Supporting Information File 1

for

Hybrid macrocycle formation and spiro annulation on cis-syn-cis-tricyclo[6.3.0.0²,6]undeca-3,11-dione and its congeners via ring-closing metathesis

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Experimental and analytical data
General

Melting points were recorded on a Buchi apparatus. Infrared (IR) spectra were recorded on a Nicolet Impact-400 FT IR spectrometer in KBr/CHCl₃. ¹H NMR (400 MHz), ¹³C NMR (100 MHz) spectral data were obtained at rt on Bruker (AVANCE IIITM) 500 MHz and Bruker (AVANCE IIITM) 400 MHz spectrometers with tetramethylsilane (TMS) as an internal standard and in CDCl₃ solution. Coupling constants (J values) are given in Hertz (Hz). High-resolution mass spectrometric (HRMS) measurements were carried out using Bruker (Maxis Impact) or Micromass Q-ToF spectrometers. Analytical thin layer chromatography (TLC) was performed on (10 × 5 cm) glass plates coated with Acme’s silica gel GF 254 (containing 13% calcium sulfate as a binder). Chromatography was performed using Acme’s silica gel (100-200 mesh) using double spray bellows for application of pressure and the column is eluted with ethyl acetate–petroleum ether mixture. All of the organic solvents used in this study were dried over appropriate drying agents and distilled prior to use.

General procedure for the preparation of diindole derivatives.

In a typical experiment, 1.5 g of an L-(+)-tartaric acid/N,N′-dimethylurea (30:70) mixture was heated to 70 °C to obtain a clear melt. To this melt, 2 mmol of N-methyl-N-phenylhydrazine and 1 mmol of diketone were added at 70 °C. After termination of the reaction (TLC monitoring by mini work up), the reaction mixture was quenched with water while it was still hot. The reaction mixture was cooled to rt and the solid was filtered through a sintered glass funnel and washed with water (2 × 5 mL). The solvent was evaporated and the crude product was purified by silica gel column chromatography with an appropriate mixture of EtOAc and petroleum ether [1,2].

Synthesis of compound 8

The tricyclic dione 2 (100 mg, 0.56 mmol), was reacted with phenylhydrazine hydrochloride (177 mg, 1.23 mmol) by following the general procedure. After termination of the reaction (TLC monitoring), the reaction mixture was worked up according to the general procedure. The crude product obtained was purified by column chromatography on silica gel.
(EtOAc/petroleum ether, 10:90) to provide the diindole derivative 8 (115 mg, 62%) as a colourless solid [2].

Mp 189-191 °C; $R_f = 0.41$ (Silica gel, 10% EtOAc/petroleum ether); $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 1.52$-$1.60$ (m, 1H), 2.45-$2.54$ (m, 3H), 2.89-$2.95$ (q, $J = 7.9$ Hz, 2H), 3.46-$3.51$ (m, 2H), 3.87-$3.89$ (m, 2H), 6.99-$7.06$ (m, 4H), 7.18-$7.20$ (m, 2H), 7.31-$7.33$ (m, 2H), 7.58 (bs, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta = 31.38$, 41.43, 48.22, 51.71, 111.82, 118.91, 119.88, 120.27, 120.94, 125.56, 141.58, 144.02; accurate mass (ESI, Q-ToF) m/z: calculated for C$_{23}$H$_{20}$KN$_2$ [M+K]$^+$: 363.1258; found: 363.1254.

**Synthesis of compound 9**

![Synthesis of compound 9](image)

**Method A**

To a suspension of NaH (8.2 mg, 0.34 mmol) in DMF (5 mL), the diindole 8 (50 mg, 0.15 mmol) was added at rt under nitrogen. Then, the reaction mixture stirred at rt for 15 min. Next, methyl iodide (0.03 mL, 0.34 mmol) was added in a dropwise manner, and then the stirring was continued for 24 h at rt. After termination of the reaction (TLC monitoring), the reaction mixture was diluted with ethyl acetate (10 mL), and the organic layer was washed with water, brine and dried over Na$_2$SO$_4$. The solvent was removed under reduced pressure. The crude product obtained was purified by silica gel column chromatography (5% EtOAc/petroleum ether) to yield compound 9 (47 mg, 87%) [3].

**Method B**

The tricyclic dione 2 (50 mg, 0.28 mmol) was reacted with N-methyl-N-phenylhydrazine (76 mg, 0.61 mmol) following the general procedure. After termination of the reaction (TLC monitoring), the reaction mixture was worked up according to the general procedure. The crude product obtained was purified by column chromatography on silica gel (EtOAc/petroleum ether, 10:90) to provide the diindole derivative 9 (75 mg, 76%) as a colourless solid [2].
Mp 206-208 °C; $R_f = 0.39$ (Silica gel, 10% EtOAc-petroleum ether); $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 1.74$-1.80 (m, 1H), 2.43-2.55 (m, 3H), 2.85-2.88 (m, 2H), 3.24 (s, 6H), 3.61-3.64 (m, 2H), 3.74-3.78 (m, 2H), 7.00-7.08 (m, 6H), 7.33 (d, $J = 7.7$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta = 30.70, 32.48, 38.39, 48.95, 54.48, 109.60, 118.82, 119.10, 120.31, 124.65, 141.29, 146.09$; accurate mass (ESI, Q-ToF) $m/z$: calculated for C$_{25}$H$_{24}$N$_2$Na $[M+Na]^+$: 375.1832; found: 375.1835.

Synthesis of compound 10

To a suspension of NaH (16.3 mg, 0.70 mmol) in DMF (10 mL), the diindole 8 (100 mg, 0.3 mmol) was added at rt under nitrogen. Then, the reaction mixture stirred at rt for 15 min. Allyl bromide (0.02 mL, 0.3 mmol) was added in a dropwise manner, and then the stirring was continued at rt for 24 h. After termination of the reaction (TLC monitoring), the reaction mixture was diluted with ethyl acetate (10 mL), and the organic layer was washed with water, brine and dried over Na$_2$SO$_4$. The solvent was removed under reduced pressure. The crude product obtained was purified by silica gel column chromatography (5% EtOAc/petroleum ether) to yield compound 10 (81 mg, 65%) as a yellow thick liquid [3].

$R_f = 0.42$ (Silica gel, 5% EtOAc-petroleum ether); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 1.77$-1.83 (m, 1H), 2.44-2.56 (m, 3H), 2.86-2.90 (m, 2H), 3.59-3.63 (m, 2H), 3.73-3.74 (m, 2H), 3.96-4.01 (m, 2H), 4.35-4.39 (m, 2H), 4.74-4.78 (m, 2H), 4.96-4.98 (m, 2H), 5.62-5.67 (m, 2H), 7.00-7.11 (m, 6H), 7.33-7.35 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 32.20, 38.29, 47.03, 49.37, 54.56, 109.37, 115.98, 118.89, 119.32, 120.05, 120.50, 125.13, 134.15, 141.02, 145.72$; accurate mass (ESI, Q-ToF) $m/z$: calculated for C$_{29}$H$_{28}$N$_2$Na $[M+Na]^+$: 427.2145; found: 427.2150.
Synthesis of compound 11

A solution of diallyldiindole 10 (65 mg, 0.16 mmol) in dry CH₂Cl₂ (15 mL) was degassed with N₂ for 10 min. Then, G-II (7.5 mol %) was added stirring was continued for 24 h at rt. After termination of the reaction (TLC monitoring), the solvent was removed at reduced pressure and the crude product was purified by silica gel column chromatography (5% EtOAc/petroleum ether) gave the RCM compound 11 (51 mg, 84%) as a white solid [3].

Mp at 235 °C decomposed; Rᵣ = 0.40 (Silica gel, 5% EtOAc/petroleum ether); ¹H NMR (400 MHz, CDCl₃): δ = 1.74-1.80 (m, 1H), 2.45-2.58 (m, 3H), 2.89-2.94 (m, 2H), 3.54-3.63 (m, 2H), 3.83-3.95 (m, 4H), 4.37-4.40 (d, J = 13.9 Hz, 2H), 5.73-5.75 (t, J = 3.6 Hz, 2H), 6.98-7.09 (m, 4H), 7.14-7.16 (m, 2H), 7.33-7.35 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 32.20, 39.80, 41.41, 49.50, 53.31, 109.31, 118.97, 119.17, 119.86, 120.51, 124.50, 127.55, 140.57, 145.39; accurate mass (ESI, Q-ToF) m/z: calculated for C₂₇H₂₄N₂Na [M+Na]⁺: 399.1832; found: 399.1835

Synthesis of compound 6

To a solution of compound 11 (50 mg, 0.13 mmol) in dry EtOAc (10 mL), 10 mol% Pd/C (15.4 mg, 0.13 mmol), was added and the reaction mixture was stirred at rt under H₂ pressure (1 atm) for 32 h. After termination of the reaction (TLC monitoring), the reaction mixture was filtered through a Celite-pad and washed with ethyl acetate (20 mL). Evaporation of the solvent at reduced pressure gave the crude product. Further purification by silica-gel column chromatography (5% EtOAc/petroleum ether) gave the hydrogenated product 6 (48 mg, 95%) as a white solid [3].
Mp 245-247 °C; \( R_f = 0.42 \) (Silica gel, 5% EtOAc-petroleum ether); \(^1\)H NMR (500 MHz, CDCl\(_3\)):
\[ \delta = 1.83-1.88 \text{ (m, 1H)}, 1.96-2.02 \text{ (m, 4H)}, 2.42-2.49 \text{ (m, 1H)}, 2.66 \text{ (d, } J = 4.4 \text{ Hz, 1H)}, 2.69 \text{ (d, } J = 4.5 \text{ Hz, 1H)}, 2.92-2.99 \text{ (m, 2H)}, 3.42-3.45 \text{ (m, 2H)}, 3.68-3.71 \text{ (m, 2H)}, 3.97-4.02 \text{ (m, 4H)}, 6.99-7.04 \text{ (m, 2H)}, 7.06-7.11 \text{ (m, 2H)}, 7.15-7.18 \text{ (m, 2H)}, 7.34 \text{ (d, } J = 7.7 \text{ Hz, 2H}); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)):
\[ \delta = 26.57, 31.89, 39.11, 43.41, 49.71, 54.25, 109.81, 118.94, 119.07, 119.72, 120.45, 124.51, 140.32, 145.42; \] accurate mass (ESI, Q-ToF) \( m/z \):
calculated for C\(_{27}\)H\(_{27}\)N\(_2\) [M+H]\(^+\): 379.2168 found: 379.2165.

**General procedure for the allylation of 2 and 3a–d**

To a suspension of NaH (6 equivalents) in THF (20 mL), added the dione 2 (or 3a–c) at rt under nitrogen and the reaction mixture was stirred at rt for 10 min. Later, allyl bromide was added to the reaction mixture in a dropwise manner, and stirring was continued overnight at rt. After termination of the reaction (TLC monitoring), the reaction mixture was diluted with ethyl acetate (10 mL), washed with water, brine and dried over Na\(_2\)SO\(_4\), concentrated at reduced pressure. The crude product obtained was purified by silica gel column chromatography with appropriate mixture of EtOAc-petroleum ether to yield the allylated product 12 (or 14a–d) [4].

**General procedure of the ring-closing metathesis of 12 and 14a–d**

A solution of compound 12 (or 14a–d) in dry CH\(_2\)Cl\(_2\) (20 mL) was degassed with N\(_2\) for 10 min, then G-I (10 mol%) was added and stirring was continued for 12–24 h at rt. After termination of the reaction (TLC monitoring), the solvent was removed under reduced pressure and the crude product was purified by silica gel column chromatography with an appropriate mixture of EtOAc/petroleum ether to deliver the desired RCM product 13 (or 15a-d) [4].

**General procedure for the hydrogenation of 13 and 15a–d**

The solution of compounds 13 (or 15a–d) in EtOAc (10 mL), 10 mol % Pd/C (1 mmol) was added and the reaction mixture was stirred at rt under H\(_2\) pressure (1 atm) for 6–24 h. After termination of the reaction (TLC monitoring), the reaction mixture was filtered through using a Celite-pad and the solvent was removed under reduced pressure. The crude product was purified by silica-gel column chromatography by using an appropriate mixture of EtOAc/petroleum ether to yield the desired hydrogenated product 7 (or 16a–d) [4].
Synthesis of compound 12

Thick colorless liquid, 59% yield (141.0 mg, starting with 100.0 mg of tricyclic dione 2)

$R_f = 0.74$ (silica gel, 10% EtOAc-petroleum ether): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 1.29-1.48 (m, 3H), 1.60-1.73 (m, 2H), 1.78-1.91 (m, 2H), 2.01-2.78 (m, 13H), 4.89-5.30 (m, 12H), 5.70-5.97 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 37.21, 38.05, 38.47, 40.38, 45.13, 52.45, 67.44, 118.25, 118.28, 118.58, 133.61, 134.13, 134.31, 220.71; IR $\nu_{max}$ = 1638, 1729, 2851, 2927 cm$^{-1}$; accurate mass (ESI, Q-ToF) $m/z$: calculated for C$_{29}$H$_{38}$NaO$_2$ [M+Na]$^+$ 441.2764 found: 441.2765.

Synthesis of compound 13

Colorless semi-solid, 80% yield (45.0 mg, starting with 70.0 mg of hexa-allyl tricyclic dione 12)

$R_f = 0.70$ (silica gel, 10% EtOAc-petroleum ether): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 1.26-1.33 (m, 1H), 1.68-1.72 (m, 3H), 1.99-2.14 (m, 4H), 2.23-2.39 (m, 6H), 2.41-2.59 (m, 2H), 2.61-2.64 (m, 2H), 3.03-3.09 (m, 2H), 5.50-5.53 (br, 2H), 5.65-5.67 (br, 2H), 5.75 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 31.34, 35.79, 44.79, 46.77, 46.87, 48.77, 56.23, 61.14, 123.76, 127.09, 129.64, 225.99; IR $\nu_{max}$ = 1651, 1725, 2857, 2928 cm$^{-1}$; accurate mass (ESI, Q-ToF) $m/z$: calculated for C$_{23}$H$_{26}$NaO$_2$ [M+Na]$^+$ 357.1825, found: 357.1827.

Synthesis of compound 7

White solid, 90% yield (27.0 mg, starting with 30.0 mg of tris-RCM product 13)

Mp 93-94 °C; $R_f = 0.71$ (silica gel, 10% EtOAc-petroleum ether): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 1.25-1.30 (m, 2H), 1.32-1.80 (m, 21H), 1.81-1.94 (m, 4H), 2.11-2.18 (m, 2H),

SI-17
2.36-2.53 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 21.72, 25.84, 26.03, 29.89, 36.03, 39.33, 41.64, 42.79, 45.04, 57.80, 62.25, 226.67; IR $v_{\text{max}}$ = 1727, 2862, 2938 cm$^{-1}$; accurate mass (ESI, Q-ToF) m/z: calculated for C$_{23}$H$_{32}$KO$_2$ [M+K]$^+$ 379.2034, found: 379.2038.

**Synthesis of compound 14a**

![Diagram of the synthesis of compound 14a](image)

white solid, 74% (125.6 mg, starting with 100.0 mg of pentacyclic dione 3a)

Mp 74-75 °C; $R_f$ = 0.60 (silica gel, 10% EtOAc-petroleum ether): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 0.73 (ABq, $J$ = 12.8 Hz, 1H), 1.93-1.99 (m, 3H), 2.19-2.33 (m, 5H), 2.37-2.44 (m, 4H), 2.51 (t, $J$ = 7.4 Hz, 1H), 2.66-2.69 (m, 1H), 2.85-2.90 (m, 1H), 3.19 (t, $J$ = 8.0 Hz, 1H), 3.32-3.37 (m, 1H), 4.96-5.08 (m, 8H), 5.37-5.38 (m, 1H), 5.55-5.62 (m, 2H), 5.71-5.80 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 32.05, 35.21, 35.25, 38.97, 39.16, 42.51, 48.58, 49.94, 51.00, 54.14, 54.48, 58.39, 58.84, 62.73, 77.83, 118.31, 118.37, 118.40, 118.61, 132.25, 132.47, 132.78, 133.00, 133.82, 133.91, 220.60, 221.62; IR $v_{\text{max}}$ = 3075, 2927, 2854, 1730, 1639, 1440, 1270, 1150, cm$^{-1}$; accurate mass (ESI, Q-ToF) m/z: calculated for C$_{27}$H$_{33}$O$_2$ [M+H]$^+$ 389.2481, found: 389.2436.

**Synthesis of compound 15a**

![Diagram of the synthesis of compound 15a](image)

white solid, 92% (47.0 mg, starting with 60.0 mg of tetra-allyl pentacyclic dione 14a)

Mp 203-205 °C; $R_f$ = 0.38 (silica gel, 10% EtOAc-petroleum ether): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 0.43 (ABq, $J$ = 12.6 Hz, 1H), 1.61-1.65 (m, 1H), 1.90-1.96 (m, 1H), 2.18-2.24 (m, 2H), 2.31-2.48 (m, 5H), 2.52-2.58 (m, 3H), 2.70-2.76 (m, 2H), 2.79-2.82 (m, 1H), 3.18 (t, $J$ = 8.0 Hz, 1H), 3.32-3.37 (m, 1H), 5.39-5.41 (m, 1H), 5.44-5.47 (m, 2H), 5.60-5.70 (m, 2H), 5.80-5.82 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ = 34.34 (t), 37.38 (t), 37.82 (t), 42.94 (t), 45.14 (t), 45.34 (t), 49.48 (d), 52.67 (d), 53.58 (d), 54.36 (d), 55.16 (d), 61.48 (d), 61.65 (s), 61.86 (s), 126.08 (d), 126.28 (d), 130.50 (d), 130.54 (d), 132.24 (d), 133.02 (d), 220.97 (s), 221.66 (s); IR $v_{\text{max}}$ = 3054, 2922, 2837, 1723, 1627, 1435, 1271, 1151, 1107, 1017 cm$^{-1}$;
accurate mass (ESI, Q-ToF) m/z: calculated for C_{23}H_{24}NaO_2 [M+Na]^+ 355.1669, found: 355.1669.

**Synthesis of compound 16a**

white solid, 98% (29.90 mg, starting with 30.0 mg of bis-RCM product 15a)
Mp 163-165 °C; R_{f} = 0.63 (silica gel, 10% EtOAc-petroleum ether); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta = 0.36\) (ABq, \(J = 12.7\) Hz, 1H), 1.34-1.46 (m, 3H), 1.51-1.62 (m, 4H), 1.64-1.95 (m, 15H), 2.32-2.45 (m, 4H), 2.61-2.65 (m, 1H), 2.97 (t, \(J = 8.6\) Hz, 1H), 3.31-3.38 (m, 1H); \(^1\)C NMR (125 MHz, CDCl\(_3\)) \(\delta = 25.62\) (t), 25.69 (t), 25.94 (t), 26.77 (t), 30.35 (t), 30.82 (t), 34.45 (t), 37.61 (t), 38.43 (t), 38.77 (t), 42.71 (t), 50.45 (d), 52.64 (d), 53.26 (d), 56.64 (d), 59.06 (d), 60.72 (d), 63.31 (s), 63.51 (s), 69.60 (s), 223.05 (s), 226.43 (s); IR \(\nu_{\text{max}} = 2928, 2861, 1725, 1627, 1459, 1268, 1122, 1073, 1044\) cm\(^{-1}\); accurate mass (ESI, Q-ToF) m/z: calculated for C_{23}H_{30}NaO_2 [M+Na]^+ 361.2138, found: 361.2131.

**Synthesis of compound 14b**

white solid, 60% (65.0 mg, starting with 67.0 mg of pentacyclic dione 3b)
Mp 149-151 °C; R_{f} = 0.40 (silica gel, 10% EtOAc-petroleum ether); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 0.55\) (ABq, \(J = 12.8\) Hz, 1H), 1.42-1.55 (m, 1H), 1.58-1.64 (m, 1H), 1.83-1.94 (m, 4H), 2.04-2.17 (m, 2H), 2.20-2.22 (d, \(J = 7.4\) Hz, 2H), 2.29-2.46 (m, 6H), 2.57-2.60 (m, 1H), 3.31 (s, 3H), 3.38-3.44 (m, 1H), 3.51-3.54 (m, 1H), 3.60 (t, \(J = 8.3\) Hz, 1H), 4.92-5.09 (m, 8H), 5.51-5.62 (m, 2H), 5.70-5.80 (m, 2H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 30.73\) (t), 31.98 (t), 32.24 (t), 34.53 (t), 34.95 (t), 36.88 (t), 38.84 (t), 48.84 (d), 50.06 (d), 50.26 (d), 51.09 (d), 56.30 (d), 57.74 (q), 58.74 (s), 59.13 (s), 61.66 (d), 73.01 (s), 86.97 (d), 118.15 (t), 118.27 (t), 118.31 (t), 133.09 (d), 133.28 (d), 134.01 (d), 221.34 (s), 223.00 (s); IR \(\nu_{\text{max}} = 3073, 2923, 1724, 1638, 1441, 1266, 1161, 1109, 1020\) cm\(^{-1}\); accurate mass (ESI, Q-ToF) m/z: calculated for C_{28}H_{37}O_3 [M+H]^+ 421.2743, found: 421.2761.
Synthesis of compound 15b

white solid, 92% (40.0 mg, starting with 50.0 mg of tetra-allyl pentacyclic dione 14b)

Mp 138-140 °C; Rf = 0.38 (silica gel, 10% EtOAc-petroleum ether); ¹H NMR (500 MHz, CDCl₃) δ = 0.27 (ABq, J = 12.8 Hz, 1H), 1.54-1.64 (m, 2H), 1.86-1.95 (m, 2H), 2.06-2.11 (m, 1H), 2.14-2.20 (m, 2H), 2.20-2.24 (m, 5H), 2.48-2.55 (m, 2H), 2.67-2.72 (m, 3H), 3.32 (s, 3H), 3.36-3.42 (m, 1H), 3.58-3.63 (m, 2H), 5.43-5.45 (m, 2H), 5.66-5.67 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ = 30.93 (t), 32.13 (t), 34.65 (t), 37.02 (t), 37.90 (t), 44.55 (t), 45.16 (t), 49.80 (d), 51.04 (d), 52.77 (d), 53.42 (d), 56.04 (d), 57.91 (q), 60.69 (d), 61.77 (s), 61.87 (s), 72.60 (s), 88.19 (d), 126.29 (d), 126.48 (d), 130.27 (d), 130.50 (d), 221.07 (s), 224.30 (s); IR νmax = 3057, 2927, 2854, 1731, 1422, 1265, 1114, 1044 cm⁻¹; accurate mass (ESI, Q-ToF) m/z: calculated for C₂₄H₂₉O₃ [M+H]+ 365.2100, found: 365.2064.

Synthesis of compound 16b

white solid, 99% (30.0 mg, starting with 30.0 mg of bis-RCM product 15b)

Mp 112-114 °C; Rf = 0.48 (silica gel, 10% EtOAc-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ = 0.36 (ABq, J = 12.7 Hz, 1H), 1.33-1.45 (m, 2H), 1.49-1.64 (m, 12H), 1.67-1.77 (m, 2H), 1.80-1.91 (m, 4H), 2.04-2.10 (m, 1H), 2.33-2.42 (m, 3H), 2.60-2.65 (m, 1H), 3.29 (s, 3H), 3.32-3.37 (m, 1H), 3.47-3.60 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ = 25.51 (t), 25.68 (t), 25.86 (t), 25.94 (t), 30.33 (t), 30.99 (t), 31.26 (t), 31.89 (t), 34.79 (t), 38.28 (t), 38.66 (t), 50.06 (d), 51.26 (d), 52.16 (d), 53.29 (d), 56.08 (d), 57.95 (q), 61.07 (d), 63.53 (s), 63.74 (s), 72.77 (s), 87.98 (d), 223.04 (s), 225.98 (s); IR νmax = 2927, 2867, 1724, 1449, 1265, 1114, 1044 cm⁻¹; accurate mass (ESI, Q-ToF) m/z: calculated for C₂₄H₃₃O₃ [M+H]+ 369.2400, found: 369.2373.
Synthesis of compound 14c

Colorless semi-solid, 70% (95.0 mg, starting with 80.0 mg of pentacyclic dione 3c)  
$R_f = 0.56$ (silica gel, 10% EtOAc-petroleum ether): $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 0.58$ (ABq, $J = 12.8$ Hz, 1H), 1.53-1.62 (m, 1H), 1.65-1.72 (m, 2H), 1.73-1.84 (m, 2H), 1.84-1.97 (m, 5H), 2.23 (t, $J = 7.0$ Hz, 4H), 2.32-2.43 (m, 3H), 2.44-2.50 (m, 1H), 2.58-2.62 (m, 1H), 3.04 (t, $J = 8.2$ Hz, 1H), 3.40-3.47 (m, 1H), 4.95-5.19 (m, 8H), 5.52-5.65 (m, 2H), 5.70-5.80 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta = 26.83$, 31.90, 34.80, 34.95, 37.49, 38.86, 38.95, 42.33, 49.46, 50.50, 51.00, 57.11, 57.81, 58.64, 58.98, 61.16, 69.80, 118.30, 118.33, 118.45, 133.02, 133.09, 134.01, 221.28, 224.09; IR $\nu_{max} = 2955, 2928, 2857, 1731, 1464, 1380, 1274, 1124, 1073$ cm$^{-1}$; accurate mass (ESI, Q-ToF) $m/z$: calculated for C$_{27}$H$_{35}$O$_2$ [M+H]$^+$ 391.2637, found: 391.2795.

Synthesis of compound 15c

White solid, 91% (32.0 mg, starting with 41.0 mg of tetra-allyl pentacyclic dione 14c)  
Mp 175-177 °C; $R_f = 0.50$ (silica gel, 10% EtOAc-petroleum ether): $^1$H NMR (500 MHz, CDCl$_3$) $\delta = 0.26$ (ABq, $J = 12.8$ Hz, 1H), 1.57-1.63 (m, 1H), 1.64-1.71 (m, 2H), 1.76-1.83 (m, 2H), 1.84-1.97 (m, 3H), 2.12-2.20 (m, 2H), 2.32-2.45 (m, 3H), 2.48-2.61 (m, 3H), 2.68-2.75 (m, 3H), 3.04 (q, $J = 8.2$ Hz, 1H), 3.37-3.43 (m, 1H), 5.43-5.46 (m, 2H), 5.66-5.70 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta = 27.00$ (t), 34.25 (t), 37.02 (t), 37.50 (t), 37.89 (t), 43.26 (t), 44.69 (t), 45.20 (t), 50.20 (d), 53.01 (d), 53.36 (d), 56.53 (d), 58.82 (d), 60.34 (d), 61.56 (s), 61.64 (s), 69.41 (s), 126.17 (d), 126.26 (d), 130.55 (d), 130.56 (d), 221.00 (s), 224.58 (s); IR $\nu_{max} = 3054, 2925, 2854, 1724, 1622, 1459, 1269, 1124$ cm$^{-1}$; accurate mass (ESI, Q-ToF) $m/z$: calculated for C$_{23}$H$_{27}$O$_2$ [M+H]$^+$ 335.2011, found: 335.1969.
Synthesis of compound 14d

white solid, 67% (127 mg, starting with 100 mg of pentacyclic dione 3a)
Mp 101-103 °C; Rf = 0.69 (silica gel, 10% EtOAc-petroleum ether); ¹H NMR (500 MHz, CDCl₃) δ = 0.99, 1.02 (ABq, J = 14.6 Hz, 1H), 1.99-2.61 (m, 16H), 3.21-3.28 (m, 2H), 4.98-5.47 (m, 10H), 5.46-5.47 (br, 1H), 5.53-5.62 (m, 3H), 5.76-5.81 (m, 2H), 5.89-5.91 (br, 1H); ¹³C NMR (100.8 MHz, CDCl₃) δ = 32.63, 34.28, 34.70, 35.84, 36.84, 37.86, 38.65, 50.26, 50.79, 52.84, 53.00, 56.83, 58.07, 59.30, 65.10, 118.43, 118.52, 118.57, 118.64, 118.81, 132.75, 132.91, 133.39, 133.84, 134.01, 134.66, 135.19, 220.24, 222.72; IR v_max = 1639, 1727, 2930 cm⁻¹; accurate mass (ESI, Q-ToF) m/z: calculated for C₃₀H₃₆NaO₂ [M+Na]⁺ 451.2608 found: 451.2610.

Synthesis of compound 15d

white solid, 85% (44 mg, starting with 60 mg of peta-allyl pentacyclic dione 14d)
Mp 116-118 °C; Rf = 0.66 (silica gel, 10% EtOAc-petroleum ether); ¹H NMR (500 MHz, CDCl₃) δ = 0.64, 0.70 (ABq, J = 12.7 Hz, 1H), 1.62-1.99 (m, 1H), 2.16-2.30 (m, 4H), 2.37-2.50 (m, 3H), 2.51-2.69 (m, 6H), 2.72-2.80 (m, 2H), 3.20-3.29 (m, 2H), 5.01-5.06 (m, 2H), 5.45-5.49 (m, 3H), 5.53-5.59 (m, 1H), 5.61-5.72 (m, 2H), 5.89-5.92 (m, 1H); ¹³C NMR (100.8 MHz, CDCl₃) δ = 34.39, 35.40, 36.98, 37.32, 39.44, 44.17, 47.37, 52.46, 52.86, 53.79, 53.84, 57.74, 61.31, 61.97, 65.15, 76.34, 118.62, 126.06, 126.48, 129.77, 130.58, 134.13, 135.20, 220.11, 225.18; IR v_max = 1621, 1637, 1730, 2845, 2922 cm⁻¹; accurate mass (ESI, Q-ToF) m/z: calculated for C₂₆H₂₈NaO₂ [M+Na]⁺ 395.1982, found: 395.1983.
Synthesis of compound 16d

![Chemical structure](image)

white solid, 97% (33 mg, starting with 35 mg of bis-RCM product 16d)

Mp 135-136 °C; $R_f = 0.68$ (silica gel, 10% EtOAc-petroleum ether). $^1$H NMR (500 MHz, CDCl$_3$) $\delta = 0.71, 0.77$ (ABq, $J = 12.6$ Hz, 1H), 0.88-0.92 (m, 3H), 1.02-1.07 (m, 1H), 1.20-1.27 (m, 2H), 1.77-1.95 (m, 24H), 2.24 (d, $J = 8.0$ Hz, 1H), 2.37-2.44 (m, 2H), 3.01 (t, $J = 7.8$ Hz, 1H), 3.21 (t, $J = 8.4$ Hz, 1H); $^{13}$C NMR (100.8 MHz, CDCl$_3$) $\delta = 15.04, 19.65, 25.42, 25.57, 25.72, 25.89, 27.19, 27.54, 30.87, 32.98, 35.11, 35.64, 38.83, 39.52, 40.12, 51.56, 52.31, 55.92, 55.97, 59.41, 62.59, 64.32, 65.24, 69.91, 226.13; IR $\nu_{max} = 1720, 2869, 2956$ cm$^{-1}$; accurate mass (ESI, Q-ToF) $m/z$: calculated for C$_{26}$H$_{36}$NaO$_2$ [M+Na]$^+$ 403.2608, found: 403.2608.

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