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Enantiospecific first total synthesis of (+)-2β-hydroxysolanascone, the aglycone of the phytoalexin isolated from flue-cured tobacco leaves

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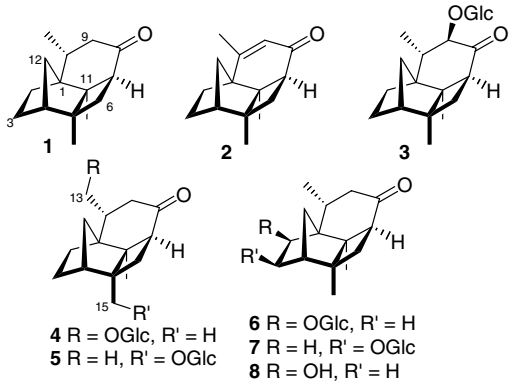
Abstract—The first total synthesis of (+)-2β-hydroxysolanascone, the aglycone of the phytoalexin 2β-hydroxysolanascone-β-glucopyranoside isolated from flue-cured tobacco leaves (*N. tabacum* L., OCL), and its 2,10-diepi- and 2α-epimers has been accomplished, starting from the readily available monoterpene (*R*)-carvone.

Phytoalexins are antibacterial, fungicidal, low molecular weight secondary metabolites produced as a means of self-defense in plants. The isolation of the structurally complex tetracyclic phytoalexin solanascone **1** was first reported by Fujimori and co-workers in 1978, from *Nicotiana tabacum* cv. Burley.[1,2] In 1983, the research group of Nishikawaji reported the isolation of dehydrosolanascone **2** from flue-cured tobacco leaves.[3] An oxygenated derivative, 9-hydroxysolanascone-β-sophoroside **3** was later isolated from flue-cured tobacco leaves by Kodama et al.[4] In 1986, Tazaki and co-workers reported two more solanascane derivatives, 13-hydroxysolanascone-β-glucopyranoside **4** and 15-hydroxysolanascone-β-glucopyranoside **5** from flue-cured tobacco.[5] Subsequently, they also reported the isolation of 2β-hydroxysolanascone-β-glucopyranoside **6** and 3β-hydroxysolanascone-β-glucopyranoside **7** from flue-cured tobacco leaves (*N. tabacum* L., OCL).[6] The strong antibacterial activity of solanascones on *Pseudomonas solanacearum* has been well established.[7]

The unusual and novel tetracyclo[5.3.1.$1^{1,4}$.$0^{5,11}$]dodecane carbon framework[2] incorporating three contiguous quaternary carbon atoms and seven chiral centres, coupled with the biological activities made solanascanes interesting and challenging synthetic targets.[8] Recently, we reported[8] the enantiospecific total synthesis of solanascone **1** and dehydrosolanascone **2**. In continuation,



herein, we report the enantiospecific first total synthesis of 2β-hydroxysolanascone **8**, the aglycone of the glycoside **6**, starting from the monoterpene (*R*)-carvone **9**.

A retrosynthetic analysis of 2-hydroxysolanascone **8** is depicted in Scheme 1. Enone **10** was identified as the key intermediate, which could be elaborated into 2-hydroxysolanascones. For the enone **10**, the diketone **11** was considered as an appropriate precursor, whose synthesis from carvone **9** via 3-butenylcarvone **12** has already been developed.[8]

The synthetic sequence (Schemes 2 and 3) was initiated with the preparation of the diketone **11** as described earlier.[8] Thus, a Barbier reaction between carvone **9** and 4-bromobut-1-ene, followed by oxidation of the resultant allylic tertiary alcohol furnished the 1,3-transposed

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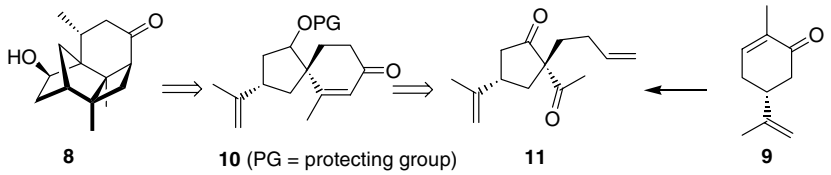
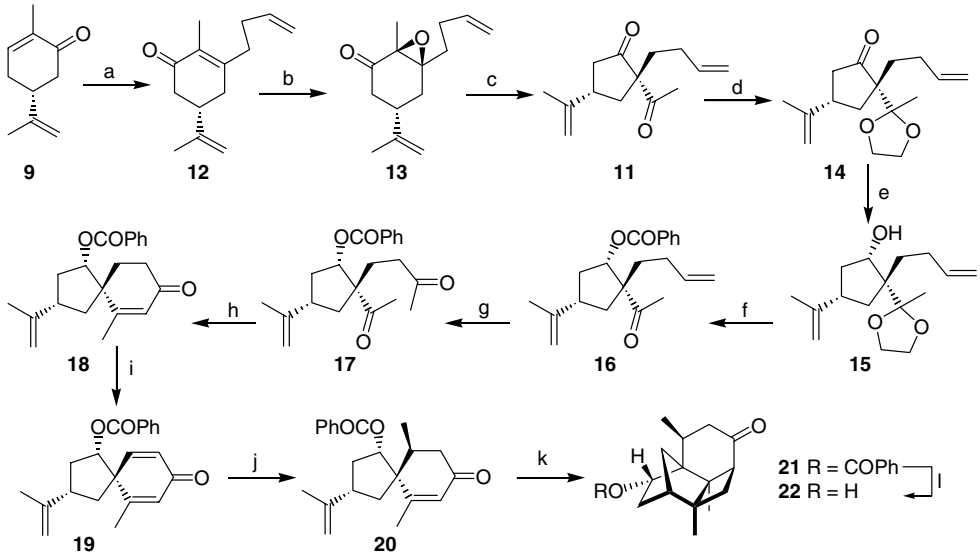


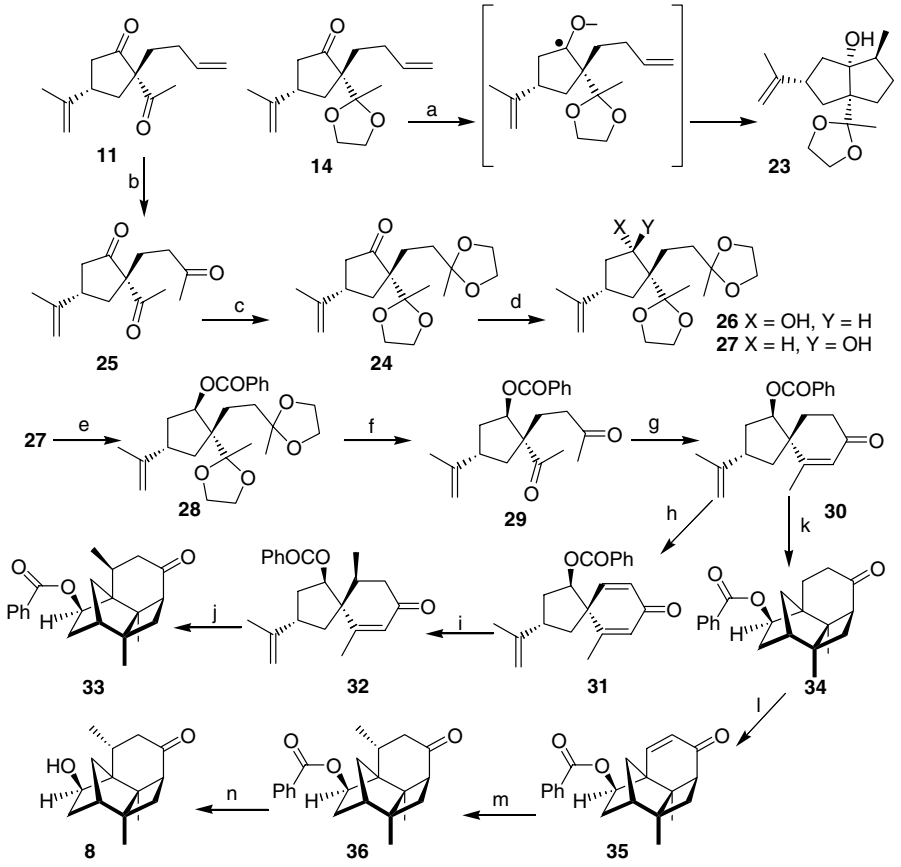
Scheme 1.



Scheme 2. Reagents, conditions and yields: (a) (i) Li, $BrCH_2CH_2CH{=}CH_2$, THF,))), 1 h; (ii) PCC, silica gel, CH_2Cl_2, rt, 4 h, 85%; (b) 30% H_2O_2, 6 N aq NaOH, MeOH, 0 °C, 20 h, 85%; (c) Amberlyst-15 (1:1 w/w), CH_2Cl_2 (0.1 M), rt, 24 h, 74%; (d) $(CH_2OH)_2$, PTSA, C_6H_6, reflux, 45 min, 68%; (e) LAH, Et_2O, 0 °C → rt, 1 h, 100%; (f) (i) C_6H_5COCl, py, DMAP, CH_2Cl_2, rt, 8 h; (ii) 3 N HCl, THF, 2 h; 91%; (g) $PdCl_2$, CuCl, DMF–H_2O (4:1), O_2, rt, 20 h, 82%; (h) piperidine, AcOH, C_6H_6, reflux, 45 min, 85%; (i) LHMDS, PhSeSePh, THF, 3.5 h, −70 °C; 30% H_2O_2, 30 min, 87%; (j) Me_2CuLi, Et_2O, −30 °C, 1 h, 76%; (k) hν, MeOH, 1 h, 84%; (l) K_2CO_3, MeOH, 50 °C, 4 h, 86%.

enone (*S*)-3-(but-3-enyl)carvone **12**.[9] Epoxidation of the enone **12** with 30% aqueous hydrogen peroxide in the presence of sodium hydroxide furnished the *anti*-epoxide **13**, in 85% yield, which on rearrangement with Amberlyst-15 generated the dione **11**.[10] Next, attention was focused on the protection of the cyclopentanone ketone in the dione **11**. Thus, refluxing a benzene solution of the diketone **11** with ethylene glycol in the presence of a catalytic amount of *p*-toluenesulfonic acid (PTSA) using a Dean–Stark water trap furnished the keto-ketal **14** in 68% yield, in a highly regioselective manner, which on reaction with LAH in ether at ice temperature furnished, stereoselectively, the alcohol **15** in quantitative yield. Reaction of the alcohol **15** with benzoyl chloride in pyridine in the presence of a catalytic amount of 4-*N*,*N*-dimethylaminopyridine (DMAP) at room temperature, followed by hydrolysis of the ketal with 3 N aqueous hydrochloric acid furnished the keto-benzoate **16** in 91% yield.

Treatment of the keto-benzoate **16** with 0.1 equiv of palladium chloride and 5 equiv of cuprous chloride in DMF and water under an oxygen atmosphere (balloon)[11] for 12 h produced, regioselectively, the diketobenzoate **17** in 82% yield. An intramolecular aldol condensation of the diketobenzoate **17** with piperidine and acetic acid in dry benzene using a Dean–Stark water trap furnished the enone **18**, in 85% yield, in a highly regioselective manner. A two-step protocol was conceived for introducing the secondary methyl group at the C-10 position via the cross-conjugated cyclohexadienone **19**. Accordingly, reaction of the enone **18** with lithium hexamethyldisilazide (LHMDS) and then diphenyl diselenide at −70 °C, followed by oxidation with 30% aqueous hydrogen peroxide at ice-bath temperature generated the dienone **19** in 87% yield. Conjugate addition of lithium dimethylcuprate to the dienone **19** at −30 °C furnished the enone **20**, in 76% yield, in a highly regio- and stereoselective manner. Even though the stereochemistry of the C-10 methyl group was not established at this stage, since only one isomer is produced in the reaction, it was tentatively assigned as *anti* to the benzoate bearing carbon. It was surprising to note that only one stereoisomer was formed in the cuprate reaction[8] even though the two substituents on the cyclopentane ring are *anti* to the C-10 carbon atom. One possible explanation for the observed stereoselectivity is the π-stacking of the dienone system with the aromatic ring of the benzoate blocking one side of the dienone in **19**. Photochemical irradiation of the enone **20** with a 450 W Hanovia medium pressure mercury vapor lamp furnished the keto-benzoate **21** in a highly regioselective and stereospecific manner, in 84% yield. Hydrolysis of the benzoate group in **21** furnished 2α-hydroxy-10-*epi*-



Scheme 3. Reagents, conditions and yields: (a) Li, liq. NH_3, THF, 10 min, 75%; (b) $PdCl_2$, CuCl, DMF, H_2O, O_2, rt, 20 h, 86%; (c) $(CH_2OH)_2$, PTSA, C_6H_6, reflux, 45 min, 72%; (d) Li, liq. NH_3, THF, 15 min, 89% (**26**:**27** 3:1); (e) C_6H_5COCl, py, DMAP, CH_2Cl_2, rt, 8 h, 95%; (f) 3 N HCl, THF, 2 h, 87%; (g) piperidine, AcOH, C_6H_6, reflux, 1 h, 90%; (h) LHMDS, TMSCl, Et_3N, THF, 2 h, −70 °C; $Pd(OAc)_2$, CH_3CN, rt, 4 h, 80%; (i) Me_2CuLi, Et_2O, 1 h, −30 °C; (j) hν, MeOH, 1 h, 65%; (k) hν, MeOH, 2 h, 87%; (l) LHMDS, TMSCl, Et_3N, THF, −70 °C, 2 h; $Pd(OAc)_2$, CH_3CN, 4 h, 80%; (m) Me_2CuLi, Et_2O, −30 °C, 1 h, 63%; (n) K_2CO_3, MeOH, 50 °C, 4 h, 100%.

solanascone **22**, mp 168–169.5 °C, in 86% yield, whose structure was confirmed by single crystal X-ray diffraction analysis (Fig. 1).[15] The stereochemistry of the hydroxy and secondary methyl groups in the keto-alcohol **22** was epimeric to those of the aglycone **8**.

For generation of the hydroxy group with correct stereochemistry, reduction of the keto-ketal **14** via single electron transfer methodology was investigated.[12] Reaction of the keto-ketal **14** with lithium in liquid ammonia and THF, however, furnished exclusively the diquinane **23** in a highly regio- and stereoselective manner, in 75% yield. Formation of the diquinane **23** can be readily explained via transfer of an electron to the ketone group in **14** followed by 5-*exo* trig cyclisation of the resultant radical anion.[13]

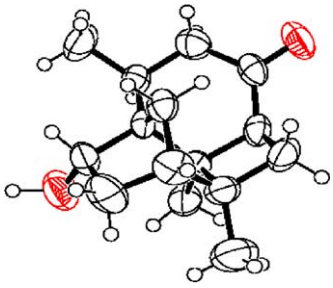


Figure 1. ORTEP diagram of the 2α-hydroxy-10-*epi*-solanascone **22**.

In order to prevent the radical cyclisation reaction, it was decided to carry out the sequence with the bisketal **24** of triketone **25**. Consequently, Wacker oxidation[11] of the dione **11** followed by selective ketalisation of the resultant trione **25** furnished the bisketal **24**. Reaction of the bisketal **24** with lithium in liquid ammonia and THF furnished a ~3:1 epimeric mixture of the alcohols **26** and **27**, which were separated by column chromatography on silica gel. The relative stereochemistry of the major alcohol **26** was established by converting it to the diketobenzoate **17**. The major alcohol **26** was reoxidised to **24** and the sequence was continued with the minor alcohol **27**. Treatment of the alcohol **27** with benzoyl chloride in the presence of a catalytic amount of DMAP in pyridine furnished the benzoate **28** in 95% yield, which on treatment with 3 N aqueous hydrochloric acid furnished the diketobenzoate **29** in 87% yield. Refluxing a benzene solution of the diketobenzoate **29** with piperidine and acetic acid using a Dean–Stark water trap furnished the enone **30** in a highly regioselective manner, in 90% yield. Reaction of the enone **30** with

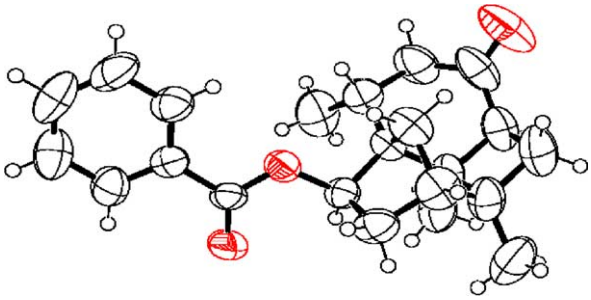


Figure 2. ORTEP diagram of the keto-benzoate **36**.

LHMDS, trimethylsilyl chloride and triethylamine followed by oxidative desilylation[14] of the resultant silyl dienolate with palladium acetate in dry acetonitrile furnished the cross-conjugated dienone **31** in 80% yield. Reaction of the dienone **31** with lithium dimethylcuprate in ether at −30 °C for 1 h furnished the enone **32**, which on photochemical irradiation with a 450 W Hanovia medium pressure mercury vapor lamp furnished 10-*epi*-solanascone derivative **33**, mp 124–125 °C,[15] in 65% yield.

In order to generate the secondary methyl group with correct stereochemistry, the sequence was altered and the secondary methyl group was introduced after the construction of the tetracyclic framework.[8] Consequently, irradiation of the enone **30** in methanol with a 450 W Hanovia medium pressure mercury vapor lamp for two hours furnished the keto-benzoate **34** in 87% yield. Treatment of the tetracyclic ketone **34** with LHMDS, trimethylsilyl chloride and triethylamine followed by reaction of the resultant silyl enol ether with palladium acetate in acetonitrile furnished the enone **35** in 80% yield. Treatment of the enone **35** with lithium dimethylcuprate at −30 °C furnished the keto-benzoate **36**, mp 168–170 °C, in 63% yield. The stereostructure of the keto-benzoate **36** was confirmed by X-ray diffraction analysis (Fig. 2).[15] Finally, hydrolysis of the benzoate group in **36** furnished the keto-alcohol[15] **8**, the aglycone of the glycoside **6**, in quantitative yield.

In summary, we have accomplished the first total synthesis of the aglycone **8** of the phytoalexin 2β-hydroxy-solanascone-β-glucopyranoside **6** isolated from flue-cured tobacco leaves, and its 2,10-diepi- and 2α-epimers, starting from the readily available monoterpene (*R*)-carvone via 3-butenylcarvone.

Acknowledgements

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15. Yields refer to isolated and chromatographically pure compounds. All the compounds exhibited spectral data (IR, ^{1}H and ^{13}C NMR and mass) consistent with their structures. Selected spectral data for (1*R*,2*S*,4*S*,5*S*,7*S*,10*S*,11*S*)-5,10,11-trimethyl-8-oxotetracyclo[5.3.1.1^{1,4}.0^{5,11}]dodecan-2-ol (**22**): mp: 168–169.5 °C; $[\alpha]_D^{24}$ +162.8 (*c* 0.7, $CHCl_3$); IR (thin film): ν_{max}/cm^{-1} 3426, 1670; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.23 (1H, dd, *J* 10.6 and 5.3 Hz), 2.68 (1H, dd, *J* 16.2 and 10.0 Hz), 2.62–2.50 (1H, m), 2.41 (1H, dd, *J* 10.8 and 7.4 Hz), 2.05 (1H, d, *J* 13.2), 2.10–2.00 (2H, m), 1.94 (1H, dd, *J* 16.0 and 4.8 Hz), 1.75 (1H, d, *J* 5.3 Hz, H-4), 1.67 (1H, ddd, *J* 11.7, 3.9 and 1.8 Hz), 1.43 (3H, s), 1.34 (1H, ddd, *J* 13.2, 5.1 and 3.6 Hz), 1.20 (1H, d, *J* 11.6 Hz), 1.15 (3H, s), 1.00 (3H, d, *J* 6.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 218.3 (C), 73.3 (CH), 54.2 (C), 51.0 (CH), 48.5 (C), 45.6 (CH_2), 44.2 (C), 43.2 (CH), 35.3 (CH_2), 33.1 (CH_2), 32.9 (CH_2), 27.3 (CH), 19.2 (CH_3), 17.9 (CH_3), 17.6 (CH_3); mass: 234 (M^+, 1%), 190 (50), 175 (9), 164 (11), 137 (68), 121 (44), 120 (100), 105 (44), 91 (28); HRMS: *m*/*z* calcd for $C_{15}H_{22}O_2Na$ (M+Na): 257.1517; Found: 257.1510. For (1*R*,2*R*,4*S*,5*S*,7*S*,10*S*,11*S*)-5,10,11-trimethyl-8-oxotetracyclo[5.3.1.1^{1,4}.0^{5,11}]dodec-2-yl benzoate (**33**): mp: 124–125 °C; $[\alpha]_D^{25}$ +19.1 (*c* 0.68, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 1714, 1601; ^{1}H NMR (300 MHz, $CDCl_3 + CCl_4$): δ 8.01 (2H, d, *J* 7.2 Hz), 7.56 (1H, t, *J* 7.2 Hz), 7.44 (2H, t, *J* 7.2 Hz), 5.22 (1H, d, *J* 6.6 Hz), 2.80–2.67 (2H, m), 2.60 (1H, dd, *J* 12.0 and 6.6 Hz), 2.20 (1H, ddd, *J* 14.7, 6.9 and 2.7 Hz), 2.11 (1H, dd, *J* 12.9 and 6.3 Hz), 1.96–1.73 (5H, m), 1.40 (1H, ddd, *J* 14.4, 4.8 and 2.4 Hz), 1.33 (3H, s), 1.10 (3H, s), 1.17 (3H, d, *J* 6.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3 + CCl_4$): δ 216.1 (C), 166.0 (C), 133.0 (CH), 130.7 (C), 129.6 (2 C, CH), 128.4 (2 C, CH), 76.7 (CH, C-2), 54.4 (C), 50.3 (C), 49.3 (CH), 45.8 (CH_2), 44.1 (C), 42.8 (CH), 35.6 (CH_2), 33.8

(CH_2), 32.3 (CH_2), 31.5 (CH), 21.6 (CH_3), 18.0 (CH_3), 17.1 (CH_3); Mass: 216 (M^+−PhCOOH, 8%), 201 (4), 190 (5), 149 (16), 121 (12), 105 (100); HRMS: *m*/*z* calcd for $C_{22}H_{26}O_3Na$ (M+Na): 361.1780; Found: 361.1796. For(1*R*,2*R*,4*S*,5*S*,7*S*,10*R*,11*S*)-5,10,11-trimethyl-8-oxotetracyclo[5.3.1.$1^{1,4}$.$0^{5,11}$]dodec-2-yl benzoate (**36**): mp: 168–170 °C; $[\alpha]_D^{24}$ −40.0 (*c* 0.5, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 1714; ^1H NMR (400 MHz, $CDCl_3$): δ 8.01 (2H, d, *J* 7.3 Hz), 7.57 (1H, t, *J* 7.3 Hz), 7.45 (2H, t, *J* 7.3 Hz), 5.15 (1H, d, *J* 6.4 Hz), 2.75 (1H, q, *J* 7.9 Hz), 2.60–2.54 (2H, m), 2.26 (1H, ddd, *J* 14.6, 6.3 and 2.7 Hz), 2.20–1.92 (4H, m), 1.82 (1H, d, *J* 4.7 Hz), 1.73 (1H, d, *J* 11.5 Hz), 1.45 (1H, dd, *J* 14.7 and 4.9 Hz), 1.38 (3H, s), 1.15 (3H, s), 1.05 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 218.0 (C), 166.0 (C), 133.0 (CH), 130.6 (C), 129.4 (2C, CH), 128.4 (2C, CH), 74.6 (CH), 53.4 (C), 49.1 (C), 48.2 (CH), 46.4 (CH_2), 45.2 (C), 43.3 (CH, C-4), 38.4 (CH_2), 36.2 (CH_2), 34.4 (CH_2), 34.1 (CH), 19.4 (CH_3), 18.0 (CH_3), 17.8 (CH_3); mass: 216 (M^+−PhCOOH, 6%), 204 (5), 190 (3), 135 (7), 121 (12), 120 (20), 105 (100), 91 (10); HRMS: *m*/*z* calcd for $C_{22}H_{26}O_3Na$ (M+Na): 361.1780; Found: 361.1779; Anal. Calcd for $C_{22}H_{26}O_3$ C, 78.07; H, 7.74. Found: C, 77.80; H, 7.72. For (1*R*,2*R*,4*S*,5*S*,7*S*,10*R*,11*S*)-5,10,11-trimethyl-8-oxotetracyclo[5.3.1.$1^{1,4}$.$0^{5,11}$]dodecan-2-ol (**8**): $[\alpha]_D^{25}$ +21.8 (*c* 0.64, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3465, 1704; ^1H NMR (300 MHz, $CDCl_3$): δ 4.03 (1H, d, *J* 6.6 Hz), 2.65–2.50 (2H, m), 2.50 (1H, dd, *J* 11.7 and 5.7 Hz), 2.20–2.05 (2H, m), 2.03 (1H, ddd, *J* 14.1, 6.6 and 2.7 Hz), 1.91 (1H, t, *J* 12.3 Hz), 1.82 (1H, br d, *J* 12.3 Hz), 1.75 (1H, d, *J* 4.5 Hz), 1.52 (1H, d, *J* 11.7 Hz), 1.35–1.20 (2H, m), 1.29 (3H, d, *J* 6.6 Hz), 1.26 (3H, s), 0.98 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 218.5 (C), 70.0 (CH), 54.2 (C), 49.0 (C), 48.2 (CH), 46.6 (CH_2), 45.0 (C), 43.1 (CH), 38.1 (CH_2), 36.8 (CH_2), 34.5 (CH_2), 33.7 (CH), 19.6 (CH_3), 18.0 (CH_3), 17.5 (CH_3); Mass: 190 (M^+−CH_3CHO, 14%), 164 (10), 147 (6), 137 (100), 135 (10), 121 (25), 120 (53), 105 (30), 91 (23); HRMS: *m*/*z* Calcd for $C_{15}H_{22}O_2Na$ (M+Na): 257.1517; Found: 257.1509. Crystal data for the alcohol **22**: X-ray data were collected at 293 K on a SMART CCD-BRUKER diffractometer with graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods (SIR92). Refinement was by full-matrix least-squares procedures on F2 using SHELXL-97. The non-hydrogen atoms were refined anisotropically whereas hydrogen atoms were refined isotropically. $C_{15}H_{22}O_2$; MW = 234.3; colourless crystal; crystal system: monoclinic; space group P2(1); cell parameters, $a = 7.719(13)$ Å, $b = 8.429(14)$ Å, $c = 9.954(17)$ Å; $V = 647.62(2)$ Å^3, $Z = 2$, $D_c = 1.202$ g cm^{-3}, $F(000) = 256$, $\mu = 0.078$ mm^{-1}. Total number of l.s. parameters = 161, $R1 = 0.064$ for 1697 $F_o > 4\sigma(F_o)$ and 0.092 for all 2255 data. $wR2 = 0.134$, GOF = 1.076, restrained GOF = 1.076 for all data. An ORTEP diagram of **22** is depicted in Figure 1. Crystallographic data has been deposited with the Cambridge Crystallographic Data Centre (CCDC 284283). Crystal data for the keto-benzoate **36**: X-ray data were collected at 293 K on a SMART CCD-BRUKER diffractometer with graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods (SIR92). Refinement was done by full-matrix least-squares procedures on F2 using SHELXL-97. The non-hydrogen atoms were refined anisotropically whereas hydrogen atoms were refined isotropically. $C_{22}H_{26}O_3$; $MW = 338.4$; colourless crystal; crystal system: monoclinic; space group *C*2; cell parameters, $a = 20.595(57)$ Å, $b = 7.798(21)$ Å, $c = 11.834(33)$ Å; $V = 1884.55(13)$ Å^3, $Z = 4$, $D_c = 1.19$ g cm^{-3}, $F(000) = 727.9$, $\mu = 0.078$ mm^{-1}. Total number of l.s. parameters = 229, $R1 = 0.066$ for 2768 $F_o > 4\sigma(F_o)$ and 0.080 for all 3282 data. $wR2 = 0.138$, GOF = 1.221, restrained GOF = 1.221 for all data. An ORTEP diagram of **36** is depicted in Figure 2. Crystallographic data has been deposited with the Cambridge Crystallographic Data Centre (CCDC 284284).