2), 41.93 (CH), 42.28 (C), 51.22 (CH), 52.19 (CH), 58.25 (CH), 67.85 (CH), 68.87 (CH), 70.30 (CH_2), 75.28 (CH), 76.00 (CH), 115.92 (d, J = 21.6 Hz, 2×CH), 129.58 (d, J = 8.4 Hz, 2×CH), 132.57 (d, J = 3.6 Hz, C), 162.81 (d, J = 248.3 Hz, C), 169.94 (C), 170.01 (C), 170.22 (C), 170.55 (C), 175.01 (C). ^{19}F NMR {^{1}H} δ -111.94 (s, 1F). HRMS: (API+) calculated for $C_{37}H_{50}FO_{10}$ ([M+H]$^+$) 673.3388, Found 673.3395.

(*22R*, *23R*)-2α,3α,22,23-tetraacetoxy-7-oxa-7a-homo-23-(4-chlorophenyl)-24-nor-5α-cholan-6-one (10e)

General procedure for Baeyer-Villiger oxidation of **10d** and chromatography on silica (EtOAc/cyclohexane - 2/3) afforded 90 mg (88 %) of the title compound **10e** as a colorless oil: IR ν (cm^{-1}) 2937, 1738, 1610, 1510, 1233. ^{1}H NMR ($CDCl_3$) δ 0.46, 0.95 (both s, 3H, CH_3), 1.00 (d, 3H, J = 6.7 Hz, CH_3), 1.86-1.93 (m, 3H), 1.990, 1.994 (both s, 3H, CH_3), 2.00-2.12 (m, 2H), 2.10, 2.11 (both s, 3H, CH_3), 2.27 (m, 1H, ΣJ = 30.6 Hz), 2.97 (dd, 1H, J = 12.4, J´ = 4.4 Hz, H-5α), 4.01 (dd, 1H, J = 12.3, J´ = 9.2 Hz, H-7a_1), 4.08 (dd, 1H, J = 12.3, J´ = 1.1 Hz, H-7a_2), 4.85 (m, 1H, ΣJ = 19.6 Hz), 5.36 (m, 1H), 5.38 (d, 1H, J = 9.8 Hz), 5.82 (d, 1H, J = 9.8 Hz), 7.31-7.37 (m, 4H, 4×Ar-H). ^{13}C NMR δ 11.29 (CH_3), 12.81 (CH_3), 15.39 (CH_3), 20.88 (CH_3), 20.97 (CH_3), 21.03 (CH_3), 21.12 (CH_3), 22.13 (CH_2), 24.54 (CH_2), 27.85 (CH_2), 29.21 (CH_2), 36.24 (CH), 38.31 (CH_2), 38.79 (C), 39.02 (CH), 39.30 (CH_2), 41.93 (CH), 42.29 (C), 51.23 (CH), 52.18 (CH), 58.25 (CH), 67.85 (CH), 68.87 (CH), 70.30 (CH_2), 75.30 (CH), 75.84 (CH), 129.14 (4×CH), 134.83 (C), 135.18 (C), 169.97 (C), 170.13 (C), 170.23 (C), 170.53 (C), 175.01 (C). HRMS: (API+) calculated for $C_{37}H_{50}ClO_{10}$ ([M+H]$^+$) 689.3093, Found 689.3092.

(*22R*, *23R*)-2α,3α,22,23-tetraacetoxy-7-oxa-7a-homo-23-(4-bromophenyl)-24-nor-5α-cholan-6-one (11e)

General procedure for Baeyer-Villiger oxidation of **11d** and chromatography on silica (EtOAc/cyclohexane - 2/3) afforded 89 mg (87 %) of the title compound **11e** as a colorless oil: IR ν (cm^{-1}) 2935, 1735, 1611, 1508, 1236. ^{1}H NMR ($CDCl_3$) δ 0.47, 0.95 (both s, 3H, CH_3), 1.00 (d, 3H, J = 6.7 Hz, CH_3), 1.86-1.93 (m, 3H), 1.988, 1.994 (both s, 3H, CH_3), 2.01-2.11 (m, 2H), 2.10, 2.11 (both s, 3H, CH_3), 2.27 (m, 1H, ΣJ = 30.6 Hz), 2.97 (dd, 1H, J = 12.4, J´ = 4.4 Hz, H-5α), 4.01 (dd, 1H, J = 12.5, J´ = 9.2 Hz, H-7a_1), 4.08 (dd, 1H, J = 12.5, J´ = 1.2 Hz, H-7a_2), 4.85 (m, 1H, ΣJ = 19.9 Hz), 5.36 (m, 1H), 5.38 (d, 1H, J = 9.8 Hz), 5.81 (d, 1H, J = 9.8 Hz), 7.27 (m, 2H), 7.52 (m, 2H). ^{13}C NMR δ 11.30 (CH_3), 12.81 (CH_3), 15.38 (CH_3), 20.87 (CH_3), 20.95 (CH_3), 21.02 (CH_3), 21.11 (CH_3), 22.12 (CH_2), 24.53 (CH_2), 27.85 (CH_2), 29.21 (CH_2), 36.24 (CH), 38.31 (CH_2), 38.79 (C), 39.02 (CH), 39.30 (CH_2), 41.93 (CH), 42.28 (C), 51.22 (CH), 52.17 (CH), 58.25 (CH), 67.83 (CH), 68.85 (CH), 70.28 (CH_2), 75.35 (CH), 75.75 (CH), 123.04 (C), 129.42 (2×CH),

132.09 (2×CH), 135.67 (C), 169.94 (2×C), 170.21 (C), 170.51 (C), 175.00 (C). HRMS: (API+) calculated for $C_{37}H_{50}{}^{79}BrO_{10}$ ($[M+H]^+$) 733.2587, Found 733.2583.

(*22R*, *23R*)-2α,3α,22,23-tetraacetoxy-7-oxa-7a-homo-23-(4-nitrophenyl)-24-nor-5α-cholan-6-one (13e)

General procedure for Baeyer-Villiger oxidation of **13d** and chromatography on silica (EtOAc/cyclohexane - 2/3) afforded 89 mg (87 %) of the title compound **13e** as a colorless oil: IR ν (cm^{-1}) 2935, 1732, 1609, 1525, 1345, 1226. ^{1}H NMR ($CDCl_3$) δ 0.45, 0.94 (both s, 3H, CH_3), 1.04 (d, 3H, J = 6.4 Hz, CH_3), 1.86-1.93 (m, 3H), 1.99, 2.03 (both s, 3H, CH_3), 2.01-2.11 (m, 2H), 2.10, 2.11 (both s, 3H, CH_3), 2.27 (m, 1H, ΣJ = 30.6 Hz), 2.97 (dd, 1H, J = 12.4, J´ = 4.4 Hz, H-5α), 4.01 (dd, 1H, J = 12.5, J´ = 9.2 Hz, H-7a_1), 4.07 (dd, 1H, J = 12.5, J´ = 1.2 Hz, H-7a_2), 4.85 (m, 1H, ΣJ = 19.9 Hz), 5.35 (m, 1H), 5.41 (d, 1H, J = 9.5 Hz), 5.91 (d, 1H, J = 9.5 Hz), 7.58 (m, 2H), 8.26 (m, 2H). ^{13}C NMR δ 11.31 (CH_3), 12.95 (CH_3), 15.39 (CH_3), 20.82 (CH_3), 20.86 (CH_3), 21.03 (CH_3), 21.12 (CH_3), 22.12 (CH_2), 24.51 (CH_2), 27.93 (CH_2), 29.21 (CH_2), 36.46 (CH), 38.31 (CH_2), 38.79 (C), 39.01 (CH), 39.29 (CH_2), 41.93 (CH), 42.32 (C), 51.21 (CH), 52.16 (CH), 58.23 (CH), 67.85 (CH), 68.86 (CH), 70.25 (CH_2), 75.02 (CH), 75.45 (CH), 124.13 (2×CH), 128.66 (2×CH), 143.83 (CH), 148.12 (C), 169.83 (C), 169.93 (C), 170.21 (C), 170.40 (C), 174.95 (C). HRMS: (API+) calculated for $C_{37}H_{50}NO_{12}$ ($[M+H]^+$) 700.3333, Found 700.3328.

(*22R*, *23R*)-2α,3α,22,23-tetraacetoxy-7-oxa-7a-homo-23-(4-methylphenyl)-24-nor-5α-cholan-6-one (14e)

General procedure for Baeyer-Villiger oxidation of **14d** and chromatography on silica (EtOAc/cyclohexane - 2/3) afforded 84 mg (82 %) of the title compound **14e** as a colorless oil: IR ν (cm^{-1}) 2934, 1733, 1609, 1508, 1237. ^{1}H NMR ($CDCl_3$) δ 0.44, 0.94 (both s, 3H, CH_3), 1.00 (d, 3H, J = 6.7 Hz, CH_3), 1.86-1.93 (m, 3H), 1.97, 1.99 (both s, 3H, CH_3), 2.01-2.11 (m, 2H), 2.09, 2.11 (both s, 3H, CH_3), 2.27 (m, 1H, ΣJ = 30.6 Hz), 2.36 (s, 3H, CH_3), 2.97 (dd, 1H, J = 12.5, J´ = 4.5 Hz, H-5α), 4.01 (dd, 1H, J = 12.5, J´ = 9.2 Hz, H-7a_1), 4.07 (dd, 1H, J = 12.5, J´ = 1.1 Hz, H-7a_2), 4.85 (m, 1H, ΣJ = 19.6 Hz), 5.35 (m, 1H), 5.41 (d, 1H, J = 9.8 Hz), 5.84 (d, 1H, J = 9.8 Hz), 7.18 (d, 2H, J = 7.9 Hz), 7.26 (d, 2H, J = 7.9 Hz). ^{13}C NMR δ 11.25 (CH_3), 12.79 (CH_3), 15.38 (CH_3), 20.93 (CH_3), 21.02 (CH_3), 21.07 (CH_3), 21.12 (CH_3), 21.25 (CH_3), 22.13 (CH_2), 24.57 (CH_2), 27.77 (CH_2), 29.21 (CH_2), 36.17 (CH), 38.31 (CH_2), 38.79 (C), 39.03 (CH), 39.31 (CH_2), 41.93 (CH), 42.27 (C), 51.22 (CH), 52.23 (CH), 58.25 (CH), 67.85 (CH), 68.87 (CH), 70.34 (CH_2), 75.93 (CH), 76.22 (CH), 127.71 (2×CH), 129.53 (2×CH), 133.54 (C), 138.80 (C), 169.96 (C), 170.11 (C), 170.25 (C), 170.64 (C), 175.06 (C). HRMS: (API+) calculated for $C_{38}H_{53}O_{10}$ ($[M+H]^+$) 669.3639, Found 669.3644.

(*22R*, *23R*)-2α,3α,22,23-tetraacetoxy-7-oxa-7a-homo-23-(4-isopropylphenyl)-24-nor-5α-cholan-6-one (16e)

General procedure for Baeyer-Villiger oxidation of **16d** and chromatography on silica (EtOAc/cyclohexane - 2/3) afforded 87 mg (85 %) of the title compound **16e** as a colorless oil: IR ν (cm^{-1}) 2930, 1732, 1611, 1506, 1230. ^{1}H NMR ($CDCl_3$) δ 0.43, 0.94 (both s, 3H, CH_3), 1.00 (d, 3H, J = 6.7 Hz, CH_3), 1.25 (d, 6H, J = 6.7 Hz, 2×CH_3), 1.86-1.93 (m, 3H), 1.98, 1.99

(both s, 3H, CH_3), 2.01-2.11 (m, 2H), 2.09, 2.10 (both s, 3H, CH_3), 2.27 (m, 1H, ΣJ = 30.6 Hz), 2.91 (septet, 1H, J = 6.7 Hz), 2.97 (dd, 1H, J = 12.4, J´ = 4.4 Hz, H-5α), 4.01 (dd, 1H, J = 12.5, J´ = 9.1 Hz, H-7a_1), 4.07 (dd, 1H, J = 12.5, J´ = 1.2 Hz, H-7a_2), 4.85 (m, 1H, ΣJ = 19.9 Hz), 5.35 (m, 1H), 5.41 (d, 1H, J = 9.6 Hz), 5.86 (d, 1H, J = 9.6 Hz), 7.22 (d, 2H, J = 8.1 Hz), 7.29 (d, 2H, J = 8.1 Hz). ^{13}C NMR δ 11.18 (CH_3), 12.81 (CH_3), 15.36 (CH_3), 20.93 (CH_3), 21.01 (CH_3), 21.07 (CH_3), 21.11 (CH_3), 22.12 (CH_2), 23.77 (CH_3), 23.85 (CH_3), 24.56 (CH_2), 27.69 (CH_2), 29.20 (CH_2), 33.80 (CH), 36.08 (CH), 38.29 (CH_2), 38.77 (C), 39.03 (CH), 39.29 (CH_2), 41.93 (CH), 42.26 (C), 51.18 (CH), 52.26 (CH), 58.24 (CH), 67.84 (CH), 68.86 (CH), 70.33 (CH_2), 75.94 (CH), 76.28 (CH), 126.85 (2×CH), 127.75 (2×CH), 133.76 (C), 149.65 (C), 169.95 (C), 170.10 (C), 170.22 (C), 170.62 (C), 175.05 (C). HRMS: (API+) calculated for $C_{40}H_{57}O_{10}$ ($[M+H]^+$) 697.3952, Found 697.3954.

(*22R*, *23R*)-2α,3α,22,23-tetraacetoxy-7-oxa-7a-homo-23-(4-cyanophenyl)-24-nor-5α-cholan-6-one (17e)

General procedure for Baeyer-Villiger oxidation of **17d** and chromatography on silica (EtOAc/cyclohexane - 2/3) afforded 81 mg (79 %) of the title compound **17e** as a colorless oil: IR ν (cm^{-1}) 2935, 2231, 1738, 1609, 1510, 1235. ^{1}H NMR ($CDCl_3$) δ 0.46, 0.95 (both s, 3H, CH_3), 1.03 (d, 3H, J = 6.7 Hz, CH_3), 1.86-1.93 (m, 3H), 1.99, 2.02 (both s, 3H, CH_3), 2.01-2.11 (m, 2H), 2.10, 2.11 (both s, 3H, CH_3), 2.27 (m, 1H, ΣJ = 30.5 Hz), 2.97 (dd, 1H, J = 12.2, J´ = 4.6 Hz, H-5α), 4.01 (dd, 1H, J = 12.5, J´ = 9.2 Hz, H-7a_1), 4.08 (dd, 1H, J = 12.5, J´ = 1.1 Hz, H-7a_2), 4.86 (m, 1H, ΣJ = 19.7 Hz), 5.35 (m, 1H), 5.38 (d, 1H, J = 9.6 Hz), 5.85 (d, 1H, J = 9.6 Hz), 7.51 (d, 2H, J = 8.3 Hz), 7.70 (d, 2H, J = 8.3 Hz). ^{13}C NMR δ 11.25 (CH_3), 12.91 (CH_3), 15.36 (CH_3), 20.80 (CH_3), 20.84 (CH_3), 21.00 (CH_3), 21.09 (CH_3), 22.11 (CH_2), 24.48 (CH_2), 26.85 (CH_2), 27.86 (CH_2), 29.18 (CH), 36.35 (CH), 38.28 (CH_2), 38.76 (C), 38.99 (CH), 39.27 (CH_2), 41.90 (CH), 42.29 (C), 51.17 (CH), 52.13 (CH), 58.20 (CH), 67.83 (CH), 68.84 (CH), 70.23 (CH_2), 75.24 (CH), 75.45 (CH), 112.91 (C), 118.18 (C), 128.42 (2×CH), 132.68 (2×CH), 141.90 (C), 169.83 (C), 169.93 (C), 170.20 (C), 170.39 (C), 174.96 (C). HRMS: (API+) calculated for $C_{38}H_{50}NO_{10}$ ($[M+H]^+$) 680.3435, Found 680.3439.

General procedure for hydrolysis of acetates

To a solution of tetraacetate (70 mg) in tetrahydrofuran (4 mL) and water (1 mL) was added potassium hydroxide (50 mg; 0.89 mmol) and mixture was heated at 60 °C for 6 hours. Then, the reaction was acidified with 5% aqueous solution of hydrochloric acid and reaction mixture was stirred at room temperature for 30 minutes. The reaction mixture was then diluted with ethyl acetate (20 mL) and extracted with water (2 × 10 mL). The combined organic fractions were dried over anhydrous magnesium sulfate and evaporated under reduced pressure. Column chromatography on silica gel afforded desired product.

(*22R*, *23R*)-2α,3α,22,23-tetrahydroxy-7-oxa-7a-homo-23-phenyl-24-nor-5α-cholan-6-one (8f)

General procedure for hydrolysis of acetates of **8e**, chromatography on silica (MeOH/$CHCl_3$ - 1/12) and lyophilization from *t*-butanol afforded 49 mg (95 %) of the title compound **8f** as an

amorphous powder: m. p. 258-260 °C, IR ν (cm^{-1}) 3393, 2942, 1707, 1608. ^{1}H NMR (DMSO-d_6) δ 0.33, 0.71 (both s, 3H, CH_3), 0.84 (d, 3H, J = 6.7 Hz, CH_3), 1.76-1.88 (m, 4H), 3.04 (dd, 1H, J = 12.1, J´ = 4.4 Hz, H-5α), 3.46-3.49 (m, 2H), 3.71 (m, 1H), 3.84 (d, 1H, J = 11.9 Hz), 4.11 (dd, 1H, J = 12.4, J´ = 9.3 Hz), 4.30 (d, 1H, J = 2.8 Hz), 4.34-4.36 (m, 2H), 4.51 (d, 1H, J = 4.3 Hz), 5.10 (d, 1H, J = 4.0 Hz), 7.23-7.33 (m, 5H, 5×Ar-H). ^{13}C NMR δ 11.18 (CH_3), 12.41 (CH_3), 15.35 (CH_3), 21.74 (CH_2), 24.13 (CH_2), 27.21 (CH_2), 31.94 (CH_2), 36.35 (CH), 37.64 (CH_2), 38.80 (CH), 39.26 (C), 40.46 (CH), 41.50 (C), 41.71 (CH_2), 50.77 (CH), 51.83 (CH), 57.19 (CH), 67.01 (CH), 67.13 (CH), 69.56 (CH_2), 75.16 (CH), 76.25 (CH), 127.02 (2×CH), 127.25 (CH), 128.10 (2×CH), 143.27 (C), 175.92 (C). HRMS: (API+) calculated for $C_{29}H_{43}O_6$ ($[M+H]^+$) 487.3060, Found 487.3063. Anal. Calcd for $C_{29}H_{42}O_6$: C, 71.57; H, 8.70. Found: C, 71.55; H, 8.73 %.

(*22R*, *23R*)-2α,3α,22,23-tetrahydroxy-7-oxa-7a-homo-23-(4-fluorophenyl)-24-nor-5α-cholan-6-one (9f)

General procedure for hydrolysis of acetates of **9e**, chromatography on silica (MeOH/$CHCl_3$ - 1/12) and lyophilization from *t*-butanol afforded 50 mg (95 %) of the title compound **9f** as an amorphous powder: m. p. 274-276 °C, IR ν (cm^{-1}) 3381, 2942, 1706, 1605. ^{1}H NMR (DMSO-d_6) δ 0.36, 0.72 (both s, 3H, CH_3), 0.83 (d, 3H, J = 6.4 Hz, CH_3), 1.76-1.88 (m, 4H), 3.04 (dd, 1H, J = 12.2, J´ = 4.6 Hz, H-5α), 3.44 (m, 1H), 3.71 (m, 1H), 3.84 (d, 1H, J = 11.9 Hz), 4.11 (dd, 1H, J = 12.5, J´ = 9.5 Hz), 4.31 (d, 1H, J = 2.8 Hz), 4.35-4.38 (m, 2H), 4.54 (d, 1H, J = 4.3 Hz), 5.15 (d, 1H, J = 3.7 Hz), 7.14 (m, 2H), 7.30 (m, 2H). ^{13}C NMR δ 11.21 (CH_3), 12.39 (CH_3), 15.37 (CH_3), 21.76 (CH_2), 24.15 (CH_2), 27.26 (CH_2), 31.95 (CH_2), 36.41 (CH), 37.66 (CH_2), 38.82 (CH), 39.28 (C), 40.47 (CH), 41.52 (C), 41.74 (CH_2), 50.78 (CH), 51.84 (CH), 57.21 (CH), 67.02 (CH), 67.15 (CH), 69.58 (CH_2), 74.39 (CH), 76.28 (CH), 114.87 (d, J = 21.6 Hz, 2×CH), 128.87 (d, J = 8.4 Hz, 2×CH), 139.57 (d, J = 3.6 Hz, C), 161.28 (d, J = 242.3 Hz, C), 175.95 (C). ^{19}F NMR {^{1}H} δ -115.34 (s, 1F). HRMS: (API+) calculated for $C_{29}H_{42}FO_6$ ($[M+H]^+$) 505.2965, Found 505.2964. Anal. Calcd for $C_{29}H_{41}FO_6$: C, 69.02; H, 8.19. Found: C, 68.58; H, 8.23 %.

(*22R*, *23R*)-2α,3α,22,23-tetrahydroxy-7-oxa-7a-homo-23-(4-chlorophenyl)-24-nor-5α-cholan-6-one (10f)

General procedure for hydrolysis of acetates of **10e**, chromatography on silica (MeOH/$CHCl_3$ - 1/12) and lyophilization from *t*-butanol afforded 51 mg (97 %) of the title compound **10f** as an amorphous powder: m. p. 282-284 °C, IR ν (cm^{-1}) 3341, 2945, 1701, 1599. ^{1}H NMR (DMSO-d_6) δ 0.37, 0.72 (both s, 3H, CH_3), 0.83 (d, 3H, J = 6.7 Hz, CH_3), 1.76-1.88 (m, 4H), 3.04 (dd, 1H, J = 12.2, J´ = 4.6 Hz, H-5α), 3.44 (m, 1H), 3.71 (m, 1H), 3.85 (d, 1H, J = 12.2 Hz), 4.12 (dd, 1H, J = 12.5, J´ = 9.5 Hz), 4.30 (d, 1H, J = 2.8 Hz), 4.34 -4.38 (m, 2H), 4.58 (d, 1H, J = 4.3 Hz), 5.21 (d, 1H, J = 3.7 Hz), 7.29 (m, 2H), 7.38 (m, 2H). ^{13}C NMR δ 11.23 (CH_3), 12.41 (CH_3), 15.35 (CH_3), 21.74 (CH_2), 24.13 (CH_2), 27.26 (CH_2), 31.94 (CH_2), 36.51 (CH), 37.64 (CH_2), 38.80 (CH), 39.26 (C), 40.45 (CH), 41.51 (C), 41.72 (CH_2), 50.77 (CH), 51.81 (CH), 57.19 (CH), 67.00 (CH), 67.13 (CH), 69.55 (CH_2), 74.39 (CH), 76.13 (CH), 128.10 (2×CH), 128.86 (2×CH), 131.52 (C), 142.40 (C), 175.91 (C). HRMS: (API+) calculated for $C_{29}H_{42}ClO_6$ ($[M+H]^+$) 521.2670, Found 521.2670. Anal. Calcd for $C_{29}H_{41}ClO_6$: C, 66.84; H, 7.93. Found: C, 66.80; H, 7.94 %.

(*22R*, *23R*)-2α,3α,22,23-tetrahydroxy-7-oxa-7a-homo-23-(4-bromophenyl)-24-nor-5α-cholan-6-one (11f)

The general procedure for hydrolysis of acetates of **11e**, chromatography on silica ($MeOH/CHCl_3$ - 1/12) and lyophilization from *t*-butanol afforded 51 mg (95 %) of the title compound **11f** as an amorphous powder: m. p. 277-279 °C, IR ν (cm^{-1}) 3372, 2942, 1707, 1592. ^1H NMR (DMSO-d_6) δ 0.37, 0.72 (both s, 3H, CH_3), 0.83 (d, 3H, J = 6.7 Hz, CH_3), 1.76-1.88 (m, 4H), 3.04 (dd, 1H, J = 12.1, J´ = 4.4 Hz, H-5α), 3.44 (m, 1H), 3.71 (m, 1H), 3.85 (d, 1H, J = 12.2 Hz), 4.12 (dd, 1H, J = 12.4, J´ = 9.6 Hz), 4.31 (d, 1H, J = 2.4 Hz), 4.34 -4.37 (m, 2H), 4.58 (d, 1H, J = 4.3 Hz), 5.21 (d, 1H, J = 3.7 Hz), 7.23 (m, 2H), 7.51 (m, 2H). ^{13}C NMR δ 11.27 (CH_3), 12.44 (CH_3), 15.37 (CH_3), 21.76 (CH_2), 24.15 (CH_2), 27.28 (CH_2), 31.95 (CH_2), 36.56 (CH), 37.66 (CH_2), 38.82 (CH), 39.28 (C), 40.47 (CH), 41.52 (C), 41.75 (CH_2), 50.78 (CH), 51.82 (CH), 57.21 (CH), 67.02 (CH), 67.15 (CH), 69.58 (CH_2), 74.48 (CH), 76.08 (CH), 120.09 (C), 129.26 (2×CH), 131.03 (2×CH), 142.83 (C), 175.95 (C). HRMS: (API+) calculated for $C_{29}H_{42}{}^{79}BrO_6$ ($[M+H]^+$) 565.2165, Found 565.2167. Anal. Calcd for $C_{29}H_{41}BrO_6$: C, 61.59; H, 7.31. Found: C, 61.51; H, 7.35 %.

(*22R*, *23R*)-2α,3α,22,23-tetrahydroxy-7-oxa-7a-homo-23-(4-nitrophenyl)-24-nor-5α-cholan-6-one (13f)

The general procedure for hydrolysis of acetates of **13e**, chromatography on silica ($MeOH/CHCl_3$ - 1/12) and lyophilization from *t*-butanol afforded 49 mg (93 %) of the title compound **13f** as an amorphous powder: m. p. 252-254 °C, IR ν (cm^{-1}) 3368, 2923, 1705, 1604, 1520, 1345. ^1H NMR (DMSO-d_6) δ 0.37, 0.72 (both s, 3H, CH_3), 0.86 (d, 3H, J = 6.7 Hz, CH_3), 1.76-1.88 (m, 4H), 3.04 (dd, 1H, J = 12.1, J´ = 4.4 Hz, H-5α), 3.49 (m, 1H), 3.71 (m, 1H), 3.84 (d, 1H, J = 12.0 Hz), 4.12 (dd, 1H, J = 12.4, J´ = 9.6 Hz), 4.30 (d, 1H, J = 2.1 Hz), 4.34 (b d, 1H, J = 5.5 Hz), 4.53 (dd, 1H, J = 7.9, J´ = 2.1 Hz), 4.74 (d, 1H, J = 4.6 Hz), 5.47 (d, 1H, J = 3.7 Hz), 7.57 (m, 2H), 8.20 (m, 2H). ^{13}C NMR δ 11.23 (CH_3), 12.55 (CH_3), 15.34 (CH_3), 21.73 (CH_2), 24.13 (CH_2), 27.28 (CH_2), 31.93 (CH_2), 36.81 (CH), 37.63 (CH_2), 38.79 (CH), 39.24 (C), 40.44 (CH), 41.50 (C), 41.74 (CH_2), 50.75 (CH), 51.83 (CH), 57.18 (CH), 66.99 (CH), 67.12 (CH), 69.53 (CH_2), 74.41 (CH), 76.00 (CH), 123.30 (2×CH), 128.22 (2×CH), 146.60 (C), 151.50 (C), 175.89 (C). HRMS: (ESI-) calculated for $C_{29}H_{41}NO_8$ ($[M^\bullet]^-$) 531.2832, Found 531.2831. Anal. Calcd for $C_{29}H_{41}NO_8$: C, 65.52; H, 7.77. Found: C, 65.45; H, 7.83 %.

(*22R*, *23R*)-2α,3α,22,23-tetrahydroxy-7-oxa-7a-homo-23-(4-methylphenyl)-24-nor-5α-cholan-6-one (14f)

The general procedure for hydrolysis of acetates of **14e**, chromatography on silica ($MeOH/CHCl_3$ - 1/12) and lyophilization from *t*-butanol afforded 50 mg (95 %) of the title compound **14f** as an amorphous powder: m. p. 253-255 °C, IR ν (cm^{-1}) 3339, 2930, 1713, 1607. ^1H NMR (DMSO-d_6) δ 0.35, 0.72 (both s, 3H, CH_3), 0.83 (d, 3H, J = 6.7 Hz, CH_3), 1.76-1.88 (m, 4H), 2.28 (s, 3H, CH_3), 3.04 (dd, 1H, J = 12.2, J´ = 4.6 Hz, H-5α), 3.46 (m, 1H), 3.71 (m, 1H), 3.84 (d, 1H, J = 11.9 Hz), 4.12 (dd, 1H, J = 12.5, J´ = 9.5 Hz), 4.29 -4.32 (m, 2H), 4.35 (d, 1H, J = 5.5 Hz), 4.46 (d, 1H, J = 4.1 Hz), 5.01 (d, 1H, J = 3.7 Hz), 7.11-7.15 (m, 4H). ^{13}C NMR δ 11.26 (CH_3), 12.34 (CH_3), 15.36 (CH_3), 20.80 (CH_3), 21.75 (CH_2), 24.14 (CH_2), 27.24 (CH_2),

31.94 (CH_2), 36.42 (CH), 37.65 (CH_2), 38.80 (CH), 39.28 (C), 40.45 (CH), 41.51 (C), 41.71 (CH_2), 50.78 (CH), 51.81 (CH), 57.20 (CH), 67.01 (CH), 67.14 (CH), 69.82 (CH_2), 74.91 (CH), 76.17 (CH), 126.96 (2×CH), 128.68 (2×CH), 136.12 (C), 140.18 (C), 175.92 (C). HRMS: (API+) calculated for $C_{30}H_{45}O_6$ ($[M+H]^+$) 501.3216, Found 501.3219. Anal. Calcd for $C_{30}H_{44}O_6$: C, 71.97; H, 8.86. Found: C, 71.93; H, 8.92 %.

(*22R*, *23R*)-2α,3α,22,23-tetrahydroxy-7-oxa-7a-homo-23-(4-isopropylphenyl)-24-nor-5α-cholan-6-one (16f)

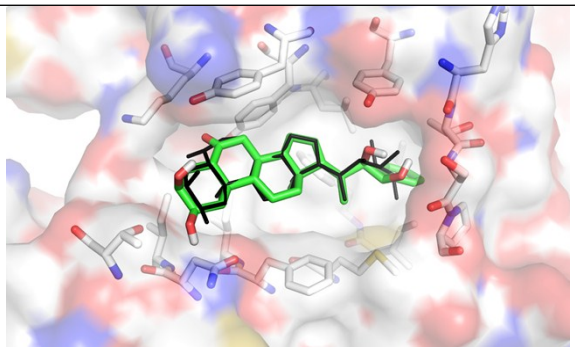
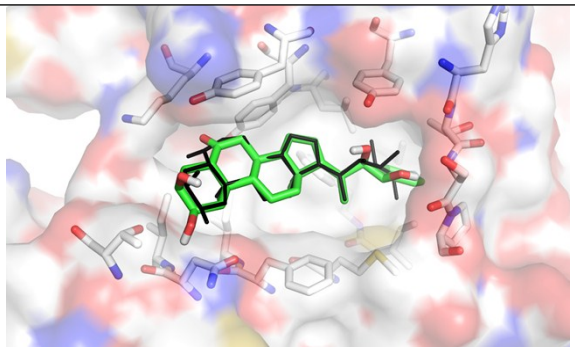
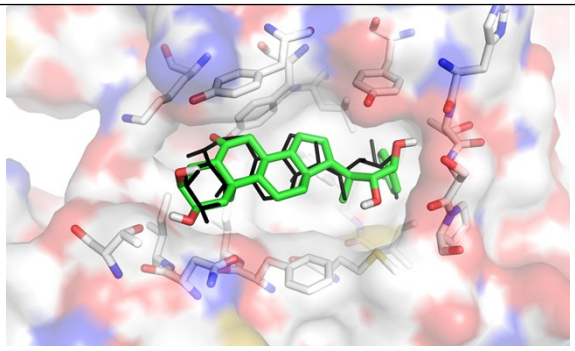
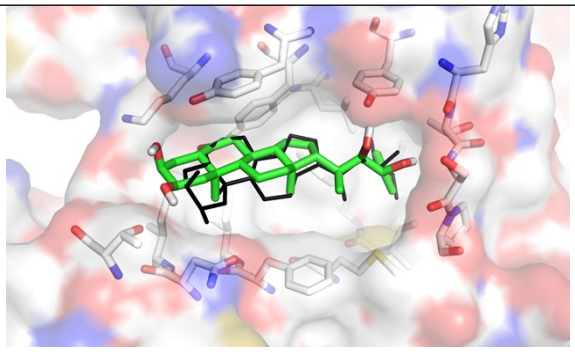
The general procedure for hydrolysis of acetates of **16e**, chromatography on silica ($MeOH/CHCl_3$ - 1/12) and lyophilization from *t*-butanol afforded 51 mg (95 %) of the title compound **16f** as an amorphous powder: m. p. 263-265 °C, IR ν (cm^{-1}) 3399, 2937, 1706, 1603. ^1H NMR (DMSO-d_6) δ 0.34, 0.71 (both s, 3H, CH_3), 0.83 (d, 3H, J = 6.7 Hz, CH_3), 1.18 (d, 6H, J = 6.9 Hz, 2×CH_3), 1.76-1.88 (m, 4H), 2.86 (septet, 1H, J = 6.9 Hz), 3.04 (dd, 1H, J = 12.2, J´ = 4.6 Hz, H-5α), 3.46 (m, 1H), 3.71 (m, 1H), 3.85 (d, 1H, J = 12.2 Hz), 4.11 (dd, 1H, J = 12.4, J´ = 9.4 Hz), 4.29 -4.32 (m, 2H), 4.35 (d, 1H, J = 5.8 Hz), 4.43 (d, 1H, J = 4.3 Hz), 5.01 (d, 1H, J = 3.7 Hz), 7.16-7.19 (m, 4H). ^{13}C NMR δ 11.23 (CH_3), 12.43 (CH_3), 15.34 (CH_3), 21.75 (CH_2), 23.91 (CH_3), 24.01 (CH_3), 24.16 (CH_2), 27.16 (CH_2), 31.34 (CH_2), 33.11 (CH), 36.37 (CH), 37.65 (CH_2), 38.81 (CH), 39.28 (C), 40.47 (CH), 41.51 (C), 41.73 (CH_2), 50.76 (CH), 51.91 (CH), 57.21 (CH), 67.02 (CH), 67.14 (CH), 69.59 (CH_2), 75.03 (CH), 76.10 (CH), 125.97 (2×CH), 127.04 (2×CH), 140.63 (C), 147.22 (C), 175.94 (C). HRMS: (API+) calculated for $C_{32}H_{49}O_6$ ($[M+H]^+$) 529.3529, Found 529.3530. Anal. Calcd for $C_{32}H_{48}O_6$: C, 72.69; H, 9.15. Found: C, 72.66; H, 9.20 %.

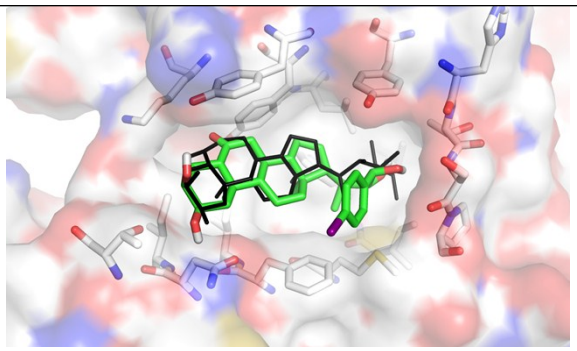
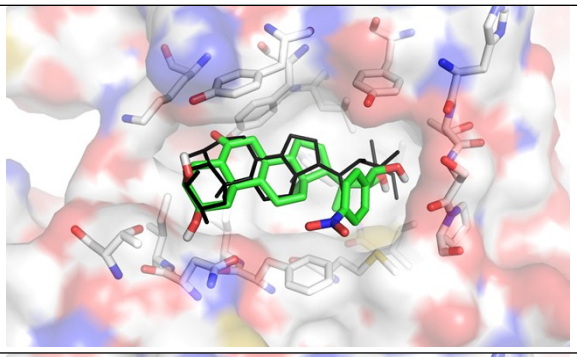
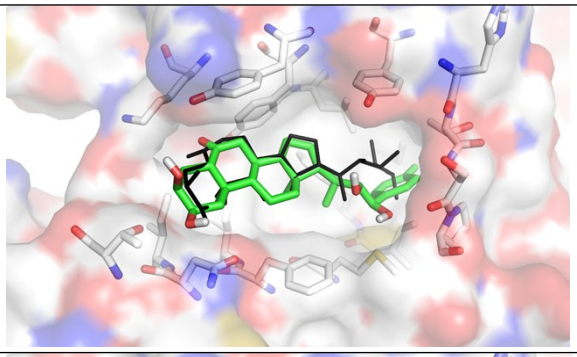
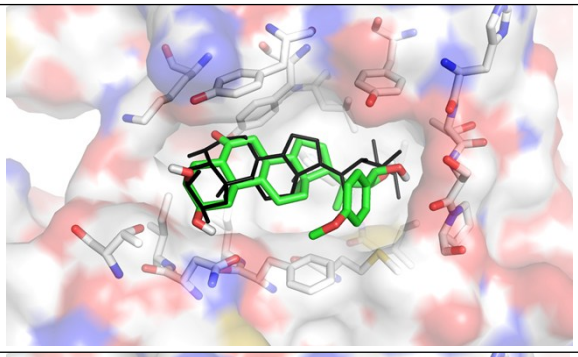
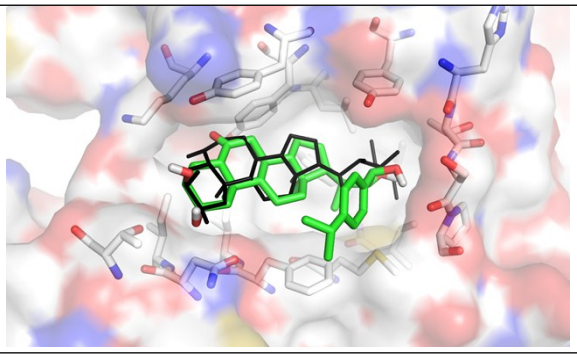
(*22R*, *23R*)-2α,3α,22,23-tetrahydroxy-7-oxa-7a-homo-23-(4-cyanophenyl)-24-nor-5α-cholan-6-one (17f)

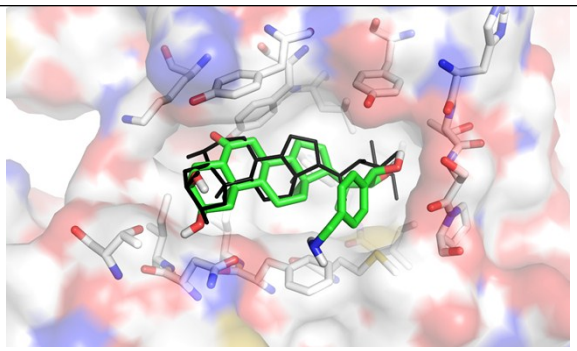
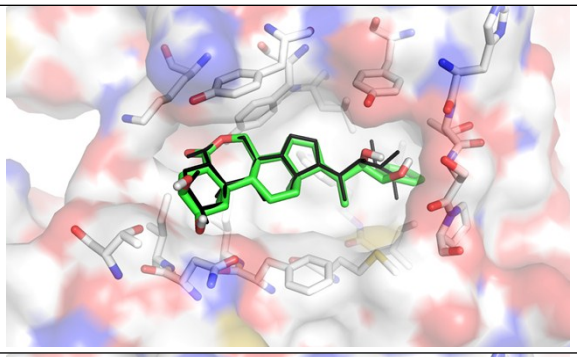
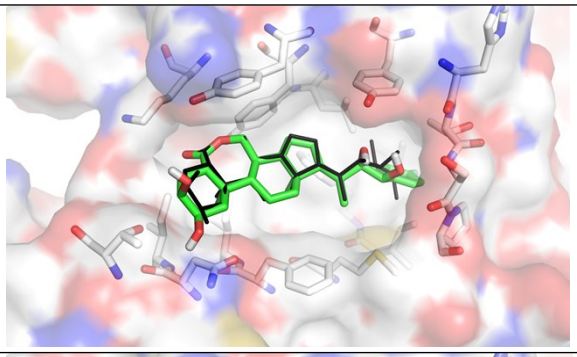
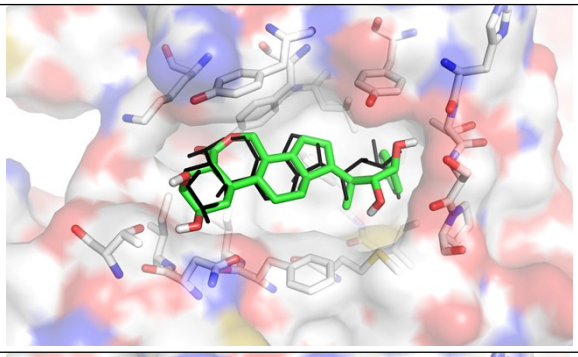
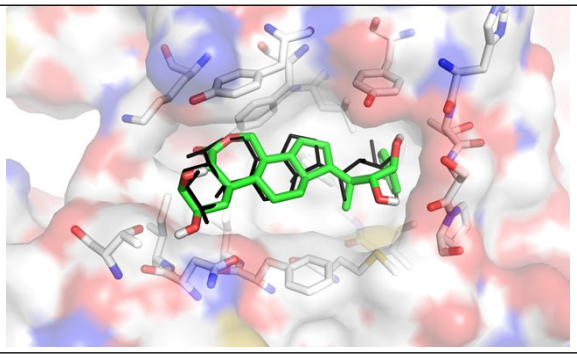
The general procedure for hydrolysis of acetates of **17e**, chromatography on silica ($MeOH/CHCl_3$ - 1/12) and lyophilization from *t*-butanol afforded 48 mg (92 %) of the title compound **17f** as an amorphous powder: m. p. 281-283 °C, IR ν (cm^{-1}) 3392, 2942, 2227, 1705, 1610. ^1H NMR (DMSO-d_6) δ 0.37, 0.72 (both s, 3H, CH_3), 0.84 (d, 3H, J = 6.7 Hz, CH_3), 1.76-1.89 (m, 4H), 3.04 (dd, 1H, J = 12.2, J´ = 4.4 Hz, H-5α), 3.47 (m, 1H), 3.71 (m, 1H), 3.84 (d, 1H, J = 12.0 Hz), 4.11 (dd, 1H, J = 12.4, J´ = 9.3 Hz), 4.30 (d, 1H, J = 2.5 Hz), 4.35 (d, 1H, J = 5.8 Hz), 4.46 (dd, 1H, J = 7.9, J´ = 2.4 Hz), 4.68 (d, 1H, J = 4.3 Hz), 5.40 (d, 1H, J = 3.7 Hz), 7.48 (d, 2H, J = 8.6 Hz, 2×Ar-H), 7.79 (d, 2H, J = 8.6 Hz, 2×Ar-H). ^{13}C NMR δ 11.20 (CH_3), 12.53 (CH_3), 15.33 (CH_3), 21.73 (CH_2), 24.12 (CH_2), 27.25 (CH_2), 31.93 (CH_2), 36.71 (CH), 37.64 (CH_2), 38.79 (CH), 39.24 (C), 40.45 (CH), 41.50 (C), 41.74 (CH_2), 50.75 (CH), 51.83 (CH), 57.19 (CH), 67.00 (CH), 67.13 (CH), 69.55 (CH_2), 74.66 (CH), 76.00 (CH), 109.83 (C), 118.98 (C), 127.99 (2×CH), 132.09 (2×CH), 149.29 (C), 175.89 (C). HRMS: (API+) calculated for $C_{30}H_{42}NO_6$ ($[M+H]^+$) 512.3012, Found 512.3009. Anal. Calcd for $C_{30}H_{41}NO_6$: C, 70.42; H, 8.08. Found: C, 70.37; H, 8.12 %.

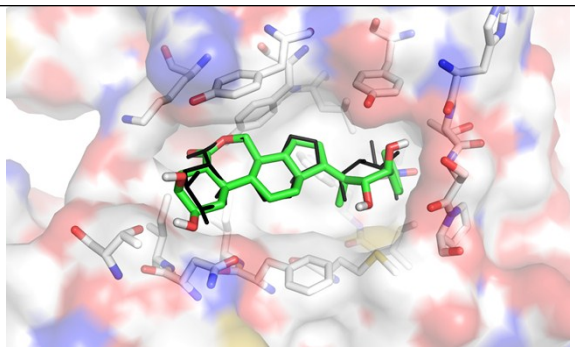
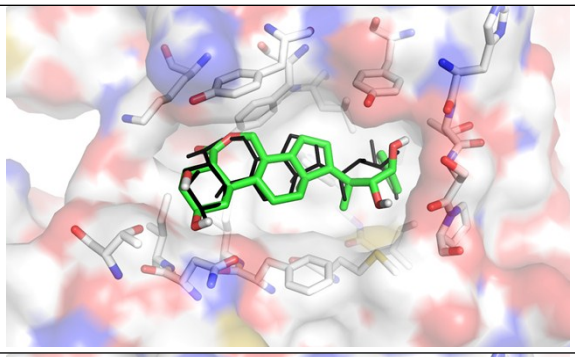
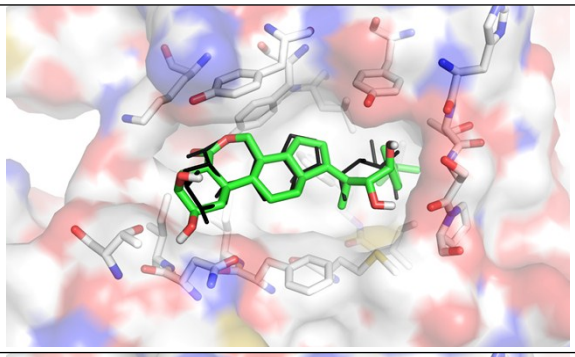
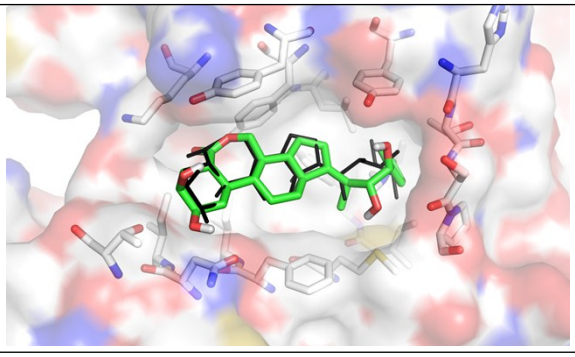
3) Molecular docking into BRI1:

Table 1 Global view on results of molecular docking to BRI receptor. Nature compound brassinolide is black.

Compound name	Result view	ΔG (kcal/mol) binding energy
MK-259B = 8c		-10.7 kcal/mol
MK-273B = 9c		-10.6 kcal/mol
MK-282 = 10c		-9.4 kcal/mol
MK-290 = 11c		-9.4 kcal/mol

MK-291 = 12c		-9.0 kcal/mol
MK-296 = 13c		-8.6 kcal/mol
MK-301 = 14c		-9.7 kcal/mol
MK-302 = 15c		-8.7 kcal/mol
MK-318 = 16c		-9.3 kcal/mol

MK-320 = 17c		-8.7 kcal/mol
MK-266 = 8f		-10.9 kcal/mol
MK-309 = 9f		-10.7 kcal/mol
MK-308 = 10f		-10.2 kcal/mol
MK-310 = 11f		-9.8 kcal/mol

MK-311 = 13f		-9.2 kcal/mol
MK-314 =14f		-10.4 kcal/mol
MK-321 = 16f		-9.8 kcal/mol
MK-322 = 17f		-9.5 kcal/mol

4) Biological activities:

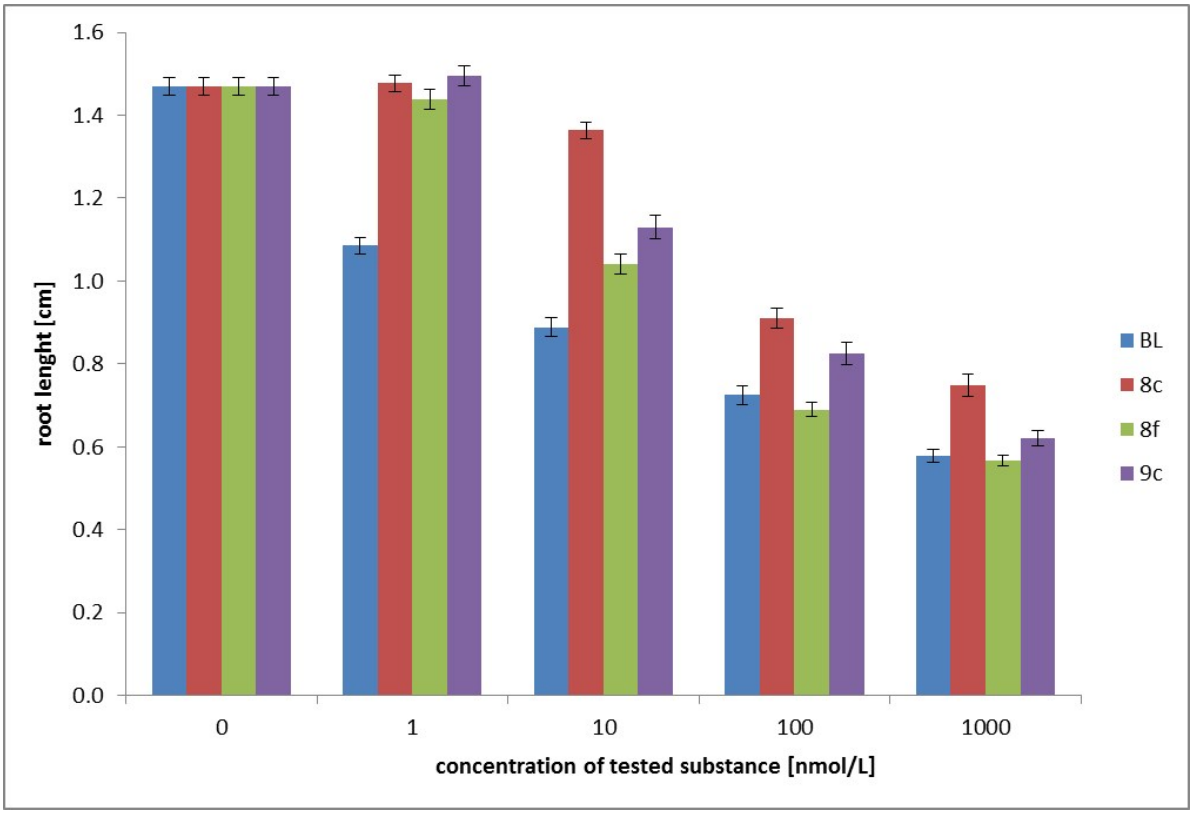


Fig. S3: Effect of selected brassinosteroid derivatives on the inhibition of Arabidopsis root lenght. 5 days old *Arabidopsis thaliana* seedlings (Columbia ecotype, Col-0) were treated by DMSO/BL/BR analogues. For each treatment more than 25 seedlings were analyzed in two biological repeats.

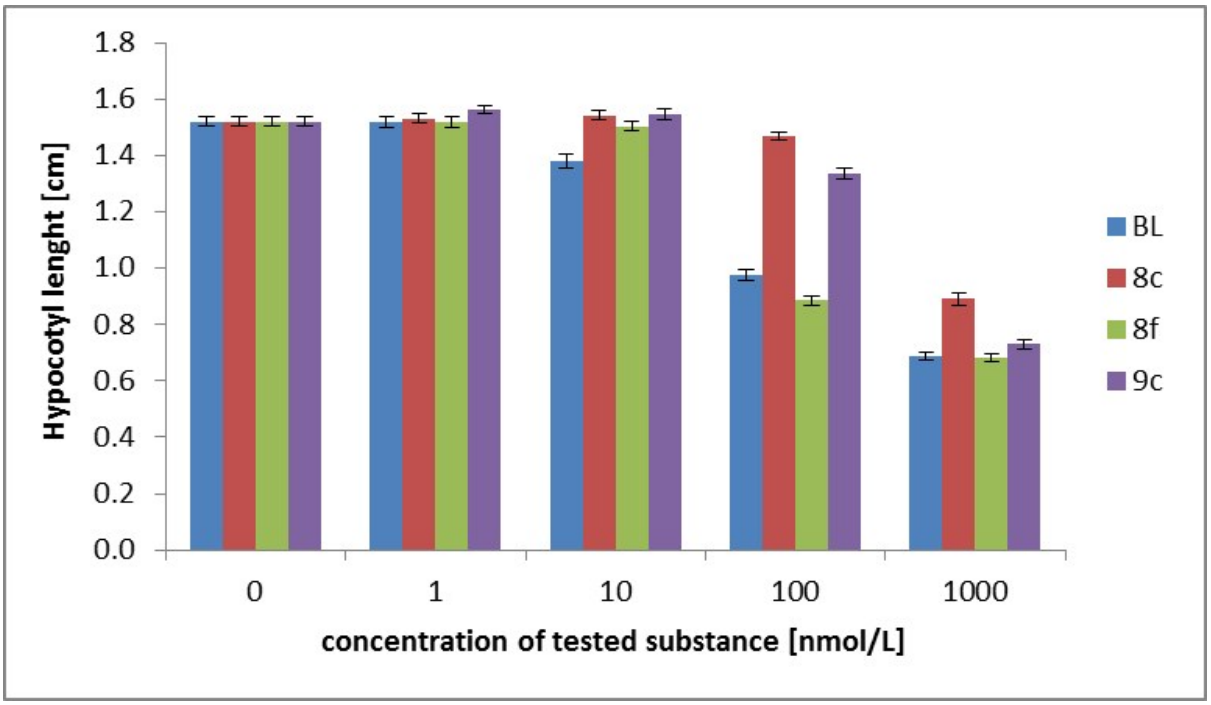


Fig. S4: Effect of selected brassinosteroid derivatives on the inhibition of Arabidopsis hypocotyl lenght. 5 days old *Arabidopsis thaliana* seedlings (Columbia ecotype, Col-0) were treated by DMSO/BL/BR analogues. For each treatment more than 25 seedlings were analyzed in two biological repeats.

Table S2.: IC_{50} (µmol/L) values obtained from the cytotoxicity assay on human cancer cell lines and normal human fibroblasts.

Compound	CEM	MCF7	HeLa	BJ
24-epibrassinolide	44.0 ± 2.2	>50	>50	>50
10c	>50	>50	>50	>50
11c	>50	>50	>50	>50
12c	>50	>50	>50	>50
13c	>50	>50	>50	>50
14c	>50	>50	>50	>50
15c	>50	>50	>50	>50
14f	50.0 ± 0.0	>50	50.0 ± 0.0	>50
17c	>50	>50	>50	>50
16f	>50	>50	>50	>50
17f	>50	>50	>50	>50
8c	>50	>50	>50	>50
8f	>50	>50	>50	>50
9c	>50	>50	>50	>50
10f	39.0 ± 0.6	>50	>50	>50
9f	>50	>50	>50	>50
11f	31.1± 0.5	>50	>50	>50
13f	>50	>50	37.2 ± 1.6	>50
16c	>50	>50	>50	>50