Supplementary Material (ESI) for Chemical Communications

Truncated cinchona alcaloids as catalysts in enantioselective monobenzoylation of meso 1,2-diols

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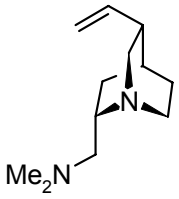
Electronic Supplementary Information

General.

Liquids were distilled under N_2 from CaH_2 in an H-tube prior to use. Molecular sieves (4Å) were activated by heating at 160 °C under high vacuum for 12 hours. NOTE: Diamines **5** and **7** slowly reacted when dissolved in CH_2Cl_2 to give the corresponding chloromethylene chloride salt.[1] Solvents were purified by filtration on drying columns using Solvtek© system. Chemicals were purchased from Aldrich, Fluka, Acros, Lancaster, TCI organics or Buchler GmbH and used without further purification unless noted. Reactions and manipulations involving organometallic or moisture sensitive compounds were carried out under N_2 atmosphere and glassware was previously dried by heating under high vacuum as necessary. Celite 545 was used as filtering material. Yields refer to homogeneous material purified by crystallisation or Flash column chromatography using Brunschwig silica gel 60 Å (32-63 mesh) or Acros neutral Alumina (50-200 micron). Proton and carbon NMR spectra were recorded on Bruker AMX-500, AMX-400 or AMX-300 FT spectrometers using an internal deuterium lock. Chemical shifts are quoted in parts per million (ppm) downfield of TMS. Coupling constants *J* are quoted in Hz. Carbon NMR and DEPT-135 spectra were recorded with broad band proton decoupling. IR spectra were recorded on a Perkin-Elmer Spectrum One spectrophotometer. Analytical HPLC was performed using an Agilent 1100 series. Electron impact (EI) mass spectra were obtained using Varian CH-4 or SM-1 instruments operating at 40-70eV and for Electrospray ionization (ESI) HRMS analyses were measured on a VG analytical 7070E instrument. Optical rotations were measured at 20ºC on a Perkin Elmer 241 polarimeter using a quartz cell (l = 10 cm) with a Na high pressure lamp (λ = 589 nm). Melting points were determined on a Büchi 510 apparatus and are

uncorrected.

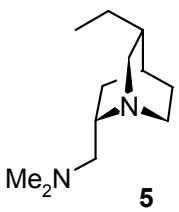
(2*S*,4*S*,5*R*)-*N*,*N*-Dimethyl-2-aminomethyl-5-ethenyl-quinuclidine.



A Schlenk tube equipped with a reflux condenser was rapidly charged with (2*S*,4*S*,5*R*)-2-aminomethyl-5-ethenyl-quinuclidine[2] (**4**) (1.41 g, 8.51 mmol), evacuated for 30 seconds, filled with N_2, and cooled to 0 °C. Then 98 % formic acid (2.04 mL, 54.1 mmol) and 36.5 % aq. formaldehyde (1.74 mL, 24.5 mmol) were added sequentially and the mixture was refluxed for 3 h. The reaction was cooled to r.t. and dissolved in a solution (1M) of HCl (30 mL) and extracted with Et_2O (3 x). The aqueous layer was then brought up to pH ≈12 with K_2CO_3 and extracted with Et_2O (3 x). The combined organic layers were dried with anh. Na_2SO_4 and volatiles removed under low pressure to give the title compound (1.56 g, 94 % yield) as a colourless oil.

MW = 194.34 g / mol; $\boldsymbol{R_F}$ = 0.58 ($CHCl_3$ 84%; MeOH 14%; $NH_{3(aq)}$ 2%); $\boldsymbol{[\alpha]_D^{20}}$: +46 (*c* = 1.64 $CHCl_3$); **IR** (neat, cm^{-1}): 3340, 3075, 2934, 2860, 2818, 2764, 1636, 1454, 1320, 1263, 1163, 1123, 1027, 990, 908; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.84 (ddd, *J* = 17.2, 10.3 and 7.6 Hz, 1H), 5.02-4.94 (m, 2H), 3.13 (dd, *J* = 13.8 and 10.1, 1H), 2.94-2.79 (m, 2H), 2.65-2.57 (m, 2H), 2.42 (dd, *J* = 12.5 and 8.3, 1H), 2.26-2.20 (m, 1H), 2.19 (s, 6H), 2.07 (dd, *J* = 12.5 and 6.5, 1H), 1.86-1.79 (m, 1H), 1.70-1.65 (m, 1H), 1.48-1.41 (m, 2H), 0.89 (dddd, *J* = 13.3, 6.7, 2.5 and 1.7, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 142.2, 114.1, 64.1, 56.2, 53.6, 45.9, 40.8, 39.9, 28.9, 27.8, 27.4; **HRMS** (ESI) calcd. for $C_{12}H_{23}N_2$ $[M+H]^+$: 195.1855, found: 195.1861.

(2*S*,4*S*,5*R*)-*N*,*N*-Dimethyl-2-aminomethyl-5-ethylquinuclidine (5).



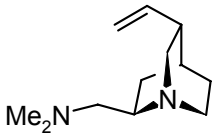
5

A two neck round bottom flask equipped charged with (2*S*,4*S*,5*R*)-*N*,*N*-dimethyl-2-aminomethyl-5-ethene-quinuclidine (1.12 g, 5.80 mmol) and 10 % Pd/Cl (123 mg, 0.12 mmol). The flask was evacuated and refilled with H_2 from a balloon. Then MeOH (27 mL) was added and the suspension was stirred at r.t. for 16 h. The reaction mixture was filtered

and the solvent evaporated under reduced pressure. The residue was dissolved aq. HCl (1M, 45 mL) and extracted with Et_2O (3 x). The aqueous layer was then brought to pH ≈ 12 with K_2CO_3 and extracted with Et_2O (3 x). The combined organic layers were dried with anh. Na_2SO_4 and volatiles removed under low pressure to give the title compound **5** (1.13 g, 95 % yield) as a colourless oil.

MW =196.34 g / mol; $\boldsymbol{R_F}$ = 0.64 ($CHCl_3$ 84%; MeOH 14%; $NH_{3(aq)}$ 2%); $\boldsymbol{[\alpha]_D^{20}}$: +12 (*c* = 0.70 $CHCl_3$); **IR** ($CHCl_3$, cm^{-1}): 3137, 2934, 2864, 2775, 2822, 1457, 1379, 1264, 1093, 1027. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.17 (dd, *J* = 13.5 and 9.4, 1H), 2.98-2.81 (m, 2H), 2.71-2.60 (m, 1H), 2.42 (dd, *J* = 12.3 and 8.0, 1H), 2.46-2.36 (m, 1H), 2.22 (s, 6H), 2.14 (dd, *J* = 12.3 and 6.8, 1H), 1.85-1.76 (m, 1H), 1.70-1.64 (m, 1H), 1.57-1.30 (m, 5H), 0.87-0.96 (m, 1H), 0.86 (t, *J* = 7.2, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 64.2, 57.8, 53.6, 46.1, 41.0, 37.4, 28.6, 27.6, 27.2, 25.6, 12.2; **HRMS** (ESI) calcd. for $C_{12}H_{25}N_2$ $[M+H]^+$: 197.2012, found: 197.2013.

(2*R*,4*S*,5*R*)-*N*,*N*-Dimethyl-2-aminomethyl-5-ethenyl-quinuclidine

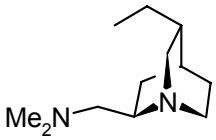


A Schlenk tube equipped with a reflux condenser was rapidly charged with (2*R*,4*S*,5*R*)-2-aminomethyl-5-ethenyl-quinuclidine[2] (1.00 g, 6.03 mmol), evacuated for 30 seconds, filled with N_2, and cooled at 0 °C. Then 98 % formic acid (1.39 mL, 36.0 mmol) and 36.5 % formaldehyde (1.22 mL, 16.4 mmol) were added and the mixture was refluxed for 3 h. Then cooled at r.t., dissolved in a solution (1M) of HCl (30 mL) and extracted with Et_2O (3 x). The aqueous layer was brought to pH ≈12 with K_2CO_3 and extracted with Et_2O (3 x). The combined organic layers were dried with anh. Na_2SO_4 and volatiles removed under low pressure to give the title compound (1.10 g, 94 % yield) as colourless oil.

MW =194.34 g / mol; $\boldsymbol{R_F}$ = 0.58 ($CHCl_3$ 84%; MeOH 14%; $NH_{3(aq)}$ 2%) ; $\boldsymbol{[\alpha]_D^{20}}$: + 181 (*c* = 1.64 $CHCl_3$); **IR** (neat, cm^{-1}): 3076, 2934, , 2862, 2818, 2763, 1682, 1636, 1455, 1321, 1263, 1202, 1029; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.86 (ddd, *J* = 17.4, 9.9 and 7.3, 1H), 5.02-4.99 (m, 1H), 4.98-4.96 (m, 1H), 2.96-2.78 (m, 4H), 2.67-2.61 (m, 1H), 2.42 (dd, *J* = 12.5 and 8.2, 1H), 2.23-2.16 (m, 1H), 2.21 (s, 6H), 2.11 (dd, *J* = 12.5 and 6.4, 1H), 1.70-1.66 (m, 1H), 1.61-1.46 (m, 3H), 1.26 (dddd, *J* = 21.6, 8.2, 2.0 and 1.8, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 141.7, 114.5, 63.1, 53.7, 49.6, 47.7, 46.2, 40.6, 28.0,

27.2, 27.1; **HRMS** (ESI) calcd. for $C_{12}H_{23}N_2$ $[M+H]^+$: 195.1855, found: 195.1848.

(2*R*,4*S*,5*R*)-*N*,*N*-Dimethyl-2-aminomethyl-5-ethylquinuclidine (7).



7

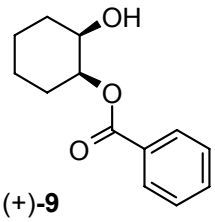
A two neck round bottom flask was charged with (2*R*,4*S*,5*R*)-*N*,*N*-dimethyl-2-aminomethyl-5-etheneyl-quinuclidine (1.11 g, 5.66 mmol) and 10 % palladium on charcoal (120 mg, 0.11 mmol). The flask was evacuated and refilled with H_2 from a balloon. Then MeOH (26 mL) was added and the suspension was stirred at r.t. for 18 h. The reaction mixture was then filtered and the solvent evaporated under reduced pressure. The residue was dissolved in aq. HCl (1 M, 45 mL) and extracted with Et_2O (3 x). The aqueous layer was brought to pH ≈12 with K_2CO_3 and extracted with Et_2O (3 x). The combined organic layers were dried with anh. Na_2SO_4 and volatiles removed under low pressure to give the title compound **7** (933 mg, 84 %) as colourless oil.

MW =196.34 g / mol; $\boldsymbol{R_F}$ = 0.46 ($CHCl_3$ 84%; MeOH 14%; $NH_{3(aq)}$ 2%); $\boldsymbol{[\alpha]_D^{20}}$: + 128 (*c* = 0.93 $CHCl_3$); **IR** (neat, cm^{-1}): 2933, 2860, 2817, 2764, 1683, 1456, 1378, 1325, 1263, 1202, 1147, 1034; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.90-2.73 (m, 4H), 2.39 (dd, *J* = 12.4 and 7.9, 1H), 2.35 (ddd, *J* = 14.0, 7.3 and 2.3, 1H), 2.20 (s, 6H), 2.11 (dd, *J* 12.4 and 6.8, 1H), 1.62-1.51 (m, 2H), 1.49-1.40 (m, 2H), 1.39-1.25 (m, 3H), 1.24-1.15 (m, 1H), 0.82 (t, *J* 7.3, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 63.2, 53.7, 49.5, 49.2, 46.1, 37.9, 27.8, 26.7, 26.1, 25.8, 12.1; **HRMS** (ESI) calcd. for $C_{12}H_{25}N_2$ $[M+H]^+$: 197.2017, found: 197.2005.

General procedure for the asymmetric acylation of *meso*-1,2-diols.

A solution of chiral diamine **5** (3.4 mg, 0.017 mmol, 2 mol %) in dry AcOEt (2 ml) was added under N_2 to a mixture of *meso*-1,2-diol (0.86 mmol) and activated molecular sieves (4Å, 113 mg) in dry AcOEt (6 ml). To the stirred, cold (-60 °C) solution, benzoyl chloride (150 μL, 1.29 mmol) followed by Et_3N (121 μL, 0.86 mmol) were added drop-wise. The resulting mixture was stirred at -60 °C for 22 hours, then quenched with a solution (10 mL) of phosphate buffer (pH = 7) and extracted with Et_2O (3 x). The organic layers were dried with $MgSO_4$ and all volatiles were removed under reduced pressure. The residue was purified by flash chromatography (Et_2O / pentane) to the monobenzoate.

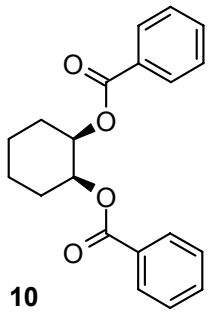
(+)-(1*S*,2*R*)-2-Hydroxy-1-cyclohexyl benzoate (+)-9[3,4]



(+)-**9**

Colourless oil; **MW** = 220.26 g / mol; $\boldsymbol{R_F}$ = 0.16 (Et_2O / pentane, 1 : 3); $\boldsymbol{[\alpha]_D^{20}}$: +16 (*c*= 0.68 $CHCl_3$); **IR** (neat, cm^{-1}): 3441, 2937, 2862, 1715, 1602, 1450, 1272; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.03-7.99 (m, 2H), 7.60-7.53 (m, 1H), 7.48-7.40 (m, 2H), 5.24-5.20 (m, 1H), 3.99-3.92 (m, 1H), 2.09-1.92 (m, 1H), 1.95 (broad s, 1H), 1.90-1.80 (m, 1H), 1.78-1.62 (m, 4H), 1.51-1.37 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.3, 133.1, 130.4, 129.6, 128.4, 74.6, 70.0, 30.4, 27.4, 21.8, 21.6; **MS** *m/z* (EI): 202 (2 [M-H_2O]$^+$), 174 (2), 149 (4), 115 (14), 105 (100), 98 (95 [M-BzOH]$^+$), 77 (79), 51 (36); **HPLC** Chiralcel OJ-H, eluent: 95:5 hexane / ^{i}PrOH, flow rate: 1 mL / min: retention times 11.3 min ((1*S*,2*R*)-enantiomer) and 13.5 min ((1*R*,2*S*)-enantiomer).

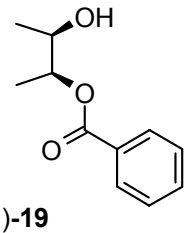
***cis*-1,2-Dibenzoyloxycyclohexane (10)** [5]



10

White solid; **MW** = 324.37 g / mol; $\boldsymbol{R_F}$ = 0.48 (Et_2O / pentane, 1: 3); **MP** = 63-64 °C (Ethanol); **IR** (neat, cm^{-1}): 2942, 1786, 1720, 1600, 1450, 1265, 1210; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.01 (d, *J* 7.1, 4H), 7.54 (t, *J* 8.8, 2H), 7.41 (t, *J* 8.8, 4H), 5.40-5.38 (m, 2H), 2.14-2.06 (m, 2H), 1.90-1.75 (m, 4H), 1.62-1.53 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.8, 132.9, 130.5, 129.6, 128.3, 71.9, 28.0, 21.9; **MS** *m/z* (EI): 202 (12 [M-BzOH]$^+$), 198 (15), 182 (5), 122 (3), 105 (100), 77 (81), 51 (62).

(+)-(2*S*,3*R*)-3-Hydroxyl-2-butyl benzoate (19)[6]:



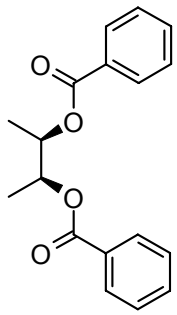
(+)-**19**

The starting material was dried over MS 4Å in CH_2Cl_2 solution.

(+)-**19**: colourless oil; **MW** = 194.23 g / mol; $\boldsymbol{R_F}$ = 0.26 (Et_2O / pentane, 1 : 3); $\boldsymbol{[\alpha]_D^{20}}$: + 17 (*c*= 0.70 CH_2Cl_2); **IR** (neat, cm^{-1}): 3441, 2981, 1714, 1451, 1315, 1275, 1119, 1091, 1071, 1026, 1008; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.03 (d, *J* 7.8, 2H), 7.54 (t, *J* 7.2, 1H), 7.42 (t, *J* 7.8, 2H), 5.15-5.07 (m, 1H), 3.99 (cd, *J* 6.4 and 3.5, 1H), 2.35 (broad s, 1H), 1.33 (d, *J* 6.4, 3H), 1.23 (d, *J* 6.4, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.2, 133.1,

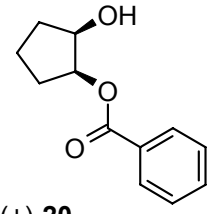
130.3, 129.6, 128.4, 75.1, 69.8, 18.0, 14.5; **MS** *m/z* (EI): 194 (2 $[M]^+$), 179 (2), 150 (48), 105 (100), 77 (80), 72 (32), 51 (14). **HPLC** Chiralcel OJ-H, eluent: 95:5 hexane / ^{i}PrOH, flow rate: 1 mL / min: retention times 10.6 min ((2*S*,3*R*)-enantiomer) and 12.0 min ((2*R*,3*S*)-enantiomer).

cis-1,2-Bisbenzoyloxybutane[7]



Colourless oil; **MW** = 298.34 g / mol; $\boldsymbol{R_F}$ = 0.65 (Et_2O / pentane, 1 : 3); **MP** = 73-75 °C (CH_2Cl_2 / cyclohexane); **IR** (neat, cm^{-1}): 2988, 1787, 1717, 1692, 1601, 1584, 1451, 1316, 1266, 1212, 1113, 1096, 1070, 1038, 1016, 996; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.04 (d, *J* 8.3, 4H), 7.55 (t, *J* 7.5, 2H), 7.43 (t, *J* 7.7, 4H), 5.42-5.36 (m, 2H), 1.45 (d, *J* 6.4, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.0, 133.2, 130.5, 129.8, 128.6, 72.5, 15.7; **MS** *m/z* (EI): 254 (6), 226 (6), 210 (27), 198 (12), 176 (14 $[M\text{-}PhCOOH]^+$), 149 (13), 132 (12), 105 (100), 77 (70), 51 (47).

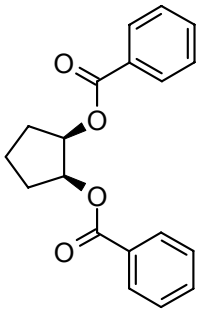
(+)-(1*S*,2*R*)-2-Hydroxy-1-cyclopentyl benzoate (20)[3,8,9]



(+)-**20**

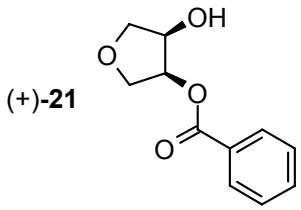
The starting material was dried over MS 4Å in CH_2Cl_2 solution. [3, 12, 13] colourless oil; **MW** = 206.24 g / mol; $\boldsymbol{R_F}$ = 0.22 (Et_2O / pentane, 1 : 3); $\boldsymbol{[\alpha]^{20}_D}$: +13 (*c* = 0.45 CH_2Cl_2); **IR** (neat, cm^{-1}): 3596, 3064, 2974, 2879, 1717, 1602, 1584, 1451, 1272, 1117; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.03 (dd, *J* 8.3, and 1.1, 2H), 7.36 (dt, *J* 7.5 and 1.5, 1H), 7.41 (dt, *J* 7.5 and 1.5, 2H), 5.24-5.16 (m, 1H), 4.32-4.25 (m, 1H), 2.64 (broad s, 1H), 2.19-1.99 (m, 1H), 1.98-1.87 (m, 3H), 1.82-1.75 (m, 1H), 1.64-1.57 (m, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 166.4, 133.1, 130.1, 129.6, 128.4, 77.4, 73.4, 30.9, 28.2, 19.5; **MS** *m/z* (EI): 206 (1 $[M]^+$), 198 (14), 188 (34 $[M\text{-}H_2O]^+$), 106 (50), 105 (100), 77 (73), 51 (50); **HRMS** (ESI) calcd. for $C_{12}H_{14}O_3Na$ $[M+Na]^+$: 229.0835, found: 229.0829; **HPLC** Chiralcel OJ-H, eluent: 95:5 hexane / ^{i}PrOH, flow rate: 0.5 mL / min: retention times 22.3 min ((1*S*,2*R*)-enantiomer) and 26.7 min ((1*R*,2*S*)-enantiomer).

***cis*-1,2-Bisbenzoyloxycyclopentane[11]**



White solid; **MW** = 310.35 g / mol; $\boldsymbol{R_F}$ = 0.59 (Et_2O / pentane, 1 : 3); **MP** = 45-47 °C (ethanol); **IR** (neat, cm^{-1}): 3065, 2962, 1720, 1602, 1584, 1451, 1315, 1283, 1272, 1258, 1177, 1122; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.97 (dd, *J* 8.5, and 1.3, 4H), 7.52 (tt, *J* 7.5, and 1.5, 2H), 7.40-7.33 (m, 4H), 5.54-5.48 (m, 2H), 2.27-2.13 (m, 2H), 2.10-1.97 (m, 3H), 1.84-1.72 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 165.9, 132.8, 130.5, 129.6, 128.2, 75.1, 28.6, 19.7; **MS** *m/z* (ESI): 311 (100 $[M]^+$), 205 (24), 189 (99), 106 (8); **HRMS** (ESI) calcd. for $C_{19}H_{19}O_4$ $[M+H]^+$: 311.1277, found: 311.1277.

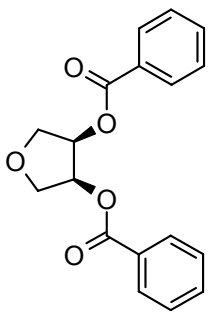
(+)- 4-Anhydro-2-acyloxyerytritol (21):



(+)-**21**

proposed absolute configuration

White solid, **MW** = 208.22 g / mol; $\boldsymbol{R_F}$ = 0.07 (Et_2O / pentane, 1 : 2); $\boldsymbol{[\alpha]_D^{20}}$: +4 (*c* = 0.86 CH_2Cl_2); **MP** = 80-81 °C (CH_2Cl_2, cyclohexane); **IR** (neat, cm^{-1}): 3417, 2926, 2874, 1715, 1601, 1584, 1451, 1269, 1177, 1118, 1068; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.05-8.00 (m, 2H), 7.58-7.52 (m, 1H), 7.37-7.34 (m, 2H), 5.34-5.30 (m, 1H), 4.51 (ddd, *J* 11.1, 5.5 and 1.6, 1H), 4.11 (ddd, *J* 10.2, 5.8 and 1.7, 1H), 3.98 (ddd, *J* 9.3, 5.8 and 9.3, 1H), 3.96 (ddd, *J* 12.1, 5.8 and 1.7, 1H), 3.74 (ddd, *J* 9.3, 5.5 and 1.8, 1H), 2.83 (broad s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 166.6, 133.7, 130.0, 129.6, 128.7, 74.5, 72.6, 71.2, 70.7; **HRMS** (ESI) calcd. for $C_{11}H_{13}O_4$ $[M^+ + H]$: 209.0808, found: 209.0817; **HPLC** Chiralcel AS-H, eluent: 95:5 hexane / ^{i}PrOH, flow rate: 1 mL / min: retention times 38.1 min ((-)-enantiomer) and 45.6 min ((+)-enantiomer).

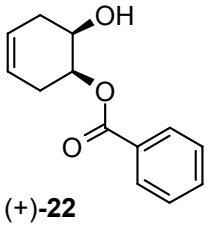


***cis*-1,2-Bisbenzoyloxy-4-anhydroerytritol[13]**

Colourless oil; **MW** = 312.33 g / mol; $\boldsymbol{R_F}$ = 0.40 (Et_2O / pentane, 1 : 2); **IR** (neat, cm^{-1}): 2925, 2872, 1721, 1602, 1584, 1491, 1451, 1345, 1315, 1277, 1177, 1126; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.98-7.93 (m, 4H), 7.56-7.50 (m, 2H), 7.39-7.32 (m, 4H), 5.70-5.66 (m, 2H), 5.32-5.26 (m, 2H), 4.08-4.03 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$):

δ 166.1, 133.6, 130.1, 129.7, 128.7, 72.6, 70.9; **HRMS** (ESI) calcd. for $C_{18}H_{17}O_5$ $[M^+ + H]$: 313.1070, found: 313.1066.

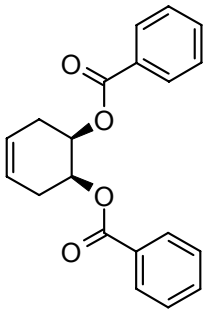
(+)-(1*S*,2*R*)- 2-Hydroxy-1-cyclohex-4-enyl benzoate (22)[10]



(+)-**22**

Colourless oil; **MW** = 218.25 g / mol; $\boldsymbol{R_F}$ = 0.08 (Et_2O / pentane, 1 : 3); $\boldsymbol{[\alpha]_D^{20}}$: + 44 (*c* = 0.92 CH_2Cl_2); **IR** (neat, cm^{-1}): 3597, 3064, 3036, 2929, 2853, 1716, 1602, 1584, 1451, 1315, 1275, 1116; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.04 (d, *J* 7.9, 2H), 7.58-7.52 (m, 1H), 7.46-7.40 (m, 2H), 5.70-5.58 (m, 2H), 5.35-5.30 (m, 1H), 4.18-4.14 (m, 1H), 2.64 (broad s, 1H), 2.52-2.43 (m, 3H), 2.39-2.32 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 166.6, 133.2, 130.3, 129.7, 128.4, 123.9, 123.4, 72.8, 67.6, 31.5, 28.4; **MS** *m/z* (EI): 218 (2 $[M]^+$), 164 (2), 123 (18), 105 (100), 96 (84), 77 (19), 67 (17), 51 (11); **HRMS** (ESI) calcd. for $C_{13}H_{15}O_3$ $[M+H]^+$: 219.1015, found: 219.1009; **HPLC** Chiralcel OJ-H, eluent: 95:5 hexane / ^{i}PrOH, flow rate: 0.5 mL / min: retention times 25.3 min ((1*S*,2*R*)-enantiomer) and 31.4 min ((1*R*,2*S*)-enantiomer).

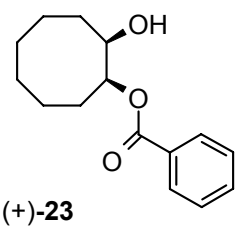
***cis*-1,2-Bisbenzoyloxycyclo-4-hexene**



Conversion: 8 % (^{1}H-NMR): colourless oil; **MW** = 322.36 g / mol; $\boldsymbol{R_F}$ = 0.47 (Et_2O / pentane, 1 : 3); **IR** (neat, cm^{-1}): 3065, 3038, 2934, 1718, 1584, 1452, 1315, 1303, 1280, 1266, 1253, 1217; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.03-8.01 (m, 4H), 7.57-7.51 (m, 2H), 7.43-7.40 (m, 4H), 5.73 (t, *J* 1.6, 2H), 5.80-5.55 (m, 2H), 2.68-2.56 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 165.9, 132.9, 130.2, 129.6, 128.3, 123.6, 69.9, 28.8; **HRMS** (ESI) calcd. for $C_{20}H_{19}O_4$ $[M+H]^+$: 323.1277, found: 323.1279.

(+)-(1*S*,2*R*)- 2-Hydroxyl-1-cyclooctanyl benzoate (23)[3]

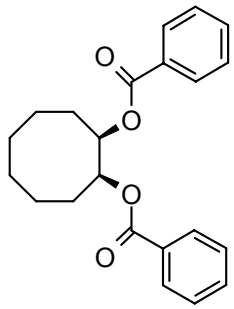
Colourless oil; **MW** = 248.32 g / mol; R_F = 0.40 (Et_2O / pentane, 1: 2). $[\alpha]^{20}_D$: + 8 (*c* = 0.90 CH_2Cl_2); **IR** (neat, cm^{-1}): 3425, 3036, 2922, 2856, 1710, 1601, 1584, 1450, 1315, 1271, 1176, 1110. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.05-8.01 (m, 2H), 7.56-7.52 (m, 1H), 7.45-7.39 (m, 2H), 5.32-5.27 (m, 1H), 4.07 (ddd, *J* 6.4, 3.9, 2.4, 1H) 2.39 (broad s, 1H),



(+)-**23**

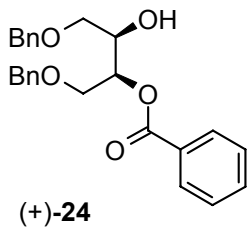
2.23-2.11 (m, 1H), 1.94-1.47 (m, 11H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.1, 132.9, 130.3, 129.5, 128.3, 77.6, 71.7, 30.5, 27.8, 26.8, 25.6, 24.1, 22.0; **HRMS** (ESI) calcd. for $C_{15}H_{21}O_3$ $[M+H]^+$: 249.1485, found: 249.1481; **HPLC** Chiralcel OJ-H, eluent: 95:5 hexane / ^{i}PrOH, flow rate: 1 mL / min: retention times 8.9 min ((1*S*,2*R*)-enantiomer) and 10.7 min ((1*R*,2*S*)-enantiomer).

***cis*-1,2-Bisbenzoyloxycyclooctane**:



Colourless oil; **MW** = 352.43 g / mol; $\boldsymbol{R_F}$ = 0.44 (Et_2O / pentane, 1 : 4); **IR** (neat, cm^{-1}): 3422, 2924, 2853, 1717, 1451, 1378, 1314, 1278, 1176, 1109, 1069, 1026; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.03-7.98 (m, 4H), 7.57-7.51 (m, 2H), 7.43-7.38 (m, 4H), 5.54-5.49 (m, 2H), 2.30-1.19 (m, 2H), 1.96-1.64 (m, 10H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.2, 133.2, 130.8, 130.0, 128.7, 75.0, 29.1, 26.7, 23.8; **HRMS** (ESI) calcd. for $C_{22}H_{25}O_4$ $[M+H]^+$: 353.1747, found: 353.1745.

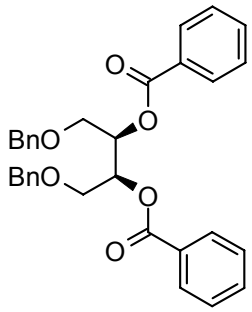
(+)-(2*S*,3*R*)-1,4-Bisbenzyloxy-3-hydroxyl-2-butyl benzoate (24):



(+)-**24**

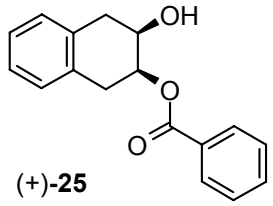
Colourless oil; **MW** = 406.48 g / mol; $\boldsymbol{R_F}$ = 0.16 (Et_2O / pentane, 1 : 2); $\boldsymbol{[\alpha]_D^{20}}$: + 55 (*c* = 0.23 CH_2Cl_2); **IR** (neat, cm^{-1}): 3464, 3063, 3031, 2865, 1716, 1452, 1270, 1108, 1070, 1026, 737, 712, 698; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.03 (d, *J* 8.3, 2H), 7.58 (t, *J* 7.4, 1H), 7.43-7.41 (m, 2H), 7.31-7.22 (m, 10H), 5.33 (ddd, *J* 6.7, 4.7, and 3.5, 1H), 4.61-4.49 (m, 4H), 4.27-4.19 (m, 1H), 3.91 (dd, *J* 10.9 and 4.8, 1H), 3.84 (dd, *J* 10.9 and 3.5, 1H), 3.65 (dd, *J* 9.7 and 3.9, 1H), 3.60 (dd, *J* 9.5 and 5.9, 1H), 2.87 (d, *J* 5.7, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 165.7, 130.8, 137.7, 133.1, 129.9, 129.7, 128.4, 128.37, 128.33, 127.8, 127.7, 127.6, 127.5, 73.4, 73.3, 73.0, 70.6, 69.8, 68.8; **HRMS** (ESI) calcd. for $C_{25}H_{27}O_5$ $[M+H]^+$: 407.1853, found: 407.1862; **HPLC** Chiralcel AS-H, Gradient 99:1 to 90:10 during 60 min, eluent: hexane / ^{i}PrOH, flow rate: 1 mL / min: retention times 35.8 min ((2*S*,3*R*)-enantiomer) and 42.6 min ((2*R*,3*S*)-enantiomer).

***cis*-2,4-Bisbenzoyloxy-1,4-benzyloxybutane**



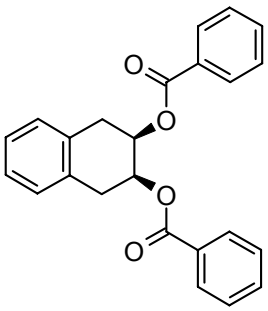
White solid; **MW** = 510.59 g / mol; $\boldsymbol{R_F}$ = 0.51 (Et_2O / pentane, 1 : 2); **MP** = 114-116 °C (CH_2Cl_2 / cyclohexane); **IR** (neat, cm^{-1}): 3064, 3032, 2928, 2856, 1788, 1719, 1601, 1585, 1451, 1258, 1096; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.03-7.99 (m, 4H), 7.57 (tt, *J* 7.5 and 1.3, 2H), 7.44 (t, *J* 7.8, 4H), 7.27-7.18 (m, 10H), 5.76-7.72 (m, 2H), 4.56 (d, *J* 12.1, 2H), 4.48 (d, *J* 12.1, 2H), 3.88 (dd, *J* 10.8 and 3.8, 2H), 3.82 (dd, *J* 10.8 and 3.8, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 165.5, 138.0, 133.4, 130.2, 130.1, 128.7, 128.6, 128.0, 127.9, 77.3, 73.8, 68.4; **MS** *m/z* (EI): 403 (2 $[M\text{-}BnO]^+$), 313 (65), 267 (2), 191 (5), 158 (4), 105 (100), 91 (84); **HRMS** (EI) calcd. for $C_{25}H_{23}O_5$ $[M\text{-}BnO]^+$: 403.1545, found: 403.1544.

(+)-(2*S*,3*R*)-3-Hydroxyl-2-tetralinyl benzoate (25):



(+)-**25**

Colourless oil; **MW** = 268.32 g / mol; $\boldsymbol{R_F}$ = 0.20 (Et_2O / pentane, 1 : 2); $\boldsymbol{[\alpha]_D^{20}}$: + 20 (*c* = 0.69 CH_2Cl_2), 81.7 % ee; **IR** (neat, cm^{-1}): 3423, 3064, 2931, 1712, 1601, 1583, 1495, 1451, 1315, 1270, 1113, 1068; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.06-8.01 (m, 2H), 7.58-7.52 (m, 1H), 7.41 (t, *J* 7.8, 2H), 7.20-7.10 (m, 4H), 5.55-5.50 (m, 1H), 4.37-4.32 (m, 1H), 3.31-3.04 (m, 4H), 2.75 (broad s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.9, 133.5, 133.2, 132.7, 130.2, 130.0, 129.5, 129.2, 128.6, 126.6, 126.5, 73.3, 68.1, 34.9, 32.1; **MS** *m/z* (EI): 146 (100 $[M\text{-}PhCOOH]^+$), 145 (56), 128 (55), 117 (60), 105 (88), 77 (69). **HRMS** (ESI) calcd. for $C_{17}H_{17}O_3$ $[M+H]^+$: 269.1172, found: 269.1179; **HPLC** Chiralcel AS-H, Gradient 99:1 to 90:10 during 60 min, eluent: hexane / ^{i}PrOH, flow rate: 1 mL / min: retention times 35.6 ((2*S*,3*R*)-enantiomer) min and 47.7 min((2*R*,3*S*)-enantiomer) .

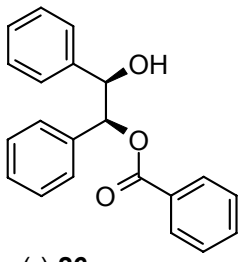


***cis*-2,4-Bisbenzoyloxytetralin.**

White solid; **MW** = 372.42 g / mol; $\boldsymbol{R_F}$ = 0.69 (Et_2O / pentane, 1 : 2); **MP** = 91 °C (Ethanol); **IR** (neat, cm^{-1}): 3066, 1787, 1720, 1600, 1584, 1451, 1315, 1278, 1212, 1174, 1109, 1040; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.02-7.95 (m, 4H), 7.57-7.51 (m,

2H), 7.44-7.34 (m, 4H), 7.23-7.15 (m, 4H), 5.75 (t, *J* 5.5, 2H), 3.44-3.30 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.2, 133.3, 132.6, 130.3, 129.9, 129.4, 128.6, 126.8, 70.5, 32.4; **MS** *m/z* (EI): 373 (2 $[M]^+$), 128 (100 $[M-2PhCOOH]^+$), 105 (85), 77 (72), 51 (32); **HRMS** (ESI) calcd. for $C_{24}H_{21}O_4$ $[M+H]^+$: 373.1434, found: 373.1439.

(-)-(1*S*,2*R*)-1,4-Diphenyl-2-hydroxyl-1-butyl benzoate (26)[3]

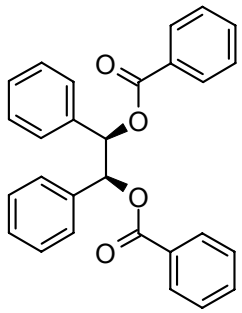


(-)-**26**

White solid; **MW** = 318.38 g / mol; $\boldsymbol{R_F}$ = 0.21 (Et_2O / pentane, 1: 3) ; $\boldsymbol{[\alpha]^{20}_D}$: -8 (*c*= 0.22 CH_2Cl_2); **MP** = 158-159 (CH_2Cl_2 / cyclohexane); **IR** (neat, cm^{-1}): 3477, 3028, 1720, 1451, 1316, 1272, 1177, 1113, 1027, 701; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.03-7.98 (m, 2H), 7.59-7.53 (m, 1H), 7.46-7.40 (m, 2H), 7.34-7.26 (m, 10H), 6.16 (d, *J* 5.8, 1H), 5.16 (d, *J* 5.8, 1H), 2.26 (broad s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 165.7, 139.8, 136.8, 133.5, 130.3, 130.0, 128.8, 128.7, 128.6, 128.5, 128.4, 127.9, 127.3, 79.8, 76.9; **MS** *m/z* (EI): 318 (2 $[M^+]$), 212 (51), 167 (15), 149 (3), 122 (5), 105 (100), 77 (64), 51 (10); **HPLC** Chiralcel OJ-H, eluent: 95:5 hexane / ^{i}PrOH, flow rate: 1 mL / min: retention times 33.8 min ((1*R*,2*S*)-enantiomer) and 57.3 min ((1*S*,2*R*)-enantiomer).

***cis*-2,3-Bisbenzoyloxy-1.4-diphenylbutane[10]**

White solid; **MW** = 422.49 g / mol; $\boldsymbol{R_F}$ = 0.39 (Et_2O / pentane, 1 : 2); **MP** = 241-239 °C (CH_2Cl_2 / cyclohexane); **IR** (neat, cm^{-1}): 2924, 2852, 1709, 1451, 1266, 1110, 1069, 710; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.01 (d, *J* 8.0, 4H), 7.56 (t, *J* 7.6, 2H), 7.43 (t, *J* 7.6, 4H), 7.29 (s, 10H), 6.49 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.5, 136.2, 133.4, 130.1, 130.0, 128.78, 128.72, 128.4, 127.8, 77.6; **HRMS** (ESI) calcd. for $C_{28}H_{22}O_4$ $[M+H]^+$: 440.1856, found: 440.1851.



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