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Unexpected Selectivity Between Pinacolic Rearrangement and Intramolecular Displacement in the Acid-promoted Epoxide Ring Opening of 6-*exo*-Cyano-3,8-dioxabicyclo[3.2.1.$0^{2,4}$]oct-6-*endo*-yl Esters.

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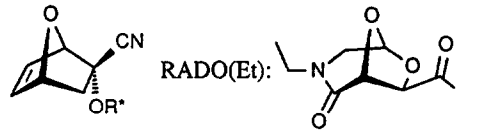
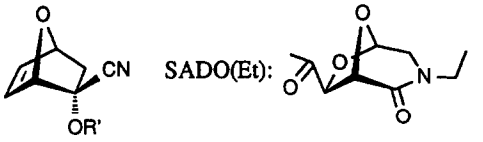
Summary: *Acid promoted epoxide ring opening of* 2-exo-*cyano-5-*exo,*6-*exo-*epoxy-7-oxa-bicyclo[2.2.1]hept-2-*endo-*yl acetate is accompanied by a Wagner-Meerwein (pinacolic) rearrangement when run in* CH_2Cl_2/HSO_3F *and by* endo *acetoxy group participation when run in* $CF_3CH(OH)CF_3/HClO_4$. *An efficient and stereoselective* trans-*double hydroxylation of centers C(5) and C(6) of the "naked sugar" (1*R,2S,4R*)-2-*exo-*cyano-7-oxabicyclo[2.2.1]-hept-2-*endo-*yl (1*S'*)-camphanate is also presented.*

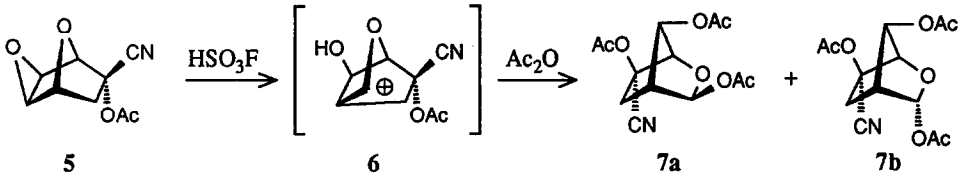
The optically pure 7-oxabicyclo[2.2.1]hept-5-en-2-yl derivatives (+)-**1**, (+)-**2** and their diastereomers (-)-**3**, (-)-**4** are useful chirons[1] ("naked sugars"[2]) in the total synthesis of rare carbohydrates and analogues, C-nucleosides, cyclitols and other compounds of biological interest.[3,4] The epoxides of 7-oxabicyclo[2.2.1]-hept-5-en-2-yl derivatives have shown a high versatility in their acid-catalyzed acetolysis.[5] For instance in



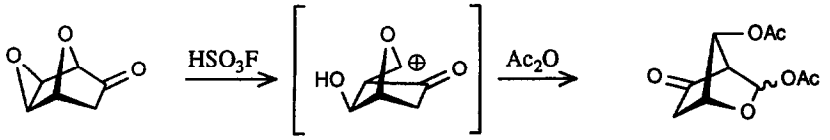
(+)-**1** R*=(1S)-camphanoyl
(+)-**2** R*=RADO(Et)-



(+)-**3** R'=(1R)-camphanoyl
(+)-**4** R'=SADO(Et)-



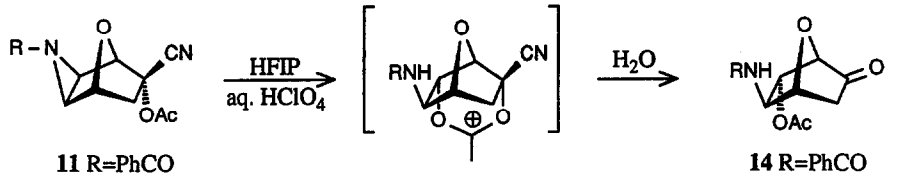
5 **6** **7a** **7b**



8 **9** **10**

the presence of HSO_3F/Ac_2O in CH_2Cl_2, *Le Drian*[5] reported that 2-*exo*-cyano-5-*exo*,6-*exo*-epoxy-7-oxabi-cyclo[2.2.1]hept-2-*endo*-yl acetate ((±)-**5**) gives products **7a** + **7b** derived from the epoxide-ring opening

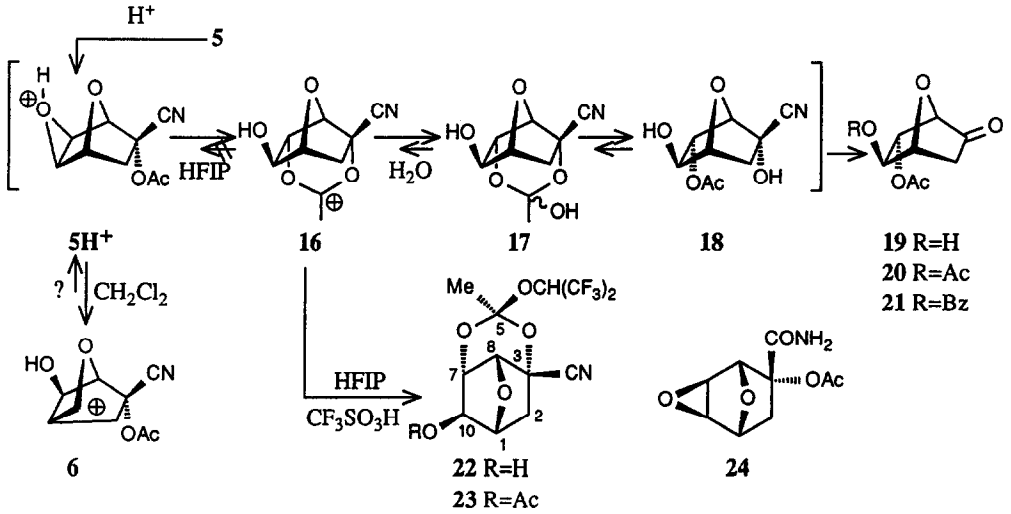
and a 1,2-shift of the unsubstituted alkyl group (σ bond C(3), C(4)), probably via the cationic intermediate **6** (pinacolic rearrangement). Products **7** are protected forms of a potential precursor of carba analogues of lyxose. Under similar conditions, epoxy-ketone **8** gave 5-oxo-2-oxabicyclo[2.2.1]heptane-3,7-diyl diacetates **10** arising from the 1,2-shift of the acyl group via ion intermediate **9**. When the aziridines **11** and **12** were treated with 70% aqueous $HClO_4$ in $CF_3CH(OH)CF_3$ (HFIP), no product of pinacolic rearrangement was detected; the products of acetoxy group migration (intramolecular displacement via cationic intermediates **13**) **14** and **15**, respectively were isolated instead.[7] In the light of these results, the non-observation of



11 R=PhCO
12 R=PhNHCO
13
14 R=PhCO
15 R=PhNHCO

products of acetoxy group migration in the acid-promoted epoxides ring opening of **5** raised a number of questions that we intend to address in this report. As we shall see, competition between pinacolic rearrangement and intramolecular displacement in the acid-promoted epoxide ring opening of 6-*exo*-cyano-3,8-dioxabicyclo[3.2.1.$0^{2,4}$]oct-6-*endo*-yl esters strongly depends on the nature of the medium.

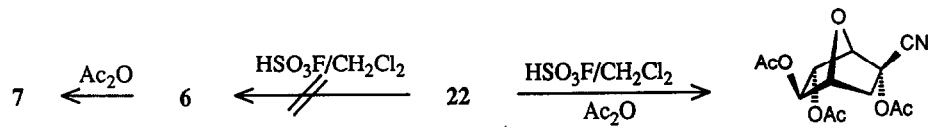
When epoxide **5** (1% in HFIP) was treated with 70% aqueous $HClO_4$ (0.2 equivalent), the product of *endo* acetoxy group migration **19** was formed slowly, together with some polymeric material. After 5 h at 20°C, 56% of **5** had been converted and **19** was isolated in 49% yield. Compound **19** was converted into the corresponding acetate **20** and benzoate **21** for complete characterization (see Experim. Section). This result can be interpreted in terms of the formation of the dialkoxycarbenium ion intermediate **16** arising from the



endo acetoxy group participation to the acid epoxide ring opening in **5**. In the presence of H_2O, this is

quenched to generate the hemiorthoester **17** which is decomposed into the cyanohydrine **18**; the latter eliminate HCN to afford **19**. When the epoxide **5** was treated in HFIP and in the presence of CF_3SO_3H (1 equivalent) to 70°C for 4 h, a mixture composed of orthoester **22** (24%), of ketone **19** (45%) and of starting material **5** (25%) was obtained and separated by column chromatography on silica gel. The isolation of **22**, characterized as its acetate **23**, confirmed the intermediacy of **16**. When HSO_3F was used instead of CF_3SO_3H, mixtures of **19**, **22** and **24** were obtained together with polymeric materials. The proportion of **19/22/24** varied with the concentration of the acid and of H_2O. If products resulting from a pinacolic rearrangement (e.g. **5** → **6**) were formed under the above conditions, they are not stable and might contribute to the formation of polymers.

In order to test whether the secondary alkoxycarbenium ion **6** could be equilibrated with the tertiary dialkoxycarbenium ion **16** we treated **22** under the conditions of *Le Drian* ($CH_2Cl_2/HSO_3F/Ac_2O$, -25°C, 4 h). No trace of products **7** could be observed in the crude reaction mixture, the triacetate **25** was isolated instead in 58% yield. In order to test also whether rearrangement of the cationic intermediates **6** → **16** could



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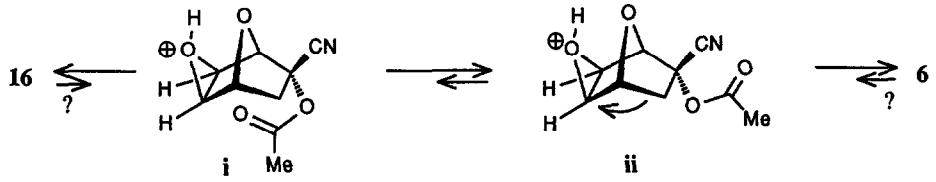
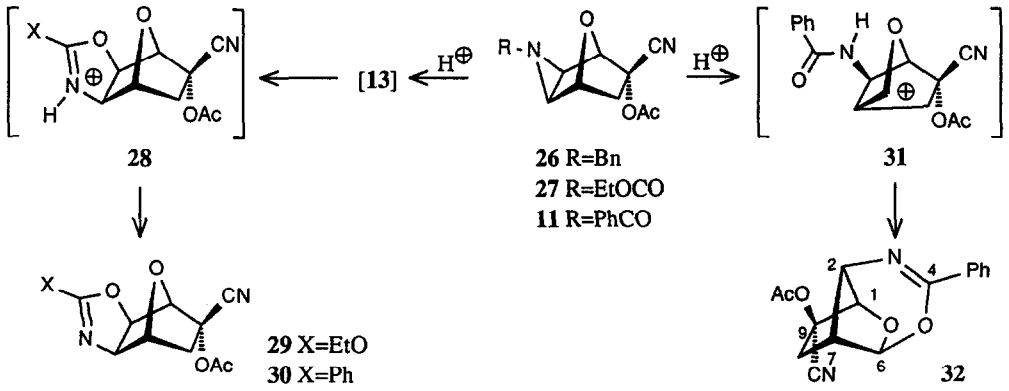
be achieved under appropriate conditions we treated epoxide **5** with HSO_3F/CH_2Cl_2 in the absence of nucleophile (Ac_2O). After 6 h at -25°C the reaction mixture was quenched with Ac_2O and the products of pinacolic rearrangement **7a** + **7b** were isolated. No trace of products of acetoxy group participation such as **19**, **20**, **22** or **23** could be detected! When compounds **7a** and **7b** were treated with $HClO_4$, HSO_3F or CF_3SO_3H in HFIP, they were **not** transformed into **19** or **22**. Only slow decomposition was observed after prolonged heating to 60°C. If ionic intermediates **6** and **16** could be equilibrated, the energy barriers for both rearrangements **6** → **16** and **16** → **6** are too high and cannot be overcome under our experimental conditions.

Our results demonstrate the importance of the medium on the relative energy barrier for the pinacolic rearrangement **5H**$^+$ → **6** and for the intramolecular nucleophilic displacement by an *endo* acetoxy group **5H**$^+$ → **16**. In the alcoholic medium (HFIP), the preferred process implies the formation of a relatively stable tertiary dialkoxycarbonium ion **16** whereas in the less ionizing and non-alcoholic medium (CH_2Cl_2), the acetoxy group participation must be retarded to render the concurrent σC(3),C(4) bond migration the fastest process although it engenders a less stable intermediate **6** which is a secondary alkoxycarbenium ion[8] (strain energy is not expected to differ significantly between **6** and **16**).[9]



Since less than 0.2 equivalent of HSO_3F was used in the reaction **5** → **6** → **7**, one cannot invoke a complete protonation of the acetoxy moiety of **5** that could suppress, under the conditions of *Le Drian*, its intervention as an intramolecular nucleophile. Therefore, one hypothesis would be to invoke that rotamer **i** of **5H⁺** which leads to **16** is less stable than other rotamers such as **ii**. The stability difference between **i** and **ii**, as well as the energy barrier for their interconversion could be solvent dependent. Together with the fact that **5H⁺** is less solvated in CH_2Cl_2 than in HFIP, its intrinsic stability (or instability) makes it to be less selective when it requires the σC(3),C(4) or the *endo* acetoxy group to get involved in the reaction. In other words, because of its high instability in CH_2Cl_2, **5H⁺** has not the time to wait for conformer **i** to be generated and the pinacolic rearrangement is thus preferred. Alternatively, one could invoke the hypothesis that the geometry of **5H⁺** is affected by solvation (e.g. *syn* protonation rather than *anti* protonation of the epoxide ring relative to the oxa bridge) in such a way that in CH_2Cl_2 it makes the approach of the *endo* acetoxy group more difficult than in HFIP.

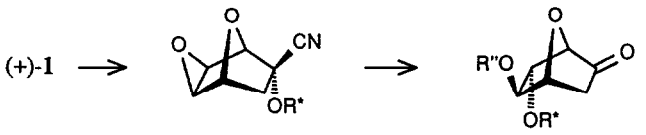
In order to test these hypotheses we have examined the reaction of the aziridine derivatives **26**, **27** and **11** in the presence HSO_3F in CH_2Cl_2. It was hoped that contrary to the reactions of aziridine ring opening that were exclusively assisted by the *endo* acetoxy group when run in HFIP[7] that the acid promoted rearrangements of these systems in CH_2Cl_2 would be accompanied by pinacolic rearrangements as in the case of the corresponding epoxide **5**. The benzylamine derivative **26** did not react under the conditions of *Le*



Drian (CH_2Cl_2, 3 equivalents of Ac_2O, 0.2 equivalents of HSO_3F, -20°C, several days). In contrast, the ethyl carbamate **27** was transformed rapidly to the ethoxyoxazolidine **29** which was isolated in 70% yield. The reaction probably proceeds via *endo* acetoxy group participation with the formation of a dialkoxy-carbenium ion intermediate of type **13**. In the absence of water, the latter is displaced by the *exo* carbamate

moiety leading to a more stable aminodialkoxycarbenium ion intermediate of type **28** which affords **29** upon neutralization.[7] No trace of products arising from a possible pinacolic rearrangement could be detected. Under similar conditions benzamide **11** gave a mixture of the known phenylisoxazolidine **30**[7] and of the 5,10-dioxa-3-azatricyclo[4.3.1.$0^{2,7}$]dec-3-en-9-yl derivative **32**, these two compounds being separated by column chromatography on silica gel and isolated in 63% and 1.8% yield, respectively. Thus, in CH_2Cl_2, the *endo* acetoxy group is not impeded to act as an intramolecular nucleophile in the acid promoted ring opening of acyl substituted aziridine moieties. In the case of the benzamide derivative **11** only, the acetoxy group participation is sufficiently retarded to allow for the concurrent pinacolic rearrangement to occur timidly. Compound **32** was not detected in the reactions run in HFIP. These results show that the competition between the pinacolic rearrangement and the *endo* acetoxy group participation depends on the nature of the three-membered onium ions grafted at the *exo* positions of centers C(5) and C(6) of the 7-oxabicyclo[2.2.1]hept-2-*endo*-yl acetate. The less stable are these ions, the greater is the chance for the pinacolic rearrangement to compete with the thermodynamically more favorable migration of the *endo* acetoxy group.

Much more work is definitively required to approach a sound explanation of the medium effect reported here. In the meantime, it has allowed one to develop a new and efficient method for the stereoselective *trans* dihydroxylation[6] of centers C(5) and C(6) of our "naked sugars". Indeed, when the optically pure epoxide (-)-**33** derived from (+)-**1** was treated with 70% aqueous $HClO_4$ in HFIP (20°C) the ester-alcohol (-)-**34** was obtained in 71% yield, together with the recovery of 29% of (-)-**33**. Compound (-)-**34** was fully characterized in the forms of the corresponding acetate (-)-**35** and benzoate (-)-**36**. The double hydroxylation method described here generates semi-protected *trans*-diols, thus allowing for a differentiation of the two hydroxy groups introduced onto the "naked sugars". The structure of the new



(-)-**33**

R*=(1*S*)-camphanoyl

(-)-**34** R''=H
(-)-**35** R''=Ac
(-)-**36** R''=Bz

compounds described in this work were established by their elemental analyses and their spectral data. ^{1}H-NMR spectra together with the help of double irradiation experiments allowed one to recognize unambiguously the relative *exo* and *endo* configurations of the CH's of the 7-oxabicyclo[2.2.1]heptyl systems.[10]

Acknowledgments. This work was supported by the *Swiss National Science Foundation*, the *Fonds Herbette* (Lausanne) and *F. Hoffmann-La Roche & Co.*, AG (Basel). We thank Miss Nadia Larbi for her technical assistance.

Experimental Part.

General remarks, see ref. 11.

(±)-(1*RS*,2*SR*,3*SR*,4*RS*)-3-*exo*-Hydroxy-6-oxo-7-oxabicyclo[2.2.1]hept-2-*endo*-yl acetate (**19**). 70% aqueous $HClO_4$ (50 µL, 11.6 M, 0.58 mmol) was added to a solution of epoxide **5**[6] (0.5 g, 2.56 mmol) in anhydrous HFIP (5 mL). After staying at 20°C for 5 h, the solution was poured into ice-cold and vigorously stirred aqueous solution saturated with $NaHCO_3$ (20 mL). The mixture was extracted with CH_2Cl_2 (20 mL, 4 times). The combined extracts were dried ($MgSO_4$) and the solvent was evaporated in vacuo to give a residue (427 mg, colorless oil) that was purified by flash chromatography on silica gel (50 g, light petroleum/EtOAc 1:2). The first fraction (R_f = 0.44) gave 60 mg (22%) of **5**, the second one (R_f = 0.33) afforded 233 mg (49%, 56% based on converted **5**) of **19**, colourless oil. IR ($CDCl_3$) ν: 3570, 3020, 2940, 1770, 1740, 1405, 1370, 1300, 1140, 1060, 1010, 975, 960, 905, 890, 825 cm^{-1}; ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 4.76 (d, $J_{2,1}$ = 5.5, $J_{2,3}$ = 1.2, H-C(2)); 4.75 (d, $J_{4,5\text{-}exo}$ = 7.0, H-C(4)); 4.53 (m, $J_{2,1}$ = 5.5, $J_{1,5\text{-}exo}$ = 1.5, $J_{1,3}$ < 1.0, H-C(1)); 4.03 (br. s, $J_{3,2}$ = 1.2, $J_{3,1}$ < 1.0, H-C(3)); 3.12 (br. s, OH); 2.57 (ddd, J_{gem} = 18.0, $J_{5\text{-}exo,4}$ = 7.0, $J_{5\text{-}exo,1}$ = 1.5, H-C(5-*exo*)); 2.12 (d, J_{gem} = 18.0, H-C(5-*endo*)); 2.09 (s, 3H, CH_3(OAc)). ^{13}C-NMR (90.55 MHz, $CDCl_3$) δ_C: 206.4 (s, C(6)); 171.0 (s, CO); 82.3 (d, ^1J(C,H) = 165), 79.7 (d, ^1J(C,H) = 160), 79.5 (d, ^1J(C,H) = 175), 78.7 (d, ^1J(C,H) = 150), (4d, C(1), C(2), C(3), C(4)); 39.4 (t, ^1J(C,H) = 135, C(5)); 20.5 (q, ^1J(C,H) = 130, CH_3). CI-MS (NH_3) m/z: 204 (2, $M^{+\cdot}$+1+NH_3), 187 (7), 186 (15, $M^{+\cdot}$), 144 (71), 143 (24), 125 (14), 115 (15), 102 (23), 98 (26), 97 (43), 85 (100), 84 (69), 83 (25), 81 (23), 73 (30), 71 (49), 70 (25). Anal. calc. for $C_8H_{10}O_5$ (186.17): C 51.61, H 5.41; found: C 51.66, H 5.32.

(±)-(1*RS*,2*RS*,3*SR*,4*RS*)-5-Oxo-7-oxabicyclo[2.2.1]hepta-2-*exo*,3-*endo*-diyl diacetate (**20**). A mixture of **19** (91 mg, 4.9 mmol), anh. pyridine (2 mL) and Ac_2O (2 mL) was stirred at 20°C for 15 h. The solvent was evaporated in vacuo, the residue taken with toluene (4 mL) and the solvent evaporated. This latter operation was repeated 3 times. The residue was filtered though a short column of silica gel (10 g, light petroleum/EtOAc 1:2, R_f = 0.55), yielding 91 mg (82%), colorless oil. IR ($CDCl_3$) ν: 3000, 1760, 1730, 1390, 1355, 1130, 1040, 1005, 970, 865 cm^{-1}; ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 5.05 (br. d, $J_{2,3}$ = 1.4, $J_{4,3}$ = 6.0, $J_{1,3}$ = 1.8, $J_{6\text{-}exo}$ <1.0, H-C(3)); 4.92 (d, $J_{3,2}$ = 1.4, H-C(2)); 4.80 (br. d, $J_{1,6\text{-}exo}$ = 6.7, $J_{1,3}$ = 1.8, $J_{1,4}$ = 1.0, H-C(1)); 4.58 (br. d, $J_{3,4}$ = 6.0, $J_{1,4}$ = 1.0, $J_{1,6\text{-}exo}$ = 1.5, H-C(4)); 2.58 (ddd, J_{gem} = 18.0, $J_{6\text{-}exo,4}$ = 1.5, $J_{6\text{-}exo,1}$ = 6.7, H-C(6-*exo*)); 2.33 (d, J_{gem} = 18.0, H-C(6-*endo*)); 2.14, 2.05 (2s, 2 Me). ^{13}C-NMR (90.55 MHz, $CDCl_3$) δ_C: 205.05 (s, C(5)); 170.4, 169.5 (2s, 2 CO); 80.5 (d, ^1J(C,H) = 170), 79.4 (d, ^1J(C,H) = 155), 79.2 (d, ^1J(C,H) = 170), 75.8 (d, ^1J(C,H) = 165, C(1), C(2), C(3), C(4)); 39.2 (t, ^1J(C,H) = 135, C(5)); 20.7, 20.4 (2q, ^1J(C,H) = 130, 2 Me). CI-MS (NH_3) m/z: 229 (5, $M^{+\cdot}$+1), 228 (15, $M^{+\cdot}$), 186 (30), 126 (18), 112 (13), 97 (100), 81 (12), 70 (13). Anal. calc. for $C_{10}H_{12}O_6$ (228.20): C 52.63, H 5.30; found: C 52.62, H 5.28.

(±)-(1*RS*,2*SR*,3*RS*,4*RS*)-3-*exo*-Benzoyloxy-6-oxo-7-oxabicyclo[2.2.1]hept-2-*endo*-yl acetate (**21**). A mixture of **19** (160 mg, 0.86 mmol) in anh. pyridine (4 mL) and benzoyl chloride (0.2 mL; 1.72 mmol) was stirred at 20°C for 15 h. The solvent was evaporated in vacuo and the residue taken with toluene (4 mL). The solvent was evaporated to dryness (3 times). The residue was filtered through a short column of silica gel (5 g, light petroleum/EtOAc, R_f = 0.50) giving 217 mg (87%), colorless crystals, m.p. 73-75°C. IR $CHCl_3$) ν: 3000, 1760, 1730, 1710, 1590, 1440, 1355, 1300, 1255, 1095, 1055, 1005, 940 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 8.06-8.11 (m, 2H, arom); 7.65-7.44 (m, 3H, arom); 5.23 (m, $J_{2,1}$ = 6.0, $J_{2,3}$ = 1.5, $J_{2,4}$ = 1.5, $J_{2,5\text{-}exo}$ <1.0, H-C(2)); 5.19 (d, $J_{3,2}$ = 1.5, H-C(3)); 4.96 (m, $J_{4,5\text{-}exo}$ = 6.5, $J_{4,2}$ = 1.5, $J_{4,1}$ = 1.0, H-C(4)); 4.66 (m, $J_{3,1}$ = 1.5, $J_{1,2}$ = 6.0, $J_{1,5\text{-}exo}$ = 1.5, $J_{1,4}$ = 1.0, H-C(1)); 2.65 (ddd, J_{gem} = 18.0, $J_{5\text{-}exo,4}$ = 6.5, $J_{5\text{-}exo,2}$ <1.0, $J_{5\text{-}exo,1}$ = 1.5, H-C(5-*exo*)); 2.33 (d, J_{gem} = 18.0, H-C(5-*endo*)); 2.09 (s, CH_3). ^{13}C-NMR (90.55 MHz, $CDCl_3$) δ_C: 205.6 (s, C(6)); 169.6, 166.0 (2s, 2 CO); 133.6, 129.9, 128.5 (3d, ^1J(C,H) = 160, CH(arom)); 129.1 (s, C(arom)); 80.6 (d, ^1J(C,H) = 165), 79.7 (d, ^1J(C,H) = 160) 79.5 (d, ^1J(C,H) = 175), 75.9 (d, ^1J(C,H) = 165, C(1), C(2), C(3), C(4)); 39.3 (t, ^1J(C,H) = 135, C(5)); 20.4 (q, ^1J(C,H) = 130, Me). CI-MS (NH_3) m/z: 291 (1, $M^{+\cdot}$+1), 290 (4, $M^{+\cdot}$), 248 (7), 106 (10), 105 (100), 97 (37), 77 (46). Anal. calc. for $C_{15}H_{14}O_6$ (290.28): C 62.07, H 4.86; found: C 61.89, H 4.92.

(±)-(1*RS*,3*SR*,7*SR*,8*RS*,10*RS*)-10-*exo*-Hydroxy-5-methyl-5-[2,2,2-trifluoro-1-(trifluoromethyl)ethyloxy]-4,6,9-trioxatricyclo[5.2.1.$0^{3,8}$]decane-3-carbonitrile (**22**). A mixture of **5** (300 mg, 1.54 mmol), HFIP (15 mL) and CF_3SO_3H (15 µL, 0.17 mmol) was heated to 70°C for 4 h. The mixture was poured into ice cold and vigorously stirred saturated aqueous solution of $NaHCO_3$ (200 mL). The mixture was extracted with CH_2Cl_2 (100 mL, 4 times). The combined extracts were dried ($MgSO_4$) and the solvent was evaporated. The colorless

residue was purified by column chromatography on silica gel (Et_2O/EtOAc 1:1). The first fraction (R_f = 0.55) gave 133 mg (24%) of **22**. The second fraction (R_f = 0.48) afforded 75 mg (25%) of **5**, and a third fraction (R_f = 0.42) gave 129 mg (45%) of **19**. Recrystallization of **22** from acetone/Et_2O (-20°C) furnished 106 mg (19%), colorless crystals, m.p. 158-159°C. IR (KBr) ν: 3460, 2950, 2260, 1400, 1370, 1350, 1280, 1230, 1185, 1165, 1100, 1080, 1025, 960, 890, 870, 685 cm^{-1}. ^{1}H-NMR (250 MHz, CD_3COCD_3) δ_H: 5.48 (heptuplet, 1H, ^3J(H,F) = 6.0); 4.97 (br. d, $J_{8,7}$ = 5.0, $J_{8,1}$ <1.0, $J_{8,2\text{-}exo}$<1.0, H-C(8)); 4.78 (d, $J_{OH,10}$ = 5.0, OH)); 4.56 (br. d, $J_{1,2\text{-}exo}$ = 5.5, $J_{1,7}$ <1.0, $J_{1,8}$ <1.0, H-C(1)); 4.09 (br. d, $J_{7,8}$ = 5.0, $J_{7,10}$ = 1.5, $J_{7,1}$ <1.0, H-C(7)); 4.04 (dd, $J_{10,OH}$ = 5.0, $J_{10,7}$ = 1.5, H-C(10)); 2.49 (dd, J_{gem} = 13.5, $J_{2\text{-}exo,1}$ = 5.5, $J_{2\text{-}exo,8}$ <1.0, H-C(2-*exo*)); 2.33 (d, J_{gem} = 13.5, H-C(2-*endo*)); 1.69 (s, MeC(5)). ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 5.08 (br. d, $J_{8,7}$ =5.0, $J_{8,1}$ <1.0, $J_{8,2\text{-}exo}$ <1.0, H-C(8)); 4.56 (br. d, $J_{1,2\text{-}exo}$ = 5.5, $J_{1,7}$ <1.0, H-C(1)); 4.43 (heptuplet, 1 H, ^3J(H,F) = 5.7, CH(CF_3)$_2$)); 4.18 (br. d, $J_{7,8}$ = 5.0, $J_{7,10}$ = 1.5, H-C(7)); 4.02 (br. d, $J_{OH,10}$ = 7.6, H-C(10)); 2.59 (dd, J_{gem} = 13.5, $J_{2\text{-}exo,1}$ = 5.5, H-C(2-*exo*)); 2.22 (d, J_{gem} = 13.5, H-C(2-*endo*)); 2.09 (d, 1H, $J_{OH,10}$ =7.6, OH); 1.61 (s, CH_3C(5)). ^{13}C-NMR (90.55 MHz, $CDCl_3$) δ_C: 127.3, 127.0 (2q, ^1J(C,H) = 285, 2 CF_3); 119.9 (s, C(3)); 114.5 (s, CN); 86.1 (d, ^1J(C,H) = 165), 81.0 (d, ^1J(C,H) = 165), 78.1 (d, ^1J(C,H) = 150), 77.2 (d, ^1J(C,H) = 170, C(1), C(7), C(8), C(10)); 72.0 (s, C(2)); 70.6, 70.1 (2dq, ^1J(C,H) = 150, ^2J(C,F) = 33, *C*H(CF_3)$_2$); 45.7 (t, ^1J(C,H) = 140, C(10)); 23.4 (q, ^1J(C,H) = 130, CH_3). CI-MS (NH_3) m/z: 364 (3), 363 (6, $M^{+\cdot}$+1), 364 (3), 196 (100, $M^{+\cdot}$+1-CF_3CH(OH)CF_3), 124 (36), 107 (19), 96 (16), 94 (24), 84 (63). Anal. calc. for $C_{12}H_{10}F_6NO_5$ (362.18): C 39.80, H 2.78, N 3.87; found: C 40.00, H 2.90, N 3.39.

(±)-(1*RS*,3*SR*,7*SR*,8*RS*,10*RS*)-7-*exo*-Cyano-5-methyl-5-[2,2,2-trifluoro-1-(trifluoromethyl)ethyloxy]-4,6,9-trioxatricyclo[5.2.1.$0^{3,8}$]dec-2-*exo*-yl acetate (**23**). This product was prepared following the same procedure as for the preparation of **20**. R_f = 0.65 (light petroleum/EtOAc 1:2), recrystallization from CH_2Cl_2/Et_2O (0°C), 95%, colorless oil, m.p. 138.5-140.5°C. IR (KBr) ν: 2960, 1750, 1370, 1290, 1240, 1190, 1165, 1105, 1080, 1030, 890, 685 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 5.11 (d, $J_{8,7}$ = 5.0, $J_{8,1}$ <1.0, $J_{8,2\text{-}exo}$ <1.0, H-C(8)); 4.89 (d, ^3J = 1.5, H-C(10)); 4.63 (d, $J_{1,2\text{-}exo}$ = 5.5, $J_{1,7}$ <1.0, $J_{1,8}$ <1.0, H-C(1)); 4.43 (heptuplet, $J_{H,F}$ = 5.5, CH(CF_3)$_2$); 4.26 (br. d, $J_{7,8}$ = 5.0, $J_{7,10}$ = 1.5, $J_{7,1}$ <1.0, H-C(7)); 2.57 (br. dd, J_{gem} = 13.5, $J_{2\text{-}exo,1}$ = 5.5, $J_{2\text{-}exo,8}$ <1.0, H-C(2-*exo*)); 2.39 (d, J_{gem} =13.5, H-C(2-*endo*)); 2.13 (s, CH_3); 1.64 (s, CH_3C(5)). ^{13}C-NMR (90.55 MHz, $CDCl_3$) δ_C: 170.4 (s, CO); 121.3, 120.7 (2q, ^1J(C,H) = 285, (CF_3)$_2$); 118.1 (s, C(5)), 113.5 (s, CN); 82.6 (d, ^1J(C,H) = 165), 79.3 (d, ^1J(C,H) = 177), 76.8 (d, ^1J(C,H) = 164), 76.4 (d, ^1J(C,H) = 184, C(1), C(7), C(8), C(10)); 67.0 (s, C(3)); 70.5, 70.1 (2qd, ^2J(C,F) = 33, ^1J(C,H) = 147, CH(CF_3)$_2$); 45.0 (t, ^1J(C,H) = 140, C(2)); 23.1 (q, ^1J(C,H) = 130, CH_3-*C*(5)); 20.5 (q, ^1J(C,H) = 130, CH_3). CI-MS(NH_3) m/z: 406 (6), 405 (11, $M^{+\cdot}$+1), 239 (21), 238 (100, $M^{+\cdot}$+1-CF_3CHOHCF_3), 126 (11), 84 (22), 81 (33). Anal. calc. for $C_{14}H_{12}F_6NO_6$ (404.24): C 41.60, H 2.99, N 3.46; found: C 41.55, H 2.90, N 3.39.

(±)-(1*RS*,2*RS*,3*SR*,4*RS*,5*SR*)-5-*exo*-Cyano-7-oxabicyclo[2.2.1]hepta-2-*exo*,3-*endo*,5-*endo*-triyl triacetate (**25**). Ac_2O (70 µL, 0.66 mmol) and HSO_3F (10 µL) were added to a solution of **22** (80 mg, 0.22 mmol) in anh. CH_2Cl_2 (4 mL) cooled to -78°C under N_2 atmosphere. After stirring at -25°C for 4 h, the reaction mixture was poured into saturated aqueous solution of $NaHCO_3$ (20 mL) and the mixture extracted with CH_2Cl_2 (15 mL, 4 times). The combined extracts were dried ($MgSO_4$) and the solvent was evaporated. The residue was filtered through a short column of silica gel (light petroleum/EtOAc 1:2, R_f = 0.55) giving 38 mg (58%) after recrystallization from Et_2O (20°C, then 0°C), colorless crystals, m.p. 137-138°C. IR (KBr) ν: 1740, 1370, 1230, 1190, 1085, 1055, 1015, 1005, 985, 970, 900, 885, 795 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 5.25 (br. d, $J_{3,4}$ = 5.5, $J_{1,4}$ = 1.0, H-C(4)); 5.22 (br. dd, $J_{3,4}$ = 5.5, $J_{3,2}$ = 2.0, H-C(3)); 4.79 (d, $J_{2,3}$ = 2.0, H-C(2)); 4.62 (br. d, $J_{1,6\text{-}exo}$ = 6.5, $J_{1,4}$ = 1.0, H-C(1)); 2.93 (dd, ^2J = 14.0, ^3J = 6.5, H-C(6-*exo*)); 2.22 (d, ^2J = 14.0, H-C(6-*endo*)); 2.18, 2.13, 2.08 (3s, 3 AcO). CI-MS (NH_3) m/z: 316 (11), 315 (70, $M^{+\cdot}$+1+NH_3), 298 (3, M+H^+), 297 (2), 238 (5), 197 (12), 196 (100). Anal. calc. for $C_{13}H_{15}NO_7$ (297.27): C 52.53, H 5.09, N 4.71; found: C 52.54, H 5.03, N 4.73.

(±)-(1*RS*,2*RS*,6*SR*,7*RS*,9*SR*)-9-Cyano-4-phenyl-5,10-dioxa-3-azatricyclo[4.3.1.$0^{2,7}$]dec-3-en-9-yl acetate (**32**). HSO_3F (20 µL, 0.3 mmol) was added to a solution of **11** (447 mg, 1.5 mmol) and Ac_2O (0.5 mL) in anhydrous CH_2Cl_2 (5 mL) cooled to -70°C. After staying at -25°C for 2 h, no reaction had occurred. The mixture was then stirred at 20°C for 15 h and HSO_3F (80 µL) were added slowly. After stirring at 20°C for another 1.5 h, the mixture was poured into a vigorously stirred saturated aqueous solution of $NaHCO_3$ cooled to 0°C. The mixture was extracted with CH_2Cl_2 (50 mL, 4 times). The combined extracts were dried ($MgSO_4$), the solvent was evaporated and the residue purified by column chromatography on silica gel (light petroleum/EtOAc 1:2). A first fraction (R_f = 0.39, UV-visible) gave 282 mg (63%) of **30**.[7] A second fraction (R_f = 0.20, UV-visible) gave 8 mg (1.8%) of **32**, colorless oil. IR (CH_2Cl_2) ν: 2920, 2240, 1760, 1640, 1575,

1490, 1370, 1350, 1320, 1220, 1195, 1125, 1060, 1005, 980, 960, 940 cm^{-1}; ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 7.93-7.89 (m, 2H, arom); 7.53-7.37 (m, 3H, arom); 5.62 (s, H-C(6)); 5.02 (br. s, H-C(1)); 4.12 (br. s, $J_{2,7}$ = 2.0, H-C(2)); 2.63 (m, $J_{8\text{-}exo,7}$ = 4.0, $J_{7,2}$ = 2.0, H-C(7)); 2.50 (d, ^2J = 15.0, H-C(8-*endo*)); 2.42 (dd, $J_{7,8\text{-}exo}$ = 4.0, ^2J = 15.0, H-C(8-*exo*)); 2.17 (s, Ac). CI-MS (NH_3) m/z: 299 (44, M+H$^+$), 298 (9, M$^{+\cdot}$), 256 (16), 172 (11), 122 (12), 105 (100), 77 (81).

(1*R*,2*S*,4*R*,5*R*,6*R*)-2-*exo*-Cyano-5-*exo*,6-*exo*-epoxy-7-oxabicyclo[2.2.1]hept-2-*endo*-yl (1*S*')-camphanate ((-)-**33**). (A) Commercial mCPBA (Fluka 55% metachloroperbenzoic acid/metachlorobenzoic acid, 1.97 g 6.27 mmol) in solution in brine (5 mL) was extracted with $CHCl_3$ (13 mL). After drying of the extract ($MgSO_4$) (+)-**1** (1.325 g, 4.18 mmol)[1a] was added and the mixture stirred at 40°C for 24 h. The solvent was evaporated and the residue purified by column chromatography on silica gel (light petroleum/EtOAc 1:2). A first fraction (R_f = 0.47) afforded the unreacted (+)-**1** (167 mg, 13%). The second fraction (R_f = 0.32) gave 1.186 g of (-)-**33** (85%, 97% based on converted (+)-**1**) after recrystallization form Et_2O/CH_2Cl_2.
(B) A solution of dimethyldioxirane[12] (freshly prepared, 0.06 M in acetone (3 mL) cooled to -10°C was added slowly to a stirred solution of (+)-**1** (30 mg, 0.09 mmol) in CH_2Cl_2 (3 mL) cooled to -10°C). After stirring at 20°C for 15 h, the solvent was evaporated and the residue purified as above giving 8 mg (25%) of (+)-**1** and 22 mg (73%), colorless crystals, m.p. 185-187°C. $[\alpha]^{25}_{589}$ = -0.6, $[\alpha]^{25}_{577}$ = -0.2, $[\alpha]^{25}_{546}$ = +4, $[\alpha]^{25}_{435}$ = +16, $[\alpha]^{25}_{405}$ = +17 (c = 1.0, CH_2Cl_2). IR (KBr) ν: 3060, 3010, 2970, 2250, 1785, 1755, 1440, 1400, 1375, 1305, 1260, 1240, 1170, 1145, 1100, 1070, 1055, 1020, 980, 950, 930, 860 cm^{-1}.^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 5.04 (s, H-C(1)); 4.71 (d, $J_{4,3\text{-}exo}$ = 5.0, H-C(4)); 3.56 (d, $J_{6,5}$ = 3.0, H-C(6)); 3.49 (d, $J_{5,6}$ = 3.0, H-C(5)); 2.84 (dd, ^2J = 14.0, $J_{3\text{-}exo,4}$ = 5.0, H-C(3-*exo*)); 2.49-2.37 (m, H-C(6')); 2.12-1.92 (m, H-C(6')), H-C(5')); 1.96 (d, ^2J = 14.0, H-C(3-*endo*)); 1.78-1.64 (m, H-C(5')); 1.14, 1.10, 1.03 (3s, 3 Me). ^{13}C-NMR (90.55 MHz, $CDCl_3$) δ_C: 177.3 (s, CO), 166.5 (s, C(3')); 117.0 (s, CN); 90.0 (s, C(1')); 78.5 (d, ^1J(C,H) = 170, C(4)); 76.1 (s, C(2)); 74.3 (d, ^1J(C,H) = 170, C(4)); 55.0 (s, C(4')); 54.8 (s, C(7')); 48.5, 46.3 (2d, ^1J(C,H) = 200, C(5), C(6)); 41.3 (t, ^1J(C,H) = 140, C(3)); 30.8, 28.7 (2t, ^1J(C,H) = 135, C(5')), C(6')); 16.7, 16.6 (2q, ^1J(C,H) = 126, 2 Me); 9.6 (q, ^1J(C,H) = 130, Me). CI-MS (NH_3) m/z: 333 (19, M$^{+\cdot}$), 305 (19), 153 (11), 137 (37), 135 (21), 125 (32), 109 (65), 97 (66), 83 (100). Anal. calc. for $C_{17}H_{19}NO_6$ (333.34): C 61.25, H 5.75, N 4.20; found: C 61.12, H 5.86, N 4.27.

(1*R*,2*S*,3*R*,4*R*)-3-*exo*-Hydroxy-6-oxo-7-oxabicyclo[2.2.1]hept-2-*endo*-yl (1*S*')-camphanate ((-)-**34**). A mixture of (-)-**33** (100 mg, 0.3 mmol), HFIP (20 mL) and 70% aqueous $HClO_4$ (20 µL, 0.22 mmol) was stirred at 20°C for 2 h and 15 min. 70% aqueous $HClO_4$ (20 µL) was added. After another 2 h, 70% aqueous $HClO_4$ (20 µL) was added and the mixture was allowed to stand another 3.5 h. It was poured into a saturated aqueous solution of $NaHCO_3$ (200 mL) cooled to 0°C. The mixture was extracted with CH_2Cl_2 (50 mL, 4 times). The solvent was evaporated and the residue purified by column chromatography on silica gel (CH_2Cl_2/Et_2O 1:1). The first fraction (R_f = 0.37) afforded 29 mg (29%) of unreacted (-)-**33**. The second fraction (R_f = 0.24) gave 69 mg (71%, 100% based on reacted (-)-**33**) of (-)-**34**. Colorless crystals, m.p. 158-161°C. $[\alpha]^{25}_{589}$ = -53, $[\alpha]^{25}_{577}$ = -56, $[\alpha]^{25}_{546}$ = -61, $[\alpha]^{25}_{435}$ = -105, $[\alpha]^{25}_{405}$ = -139 (c = 1.0, CH_2Cl_2). IR (KBr) ν: 3550, 2970, 2940, 1780, 1750, 1450, 1400, 1380, 1320, 1300, 1260, 1230, 1170, 1150, 1105, 1060, 1015, 985, 960, 930, 895, 830, 780 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 4.89 (br. d, $J_{2,1}$ = 5.5, $J_{2,3}$ = 1.0, $J_{2,4}$ <1.0, $J_{2,5\text{-}exo}$ <1.0, H-C(2)); 4.79 (br. d, $J_{4,5\text{-}exo}$ = 6.0, $J_{4,1}$ <1.0, H-C(4)); 4.64 (d, $J_{1,2}$ = 5.5, $J_{1,5\text{-}exo}$ = 1.0, H-C(1)); 4.19 (dd, $J_{3,OH}$ = 6.3, $J_{3,2}$ = 1.0, H-C(3)); 2.71 (d, $J_{OH,3}$ = 6.3, OH); 2.59 (dd, ^2J = 18.0, $J_{5\text{-}exo,4}$ = 6.0, $J_{5\text{-}exo,1}$ = 1.0, H-C(5-*exo*)); 2.40-2.28 (m, H-C(6')); 2.14 (d, ^2J = 18.0, H-C(5-*endo*)); 2.07-1.63 (m, 3H, H-C(6'), H_2C(5')); 1.12, 1.05, 0.97 (3s, 3 Me). ^{13}C-NMR (90.55 MHz, $CDCl_3$) δ_C: 206.0 (s, C(6)); 177.9 (s, CO); 167.1 (s, C(3')); 90.5 (s, C(1')); 82.4 (d, ^1J(C,H) = 165, C(2)); 80.2 (d, ^1J(C,H) = 165, C(4)); 79.4 (d, ^1J(C,H) = 170, C(1)); 78.1 (d, ^1J(C,H) = 155, C(3)); 54.8 (s, C(4')); 54.3 (s, C(7')); 39.1 (t, ^1J(C,H) = 140, C(5)); 30.8, 28.8 (2t, ^1J(C,H) = 135, C(5'), C(6')); 16.6, 16.5 (2q, ^1J(C,H) = 126, 2 Me); 9.6 (q, ^1J(C,H) = 130, Me). CI-MS (NH_3) m/z: 343 (11), 342 (65, M$^{+\cdot}$+1+NH_3), 324 (4, M$^{+\cdot}$), 279 (12), 278 (11), 164 (12), 137 (32), 136 (20), 135 (18), 126 (37), 125 (32), 109 (65), 99 (12), 98 (50), 97 (69), 95 (33), 84 (24), 83 (100), 82 (37), 81 (44). Anal. calc. for $C_{16}H_{20}O_7$ (324.33): C 59.25, H 6.22; found: C 59.44, H 6.24.

(1*R*,2*R*,3*S*,4*R*)-3-*endo*-(1'*S*)-Camphanoyloxy-5-oxo-7-oxabicyclo[2.2.1]hept-2-*exo*-yl acetate ((-)-**35**). This product was prepared according to the procedure described for the preparation of **20** starting with (-)-**34** (50 mg, 0.154 mmol). Recrystallization from CH_2Cl_2/Et_2O (4°C) afforded 54 mg (96%), colorless crystals, m.p. 169-171°C. $[\alpha]^{25}_{589}$ = -71, $[\alpha]^{25}_{577}$ = -74, $[\alpha]^{25}_{546}$ = -80, $[\alpha]^{25}_{435}$ = -135, $[\alpha]^{25}_{405}$ = -171 (c = 1.0, CH_2Cl_2). IR (KBr): 2960, 2920, 1780, 1750, 1730, 1445, 1395, 1370, 1325, 1310, 1300, 1250, 1225, 1165, 1105, 1060, 985, 955, 925, 830, 780 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 5.11 (m, $J_{3,4}$ = 5.6, $J_{3,2}$ = 1.4, H-C(3)); 4.97 (d,

$J_{1,4}$ = 1.4, H-C(2)); 4.86 (br. d, $J_{1,6\text{-}exo}$ = 6.6, H-C(1)); 4.67 (br. d, $J_{4,3}$ = 5.6, $J_{4,6\text{-}exo}$ = 1.5, H-C(4)); 2.63 (ddd, ^2J = 18.0, $J_{6\text{-}exo,1}$ = 6.6, $J_{6\text{-}exo,3}$ <1.0, H-C(6-*exo*)); 2.42-2.31 (m, H-C(6')); 2.26 (d, ^2J = 18.0, H-C(6-*endo*)); 2.16 (s, Me); 2.09-1.86 (m, 2H, H-C(6'), H-C(5')); 1.74-1.63 (m, H-C(5')); 1.11, 1.03, 0.99 (3s, 3 Me).^{13}C-NMR (90.55 MHz, $CDCl_3$) δ_C: 205.1 (s, C(5)); 177.7, 170.3 (2s, 2 CO); 166.5 (s, C(3')); 90.4 (s, C(1')); 80.3 (d, ^1J(C,H) = 165, C(3)); 79.2 (d, ^1J(C,H) = 175, C(2)); 79.1 (d, ^1J(C,H) = 160, C(1)); 76.9 (d, ^1J(C,H) = 165, C(4)); 54.8 (s, C(4')); 54.3 (s, C(7')); 39.3 (t, ^1J(C,H) = 135, C(6)); 30.9, 28.8 (2t, ^1J(C,H) = 135, C(5'), C(6')); 20.7 (q, ^1J(C,H) = 130, CH_3); 16.5, 16.3 (2q, ^1J(C,H) = 126), 9.6 (q, ^1J(C,H) = 130, 4 Me). CI-MS (NH_3) m/z: 384 (18, $M^{+\cdot}$+1+NH_3), 366 (1, $M^{+\cdot}$), 324 (8); 321 (9), 277 (13), 137 (23), 136 (17), 135 (13), 127 (27), 126 (72), 125 (36), 109 (98), 108 (14), 107 (11), 98 (23), 97 (66), 96 (12), 93 (11), 91 (22), 85 (17), 84 (12), 83 (100), 82 (20), 81 (44), 79 (15), 77 (11). Anal. calc. for $C_{18}H_{22}O_8$ (366.37): C 59.01, H 6.05; found: C 58.96, H 6.06.

(1*R*,2*R*,3*S*,4*R*)-3-*endo*-(1'*S*)-Camphanoyloxy-5-oxo-7-oxabicyclo[2.2.1]hept-2-*exo*-yl benzoate ((-)-**36**). Prepared according to the procedure described for the preparation of **21** starting with (-)-**34** (70 mg, 0.216 mmol). Recrystallization from CH_2Cl_2/Et_2O (4°C) gave 67 mg (72%), colorless crystals, m.p. 190-191.5°C. $[\alpha]^{25}_{589}$ = -115, $[\alpha]^{25}_{577}$ = -120, $[\alpha]^{25}_{546}$ = -133, $[\alpha]^{25}_{435}$ = -228, $[\alpha]^{25}_{405}$ = -284 (c = 1.0, CH_2Cl_2). IR (KBr) ν: 2960, 2920, 1780, 1760, 1745, 1720, 1440, 1270, 1100, 1060, 1020, 955, 710 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 8.11-8.06 (m, 2H, arom); 7.66-7.45 (m, 3H, arom); 5.28 (br. d, $J_{2,1}$ = 5.6, $J_{2,3}$ = 1.4, H-C(2)); 5.24 (d, $J_{3,2}$ = 1.4, H-C(3)); 5.00 (br. d, $J_{4,5\text{-}exo}$ = 6.6, $J_{4,2}$ <1.0, $J_{4,1}$ <1.0, H-C(4)); 4.74 (br. d, $J_{1,2}$ = 5.6, $J_{1,5\text{-}exo}$ = 1.2, H-C(1)); 2.69 (ddd, ^2J = 18.0, $J_{5\text{-}exo,4}$ = 6.6, $J_{5\text{-}exo,1}$ = 1.2, H-C(5-*exo*)); 2.46-2.35 (m, 1H, H-C(6')); 2.35 (d, ^2J = 18.0, H-C(5-*endo*)); 2.12-1.87 (m, H-C(6'), H-C(5')); 1.75-1.64 (m, H-C(5')); 1.12, 1.05, 1.02 (3s, 3 Me). ^{13}C-NMR (90.55 MHz, $CDCl_3$) δ_C: 205.2 (s, C(5)); 177.7, 170.2 (2s), 166.5 (s, C(3')); 133.8, 129.9 (2d, ^1J(C,H) = CH(arom)); 128.8 (s, arom), 128.6 (d, ^1J(C,H) = 160, CH(arom)); 90.4 (s, C(1')); 80.4 (d, ^1J(C,H) = 170, C(2)); 79.5 (d, ^1J(C,H) = 165, C(3)); 79.3 (d, ^1J(C,H) = 155, C(4)); 77.0 (d, ^1J(C,H) = 165, C(1)); 54.8 (s, C(4')); 54.4 (s, C(7')); 39.4 (t, ^1J(C,H) = 135, C(5)); 30.9, 28.8 (2t, ^1J(C,H) = 135, C(5'), C(6')); 16.5, 16.4 (2q, ^1J(C,H) = 126, Me-C(4',7')); 9.6 ^1J(C,H) = 130, Me-C(7')). CI-MS (NH_3) m/z: 446 (7, $M^{+\cdot}$+1+NH_3), 428 (4, $M^{+\cdot}$), 188 (13), 137 (9), 109 (14), 106 (10), 105 (100), 97 (15), 83 (26), 77 (29). Anal. calc. for $C_{23}H_{24}O_8$ (428.44): C 64.48, H 5.65; found: C 64.63, H 5.76.

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