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Protocol

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# Biomimetic tail-to-head terpene cyclizations using the resorcin[4]arene capsule catalyst

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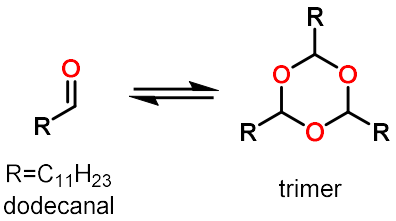
## Supplementary Information




R=$C_{11}H_{23}$
dodecanal

trimer

**Fig S1 |** Trimerization of dodecanal

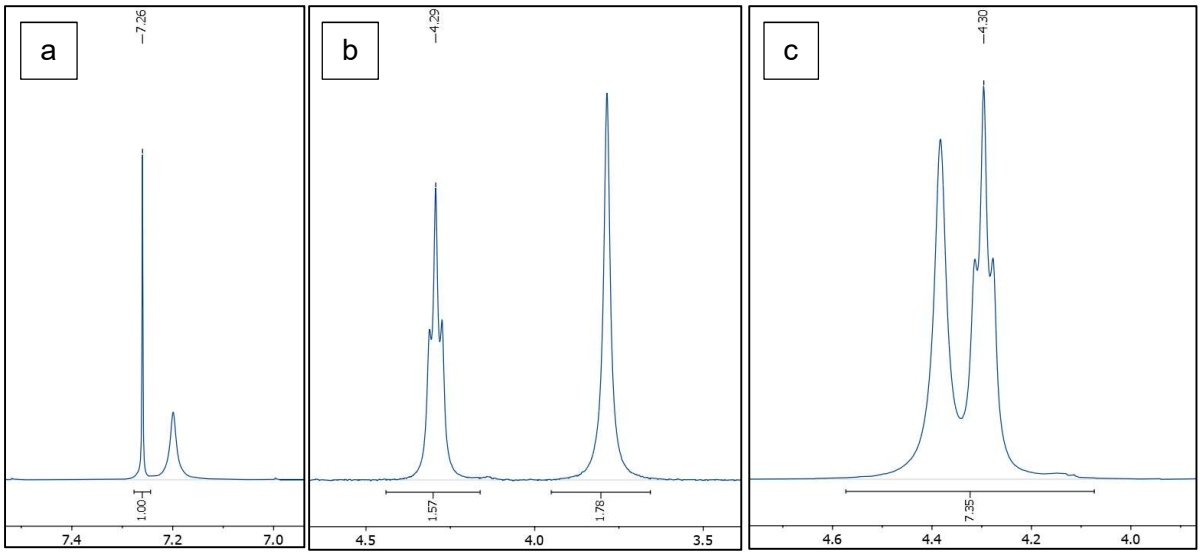



**Fig. S2 |** Example of $^{1}$H NMR spectra for the determination of water in resorcin[4]arene (a) the $CHCl_3$ residual solvent is integrated first, (b) then the CH triplet (4.30 ppm) and the water signal (variable chemical shift). (c) If the CH triplet and the water singlet overlap, the aromatic CH singlet (6.11 ppm) should be used to deduce the water integral.

## Derivation of the equations

Equation 2

$$c_M(Et_3N\ titrant) = \frac{n(Et_3N)}{V(volumetric\ flask)} = \frac{m(Et_3N)}{V(volumetric\ flask) \times M_w(Et_3N)} =$$

$n\ (mol)$: $molar\ amount$

$m\ (g)$: $mass$

$V\ (L)$: $volume$

$Mw\ \left(\frac{g}{mol}\right)$: $molar\ weight$

$c_M\left(\frac{mol}{L}\right)$: $molar\ concentration$

Equation 3

$$c_M(HCl\ stock\ solution) = \frac{\mathrm{n}(HCl\ stock\ solution)}{V(HCl\ stock\ solution)} = \frac{n(Et_3N\ titrant)}{V(HCl\ stock\ solution)} = \frac{c_M(Et_3N\ titrant) \times V(Et_3N\ titrant)}{V(HCl\ stock\ solution)}$$

$V\ (\mu L)$: $volume$

$n\ (mol)$: $molar\ amount$

$c_M\left(\frac{mol}{L}\right)$: $molar\ concentration$

Equation 4

$$r\left(\frac{H_2O\ present}{capsule}\right) = \frac{n(H_2O\ in\ sample) - n(H_2O\ in\ CDCl_3)}{n(resorcin[4]arene\ in\ sample)} \times 6$$

$$= \frac{\frac{int(H_2O\ in\ sample)}{2}}{\frac{int(CHCl_3\ in\ sample)}{\frac{int(CH-resorcin[4]arene\ in\ sample)}{4}}} - \frac{\frac{int(H_2O\ in\ CDCl_3)}{2}}{\frac{int(CHCl_3\ in\ CDCl_3)}{int(CHCl_3\ in\ sample)}} \times 6$$

$r$: $ratio$

$n$ : $amount$

$int$: $peak\ integral$

Equation 5 and 10

$$m(H_2O\ to\ add) = n(H_2O\ to\ add) \times Mw(H_2O) = \frac{r\left(\frac{H_2O\ to\ add}{capsule}\right) \times n(RS) \times Mw(H_2O)}{6} =$$

$$= \frac{r\left(\frac{H_2O\ to\ add}{capsule}\right) \times m(RS) \times Mw(H_2O)}{Mw(RS) \times 6}$$

$$= \frac{\left(r\left(\frac{H_2O\ target}{capsule}\right) - r\left(\frac{H_2O\ present}{capsule}\right)\right) \times m(RS) \times Mw(H_2O)}{Mw(RS) \times 6}$$

$n\ (mol)$: $molar\ amount$

$m\ (g)$: $mass$

$r\ (-)$: $ratio$

$Mw\ \left(\frac{g}{mol}\right)$: $molar\ weight$

$RS$ : $resorcin[4]arene$

Equation 6

$$r\left(\frac{H_2O}{capsule}\right) = \frac{n(H_2O\ in\ sample)}{n(resorcin[4]arene)} \times 6 = \frac{\frac{int(H_2O\ in\ sample)}{2}}{\frac{int(CH-resorcin[4]arene)}{4}} \times 6$$

$r: ratio$

$n\ (mol): molar\ amount$

$int: peak\ integral$

Equation 7

$$r\left(\frac{H_2O}{capsule}\right) = \frac{n(H_2O) \times 6}{n(RS)} = \frac{m(H_2O) \times 6}{n(RS) \times M_w(H_2O)} = \frac{ppm(H_2O) \times m(sol) \times 6}{10^6 \times n(RS) \times M_w(H_2O)}$$

$$= \frac{ppm(H_2O) \times m(sol) \times M_w(RS) \times 6}{10^6 \times m(RS) \times M_w(H_2O)}$$

$$= \frac{ppm(H_2O) \times m(sol) \times Mw(RS) \times 6}{10^6 \times V(sol) \times M_w(H_2O) \times c_w(RS)}$$

$r\ (-): ratio$

$m\ (g): mass$

$n\ (mol): molar\ amount$

$V\ (mL): volume$

$Mw\ \left(\frac{g}{mol}\right): molar\ weight$

$c_w\ \left(\frac{g}{mL}\right): weight\ concentration$

$RS:\ resorcinarene$

$sol:\ solution$

## NMR spectra

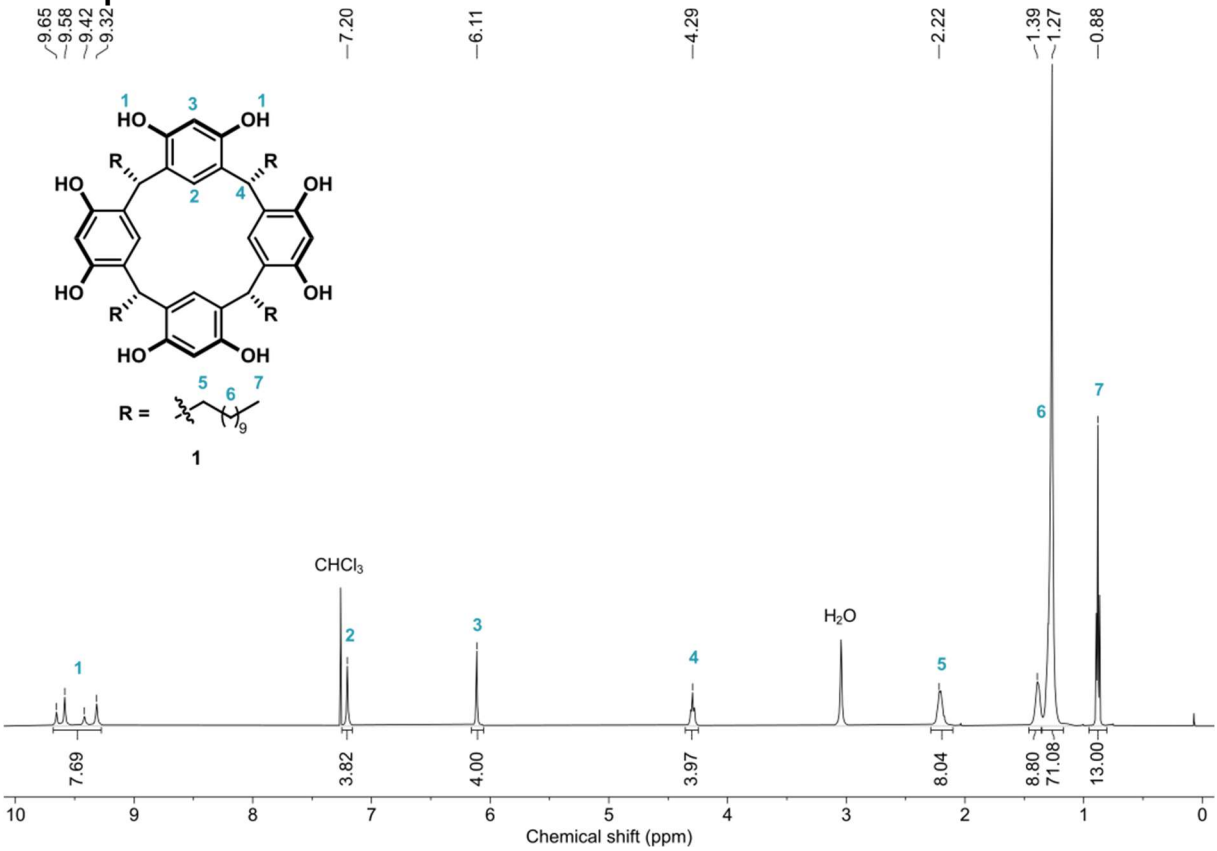



**Fig. S3 |** $^{1}$H NMR spectrum of resorcin[4]arene **1** (500 MHz, chloroform-d, 298K)

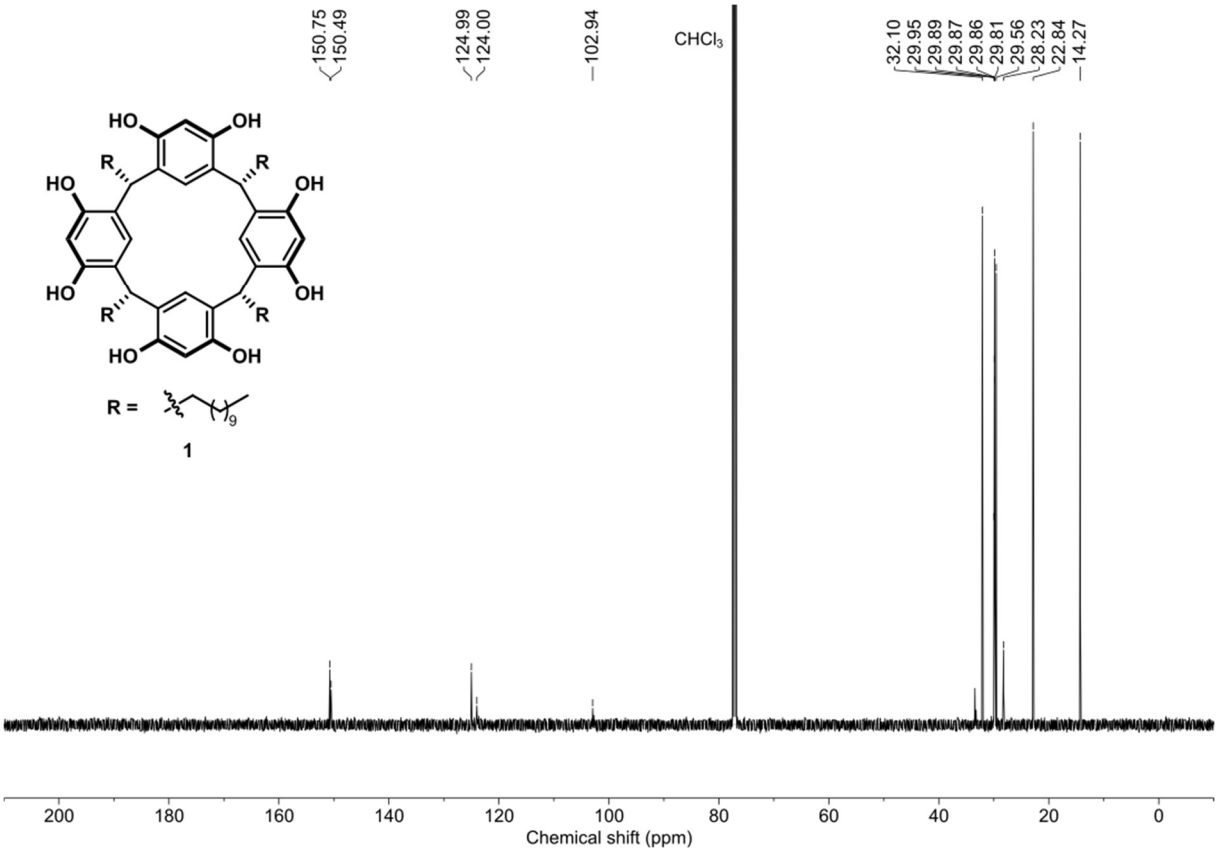



**Fig. S4 |** $^{13}$C NMR spectrum of resorcin[4]arene **1** (126 MHz, chloroform-d, 298K)

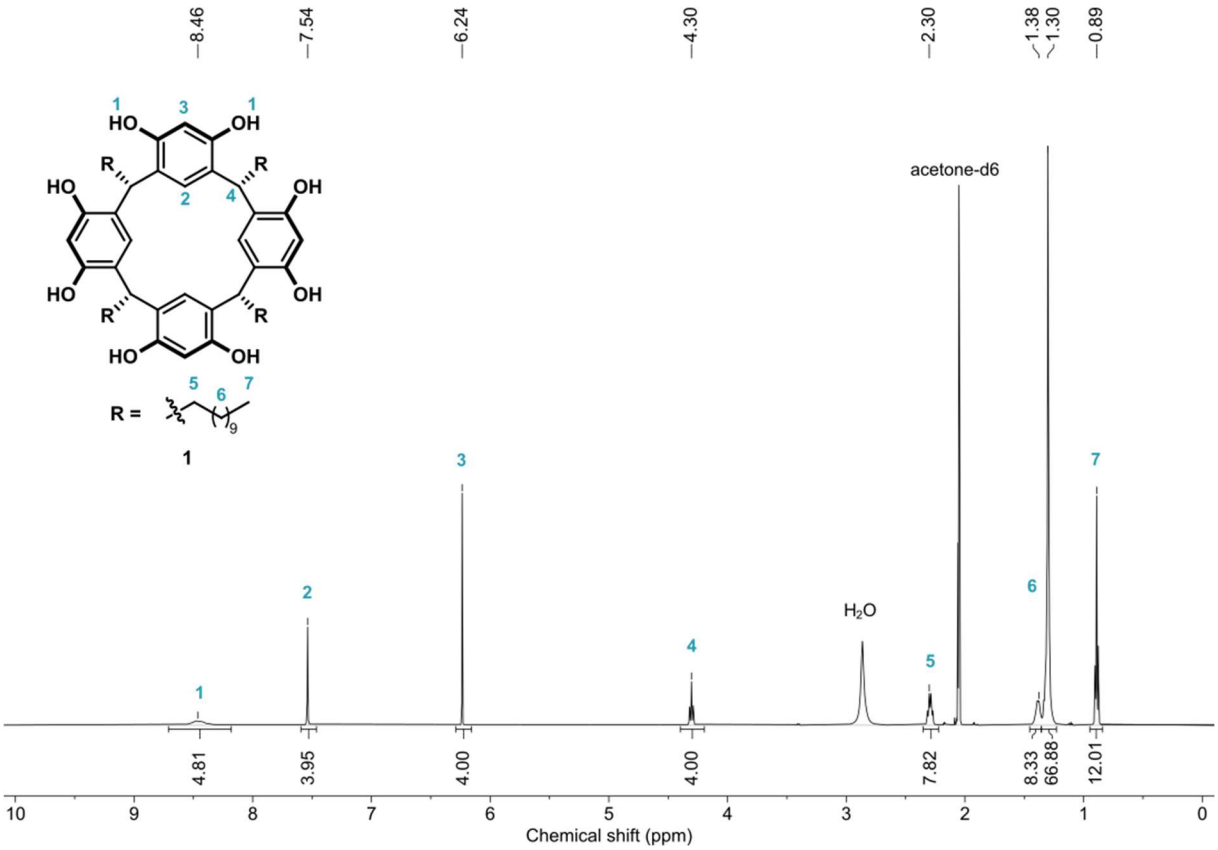



**Fig. S5 |** $^{1}$H NMR spectrum of resorcin[4]arene **1** (500 MHz, acetone-d6, 298K)

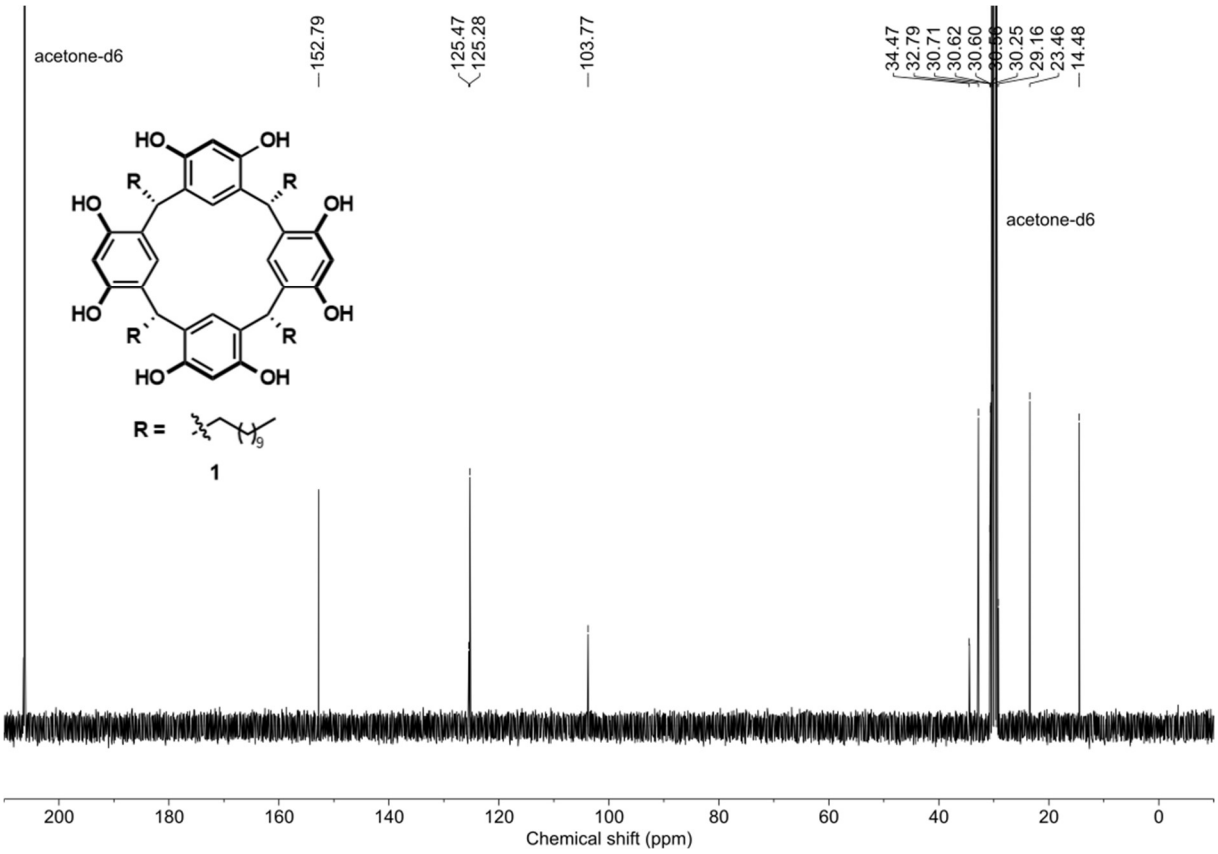



**Fig. S6 |** $^{13}$C NMR spectrum of resorcin[4]arene **1** (126 MHz, acetone-d6, 298K)

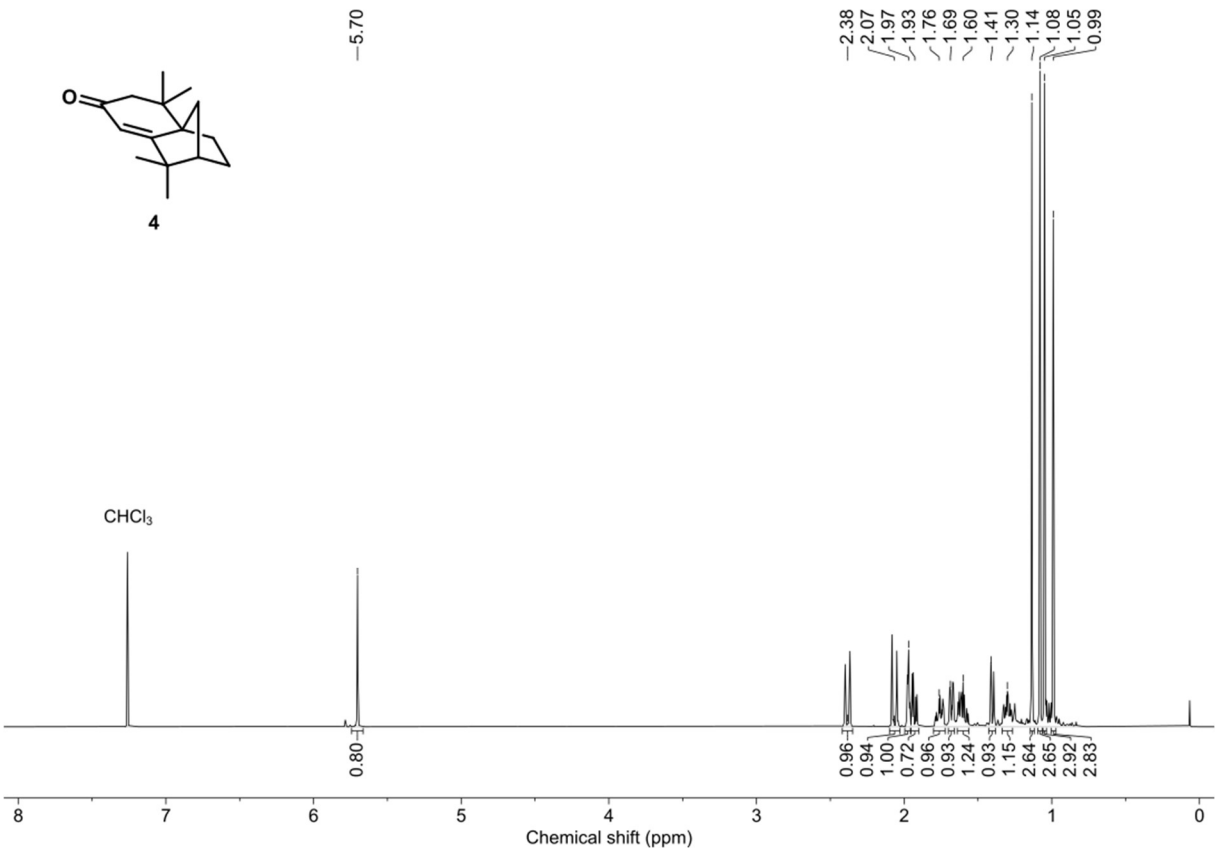



**Fig. S7 |** $^{1}$H NMR spectrum of isolongifolenone **4** (500 MHz, chloroform-d, 298K)

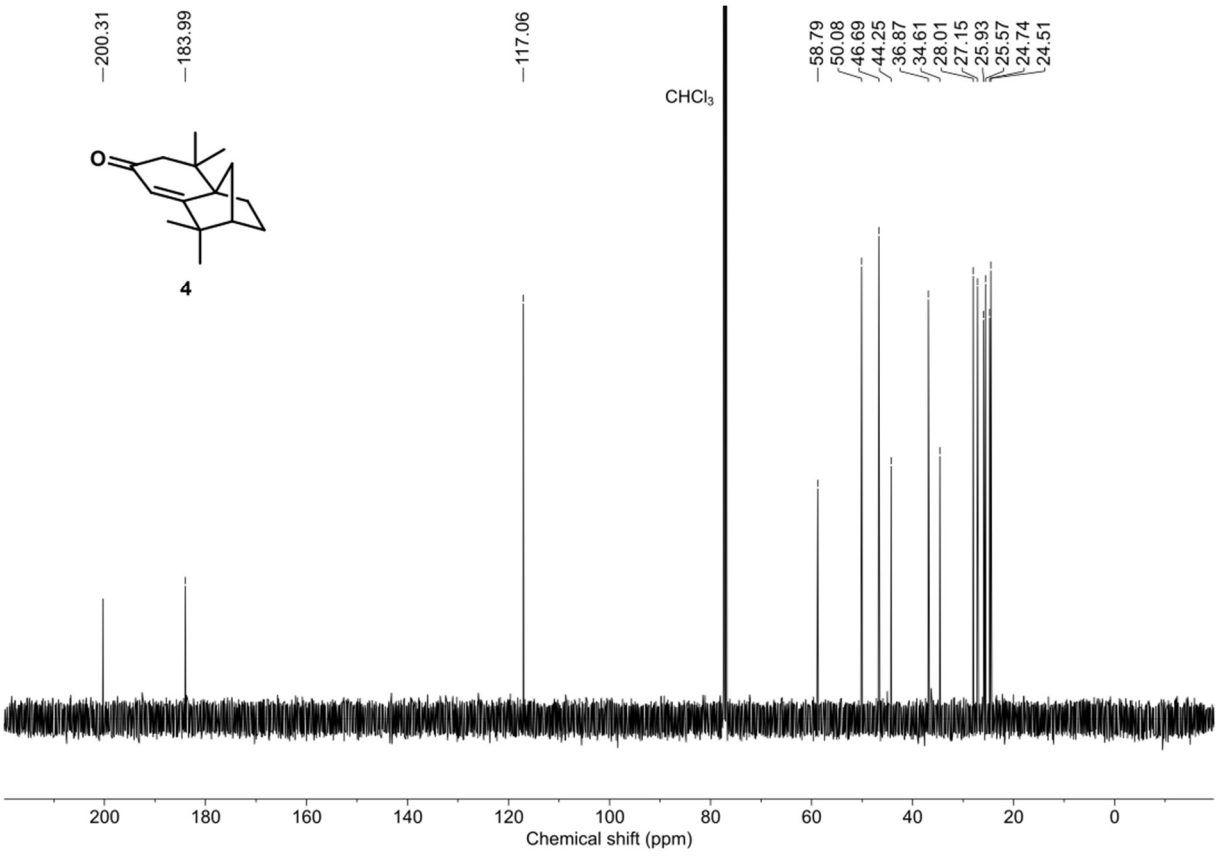



**Fig. S8 |** $^{13}$C NMR spectrum of isolongifolenone **4** (126 MHz, chloroform-d, 298K)

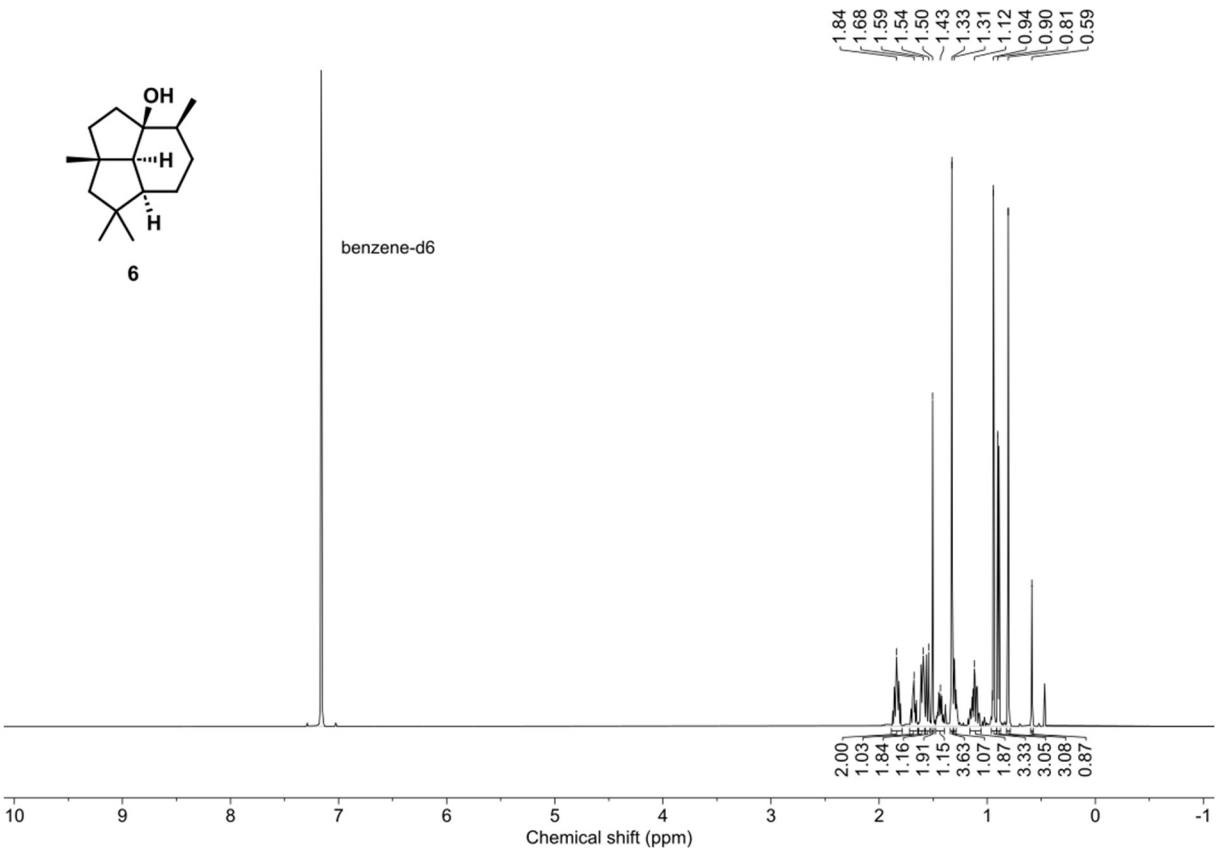



**Fig. S9 |** $^{1}$H NMR spectrum of presilphiperfolan-1β-ol **6** (500 MHz, benzene-d6, 298K)

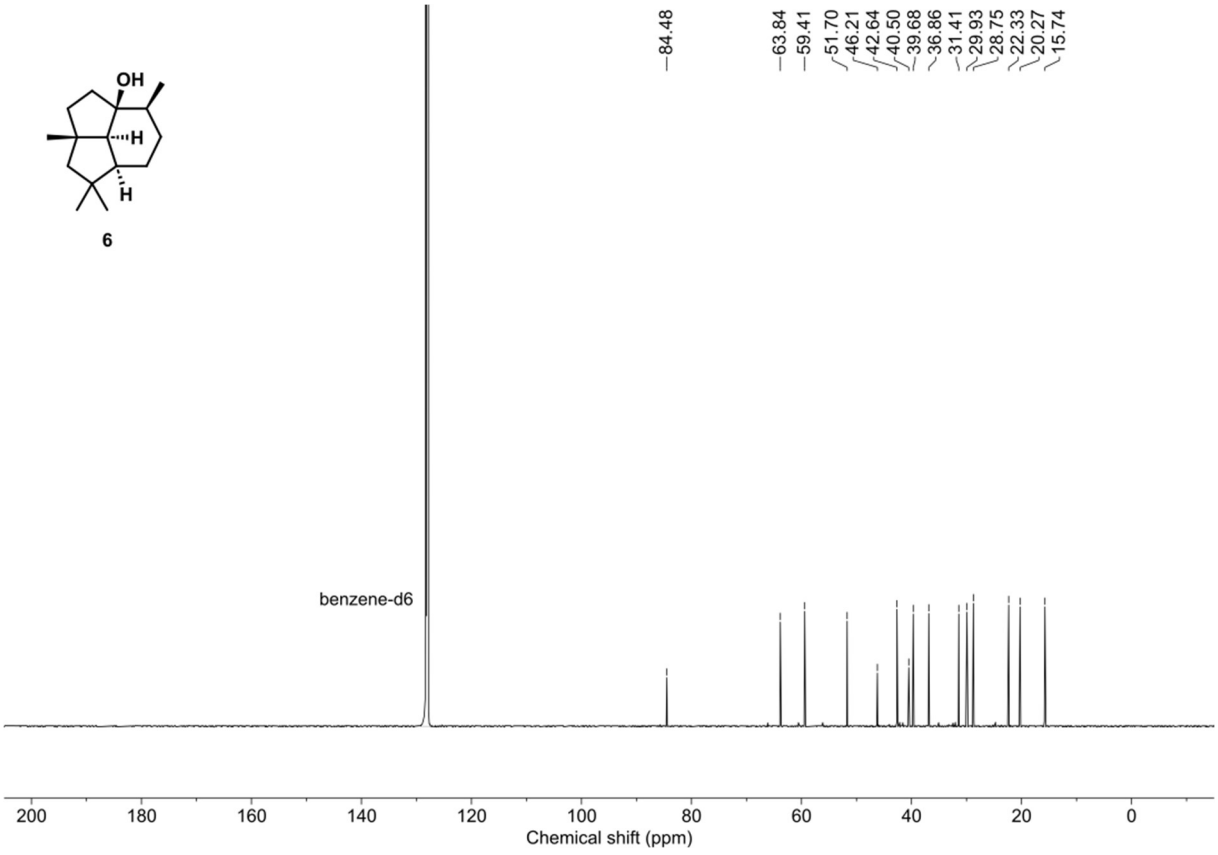



**Fig. S10 |** $^{13}$C NMR spectrum of presilphiperfolan-1β-ol **6** (126 MHz, benzene-d6, 298K)