Supporting Information

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Transannular Radical Cascade
as a New Approach to the Synthesis
of Linear Triquinane

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Supplementary Material Available: Summary of procedures and characterization data for 6 (from but-3-yn-1-ol), 7, 8, 9, 5, 10, 3, 1, 11 and all the intermediacy products (19 pages).
Procedures and characterization data :

**Methyl 5-tert-butyldimethylsilyloxy pent-2-ynoate** : To a solution of DMAP (1.22 g, 0.1 eq.) and TBSCl (15.8g, 1.1 eq.) at 0°C in CH₂Cl₂ was added a molar solution of but-3-yne-1-ol (100 mmol). Then Et₃N (15.3 mL, 1.1 eq.) was added dropwise and the reaction mixture was allowed to warm up to room temperature for 30 min. The organic layer was diluted and washed with a saturated solution of NH₄Cl then with brine, dried with MgSO₄ and the solvent was evaporated under reduced pressure. This crude product was then diluted in 500 mL of THF and cooled to -78°C and n-butyllithium (1.4 M, 1.05 eq. 75 ml) was added in 15 min. The reaction mixture was allowed to stay at -78°C for 1.5 h and methylchloroformate (1.1 eq. 8.5 mL) was added dropwise. Warming up slowly to room temperature, the mixture was quenched with a saturated solution of NH₄Cl, diluted with diethyl ether, washed with brine and dried with MgSO₄. The solvent was evaporated under reduced pressure. Filtration through a short pad of silica gel afforded the pentynoate (24 g, 99 mmol) in almost quantitative yield. Yellow oil. Rₓ=0.32, (eluant : AcOEt/ PE : 2/98). ¹H, ¹³C NMR and IR spectra were in total accordance with those previously described by Thomas E. J. et al. *J. Chem. Soc. Perkin Trans I*, 1998, 2853-2864. Elementary analysis calcd (%) for C₁₂H₂₂O₃Si (M=242.391 g.mol⁻¹) : C 59.46, H 9.15 ; found : C 59.44, H 9.20.

**(2E)Methyl 5-tert-butyldimethylsilyloxy-3-thiophenyl pent-2-enoate** : Sodium thiophenate solution was prepared by addition, at 0°C, of small pieces of sodium (1.1g) to a solution of thiophenol (4.95 mL, 1 eq.) in 48mL of methanol. To a solution of previous ynoate (11.65 g, 48 mmol) in 240 mL of MeOH at 0°C was added via canula the freshly prepared thiophenate solution. After stirring for
30 min, the mixture was diluted with ethyl ether, washed successively with a solution of NaOH 1M, a saturated solution of NH₄Cl and brine. The organic layer was dried with MgSO₄, filtered and the solvent was removed under reduce pressure. The crude residue was purified by flash chromatography on silica gel to yield 10.65 g of expected thioenoate. Yield = 62%, ¹H NMR (CDCl₃, 400 MHz) δ = 7.55 (dd, 2H, J=7.6 and 2.0 Hz), 7.40 (m, 1H + 2H), 5.94 (s, 1H), 3.78 (s, 3H), 3.56 (t, 2H, J=6.8 Hz), 2.37 (t, 2H, J=6.4 Hz), 0.83 (s, 9H), 0.04 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ = 166.7, 158.2, 136.0, 131.2, 129.7 (2C), 129.6 (2C), 113.5, 62.2, 51.5, 39.9, 26.2 (3C), 18.5, -5.1 (2C).

(2E)Methyl 5-tert-butyldimethylsilyloxy-3-methyl pent-2-enoate: methyl grignard (46mL, 3.25 molL⁻¹, 5eq.) was added dropwise at -78°C under argon atmosphere, on a solution of CuBr.Me₂S (12.24 g, 2 eq.) in 280 mL of THF. After stirring for 30 minutes, a solution of the thioenoate (29.8 mmol) in 95 mL of THF was canulated. After stirring for 3 h at -78°C, the reaction mixture was quenched with a saturated solution of NH₄Cl/NH₄OH (2/1). After dilution with ethyl ether, the temperature was allowed to reach the room temperature. Organic layer was washed with a saturated solution of NH₄Cl/NH₄OH (2/1) and then, with brine, dried with MgSO₄, filtered and the solvent was removed under reduce pressure. Enoate (7.6 g) was obtained in quantitative yield as a yellow oil. ¹H NMR (CDCl₃, 400 MHz) δ = 5.71 (s, 1H), 3.77 (t, 2H, J=6.6 Hz), 3.71 (s, 3H), 2.37 (t, 2H, J=6.6 Hz), 2.21 (s, 3H), 0.90 (s, 9H), 0.06 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ = 166.9, 157.2, 116.7, 61.2, 50.6, 43.9, 25.8 (3C), 19.0, 16.2, -5.5 (2C); IR (neat), cm⁻¹ 2940, 2920, 2840, 1720, 1640, 1150, 1100, 830, 770.
(2E)\textit{5-tert-butyldimethylsilyloxy-3-methyl pent-2-en-1-ol}:
To a solution of LiAlH$_4$ (565 mg, 0.5 eq.) in 120 mL of Et$_2$O at -30°C was added via canula a solution of previous pentenoate (29.7 mmol). After stirring for 20 min, another portion of LiAlH$_4$ (565 mg, 0.5 eq.) was added and led to the completion of reaction after 1h. The diluted reaction mixture was then quenched with a saturated solution of Na$_2$SO$_4$ and filtered through a short pad of Celite. The white salts were carefully washed several times with AcOEt. The solvents were evaporated under reduced pressure. Purification by flash chromatography on silica gel (eluant: AcOEt/PE: 2/8) afforded the pentenol in quantitative yield, as a yellow oil. $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ = 5.46 (t, 1H, $J$=7.1 Hz), 4.17 (m, 2H), 3.72 (t, 2H, $J$=7.1 Hz), 2.26 (t, 2H, $J$=7.1 Hz), 1.72 (s, 3H), 0.91 (s, 9H), 0.07 (s, 6H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ = 137.0, 125.2, 62.1, 59.4, 42.8, 26.0 (3C), 16.7, 16.0, -5.3 (2C); IR (neat), cm$^{-1}$ 3330, 2980, 2920, 2860, 1670, 1470, 1380, 1250, 1100, 1070, 845, 775, 665; Elementary analysis calcd (%) for C$_{12}$H$_{26}$O$_2$Si (M=230.42 g.mol$^{-1}$) : C 62.55, H 11.37; found : C 62.60, H 11.26.

(2E)\textit{1-tert-butyldimethylsilyloxy-5-chloro-3-methyl pent-3-ene}:
To a solution of previous alcohol (43 mmol) and 2,6-lutidine (8.25 mL, 1.65 eq) in 40 mL of DMF at 0°C was added at once anhydrous LiCl (2.71 g, 1.5 eq.). Then MsCl (5 mL, 1.5 eq.) was added dropwise. After 2h at 0°C, the reaction mixture was dropped into cooled water. The aqueous layer was washed with a 1 to 1 Et$_2$O/pentane mixture. The organic layer was washed with brine, dried with Na$_2$SO$_4$, concentrated. The crude was purified by flash chromatography to afford the desired allylic alcohol as a colorless oil.
(4E) \textbf{Ethyl 7-\textit{tert}-butyldiméthylsilyloxy-2,2,5-triméthyl hept-4-ènoate}: The crude oil thus obtained, was diluted in 60 mL of THF and added via canula to a solution of enolate in 150 mL of THF at \(-78^\circ\text{C}\). The enolate had been previously prepared by addition via syringe pump (3.54 mL/h) of ethyl isobutyrate (7.46 mL, 1.3 eq.) in 2 mL of THF, at \(-78^\circ\text{C}\), over a LDA solution \([\text{prepared at } 0^\circ\text{C from } n\text{-butyllithium (1.42 M, 38.15 mL, 1.26 eq.) and diisopropylamine (7.82 mL, 1.3 eq.)}]\) followed by a one hour-stirring period. After one night at \(-20^\circ\text{C}\), the organic layer was diluted and washed with a saturated solution of \(\text{NH}_4\text{Cl}\) then with brine, dried with MgSO\(_4\) and the solvent was evaporated under reduced pressure. Purification by flash chromatography on silica gel \(\text{eluant: Et}_2\text{O/PE: 1/99}\) furnished in a 85% yield, 12.43 g of heptenoate as pure \(\text{E}\) isomer. \(^1\text{H NMR (CDCl}_3, 400 \text{MHz}) \delta = 5.14 \text{ (t, 1H, } J=7.6 \text{ Hz)}, 4.12 \text{ (q, 2H, } J=7.1 \text{ Hz)}, 3.66 \text{ (t, 2H, } J=6.6 \text{ Hz)}, 2.23 \text{ (m, 4H)}, 1.63 \text{ (s, 3H)}, 1.25 \text{ (t, 3H, } J=7.1 \text{ Hz)}, 1.17 \text{ (s, 6H)}, 0.90 \text{ (s, 9H)}, 0.05 \text{ (s, 6H)}; \(^{13}\text{C NMR (CDCl}_3, 100 \text{ MHz}) \delta = 177.0, 134.9, 121.9, 62.5, 60.3, 43.4, 42.7, 38.6, 26.0, 24.8, 18.4, 16.7, 14.3, -5.3; \text{IR (neat), cm}^{-1} 2970, 2960, 2920, 1725, 1465, 1380, 1305, 1250, 1090, 830, 770; \text{Anal. for } \text{C}_{18}\text{H}_{36}\text{O}_3\text{Si calcd C: } 65.85\%; \text{H: } 10.98\%; \text{found C: } 65.20\%; \text{H: } 11.15\%.

(4E)-7-\textit{tert}-butyldiméthylsilyloxy-2,2,5-triméthyl \textbf{hept-4-enol}: To a suspension of LiAlH\(_4\) (306 mg, 0.5 eq.) in 14 mL of Et\(_2\)O at \(0^\circ\text{C}\), was added via canula a 26 mL THF solution of the heptenoate (5.27 g, 16.1 mmol). After stirring at room temperature for 20 min, another portion of LiAlH\(_4\) (306 mg, 0.5 eq.) was added and led to the completion of reaction after 1h. The reaction mixture was then quenched with a saturated solution of Na\(_2\)SO\(_4\) and filtered through a short pad of Celite. The white salts were carefully washed several times with AcOEt. The solvents were evaporated
under reduced pressure to give the expected alcohol as a yellow oil (Rf = 0.29 with Et₂O/PE: 2/80). ³¹H NMR (CDCl₃, 400 MHz) δ = 5.28 (t, 1H, J=7.6 Hz), 3.69 (t, 2H, J=7.1 Hz), 3.33 (d, 2H, J=6.1 Hz), 2.24 (t, 2H, J=7.1 Hz), 1.97 (d, 2H, J=7.6 Hz), 1.65 (s, 3H), 0.90 (2s, 9H+ 6H), 0.06 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ = 134.2, 122.7, 71.9, 62.4, 45.4, 37.0, 36.3, 26.0 (3C), 23.9 (2C), 18.4, 16.5, −5.2 (2C); IR (neat), cm⁻¹ 3360, 2940, 2920, 2840, 1660, 1465, 1380, 1355, 1250, 1090, 1040, 905, 830, 770, 730; Anal. for C₁₆H₃₃O₂Si calcd C: 67.13%; H: 11.89%, found C: 64.88%; H: 11.85%.

(4E)-7-tert-butyldimethylsilyloxy-2,2,5-trimethyl hept-4-enal (6): The crude alcohol was then submitted to a classical Swern oxidation. A solution of (COCl)₂ (1.8 mL, 1.3 eq.) in 50 mL anhydrous CH₂Cl₂ was cooled to −78°C and treated with a solution of DMSO (3 mL, 2.6 eq.) in CH₂Cl₂. After 10 min, a molar solution of alcohol (15.73 mmol) in CH₂Cl₂ was added. After 10 min, triethylamine (11.0 mL, 5 eq.) was introduced, and the mixture was allowed to react at room temperature until complete at TLC (15 min.). The reaction was then quenched with a saturated NH₄Cl solution and extracted with CH₂Cl₂. The combined organic phases were washed with brine (3x), dried on MgSO₄ and concentrated. Chromatography of the residue (elution with 5% ether in petroleum ether) afforded 4.26 g (93% on two steps) of the aldehyde as a yellow oil (Rf = 0.86 with Et₂O/PE: 2/80). ¹H NMR (CDCl₃, 400 MHz) δ = 9.50 (s, 1H), 5.14 (t, 1H, J=7.6 Hz), 3.67 (t, 2H, J=7.1 Hz), 2.23 (t, 2H, J=7.1 Hz), 2.18 (d, 2H, J=7.6 Hz), 1.64 (s, 3H), 1.06 (s, 6H), 0.91 (s, 9H), 0.06 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ = 206.2, 135.6, 120.5, 62.2, 46.5, 43.2, 35.3, 25.9 (3C), 21.1 (2C), 18.3, 16.5, −5.3 (2C); IR (neat), cm⁻¹ 2970, 2960, 2920, 2965, 1725, 1465, 1380, 1250,
Ethyl 9-tert-butyldimethylsilyloxy-4,4,7-trimethyl-nona-2,6-dienoate: To a solution of 1.94 g (1.44 eq) of dried LiCl in MeCN (15 mL), was added 7.65 mL (1.2 eq) of triethyl phosphonoacetate. Then, at 0°C, 5.9 mL (1.32 eq) of Et₃N in 10 mL of MeCN was added via canula and the mixture was allowed to stir 10 min before adding the aldehyde (32 mmol) in 13 mL of MeCN. After stirring overnight at room temperature, the thick mixture was quenched with a 5% HCl solution and the aqueous layer was extracted 3 times with Et₂O. The organic layer was then washed with brine, dried with MgSO₄ and the solvents were evaporated under reduced pressure. The crude residue was purified by flash chromatography on silica gel (Rf = 0.40 eluant: AcOEt/PE: 3/97) and yielded 8.96 g of the expected dienoate. Yield = 79%, yellow oil. ¹H NMR (CDCl₃, 400 MHz) δ = 6.96 (d, 1H, J=16.0 Hz), 5.73 (d, 1H, J=16Hz), 5.15 (t, 1H, J=7.6Hz), 4.21 (q, 2H, J=7.1 Hz), 3.67 (t, 2H, J=7.1 Hz), 2.23 (t, 2H, J=7.1 Hz), 2.07 (d, 2H, J=7.6 Hz), 1.61 (s, 3H), 1.32 (t, 3H, J=7.1 Hz), 1.06 (s, 6H), 0.91 (s, 9H), 0.06 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ = 167.2, 158.3, 134.8, 122.0, 117.7, 62.5, 60.3, 43.4, 40.1, 37.7, 26.0 (3C+2C), 18.4, 16.7, 14.4, -5.1 (2C); IR (neat), cm⁻¹ 2960, 2920, 2840, 1720, 1645, 1465, 1305, 1250, 1170, 1100, 840, 770.

Ethyl 9-hydroxy-4,4,7-trimethyl-nona-2,6-dienoate (7): To a solution of previous ester (22.4 mmol) in 50 mL of THF was added 23.5 mL of Bu₄NF solution (1.05 eq, 1M). After completion of the reaction, the mixture was diluted with diethyl ether (150 mL) and quenched with a saturated solution of NH₄Cl. The organic layer was washed with brine,
dried with MgSO₄ and the solvent was evaporated under reduced pressure. A rapid filtration on silica gel (RF = 0.35 with AcOEt/PE: 25/75) furnished 4.91 g of dienoate (7). Yield = 91%; colorless oil; ¹H NMR (CDCl₃, 400 MHz) δ = 6.96 (d, 1H, J=16.0 Hz), 5.73 (d, 1H, J=16 Hz), 5.23 (t, 1H, J=7.6Hz), 4.21 (q, 2H, J=7.1 Hz), 3.68 (q, 2H, J=6.1 Hz), 2.29 (t, 2H, J=6.1 Hz), 2.12 (d, 2H, J=7.6 Hz), 1.61 (s, 3H), 1.32 (t, 3H, J=7.1 Hz), 1.08 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ = 167.3, 158.1, 134.1, 123.3, 117.9, 60.4 (2C), 43.1, 40.1, 37.7, 26.2 (2C), 16.1, 14.4; IR (neat), cm⁻¹ 3420 (br), 2960, 2930, 2875, 1710, 1650, 1385, 1365, 1305, 1180, 1040, 915, 865, 730; Anal. for C₁₄H₂₄O₃ calcd C: 69.96%; H: 10.07%, found C: 69.95%; H: 10.02%.

(2E,6E) Ethyl 9-oxo-4,4,7-trimethyl undeca-2,6-dienoate:
To a solution of 17.7 mmol of alcohol (7) in 325 mL of CH₂Cl₂ was added at once 9.0 g (1.2 eq) of Dess–Martin periodinane. After 30 min., the mixture was diluted with diethyl ether and quenched by adding a saturated solution of NaHCO₃ as well as a saturated solution of Na₂S₂O₃. The organic layer was washed with brine, dried with MgSO₄ and the solvents were evaporated under reduced pressure. The crude residue was purified by simple filtration on desactivated alumina (10% water) (eluant: AcOEt/PE: 1/9) to furnish a yellow oil.

(2E,6E) Ethyl 11-trimethylsilyl-9-hydroxy-4,4,7-trimethyl-undeca-2,6-dien-10-ynoate (8):
To a solution of anhydrous CeCl₃ (6.55 g, 1.5 eq) in 115 mL of THF was added the crude aldehyde in 35 mL of THF. After 75 min. the temperature was decreased to -78°C and a solution of trimethylsilylacetylide in 75 mL of THF was added via canula. The acetylide had been previously prepared by addition of 16.6 mL of BuLi (1.5 eq, 1.6M in hexane) to a solution of 4.64
mL of trimethylsilylacetylene (1.75 eq) in 75 mL of THF at -78°C and by stirring this mixture at the same temperature for 90 min. After 12 hours at -78°C, the reaction mixture was diluted with diethyl ether (700 mL) and quenched with a saturated solution of NH₄Cl. The aqueous layer was filtered on Celite and the brown salts were washed with ethyl acetate. The aqueous layer was extracted once more with diethyl ether. Organic layers were washed with brine, dried with MgSO₄ and the solvents were evaporated under reduced pressure. The crude residue was purified by flash chromatography on silica gel (eluant: AcOEt/PE: 1/9) and yielded 4.73 g of ynol (8). Yield=79% (on two steps), yellow oil. Rf = 0.3, (eluant: AcOEt/PE: 1/9); 1H NMR (CDCl₃, 400 MHz) δ = 6.79 (d, 1H, J=16.0 Hz), 5.56 (d, 1H, J=16Hz), 5.12 (t, 1H, J=7.6Hz), 4.27 (t, 1H, J=6.6 Hz), 4.03 (q, 2H, J=7.1 Hz), 2.27 (d, 2H, J=6.6 Hz), 1.93 (d, 2H, J=7.6 Hz), 1.50 (s, 3H), 1.14 (t, 3H, J=7.1 Hz), 0.90 (s, 6H), 0.00 (s, 9H); 13C NMR (CDCl₃, 100 MHz) δ = 167.3, 158.1, 133.1, 124.9, 117.9, 106.9, 89.4, 61.2, 60.4, 48.3, 40.3, 37.8, 26.2 (2C), 16.8, 14.4, 0.0 (3C); IR (neat), cm⁻¹ 3420 (br), 2960, 2930, 2170, 1710, 1645, 1385, 1365, 1305, 1250, 1170, 1040, 850, 760 ; Anal. for C₁₉H₃₂O₃Si calcd C: 67.81%; H: 9.58%, found C: 67.67%; H: 9.71%.

(2E,6E) Ethyl 19-hydroxy-4,4,7-trimethyl-undeca-2,6-dien-10-ynoate : To a solution of 14.06 mmol of alkyne (8) in 350 mL of EtOH was added at 0°C 15.52 g of K₂CO₃ (8 eq). After stirring overnight at room temperature, the reaction mixture was quenched with brine and the aqueous layer was extracted 3 times with CH₂Cl₂ (150 mL). Then the organic layer was dried with MgSO₄ and the solvents were evaporated under reduced pressure. The crude residue was rapidly filtrated on silica gel to afford the expected alkyne. 1H NMR (CDCl₃, 400 MHz) δ = 6.96 (d, 1H, J=16.0 Hz), 5.73 (d,
$^{1}$H, $J=16$ Hz), 5.30 (t, 1H, $J=7.6$ Hz), 4.48 (m, 1H), 4.21 (q, 2H, $J=7.1$ Hz), 2.49 (d, 1H, $J=2$ Hz), 2.45 (d, 2H, $J=6.7$ Hz), 2.12 (d, 2H, $J=7.6$ Hz), 1.68 (s, 3H), 1.32 (t, 3H, $J=7.1$ Hz), 1.08 (s, 6H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta = 167.3$, 158.0, 132.7, 125.0, 117.9, 84.9, 73.1, 60.6, 60.4, 48.2, 40.3, 37.7, 26.3, 26.1, 16.6, 14.3; IR (neat), cm$^{-1}$ 3440, 3300, 2960, 2940, 2120, 1715, 1650, 1460, 1385, 1365, 1310, 1190.

(2E,6E) Ethyl 9-tert-butyldimethylsilyloxy-4,4,7-triméthyl-undeca-2,6-dien-10-ynoate (9): The crude alcohol is added to a 17 mL DMF solution of imidazole (1.91 g, 2.0 eq.). At 0°C, under argon atmosphere, TBSCl (2.23 g, 1.05 eq.) is added dropwise via a canula. The reaction mixture was diluted with diethyl ether and quenched with a saturated solution of NaCl. The organic layer was washed twice, with water and brine, dried with MgSO$_4$ and the solvents were evaporated under reduced pressure. The crude residue was purified by flash chromatography on silica gel (eluant: AcOEt/PE: 2/98) to furnish 4.41 g of the expected alkyne (9). Yield=83%(on two steps), colorless oil. $R_f$ = 0.6, (eluant: AcOEt/PE: 1/9); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta = 6.97$ (d, 1H, $J=16.0$ Hz), 5.73 (d, 1H, $J=16$Hz), 5.24 (t, 1H, $J=7.6$Hz), 4.44 (t, 1H, $J=6.6$ Hz), 4.20 (q, 2H, $J=7.1$ Hz), 2.41 (d, 1H, $J=2.1$ Hz), 2.38 (d, 2H, $J=6.6$ Hz), 2.08 (td, 2H, $J=7.6$ Hz, $J=2$Hz), 1.64 (s, 3H), 1.31 (t, 3H, $J=7.1$ Hz), 1.07 (s, 6H), 0.91 (s, 9H), 0.10 (s, 6H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta = 167.3$, 158.0, 132.9, 124.1, 117.8, 85.4, 72.7, 62.2, 60.1, 49.0, 40.2, 37.6, 26.1 (2C), 25.8 (3C), 18.1, 16.9, 14.3, -4.7, -5.1; IR (neat), cm$^{-1}$ 3300, 2940, 2920, 2840, 2100, 1715, 1640, 1380, 1360, 1250, 1160, 1080, 830, 770; Anal. for C$_{22}$H$_{38}$O$_3$Si calcd C: 69.79%; H: 10.12%, found C: 69.23%; H: 10.29%.
(2E,6E) 9-tert-butyldimethylsilyloxy-4,4,7-trimethyl
undeca-2,6-dien-10-ynol: To a solution of 11.36 mmol of
ester (9) in 22 mL of CH₂Cl₂ was added 25 mL of DiBAI-H
(2.2 eq, 1M in hexane) at -78°C. After 90 min. at room
temperature, 22 mL of a saturated solution of potassium and
sodium tartrate (Rochelle's salts) was added at once. Stirring
was maintained until two layers clearly appeared in the flask. The organic layer was washed with brine, dried with MgSO₄ and the solvents were evaporated under reduced pressure. The crude residue was purified by flash chromatography on silica gel (eluant: AcOEt/PE: 13/87) and yielded 3.18 g of alcohol. Yield=83%, yellow oil. Rₜ= 0.25,
(eluant: AcOEt/PE: 1/9); ¹H NMR (CDCl₃, 400 MHz) δ = 5.70
(d, 1H, J=16.0 Hz), 5.56 (dt, 1H, J=16Hz, J=6.1 Hz), 5.28
(t, 1H, J=7.6Hz), 4.45 (td, 1H, J=6.6 Hz, J=2.1 Hz), 4.12
(t, 2H, J=6.1 Hz), 2.41 (d, 1H, J=2.1 Hz), 2.39 (d, 2H, J=7.6 Hz), 2.01 (t, 2H, J=6.6 Hz), 1.65 (s, 3H), 1.02 (s, 6H), 0.92 (s, 9H), 0.14 (s, 3H), 0.11 (s, 3H); ¹³C NMR
(CDCl₃, 50 MHz) δ = 142.8, 132.0, 125.2, 125.0, 85.7, 72.5,
64.1, 62.3, 49.0, 40.9, 36.6, 27.0, 26.8, 25.8 (3C), 18.3, 16.9, -4,6, -5.0; IR (neat), cm⁻¹ 3320 (br), 3300 (thin),
2940, 2920, 2860, 2100, 1665, 1465, 1380, 1360, 1250, 1090,
835, 775; Anal. for C₂₀H₃₆O₂Si calcd C: 71.37%; H: 10.78%,
found C: 71.29%; H: 10.77%.

(2E,6E) 9-tert-butyldimethylsilyloxy-4,4,7-trimethyl
undeca-2,6-dien-10-ynal: To a solution of 2.2 mmol of
previous alcohol in 39 mL of CH₂Cl₂ was added at once 1.11
g (1.2 eq) of Dess-Martin periodinane. After 30 min., the
mixture was diluted with diethyl ether and quenched by
adding a saturated solution of NaHCO₃ as well as a
saturated solution of Na₂S₂O₃. The organic layer was washed
with brine, dried with MgSO₄ and the solvents were
evaporated under reduced pressure. The crude residue was
purified by simple filtration on silica gel (eluant: AcOEt/PE: 1/9) to furnish 671 mg of the expected aldehyde. Yield=91%, yellow oil. Rf= 0.8, (eluant: AcOEt/PE: 1/9); \( ^1H \) NMR (CDCl\(_3\), 400 MHz) \( \delta = 9.51 \) (d, 1H, \( J=7.8 \) Hz), 6.82 (d, 1H, \( J=16.0 \) Hz), 6.04 (dd, 1H, \( J=16Hz, J=7.8 \) Hz), 5.24 (t, 1H, \( J=7.6Hz \)), 4.44 (td, 1H, \( J=6.6 \) Hz, \( J=2.1 \) Hz), 2.39 (d, 1H, \( J=2.1 \) Hz), 2.37 (d, 2H, \( J=7.6 \) Hz), 2.14 (m, 2H), 1.63 (s, 3H), 1.10 (s, 6H), 0.89 (s, 9H), 0.13 (s, 3H), 0.10 (s, 3H); \( ^{13}C \) NMR (CDCl\(_3\), 50 MHz) \( \delta = 194.4, 167.7, 133.5, 129.4, 123.6, 85.4, 72.7, 62.1, 48.8, 40.1, 38.3, 26.1 \) (2C), 25.8 (3C), 18.3, 16.9, \(-4.6, -5.1\); IR (neat), cm\(^{-1}\) 3300 (thin), 2960, 2920, 2840, 2720, 2100, 1690, 1630, 1460, 1385, 1360, 1250, 1100, 830, 775; Anal. for C\(_{20}\)H\(_{34}\)O\(_2\)Si calcd C: 71.80%; H: 10.24%, found C: 71.79%; H: 10.31%.

\( (2E, 6E) \) 9-tert-butyldimethylsilyloxy-11-iodo-4,4,7-trimethyl undeca-2,6-dien-10-ynal (5) : To a solution of 0.55 mmol of previous alkyne in 27 mL of acetone was added 186 mg of N-iodosuccinimide (1.5 eq) and 19 mg of silver nitrate (0.2 eq). After 30 min., the reaction mixture was diluted with diethyl oxide and washed with cold water. The organic layer was washed with brine, dried with Na\(_2\)SO\(_4\) and the solvents were evaporated under reduced pressure. Filtration on desactivated alumina (10%) afforded 244 mg of the expected iodoalkyne (5). Yield=96%, yellow oil. Rf= 0.35, (eluant: AcOEt/PE: 5/95); \( ^1H \) NMR (C\(_6\)D\(_6\), 400 MHz) \( \delta = 9.54 \) (d, 1H, \( J=7.6 \) Hz), 6.42 (d, 1H, \( J=16.0 \) Hz), 6.09 (dd, 1H, \( J=16Hz, J=7.6Hz \)), 5.22 (t, 1H, \( J=7.6Hz \)), 4.62 (t, 1H, \( J=6.6 \) Hz), 2.42 (d, 2H, \( J=6.6 \) Hz), 1.92 (m, 2H), 1.56 (s, 3H), 1.05 (s, 9H), 0.91 (s, 6H), 0.27 (s, 3H), 0.18 (s, 3H); \( ^{13}C \) NMR (C\(_6\)D\(_6\), 100 MHz) \( \delta = 193.0, 165.9, 133.3, 130.0, 124.0, 110.8, 96.1, 64.1, 49.0, 40.0, 37.8, 25.8 \) (5C), 18.2, 16.7, \(-4.5, -5.1\); IR (neat), cm\(^{-1}\) 2960, 2920, 2840,
2720, 2180, 1690, 1630, 1380, 1360, 1340, 1250, 1090, 840, 775; Anal. for C_{20}H_{33}O_{2}SiI calcd C: 52.17%; H: 7.22%,
found C: 53.03%; H: 7.60%.

(2E,6E) 9-tert-butyldimethylsilyloxy-4,4,7-trimethyl
cycloundeca-2,6-dien-10-yn-1-ol (10): To a suspension of
CrCl₂ (400 mg, 7.0 eq.) in 35 mL of anhydrous and degassed
THF, sonicated 30 minutes, was added a solution of the iodo
alkyne 5 (214 mg, 0.46 mmol) in THF (15 mL) via a syringe-
pump (15 mL/h). After overnight, the reaction was quenched
with a saturated NH₄Cl solution and diluted with ethyl
acetate. After 10 min stirring, the aqueous layer was
filtered on silica pad and residues were carefully washed
with ethyl acetate. The aqueous layer was extracted with
ethyl acetate. The organic layers were washed with brine,
dried over MgSO₄ and finally concentrated under vacuum to
give a yellow oil which was chromatographed (EE/PE : 5/95). Purification yielded 153 mg (88%) of the macrocycle
(10) as a 2 to 1 mixture of diastereomers.

¹H NMR (CDCl₃, 400 MHz) δ = major diastereomer: 5.60 (m,
1H₃ + 1H₂), 5.09 (t, 1H₆, J=7.1 Hz), 4.90 (m, 1H₁), 4.63 (t,
1H₉, J=6.1 Hz), 2.42 (dd, 1H₈, J=12.7 Hz, J=5.6 Hz), 2.36
(dd, 1H₈, J=12.7 Hz, J=6.6 Hz), 2.03 (d, 2H₅, J=8.1 Hz),
1.61 (s, 3H₇), 1.13 (s, 3H₄), 1.12 (s, 3H₄), 0.91 (s, 9H),
0.13 (s, 6H), minor diastereomer: 5.53 (dd, 1H₂, J=16.3 Hz,
J=7.1 Hz), 5.31 (d, 1H₃, J=16.3 Hz), 5.20 (dd, 1H₆, J=7.1
Hz, J=2.6 Hz), 4.90 (m, 1H₁), 4.59 (m, 1H₉), 2.53 (dd, 1H₅,
J=12.2 Hz, J=5.1 Hz), 2.28 (1H₈, J=12.7 Hz, J=10.2 Hz),
2.12 (dd, 1H₈, J=13.7 Hz, J=11.7 Hz), 1.80 (m, 1H₅), 1.59
(s, 3H₇), 1.14 (s, 3H₄), 1.11 (s, 3H₄), 0.91 (s, 9H), 0.12
(s, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ = major diastereomer:
140.1 (t, C₃), 132.2 (q, C₇), 129.5 (t, C₂), 126.7 (t, C₆),
89.9 (q, C₁₀), 88.9 (q, C₁₁), 63.0 (t, C₉), 62.5 (t, C₁),
50.2 (s, C₈), 41.5 (s, C₅), 37.4 (q, C₄), 25.9 (p, 2CH₃-4 +
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3C), 18.2 (q), 16.4 (p, CH₃-7), -4.6 (p), -5.0 (p), minor
diastereomer : 139.2 (t, C₃), 132.2 (q, C₇), 130.7 (t, C₂),
126.6 (t, C₆), 89.9 (q, C₁₀), 88.9 (q, C₁₁), 63.8 (t, C₉),
62.3 (t, C₁), 50.7 (s, C₈), 41.0 (s, C₅), 37.5 (q, C₄), 29.8
(p, 3C), 26.7 (p, CH₃-4), 26.8 (p, CH₃-4), 18.2 (q), 15.7
(p, CH₃-7), -4.6 (p), -5.0 (p); IR (neat), cm⁻¹ 3460 (br),
2980, 2960, 2850, 1460, 1385, 1360, 1250, 1070, 830, 775;
C₂₀H₃₄O₂Si (M=334.576 g.mol⁻¹); Mass (IC, CH₄) m/z: 352 (16,
MNH₄⁺), 335 (19, MH⁺), 317 (22, MH⁺-H₂O), 249 (100); exact
mass (IC, CH₄) for [MH⁺] 335.2406, mes. 335.2408.

(2E,6E) 9-tert-butyldimethylsilyloxy-4,4,7-trimethyl-1-
methoxy cycloundeca-2,6-dien-10-yne :

To a suspension of NaH (69 mg, 2 eq., 60% masse) in THF 3
mL, was added under inert atmosphere, a large excess of MeI
(2 mL). After 10 minutes at 40°C, a 2 mL THF solution of
macrocycle (10) (287 mg, 0.86 mmol) was added dropwise via
a canula. After stirring 1h around 40°C, the reaction was
quenched at room temperature with MeOH. After complete
neutralization of the excess of NaH, the organic layer was
washed with brine, dried over MgSO₄, filtered off and
concentrated under reduced pressure to give a yellow oil
which was chromatographed (EA/PE : 1/99). Purification
yielded 279 mg (94%) of the expected methoxy macrocycle as
a 2 to 1 mixture of diastereomers.

¹H NMR (CDCl₃, 200 MHz) δ = major diastereomer : 5.60-5.40
(m, 1H₃ + 1H₂), 5.05 (t, 1H₆, J=7.9 Hz), 4.59 (t, 1H₉, J=5.4
Hz), 4.41 (d, 1H₁, J=4.4 Hz), 3.32 (s, -OCH₃), 2.34 (d, 2H₈,
J=5.9 Hz), 1.99 (d, 2H₅, J=7.9 Hz), 1.58 (s, 3H₇), 1.09 (s,
6H₄), 0.89 (s, 9H), 0.11 (s, 3H), 0.09 (s, 3H), minor
diastereomer : 5.60-5.40 (m, 1H₂), 5.30 (d, 1H₃, J=16.2
Hz), 5.13 (m, 1H₆), 4.59 (t, 1H₉, J=5.4 Hz), 4.50 (dd, 1H₁,
J=6.9 Hz, J=3 Hz), 3.33 (s, -OCH₃), 2.53 (dd, 1H₈, J=11.8
Hz, J=5.4 Hz), 2.32 (1H₈, J=12.3 Hz, J=10.2 Hz), 2.10 (dd,
$^{1}H$ NMR (CDCl$_3$, 200 MHz) $\delta =$

major diastereomer : 5.64-5.45 (m, 1H$_5$ + 1H$_8$), 5.08 (t, 1H$_9$, $J$=7.9 Hz), 4.66 (m, 1H$_1$), 4.42 (d, 1H$_4$, $J$=4.9 Hz), 3.35 (s, -OCH$_3$), 2.48 (dd, 1H$_{11}$, $J$=13.4 Hz, $J$=5.9 Hz), 2.34 (dd, 1H$_{11}$, $J$=12.8 Hz, $J$=6.4 Hz), 2.00 (d, 2H$_8$, $J$=7.4 Hz), 1.61 (s, 3H$_{10}$), 1.10 (s, 2CH$_3$),

minor diastereomer : 5.50 (m, 1H$_5$), 5.32 (d, 1H$_6$, $J$=16.2 Hz), 5.14 (m, 1H$_9$), 4.66 (m, 1H$_5$), 1.77 (m, 1H$_5$, $J$=13.8 Hz, $J$=3.0 Hz), 1.49 (s, 3H$_7$), 1.11 (s, 3H$_4$), 1.07 (s, 3H$_4$), 0.89 (s, 9H), 0.13 (s, 6H), 0.12 (s, 3H); $^{13}C$ NMR (CDCl$_3$, 50 MHz) $\delta =$

major diastereomer : 141.5 (t, C$_3$), 132.2 (q, C$_7$), 127.2 (t, C$_2$), 126.2 (t, C$_6$), 89.5 (q, C$_{10}$), 88.4 (q, C$_{11}$), 71.5 (t, C$_1$), 63.0 (t, C$_5$), 56.6 (p, -OCH$_3$), 50.1 (s, C$_8$), 41.5 (s, C$_5$), 37.5 (q, C$_4$), 27.2 (p), 26.4 (p), 25.9 (p, 3C), 18.2 (q, C), 16.5 (p), -4.6 (p), -5.1 (p),

minor diastereomer : 140.1 (t, C$_3$), 130.8 (q, C$_7$), 128.5 (t, C$_2$), 126.5 (t, C$_6$), 89.1 (q, C$_{10}$), 87.6 (q, C$_{11}$), 72.3 (t, C$_1$), 62.2 (t, C$_9$), 56.5 (p, -OCH$_3$), 50.6 (s, C$_8$), 41.0 (s, C$_5$), 37.8 (q, C$_4$), 29.9 (p), 25.9 (p, 3C), 23.3 (p), 18.2 (q), 15.7 (p), -4.6 (p), -5.0 (p); IR (neat), cm$^{-1}$ 2950, 2870, 1660, 1470, 1385, 1360, 1250, 1090 (br), 965, 930, 860, 840, 780; C$_{21}$H$_{36}$O$_2$Si (M$\text{=}$348.603 g.mol$^{-1}$).

$(5E,9E)$ 4-methoxy-7,7,10-trimethyl cycloundeca-5,9-dien-2-yn-1-ol : To a solution of previous macrocycle (279 mg, 0.80 mmol) in THF (1.6 mL) was added a 1M THF solution of $n$-Bu$_4$NF (0.84 mL, 1.05 eq.). After complete transformation of the starting material (TLC control), the mixture was quenched with a saturated NH$_4$Cl solution and extracted with ether. The combined organic layers were washed with a brine solution, dried over MgSO$_4$ and the solvent was removed in vacuo. The residue was purified on a silica gel column eluting with a mixture of pentane/EA 85/15 and afforded 198 mg (99%) of the expected alcohol as a 2 to 1 mixture of diastereomers as a yellow oil.

$^1$H NMR (CDCl$_3$, 200 MHz) $\delta =$

major diastereomer : 5.64-5.45 (m, 1H$_5$ + 1H$_8$), 5.08 (t, 1H$_9$, $J$=7.9 Hz), 4.66 (m, 1H$_1$), 4.42 (d, 1H$_4$, $J$=4.9 Hz), 3.35 (s, -OCH$_3$), 2.48 (dd, 1H$_{11}$, $J$=13.4 Hz, $J$=5.9 Hz), 2.34 (dd, 1H$_{11}$, $J$=12.8 Hz, $J$=6.4 Hz), 2.00 (d, 2H$_8$, $J$=7.4 Hz), 1.61 (s, 3H$_{10}$), 1.10 (s, 2CH$_3$),

minor diastereomer : 5.50 (m, 1H$_5$), 5.32 (d, 1H$_6$, $J$=16.2 Hz), 5.14 (m, 1H$_9$), 4.66 (m,
1H NMR (CDCl₃, 50 MHz) δ = major diastereomer: 141.9 (t, C₆), 131.6 (q, C₁₀), 126.9 (t, C₅), 126.6 (t, C₉), 89.4 (q, C₂), 88.8 (q, C₃), 71.1 (t, C₄), 62.5 (t, C₁), 56.8 (p, -OCH₃), 49.1 (s, C₁₁), 41.5 (s, C₈), 37.5 (q, C₇), 26.8 (p), 26.7 (p), 16.5 (p), minor diastereomer: 140.5 (t, C₆), 130.6 (q, C₁₀), 128.4 (t, C₅), 126.9 (t, C₉), 88.6 (q, C₂), 88.3 (q, C₃), 72.5 (t, C₄), 61.7 (t, C₁), 56.8 (p, -OCH₃), 50.1 (s, C₁₁), 40.1 (s, C₈), 37.7 (q, C₇), 30.0 (p), 23.2 (p), 15.6 (p); IR (neat), cm⁻¹: 3400 (br), 2960, 2840, 1650, 1440, 1380, 1360, 1100 (br), 1020, 960, 895, 830; C₁₅H₂₂O₂ (M=234.339 g.mol⁻¹).

(2E,6E)-9-bromomethyldimethylsilyloxy-4,4,7-trimethyl-1-methoxy cycloundeca-2,6-dien-10-yne (3): To a solution of BMDMScI (0.27 mL, 1.22 eq.) and 4-DMAP (13.0 mg, 0.12 eq.) in 2 mL of CH₂Cl₂, at 0 °C, were added triethylamine (0.31 mL, 2.44 eq.) and a solution of previous alcohol (211 mg, 0.9 mmol) in 1 mL. At completion of the addition, the resulting solution was allowed to rise to room temperature and stir until complete at TLC (1h). At this time, the reaction mixture was quenched with a saturated NaCl solution and extracted with methylene chloride. The combined organic layers dried over Na₂SO₄ and the solvent was removed under vacuum. The residue was chromatographed on silica (10 g), eluting with a 150 mL mixture of 2% ethyl acetate in petroleum ether to afford the expected silyl ether (3) as a yellow oil, as a 2 to 1 mixture of diastereomers.

¹H NMR (C₆D₆, 200 MHz) δ = major diastereomer: 5.64-5.45 (m, 1H₃ + 1H₂), 5.08 (t, 1H₆, J=7.4 Hz), 4.60 (t, 1H₉, J=5.4 Hz), 4.31 (d, 1H₁, J=4.4 Hz), 3.19 (s, -OCH₃), 2.50-2.30
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Radical cyclization:

To a degassed solution of the BMDMS ether 3 (154 mg, 0.4 mmol), enriched in a 3 to 1 mixture of diastereomers in 14 mL of dry benzene under reflux, was added a solution of Ph3SnH (182 mg, 0.52 mmol) and AIBN (20 mg, 0.12 mmol) in 4 mL of dry and degassed benzene via a syringe pump (2.12 mL/h). At completion of the addition, starting material was consumed, benzene was removed under vacuum and stannylated derivatives were precipitated by stirring on pentane at 0°C. Filtration on celite pad furnished, after two treatments, the residue, which was poured in the mixture THF/MeOH (1:1, 6 mL) with 248 mg (2.48 mmol) of KHCO3, KF (93 mg, 1.6 mmol) and a solution of H2O2 35% (4 mL). After
heated 1 h at 70 °C, the reaction mixture was allowed to cool to room temperature was filtered through celite, and rinsed 3 times with ethyl acetate. The aqueous layer were extracted twice more with ethyl acetate. Organic layers were washed with a brine, dried with MgSO₄ and the solvent was removed under reduce pressure. The residue was purified via a silica gel column eluting with 3% of MeOH in CH₂Cl₂ and afforded two fractions: 47 mg (45 %) of triquinane 1, 13 mg of cyclopentane 11 (12%).

1-Hydroxymethyl-7-methoxy-3a,5,5-trimethyl-3,3a,3b,4,5,6,6a,7-octahydro-2H-cyclopenta[a]pentalen-2-ol (1): ^1^H NMR (200 MHz, CDCl₃, 25°C) δ = 5.27 (t, 1H-2, J=6.6 Hz), 4.47 (d, 1H, CH₂OH, J=12.6 Hz), 4.32 (d, 1H, CH₂OH J=12.6 Hz), 4.03 (d, 1H-7, J=6.4 Hz), 3.15 (s, 3H, OMe), 2.88 (m, 1H-6a), 2.38 (dd, 1H-3b, J=11.3 Hz, J=9.5 Hz), 2.36 (dd, 1H-3, J=12.1 Hz, J=6.4 Hz), 1.68 (dd, 1H-6, J=12.1 Hz, J=10.7 Hz), 1.53 (dd, 1H-3', J=11.9 Hz, J=7.8 Hz), 1.32 (d, 2H-4, J=9.6 Hz), 1.24 (dd, 1H-6, J=8.4 Hz, J=3.5 Hz), 1.07 (s, 3H-5α), 1.00 (s, 3H-3a), 0.92 (s, 3H-5β); ^1^C NMR (CDCl₃, 50 MHz) δ = 154.8 (q, C-7a), 135.4 (q, C-1), 81.3 (t, C-7), 75.6 (t, C-2), 58.3 (s, CH₂OH), 56.3 (p, CH₃O), 55.0 (s, C-3), 53.6 (t, C-3b), 50.8 (q, C-3a), 49.9 (t, C-6a), 43.2 (q, C-5), 41.2 (s, C-6), 38.2 (s, C-4), 29.2 (p, CH₃-5), 27.4 (p, CH₃-5), 23.4 (p, CH₃-3a); IR (neat), cm⁻¹ 3450 (br), 2940, 2850, 1650 (br), 1455, 1360, 1090, 995, 760; Elementary analysis calcd (%) for C₁₆H₂₆O₃ (M=266.381 g mol⁻¹): C 72.14, H 9.83; found: C 72.11, H 9.80; MS (C.I, CH₄) m/z (relative intensity) 266 (M⁺, 4%), 265 (M⁺-1, 7%), 249 (M⁺-OH, base peak), 231 (47%), 217 (47%).

2-hydroxymethyl-3-methoxymethylene-4-methyl-4-[4',4'-dimethyl cyclopent-2-enyl] cyclopentan-1-ol (11). Yield =12%. Two diastereomers. ^1^H NMR (CDCl₃, 200 MHz) δ = 5.80
(s, CHOMe), 5.47 (m, 1H 2' + 1H 3'), 4.54 (dt, 1H, J=10.3 Hz, J=6.9 Hz), 3.97 (dd, 1H, CH 3 OH, J=10.3 Hz, J=10.3 Hz), 3.36 (td, 1H, J=11.3 Hz, J=5.1 Hz), 3.35 (d, 1H, CH 3 OH, J=8.9 Hz), 2.81 (m, 1H 2), 1.73 (dd, 1H, J=12.8 Hz, J=10.3 Hz), 1.61 (dd, 1H 3', J=12.8 Hz, J=7.9 Hz), 1.51 (dd, 1H 5, J=13.4 Hz, J=6.9 Hz), 1.44 (dd, 1H 5', J=12.8 Hz, J=6.9 Hz), 1.18 (s, 3H), 1.08 (s, 3H), 0.98 (s, 3H); 13C NMR (CDCl 3 , 50 MHz) δ = 143.2 (t, CHOMe), 142.8 (t, C 3'), 129.7 (t, C 2'), 123.8 (q, C 3), 73.8 (t, C 1), 65.1 (s, CH 3 OH), 59.8 (p, -OCH 3 ), 52.6 (t, C 2), 47.0 (t, C 1'), 44.9 (q, C 4), 44.4 (q, C 4'), 42.1 (s, C 5), 42.0 (s, C 5'), 29.7 (p, CH 3), 28.5 (p, CH 3), 26.2 (p, CH 3); IR (neat), cm⁻¹ 3350 (br), 2940, 2920, 1670, 1450, 1355, 1060, 750; C 16 H 26 O 3 (M=266.381 g.mol⁻¹).