Supporting Information

for

Novel supramolecular affinity materials based on
(−)-isosteviol as molecular templates

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Characterization data, spectra of synthesized compounds, QCM set up, and
QCM screening details.

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A. Materials and methods

All reagents were used in analytical grades. Solvents were dried if necessary, by standard methods. Nitrogen which was used in the QMB screening experiments was used in a purity of 99.998%. Melting points were determined by a Melting Point apparatus B-545 (Büchi, Flawil, Switzerland) and were uncorrected. Microanalysis was performed with a VarioMICRO cube (Elementaranalysensysteme, Hanau, Germany). NMR spectra were recorded with a Bruker AC 300 or AV II 400 instrument (Bruker Analytische Messtechnik, Karlsruhe, Germany) by calibration on traces of CHCl₃ in the corresponding deuterated solvent with δ = 7.26 ppm for ¹H NMR and δ = 77.0 ppm for ¹³C NMR, respectively; chemical shifts are expressed in ppm. The assignment of signals, if given, was determined via 2D NMR spectroscopy (COSY, HSQC, HMBC) or in accordance with literature [1]. Mass spectra and high resolution mass spectra were obtained on a QTof Ultima 3 apparatus (Waters, Milford, Massachusetts) employing ESI or on a MAT 95 (Thermo Finnigan, Bremen, Germany) employing FD. Optical rotations were measured using a JASCO P-2000 apparatus (Jasco Deutschland GmbH, Gross-Umstadt, Germany, path length 100 mm). All reactions were monitored by thin layer chromatography (TLC), visualization was effected by UV and heating with a 1% aqueous solution of Ce(SO₄)₂·4H₂O containing 2.5% of molybdatophosphoric acid and 6% of sulfuric acid. Column chromatography was performed on silica gel (particle size 63–200 μm, Merck, Darmstadt, Germany) or using a Büchi chromatography system (silica gel, particle size 40-63 μm, Macherey-Nagel GmbH, Düren, Germany) using mixtures of cyclohexane with ethyl acetate or dichloromethane with methanol as eluents. X-ray analysis data were collected on a STOE IPDS-2T diffractometer (Stoe, Darmstadt, Germany) using Incoatec microSource Cu Kα radiation (λ = 1.54186 Å). The structures were solved by direct methods and refined anisotropically by the least-
squares procedure implemented in the SHELX program system. CCDC-942549 (for all-syn-17) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

The experimental primary data of the QCM experiments were processed with Matlab 7.11.0 (R2010b) (The MathWorks Inc., Natick, Massachusetts, USA).

For the preparation of the diagrams OriginPro 8 SR0 (OriginLab Corporation, Northampton, Massachusetts, USA) were used.

HFF-QCMs with a fundamental frequency of 195 MHz were used (KVG Quartz Crystal Technology GmbH, Neckarbischofsheim, Germany. Type: XA 1600).

The QCM is excited using an aperiodic oscillator circuit and oscillates with its specific load resonance frequency [2]. Frequency counting is performed using a FPGA (field programmable gate array) which allows asynchronous 28-bit counting with an accuracy of ±0.5 Hz.

B. Experimental procedures and characterization

(+)-all-syn-Trispiro[tris-ent-beyerane-16,2´;16´,7´;16´´,12´-triphenyleno-[2,3-d;6,7-d´;10,11-d´]-tris[1,3]dioxole]-19,19´,19´´-nor-4,4´,4´´-tri-N-p-toluenesulfonamide (all-syn-3)

To a solution of all-syn-2a [1] (153 mg, 0.13 mmol) in pyridine (10 mL), para-toluenesulfonyl chloride (3.21 g, 16.8 mmol) was added at 25 °C. The reaction mixture was left to stand for seven days. After that, the solution was poured on ice
and left to stand for 45 minutes. 10% citric acid (10 mL) was added, the resulting orange precipitate was filtered off and washed with cold water (5 mL). The aqueous layer was extracted with dichloromethane (20 mL) and the organic fractions were washed with water (2 x 20 mL) and brine (20 mL), dried (Na$_2$SO$_4$) and concentrated under reduced pressure. The crude product was purified by column chromatography on silica (cyclohexane/ethyl acetate 9:1 to 75:25).

Yield: 68 mg (0.043 mmol, 32%) of a pale brown solid. $R_f$ (CH:EE = 75:25): 0.39; Mp: decomposition >310 °C; $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ [ppm] = 0.80 – 0.83 (m, 3H), 0.85 (s, 9H, H-20), 0.87 – 0.94 (m, 8H), 1.08 (s, 9H, H-17), 1.11 – 1.16 (m, 3H), 1.20 (s, 9H, H-18), 1.23 – 1.28 (m, 11H), 1.31 – 1.34 (m, 5H), 1.49 (dt, $J = 4.0$ Hz, 13.3 Hz, 3H), 1.63 – 1.66 (m, 9H), 1.70 – 1.72 (m, 3H), 1.79 (d, $J = 11.9$ Hz, 3H), 1.90 (d, $J = 10.2$ H, 3H), 2.01 (d, $J = 15.4$ Hz, 3H), 2.36 (d, $^2$J$_{15\alpha,15\beta}$ = 13.9 Hz, 3H, H-15$_\alpha$), 2.42 (s, 9H, H-25), 2.70 (d, $^2$J$_{3ax,3eq}$ = 15.1 Hz, 3H, H-3$_{eq}$), 4.30 (s, 3H, 19-$N$H), 7.27 (d, $^3$J$_{22,23}$ = 8.8 Hz, 6H, H-23), 7.65, 7.68 (every s, every 3H, H-4', H-15'), 7.75 (d, $^3$J$_{22,23}$ = 8.3 Hz, 6H, H-22); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ [ppm] = 14.8 (C20), 17.1 (C2), 19.1 (C11), 19.4 (C17), 19.6 (C6), 21.5 (C25), 28.9 (C18), 34.8 (C12), 37.1 (C3), 37.5 (C10), 38.7 (C1), 40.6 (C7), 40.7 (C13), 46.8 (C8), 48.0 (C15), 54.2 (C14), 55.7, 56.9 (C5, C9), 58.7 (C4), 99.9, 100.0 (C4', C15'), 124.1, 124.5 (C4a', C14b'), 126.9 (C22), 127.8 (C16), 129.5 (C23), 140.5 (C24), 142.8 (C21), 147.4, 148.4 (C3a', C15a'); MS (ESI pos. mode): m/z =1623.8 [M+Na]$^+$; HRMS (ESI, pos. mode): m/z for C$_{96}$H$_{117}$NaN$_3$O$_{12}$S$_3$ [M+Na]$^+$ calc.: 1622.7692, found: 1622.7686; elem. anal.

C$_{96}$H$_{117}$NaN$_3$O$_{12}$S$_3$ (1601.16): calc. C 72.01 H 7.37 N 2.62 S 6.01, found: C 69.78 H 8.63 N 2.41 S 6.12; optical rotation [\alpha]$_D^{20}$ = +55.9° (c 1.00, CHCl$_3$).
Deviations in the elemental analysis are probably caused by solvent molecules within the cavities of the molecules. The measurement of the optical rotation was therefore carried out to determine the orientation thereof.

Methyl (+)-ent-beyeran-19-oate-[15,16-b]quinoxaline (6)

To a suspension of (+)-ent-15,16-dioxobeyeran-19-oic acid methyl ester 5b [3] (100 mg, 0.29 mmol) in glacious acetic acid (10 mL), o-phenylenediamine (31 mg, 0.29 mmol) was added. The reaction mixture was refluxed for 4 hours. After bringing to room temperature, the mixture was fractionated between aqueous NaHCO₃ (50 mL) and tert-butyl methyl ether (TBME, 50 mL). The aqueous layer was extracted with TBME (2 x 20 mL), the combined organic fractions were washed with water (5 x 50 mL) and brine (50 mL), dried (MgSO₄), and concentrated under reduced pressure. The crude product was purified by column chromatography on silica (Büchi chromatography system, cyclohexane/ethyl acetate 98:2).

Yield: 50 mg (0.12 mmol, 41%) of a colorless solid. Rᵣ (SiO₂, cyclohexane/ethyl acetate, 9:1) = 0.37; Mp. = 155 °C (ethyl acetate); ¹H-NMR (300 MHz, CDCl₃) δ [ppm] = 0.52 (s, 3H, H-20), 0.61 – 0.77 (m, 1H), 0.92 (dt, ²J₁ax,1eq = 3 J₁ax,2ax = 13.1 Hz,³J₁ax,2eq = 4.1 Hz, 1H, H-1ₐx), 1.05 (dt, ²J₃ax,3eq = ³J₂ax,3ax = 13.4 Hz,³J₂eq,3ax = 4.1 Hz, 1H, H-3ₐx), 1.23 – 1.28 (m, 1H), 1.26 (s, 3H; H-17), 1.35 – 1.43 (m, 1H), 1.41 (s, 3H, H-18), 1.45 – 1.91 (m, 9H), 2.01 – 2.08 (m, 1H), 2.18 – 2.25 (m, 2H), 2.79 (dq,
$^3J_{6ax,7eq} = 3.4$ Hz, $^2J_{6ax,6eq} = J_{6ax,5} = 13.7$ Hz, (1H, H-6ax), 3.72 (s, 3H, H-21),
7.60 – 7.66 (m, 2H, H-6', H-7'), 8.00 – 8.06 (m, 2H, H-5', H-8'); $^{13}$C-NMR (75 MHz,
CDCl$_3$) $\delta$ [ppm] = 11.7 (C20), 19.0 (C2), 21.2 (C6), 21.7 (C11), 22.1 (C17), 29.1
(C18), 36.7 (CH$_2$), 37.9 (CH$_2$), 38.4 (CH$_2$), 38.9 (C10), 40.5 (CH$_2$), 43.1, 44.1, 46.1
(C4, C8, C13), 51.3 (C21), 56.2, 57.1 (C5, C9), 58.8 (C14), 128.3, 128.6, 128.8,
129.6 (C5' – C8'), 141.4, 141.9 (C4a', C8a'), 165.7, 166.1 (C15, C16), 178.2 (C19);
MS (ESI, pos. mode): m/z = 441.24 [M+Na]$^+$; 859.5 [2M+Na]$^+$; HRMS (ESI, pos.
mode): m/z for C$_{27}$H$_{34}$N$_2$NaO$_2$ [M+Na]$^+$ calc.: 441.2518, found 441.2518; elem. anal.
C$_{27}$H$_{34}$N$_2$O$_2$ (418.57): calc. C 77.4 H 8.19 N 6.69, found C 77.80 H 8.56 N 6.67;
optical rotation $[\alpha]_D^{20} = +104.9^\circ$ (c 1.00, CHCl$_3$).

Methyl (+)-ent-beyeran-19-oate-[15,16-b]-6´,7´-dimethylquinoxaline (7)

To a suspension of (+)-ent-15,16-dioxobeyeran-19-oic acid methyl ester 5b [3] (500
mg, 1.45 mmol) in glacious acetic acid (50 mL), 4,5-dimethyl-1,2-phenylenediamine
(195 mg, 1.45 mmol) was added. The reaction mixture was refluxed for 4 hours. After
bringing to room temperature, the mixture was fractionated between aqueous
NaHCO$_3$ (100 mL) and ethyl acetate (50 mL). The aqueous layer was extracted with
EtOAc (2 x 50 mL), the combined organic fractions were washed with water (5 x 50
mL) and brine (50 mL), dried (MgSO$_4$), and concentrated under reduced pressure.
The crude product was purified by column chromatography on silica (Büchi chromatography system, cyclohexane/ethyl acetate 99:1).

Yield: 373 mg (0.87 mmol, 60%) of a colorless foam. $R_f$ (SiO$_2$, cyclohexane/ethyl acetate, 4:1) = 0.63; $^1$H-NMR (400 MHz, CDCl$_3$) δ [ppm] = 0.51 (s, 3H, H-20), 0.62 – 0.71 (m, 1H), 0.92 (dt, $^2$J$_{1ax,1eq} = ^3$J$_{1ax,2ax} = 13.3$ Hz, $^3$J$_{1ax,2eq} = 4.2$ Hz, 1H, H-1$_{ax}$), 1.05 (dt, $^2$J$_{3ax,3eq} = ^3$J$_{3ax,2ax} = 13.5$ Hz, $^3$J$_{3ax,2eq} = 4.1$ Hz, 1H, H-3$_{ax}$), 1.23 – 1.27 (m, 1H), 1.26 (s, 3H; H-17), 1.37 – 1.42 (m, 1H), 1.41 (s, 3H, H-18), 1.43 – 1.54 (m, 2H), 1.61 – 1.88 (m, 7H), 2.02 – 2.06 (m, 1H), 2.17 – 2.23 (m, 2H), 2.45, 2.46 (every s, every 3H, H-9', H-10'), 2.77 (dq, $^3$J$_{6ax,7eq} = 3.5$ Hz, $^2$J$_{6ax,6eq} = ^3$J$_{6ax,7ax} = ^3$J$_{6ax,5} =$13.7 Hz, 1H, H-6$_{ax}$), 3.72 (s, 3H, H-21), 7.78, 7.83 (every s, every 1H, H-5', H-8'); $^{13}$C-NMR (100 MHz, CDCl$_3$) δ [ppm] = 11.8 (C20), 19.0 (CH$_2$), 20.06, 20.11 (C9', C10'), 21.2 (CH$_2$), 21.7 (CH$_2$), 22.2 (C17), 28.9 (C18), 36.5 (CH$_2$), 37.6 (CH$_2$), 38.2 (CH$_2$), 38.6 (C), 40.3 (CH$_2$), 42.7 (C), 43.9 (C), 45.7 (C), 51.2 (C21), 55.9, 56.9 (C5, C9), 58.7 (C14), 128.7 (C5', C8'), 138.1, 138.4 (C4a', C8a'), 140.4 (C6', C7'), 164.2, 164.8 (C15, C16), 178.1 (C19); MS (ESI, pos. mode): m/z = 447.32 [M+H]$^+$; HRMS (ESI, pos. mode): m/z for C$_{29}$H$_{39}$N$_2$O$_2$[M+H]$^+$ calc.:447.3012, found 447.3003; elem. anal. C$_{29}$H$_{38}$N$_2$O$_2$ (446.62): calc. C 77.99 H 8.58 N 6.27, found C 77.90 H 9.06 N 6.16; optical rotation [α]$_D^{20}$ = +140.0° (c 1.00, CHCl$_3$).

Hexaammoniumtriptycene hexachloride 4 [4] (54 mg, 0.07 mmol), (+)-ent-15,16- dioxobeyeran-19-oic acid methyl ester 5b [3] (225 mg, 0.65 mmol), sodium acetate (71 mg, 0.87 mmol) and THF (2 mL) were placed in a sealed tube and heated to 100 °C for 16 h. After cooling to room temperature, the reaction mixture was fractionated between H₂O (50 mL) and CH₂Cl₂ (50 mL). The aqueous layer was extracted with CH₂Cl₂ (20 mL). The combined organic fractions were washed with H₂O (2 x 50 mL) and brine (50 mL), dried (Na₂SO₄), and concentrated under reduced pressure. The crude product was purified by column chromatography on silica (CH₂Cl₂/MeOH, 99.5:0.5 to 99:1).

Combined yield: 55 mg (0.042 mmol, 59% [all-syn + anti,anti,syn]) of an orange glassy solid.

Chromatographic separation of isomers:  

anti,anti,syn 23 mg (25%)  
all-syn 3 mg (3%)

The remaining 31% were reisolated as isomeric mixture after column chromatography.
all-syn:

$R_f$ (SiO$_2$, dichloromethane/methanol, 98:2) = 0.21; $^1$H-NMR (600 MHz, CDCl$_3$) $\delta$

[ppm] = 0.42 (s, 9H, H-20), 0.52 – 0.59 (m, 3H), 0.85 – 0.90 (m, 5H), 1.03 (dt, $^2J_{3ax,3eq}$

$= \frac{3}{2}J_{3ax,2ax} = 13.5$ Hz, $^3J_{3ax,2eq} = 4.1$ Hz, 3H, H-3$_{ax}$), 1.22 (d, $J = 12.5$ Hz, 3H), 1.26 (s, 9H, H-17), 1.38 (s, 9H, H-18), 1.41 – 1.49 (m, 7H), 1.56 (d, $J = 12.6$ Hz, 3H), 1.60 – 1.63 (m, 6H), 1.68 – 1.77 (m, 9H), 1.83 – 1.84 (m, 3H), 2.00 (d, $J = 12.6$ Hz, 3H),

2.10 (d, $J = 13.2$ Hz, 3H), 2.18 (d, $J = 13.9$ Hz, 3H), 2.73 (dq, $^3J_{6ax,7eq} = 3.5$ Hz,

$^2J_{6ax,6eq} = ^3J_{6ax,5} = 13.6$ Hz, 3H, H-6$_{ax}$), 3.76 (s, 9H, H-21), 5.96, 5.99 (every s, every 1H, H-9*, H-10*), 8.11 – 8.19 (m, 6H, H-ar*); $^{13}$C-NMR (150 MHz, CDCl$_3$) $\delta$

[ppm] = 11.6 (C20), 19.0 (C2), 21.1 (C6), 21.6 (C11), 22.1 (C17), 28.9 (C18), 29.7 (CH$_2$), 31.9 (C), 36.4 (CH$_2$), 37.4 (CH$_2$), 38.2 (CH$_2$), 38.6 (C), 40.2 (CH$_2$), 42.8 (C), 43.9 (C), 45.8 (C), 51.2 (C21), 52.9, 53.1, 55.8, 56.8 (C5, C9, C9*, C10*), 58.7 (C14),

123.3, 123.9 (C1*, C4*, C5*, C8*, C13*, C16*), 140.5 (C*), 143.0 (C*), 143.2 (C*),

165.0, 165.7 (C15, C16), 178.1 (C19); MS (MALDI-TOF, pos. mode): m/z = 1275.47

[M+H]$^+$; HRMS (ESI, pos. mode): m/z for C$_{83}$H$_{99}$N$_6$O$_6$ [M+H]$^+$ calc. 1275.7626, found 1275.7592; elem. anal. C$_{83}$H$_{99}$N$_6$O$_6$ (1275.70): calc. C 78.14 H 7.74 N 6.59, found C 75.42 H 8.33 N 5.48; optical rotation $[\alpha]_D^{20} = +64.7^\circ$ (c 1.00, CHCl$_3$).

Deviations in the elemental analysis are probably caused by solvent molecules within the cavities of the molecules. The measurement of the optical rotation was therefore carried out to determine the orientation thereof.

anti,anti,syn

$R_f$ (SiO$_2$, dichloromethane/methanol, 98:2) = 0.25; $^1$H-NMR (600 MHz, CDCl$_3$) $\delta$

[ppm] = 0.40, 0.41 (every s, 9H, H-20), 0.47 – 0.55 (m, 3H), 0.85 – 1.05 (m, 9H), 1.18 – 1.22 (m, 5H), 1.25 (s, 9H; H-17), 1.34 – 1.37 (m, 12H), 1.40 – 1.49 (m, 6H), 1.53 – 1.63 (m, 9H), 1.65 – 1.73 (m, 6H), 1.79 – 1.80 (m, 5H), 1.98 – 2.19 (m, 9H), 2.68 –
2.77 (m, 3H, H-6ax), 3.74, 3.75, 3.77 (every s, 9H, H-21), 5.94, 5.96 (every s, every 1H, H-9*, H-10*), 8.04 – 8.17 (m, 6H, H-ar*); $^{13}$C-NMR (150 MHz, CDCl$_3$) $\delta$ [ppm] = 11.6, 11.7 (C20), 18.9 (CH$_2$), 19.0 (CH$_2$), 21.02 (CH$_2$), 21.05 (CH$_2$), 21.07 (CH$_2$), 21.54 (CH$_2$), 21.60 (CH$_2$), 21.62 (CH$_2$), 22.1 (C17), 28.87, 28.89 (C18), 36.35 (CH$_2$), 36.42 (CH$_2$), 37.39 (CH$_2$), 37.47 (CH$_2$), 37.49 (CH$_2$), 38.1 (CH$_2$), 38.5 (C), 40.2 (CH$_2$), 42.71 (C), 42.75 (C), 42.76 (C), 43.8 (C), 45.72 (C), 45.74 (C), 45.76 (C), 51.18, 51.20, 51.21 (C21), 52.9, 53.0, 55.7, 55.8, 56.80, 56.83 (C5, C9, C9*, C10*), 58.64, 58.66, 58.72 (C14), 123.2, 123.3, 123.8, 123.96, 124.0 (C1*, C4*, C5*, C8*, C13*, C16*), 140.2 (C*), 140.46 (C*), 140.48 (C*), 140.55 (C*), 142.8 (C*), 142.9 (C*), 143.0 (C*), 143.1 (C*), 143.3 (C*), 165.1, 165.4, 165.5, 165.6 (C15, C16), 178.00, 178.01 (C19); MS (MALDI-TOF, pos. mode): m/z = 1275.47 [M+H]$^+$; HRMS (ESI, pos. mode): m/z for C$_{83}$H$_{99}$N$_6$O$_6$ [M+H]$^+$ calc. 1275.7626, found 1275.7592; elem. anal. C$_{83}$H$_{99}$N$_6$O$_6$ (1275.70): calc. C 78.14 H 7.74 N 6.59, found C 75.49 H 9.27 N 5.69; optical rotation $[\alpha]_{D}^{20}$ = +87.2° (c 1.00, CHCl$_3$).

General remarks for the anti,anti,syn-isomers:

Due to isochronic effects caused by pseudo-symmetries within the anti,anti,syn-isomers, the number of signals in the corresponding $^{13}$C NMR spectra does not necessarily correlate with the number of C-atoms in the molecules. Deviations in the elemental analysis are probably caused by solvent molecules within the cavities of the molecules. The measurement of the optical rotation was therefore carried out to determine the orientation thereof.
3,5-Dinitrobenzyl-(−)-ent-16-oxobeyeran-19-oate (12)

To a solution of (−)-isosteviol 1 (3.09 g, 9.7 mmol) in DMF (20 mL), triethylamine (2.3 mL, 17.1 mmol) and 3,5-dinitrobenzyl chloride (2.1 g, 9.7 mmol) were added at 25 °C. The solution was stirred at 25 °C for 16 h. After fractionation between 0.5 M HCl (50 mL) and EtOAc (150 mL), the aqueous layer was extracted with EtOAc (2 x 100 mL). The combined organic fractions were washed with aqueous NaHCO₃ (100 mL), H₂O (2 x 100 mL) and brine (100 mL), dried (MgSO₄), and concentrated under reduced pressure. The crude product was purified by column chromatography on silica (Büchi chromatography system, cyclohexane/ethyl acetate 99:1 to 96:4).

Yield: 2.94 g (5.9 mmol, 61%) of a colorless solid. Rᵣ (SiO₂, cyclohexane/ethyl acetate, 4:1) = 0.38; Mp. 132 °C (ethyl acetate); ¹H NMR (300 MHz, CDCl₃) δ [ppm] = 0.66 (s, 3H, H-20), 0.84 – 0.94 (m, 1H, H-1ₐₓ), 0.96 (s, 3H, H-17), 1.05 – 1.15 (m, 1H, H-3ₐₓ), 1.16 – 1.23 (m, 3H, H-5, H-9, H-11ₐₓ), 1.26 (s, 3H, H-18), 1.33 – 1.40 (m, 1H, H-12ₐₓ), 1.42 – 1.50 (m, 2H, H-2ₑ𝑞, H-14ₐₓ), 1.53 – 1.58 (m, 2H, H-7ₐₓ, H-1₄ₑ𝑞), 1.61 – 1.83 (m, 7H, H-1ₑ𝑞, H-2ₐₓ, H-6ₐₓ, H-7ₑ𝑞, H-11ₑ𝑞, H-1₂ₑ𝑞, H-1₅₂), 1.94 – 1.98 (m, 1H, H-6ₑ𝑞), 2.22 (d, 2J₃ₑ𝑞,₃ₐₓ = 13.3 Hz, 1H, H-3ₑ𝑞), 2.56 (dd, 2J₁₅₂,₁₅₃ = 18.7 Hz, 4J₁₅₂,₁₄ = 3.8 Hz, 1H, H-1₅₂), 5.19 – 5.36 (m, 2H, H-2₁), 8.55 (d, 4J₂₃,₂₅ = 2.1 Hz, 2H, H-2₃), 9.00 (dd, 4J₂₃,₂₅ = 2.1 Hz, 1H, H-2₅); ¹³C NMR (75 MHz, CDCl₃) δ [ppm] = 13.5 (C20), 18.8 (C2), 19.8 (C17), 20.3 (C11), 21.9 (C6), 28.9 (C18), 37.2 (C12), 37.8 (C3), 38.0 (C10), 39.4 (C13), 39.5 (C1), 41.3 (C7), 44.0 (C4), 48.3 (C15), 48.6 (C8), 54.1 (C14), S11
54.6, 57.0 (C5, C9), 63.6 (C21), 118.3 (C25), 127.5 (C23), 140.8 (C22), 148.6 (C24), 176.7 (C19), 219.5 (C16); MS (ESI, pos. mode): m/z = 499.28 [M+H]+; HRMS (ESI, pos. mode): m/z for C$_{27}$H$_{35}$N$_{2}$O$_{7}$ [M+H]$^+$ calc. 499.2444, found 499.2436; elem. anal. C$_{27}$H$_{34}$N$_{2}$O$_{7}$ (498.57): calc. C 65.04 H 6.87 N 5.62, found C 65.08 H 6.98 N 5.46; optical rotation [α]$_{D}^{20}$ = −45.5° (c 1.00, CHCl$_{3}$).

3,5-Dinitrobenzyl-(-)-ent-15,16-dioxobeyeran-19-oate (10)

![Chemical structure](image)

**Procedure A**

To a solution of (-)-ent-15,16-dioxobeyeran-19-oic acid (9, 100 mg, 0.3 mmol) in DMF (3 mL), triethylamine (0.07 mL, 0.52 mmol) and 3,5-dinitrobenzyl chloride (65 mg, 0.3 mmol) were added at 25 °C. The solution was stirred at 25 °C for 16 h. After fractionation between 0.5 M HCl (10 mL) and EtOAc (20 mL), the aqueous layer was extracted with EtOAc (2 x 10 mL). The combined organic fractions were washed with aqueous NaHCO$_{3}$ (10 mL), H$_{2}$O (2 x 50 mL) and brine (50 mL), dried (MgSO$_{4}$), and concentrated under reduced pressure. The crude product was purified by column chromatography on silica (Büchi chromatography system, cyclohexane/ethyl acetate 98:2 to 94:6) to give an orange foam (85 mg, 57%).

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Procedure B

To a solution of 3,5-dinitrobenzyl-(-)-ent-16-oxobeyeran-19-oate 12 (2.9 g, 5.81 mmol) in p-xylene (100 mL), SeO₂ (0.95 g, 11.6 mmol) was added at 25 °C. The reaction mixture was heated to reflux for 2 d. After cooling to room temperature, the crude product was filtered by the aid of Celite™ and rinsed with dichloromethane (100 mL). The solvent was removed under reduced pressure and the product was purified by column chromatography on silica (Büchi chromatography system, cyclohexane/ethyl acetate 1:0 to 92:8).

Yield: 2.31 g (4.51 mmol, 78%) of an orange foam. R₁ (SiO₂, cyclohexane/ethyl acetate, 4:1) = 0.32; ¹H NMR (300 MHz, CDCl₃) δ [ppm] = 0.47 (s, 3H, H-20), 0.84 – 1.10 (m, 3H), 1.12 (s, 3H, H-17), 1.18 – 1.26 (m, 3H), 1.29 (s, 3H, H-18), 1.44 – 1.55 (m, 2H), 1.58 – 1.65 (m, 2H), 1.73 – 1.82 (m, 3H), 1.90 – 2.03 (m, 3H), 2.19 – 2.38 (m, 2H, H-3eq, H-6eq), 5.26 – 5.37 (m, 2H, H-21), 8.60 (d, ⁴J₂₃,₂₅ = 2.1 Hz, 2H, H-23), 9.02 (dd, ⁴J₂₃,₂₅ = 2.1 Hz, 1H, H-25); ¹³C NMR (75 MHz, CDCl₃) δ [ppm] = 11.5 (C20), 18.8 (C2), 20.1 (C17), 21.1 (C11), 21.4 (C6), 28.7 (C18), 33.9 (C7), 37.9 (C3), 38.8 (C10), 39.6, 39.7 (C1, C12), 44.0 (C4), 46.9 (C13), 47.1 (C14), 50.4 (C8), 56.1, 59.3 (C5, C9), 63.7 (C21), 118.8 (C25), 127.8 (C23), 140.6 (C22), 148.6 (C24), 176.5 (C19), 208.6, 210.1 (C15, C16); MS (ESI, pos. mode): m/z = 535.2 [M+Na]⁺; HRMS (ESI, pos. mode): m/z for C₂₇H₃₂NaN₂O₈ [M+Na]⁺ calc. 535.2056, found 535.2080; elem. anal. C₂₇H₃₂NaN₂O₈ (512.55): calc. C 63.27 H 6.29 N 5.47, found C 63.37 H 7.07 N 5.20; optical rotation [α]₀²⁰ = –2.7° (c 1.00, CHCl₃).
To a solution of (–)-isosteviol 1 (9.1 g, 28.2 mmol) in DMF (100 mL), cesium carbonate (13.8 g, 42.3 mmol) and 4-nitrobenzyl chloride (9.68 g, 56.4 mmol) were added at 25 °C under argon atmosphere. The solution was stirred at 25 °C for 5 h. After fractionation between H₂O (150 mL) and EtOAc (150 mL), the aqueous layer was extracted with EtOAc (2 x 150 mL). The combined organic fractions were washed with H₂O (2 x 150 mL) and brine (100 mL), dried (MgSO₄), and concentrated under reduced pressure. The crude product was purified by column chromatography on silica (cyclohexane/ethyl acetate 95:5 to 9:1).

Yield: 9.98 g (22 mmol, 77%) of a colorless solid. Rf (SiO₂, cyclohexane/ethyl acetate, 4:1) = 0.44; Mp. 118 °C (ethyl acetate); ¹H NMR (300 MHz, CDCl₃) δ [ppm] = 0.61 (s, 3H, H-20), 0.84 – 0.91 (m, 1H, H-1ₐₓ), 0.92 (s, 3H, H-1ₗ), 1.03 (dt, ²J₃ₐₓ,₃ₑₒₚ = ³J₃ₐₓ,₂ₐₓ = 13.3 Hz, ³J₃ₐₓ,₂ₑₒₚ = 4.1 Hz, 1H, H-3ₐₓ), 1.12 – 1.17 (m, 3H, H-5, H-9, H-1₁ₐₓ), 1.20 (s, 3H, H-1ₜₘ), 1.29 – 1.45 (m, 4H), 1.47 – 1.49 (m, 1H), 1.52 – 1.54 (m, 1H), 1.65 – 1.68 (m, 4H), 1.71 – 1.79 (m, 2H), 1.88 (d, J = 14.1 Hz, 1H, H-6ₑₒₚ), 2.17 (d, ²J₃ₐₓ,₃ₑₒₚ = 13.3 Hz, 1H, H-3ₑₒₚ), 2.52 (dd, ²J₁₅α,₁₅β = 18.6 Hz, ⁴J₁₅α,₁₄ = 3.7 Hz, 1H, H-1₅ₐ), 5.06 (d, ²J₂₁,₂₁ = 9.9 Hz, 1H, H-2₁), 5.21 (d, ²J₂₁,₂₁ = 9.9 Hz, 1H, H-2₁), 7.49 (d, ³J₂₃,₂₄ = 8.6 Hz, 2H, H-2₃), 8.18 (d, ³J₂₃,₂₄ = 8.7 Hz, 2H, H-2₄); ¹³C NMR (75 MHz, CDCl₃) δ [ppm] = 13.3 (C20), 18.8 (C2), 19.7 (C17), 20.2 (C11), 21.6 (C6), 28.8 (C18), 37.1 (C12), 37.7 (C3), 37.9 (C10), 39.3 (C13), 39.5 (C1), 41.2 (C7), 43.8 (C4), 44.1 (C4), 49.7 (C12), 50.4 (C13), 50.5 (C14), 51.3 (C15), 53.4 (C16), 67.1 (C19), 70.6 (C21), 71.7 (C21), 104.6 (C23), 110.4 (C24), 122.6 (C25), 126.2 (C26), 131.9 (C27), 139.3 (C28), 143.8 (C29), 157.0 (C30).
48.2 (C15), 48.5 (C8), 54.1 (C14), 54.4, 56.9 (C5, C9), 64.5 (C21), 123.7 (C24), 128.4 (C23), 143.2 (C22), 147.5 (C25), 176.6 (C19), 219.3 (C16); MS (ESI, pos. mode): m/z = 476.27 [M+Na]+; HRMS (ESI, pos. mode): m/z for C_{27}H_{35}NaNO_{5} [M+Na]^+ calc. 476.2413, found 476.2414; elem. anal. C_{27}H_{35}NO_{5} (453.57): calc. C 71.50 H 7.78 N 3.09, found C 71.10 H 7.95 N 3.16; optical rotation [α]_{D}^{20} = +36.3° (c 1.00, CHCl_{3}).

4-Nitrobenzyl-(−)-ent-15,16-dioxobeyeran-19-oate (11)

**Procedure A**

To a solution of (−)-ent-15,16-dioxobeyeran-19-oic acid (9, 911 mg, 2.73 mmol) in DMF (50 mL), cesium carbonate (1.34 g, 4.1 mmol) and 4-nitrobenzyl chloride (937 mg, 5.46 mmol) were added at 25 °C under argon atmosphere. The solution was stirred at 25 °C for 5 h. After fractionation between H_{2}O (100 mL) and EtOAc (150 mL), the aqueous layer was extracted with EtOAc (2 x 150 mL). The combined organic fractions were washed with H_{2}O (2 x 50 mL) and brine (50 mL), dried (MgSO_{4}), and concentrated under reduced pressure. The crude product was purified by column chromatography on silica (Büchi chromatography system, cyclohexane/ethyl acetate 98:2 to 96:4) to give an orange foam (863 mg, 68%).
Procedure B

To a solution of 4-nitrobenzyl-\textit{(+)-ent}\textendash\textit{16-oxobeyeran-19-oate} (13, 8.97 g, 19.8 mmol) in \textit{p}-xylene (150 mL), SeO$_2$ (3.24 g, 39.6 mmol) was added at 25 °C. The reaction mixture was heated to reflux for 2 d. After cooling to room temperature, the crude product was filtered by the aid of Celite$^{\text{TM}}$ and rinsed with dichloromethane (150 mL). The solvent was removed under reduced pressure and the product was purified by column chromatography on silica (Büchi chromatography system, cyclohexane/ethyl acetate 98:2 to 94:6).

Yield: 6.86 g (14.7 mmol, 74%) of an orange foam. \(R_l\) (SiO$_2$, cyclohexane/ethyl acetate, 4:1) = 0.33; $^1$H NMR (300 MHz, CDCl$_3$) \(\delta\) [ppm] = 0.53 (s, 3H, H-20), 0.90 (dt, $^2$J$_{1ax,1eq} = 3$J$_{1ax,2ax} = 13.2$ Hz, $^3$J$_{1ax,2eq} = 4.1$ Hz, 1H, H-1$ax$), 1.05 (dt, $^2$J$_{3ax,3eq} = 3$J$_{3ax,2ax} = 13.5$ Hz, $^3$J$_{3ax,2eq} = 4.1$ Hz, 1H, H-3$ax$), 1.13 (s, 3H, H-17), 1.19 – 1.23 (m, 2H, H-5, H-7$ax$), 1.24 (s, 3H, H-18), 1.26 – 1.28 (m, 1H, H-11$ax$), 1.42 – 1.47 (m, 1H, H-2$eq$), 1.55 – 1.66 (m, 3H, H-9, H-14$ax$), 1.69 – 1.85 (m, 4H, H-2$ax$, H-11$eq$, H-12$ax$, H-14$eq$), 1.89 – 1.95 (m, 2H, H-6$ax$, H-7$eq$), 1.99 – 2.03 (m, 1H, H-12$eq$), 2.21 (d, $^2$J$_{3ax,3eq} = 13.5$ Hz, 1H, H-3$eq$), 2.30 – 2.41 (m, 1H, H-6$eq$), 5.12 – 5.21 (m, 2H, H-21), 7.59 (d, $^3$J$_{23,24} = 8.7$ Hz, 2H, H-23), 8.25 (d, $^3$J$_{23,24} = 8.7$ Hz, H-24); $^{13}$C NMR (75 MHz, CDCl$_3$) \(\delta\) [ppm] = 11.7 (C20), 18.8 (C2), 20.1 (C17), 20.9 (C11), 21.4 (C6), 28.7 (C18), 34.0 (C7), 38.0 (C3), 38.9 (C10), 39.7 (C1, C12), 43.9 (C4), 46.9 (C13), 47.2 (C14), 50.5 (C8), 56.2, 59.3 (C5, C9), 65.0 (C21), 123.8 (C24), 128.9 (C23), 143.1 (C22), 147.7 (C25), 176.7 (C19), 208.8, 210.2 (C15, C16); MS (ESI, pos. mode): m/z = 957.51 [2M+Na]$^+$; HRMS (ESI, pos. mode): m/z for C$_{27}$H$_{33}$NaNO$_6$ [M+Na]$^+$ calc. 490.2206, found 490.2190; elem. anal. C$_{27}$H$_{34}$NO$_6$ (467.55): calc. C 69.36 H 7.11 N 3.00, found C 68.77 H 7.25 N 3.11; optical rotation [\(\alpha\)]$_D^{20}$ = $-12.5^\circ$ (c 1.00, CHCl$_3$).


Hexaammoniumtriptycene hexachloride 4 [4] (344 mg, 0.42 mmol), 3,5-dinitrobenzyl-(-)-ent-15,16-dioxobeyeran-19-oate (10, 1.93 g, 3.76 mmol), sodium acetate (411 mg, 5.04 mmol) and THF (15 mL) were placed in a sealed tube and heated to 100 °C for 16 h. After cooling to room temperature, the reaction mixture was fractionated between H₂O (150 mL) and CH₂Cl₂ (150 mL). The aqueous layer was extracted with CH₂Cl₂ (100 mL). The combined organic fractions were washed with H₂O (3 x 50 mL) and brine (50 mL), dried (Na₂SO₄), and concentrated under reduced pressure. The crude product was purified by column chromatography on silica (A: Büchi chromatography system, cyclohexane/ethyl acetate 95:5 to 4:1 [removal of excess starting material]; B: CH₂Cl₂/MeOH, 99.5:0.5 [separation of isomers]). Combined yield: 642 mg (0.36 mmol, 86% % [all-syn + anti,anti,syn]) of an orange glassy solid.

Chromatographic separation of isomers: 

- anti,anti,syn 361 mg (48%)
- all-syn 117 mg (17%)
The remaining 21% were reisolated as isomeric mixture after column chromatography.

**all-syn**

\[ R_f (\text{SiO}_2, \text{dichloromethane/methanol, 98:2}) = 0.22; \]  
\[ ^1H \text{ NMR (400 MHz, CDCl}_3 \]  
\[ \delta \text{ [ppm]} = 0.41 (s, 9H, H-20), 0.48 - 0.54 (m, 3H), 0.84 - 0.91 (m, 3H), 1.05 - 1.13 (m, 3H), 1.23 - 1.30 (m, 5H), 1.32, 1.34 (every s, every 9H, H-17, H-18), 1.36 - 1.48 (m, 9H), 1.52 - 1.60 (m, 9H), 1.65 - 1.76 (m, 10H), 2.04 - 2.11 (m, 6H), 2.20 - 2.23 (m, 3H), 2.72 - 2.81 (m, 3H, H-6_{ax}), 5.30 (d, \text{ }^2J_{21,21'} = 13.7 \text{ Hz, 3H, H-21}), 5.60 (d, \text{ }^2J_{21,21'} = 13.7 \text{ Hz, 3H, H-21'}), 5.85, 5.88 \text{ (every s, every 1H, H-9*, H-10*)}, 7.80, 8.07 \text{ (every s, every 3H, H-ar*)}, 8.76 (d, \text{ }^4J_{23,25} = 2.0 \text{ Hz, 6H, H-23}), 8.98 (dd, \text{ }^4J_{23,25} = \text{ }^4J_{23,25} = 2.0 \text{ Hz, 3H, H-25}); \]  
\[ ^{13}C \text{ NMR (100 MHz, CDCl}_3 \]  
\[ \delta \text{ [ppm]} = 11.8 (C20), 18.8 (C2), 21.0 (C11), 21.8 (C6), 22.0 (C17), 28.7 (C18), 36.3 (CH2), 37.3 (CH2), 38.1 (CH2), 38.6 (C), 39.9 (CH2), 42.7 (C), 44.0 (C), 45.6 (C), 52.8, 53.0, 55.5, 56.7 (C5, C9, C9*, C10*), 58.5 (C14), 63.8 (C21), 118.2 (C25), 123.4, 123.6 (C1*, C4*, C5*, C8*, C13*, C16*), 128.1 (C23), 140.3, 140.4, 141.3, 142.9, 143.1 (C22, C*), 148.6 (C24), 165.1, 165.3 (C15, C16), 177.0 (C19); MS (MALDI-TOF, pos. mode): m/z = 1774.2 [M+H]^+  
\text{(Deviation from HRMS lies within the error margin of the instrument); HRMS (ESI, pos. mode): m/z for C}_{101}H_{105}N_{12}O_{18} [M+H]^+ \text{ calc. 1773.7670, found 1773.7678; elem. anal. C}_{101}H_{104}N_{12}O_{18} (1773.98): calc. C 68.38 H 5.91 N 9.47, found C 66.13 H 6.36 N 8.17; optical rotation } [\alpha]_D^{20} = +67.5^\circ (c 1.00, \text{CHCl}_3). \]

Deviations in the elemental analysis are probably caused by solvent molecules within the cavities of the molecules. The measurement of the optical rotation was therefore carried out to determine the orientation thereof.
anti, anti, syn

$R_t$ (SiO$_2$, dichloromethane/methanol, 98:2) = 0.32; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$

[ppm] = 0.40, 0.41 (every s, 9H, H-20), 0.45 – 0.55 (m, 3H), 0.83 – 0.94 (m, 3H), 1.07 – 1.15 (m, 3H), 1.24 – 1.31 (m, 5H), 1.33 – 1.38 (m, 16H), 1.41 – 1.52 (m, 9H), 1.58 – 1.63 (m, 9H), 1.69 – 1.73 (m, 6H), 1.76 – 1.81 (m, 6H), 2.03 – 2.15 (m, 6H), 2.18 – 2.24 (m, 3H), 2.67 – 2.84 (m, 3H, H-6$_{ax}$), 5.23 – 5.34 (m, 3H, H-21), 5.44 – 5.57 (m, 3H, H-21'), 5.91, 5.94 (every s, every 1H, H-9*, H-10*), 7.73 (s, 1H, H-ar*), 7.83 (s, 1H, H-ar*), 7.85 (s, 1H, H-ar*), 8.10 (s, 1H, H-ar*), 8.20 (s, 1H, H-ar*), 8.23 (s, 1H, H-ar*), 8.70, 8.71, 8.76 (every d, $^4J_{23,25} = 2.1$ Hz, 6H, H-23), 9.02, 9.09, 9.11 (every dd, $^4J_{23,25} = ^4J_{23',25} = 2.1$ Hz, 3H, H-25); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ [ppm] = 11.8, 11.9, 12.0 (C20), 18.8 (CH$_2$), 18.9 (CH$_2$), 21.05 (CH$_2$), 21.08 (CH$_2$), 21.8 (CH$_2$), 21.9 (CH$_2$), 22.1 (C17), 28.8, 28.9, 29.0 (C18), 36.2 (CH$_2$), 36.3 (CH$_2$), 37.36 (CH$_2$), 37.41 (CH$_2$), 38.0 (CH$_2$), 38.1 (CH$_2$), 38.63 (C), 38.65 (C), 38.66 (C), 40.0 (CH$_2$), 42.74 (C), 42.78 (C), 42.82 (C), 44.1 (C), 45.7 (C), 45.8 (C), 52.8, 52.9, 55.6, 55.7, 56.74, 56.78, 56.83 (C5, C9, C9*, C10*), 58.55, 58.62, 58.66 (C14), 63.8 (C21), 118.36, 118.37, 118.48 (C25), 123.4, 123.5, 123.6 (C1*, C4*, C5*, C8*, C13*, C16*), 127.9, 128.0, 128.3 (C23), 140.3, 140.40, 140.43, 140.5, 141.0; 141.1; 141.3; 142.9, 143.1, 143.3, 143.5 (C22, C*), 148.59, 148.67, 148.71 (C24), 165.0, 165.1, 165.2, 165.3, 165.5 (C15, C16), 176.88, 176.98, 177.02 (C21); MS (MALDI-TOF, pos. mode): m/z = 1774.2 [M+H]$^+$ (Deviation from HRMS lies within the error margin of the instrument); HRMS (ESI, pos. mode): m/z for C$_{101}$H$_{105}$N$_{12}$O$_{18}$ [M+H]$^+$ calc. 1773.7670, found 1773.7678; elem. anal. C$_{101}$H$_{104}$N$_{12}$O$_{18}$ (1773.98): calc. C 68.38 H 5.91 N 9.47, found C 67.80 H 6.00 N 9.17; optical rotation $[\alpha]_D^{20} = +106.9^\circ$ (c 1.00, CHCl$_3$).
Hexaammoniumtriptylene hexachloride 4 \([4]\) (1.34 g, 1.63 mmol), 4-nitrobenzyl-(−)-\(ent\)-15,16-dioxobeyeran-19-oate (11, 6.86 g, 14.7 mmol), sodium acetate (1.6 g, 19.6 mmol) and THF (10 mL) were placed in a sealed tube and heated to 100 °C for 16 h. After cooling to room temperature, the reaction mixture was fractionated between \(\text{H}_2\text{O}\) (150 mL) and \(\text{CH}_2\text{Cl}_2\) (150 mL). The aqueous layer was extracted with \(\text{CH}_2\text{Cl}_2\) (100 mL). The combined organic fractions were washed with \(\text{H}_2\text{O}\) (3 x 50 mL) and brine (50 mL), dried (\(\text{Na}_2\text{SO}_4\)), and concentrated under reduced pressure. The crude product was purified by column chromatography on silica (\(A\): Büchi chromatography system, cyclohexane/ethyl acetate 98:2 to 88:12 [removal of excess starting material]; \(B\): \(\text{CH}_2\text{Cl}_2/\text{MeOH}\), 99.5:0.5 [separation of isomers]).

Combined yield: 2.47 g (1.55 mmol, 95% [all\(-\text{syn} + \text{anti,anti,syn}\]) of an orange glassy solid.

Chromatographic separation of isomers: \(\text{anti,anti,syn}\) 861 mg (34%)

\(\text{all-syn}\) 303 mg (12%)
The remaining 49% were reisolated as isomeric mixture after column chromatography.

**all-syn**

\( R_f \) (SiO\(_2\), dichloromethane/methanol, 98:2) = 0.23; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \( \delta \) [ppm] = 0.45 (s, 9H, H-20), 0.49 – 0.58 (m, 3H), 0.90 (dt, \( ^2J_{1ax,1eq} = \ ^3J_{1ax,2ax} = 13.0 \) Hz, \( ^3J_{1ax,2eq} = 3.9 \) Hz, 3H, H-1ax), 1.08 (dt, \( ^2J_{3ax,3eq} = \ ^3J_{3ax,2ax} = 13.5 \) Hz, \( ^3J_{3ax,2eq} = 3.9 \) Hz, 3H, H-3ax), 1.27 – 1.29 (m, 3H), 1.31, 1.36 (every s, every 9H, H-17, H-18), 1.40 – 1.50 (m, 9H), 1.57 – 1.63 (m, 9H), 1.67 – 1.76 (m, 9H), 1.81 – 1.83 (m, 3H), 2.06 (dd, \( J = 2.8 \) Hz, 14.6 Hz, 3H), 2.13 (d, \( J = 13.2 \) Hz, 3H), 2.21 (d, \( ^2J_{3ax,3eq} = 13.5 \) Hz, 3H, H-3eq), 2.80 (dq, \( ^3J_{6ax,7eq} = 3.5 \) Hz, \( ^2J_{6ax,6eq} = \ ^3J_{6ax,7ax} = ^3J_{6ax,5} =13.5 \) Hz, 3H, H-6ax), 5.26 (d, \( ^2J_{21,21} = 13.9 \) Hz, 3H, H-21), 5.36 (d, \( ^2J_{21,21} = 13.8 \) Hz, 3H, H-21'), 5.80, 5.91 (every s, every 1H, H-9*, H-10*), 7.72 (d, \( ^3J_{23,24} = 8.7 \) Hz, 6H, H-23), 7.88, 8.13 (every s, every 3H, H-ar*), 8.30 (d, \( ^3J_{23,24} = 8.7 \) Hz, 6H, H-24); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \( \delta \) [ppm] = 11.9 (C20), 18.9 (C2), 21.1 (C11), 21.8 (C6), 22.1 (C17), 28.9 (C18), 36.3 (CH\(_2\)), 37.4 (CH\(_2\)), 38.2 (CH\(_2\)), 38.7 (C), 40.1 (CH\(_2\)), 42.8 (C), 44.0 (C), 45.9 (C), 52.9, 53.0 (C9*, C10*), 53.4 (CH\(_2\)), 55.8, 56.8 (C5, C9), 58.7 (C14), 65.0 (C21), 123.7 (CH*, C24), 128.6 (C23), 140.5, 142.9, 143.2, 144.0 (C22, C*), 147.5 (C25), 164.9, 165.6 (C15, C16), 177.2 (C19); MS (MALDI-TOF, pos. mode): m/z = 1638.97 [M]*; HRMS (ESI, pos. mode): m/z for C\(_{101}\)H\(_{108}\)N\(_9\)O\(_{12}\) [M+H]* calc. 1638.8117, found 1638.8156; elem. anal. C\(_{101}\)H\(_{107}\)N\(_9\)O\(_{12}\) (1638.98): calc. C 74.01 H 6.58, N 7.69, found C 73.38 H 7.68 N 7.27; optical rotation \( [\alpha]_D^{20} = +126.6^{\circ} \) (c 1.00, CHCl\(_3\)).
**anti,anti,syn**

\( R_t (\text{SiO}_2, \text{dichloromethane/methanol, 98:2}) = 0.33; \) \(^1\text{H} \text{NMR (600 MHz, CDCl}_3\) δ [ppm] = 0.35, 0.36, 0.44 (every s, every 3H, H-20), 0.50 – 0.60 (m, 3H), 0.82 – 0.92 (m, 5H), 1.04 – 1.10 (m, 3H), 1.24 – 1.29 (m, 5H), 1.30, 1.31, 1.32 (every s, every 3H, CH\(_3\)), 1.38 (s, 7H), 1.41 (s, 3H, CH\(_3\)_3), 1.44 – 1.50 (m, 5H), 1.55 – 1.64 (m, 10H), 1.67 – 1.73 (m, 5H), 1.79 – 1.83 (m, 5H), 2.06 – 2.23 (m, 9H), 2.78 – 2.85 (m, 3H, H-6\(_{ax}\)), 5.19 – 5.30 (m, 5 H, H-21), 5.41 – 5.43 (d, 1H, H-21), 5.84, 5.91 (every s, every 1H, H-9*, H-10*), 7.68 – 7.73 (m, 7H, H-ar), 7.87 (s, 1H, H-ar), 8.00 (s, 1H, H-ar), 8.16 (s, 1H, H-ar), 8.21 (s, 2H, H-ar), 8.28 – 8.31 (m, 4H, H-ar), 8.33 – 8.34 (d, 2H, H-ar); \(^{13}\text{C} \text{NMR (150 MHz, CDCl}_3\) δ [ppm] = 11.9, 12.0, 12.1 (C20), 18.86 (CH\(_2\)), 18.89 (CH\(_2\)), 18.91 (CH\(_2\)), 21.1 (CH\(_2\)), 21.7 (CH\(_2\)), 21.8 (CH\(_2\)), 22.1, 22.15, 22.18 (C17), 26.9 (CH\(_2\)), 28.81, 28.87, 28.93 (C18), 36.29 (CH\(_2\)), 36.33 (CH\(_2\)), 37.36 (CH\(_2\)), 37, 43 (CH\(_2\)), 38.18 (CH\(_2\)), 38.21 (CH\(_2\)), 38.66 (C), 38.67 (C), 40.1 (CH\(_2\)), 42.80 (C), 42.89 (C), 42.99 (C), 44.01 (C), 44.09 (C), 44.12 (C), 45.8 (C), 45.9 (C), 46.0 (C), 52.89, 52.92, 55.6, 55.7, 55.8, 56.76, 56.78, 56.80 (C5, C9, C9*, C10*), 58.6, 58.7 (C14), 64.9, 65.0, 65.1 (C21), 123.4 (CH), 123.6 (CH), 123.7 (CH), 123.76 (CH), 123.77 (CH), 123.8 (CH), 128.5, 128.68, 128.74 (C23), 140.54 (C), 140.56 (C), 142.6 (C), 142.9 (C), 143.6 (C), 143.7 (C), 144.1 (C), 147.49, 147.54, 147.6 (C25), 165.0, 165.5, 165.7, 165.8 (C15, C16), 177.1, 177.2, 177.3 (C19); MS (MALDI-TOF, pos. mode): m/z = 1638.97 [M]+; HRMS (ESI, pos. mode): m/z for C\(_{101}\)H\(_{108}\)N\(_9\)O\(_{12}\) [M+H]+ calc. 1638.8117, found 1638.8156; elem. anal. C\(_{101}\)H\(_{107}\)N\(_9\)O\(_{12}\) (1638.98): calc. C 74.01 H 6.58 N 7.69, found C 73.72 H 7.07 N 7.39; optical rotation [\(\alpha\)]\(_D\)\(^{20}\) = +137.5° (c 1.00, CHCl\(_3\)).

To a solution of all-syn-15 (283 mg, 0.17 mmol) in THF (10 mL), palladium on activated charcoal (10% Pd on charcoal, 50% H₂O, 30 mg) was added under an argon atmosphere. The argon atmosphere was replaced by hydrogen atmosphere and the mixture was stirred at 25 °C for 3 d. The catalyst was then filtered off by the aid of Celite™. The filter cake was rinsed with CH₂Cl₂ (50 mL) and the filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography on silica (Büchi chromatography system, cyclohexane/ethyl acetate 95:5 to 4:1).

Yield: 197 mg (0.16 mmol, 94%) of a colorless solid. R\text{f} (SiO₂, dichloromethane/methanol, 95:5) = 0.35; \textsuperscript{1}H NMR (400 MHz, THF-d₈) δ [ppm] = 0.58 (s, 9H, H-20), 0.88 – 0.93 (m, 4H), 0.97 – 1.03 (m, 4H), 1.12 – 1.22 (m, 3H), 1.25 (s, 9H, H-17), 1.25 – 1.29 (m, 3H), 1.30 (s, 9H, H-18), 1.40 (s, 3H), 1.45 – 1.50 (m, 6H), 1.56 – 1.58 (m, 3H), 1.61 – 1.71 (m, 12H), 1.82 – 1.86 (m, 3H), 1.98 – 2.00 (m, 3H), 2.10 – 2.12 (m, 6H), 2.82 – 2.89 (m, 4H), 6.01, 6.13 (every s, every 1H, H-9*, H-10*), 8.06, 8.08 (every s, every 3H, H-ar*); \textsuperscript{13}C NMR (100 MHz, THF-d₈) δ [ppm] = 12.6
(C20), 20.2 (CH2), 22.2 (CH2), 22.6 (C17), 22.9 (CH2), 29.7 (C18), 37.6 (CH2), 38.5
(CH2), 39.4 (CH2), 39.8 (C), 41.4 (CH2), 43.7 (C), 44.3 (C), 46.9 (C), 53.8, 54.1, 57.1,
57.8 (C5, C9, C9*, C10*), 60.0 (C14), 124.7 (CH-ar*), 141.6 (C*), 142.0 (C*), 144.5
(C*), 144.7 (C*), 165.9, 166.3 (C15, C16), 178.9 (C19) (The product is contaminated
with about two equivalents of p-toluidine which is formed as side product by reductive
cleavage of the p-nitrobenzyl protecting group); MS (MALDI-TOF, pos. mode): m/z =
1234.99 [M+H]+ (Deviation from HRMS can be explained by the isotope distribu-
tion; 1:1-ratio of the two most intensive signals); HRMS (ESI, pos. mode): m/z for
C80H93N6O6 [M+H]+ calc. 1233.7157, found 1233.7184; elem. anal. C80H92N6O6
(1233.62): calc. C 77.89 H 7.52 N 6.81, found C 66.02 H 8.44 N 5.18; optical rotation
[α]D20 = +100.8° (c 1.00, CHCl3).
Deviations in the elemental analysis are probably caused by solvent molecules within
the cavities of the molecules. The measurement of the optical rotation was therefore
carried out to determine the orientation thereof.

Pent-4-enyl (+)-tris-ent-beyeran-19-oate-[16,15-e:15′,16′-e′:16″,15′′-e″]triptyceno*-
[2*,3*-b:6*:7*-b′:14*,15*-b′]tripyrarazine (all-syn-17)
To a solution of all-syn-16 (84 mg, 0.07 mmol) in DMF (5 mL), potassium carbonate (87 mg, 0.63 mmol) was added at 25 °C under argon atmosphere. The solution was stirred at 25 °C for 10 min. 5-Bromo-1-pentene (0.03 mL, 0.23 mmol) and TBAI (10 mg) were added, the reaction mixture was stirred at 25 °C for 3 h. After fractionation between H₂O (20 mL) and DCM (20 mL), the aqueous layer was extracted with DCM (2 x 20 mL). The combined organic fractions were washed with H₂O (2 x 50 mL) and brine (50 mL), dried (Na₂SO₄), and concentrated under reduced pressure. The crude product was purified by column chromatography on silica (Büchi chromatography system, cyclohexane/ethyl acetate 95:5 to 4:1).

Yield: 31 mg (0.022 mmol, 31%) of a pale yellow solid. Rf (SiO₂, dichloromethane/methanol, 98:2) = 0.22; ¹H NMR (400 MHz, CDCl₃) δ [ppm] = 0.44 (s, 9H, H-20), 0.49 – 0.60 (m, 3H), 0.86 (dt, 2J₁ax,1eq = 3J₁ax,2ax = 12.6 Hz, 3J₁ax,2eq = 3.4 Hz, 3J₂ax,3eq = 3J₂ax,2ax = 13.3 Hz, 3J₂ax,2eq = 3.9 Hz, 3H, H-3ax), 1.00 (dt, 2J₃ax,3eq = 3J₃ax,2ax = 13.3 Hz, 3J₃ax,2eq = 3.9 Hz, 3H, H-3ax), 1.20 – 1.23 (m, 3H), 1.26 (s, 9H, H-17), 1.33 (s, 9H, H-18), 1.35 – 1.46 (m, 9H), 1.53 – 1.73 (m, 19H), 1.79 – 1.82 (m, 3H), 1.92 – 2.05 (m, 9H), 2.09 – 2.20 (m, 6H), 2.38 – 2.44 (m, 6H), 2.78 (dq, 3J₆ax,7eq = 3.0 Hz, 2J₆ax,6eq = 3J₆ax,7ax = 3J₆ax,5 = 13.1 Hz, 3H, H-6ax), 4.08 (dt, 2J₂₁,2₁′ = 11.0 Hz, 3J₂₁,2₂ = 6.6 Hz, 3H, H-21), 4.20 (dt, 2J₂₁,2₁′ = 11.0 Hz, 3J₂₁,2₂ = 6.4 Hz, 3H, H-21′), 5.19 – 5.30 (m, 6H, H-25), 5.86, 5.88 (every s, every 1H, H-9*, H-10*), 6.05 (ddt, J = 6.7 Hz, 10.1 Hz, 16.9 Hz, 3H, H-24), 8.04, 8.08 (every s, every 3H, H-ar*); ¹³C NMR (100 MHz, CDCl₃) δ [ppm] = 11.9 (C20), 19.0 (C2), 21.1 (C6), 21.7 (C11), 22.1 (C17), 28.0 (C22), 29.0 (C18), 30.7 (C23), 36.5 (CH₂), 37.4 (CH₂), 38.3 (CH₂), 38.7 (C), 40.3 (CH₂), 42.7 (C), 43.9 (C), 45.8 (C), 52.9, 53.1, 55.8, 56.9 (C5, C9, C9*, C10*), 58.8 (C14), 63.7 (C21), 115.8 (C25), 123.4, 123.8 (CH*), 137.9 (C24), 140.3, 140.5, 142.9, 143.1 (C*), 165.2, 165.5 (C15, C16), 177.7 (C19); MS (MALDI-TOF, pos. mode): m/z = 1440.55 [M+H]+ (Deviation from HRMS can be S25
explained by the isotope distribution; 1:1-ratio of the two most intensive signals);
HRMS (ESI, pos. mode): m/z for C_{95}H_{117}N_6O_6 [M+H]^+ calc. 1437.9035, found 1437.9037; elem. anal. C_{95}H_{116}N_6O_6 (1437.97): calc. C 79.35 H 8.13 N 5.84, found C 79.00 H 9.89 N 5.60; optical rotation [α]_D^{20} = +86.1° (c 1.00, CHCl₃).

Crystal structure determination:

A suitable single crystal for X-ray analysis of all-syn-17 was obtained by diffusion of n-heptane into a solution of 17 in CH₂Cl₂/MeOH at ambient conditions to give colorless needles.

Formula C_{95}H_{116}N_6O_6, M = 1437.94, 0.02 x 0.13 x 0.35 mm³, orthorhombic, space group P2₁2₁2₁, a = 14.1535(6), b = 23.4332(16), c = 24.6827(11) Å, α = 90°, β = 90°, γ = 90°, V = 8186.3(8) Å³, ρ_{calc} = 1.167 gcm⁻³, μ = 0.56 mm⁻¹, Z = 4, λ= 1.54178 Å, T = 193(2) K, F(000) = 3104, 111207 reflections collected, 14263 independent (R_{int} = 0.2386), 14263 observed, 974 refined parameters, GOF = 1.157, R^f = 0.1344 for
observed and 0.2440 for all reflections, $wR^2 = 0.4470$, largest difference peak and hole: 0.53 and −0.48 eÅ$^{-3}$.

The size of the cavity which is formed ranges approximately to the quinoxaline-nitrogen atoms of the triptycene core which exhibit a mutual distance of 8.1 Å, 8.8 Å and 8.9 Å, whereas the carboxylic carbon atoms exhibit a distance of about 12 Å. The cavity of all-syn-17 is “roofed” by the alkyl chains of the (−)-isosteviol units, whose terminal carbon atoms show a mutual distance in the range of 4.2–5.2 Å. Within a plane, the voids which are created by the aromatic faces of the triptycene are filled by (−)-isosteviol fragments of a neighbouring molecule.

Pent-4-enyl-(−)-ent-15,16-dioxobeyeran-19-oate (18)

To a solution of (−)-ent-15,16-dioxobeyeran-19-oic acid (9, 7.07 g, 21.3 mmol) in DMF (200 mL), potassium carbonate (8.82 g, 63.9 mmol) was added at 25 °C under argon atmosphere. The solution was stirred at 25 °C for 10 min. 5-Bromo-1-pentene (3.03 mL, 23.4 mmol) and TBAI (20 mg) were added, the reaction mixture was stirred at 25 °C for 4 h. After fractionation between H$_2$O (20 mL) and EtOAc (200 mL), the aqueous layer was extracted with EtOAc (2 x 150 mL). The combined organic fractions were washed with H$_2$O (2 x 150 mL) and brine (100 mL), dried (MgSO$_4$), and concentrated under reduced pressure. The crude product was purified by column chromatography on silica (cyclohexane/ethyl acetate 96:4).
Yield: 7.3 g (18.2 mmol, 85%) of an orange solid. $R_f$ (SiO$_2$, cyclohexane/ethyl acetate, 4:1) = 0.5; Mp. = 100 °C (ethyl acetate); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ [ppm] = 0.55 (s, 3H, H-20), 0.86 (dt, $^2$J$_{1ax,1eq}$ = $^3$J$_{1ax,2ax}$ = 13.1 Hz, $^3$J$_{1ax,2eq}$ = 4.2 Hz, 1H, H-1$_{ax}$), 0.98 (dt, $^2$J$_{3ax,3eq}$ = $^3$J$_{3ax,2ax}$ = 13.5 Hz, $^3$J$_{3ax,2eq}$ = 4.1 Hz, 1H, H-3$_{ax}$), 1.11 (s, 3H, H-17), 1.17 – 1.18 (m, 1H, H-5), 1.19 (s, 3H, H-18), 1.21 – 1.28 (m, 2H, H-7$_{ax}$, H-11$_{ax}$), 1.36 – 1.44 (m, 1H, H-2$_{eq}$), 1.52 – 1.65 (m, 3H), 1.70 – 1.84 (m, 6H), 1.88 – 1.90 (m, 1H), 1.93 – 2.01 (m, 2H), 2.13 – 2.21 (m, 3H), 2.28 – 2.42 (m, 1H), 4.03 (t, $^3$J$_{21,22}$ = 6.6 Hz, 2H, H-21), 4.95 – 5.09 (m, 2H, H-25), 5.81 (ddt, $J$ = 6.7 Hz, 10.2 Hz, 16.9 Hz, 1H, H-24); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ [ppm] = 11.6 (C20), 18.9 (C2), 20.1 (C17), 20.8 (C6), 21.4 (C11), 27.6 (C22), 28.8 (C18), 30.2 (C23), 34.1 (C7), 37.9 (C3), 38.8 (C10), 39.7, 39.8 (C1, C12), 43.7 (C4), 46.9 (C13), 47.2 (C14), 50.5 (C8), 56.2, 59.4 (C5, C9), 63.7 (C21), 115.3 (C25), 137.4 (C24), 177.1 (C19), 208.9, 210.0 (C15, C16); MS (FD): m/z = 400.6 [M]$^{++}$ (Deviation from HRMS lies within the error margin of the instrument); HRMS (ESI, pos. mode): m/z for C$_{25}$H$_{36}$NaO$_4$ [M+Na]$^+$ calc. 423.2511, found 423.2514; elem. anal. C$_{25}$H$_{36}$O$_4$ (400.55): calc. C 74.96 H 9.06, found C 74.78 H 9.03; optical rotation $[\alpha]_D^{20} = -116.7^\circ$ (c 1.00, CHCl$_3$).


Hexaammoniumtriptycene hexachloride 4 [4] (1.17 g, 1.42 mmol), pent-4-enyl-(−)-
ent-15,16-dioxobeyeran-19-oate (18, 5.12 g, 12.9 mmol), sodium acetate (1.39 g,
17.0 mmol) and THF (20 mL) were placed in a sealed tube and heated to 100 °C for
16 h. After cooling to room temperature, the reaction mixture was fractionated
between H₂O (150 mL) and CH₂Cl₂ (150 mL). The aqueous layer was extracted with
CH₂Cl₂ (100 mL). The combined organic fractions were washed with H₂O (3 x 50 mL)
and brine (50 mL), dried (Na₂SO₄), and concentrated under reduced pressure. The
crude product was purified by column chromatography on silica (A: Büchi
chromatography system, cyclohexane/ethyl acetate 98:2 to 4:1 [removal of excess
starting material]; B: CH₂Cl₂/MeOH, 99.5:0.5 to 99:1 [separation of isomers]).
Combined yield: 1.34 g (0.96 mmol, 67% [all-syn + anti,anti,syn]) of a pale yellow
solid.

Chromatographic separation of isomers: anti,anti,syn 879 mg (44%) 
all-syn 461 mg (23%)
all-syn: see above

anti,anti,syn

$R_t$ (SiO$_2$, dichloromethane/methanol, 98:2) = 0.24; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ [ppm] = 0.39, 0.43 (every s, 9H, H-20), 0.46 – 0.56 (m, 3H), 0.79 – 0.87 (m, 3H), 0.93 – 1.04 (m, 3H), 1.14 – 1.22 (m, 3H), 1.25, 1.26 (every s, 9H, H-17), 1.32, 1.35 (every s, 9H, H-18), 1.32 – 1.48 (m, 9H), 1.53 – 1.59 (m, 9H), 1.62 – 1.71 (m, 6H), 1.74 – 1.76 (m, 6H), 1.91 – 2.05 (m, 9H), 2.09 – 2.20 (m, 6H), 2.37 – 2.45 (m, 6H), 2.73 – 2.79 (m, 3H, H-6$_{ax}$), 4.03 – 4.09 (m, 3H, H-21), 4.17 – 4.23 (m, 3H, H-21*), 5.23 – 5.32 (m, 6H, H-25), 5.86, 5.87 (every s, every 1H, H-9*, H-10*), 6.02 – 6.13 (m, 3H, H-24), 8.01 (s, 1H, H-ar*), 8.05 (s, 1H, H-ar*), 8.06 (s, 1H, H-ar*), 8.07 (s, 1H, H-ar*), 8.11 (s, 2H, H-ar*); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ [ppm] = 11.9, 12.0 (C20), 18.90 (CH$_2$), 18.94 (CH$_2$), 21.1 (CH$_2$), 21.6 (CH$_2$), 21.7 (CH$_2$), 22.1 (C17), 27.9 (CH$_2$), 28.00 (CH$_2$), 28.04 (CH$_2$), 28.9 (C18), 30.60 (CH$_2$), 30.68 (CH$_2$), 30.73 (CH$_2$), 36.4 (CH$_2$), 37.4 (CH$_2$), 37.5 (CH$_2$), 38.2 (CH$_2$), 38.3 (CH$_2$), 38.62 (C), 38.63 (C), 38.65 (C), 40.2 (CH$_2$), 40.3 (CH$_2$), 42.68 (C), 42.71 (C), 43.88 (C), 43.91 (C), 45.8 (C), 52.9, 53.0, 55.75, 55.77, 56.8 (C5, C9, C9*, C10*), 58.7, 58.8 (C14), 63.70, 63.75, 63.83 (C21), 115.80, 115.83, 115.86 (C24), 123.2, 123.3, 123.8, 123.99, 124.00 (CH*), 137.88, 137.91, 137.98 (C24), 140.3, 140.46, 140.51, 142.7, 142.9, 143.0, 143.08, 143.10 (C*), 165.09, 165.16, 165.19, 165.4, 165.5, 165.6 (C15, C16), 177.6, 177.7 (C19); MS (MALDI-TOF, pos. mode): m/z = 1440.55 [M+H]$^+$ (Deviation from HRMS can be explained by the isotope distribution; 1:1-ratio of the two most intensive signals); HRMS (ESI, pos. mode): m/z for C$_{95}$H$_{117}$N$_6$O$_6$ [M+H]$^+$ calc. 1437.9035, found 1437.9037; elem. anal. C$_{95}$H$_{117}$N$_6$O$_6$ (1437.97): calc. C 79.35 H 8.13 N 5.84, found C 79.34 H 9.18 N 6.03; optical rotation $[\alpha]_D^{20} = +120.9^\circ$ (c 1.00, CHCl$_3$).
Under argon atmosphere, all-syn-17 (50 mg, 0.036 mmol) and Grubbs catalyst (2nd generation, 12 mg, 0.012 mmol) were solved in degassed dichloromethane (100 mL each) in separated flasks. The solution of all-syn-17 was then added to the catalyst solution and the resulting mixture was refluxed for 34 days. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography on silica (dichloromethane/methanol, 99.5:0.5 to 98:2) to yield a brown solid.

\[ R_f \text{ (dichloromethane/methanol, 98:2)} = 0.20; \]  
\[ ^{13}\text{C NMR (150 MHz, CDCl}_3\text{)} \delta \text{ [ppm]} = \]  
11.6, 12.0, 12.3, 13.9 (every CH\(_3\)), 18.8, 19.2, 21.0, 21.1, 21.4, 21.7 (every CH\(_2\)), 21.9, 22.1, 22.2 (every CH\(_3\)), 28.48, 28.57 (every CH\(_2\)), 28.61, 28.9, 29.2 (every CH\(_3\)), 29.3, 29.7, 30.2, 30.6, 30.9, 31.6 (every CH\(_2\)), 31.9 (C), 34.9, 35.3 (every CH\(_3\)), 36.4, 36.5, 36.6, 37.4, 37.6, 38.5 (every CH\(_2\)), 38.8 (C), 40.0, 40.3 (every CH\(_2\)), 42.9, 43.1, 43.2, 43.8 (every C), 50.8, 53.0, 53.4, 55.1, 55.3, 55.6, 56.6, 56.7, 56.8 (every CH), 58.3, 58.5, 58.7, 61.8, 63.2, 63.3, 64.1, 64.3, 65.2, 70.2, 70.5, 71.3,
72.5 (every CH₂), 123.3, 123.6, 124.2, 129.6, 130.3, 131.5 (every CH), 140.4, 140.6, 142.2, 143.4, 165.1, 165.4, 177.0, 178.1 (every C); MS (MALDI-TOF, pos. mode): m/z = 2793.59 [M+H]⁺.

*Note:* Complete conversion of the starting material could not be achieved. The brown color of the product as well corresponding signals in the NMR spectra indicate the presence of catalyst fragments within the product. Due to a very small amount of product with a comparatively high molecular weight, a complete characterization by NMR methods has not been achieved yet. For discussion on this topic, see publication.
C. $^1$H and $^{13}$C NMR spectra

Compound all-syn-3:

$^1$H NMR, 400 MHz, CDCl$_3$

$^{13}$C NMR, 100 MHz, CDCl$_3$
Compound 6:

\( ^{13}C \text{ DEPT NMR, 100 MHz, CDCl}_3 \)

\( ^1H \text{ NMR, 300 MHz, CDCl}_3 \)
$^{13}$C NMR, 75 MHz, CDCl$_3$

13C DEPT NMR, 75 MHz, CDCl$_3$
Compound 7:

$^1$H NMR, 400 MHz, CDCl$_3$

$^{13}$C NMR, 100 MHz, CDCl$_3$
Compound 8:

$^{13}\text{C}$ DEPT NMR, 100 MHz, CDCl$_3$

$^1\text{H}$ NMR, 600 MHz, CDCl$_3$
$^1$H NMR, 600 MHz, CDCl$_3$

$^{13}$C NMR, 150 MHz, CDCl$_3$
Compound 12:

\[ 1^3 \text{C DEPT NMR, 150 MHz, CDCl}_3 \]

\[ 1^1 \text{H NMR, 300 MHz, CDCl}_3 \]
$^{13}$C NMR, 75 MHz, CDCl$_3$

$^{13}$C DEPT NMR, 75 MHz, CDCl$_3$
Compound 10:

$^1$H NMR, 300 MHz, CDCl$_3$

$^{13}$C NMR, 75 MHz, CDCl$_3$
Compound 13:

$\text{C DEPT NMR, 75 MHz, CDCl}_3$

$\text{H NMR, 300 MHz, CDCl}_3$
Compound 11:

\[^{1}H\text{ NMR, 300 MHz, CDCl}_3\]

\[^{13}C\text{ NMR, 75 MHz, CDCl}_3\]
**Compound 14:**

$^{13}$C DEPT NMR, 75 MHz, CDCl$_3$

$^1$H NMR, 400 MHz, CDCl$_3$
$^{1}$H NMR, 400 MHz, CDCl$_3$

$^{13}$C NMR, 100 MHz, CDCl$_3$
Compound 15:

$^{13}$C DEPT NMR, 100 MHz, CDCl$_3$

$^1$H NMR, 600 MHz, CDCl$_3$
$^{13}$C NMR, 150 MHz, CDCl$_3$

$^{13}$C DEPT NMR, 150 MHz, CDCl$_3$
$^1$H NMR, 600 MHz, CDCl$_3$

$^{13}$C NMR, 150 MHz, CDCl$_3$
Compound 16: [* Contamination with p-toluidine, see characterization]
\[ ^{13}C \text{ NMR, 100 MHz, CDCl}_3 \]

\[ ^{13}C \text{ DEPT NMR, 100 MHz, CDCl}_3 \]
Compound 17:

$^1$H NMR, 400 MHz, CDCl$_3$

$^{13}$C NMR, 100 MHz, CDCl$_3$
$^{13}$C DEPT NMR, 100 MHz, CDCl$_3$

$^1$H NMR, 400 MHz, CDCl$_3$
$^{13}$C NMR, 100 MHz, CDCl$_3$

anti,anti,syn

$^{13}$C DEPT NMR, 100 MHz, CDCl$_3$
D. Evaluation of affinity

QCM setup
The resonance frequency of thickness-shear resonators, like the employed quartz crystal microbalances, is largely influenced by the oscillating mass. The sensitivity of the quartz resonator is influenced by several environmental factors and is described by the Sauerbrey equation (formula 1),[5] wherein \( A \) is the oscillating area, \( N \) the frequency constant and \( \rho \) the density of the quartz material. A variation in the oscillating mass \( \Delta m \) directly results in a linear shift \( \Delta f_0 \) of the fundamental resonance frequency \( f_0 \).

\[
\Delta f_0 = -\frac{f_0^2}{N \cdot \rho \cdot A} \cdot \Delta m
\]

The Sauerbrey equation applies to homogeneous films with nearly the same viscoelastic properties as the quartz crystal so that no damping of the oscillator appears. Also, the maximum frequency shift has to be lower than 2% of the fundamental frequency, in this case 2000 kHz. This correlation is an easy way to determine affinities from various analytes towards selected affinity materials [6].

Coating protocol
The coating of the quartz crystal microbalances is performed using an electrospray protocol [7]. This particular method is well established and allows the continuously monitoring of mass deposition onto the quartz upon spraying process. The electrospray solutions are prepared at concentrations of approx. 0.1 mg/mL in a 9:1 mixture of tetrahydrofuran/methanol.

The experimental setup for the coating unit is schematically displayed in Figure S1. The solution for coating is placed in a glass syringe equipped with metal cannula. The metallic part of the needle is contacted with an applied voltage of 5 kV relative to a counter electrode which is represented by the electrode of the QCM to be coated (distance 0.15 m needle tip/electrode). The cannula represents the anode. A constant delivery of the solution during the coating process is achieved by using a syringe pump (5 μL/min, Figure S1/2). The coating process is monitored by measuring the frequency shift of the QCM. Since it is not possible to determine the
thickness of the deposited film directly, the amount of affinity material on the quartz device is given by the frequency shift. For screening purposes, all compounds are deposited on 195 MHz QCMs until a frequency shift of 50 kHz is reached. This shift corresponds to a mass of approx. 10.4 ng of the deposited material on the electrodes.

**Figure S1**: Setup of the coating unit for electrospray.

**Figure S2**: The electrospray setup in the lab.
Setup for measurement of affinity

For determination of affinities precise conditions and concentration of analytes are required. Therefore, a “closed” system connected to a gas mixing unit is used (Figure S2). In this gas mixing unit, the inert nitrogen flow is divided into two streams, both controlled by an individual mass flow controller (MFC) from the Brooks Instrument company (Model 5050S). Flow 1 remains unchanged in temperature and composition and is used as gas source for dilution purposes, whereas, flow 2 is led through an interchangeable analyte-reservoir which is adjusted to 293.1±0.2 K. The analyte-saturated gas flow 2 is recombined with the pure inert gas flow 1 and led to the measuring chamber. The overall gas flow is set to 200 mL/min. By carefully controlling the flow of the both streams by the MFCs, it is possible to produce gas mixtures with a concentration of 1 to 100% of the vapor pressure of the pure analyte at 293.1±0.2 K.

The central part of the screening setup is the measuring cell which is connected to the gas mixing unit and placed in a temperature controlled environment. We employed a slightly modified GC oven (Hewlett Packard, Palo Alto, CA, USA. Type: HP 5890; Figure S4). The cell is kept constantly at 308 K±0.5 K to exclude temperature influences and to prevent condensation effects within the cell. The cell is designed to operate up to 12 QCM in a parallel fashion.

Figure S3: Setup for measurement.
Evaluation of the affinity materials
The following example will show the procedure for determination of affinity. The applied affinity material in this example is the triptycene derivative \textit{anti,anti,syn-8} and employed analyte is pseudocumene. This procedure is carried out for every affinity material with the individual analyte. In Figure S5 the primary data of a typical measurement for an analyte are depicted. The sensor responses (Figure S5, $\Delta F_c$) were determined by referencing the frequency of the QCM (Figure S5, a) just prior to
the admittance of analyte into the chamber to the frequency in equilibrium (Figure S5, b). The given recovery time between two concentration steps was 1500 seconds in each experiment. The given adsorption time was 1000 seconds for the first five concentration steps and 2000 seconds for the last three.

![Graph showing frequency shifts for different pseudocumene concentrations.](image)

**Figure S5:** Frequency shifts for different pseudocumene concentrations (primary data, affinity material *anti*,*anti*,syn-*8*).

By plotting the frequency shift vs. the ethanol concentration the constants of the *Langmuir* adsorption isotherm was determined (Figure S6). The graph is obtained by fitting to equation 2.
The slope of the linear part of the Langmuir equation is the product of the Langmuir constants in equation 2.

$$\Delta F = \frac{\Delta F_{\text{max}} \cdot K \cdot c_{\text{analyte}}}{1 + K \cdot c_{\text{analyte}}}$$  

Since the resulting number is a general information about the affinity of a film or porous material to a respective analyte, $\Delta F_{\text{max}}K$ will be used as the affinity within this study.

Table S1: Overview of screened analytes.

<table>
<thead>
<tr>
<th>analyte</th>
<th>vapor pressure at 20 °C [ppm]</th>
<th>applied concentration range [ppm][a]</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzene</td>
<td>99458</td>
<td>99458 - 994</td>
</tr>
<tr>
<td>toluene</td>
<td>29331</td>
<td>29331 - 293</td>
</tr>
<tr>
<td>water</td>
<td>23000</td>
<td>23000 - 230</td>
</tr>
<tr>
<td>H_2O_2</td>
<td>14500</td>
<td>7250 - 73</td>
</tr>
<tr>
<td>p-xylene</td>
<td>8700</td>
<td>8700 - 87</td>
</tr>
<tr>
<td>m-xylene</td>
<td>8000</td>
<td>8000 - 80</td>
</tr>
<tr>
<td>o-xylene</td>
<td>7000</td>
<td>7000 - 70</td>
</tr>
<tr>
<td>mesitylene</td>
<td>2800</td>
<td>2800 - 28</td>
</tr>
<tr>
<td>pseudocumene</td>
<td>2300</td>
<td>2300 - 23</td>
</tr>
</tbody>
</table>

[a] For all analytes eight concentrations between 1 % and 100 % of the saturation concentration in the gas phase at 20 °C were chosen.
Screening results
In order to obtain comparable results, the coating of the QCM was always made with the same mass of affinity material (50 kHz which corresponds to 10.4 ng). By that, a comparable film thickness is achieved. In the following table, the affinity is presented for the analytes.

**Table S2:** Affinities of the affinity materials all-syn-3, 7, 8 and 14.

<table>
<thead>
<tr>
<th>analyte</th>
<th>all-syn-3 [Hz/ppm]</th>
<th>7 [Hz/ppm]</th>
<th>all-syn-8 [Hz/ppm]</th>
<th>anti,anti,syn-8 [Hz/ppm]</th>
<th>all-syn-14 [Hz/ppm]</th>
<th>anti,anti,syn-14 [Hz/ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzene</td>
<td>0.1238</td>
<td>0.1110</td>
<td>0.0729</td>
<td>0.1410</td>
<td>0.0739</td>
<td>0.0773</td>
</tr>
<tr>
<td>toluene</td>
<td>0.453</td>
<td>0.404</td>
<td>0.204</td>
<td>0.430</td>
<td>0.395</td>
<td>0.240</td>
</tr>
<tr>
<td>water</td>
<td>0.23</td>
<td>0.54</td>
<td>0.53</td>
<td>0.46</td>
<td>1.23</td>
<td>0.90</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>0.29</td>
<td>0.66</td>
<td>0.75</td>
<td>1.69</td>
<td>1.60</td>
<td>3.33</td>
</tr>
<tr>
<td>p-xylene</td>
<td>1.43</td>
<td>1.12</td>
<td>0.70</td>
<td>1.90</td>
<td>1.43</td>
<td>0.71</td>
</tr>
<tr>
<td>m-xylene</td>
<td>1.73</td>
<td>1.64</td>
<td>0.94</td>
<td>1.05</td>
<td>1.44</td>
<td>0.81</td>
</tr>
<tr>
<td>o-xylene</td>
<td>1.98</td>
<td>1.47</td>
<td>0.85</td>
<td>3.34</td>
<td>1.34</td>
<td>0.94</td>
</tr>
<tr>
<td>mesitylene</td>
<td>4.11</td>
<td>2.88</td>
<td>1.35</td>
<td>4.96</td>
<td>4.05</td>
<td>1.86</td>
</tr>
<tr>
<td>pseudocumene</td>
<td>5.95</td>
<td>4.02</td>
<td>2.79</td>
<td>7.06</td>
<td>6.56</td>
<td>4.46</td>
</tr>
</tbody>
</table>

**Table S3:** Affinities of the affinity materials 15, 17 and 19.

<table>
<thead>
<tr>
<th>analyte</th>
<th>all-syn-15 [Hz/ppm]</th>
<th>anti,anti,syn-15 [Hz/ppm]</th>
<th>all-syn-17 [Hz/ppm]</th>
<th>anti,anti,syn-17 [Hz/ppm]</th>
<th>19 [Hz/ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzene</td>
<td>0.0751</td>
<td>0.0756</td>
<td>0.0605</td>
<td>0.072</td>
<td>0.0571</td>
</tr>
<tr>
<td>toluene</td>
<td>0.223</td>
<td>0.239</td>
<td>0.175</td>
<td>0.228</td>
<td>0.122</td>
</tr>
<tr>
<td>water</td>
<td>1.00</td>
<td>0.73</td>
<td>1.20</td>
<td>0.67</td>
<td>0.37</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>1.33</td>
<td>2.43</td>
<td>2.80</td>
<td>2.54</td>
<td>1.49</td>
</tr>
<tr>
<td>p-xylene</td>
<td>1.20</td>
<td>0.80</td>
<td>0.60</td>
<td>0.67</td>
<td>0.43</td>
</tr>
<tr>
<td>m-xylene</td>
<td>1.25</td>
<td>0.80</td>
<td>0.68</td>
<td>0.75</td>
<td>0.44</td>
</tr>
<tr>
<td>o-xylene</td>
<td>1.17</td>
<td>0.93</td>
<td>0.80</td>
<td>0.85</td>
<td>0.53</td>
</tr>
<tr>
<td>mesitylene</td>
<td>3.48</td>
<td>2.17</td>
<td>1.52</td>
<td>1.65</td>
<td>0.77</td>
</tr>
<tr>
<td>pseudocumene</td>
<td>5.61</td>
<td>4.1</td>
<td>3.26</td>
<td>3.75</td>
<td>2.69</td>
</tr>
</tbody>
</table>
E. Structure of the compared organic cage compound

(X = -C$_2$H$_4$-)
E. References


9. *Chemicals & Reagents*, Merck KGaA, Darmstadt, **2011**.