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Bicyclic Peroxides and Perorthoesters with 1,2,4-Trioxane Structures

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General Experimental Informations.

IR: Infrared spectra were obtained using Perkin-Elmer 1600 series FTIR spectrometer and are given in cm^{-1} units. Solid samples are measured as CsI or KBr discs while liquids are measured as neat between two NaCl plates.

^{1}H-NMR: The ^{1}H-NMR spectra were recorded on Bruker AC 300, Bruker DPX 300 spectrometers operating at 300 MHz or on Bruker DRX 500 spectrometer instrument operating at 500 MHz. Chemical shifts are reported as δ in ppm and the coupling constant, *J*, in Hz units. In all spectra solvent peaks were used as internal standard. Solvent used are $CDCl_3$ (δ = 7.24 ppm), DMSO-d_6 (δ = 2.49 ppm), acetone-d_6 (δ = 2.04 ppm), and MeOH-d_4 (δ = 3.35, 4.78 ppm). Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad.

^{13}C-NMR: The ^{13}C-NMR spectra were recorded either on a Bruker AC 300 spectrometer instrument operating at 75 MHz or on Bruker DRX 500 spectrometer instrument operating at 125 MHz.

HRMS: High resolution mass spectra were recorded on Finnigan MAT 900 spectrometer and are measured for the molecular ion peak (M^+).

Elemental analysis: CHN-combustion analyses were measured using Elementar Vario EL Instrument.

Syntheses of 2,3,8-trioxabicyclo[3.2.1]octanes 5 und 6:

7-Methyl-oct-6-ene-2,5-dione (1a)
A solution of 3,3-dimethylacrolein (10.0 g, 119 mmol), methylvinylketone (8.33 g, 119 mmol), 3-benzyl-5-(2-hydroxyethyl)-4-methyl-1,3-thiazolium chloride[16] (3.20 g, 11.9 mmol) and sodium acetate (3.90 g, 47.6 mmol) in ethanol (100 mL) was stirred under nitrogen at 80 °C for 15 h, then the reaction mixture was cooled to r.t. and the solvent removed under reduced pressure followed by fractional distillation (b.p. 84 °C, 1.39 torr, lit. 87-89 °C, 2.5 torr[16]) of the residue to afford the pure 1,4-dione **1a** (9.1 g, 59.1 mmol) as yellow oil, yield: 50 %; ^{1}H-NMR: (300 MHz, $CDCl_3$) δ (ppm) = 1.81 (s, 3H, C$\underline{H_3}$C=), 2.04 (s, 3H, C$\underline{H_3}$C=), 2.12 (t, 3H, *J* = 2.8 Hz, C$\underline{H_3}$CO), 2.63 (m, 4H, C$\underline{H_2}$C$\underline{H_2}$), 6.02 (m, 1H, C$\underline{H}$=C); ^{13}C-NMR: (75.5 MHz, $CDCl_3$) δ (ppm) = 20.6 (q, $\underline{C}H_3$C=), 27.5 (q, $\underline{C}H_3$C=), 29.9 (q, $\underline{C}H_3$CO), 36.9 (t, $\underline{C}H_2$), 37.4 (t, $\underline{C}H_2$) 123.3 (d, $\underline{C}$H=C), 155.3 (s, $\underline{C}$=CH), 198.6 (s, $\underline{C}$OCH=), 207.4 (s, $\underline{C}OCH_3$).

8-Methyl-non-7-ene-3,6-dione (1b)
A solution of 3,3-dimethylacrolein (18.75 g, 223.2 mmol), ethylvinylketone (25 g, 297.6 mmol), 3-benzyl-5-(2-hydroxyethyl)-4-methyl-1,3-thiazolium chloride (6.0 g, 22.3 mmol) and sodium acetate (7.32 g, 89.3 mmol) in ethanol (250 mL) was stirred under nitrogen at 80 °C for 15 h, then the reaction mixture was cooled to r.t. and the solvent removed under reduced pressure followed by fractional distillation (b.p. 119 °C, 0.33 torr) of the residue gives the pure 1,4-dione **1b** (33.4 g, 198.8 mmol) as yellow oil; yield: 89 %; ^{1}H-NMR: (300 MHz, $CDCl_3$) δ (ppm) = 0.95 (dt, 3H, *J* = 1.3, 7.4 Hz, C$\underline{H_3}$CH$_2$), 1.78 (s, 3H, C$\underline{H_3}$C=), 2.01 (s, 3H, C$\underline{H_3}$C=), 2.39 (q, 2H, *J* = 7.4 Hz, C$\underline{H_2}$CH$_3$), 2.60 (m, 4H, C$\underline{H_2}$C$\underline{H_2}$), 6.0 (m, 1H, C$\underline{H}$=C); ^{13}C-NMR: (75.5 MHz, $CDCl_3$) δ (ppm) = 7.6 (q, $\underline{C}H_3CH_2$), 20.5 (q, $\underline{C}H_3$C=), 27.4 (q, $\underline{C}H_3$C=), 35.6 (t, $\underline{C}H_2$), 35.7 (t, $\underline{C}H_2$), 37.4 (t, $\underline{C}H_2$), 123.3 (d, $\underline{C}$H=C), 155.0 (s, $\underline{C}$=CH), 198.7 (s, $\underline{C}$OCH=), 209.9 (s, $\underline{C}OCH_2$). Elemental analysis: ($C_{10}H_{16}O_2$, M = 168.12) Calcd: C 71.39 H 9.59, Found: C 71.46 H 9.46.

5-Methyl-1-(2-methyl-1,3-dioxolan-2-yl)hex-4-en-3-one (2a)
A solution of 7-methyl-oct-6-ene-2,5-dione (**1a**) (14.5 g, 94.2 mmol), ethylene glycol (10.0 g, 161.3 mmol), and pyridinium tosylate (3.58 g, 14.3 mmol) in benzene (100 mL) was refluxed using a Dean-Stark apparatus with continuous removal of the separated water. The solvent was then removed under reduced pressure and the residue mixed with ether, washed with saturated $NaHCO_3$ solution (2 x 30 mL), and dried over Na_2SO_4. After evaporation of the solvent, fractional distillation (b.p. 100 °C, 0.90 torr, Lit. 48 °C, 0.02 torr[24]) of the residue gave the pure enone acetal **2a** (7.46 g, 37.7 mmol) as yellow oil; yield: 40 %; ^{1}H-NMR: (300 MHz, $CDCl_3$) δ (ppm) = 1.19 (s, 3H, C$\underline{H}_3$), 1.76 (d, 3H, *J* = 1.3 Hz, C$\underline{H}_3$C=), 1.85 (t, 2H, *J* = 7.7 Hz C$\underline{H}_2$), 2.01 (d, 3H, *J* = 1.0 Hz, C$\underline{H}_3$C=), 2.39 (t, 2H, *J* = 7.7 Hz C$\underline{H}_2$), 3.81 (m, 4H, 2 x C$\underline{H}_2$O), 5.97 (m, 1H, C$\underline{H}$=C); ^{13}C-NMR: (75.5 MHz, $CDCl_3$) δ (ppm) = 20.4 (q, $\underline{C}H_3$C=), 23.7 (q, $\underline{C}H_3$), 27.4 (q, $\underline{C}H_3$C=), 32.8 (t, $\underline{C}H_2$), 38.5 (t, $\underline{C}H_2$CO), 64.4 (t, 2 x O$\underline{C}H_2$), 109.2 (s, O$\underline{C}$O), 123.6 (d, $\underline{C}$H=C), 154.4 (s, $\underline{C}$=CH), 199.9 (s, $\underline{C}$O).

1-(2-Ethyl-1,3-dioxolan-2-yl)-5-methylhex-4-en-3-one (2b)
A solution of 8-methyl-non-7-ene-3,6-dion (**1b**) (30.0 g, 178.6 mmol), ethylene glycol (12.5 g, 201.6 mmol) and pyridinium tosylate (4.46 g, 17.8 mmol) in benzene (100 mL) was refluxed using a Dean-Stark apparatus with continuous removal of the separated water. The solvent was then removed under reduced pressure and the residue mixed with ether, washed with saturated $NaHCO_3$ solution (2 x 30 mL), and dried over Na_2SO_4. Evaporation of the solvent afforded the enone acetal **2b** (30.2 g, 142.3 mmol) as yellow oil; yield: 80 %; ^{1}H-NMR: (300 MHz, $CDCl_3$) δ (ppm) = 0.80 (t, 3H, *J* = 7.4 Hz, C$\underline{H}_3$CH$_2$), 1.51 (q, 2H, *J* = 7.5 Hz, C$\underline{H}_2$CH$_3$), 1.76 (s, 3H, C$\underline{H}_3$C=), 1.83 (m, 2H, C$\underline{H}_2$), 2.02 (s, 3H, C$\underline{H}_3$C=), 2.39 (m, 2H, C$\underline{H}_2$), 3.81 (m, 4H, 2 x C$\underline{H}_2$O), 5.96 (m, 1H, C$\underline{H}$=C); ^{13}C-NMR: (75.5 MHz, $CDCl_3$) δ (ppm) = 7.9 (q, $\underline{C}$H$_3$CH$_2$), 20.5 (q, $\underline{C}$H$_3$C=), 27.5 (q, $\underline{C}$H$_3$C=), 30.0 (t, $\underline{C}$H$_2$), 30.5 (t, $\underline{C}$H$_2$), 38.5 (t, $\underline{C}$H$_2$CO), 64.9 (t, 2 x O$\underline{C}$H$_2$), 111.3 (s, O$\underline{C}$O), 123.7 (d, $\underline{C}$H=C), 154.5 (s, $\underline{C}$=CH), 200.2 (s, $\underline{C}$O). Elemental analysis: ($C_{12}H_{20}O_3$, M = 212.14) Calcd: C 67.89 H 9.50, Found: C 68.12 H 9.35.

5-Methyl-1-(2-methyl-1,3-dioxolan-2-yl)hex-4-en-3-ol (3a)
Under a nitrogen atmosphere, an etheral solution of 5-methyl-1-(2-methyl-1,3-dioxolan-2-yl)hex-4-en-3-one (**2a**) (8.6 g, 43.4 mmol) was added dropwise at r.t. to a suspension of $LiAlH_4$ (0.64 g, 16.8 mmol) in dry ether at such a rate as to maintain gentle reflux. After complete addition the reaction mixture was treated slowly (**Caution**, vigorous evolution of hydrogen gas!) with 2N aqueous NaOH solution. The precipitate was removed by filteration, digested with ether and the combined ether extracts were washed with brine and dried over $MgSO_4$. Evaporation of the solvent under reduced pressure gave the pure allylic alcohol **3a** (5.40 g, 0.027 mmol) as faint yellow oil; yield: 62 %; ^{1}H-NMR: (300 MHz, $CDCl_3$) δ (ppm) = 1.25 (s, 3H, C$\underline{H}_3$), 1.44-1.78 (m, 4H, C$\underline{H}_2$C$\underline{H}_2$), 1.61 (d, 2H, *J* = 1.2 Hz, C$\underline{H}_3$C=), 1.65 (d, 3H, *J* = 1.0 Hz, C$\underline{H}_3$C=), 3.87 (m, 4H, 2 x OC$\underline{H}_2$), 4.26 (m, 1H, OC$\underline{H}$), 5.10 (m, 1H, C$\underline{H}$=C); ^{13}C-NMR: (75.5 MHz, $CDCl_3$)δ (ppm) = 18.1 (q, $\underline{C}$H$_3$C=), 23.7 (q, $\underline{C}$H$_3$), 25.6 (q, $\underline{C}$H$_3$C=), 31.9 (t, $\underline{C}$H$_2$), 34.9 (t, $\underline{C}$H$_2$), 64.5 (t, 2 x O$\underline{C}$H$_2$), 109.9 (s, O$\underline{C}$O), 128.0 (d, $\underline{C}$H=C), 134.6 (s, $\underline{C}$=CH). Elemental analysis: ($C_{11}H_{20}O_3$, M = 200.14) Calcd: C 65.97 H 10.07, Found: C 66.21 H 10.01.

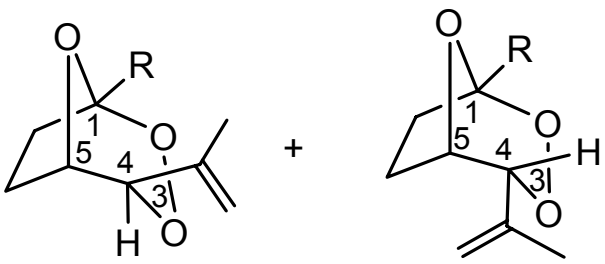
1-(2-Ethyl-1,3-dioxolan-2-yl)-5-methylhex-4-en-3-ol (3b)
Under a nitrogen atmosphere, an etheral solution of 1-(2-ethyl-1,3-dioxolan-2-yl)-5-methylhex-4-en-3-one (**2b**) (28.87 g, 136.2 mmol) was added dropwise at r.t. to a suspension of $LiAlH_4$ (2.0 g, 52.6 mmol) in dry ether at such a rate as to maintain gentle reflux. After complete addition the reaction mixture was treated slowly (**Caution**, vigorous evolution of hydrogen gas!) with 2N aqueous NaOH solution. The precipitate was removed by filteration, digested with ether and the combined ether extracts were washed with brine and dried over $MgSO_4$. Evaporation of the solvent under reduced pressure followed by fractional distillation (b.p. 110 °C, 0.22 torr) gives

the pure allylic alcohol **3b** (18.0 g, 84.1 mmol) as faint yellow oil; yield: 62 %; ^{1}H-NMR: (300 MHz, $CDCl_3$) δ (ppm) = 0.71 (t, 3H, *J* = 7.7 Hz, CH_3CH_2), 1.25-1.59 (m, 6H, 3 x CH_2), 1.48 (d, 3H, *J* = 1.0 Hz, CH_3C=), 1.53 (s, 3H, CH_3C=), 2.65 (br. s, 1H, OH), 3.73 (m, 4H, 2 x OCH_2), 4.11 (m, 1H, OCH), 4.96 (m, 1H, CH=C); ^{13}C-NMR: (75.5 MHz, $CDCl_3$) δ (ppm) = 7.7 (q, CH_3CH_2), 17.8 (q, CH_3C=), 25.3 (q, CH_3C=), 29.5 (t, CH_2), 31.5 (t, CH_2), 32.0 (t, CH_2), 64.5 (t, 2 x OCH_2), 68.0 (d, OCH), 111.6 (s, OCO), 128.1 (d, CH=C), 133.6 (s, C=CH). Elemental analysis: ($C_{12}H_{22}O_3$, M = 214.16) Calcd: C 67.26 H 10.35, Found: C 67.53 H 10.55.

General procedure for photooxygenation of allylic alcohols:
Commercially (Aldrich) available polystyrene-divinylbenzene copolymer beads (2.5 g) are distributed over a petri dish (19 cm diameter) and swollen by CH_2Cl_2 (20 mL). The substrate (ca. 10 mmol) and the nonpolar sensitizer (TPP or TTP, ca. 3-6 mg) in ethyl acetate (20 mL) are subsequently added and the excess solvent is evaporated by leaving the Petri dish in a well ventilated hood. The Petri dish is then covered with a glass plate and the sandy solid is irradiated with halogen lamp or sodium street lamp. The polymer beads are subsequently rinsed with ethanol (3 x 30 mL) and filtered (the beads are kept for regeneration and reuse). The solvent is evaporated under reduced pressure (**Caution**, water bath temperature should not exceed 30 °C).

(*syn*/*anti*)-4-Hydroperoxy-5-methyl-1-(2-methyl-1,3-dioxolan-2-yl)hex-5-en-3-ol (4a)
Photooxygenation of 5-methyl-1-(2-methyl-1,3-dioxolan-2-yl)hex-4-en-3-ol (**3a**) (1.13 g, 5.65 mmol) for 108 h afforded a diastereomeric mixture (d.r. *syn*:*anti*, 77:23) of □-hydroxy allylic hydroperoxides **4a** (1.10 g, 4.74 mmol, 84%) as yellow oil which was used immediately for the peroxyacetalization; *syn*-diastereoisomer: ^{1}H-NMR: (300 MHz, $CDCl_3$) δ (ppm) = 1.21 (s, 3H, CH_3), 1.64 (s, 3H, CH_3C=), 1.30-1.90 (m, 4H, CH_2CH_2), 3.84 (br, 4H, 2 x OCH_2), 4.07 (d, 1H, *J* = 8.1 Hz, OOCH), 4.08 (m, 1H, OCH), 4.95 (br. s, 2H, CH_2=C); ^{13}C-NMR: (75.5 MHz, $CDCl_3$) δ (ppm) = 17.9 (q, CH_3), 23.5 (q, CH_3), 27.0 (t, CH_2), 34.3 (t, CH_2), 64.3 (t, 2 x OCH_2), 70.4 (d, OCH), 93.2 (d, OOCH), 109.8 (s, OCO), 116.1 (t, CH_2=C), 141.5 (s, C=CH_2); *anti*-diastereoisomer: ^{1}H-NMR: (300 MHz, $CDCl_3$, additional significant signals) δ (ppm) = 1.23 (s, 3H, CH_3), 1.71 (s, 3H, CH_3C=), 3.60 (s, 4H, 2 x OCH_2), 3.70 (m, 1H, OCH); ^{13}C-NMR: (75.5 MHz, $CDCl_3$, additional significant signals) δ (ppm) = 64.6 (t, 2 x OCH_2), 70.3 (d, OCH), 91.5 (d, OOCH), 110.0 (s, OCO), 115.1 (t, CH_2=C), 141.5 (s, C=CH_2).

(3RS,4RS)-1-(2-Ethyl-1,3-dioxolan-2-yl)-4-hydroperoxy-5-methylhex-5-en-3-ol (4b)
Photooxygenation of 1-(2-ethyl-1,3-dioxolan-2-yl)-5-methylhex-4-en-3-ol (**3b**) (1.12 g, 5.23 mmol) for 120 h afforded a diastereomeric mixture (d.r. *syn*:*anti*, 74:26) of □-hydroxy allylic hydroperoxides **4b** (1.17 g, 4.76 mmol, 91 %) as yellow oil which was used immediately for the peroxyacetalization; *syn*-diastereoisomer: ^{1}H-NMR: (300 MHz, $CDCl_3$) δ (ppm) = 0.78 (m, 3H, CH_3CH_2), 1.14-1.91 (m, 6H, overlapped signals CH_2CH_3 and CH_2CH_2), 1.62 (s, 3H, CH_3C=), 3.82 (s, 4H, 2 x OCH_2), 4.05 (d, 1H, *J* = 8.3 Hz, OOCH), 4.09 (m, 1H, OCH), 4.93 (br. s, 2H, CH_2=C).^{13}C-NMR: (75.5 MHz, $CDCl_3$) δ (ppm) = 7.8 (q, CH_3CH_2), 17.8 (q, CH_3C=), 26.3 (t, CH_2), 29.5 (t, CH_2), 31.8 (t, CH_2), 64.7 (t, 2 x OCH_2), 70.5 (d, OCH), 93.1 (d, OOCH), 111.8 (s, OCO), 116.0 (t, CH_2=C), 141.4 (s, C=CH_2); *anti*-diastereoisomer: ^{1}H-NMR: (300 MHz, $CDCl_3$, additional significant signals) δ (ppm) = 1.69 (s, 3H, CH_3C=), 3.68 (m, 1H, OCH), 3.83 (s, 4H, 2 x OCH_2), 4.17 (d, 1H, *J* = 5.2 Hz, OOCH), 4.96 (m, 2H, CH_2=C). ^{13}C-NMR: (75.5 MHz, $CDCl_3$, additional significant signals) δ (ppm) = 64.6 (t, 2 x OCH_2), 70.5 (d, OCH), 91.4 (d, OOCH), 111.9 (s, OCO), 115.0 (t, CH_2=C), 141.5 (s, C=CH_2).



5a,b **6a,b**

1-Methyl-4-(prop-1-en-2-yl)-2,3,8-trioxa-bicyclo[3.2.1]octane (*exo*-5a and *endo*-6a)
A solution of 4-hydroperoxy-5-methyl-1-(2-methyl-1,3-dioxolan-2-yl)hex-5-en-3-ol (**4a**) (2.20 g, 9.48 mmol) in dichloromethane (100 ml) was treated with a catalytic amount of $BF_3.Et_2O$ (0.2 ml) and then stirred at r.t. for 24 h. Usual work-up and further purification of the crude product by preparative thick-layer chromatography allowed the separation of the pure major (*exo*) 1,2,4-trioxane as yellow oil (SiO_2, EA/*n*-hex, 1:10, $R_f = 0.39$) beside a diastereomeric mixture of the pure *exo*- and *endo*-1,2,4-trioxanes **5a**, **6a** in a ratio 77:23 (0.30 g, 1.76 mmol, 19 %).

exo-**5a**: ^{1}H-NMR: (300 MHz, $CDCl_3$) δ (ppm) = 1.41 (s, 3H, C$\underline{H}_3$), 1.88 (t, 3H, *J* = 0.8 Hz, C$\underline{H}_3$C=), 1.81-1.90 (m, 1H, C$\underline{H}_2$), 2.02-2.23 (m, 2H, C$\underline{H}_2$), 2.45-2.55 (m, 1H, C$\underline{H}_2$), 3.94 (d, 1H, *J* = 0.6 Hz, OOC$\underline{H}$), 4.60 (dd, 1H, *J* = 0.6, 6.5 Hz, OC$\underline{H}$), 5.13 (q, 1H, *J* = 1.6 Hz, C$\underline{H}_2$=C), 5.26 (d, 1H, *J* = 0.8 Hz, C$\underline{H}_2$=C); ^{13}C-NMR: (75.5 MHz, $CDCl_3$) δ (ppm) = 20.4 (q, $\underline{C}H_3$), 20.9 (q, $\underline{C}H_3$), 28.9 (t, $\underline{C}H_2$), 33.7 (t, $\underline{C}H_2$), 75.0 (d, O$\underline{C}$H), 85.8 (d, OO$\underline{C}$H), 111.0 (s, OO$\underline{C}$O), 113.9 (t, $\underline{C}H_2$=C), 141.5 (s, $\underline{C}$=CH_2). IR: (Film) ν (cm^{-1}) = 3092, 2993, 2954, 1650, 1452, 1381, 1189, 1147, 1055, 900, 865. Elemental analysis: ($C_9H_{14}O_3$, M = 170.21) Calcd: C 63.51 H 8.29, Found: C 63.17 H 8.29.
endo-**6a**: ^{1}H-NMR: (300 MHz, $CDCl_3$) δ (ppm) = 1.34 (s, 3H, C$\underline{H}_3$), 1.61 (d, 3H, *J* = 0.6 Hz, C$\underline{H}_3$C=), 1.71-1.81 (m, 1H, C$\underline{H}_2$), 1.92-2.13 (m, 2H, C$\underline{H}_2$), 2.21-2.27 (m, 1H, C$\underline{H}_2$), 4.30 (dd, 1H, *J* = 5.4, 0.6 Hz, OC$\underline{H}$), 4.65 (br. s, 1H, OOC$\underline{H}$), 4.67 (d, 1H, *J* = 0.9 Hz, C$\underline{H}_2$=C), 4.84 (q, 1H, *J* = 1.5 Hz, C$\underline{H}_2$=C); ^{13}C-NMR: (75.5 MHz, $CDCl_3$) δ (ppm) = 19.7 (2 x q, 2 x $\underline{C}H_3$), 23.9 (t, $\underline{C}H_2$), 34.1 (t, $\underline{C}H_2$), 76.3 (d, O$\underline{C}$H), 84.4 (d, OO$\underline{C}$H), 110.0 (s, OO$\underline{C}$O), 112.4 (t, $\underline{C}H_2$=C), 138.8 (s, $\underline{C}$=CH_2).

1-Ethyl-4-(prop-1-en-2-yl)-2,3,8-trioxa-bicyclo[3.2.1]octane (*exo*-5b and *endo*-6b)
A solution of 1-(2-ethyl-1,3-dioxolan-2-yl)-4-hydroperoxy-5-methylhex-5-en-3-ol (**4b**) (2.20 g, 8.94 mmol) in dichloromethane (100 ml) was treated with a catalytic amount of $BF_3.Et_2O$ (0.2 ml) and then stirred at r.t. for 24 h. Usual work-up and further purification of the crude product by preparative thick-layer chromatography (SiO_2, EA/*n*-hex, 1:10, $R_f = 0.68$) afforded a diastereomeric mixture of the pure *exo*- and *endo*-trioxanes **5b, 6b** in a ratio 77:23 (0.19 g, 1.03 mmol, 12 %).

exo-**5b**: ^{1}H-NMR: (300 MHz, $CDCl_3$) δ (ppm) = 0.88 (t, 3H, *J* = 7.6, C$\underline{H}_3$CH$_2$), 1.82 (d, 3H, *J* = 0.8 Hz, C$\underline{H}_3$C=), 1.53-1.85 (m, 3H, C$\underline{H}_2$CH$_3$ and CH$_2$), 1.99-2.08 (m, 2H, C$\underline{H}_2$), 2.30-2.40 (m, 1H, C$\underline{H}_2$), 3.89 (s, 1H, OOC$\underline{H}$), 4.54 (m, 1H, OC$\underline{H}$), 5.05 (q, 1H, *J* = 1.5 Hz, C$\underline{H}_2$=C), 5.19 (d, 1H, *J* = 0.7 Hz, C$\underline{H}_2$=C); ^{13}C-NMR: (75.5 MHz, $CDCl_3$) δ (ppm) = 7.5 (q, $\underline{C}H_3$CH$_2$), 20.3 (q, $\underline{C}H_3$C=), 27.6 (t, $\underline{C}H_2$), 28.3 (t, $\underline{C}H_2$), 31.2 (t, $\underline{C}H_2$), 74.8 (d, O$\underline{C}$H), 85.8 (d, OO$\underline{C}$H), 113.1 (s, OO$\underline{C}$O), 113.6 (t, $\underline{C}H_2$=C), 141.5 (s, $\underline{C}$=CH_2); IR: (Film) ν (cm^{-1}) = 3094, 2975, 2946, 2883, 1651, 1456, 1178, 1097, 1061, 961, 904; Elemental analysis: ($C_{10}H_{16}O_3$, M = 184.23) Calcd: C 65.19 H 8.75, Found: C 65.13 H 8.58
endo-**6b**: ^{1}H-NMR: (300 MHz, $CDCl_3$) δ (ppm) = 0.91 (t, 3H, *J* = 7.5, C$\underline{H}_3$CH$_2$), 1.64 (s, 3H, C$\underline{H}_3$C=), 1.53-1.85 (m, 3H, C$\underline{H}_2$CH$_3$ and CH$_2$), 1.99-2.08 (m, 2H, C$\underline{H}_2$), 2.18-2.28 (m, 1H, CH$_2$), 4.35 (d, 1H, *J* = 6.0 Hz, OC$\underline{H}$), 4.70 (br. s, 2H, OOC$\underline{H}$ and C$\underline{H}_2$=C), 4.87 (d, 1H, *J* = 1.3 Hz,

CH_2=C); ^{13}C-NMR: (75.5 MHz, $CDCl_3$) δ (ppm) = 7.7 (q, CH_3CH_2), 19.9 (q, CH_3C=), 23.6 (t, CH_2), 27.0 (t, CH_2), 32.1 (t, CH_2), 76.3 (d, OCH), 84.8 (d, OOCH), 112.4 (s, OOCO), 112.5 (t, CH_2=C), 139.0 (s, C=CH_2).

Syntheses of 2,3,7,8-tetraoxabicyclo[3.2.1]octane 10 and 1-ethyl-4-(prop-1-ene-2-yl)-2,3,8,9-tetraoxa-bicylco[3.3.1]nonane (13d)

Synthesis of (S)-2,4-dimethylhex-4-ene-2,3-diol
To a well stirred mixture of water (10 mL) and tert-butanol (10 mL) were added AD-mix a (3 g) and methane sulphonamide (2 mmol, 180 mg) at 20 °C. After 10 minutes 2,5-dimethyl-2,4-hexadiene **7** (2 mmol, 0.22 g) was added and the mixture was stirred for 2 h. Sodium bisulfite (3 g) was added and the resulting grey mixture was stirred for 1 h and extracted with ethyl acetate (3 x 14 mL). The combined organic layers were washed with brine (2 x 4 mL) and dried over $MgSO_4$. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography (SiO_2, Et_2O) to yield the diol **8** (0.253 mg, 1.76 mmol, 88 %) as pale yellow oil.
^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 1.21 (s, 3H, CH_3), 1.66 (s, 3H, CH_3), 1.71 (s, 6H, CH_3), 2.70 (br, 2H, 2 OH), 4.10 (d, 1H, *J* = 9.3 Hz, CHOH), 5.16 (d, 1H, *J* = 9.3 Hz, CH=C); ^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) = 18.4 (CH_3C=C), 23.2 (CH_3C=C), 26.0 (CH_3), 26.1 (CH_3), 74.9 (CH_3COH), 76.6 (COH), 123.6 (C=CH), 137.1 (($CH_3)_2$C=C).

General procedure for photooxygenation (GP1):
The substrate (1 mmol) and the sensitizer (TPP, 2 mg) were dissolved in 30 ml of CCl_4 and irradiated at 10 °C under an atmosphere of oxygen with a mercury-medium-pressure lamp (λ ≥ 370, edge filter). After evaporation of the solvent under reduced pressure the hydroperoxide was obtained.

Synthesis of (3R,4S)-4-hydroperoxy-2,5-dimethylhex-5-ene-2,3-diol (9)

Photooxygenation of (S)-2,4-dimethyl-hex-4-ene-2,3-diol (**8**) (1 mmol, 144 mg) for 6 h according to GP1 afforded a diastereomeric mixture (d.r. = 87:13) of the hydroperoxide **9** and starting material.

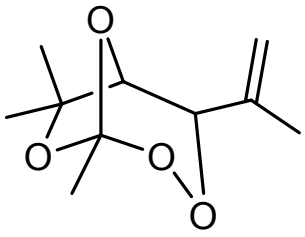
^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) = 1.35 (s, 6H, 2 CH_3), 1.82 (s, 3H, CH_3=C), 3.47 (d, 1H, *J* = 2.7 Hz, CHOH), 4.61 (d, 1H, *J* = 2.4 Hz, HCOOH), 5.09 (d, 2H, *J* = 6.6 Hz, H_2C=C); ^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) = 19.8 (CH_3C=C), 24.9 (CH_3), 27.3 (CH_3), 72.9 (($CH_3)_2$COH), 76.1 (HCOH), 87.0 (HCOOH), 114.3 (H_2C=C), 141.5 ((CH_3C=C). ^{1}H-NMR (300 MHz, $CDCl_3$, additional signals) δ (ppm) = 3.37 (d, 1H, *J* = 8.1 Hz, HCOH), 4.43 (d, 1H, *J* = 8.1 Hz, HCOOH).

Synthesis of 4-hydroperoxy-5-methylhex-5-ene-1,3-diol (12a)

Photooxygenation of 5-methylhex-4-ene-1,3-diol (**11a**) (1 mmol, 130 mg) for 6 h according to GP1 afforded a diastereomeric mixture (ds = 83:17) of the hydroperoxide **12a** and starting material.
^{1}H-NMR: (300 MHz, $CDCl_3$) δ (ppm) = 1.62 (m, 2H, CH_2), 1.70 (s, 3H, CH_3), 3.73 (sext, 2H, *J* = 5.6 Hz, CH_2OH), 3.88 (dt, 1H, *J* = 3.2 Hz, 5.5 Hz, CHOH), 4.17 (d, 1H, *J* = 8.4, CHOOH), 5.01 (d, 2H, C=CH_2); ^{13}C-NMR: (75 MHz, $CDCl_3$) δ (ppm) = 17.89 (CH_3), 34.33 (CH_2), 60.05 (CH_2OH), 69.64 (CHOH), 93.24 (CHOOH), 116.50 (C=CH_2), 141.33 (H_2C=C). ^{1}H-NMR: (300 MHz, $CDCl_3$, additional signals) δ (ppm) = 1.77 (s, 3H, CH_3), 4.27 (d, 1H, *J* = 4.8, CHOOH); ^{13}C-NMR: (75 MHz, $CDCl_3$, additional signals) δ (ppm) = 18.11 (CH_3), 91.41 (CHOOH), 115.30 (C=CH_2).

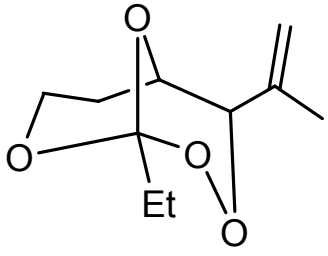
General procedure for peroxyacetalisation (GP2):
To a stirred solution of the dihydroxyhydroperoxide (1 mmol) in DCM (12 mL) were added an orthoester (3 mmol) and a catalytic amount of pyridinium-*p*-toluenesulfonate(PPTS). The reaction was stirred at RT and then filtered through a short plug of silica. Evaporation of the solvent under reduced pressure obtained the crude product, which was purified by column chromatography to yield a diastereomeric mixture of the trioxane.

1- Methyl-4-(prop-1-ene-2-yl)-2,3,8,9-tetraoxa-bicylco[3.3.1]nonane (10)



Following GP2, a solution of (3R,4S)-4-hydroperoxy-2,5-dimethylhex-5-ene-2,3-diol (**9)** (176 mg, 1 mmol) and trimethylorthoacetate (0.16 mL, 3 mmol) in DCM (12 mL) were treated with a catalytic amount of PPTS. Usual work-up and purification of the crude product by column chromatography (SiO_2, EA/*n*-hex, 1:9, $r_f = 0.42$) afforded a mixture of diastereoisomers of **10** (ds = 81:19, 37 mg, 0.19 mmol, 19 %).
^{1}H-NMR: (300 MHz, $CDCl_3$) δ (ppm) = 1.36 (s, 3H, C(C$\underline{H}_3$)$_2$), 1.56 (s, 3H, C$\underline{H}_3$COO), 1.62 (s, 3H, C(C$\underline{H}_3$)$_2$), 1.90 (s, 3H, C$\underline{H}_3$C=C), 4.10 (d, 1H, *J* = 1.2 Hz, C$\underline{H}$O), 4.33 (s, 1H, C$\underline{H}$OO), 5.23 (d, C$\underline{H}_2$=C); ^{13}C-NMR: (75 MHz, $CDCl_3$) δ (ppm) = 20.29 (C$\underline{H}_3$C=C, C$\underline{H}_3$), 21.06 (C(C$\underline{H}_3$)$_2$), 27.42 (C(C$\underline{H}_3$)$_2$), 78.53 (C$\underline{H}$O), 80.19 (C$\underline{H}$OO), 82.10 (C$\underline{(}$CH$_3$)$_2$), 114.10 (C$\underline{H}_2$=C), 122.15 (CH$_3$C$\underline{O}$O), 140.55 (C$\underline{=}$CH$_2$).
^{1}H-NMR: (300 MHz, $CDCl_3$, additional signals) δ (ppm) = 1.33 (s, 3H, C(C$\underline{H}_3$)$_2$), 1.51 (s, 3H, C$\underline{H}_3$COO), 1.60 (s, 3H, C(C$\underline{H}_3$)$_2$), 1.78 (s, 3H, C$\underline{H}_3$C=C), 4.10 (d, 1H, *J* = 0.9 Hz, C$\underline{H}$O), 4.33 (s, 1H, C$\underline{H}$OO), 5.23 (dd, Hz, C$\underline{H}_2$=C); ^{13}C-NMR: (75 MHz, $CDCl_3$, additional signals) δ (ppm) = 19.30 (C$\underline{H}_3$C=C), 21.43 (C$\underline{H}_3$), 28.39 (C(C$\underline{H}_3$)$_2$), 83.13 (C$\underline{H}$OO), 112.21 (H$_2$C$\underline{=}$C).

1-Ethyl-4-(prop-1-ene-2-yl)-2,3,8,9-tetraoxa-bicyclo[3.3.1]nonane (13d)



Following GP2, a solution of 4-hydroperoxy-5-methylhex-5-ene-1,3-diol (**12a)** (162 mg, 1 mmol) and triethylisopropylate (0.6 mL, 3 mmol) in DCM (12 mL) were treated with a catalytic amount of PPTS. Usual work-up and purification of the crude product by column chromatography (SiO_2, Et_2O/PE, 1:9, $r_f = 0.65$, 0.44) afforded the separated diastereoisomers (36 mg, 0.18 mmol, 18 %, 16 mg, 0.08 mmol, 8 %).

^{1}H-NMR: (300 MHz, $CDCl_3$) δ (ppm) = 0.95 (t, 3H, *J* = 7.8 Hz, C$\underline{H}_3$CH$_2$), 1.71 (m, 3H, C$\underline{H}_2$, CC$\underline{H}_2$), 1.86 (s, 3H, C$\underline{H}_3$), 2.45 (m, 1H, C$\underline{H}_2$), 3.91 (m, 1H, C$\underline{H}_2$O), 4.26 (dt, 1H, *J* = 6.6Hz, 1.5 Hz C$\underline{H}$O), 4.38 (s, 1H, C$\underline{H}$OO), 4.63 (m, 1H, C$\underline{H}_2$O), 5.13 (d, 2H, =C$\underline{H}_2$); ^{13}C-NMR: (75

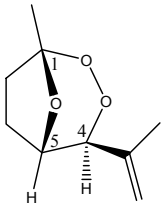
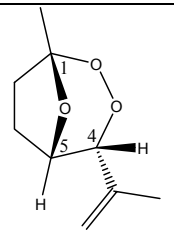
MHz, $CDCl_3$) δ (ppm) = 6.60 ($\underline{C}H_3CH_2$) 19.4 ($\underline{C}H_3$), 27.7 ($\underline{C}H_2$), 30.6 ($C\underline{C}H_2$), 59.7 ($\underline{C}H_2O$), 65.5 ($\underline{C}HO$), 84.5 ($\underline{C}HOO$), 114.5 ($OO\underline{C}CH_2$), 115.0 ($=\underline{C}H_2$), 141.2 ($\underline{C}=CH_2$).

^{1}H-NMR: (300 MHz, $CDCl_3$) δ (ppm) = 0.98 (t, 3H, *J* = 7.6 Hz, $C\underline{H}_3CH_2$), 1.73 (m, 5H, $C\underline{H}_3$, $CC\underline{H}_2$), 2.01 (m, 1H, $C\underline{H}_2$), 2.15 (m, 1H, $C\underline{H}_2$), 3.92 (m, 1H, $C\underline{H}_2O$), 4.21 (dt, 1H, *J* = 7.6Hz, 2.3 Hz $C\underline{H}O$), 4.50 (m, 1H, $C\underline{H}_2O$), 5.13 (d, 3H, $C=C\underline{H}_2$, $C\underline{H}OO$); ^{13}C-NMR: (75 MHz, $CDCl_3$) δ (ppm) = 6.75 ($\underline{C}H_3CH_2$) 19.8 ($\underline{C}H_3$), 22.71 ($\underline{C}H_2$), 30.1 ($C\underline{C}H_2$), 61.4 ($\underline{C}H_2O$), 66.3 ($\underline{C}HO$), 83.4 ($\underline{C}HOO$), 112.7 ($OO\underline{C}CH_2$), 113.7 ($=\underline{C}H_2$), 138.3 ($\underline{C}=CH_2$).

Reference [26]:
Gaussian 03, Revision C.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hrahian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Wallingford CT, 2004.

Summary of Calculated Properties of the Optimized (B3LYP/6-311G(d)) Bicycles 5a, 6a, 10 and epi-10

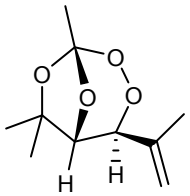
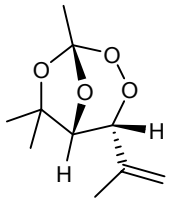
Table 1S: Calculated relative energies (B3LYP/6-311G(d)), local minima contributions of conformers and ring isomers, ^{3}J-coupling constants and chemical shifts of **5a** and **6a**.

	Confor-mer	ΔE[a] [kJ/mol]	Contrib.[b] $\frac{N_i}{N_0}$	Contrib. %	Ring conf.[c]	∠ ϕ_1 (CCC=C)	∠ ϕ_2 (4-H/5-H)	^{3}J-Coupling[d] (4-H/5-H) [Hz]	δ 4-H[e] [ppm]	δ 5-H[e] [ppm]
 **5a**	I	0.00	1.0	45	C^6/B^7	108.3	73.0	0.4	3.8	4.2
	II	0.91	0.7	31	C^6/B^7	-0.3	69.9	0.7	3.6	4.6
	III	1.69	0.5	23	C^6/B^7	-130.7	68.9	0.8	3.8	4.5
	IV	19.20	0.0	0	B^6/C^7	113.7	104.5	0.3	4.2	4.0
	V	24.09	0.0	0	B^6/C^7	-95.1	105.0	0.4	4.1	4.0
 **6a**	I	0.00	1.0	63	C^6/B^7	108.1	-65.2	1.2	4.8	4.2
	II	1.69	0.5	32	C^6/B^7	-10.2	-66.7	1.0	4.8	4.4
	III	6.33	0.1	5	C^6/B^7	-80.8	-65.0	1.2	5.2	4.0
	IV	29.92	0.0	0	B^6/C^7	119.8	-33.7	5.6	4.7	4.4
	V	34.47	0.0	0	B^6/C^7	-74.3	-33.6	5.6	5.0	4.4

a: relative energy with respect to the conformer of lowest energy; b: contribution of the respective rotamer to the overall population according Boltzmann's equation;

c: description of ring conformation - C^6/B^7: *trioxane chair*, B^6/C^7: *trioxane boat*; d: $^3J_{HH}$-coupling calculated according Karplus' equation; e: relative chemical shift with respect to TMS calculated with the GIAO algorithm at the B3LYP/6-311G(d) level of theory.

Table 2S: Calculated relative energies (B3LYP/6-311G(d)), local minima contributions of conformers and ring isomers, $^3J_{HH}$-coupling constants and chemical shifts of **10** and epi-**10**.

	Confor-mer	ΔE[a] [kJ/mol]	Contrib.[b] $\frac{N_i}{N_0}$	Contrib. %	Ring conf.[c]	∠ ϕ_1 (CCC=C)	∠ ϕ_2 (4-H/5-H)	^{3}J-Coupling[d] (4-H/5-H) [Hz]	δ 4-H[e] [ppm]	δ 5-H[e] [ppm]
 **10**	I	0.00	1.0	53	C^6/B^7	106.4	71,4	0.6	4.1	3.7
	II	1.74	0.5	26	C^6/B^7	-128.2	67,9	0.9	4.1	3.9
	III	2.26	0.4	21	C^6/B^7	0.7	69,0	0.8	3.9	4.0
	IV	14.98	0.0	0	B^6/C^7	114.9	191,1	8.9	4.8	3.6
	V	19.86	0.0	0	B^6/C^7	-92.7	101,2	0.1	4.6	3.6
 epi-**10**	I	0,00	1,0	51	C^6/B^7	132,6	-67,5	1,0	5,0	3,8
	II	0,10	1,0	49	C^6/B^7	-18,5	-69,3	0,8	5,0	4,0
	III	30,13	0,0	0	B^6/C^7	125,9	-39,3	4,8	4,9	4,1
	IV	34,41	0,0	0	B^6/C^7	-61,8	-38,2	5,0	5,2	4,1

a: relative energy with respect to the conformer of lowest energy; b: contribution of the respective rotamer to the overall population according Boltzmann's equation; c: description of ring conformation - C^6/B^7: *trioxane chair*, B^6/C^7: *trioxane boat*; d: $^3J_{HH}$-coupling calculated according Karplus' equation; e: relative chemical shift with respect to TMS calculated with the GIAO algorithm at the B3LYP/6-311G(d) level of theory.

Relaxed potential energy profiles according the rotation of the isopropenyl group of 5a, 6a, 10 and epi-10

In order to locate the relative energetic minima with respect to the rotation of the isopropenyl group, relaxed potential energy scans have been performed on the B3LYP/6-31G level of theory shown in Figures 1S-8S.

In these scans all internal coordinates of the structures were free for optimization with the exception of the dihedral angle defining the orientation of the isopropenyl group with respect to the ring system. The minima located by these tentative scans have subsequently been refined without any restrictions employing the larger basis set 6-311G(d), cf. Tables 3S ff. Note that the energy differences between the relative minima which could be estimated from the graphs differ remarkably from the thoroughly calculated ones obtained from the fully optimized structures using the larger basis set. Thus, these graphs should only be used to localize the relative minima; for any further calculations or interpretations the fully optimized structures compiled in Tables 3S-42S have been be applied.

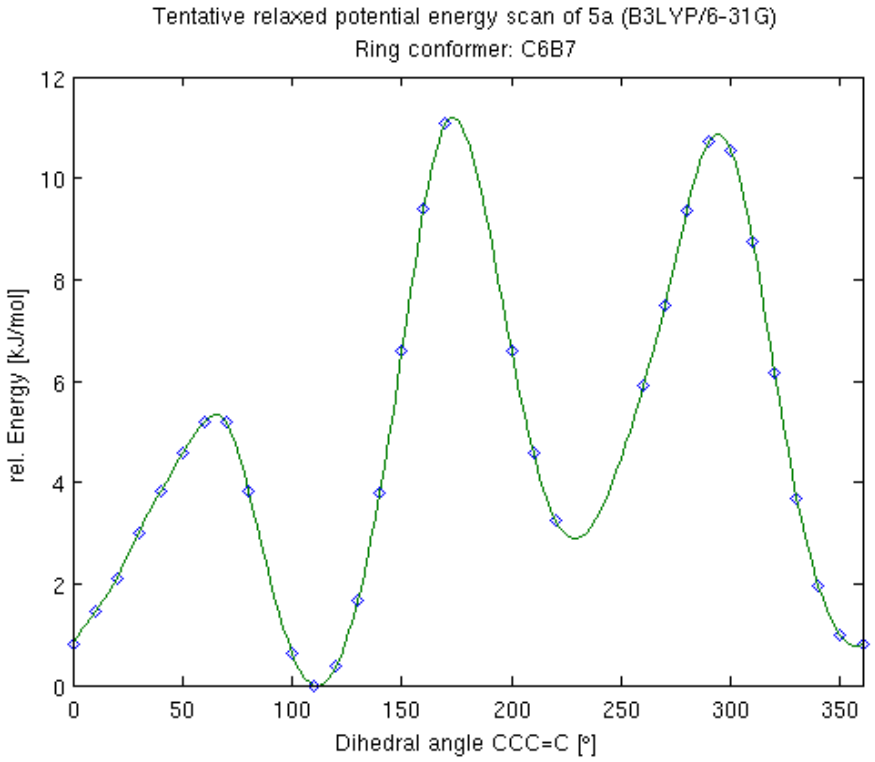


Figure 1S: Relaxed energy profile of the rotation of the isopropenyl group of **5a**, ring conformer C^6/B^7.

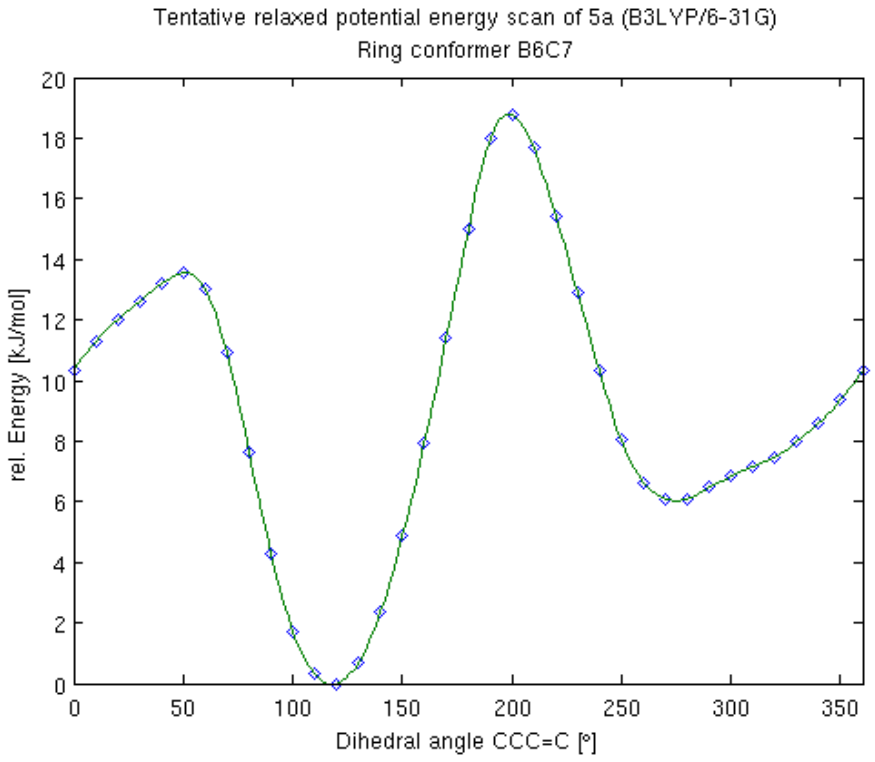


Figure 2S: Relaxed energy profile of the rotation of the isopropenyl group of **5a**, ring conformer B^6/C^7.

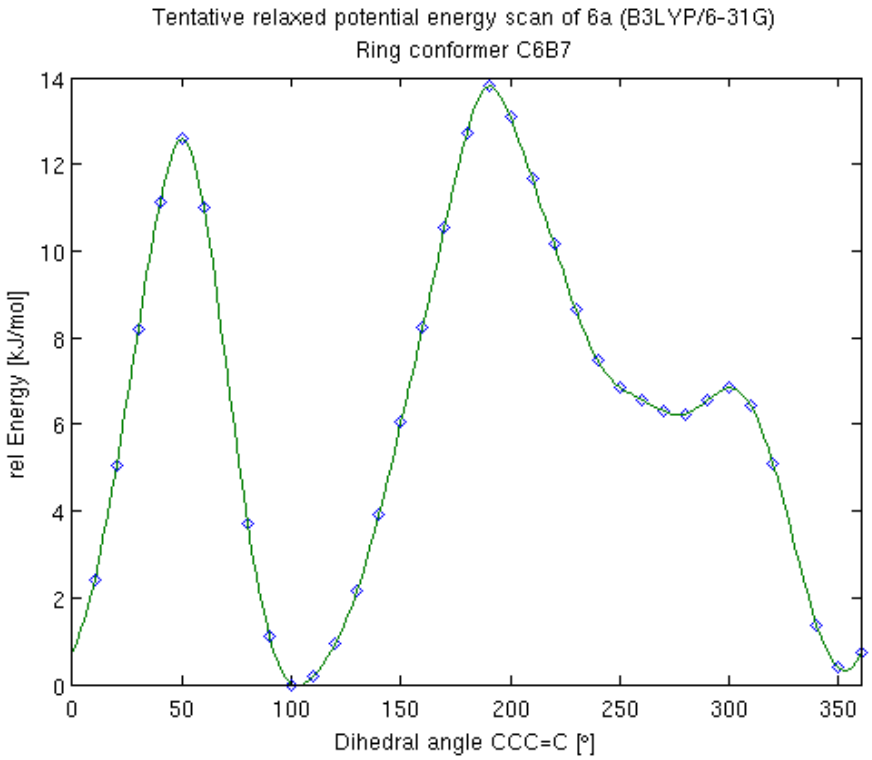


Figure 3S: Relaxed energy profile of the rotation of the isopropenyl group of **6a**, ring conformer C^6/B^7.

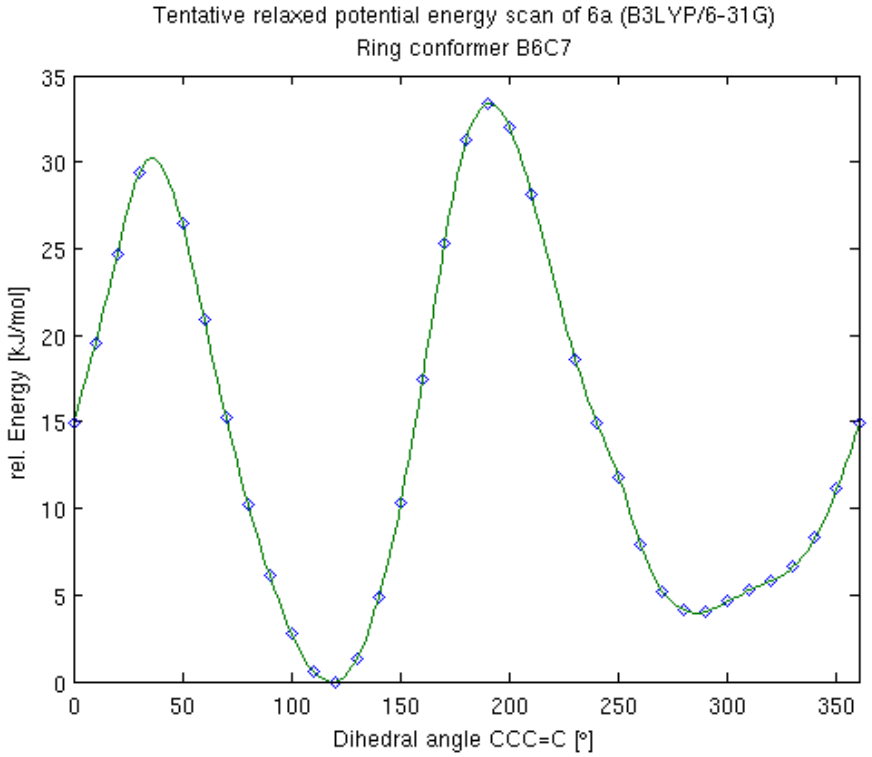


Figure 4S: Relaxed energy profile of the rotation of the isopropenyl group of **6a**, ring conformer B^6/C^7.

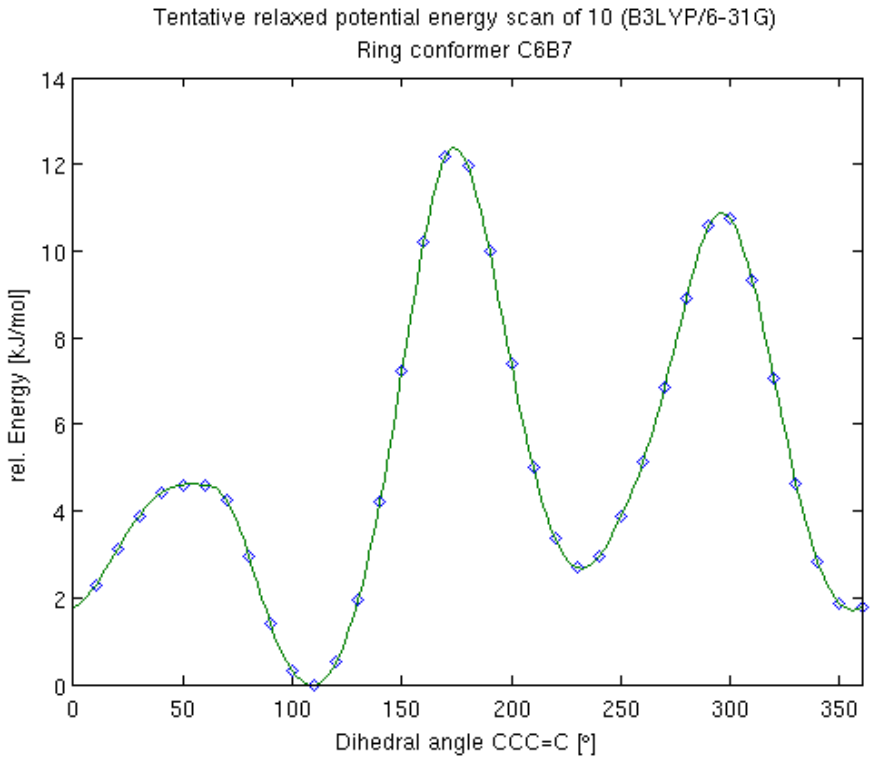


Figure 5S: Relaxed energy profile of the rotation of the isopropenyl group of **10**, ring conformer C^6/B^7.

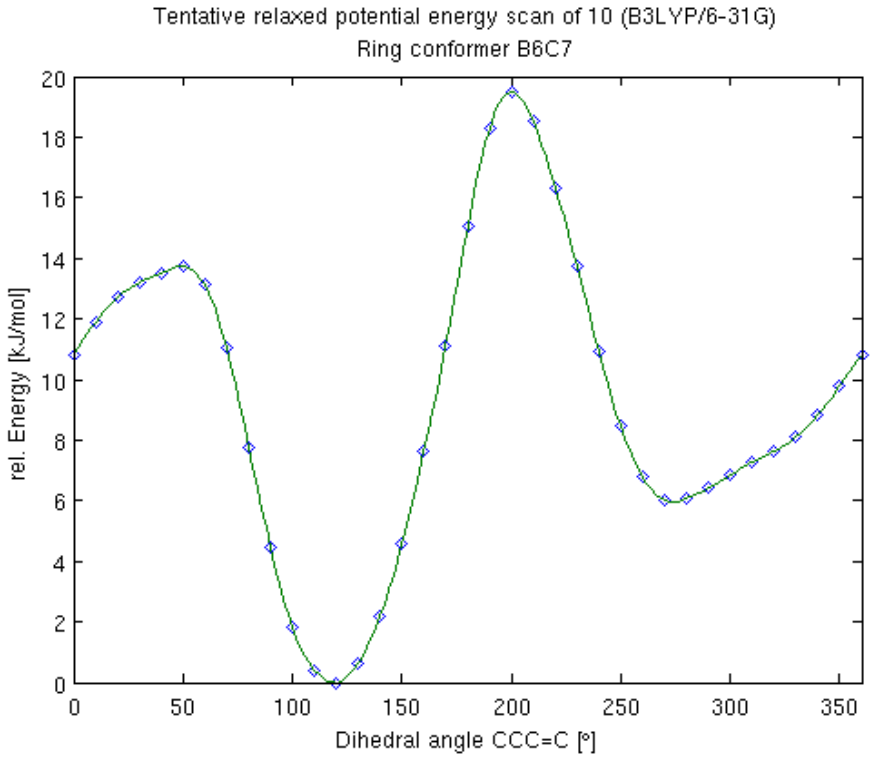


Figure 6S: Relaxed energy profile of the rotation of the isopropenyl group of **10**, ring conformer B^6/C^7.

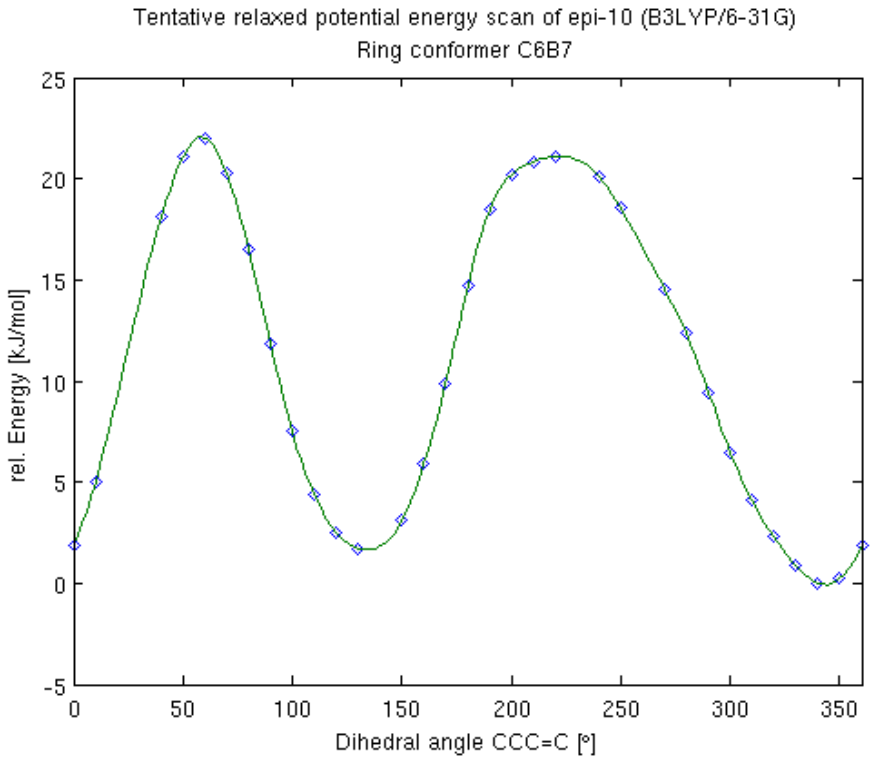


Figure 7S: Relaxed energy profile of the rotation of the isopropenyl group of epi-**10**, ring conformer C^6/B^7.

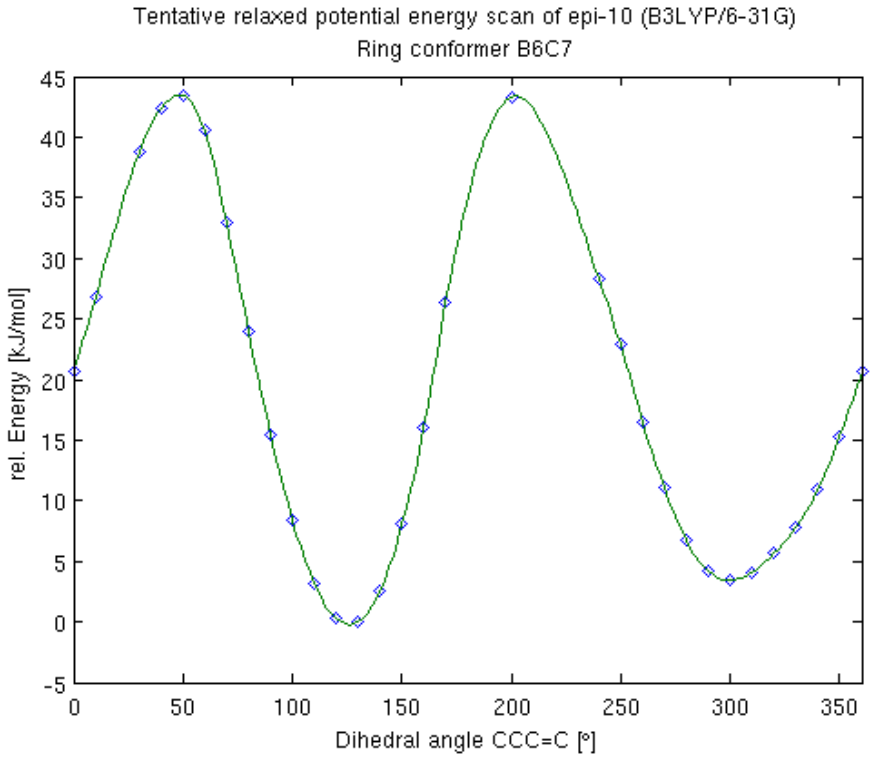
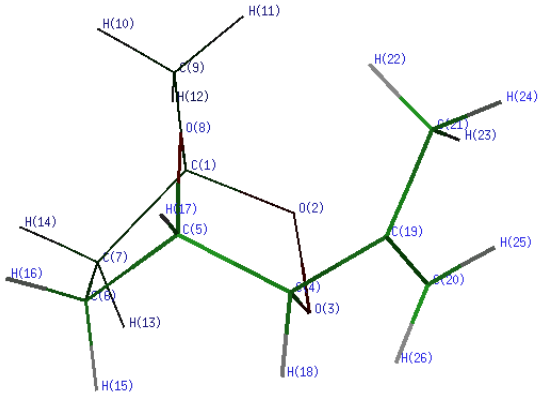


Figure 8S: Relaxed energy profile of the rotation of the isopropenyl group of epi-**10**, ring conformer B^6/C^7.

Optimized structures (B3LYP/6-311G(d)) of 5a, 6a, 10, epi-10 and TMS

Table 3S: Absolute energy and coordinates of compound **5a**, conformer I
Level of theory: B3LYP/6-311G(d)
Point group: C1
Number of negative eigenvalues in the Hessian matrix: 0
E(RB+HF-LYP) = -577.076657076 a.u.



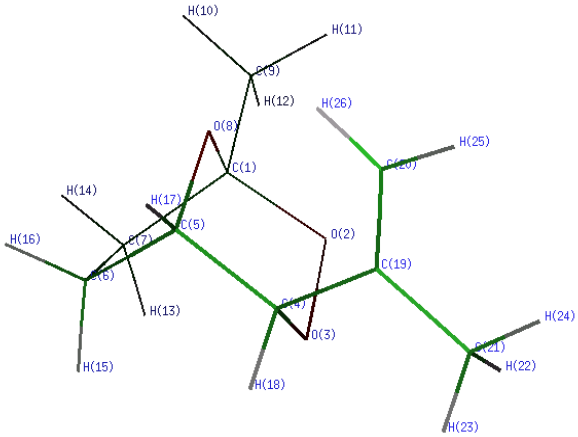
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.484429	0.455221	-0.019859
2	8	0	0.627670	0.907535	1.033121
3	8	0	-0.237081	-0.194792	1.459154
4	6	0	-0.996402	-0.706991	0.336209
5	6	0	-0.005582	-1.018002	-0.803246
6	6	0	1.140641	-1.927839	-0.311173
7	6	0	2.123925	-0.911453	0.314685
8	8	0	0.679121	0.191704	-1.165188
9	6	0	2.416800	1.612429	-0.297202
10	1	0	3.007932	1.391167	-1.187252
11	1	0	1.844042	2.523716	-0.474128
12	1	0	3.086466	1.774460	0.548697
13	1	0	2.231298	-1.028931	1.392111
14	1	0	3.114418	-0.973027	-0.139766
15	1	0	0.803809	-2.684278	0.399599
16	1	0	1.589562	-2.441156	-1.163774
17	1	0	-0.530561	-1.383681	-1.685975
18	1	0	-1.357723	-1.656545	0.743137
19	6	0	-2.198303	0.137432	-0.038661
20	6	0	-3.393999	-0.453596	-0.092885
21	6	0	-2.014046	1.599794	-0.346510
22	1	0	-1.338492	1.744943	-1.192105
23	1	0	-1.562040	2.117369	0.502586
24	1	0	-2.973446	2.070065	-0.572919
25	1	0	-4.285978	0.091771	-0.385077
26	1	0	-3.531740	-1.503404	0.150019

Table 4S: GIAO-B3LYP/6-311G(d) NMR absolute isotropic shielding tensor elements (σ, ppm) of **5a**, conformer I, and relative chemical shifts with respect to TMS (ppm).

1	C	Isotropic =	67.2457	ppm; relative to TMS:	117.2209	ppm
2	O	Isotropic =	0.7773	ppm; relative to TMS:	---	
3	O	Isotropic =	4.8423	ppm; relative to TMS:	---	
4	C	Isotropic =	89.4870	ppm; relative to TMS:	94.9796	ppm
5	C	Isotropic =	99.1356	ppm; relative to TMS:	85.3310	ppm
6	C	Isotropic =	150.3160	ppm; relative to TMS:	34.1506	ppm
7	C	Isotropic =	147.5112	ppm; relative to TMS:	36.9554	ppm
8	O	Isotropic =	201.2284	ppm; relative to TMS:	---	
9	C	Isotropic =	161.4176	ppm; relative to TMS:	23.0490	ppm
10	H	Isotropic =	31.2020	ppm; relative to TMS:	1.0783	ppm
11	H	Isotropic =	30.7932	ppm; relative to TMS:	1.4871	ppm
12	H	Isotropic =	30.9579	ppm; relative to TMS:	1.3224	ppm
13	H	Isotropic =	29.8001	ppm; relative to TMS:	2.4802	ppm
14	H	Isotropic =	30.5935	ppm; relative to TMS:	1.6868	ppm
15	H	Isotropic =	30.2558	ppm; relative to TMS:	2.0245	ppm
16	H	Isotropic =	30.2246	ppm; relative to TMS:	2.0557	ppm
17	H	Isotropic =	28.0680	ppm; relative to TMS:	4.2123	ppm
18	H	Isotropic =	28.4676	ppm; relative to TMS:	3.8127	ppm
19	C	Isotropic =	25.9810	ppm; relative to TMS:	158.4856	ppm
20	C	Isotropic =	67.9393	ppm; relative to TMS:	116.5273	ppm
21	C	Isotropic =	160.1817	ppm; relative to TMS:	24.2849	ppm
22	H	Isotropic =	29.6751	ppm; relative to TMS:	2.6052	ppm
23	H	Isotropic =	29.7386	ppm; relative to TMS:	2.5417	ppm
24	H	Isotropic =	30.5140	ppm; relative to TMS:	1.7663	ppm
25	H	Isotropic =	27.3797	ppm; relative to TMS:	4.9006	ppm
26	H	Isotropic =	27.5653	ppm; relative to TMS:	4.7150	ppm

Table 5S: Absolute energy and coordinates of compound **5a**, conformer II
Level of theory: B3LYP/6-311G(d)
Point group: C1
Number of negative eigenvalues in the Hessian matrix: 0
E(RB+HF-LYP) = -577.076309346 a.u.



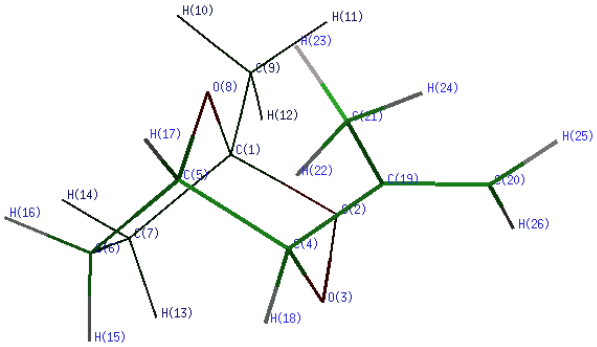
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.446003	-0.568422	-0.061885
2	8	0	0.452414	-0.925588	-1.031321
3	8	0	-0.316402	0.271858	-1.370846
4	6	0	-0.946276	0.777230	-0.165864
5	6	0	0.170657	1.022274	0.858813
6	6	0	1.326946	1.835487	0.235139
7	6	0	2.171870	0.737629	-0.455800
8	8	0	0.791107	-0.238194	1.158806
9	6	0	2.281767	-1.813249	0.124717
10	1	0	2.979626	-1.657943	0.949012
11	1	0	1.637401	-2.660002	0.364517
12	1	0	2.841401	-2.038696	-0.784196
13	1	0	2.210085	0.846060	-1.538774
14	1	0	3.194326	0.715131	-0.073966
15	1	0	0.976500	2.598136	-0.462387
16	1	0	1.890965	2.333613	1.026071
17	1	0	-0.217747	1.438630	1.788192
18	1	0	-1.321205	1.746520	-0.521365
19	6	0	-2.130373	-0.071782	0.252148
20	6	0	-2.249836	-0.621524	1.459622
21	6	0	-3.179946	-0.234243	-0.817529
22	1	0	-2.755757	-0.721174	-1.699616
23	1	0	-3.568137	0.736005	-1.150072
24	1	0	-4.021532	-0.832482	-0.463898
25	1	0	-3.132786	-1.195410	1.725222
26	1	0	-1.474964	-0.553391	2.211978

Table 6S: GIAO-B3LYP/6-311G(d) NMR absolute isotropic shielding tensor elements (σ, ppm) of **5a**, conformer II, and relative chemical shifts with respect to TMS (ppm).

1	C	Isotropic =	66.7661	ppm; relative to TMS:	117.7005	ppm
2	O	Isotropic =	-2.1256	ppm; relative to TMS:	---	
3	O	Isotropic =	14.7112	ppm; relative to TMS:	---	
4	C	Isotropic =	93.9336	ppm; relative to TMS:	90.5330	ppm
5	C	Isotropic =	104.2594	ppm; relative to TMS:	80.2072	ppm
6	C	Isotropic =	150.3097	ppm; relative to TMS:	34.1569	ppm
7	C	Isotropic =	146.7588	ppm; relative to TMS:	37.7078	ppm
8	O	Isotropic =	201.4966	ppm; relative to TMS:	---	
9	C	Isotropic =	162.0037	ppm; relative to TMS:	22.4629	ppm
10	H	Isotropic =	31.2435	ppm; relative to TMS:	1.0368	ppm
11	H	Isotropic =	30.7972	ppm; relative to TMS:	1.4831	ppm
12	H	Isotropic =	31.0414	ppm; relative to TMS:	1.2389	ppm
13	H	Isotropic =	29.7884	ppm; relative to TMS:	2.4919	ppm
14	H	Isotropic =	30.5706	ppm; relative to TMS:	1.7097	ppm
15	H	Isotropic =	30.2333	ppm; relative to TMS:	2.0470	ppm
16	H	Isotropic =	30.1624	ppm; relative to TMS:	2.1179	ppm
17	H	Isotropic =	27.7352	ppm; relative to TMS:	4.5451	ppm
18	H	Isotropic =	28.7048	ppm; relative to TMS:	3.5755	ppm
19	C	Isotropic =	32.8333	ppm; relative to TMS:	151.6333	ppm
20	C	Isotropic =	63.2762	ppm; relative to TMS:	121.1904	ppm
21	C	Isotropic =	160.2264	ppm; relative to TMS:	24.2402	ppm
22	H	Isotropic =	29.7802	ppm; relative to TMS:	2.5001	ppm
23	H	Isotropic =	30.6845	ppm; relative to TMS:	1.5958	ppm
24	H	Isotropic =	30.5229	ppm; relative to TMS:	1.7574	ppm
25	H	Isotropic =	26.9200	ppm; relative to TMS:	5.3603	ppm
26	H	Isotropic =	26.7184	ppm; relative to TMS:	5.5619	ppm

Table 7S: Absolute energy and coordinates of compound **5a**, conformer III
Level of theory: B3LYP/6-311G(d)
Point group: C1
Number of negative eigenvalues in the Hessian matrix: 0
E(RB+HF-LYP) = -577.076014066 a.u.



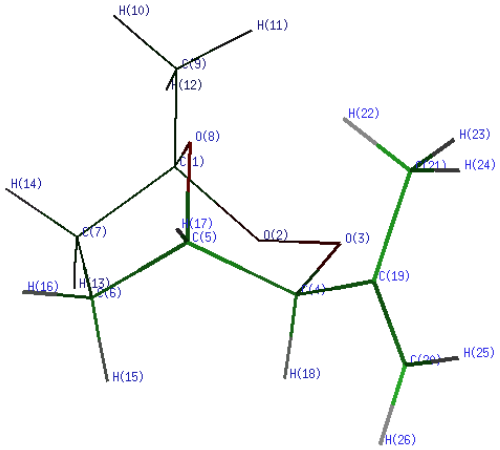
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.458701	-0.464397	0.261176
2	8	0	0.659436	-1.227093	-0.648933
3	8	0	-0.124818	-0.308428	-1.480633
4	6	0	-0.943427	0.519538	-0.636837
5	6	0	-0.006027	1.219331	0.368728
6	6	0	1.199607	1.867818	-0.345718
7	6	0	2.190722	0.686350	-0.463206
8	8	0	0.595792	0.199988	1.179027
9	6	0	2.300069	-1.485699	0.991515
10	1	0	2.841959	-0.992839	1.800149
11	1	0	1.658492	-2.257922	1.417656
12	1	0	3.013832	-1.951645	0.310607
13	1	0	2.411271	0.412439	-1.494150
14	1	0	3.132295	0.898043	0.046999
15	1	0	0.932967	2.291568	-1.315292
16	1	0	1.606150	2.669681	0.273782
17	1	0	-0.547298	1.896341	1.028544
18	1	0	-1.312196	1.269126	-1.351116
19	6	0	-2.134089	-0.197361	-0.026293
20	6	0	-2.438427	-1.450172	-0.352579
21	6	0	-2.971971	0.621309	0.923352
22	1	0	-3.208750	1.610750	0.513400
23	1	0	-2.452904	0.785757	1.873589
24	1	0	-3.915382	0.119645	1.145095
25	1	0	-3.316435	-1.938503	0.058910
26	1	0	-1.818231	-2.028483	-1.024700

Table 8S: GIAO-B3LYP/6-311G(d) NMR absolute isotropic shielding tensor elements (σ, ppm) of **5a**, conformer III, and relative chemical shifts with respect to TMS (ppm).

1	C	Isotropic =	66.7647	ppm; relative to TMS:	117.7019	ppm
2	O	Isotropic =	-5.2044	ppm; relative to TMS:	---	
3	O	Isotropic =	22.0958	ppm; relative to TMS:	---	
4	C	Isotropic =	91.8890	ppm; relative to TMS:	92.5776	ppm
5	C	Isotropic =	104.4634	ppm; relative to TMS:	80.0032	ppm
6	C	Isotropic =	150.9971	ppm; relative to TMS:	33.4695	ppm
7	C	Isotropic =	146.9378	ppm; relative to TMS:	37.5288	ppm
8	O	Isotropic =	206.2812	ppm; relative to TMS:	---	
9	C	Isotropic =	161.8441	ppm; relative to TMS:	22.6225	ppm
10	H	Isotropic =	31.2814	ppm; relative to TMS:	0.9989	ppm
11	H	Isotropic =	30.8093	ppm; relative to TMS:	1.4710	ppm
12	H	Isotropic =	31.0399	ppm; relative to TMS:	1.2404	ppm
13	H	Isotropic =	29.8239	ppm; relative to TMS:	2.4564	ppm
14	H	Isotropic =	30.5917	ppm; relative to TMS:	1.6886	ppm
15	H	Isotropic =	30.2146	ppm; relative to TMS:	2.0657	ppm
16	H	Isotropic =	30.2090	ppm; relative to TMS:	2.0713	ppm
17	H	Isotropic =	27.8225	ppm; relative to TMS:	4.4578	ppm
18	H	Isotropic =	28.4304	ppm; relative to TMS:	3.8499	ppm
19	C	Isotropic =	37.1782	ppm; relative to TMS:	147.2884	ppm
20	C	Isotropic =	65.7774	ppm; relative to TMS:	118.6892	ppm
21	C	Isotropic =	162.2184	ppm; relative to TMS:	22.2482	ppm
22	H	Isotropic =	30.8350	ppm; relative to TMS:	1.4453	ppm
23	H	Isotropic =	30.2569	ppm; relative to TMS:	2.0234	ppm
24	H	Isotropic =	30.3443	ppm; relative to TMS:	1.9360	ppm
25	H	Isotropic =	26.9934	ppm; relative to TMS:	5.2869	ppm
26	H	Isotropic =	26.5902	ppm; relative to TMS:	5.6901	ppm

Table 9S: Absolute energy and coordinates of compound **5a**, conformer IV
Level of theory: B3LYP/6-311G(d)
Point group: C1
Number of negative eigenvalues in the Hessian matrix: 0
E(RB+HF-LYP) = -577.069344615 a.u.



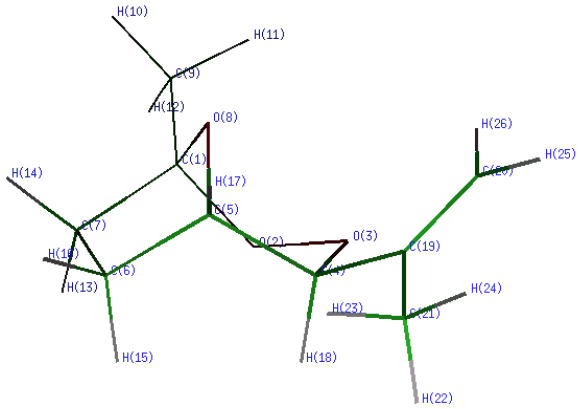
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.703982	-0.325373	-0.006079
2	8	0	-1.010361	-0.429710	1.302291
3	8	0	0.378978	-0.768903	1.084116
4	6	0	0.988897	0.376110	0.469414
5	6	0	0.060567	0.822792	-0.709247
6	6	0	-0.973462	1.919608	-0.338358
7	6	0	-2.247961	1.108170	0.006868
8	8	0	-0.747841	-0.319977	-1.031601
9	6	0	-2.656305	-1.482084	-0.170505
10	1	0	-3.190707	-1.406639	-1.120343
11	1	0	-2.098166	-2.419108	-0.150209
12	1	0	-3.381391	-1.490182	0.645232
13	1	0	-2.675419	1.363204	0.977083
14	1	0	-3.021609	1.224774	-0.755893
15	1	0	-0.631678	2.535046	0.495149
16	1	0	-1.145155	2.582588	-1.188174
17	1	0	0.647059	1.071703	-1.592839
18	1	0	1.068756	1.179629	1.210534
19	6	0	2.365448	-0.056809	0.019525
20	6	0	3.432028	0.662929	0.368975
21	6	0	2.450557	-1.289462	-0.842180
22	1	0	1.792426	-1.220307	-1.713247
23	1	0	2.122709	-2.169306	-0.283060
24	1	0	3.471782	-1.458219	-1.189262
25	1	0	4.428542	0.408118	0.021719
26	1	0	3.351923	1.532129	1.014371

Table 10S: GIAO-B3LYP/6-311G(d) NMR absolute isotropic shielding tensor elements (σ, ppm) of **5a**, conformer IV, and relative chemical shifts with respect to TMS (ppm).

1	C	Isotropic =	66.8316	ppm; relative to TMS:	117.6350	ppm
2	O	Isotropic =	3.1713	ppm; relative to TMS:	---	
3	O	Isotropic =	52.6204	ppm; relative to TMS:	---	
4	C	Isotropic =	86.3366	ppm; relative to TMS:	98.1300	ppm
5	C	Isotropic =	100.9910	ppm; relative to TMS:	83.4756	ppm
6	C	Isotropic =	150.2416	ppm; relative to TMS:	34.2250	ppm
7	C	Isotropic =	145.8537	ppm; relative to TMS:	38.6129	ppm
8	O	Isotropic =	210.5851	ppm; relative to TMS:	---	
9	C	Isotropic =	162.3308	ppm; relative to TMS:	22.1358	ppm
10	H	Isotropic =	31.0539	ppm; relative to TMS:	1.2264	ppm
11	H	Isotropic =	30.2958	ppm; relative to TMS:	1.9845	ppm
12	H	Isotropic =	30.8616	ppm; relative to TMS:	1.4187	ppm
13	H	Isotropic =	30.4641	ppm; relative to TMS:	1.8162	ppm
14	H	Isotropic =	30.7454	ppm; relative to TMS:	1.5349	ppm
15	H	Isotropic =	30.6416	ppm; relative to TMS:	1.6387	ppm
16	H	Isotropic =	30.1487	ppm; relative to TMS:	2.1316	ppm
17	H	Isotropic =	28.2742	ppm; relative to TMS:	4.0061	ppm
18	H	Isotropic =	28.0715	ppm; relative to TMS:	4.2088	ppm
19	C	Isotropic =	29.1555	ppm; relative to TMS:	155.3111	ppm
20	C	Isotropic =	66.9993	ppm; relative to TMS:	117.4673	ppm
21	C	Isotropic =	164.6788	ppm; relative to TMS:	19.7878	ppm
22	H	Isotropic =	30.2289	ppm; relative to TMS:	2.0514	ppm
23	H	Isotropic =	30.1301	ppm; relative to TMS:	2.1502	ppm
24	H	Isotropic =	30.7554	ppm; relative to TMS:	1.5249	ppm
25	H	Isotropic =	27.4173	ppm; relative to TMS:	4.8630	ppm
26	H	Isotropic =	27.3241	ppm; relative to TMS:	4.9562	ppm

Table 11S: Absolute energy and coordinates of compound **5a**, conformer V
Level of theory: B3LYP/6-311G(d)
Point group: C1
Number of negative eigenvalues in the Hessian matrix: 0
E(RB+HF-LYP) = -577.067479847 a.u.



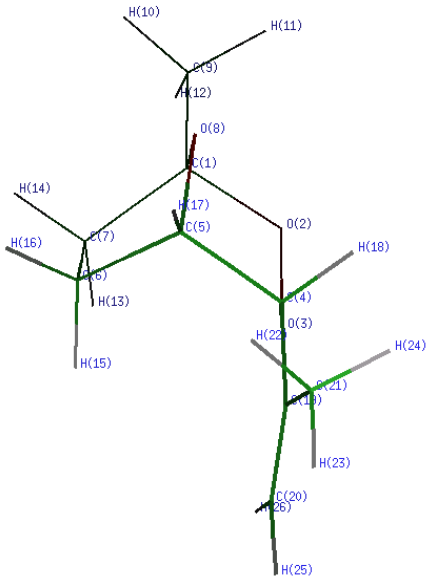
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.747525	-0.267642	-0.089201
2	8	0	-1.078408	-0.644957	1.181184
3	8	0	0.286140	-1.037613	0.904306
4	6	0	0.976981	0.148701	0.504897
5	6	0	0.093249	0.871343	-0.571601
6	6	0	-0.873251	1.947000	-0.008048
7	6	0	-2.202442	1.172415	0.176320
8	8	0	-0.777690	-0.141667	-1.093175
9	6	0	-2.765185	-1.315711	-0.459922
10	1	0	-3.280772	-1.040135	-1.382770
11	1	0	-2.263479	-2.273273	-0.605974
12	1	0	-3.500821	-1.425498	0.338953
13	1	0	-2.632242	1.278117	1.172998
14	1	0	-2.952532	1.471602	-0.559754
15	1	0	-0.505772	2.371040	0.927765
16	1	0	-0.988130	2.767344	-0.718984
17	1	0	0.703491	1.231618	-1.398694
18	1	0	1.099229	0.798964	1.382491
19	6	0	2.333950	-0.253897	-0.026079
20	6	0	2.575038	-1.472492	-0.505895
21	6	0	3.372623	0.836875	0.016243
22	1	0	3.594199	1.132409	1.048116
23	1	0	3.035128	1.743042	-0.501489
24	1	0	4.305018	0.516533	-0.451669
25	1	0	3.554082	-1.737840	-0.893105
26	1	0	1.811635	-2.239588	-0.516699

Table 12S: GIAO-B3LYP/6-311G(d) NMR absolute isotropic shielding tensor elements (σ, ppm) of **5a**, conformer V, and relative chemical shifts with respect to TMS (ppm).

1	C	Isotropic =	66.1699	ppm; relative to TMS:	118.2967	ppm
2	O	Isotropic =	5.4466	ppm; relative to TMS:	---	
3	O	Isotropic =	54.9961	ppm; relative to TMS:	---	
4	C	Isotropic =	90.4843	ppm; relative to TMS:	93.9823	ppm
5	C	Isotropic =	101.4119	ppm; relative to TMS:	83.0547	ppm
6	C	Isotropic =	149.8962	ppm; relative to TMS:	34.5704	ppm
7	C	Isotropic =	145.5813	ppm; relative to TMS:	38.8853	ppm
8	O	Isotropic =	214.2948	ppm; relative to TMS:	---	
9	C	Isotropic =	162.4464	ppm; relative to TMS:	22.0202	ppm
10	H	Isotropic =	31.0535	ppm; relative to TMS:	1.2268	ppm
11	H	Isotropic =	30.2799	ppm; relative to TMS:	2.0004	ppm
12	H	Isotropic =	30.8549	ppm; relative to TMS:	1.4254	ppm
13	H	Isotropic =	30.4428	ppm; relative to TMS:	1.8375	ppm
14	H	Isotropic =	30.7332	ppm; relative to TMS:	1.5471	ppm
15	H	Isotropic =	30.6287	ppm; relative to TMS:	1.6516	ppm
16	H	Isotropic =	30.1810	ppm; relative to TMS:	2.0993	ppm
17	H	Isotropic =	28.3199	ppm; relative to TMS:	3.9604	ppm
18	H	Isotropic =	28.2000	ppm; relative to TMS:	4.0803	ppm
19	C	Isotropic =	35.5791	ppm; relative to TMS:	148.8875	ppm
20	C	Isotropic =	68.6883	ppm; relative to TMS:	115.7783	ppm
21	C	Isotropic =	161.1412	ppm; relative to TMS:	23.3254	ppm
22	H	Isotropic =	30.5489	ppm; relative to TMS:	1.7314	ppm
23	H	Isotropic =	30.7103	ppm; relative to TMS:	1.5700	ppm
24	H	Isotropic =	30.5029	ppm; relative to TMS:	1.7774	ppm
25	H	Isotropic =	27.2753	ppm; relative to TMS:	5.0050	ppm
26	H	Isotropic =	26.9615	ppm; relative to TMS:	5.3188	ppm

Table 13S: Absolute energy and coordinates of compound **6a**, conformer I
Level of theory: B3LYP/6-311G(d)
Point group: C1
Number of negative eigenvalues in the Hessian matrix: 0
E(RB+HF-LYP) = -577.078434458 a.u.



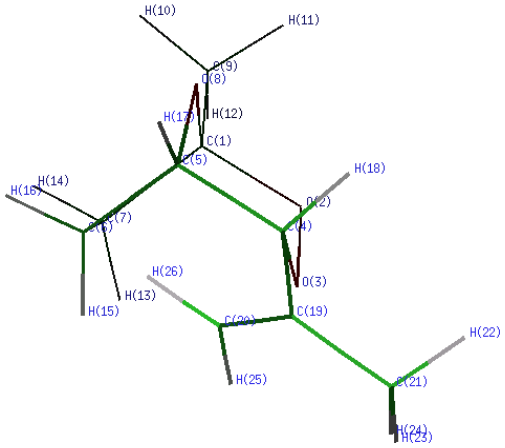
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.813961	-0.072314	-0.114748
2	8	0	-1.180555	-1.293989	-0.523116
3	8	0	0.189533	-1.309272	-0.022731
4	6	0	0.882207	-0.171578	-0.561457
5	6	0	0.093004	1.092231	-0.147538
6	6	0	-0.266331	1.085320	1.351002
7	6	0	-1.552334	0.224157	1.377856
8	8	0	-1.186617	1.005876	-0.796833
9	6	0	-3.249923	-0.205198	-0.567378
10	1	0	-3.764593	0.744380	-0.413236
11	1	0	-3.283933	-0.454413	-1.628782
12	1	0	-3.759195	-0.987284	-0.002566
13	1	0	-1.434460	-0.702747	1.937990
14	1	0	-2.398656	0.773750	1.794423
15	1	0	0.534308	0.674618	1.966701
16	1	0	-0.463634	2.105250	1.686525
17	1	0	0.577430	2.003747	-0.498049
18	1	0	0.851491	-0.234216	-1.656999
19	6	0	2.313845	-0.208707	-0.084265
20	6	0	2.723887	-1.026184	0.885083
21	6	0	3.247825	0.729358	-0.807251
22	1	0	2.938538	1.775974	-0.712475
23	1	0	4.263466	0.648347	-0.416574
24	1	0	3.279294	0.507796	-1.879776
25	1	0	3.763115	-1.044611	1.198432
26	1	0	2.048630	-1.714030	1.378000

Table 14S: GIAO-B3LYP/6-311G(d) NMR absolute isotropic shielding tensor elements (σ, ppm) of **6a**, conformer I, and relative chemical shifts with respect to TMS (ppm).

1	C	Isotropic =	67.4248	ppm; relative to TMS:	117.0418	ppm
2	O	Isotropic =	-27.1373	ppm; relative to TMS:	---	
3	O	Isotropic =	26.5834	ppm; relative to TMS:	---	
4	C	Isotropic =	94.1876	ppm; relative to TMS:	90.2790	ppm
5	C	Isotropic =	101.8652	ppm; relative to TMS:	82.6014	ppm
6	C	Isotropic =	156.3665	ppm; relative to TMS:	28.1001	ppm
7	C	Isotropic =	146.0082	ppm; relative to TMS:	38.4584	ppm
8	O	Isotropic =	186.1043	ppm; relative to TMS:	---	
9	C	Isotropic =	162.4947	ppm; relative to TMS:	21.9719	ppm
10	H	Isotropic =	31.1640	ppm; relative to TMS:	1.1163	ppm
11	H	Isotropic =	30.7655	ppm; relative to TMS:	1.5148	ppm
12	H	Isotropic =	30.9779	ppm; relative to TMS:	1.3024	ppm
13	H	Isotropic =	29.9270	ppm; relative to TMS:	2.3533	ppm
14	H	Isotropic =	30.5777	ppm; relative to TMS:	1.7026	ppm
15	H	Isotropic =	30.2082	ppm; relative to TMS:	2.0721	ppm
16	H	Isotropic =	30.5641	ppm; relative to TMS:	1.7162	ppm
17	H	Isotropic =	28.0941	ppm; relative to TMS:	4.1862	ppm
18	H	Isotropic =	27.4753	ppm; relative to TMS:	4.8050	ppm
19	C	Isotropic =	35.1788	ppm; relative to TMS:	149.2878	ppm
20	C	Isotropic =	67.6367	ppm; relative to TMS:	116.8299	ppm
21	C	Isotropic =	161.3233	ppm; relative to TMS:	23.1433	ppm
22	H	Isotropic =	30.6379	ppm; relative to TMS:	1.6424	ppm
23	H	Isotropic =	30.5070	ppm; relative to TMS:	1.7733	ppm
24	H	Isotropic =	30.5137	ppm; relative to TMS:	1.7666	ppm
25	H	Isotropic =	27.2466	ppm; relative to TMS:	5.0337	ppm
26	H	Isotropic =	27.3608	ppm; relative to TMS:	4.9195	ppm

Table 15S: Absolute energy and coordinates of compound **6a**, conformer II
Level of theory: B3LYP/6-311G(d)
Point group: C1
Number of negative eigenvalues in the Hessian matrix: 0
E(RB+HF-LYP) = -577.077791190 a.u.



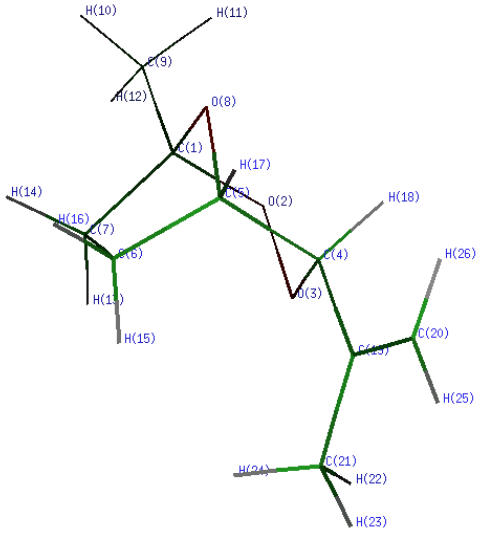
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.801385	-0.202590	-0.016307
2	8	0	-1.046021	-1.408934	0.175814
3	8	0	0.314227	-1.048603	0.560182
4	6	0	0.886362	-0.246229	-0.499780
5	6	0	-0.017676	0.982245	-0.677088
6	6	0	-0.383354	1.644281	0.668722
7	6	0	-1.580979	0.787799	1.146808
8	8	0	-1.281492	0.478472	-1.150325
9	6	0	-3.213981	-0.663859	-0.293189
10	1	0	-3.822489	0.194773	-0.580796
11	1	0	-3.216126	-1.385419	-1.111221
12	1	0	-3.645425	-1.130918	0.593265
13	1	0	-1.378477	0.252973	2.074006
14	1	0	-2.479801	1.391744	1.285416
15	1	0	0.446011	1.633402	1.375199
16	1	0	-0.677574	2.682434	0.501881
17	1	0	0.363022	1.663306	-1.438281
18	1	0	0.831986	-0.836214	-1.424705
19	6	0	2.337787	-0.034152	-0.130385
20	6	0	2.912923	1.168454	-0.146710
21	6	0	3.103340	-1.290303	0.198776
22	1	0	3.030767	-2.019223	-0.615845
23	1	0	4.158986	-1.076094	0.375140
24	1	0	2.692546	-1.776351	1.086831
25	1	0	3.971356	1.284113	0.064287
26	1	0	2.373275	2.080116	-0.375625

Table 16S: GIAO-B3LYP/6-311G(d) NMR absolute isotropic shielding tensor elements (σ, ppm) of **6a**, conformer II, and relative chemical shifts with respect to TMS (ppm).

1	C	Isotropic =	67.1649	ppm; relative to TMS:	117.3017	ppm
2	O	Isotropic =	-32.8285	ppm; relative to TMS:	---	
3	O	Isotropic =	20.1812	ppm; relative to TMS:	---	
4	C	Isotropic =	93.5843	ppm; relative to TMS:	90.8823	ppm
5	C	Isotropic =	102.4434	ppm; relative to TMS:	82.0232	ppm
6	C	Isotropic =	153.6742	ppm; relative to TMS:	30.7924	ppm
7	C	Isotropic =	146.1317	ppm; relative to TMS:	38.3349	ppm
8	O	Isotropic =	186.8741	ppm; relative to TMS:	---	
9	C	Isotropic =	162.4318	ppm; relative to TMS:	22.0348	ppm
10	H	Isotropic =	31.1507	ppm; relative to TMS:	1.1296	ppm
11	H	Isotropic =	30.7481	ppm; relative to TMS:	1.5322	ppm
12	H	Isotropic =	30.9742	ppm; relative to TMS:	1.3061	ppm
13	H	Isotropic =	29.9351	ppm; relative to TMS:	2.3452	ppm
14	H	Isotropic =	30.5506	ppm; relative to TMS:	1.7297	ppm
15	H	Isotropic =	30.1482	ppm; relative to TMS:	2.1321	ppm
16	H	Isotropic =	30.3486	ppm; relative to TMS:	1.9317	ppm
17	H	Isotropic =	27.8395	ppm; relative to TMS:	4.4408	ppm
18	H	Isotropic =	27.4801	ppm; relative to TMS:	4.8002	ppm
19	C	Isotropic =	31.7606	ppm; relative to TMS:	152.7060	ppm
20	C	Isotropic =	68.7082	ppm; relative to TMS:	115.7584	ppm
21	C	Isotropic =	160.7151	ppm; relative to TMS:	23.7515	ppm
22	H	Isotropic =	30.5340	ppm; relative to TMS:	1.7463	ppm
23	H	Isotropic =	30.6937	ppm; relative to TMS:	1.5866	ppm
24	H	Isotropic =	30.1014	ppm; relative to TMS:	2.1789	ppm
25	H	Isotropic =	27.2794	ppm; relative to TMS:	5.0009	ppm
26	H	Isotropic =	27.7343	ppm; relative to TMS:	4.5460	ppm

Table 17S: Absolute energy and coordinates of compound **6a**, conformer III
Level of theory: B3LYP/6-311G(d)
Point group: C1
Number of negative eigenvalues in the Hessian matrix: 0
E(RB+HF-LYP) = -577.076023118 a.u.



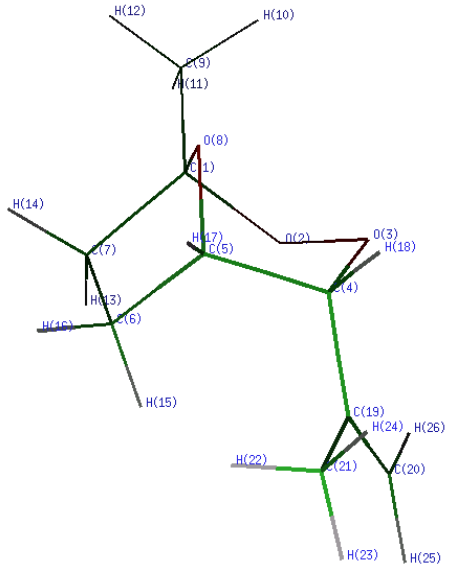
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.798920	-0.118919	-0.081911
2	8	0	-1.128006	-1.342201	-0.421770
3	8	0	0.260624	-1.258471	0.014403
4	6	0	0.873987	-0.128967	-0.635870
5	6	0	0.047439	1.126155	-0.285010
6	6	0	-0.278032	1.254210	1.215171
7	6	0	-1.490245	0.304374	1.372085
8	8	0	-1.251250	0.928184	-0.872994
9	6	0	-3.244672	-0.348381	-0.458226
10	1	0	-3.795878	0.587086	-0.351565
11	1	0	-3.310773	-0.678371	-1.495797
12	1	0	-3.693199	-1.106791	0.184992
13	1	0	-1.272461	-0.569319	1.985131
14	1	0	-2.354442	0.817528	1.798017
15	1	0	0.558712	0.993073	1.862393
16	1	0	-0.557724	2.286930	1.432510
17	1	0	0.488555	2.016401	-0.733915
18	1	0	0.795787	-0.270196	-1.718827
19	6	0	2.333024	-0.089213	-0.218063
20	6	0	3.203536	0.565610	-0.987376
21	6	0	2.748943	-0.799603	1.044471
22	1	0	2.518994	-1.866347	0.980741
23	1	0	3.821250	-0.686020	1.213979
24	1	0	2.222214	-0.425588	1.926795
25	1	0	4.250345	0.650342	-0.714532
26	1	0	2.907313	1.039576	-1.918651

Table 18S: GIAO-B3LYP/6-311G(d) NMR absolute isotropic shielding tensor elements (σ, ppm) of **6a**, conformer III, and relative chemical shifts with respect to TMS (ppm).

1	C	Isotropic =	67.5931	ppm; relative to TMS:	116.8735	ppm
2	O	Isotropic =	-25.7307	ppm; relative to TMS:	---	
3	O	Isotropic =	29.0880	ppm; relative to TMS:	---	
4	C	Isotropic =	92.3983	ppm; relative to TMS:	92.0683	ppm
5	C	Isotropic =	97.0278	ppm; relative to TMS:	87.4388	ppm
6	C	Isotropic =	153.8857	ppm; relative to TMS:	30.5809	ppm
7	C	Isotropic =	146.1731	ppm; relative to TMS:	38.2935	ppm
8	O	Isotropic =	177.0378	ppm; relative to TMS:	---	
9	C	Isotropic =	162.2859	ppm; relative to TMS:	22.1807	ppm
10	H	Isotropic =	31.1760	ppm; relative to TMS:	1.1043	ppm
11	H	Isotropic =	30.7731	ppm; relative to TMS:	1.5072	ppm
12	H	Isotropic =	30.9806	ppm; relative to TMS:	1.2997	ppm
13	H	Isotropic =	29.8481	ppm; relative to TMS:	2.4322	ppm
14	H	Isotropic =	30.5434	ppm; relative to TMS:	1.7369	ppm
15	H	Isotropic =	30.3613	ppm; relative to TMS:	1.9190	ppm
16	H	Isotropic =	30.3859	ppm; relative to TMS:	1.8944	ppm
17	H	Isotropic =	28.3115	ppm; relative to TMS:	3.9688	ppm
18	H	Isotropic =	27.1174	ppm; relative to TMS:	5.1629	ppm
19	C	Isotropic =	30.9334	ppm; relative to TMS:	153.5332	ppm
20	C	Isotropic =	69.2773	ppm; relative to TMS:	115.1893	ppm
21	C	Isotropic =	162.6888	ppm; relative to TMS:	21.7778	ppm
22	H	Isotropic =	30.2829	ppm; relative to TMS:	1.9974	ppm
23	H	Isotropic =	30.7555	ppm; relative to TMS:	1.5248	ppm
24	H	Isotropic =	30.5794	ppm; relative to TMS:	1.7009	ppm
25	H	Isotropic =	27.2700	ppm; relative to TMS:	5.0103	ppm
26	H	Isotropic =	27.4438	ppm; relative to TMS:	4.8365	ppm

Table 19S: Absolute energy and coordinates of compound **6a**, conformer IV
Level of theory: B3LYP/6-311G(d)
Point group: C1
Number of negative eigenvalues in the Hessian matrix: 0
E(RB+HF-LYP) = -577.067038706 a.u.



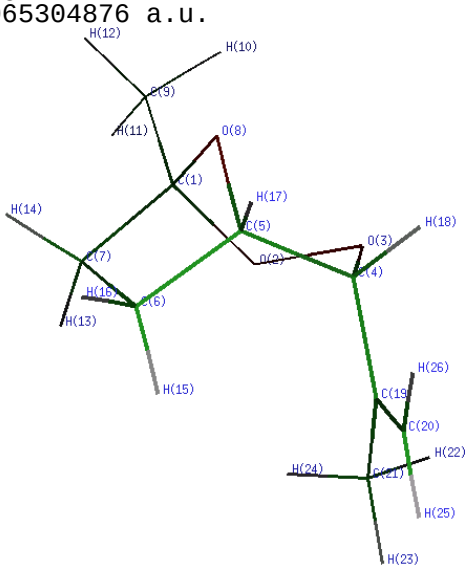
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.755890	-0.051948	0.081486
2	8	0	-0.826212	-1.118317	0.524211
3	8	0	0.074159	-1.453254	-0.561089
4	6	0	0.929032	-0.326303	-0.789133
5	6	0	0.047225	0.963369	-0.715847
6	6	0	-0.155557	1.586416	0.695185
7	6	0	-1.531839	1.033843	1.137917
8	8	0	-1.264370	0.522775	-1.100361
9	6	0	-3.133856	-0.621464	-0.136901
10	1	0	-3.093577	-1.380560	-0.919399
11	1	0	-3.499106	-1.084633	0.781376
12	1	0	-3.829867	0.164170	-0.439987
13	1	0	-1.528786	0.622588	2.147916
14	1	0	-2.318489	1.789339	1.069577
15	1	0	0.637981	1.294708	1.382462
16	1	0	-0.162986	2.675989	0.631048
17	1	0	0.377921	1.690957	-1.456060
18	1	0	1.209665	-0.466324	-1.842005
19	6	0	2.185486	-0.306175	0.052844
20	6	0	2.402697	-1.196017	1.018526
21	6	0	3.181077	0.765026	-0.317610
22	1	0	2.777759	1.772950	-0.165431
23	1	0	4.092974	0.681141	0.275914
24	1	0	3.461913	0.697660	-1.375438
25	1	0	3.318995	-1.182409	1.600958
26	1	0	1.676738	-1.965695	1.248174

Table 20S: GIAO-B3LYP/6-311G(d) NMR absolute isotropic shielding tensor elements (σ, ppm) of **6a**, conformer IV, and relative chemical shifts with respect to TMS (ppm).

1	C	Isotropic =	66.0458	ppm; relative to TMS:	118.4208	ppm
2	O	Isotropic =	5.1247	ppm; relative to TMS:	---	
3	O	Isotropic =	46.2184	ppm; relative to TMS:	---	
4	C	Isotropic =	91.4909	ppm; relative to TMS:	92.9757	ppm
5	C	Isotropic =	104.8489	ppm; relative to TMS:	79.6177	ppm
6	C	Isotropic =	157.9406	ppm; relative to TMS:	26.5260	ppm
7	C	Isotropic =	146.7073	ppm; relative to TMS:	37.7593	ppm
8	O	Isotropic =	209.5903	ppm; relative to TMS:	---	
9	C	Isotropic =	162.7391	ppm; relative to TMS:	21.7275	ppm
10	H	Isotropic =	30.2771	ppm; relative to TMS:	2.0032	ppm
11	H	Isotropic =	30.9080	ppm; relative to TMS:	1.3723	ppm
12	H	Isotropic =	31.0589	ppm; relative to TMS:	1.2214	ppm
13	H	Isotropic =	30.5975	ppm; relative to TMS:	1.6828	ppm
14	H	Isotropic =	30.8209	ppm; relative to TMS:	1.4594	ppm
15	H	Isotropic =	30.4189	ppm; relative to TMS:	1.8614	ppm
16	H	Isotropic =	30.5580	ppm; relative to TMS:	1.7223	ppm
17	H	Isotropic =	27.8346	ppm; relative to TMS:	4.4457	ppm
18	H	Isotropic =	27.5834	ppm; relative to TMS:	4.6969	ppm
19	C	Isotropic =	35.5419	ppm; relative to TMS:	148.9247	ppm
20	C	Isotropic =	66.7950	ppm; relative to TMS:	117.6716	ppm
21	C	Isotropic =	163.1393	ppm; relative to TMS:	21.3273	ppm
22	H	Isotropic =	30.8866	ppm; relative to TMS:	1.3937	ppm
23	H	Isotropic =	30.4823	ppm; relative to TMS:	1.7980	ppm
24	H	Isotropic =	30.7673	ppm; relative to TMS:	1.5130	ppm
25	H	Isotropic =	27.1312	ppm; relative to TMS:	5.1491	ppm
26	H	Isotropic =	26.7043	ppm; relative to TMS:	5.5760	ppm

Table 21S: Absolute energy and coordinates of compound **6a**, conformer V
Level of theory: B3LYP/6-311G(d)
Point group: C1
Number of negative eigenvalues in the Hessian matrix: 0
E(RB+HF-LYP) = -577.065304876 a.u.



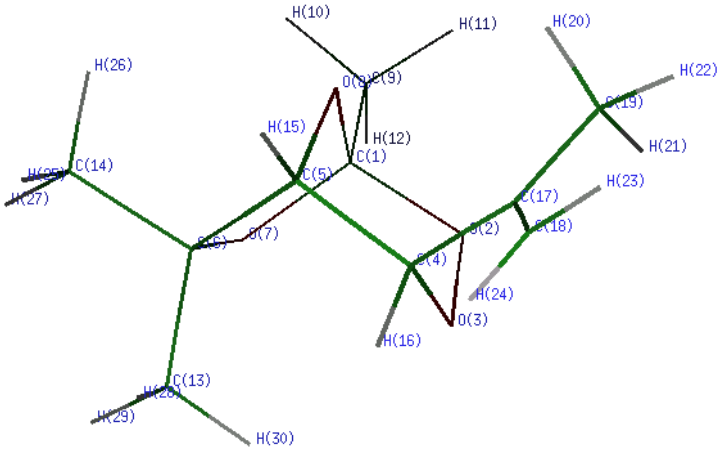
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.724146	-0.098068	0.080637
2	8	0	-0.729369	-1.151592	0.399878
3	8	0	0.152517	-1.341762	-0.735743
4	6	0	0.943095	-0.151667	-0.880110
5	6	0	-0.001309	1.074945	-0.673758
6	6	0	-0.201606	1.584328	0.781283
7	6	0	-1.518936	0.902052	1.223525
8	8	0	-1.301053	0.601348	-1.059747
9	6	0	-3.078162	-0.718386	-0.147352
10	1	0	-3.023976	-1.408554	-0.990496
11	1	0	-3.392780	-1.272361	0.738826
12	1	0	-3.820346	0.052549	-0.366975
13	1	0	-1.449494	0.402343	2.190504
14	1	0	-2.352828	1.607453	1.255995
15	1	0	0.641451	1.333383	1.423049
16	1	0	-0.297952	2.671380	0.784181
17	1	0	0.278777	1.872981	-1.359968
18	1	0	1.202645	-0.188500	-1.943242
19	6	0	2.219532	-0.147098	-0.052266
20	6	0	3.214751	0.675107	-0.387675
21	6	0	2.309190	-1.103929	1.105560
22	1	0	2.239348	-2.136173	0.751552
23	1	0	3.252310	-0.981999	1.641718
24	1	0	1.481262	-0.972883	1.806686
25	1	0	4.134633	0.721495	0.186255
26	1	0	3.155728	1.331221	-1.252258

Table 22S: GIAO-B3LYP/6-311G(d) NMR absolute isotropic shielding tensor elements (σ, ppm) of **6a**, conformer V, and relative chemical shifts with respect to TMS (ppm).

1	C	Isotropic =	65.9528	ppm; relative to TMS:	118.5138	ppm
2	O	Isotropic =	3.2615	ppm; relative to TMS:	---	
3	O	Isotropic =	40.6951	ppm; relative to TMS:	---	
4	C	Isotropic =	92.4018	ppm; relative to TMS:	92.0648	ppm
5	C	Isotropic =	103.1006	ppm; relative to TMS:	81.3660	ppm
6	C	Isotropic =	157.1077	ppm; relative to TMS:	27.3589	ppm
7	C	Isotropic =	146.4285	ppm; relative to TMS:	38.0381	ppm
8	O	Isotropic =	204.3181	ppm; relative to TMS:	---	
9	C	Isotropic =	162.6082	ppm; relative to TMS:	21.8584	ppm
10	H	Isotropic =	30.2891	ppm; relative to TMS:	1.9912	ppm
11	H	Isotropic =	30.9129	ppm; relative to TMS:	1.3674	ppm
12	H	Isotropic =	31.0699	ppm; relative to TMS:	1.2104	ppm
13	H	Isotropic =	30.5696	ppm; relative to TMS:	1.7107	ppm
14	H	Isotropic =	30.7776	ppm; relative to TMS:	1.5027	ppm
15	H	Isotropic =	30.4859	ppm; relative to TMS:	1.7944	ppm
16	H	Isotropic =	30.4740	ppm; relative to TMS:	1.8063	ppm
17	H	Isotropic =	27.9293	ppm; relative to TMS:	4.3510	ppm
18	H	Isotropic =	27.2744	ppm; relative to TMS:	5.0059	ppm
19	C	Isotropic =	25.6456	ppm; relative to TMS:	158.8210	ppm
20	C	Isotropic =	72.3936	ppm; relative to TMS:	112.0730	ppm
21	C	Isotropic =	160.8969	ppm; relative to TMS:	23.5697	ppm
22	H	Isotropic =	29.8659	ppm; relative to TMS:	2.4144	ppm
23	H	Isotropic =	30.6656	ppm; relative to TMS:	1.6147	ppm
24	H	Isotropic =	30.1695	ppm; relative to TMS:	2.1108	ppm
25	H	Isotropic =	27.3564	ppm; relative to TMS:	4.9239	ppm
26	H	Isotropic =	27.7468	ppm; relative to TMS:	4.5335	ppm

Table 23S: Absolute energy and coordinates of compound **10**, conformer I
Level of theory: B3LYP/6-311G(d)
Point group: C1
Number of negative eigenvalues in the Hessian matrix: 0
E(RB+HF-LYP) = -691.641591582 a.u.



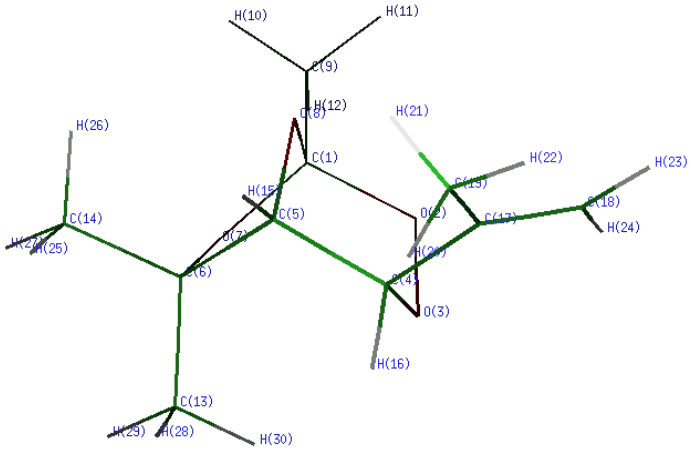
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.865906	1.235563	0.063117
2	8	0	-0.139082	1.414004	1.060299
3	8	0	-0.659970	0.116904	1.488575
4	6	0	-1.061399	-0.700034	0.364530
5	6	0	0.066188	-0.674712	-0.680588
6	6	0	1.473479	-0.994336	-0.102126
7	8	0	1.832798	0.304527	0.459030
8	8	0	0.257971	0.687996	-1.091157
9	6	0	1.444825	2.604045	-0.190821
10	1	0	2.139739	2.540476	-1.028072
11	1	0	0.652206	3.312770	-0.430012
12	1	0	1.977354	2.942984	0.697186
13	6	0	1.538140	-2.039021	1.004689
14	6	0	2.455308	-1.312051	-1.231290
15	1	0	-0.191604	-1.267379	-1.558124
16	1	0	-1.095512	-1.692642	0.821874
17	6	0	-2.445606	-0.379288	-0.168814
18	6	0	-3.321307	-1.377932	-0.299091
19	6	0	-2.787632	1.042561	-0.526563
20	1	0	-2.155313	1.412321	-1.336449
21	1	0	-2.618859	1.703924	0.326455
22	1	0	-3.833656	1.123362	-0.829188
23	1	0	-4.317553	-1.213030	-0.697108
24	1	0	-3.081638	-2.398717	-0.014621
25	1	0	2.282996	-2.314964	-1.633216
26	1	0	2.357385	-0.589403	-2.043052
27	1	0	3.478827	-1.266987	-0.853127
28	1	0	1.166614	-3.006513	0.652951
29	1	0	2.575227	-2.177206	1.318541
30	1	0	0.962654	-1.725216	1.873720

Table 24S: GIAO-B3LYP/6-311G(d) NMR absolute isotropic shielding tensor elements (σ, ppm) of **10**, conformer I, and relative chemical shifts with respect to TMS (ppm).

1	C	Isotropic =	54.6085	ppm; relative to TMS:	129.8581	ppm
2	O	Isotropic =	4.8556	ppm; relative to TMS:	---	
3	O	Isotropic =	5.7650	ppm; relative to TMS:	---	
4	C	Isotropic =	95.7043	ppm; relative to TMS:	88.7623	ppm
5	C	Isotropic =	96.2624	ppm; relative to TMS:	88.2042	ppm
6	C	Isotropic =	96.0304	ppm; relative to TMS:	88.4362	ppm
7	O	Isotropic =	168.9446	ppm; relative to TMS:	---	
8	O	Isotropic =	198.1045	ppm; relative to TMS:	---	
9	C	Isotropic =	162.2226	ppm; relative to TMS:	22.2440	ppm
10	H	Isotropic =	31.0904	ppm; relative to TMS:	1.1899	ppm
11	H	Isotropic =	30.8685	ppm; relative to TMS:	1.4118	ppm
12	H	Isotropic =	30.7162	ppm; relative to TMS:	1.5641	ppm
13	C	Isotropic =	161.9016	ppm; relative to TMS:	22.5650	ppm
14	C	Isotropic =	156.2143	ppm; relative to TMS:	28.2523	ppm
15	H	Isotropic =	28.6168	ppm; relative to TMS:	3.6635	ppm
16	H	Isotropic =	28.1545	ppm; relative to TMS:	4.1258	ppm
17	C	Isotropic =	26.7018	ppm; relative to TMS:	157.7648	ppm
18	C	Isotropic =	68.1872	ppm; relative to TMS:	116.2794	ppm
19	C	Isotropic =	161.0991	ppm; relative to TMS:	23.3675	ppm
20	H	Isotropic =	29.7345	ppm; relative to TMS:	2.5458	ppm
21	H	Isotropic =	29.7278	ppm; relative to TMS:	2.5525	ppm
22	H	Isotropic =	30.5081	ppm; relative to TMS:	1.7722	ppm
23	H	Isotropic =	27.3485	ppm; relative to TMS:	4.9318	ppm
24	H	Isotropic =	27.5220	ppm; relative to TMS:	4.7583	ppm
25	H	Isotropic =	31.3025	ppm; relative to TMS:	0.9778	ppm
26	H	Isotropic =	30.7051	ppm; relative to TMS:	1.5752	ppm
27	H	Isotropic =	30.9773	ppm; relative to TMS:	1.3030	ppm
28	H	Isotropic =	31.2692	ppm; relative to TMS:	1.0111	ppm
29	H	Isotropic =	30.6873	ppm; relative to TMS:	1.5930	ppm
30	H	Isotropic =	30.1696	ppm; relative to TMS:	2.1107	ppm

Table 25S: Absolute energy and coordinates of compound **10**, conformer II Level of theory: B3LYP/6-311G(d)
Point group: C1
Number of negative eigenvalues in the Hessian matrix: 0
E(RB+HF-LYP) = -691.640930134 a.u.



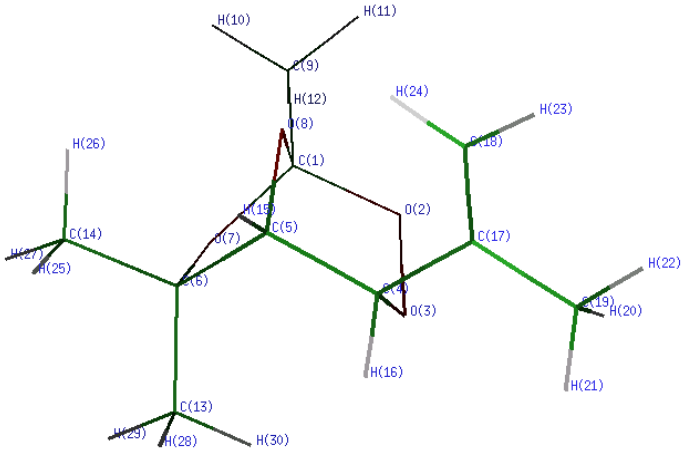
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.828333	1.256590	-0.192341
2	8	0	-0.144603	1.604626	0.793063
3	8	0	-0.603718	0.396995	1.480066
4	6	0	-1.046767	-0.591134	0.536981
5	6	0	0.064396	-0.778325	-0.511804
6	6	0	1.490338	-0.946051	0.081603
7	8	0	1.836467	0.446685	0.346584
8	8	0	0.205291	0.475772	-1.192830
9	6	0	1.351125	2.561988	-0.733982
10	1	0	2.024851	2.352186	-1.564621
11	1	0	0.524524	3.179746	-1.084189
12	1	0	1.893981	3.090230	0.049112
13	6	0	1.602820	-1.739420	1.377420
14	6	0	2.452622	-1.476371	-0.983155
15	1	0	-0.182966	-1.544923	-1.244595
16	1	0	-1.106217	-1.489886	1.165252
17	6	0	-2.421336	-0.319993	-0.050393
18	6	0	-3.153773	0.717097	0.344660
19	6	0	-2.913302	-1.328741	-1.057724
20	1	0	-2.769478	-2.358953	-0.709649
21	1	0	-2.382885	-1.237043	-2.011714
22	1	0	-3.976883	-1.192840	-1.259720
23	1	0	-4.151343	0.880563	-0.051045
24	1	0	-2.779992	1.436569	1.061333
25	1	0	2.292617	-2.543512	-1.164486
26	1	0	2.322427	-0.938544	-1.923717
27	1	0	3.483051	-1.338006	-0.648879
28	1	0	1.252464	-2.767088	1.238653
29	1	0	2.648591	-1.786397	1.689569
30	1	0	1.033021	-1.268578	2.176049

Table 26S: GIAO-B3LYP/6-311G(d) NMR absolute isotropic shielding tensor elements (σ, ppm) of **10**, conformer II, and relative chemical shifts with respect to TMS (ppm).

1	C	Isotropic =	54.1397	ppm; relative to TMS:	130.3269	ppm
2	O	Isotropic =	0.9017	ppm; relative to TMS:	---	
3	O	Isotropic =	21.6119	ppm; relative to TMS:	---	
4	C	Isotropic =	97.5596	ppm; relative to TMS:	86.9070	ppm
5	C	Isotropic =	101.7814	ppm; relative to TMS:	82.6852	ppm
6	C	Isotropic =	95.9977	ppm; relative to TMS:	88.4689	ppm
7	O	Isotropic =	167.8265	ppm; relative to TMS:	---	
8	O	Isotropic =	202.5829	ppm; relative to TMS:	---	
9	C	Isotropic =	162.7599	ppm; relative to TMS:	21.7067	ppm
10	H	Isotropic =	31.1607	ppm; relative to TMS:	1.1196	ppm
11	H	Isotropic =	30.9095	ppm; relative to TMS:	1.3708	ppm
12	H	Isotropic =	30.8025	ppm; relative to TMS:	1.4778	ppm
13	C	Isotropic =	162.2512	ppm; relative to TMS:	22.2154	ppm
14	C	Isotropic =	155.7985	ppm; relative to TMS:	28.6681	ppm
15	H	Isotropic =	28.4161	ppm; relative to TMS:	3.8642	ppm
16	H	Isotropic =	28.1617	ppm; relative to TMS:	4.1186	ppm
17	C	Isotropic =	37.7428	ppm; relative to TMS:	146.7238	ppm
18	C	Isotropic =	65.1066	ppm; relative to TMS:	119.3600	ppm
19	C	Isotropic =	162.7185	ppm; relative to TMS:	21.7481	ppm
20	H	Isotropic =	30.8770	ppm; relative to TMS:	1.4033	ppm
21	H	Isotropic =	30.3520	ppm; relative to TMS:	1.9283	ppm
22	H	Isotropic =	30.3014	ppm; relative to TMS:	1.9789	ppm
23	H	Isotropic =	26.9590	ppm; relative to TMS:	5.3213	ppm
24	H	Isotropic =	26.5097	ppm; relative to TMS:	5.7706	ppm
25	H	Isotropic =	31.2795	ppm; relative to TMS:	1.0008	ppm
26	H	Isotropic =	30.6656	ppm; relative to TMS:	1.6147	ppm
27	H	Isotropic =	30.9601	ppm; relative to TMS:	1.3202	ppm
28	H	Isotropic =	31.3054	ppm; relative to TMS:	0.9749	ppm
29	H	Isotropic =	30.6855	ppm; relative to TMS:	1.5948	ppm
30	H	Isotropic =	30.0805	ppm; relative to TMS:	2.1998	ppm

Table 27S: Absolute energy and coordinates of compound **10**, conformer III
Level of theory: B3LYP/6-311G(d)
Point group: C1
Number of negative eigenvalues in the Hessian matrix: 0
E(RB+HF-LYP) = -691.640729046 a.u.



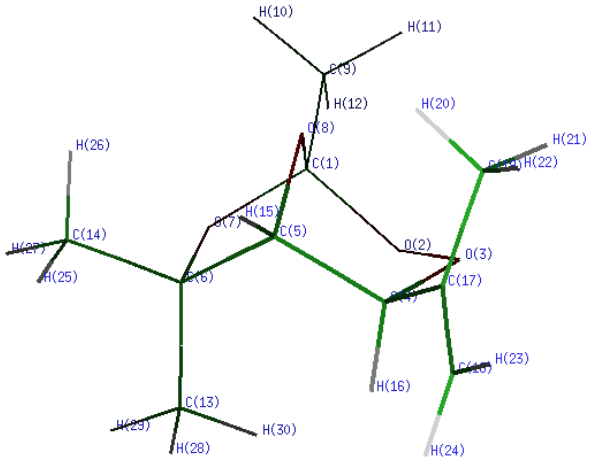
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.839360	1.252185	-0.148715
2	8	0	0.258076	1.347012	-1.059738
3	8	0	0.729175	0.004756	-1.385165
4	6	0	1.050788	-0.721105	-0.173383
5	6	0	-0.163324	-0.634481	0.757607
6	6	0	-1.518134	-0.952745	0.062952
7	8	0	-1.794600	0.325514	-0.586529
8	8	0	-0.362314	0.749863	1.083512
9	6	0	-1.391020	2.647849	-0.016415
10	1	0	-2.155379	2.651303	0.760522
11	1	0	-0.594823	3.341083	0.254192
12	1	0	-1.833834	2.955175	-0.963207
13	6	0	-1.508857	-2.051630	-0.992440
14	6	0	-2.607087	-1.196879	1.109812
15	1	0	-0.015564	-1.193346	1.681087
16	1	0	1.138990	-1.743041	-0.563347
17	6	0	2.398347	-0.314279	0.393026
18	6	0	2.580529	0.097126	1.646810
19	6	0	3.534712	-0.433598	-0.590413
20	1	0	3.359053	0.205947	-1.459185
21	1	0	3.631965	-1.458363	-0.968663
22	1	0	4.485608	-0.148165	-0.137461
23	1	0	3.572898	0.343785	2.012031
24	1	0	1.765422	0.233593	2.345438
25	1	0	-2.498511	-2.184033	1.569087
26	1	0	-2.565375	-0.439867	1.894573
27	1	0	-3.589922	-1.146865	0.636431
28	1	0	-1.199045	-3.007396	-0.558125
29	1	0	-2.516220	-2.182685	-1.394133
30	1	0	-0.847536	-1.798946	-1.818926

Table 28S: GIAO-B3LYP/6-311G(d) NMR absolute isotropic shielding tensor elements (σ, ppm) of **10**, conformer III, and relative chemical shifts with respect to TMS (ppm).

1	C	Isotropic =	54.2475	ppm; relative to TMS:	130.2191	ppm
2	O	Isotropic =	3.2676	ppm; relative to TMS:	---	
3	O	Isotropic =	15.1347	ppm; relative to TMS:	---	
4	C	Isotropic =	99.7866	ppm; relative to TMS:	84.6800	ppm
5	C	Isotropic =	101.4377	ppm; relative to TMS:	83.0289	ppm
6	C	Isotropic =	95.8305	ppm; relative to TMS:	88.6361	ppm
7	O	Isotropic =	167.0911	ppm; relative to TMS:	---	
8	O	Isotropic =	197.7836	ppm; relative to TMS:	---	
9	C	Isotropic =	162.7455	ppm; relative to TMS:	21.7211	ppm
10	H	Isotropic =	31.1346	ppm; relative to TMS:	1.1457	ppm
11	H	Isotropic =	30.9092	ppm; relative to TMS:	1.3711	ppm
12	H	Isotropic =	30.8043	ppm; relative to TMS:	1.4760	ppm
13	C	Isotropic =	162.2934	ppm; relative to TMS:	22.1732	ppm
14	C	Isotropic =	155.9087	ppm; relative to TMS:	28.5579	ppm
15	H	Isotropic =	28.3145	ppm; relative to TMS:	3.9658	ppm
16	H	Isotropic =	28.4136	ppm; relative to TMS:	3.8667	ppm
17	C	Isotropic =	32.6754	ppm; relative to TMS:	151.7912	ppm
18	C	Isotropic =	64.2146	ppm; relative to TMS:	120.2520	ppm
19	C	Isotropic =	160.2466	ppm; relative to TMS:	24.2200	ppm
20	H	Isotropic =	29.7045	ppm; relative to TMS:	2.5758	ppm
21	H	Isotropic =	30.6359	ppm; relative to TMS:	1.6444	ppm
22	H	Isotropic =	30.4895	ppm; relative to TMS:	1.7908	ppm
23	H	Isotropic =	26.9396	ppm; relative to TMS:	5.3407	ppm
24	H	Isotropic =	26.8547	ppm; relative to TMS:	5.4256	ppm
25	H	Isotropic =	31.2757	ppm; relative to TMS:	1.0046	ppm
26	H	Isotropic =	30.6225	ppm; relative to TMS:	1.6578	ppm
27	H	Isotropic =	30.9563	ppm; relative to TMS:	1.3240	ppm
28	H	Isotropic =	31.3380	ppm; relative to TMS:	0.9423	ppm
29	H	Isotropic =	30.6885	ppm; relative to TMS:	1.5918	ppm
30	H	Isotropic =	30.0861	ppm; relative to TMS:	2.1942	ppm

Table 29S: Absolute energy and coordinates of compound **10**, conformer IV
Level of theory: B3LYP/6-311G(d)
Point group: C1
Number of negative eigenvalues in the Hessian matrix: 0
E(RB+HF-LYP) = -691.635886296 a.u.



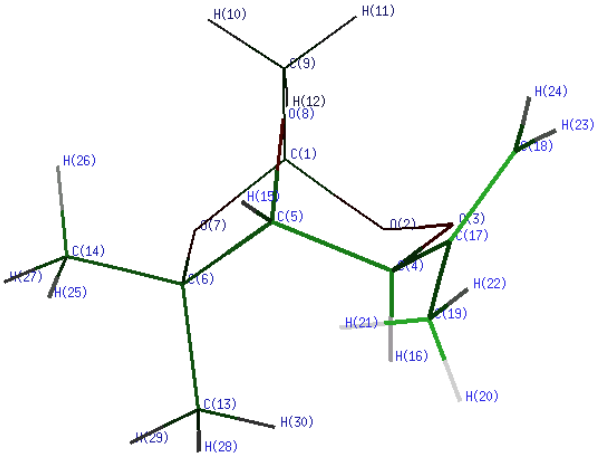
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.291601	-1.067005	-0.036551
2	8	0	0.520854	-1.201523	-1.287187
3	8	0	-0.901964	-1.114473	-1.015947
4	6	0	-1.170888	0.200391	-0.505549
5	6	0	-0.086090	0.506316	0.570969
6	6	0	1.237380	1.207195	0.103014
7	8	0	2.090780	0.063756	-0.201917
8	8	0	0.413013	-0.769002	1.004573
9	6	0	2.098396	-2.311494	0.199067
10	1	0	2.714195	-2.192808	1.091328
11	1	0	1.426076	-3.160243	0.322873
12	1	0	2.742488	-2.491551	-0.662005
13	6	0	1.139433	2.095615	-1.131320
14	6	0	1.879199	1.943540	1.278988
15	1	0	-0.519500	1.015052	1.430938
16	1	0	-1.127244	0.924124	-1.323281
17	6	0	-2.572507	0.162555	0.064255
18	6	0	-3.462138	1.078223	-0.320531
19	6	0	-2.884000	-0.915819	1.068687
20	1	0	-2.187800	-0.899636	1.912666
21	1	0	-2.785153	-1.903281	0.611859
22	1	0	-3.899324	-0.810991	1.455674
23	1	0	-4.462844	1.109921	0.098886
24	1	0	-3.227647	1.829128	-1.068644
25	1	0	1.329924	2.859130	1.517815
26	1	0	1.900845	1.306229	2.165296
27	1	0	2.907110	2.215852	1.030718
28	1	0	0.413008	2.901608	-0.987290
29	1	0	2.111241	2.553747	-1.328533
30	1	0	0.860848	1.516564	-2.010638

Table 30S: GIAO-B3LYP/6-311G(d) NMR absolute isotropic shielding tensor elements (σ, ppm) of **10**, conformer IV, and relative chemical shifts with respect to TMS (ppm).

1	C	Isotropic =	51.9356	ppm; relative to TMS:	132.5310	ppm
2	O	Isotropic =	-9.4999	ppm; relative to TMS:	---	
3	O	Isotropic =	38.9353	ppm; relative to TMS:	---	
4	C	Isotropic =	95.1517	ppm; relative to TMS:	89.3149	ppm
5	C	Isotropic =	96.1482	ppm; relative to TMS:	88.3184	ppm
6	C	Isotropic =	98.0133	ppm; relative to TMS:	86.4533	ppm
7	O	Isotropic =	154.6805	ppm; relative to TMS:	---	
8	O	Isotropic =	196.9911	ppm; relative to TMS:	---	
9	C	Isotropic =	162.7379	ppm; relative to TMS:	21.7287	ppm
10	H	Isotropic =	30.9096	ppm; relative to TMS:	1.3707	ppm
11	H	Isotropic =	30.6248	ppm; relative to TMS:	1.6555	ppm
12	H	Isotropic =	30.6793	ppm; relative to TMS:	1.6010	ppm
13	C	Isotropic =	158.9906	ppm; relative to TMS:	25.4760	ppm
14	C	Isotropic =	154.5318	ppm; relative to TMS:	29.9348	ppm
15	H	Isotropic =	28.6685	ppm; relative to TMS:	3.6118	ppm
16	H	Isotropic =	27.5185	ppm; relative to TMS:	4.7618	ppm
17	C	Isotropic =	28.9964	ppm; relative to TMS:	155.4702	ppm
18	C	Isotropic =	66.1396	ppm; relative to TMS:	118.3270	ppm
19	C	Isotropic =	164.6474	ppm; relative to TMS:	19.8192	ppm
20	H	Isotropic =	30.2786	ppm; relative to TMS:	2.0017	ppm
21	H	Isotropic =	30.0842	ppm; relative to TMS:	2.1961	ppm
22	H	Isotropic =	30.7271	ppm; relative to TMS:	1.5532	ppm
23	H	Isotropic =	27.3506	ppm; relative to TMS:	4.9297	ppm
24	H	Isotropic =	27.2571	ppm; relative to TMS:	5.0232	ppm
25	H	Isotropic =	31.2688	ppm; relative to TMS:	1.0115	ppm
26	H	Isotropic =	30.7630	ppm; relative to TMS:	1.5173	ppm
27	H	Isotropic =	30.8718	ppm; relative to TMS:	1.4085	ppm
28	H	Isotropic =	31.3125	ppm; relative to TMS:	0.9678	ppm
29	H	Isotropic =	30.7691	ppm; relative to TMS:	1.5112	ppm
30	H	Isotropic =	30.5187	ppm; relative to TMS:	1.7616	ppm

Table 31S: Absolute energy and coordinates of compound **10**, conformer V
Level of theory: B3LYP/6-311G(d)
Point group: C1
Number of negative eigenvalues in the Hessian matrix: 0
E(RB+HF-LYP) = -691.634026615 a.u.



Standard orientation:

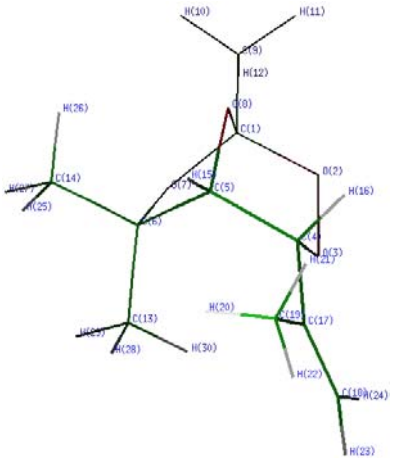
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.383426	-1.009278	-0.064667
2	8	0	-0.633296	-1.291752	1.175562
3	8	0	0.791873	-1.314640	0.905416
4	6	0	1.175246	0.000862	0.495249
5	6	0	0.117784	0.490815	-0.544320
6	6	0	-1.148206	1.254475	-0.017636
7	8	0	-2.095080	0.162765	0.185368
8	8	0	-0.474617	-0.702582	-1.075993
9	6	0	-2.278944	-2.168067	-0.396252
10	1	0	-2.873282	-1.938221	-1.281349
11	1	0	-1.671083	-3.054027	-0.578762
12	1	0	-2.944989	-2.361416	0.444995
13	6	0	-0.985207	2.017658	1.291420
14	6	0	-1.719998	2.141590	-1.123090
15	1	0	0.592545	1.025628	-1.365560
16	1	0	1.196398	0.660332	1.370181
17	6	0	2.562954	-0.083691	-0.104232
18	6	0	3.033865	-1.207403	-0.641233
19	6	0	3.347887	1.201218	-0.053516
20	1	0	3.548704	1.501819	0.981061
21	1	0	2.803750	2.032265	-0.519162
22	1	0	4.304704	1.103551	-0.568946
23	1	0	4.029072	-1.246633	-1.073365
24	1	0	2.450114	-2.118463	-0.653337
25	1	0	-1.094652	3.025027	-1.283022
26	1	0	-1.790837	1.587222	-2.061023
27	1	0	-2.722395	2.477528	-0.849642
28	1	0	-0.200524	2.777302	1.217056
29	1	0	-1.920131	2.527219	1.535503
30	1	0	-0.750161	1.341465	2.112212

Table 32S: GIAO-B3LYP/6-311G(d) NMR absolute isotropic shielding tensor elements (σ, ppm) of **10**, conformer V, and relative chemical shifts with respect to TMS (ppm).

1	C	Isotropic =	51.3157	ppm; relative to TMS:	133.1509	ppm
2	O	Isotropic =	-6.4645	ppm; relative to TMS:	---	
3	O	Isotropic =	41.1515	ppm; relative to TMS:	---	
4	C	Isotropic =	99.3187	ppm; relative to TMS:	85.1479	ppm
5	C	Isotropic =	96.5150	ppm; relative to TMS:	87.9516	ppm
6	C	Isotropic =	97.9303	ppm; relative to TMS:	86.5363	ppm
7	O	Isotropic =	153.5844	ppm; relative to TMS:	---	
8	O	Isotropic =	201.7760	ppm; relative to TMS:	---	
9	C	Isotropic =	162.8635	ppm; relative to TMS:	21.6031	ppm
10	H	Isotropic =	30.8978	ppm; relative to TMS:	1.3825	ppm
11	H	Isotropic =	30.6040	ppm; relative to TMS:	1.6763	ppm
12	H	Isotropic =	30.6855	ppm; relative to TMS:	1.5948	ppm
13	C	Isotropic =	158.8887	ppm; relative to TMS:	25.5779	ppm
14	C	Isotropic =	154.7618	ppm; relative to TMS:	29.7048	ppm
15	H	Isotropic =	28.7192	ppm; relative to TMS:	3.5611	ppm
16	H	Isotropic =	27.6472	ppm; relative to TMS:	4.6331	ppm
17	C	Isotropic =	35.5435	ppm; relative to TMS:	148.9231	ppm
18	C	Isotropic =	66.7804	ppm; relative to TMS:	117.6862	ppm
19	C	Isotropic =	161.3664	ppm; relative to TMS:	23.1002	ppm
20	H	Isotropic =	30.5154	ppm; relative to TMS:	1.7649	ppm
21	H	Isotropic =	30.7716	ppm; relative to TMS:	1.5087	ppm
22	H	Isotropic =	30.4649	ppm; relative to TMS:	1.8154	ppm
23	H	Isotropic =	27.1572	ppm; relative to TMS:	5.1231	ppm
24	H	Isotropic =	26.8445	ppm; relative to TMS:	5.4358	ppm
25	H	Isotropic =	31.2654	ppm; relative to TMS:	1.0149	ppm
26	H	Isotropic =	30.7740	ppm; relative to TMS:	1.5063	ppm
27	H	Isotropic =	30.8848	ppm; relative to TMS:	1.3955	ppm
28	H	Isotropic =	31.3488	ppm; relative to TMS:	0.9315	ppm
29	H	Isotropic =	30.7668	ppm; relative to TMS:	1.5135	ppm
30	H	Isotropic =	30.4986	ppm; relative to TMS:	1.7817	ppm

Table 33S: Absolute energy and coordinates of compound epi-**10**, conformer I

Level of theory: B3LYP/6-311G(d)
Point group: C1
Number of negative eigenvalues in the Hessian matrix: 0
E(RB+HF-LYP) = -691.639529378 a.u.



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.707456	-0.662062	-0.078660
2	8	0	-0.960572	-1.798645	0.375940
3	8	0	0.399457	-1.391123	0.695427
4	6	0	0.979417	-0.741270	-0.443523
5	6	0	0.046514	0.418797	-0.853391
6	6	0	-0.523092	1.293745	0.296864
7	8	0	-1.581679	0.418144	0.798849
8	8	0	-1.161303	-0.223807	-1.304990
9	6	0	-3.129073	-1.140461	-0.226645
10	1	0	-3.721929	-0.344695	-0.677197
11	1	0	-3.163859	-2.024119	-0.863651
12	1	0	-3.534905	-1.384374	0.754519
13	6	0	0.408846	1.635288	1.451157
14	6	0	-1.183710	2.550952	-0.273959
15	1	0	0.446709	0.998552	-1.684251
16	1	0	0.957960	-1.442057	-1.290602
17	6	0	2.425783	-0.415240	-0.139363
18	6	0	3.043435	-0.874819	0.947096
19	6	0	3.138397	0.386076	-1.200504
20	1	0	2.774681	1.418291	-1.252202
21	1	0	2.998097	-0.048281	-2.196817
22	1	0	4.210349	0.425593	-1.001614
23	1	0	4.096444	-0.673387	1.116971
24	1	0	2.527026	-1.463556	1.694463
25	1	0	-0.432844	3.282469	-0.587564
26	1	0	-1.811799	2.304378	-1.131463
27	1	0	-1.811608	3.014084	0.490173
28	1	0	1.266768	2.217955	1.105057
29	1	0	-0.132148	2.239381	2.183684
30	1	0	0.769471	0.737175	1.944242

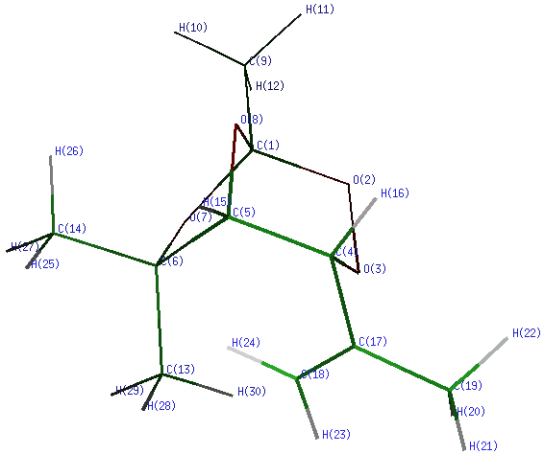
Table 34S: GIAO-B3LYP/6-311G(d) NMR absolute isotropic shielding tensor elements (σ, ppm) of epi-**10**, conformer I, and relative chemical shifts with respect to TMS (ppm).

1 C Isotropic = 54.7903 ppm; relative to TMS: 129.6763 ppm
2 O Isotropic = -25.2701 ppm; relative to TMS: ---
3 O Isotropic = 28.0104 ppm; relative to TMS: ---

```
 4 C Isotropic =  95.2016 ppm; relative to TMS:  89.2650 ppm
 5 C Isotropic = 100.8243 ppm; relative to TMS:  83.6423 ppm
 6 C Isotropic =  94.0723 ppm; relative to TMS:  90.3943 ppm
 7 O Isotropic = 162.0459 ppm; relative to TMS:    ---
 8 O Isotropic = 178.2076 ppm; relative to TMS:    ---
 9 C Isotropic = 163.3211 ppm; relative to TMS:  21.1455 ppm
10 H Isotropic =  31.0731 ppm; relative to TMS:   1.2072 ppm
11 H Isotropic =  30.8490 ppm; relative to TMS:   1.4313 ppm
12 H Isotropic =  30.7424 ppm; relative to TMS:   1.5379 ppm
13 C Isotropic = 161.9094 ppm; relative to TMS:  22.5572 ppm
14 C Isotropic = 155.0694 ppm; relative to TMS:  29.3972 ppm
15 H Isotropic =  28.4941 ppm; relative to TMS:   3.7862 ppm
16 H Isotropic =  27.2561 ppm; relative to TMS:   5.0242 ppm
17 C Isotropic =  37.0288 ppm; relative to TMS: 147.4378 ppm
18 C Isotropic =  67.0746 ppm; relative to TMS: 117.3920 ppm
19 C Isotropic = 161.7288 ppm; relative to TMS:  22.7378 ppm
20 H Isotropic =  30.6217 ppm; relative to TMS:   1.6586 ppm
21 H Isotropic =  30.5909 ppm; relative to TMS:   1.6894 ppm
22 H Isotropic =  30.4309 ppm; relative to TMS:   1.8494 ppm
23 H Isotropic =  27.2172 ppm; relative to TMS:   5.0631 ppm
24 H Isotropic =  27.1060 ppm; relative to TMS:   5.1743 ppm
25 H Isotropic =  31.2947 ppm; relative to TMS:   0.9856 ppm
26 H Isotropic =  30.6728 ppm; relative to TMS:   1.6075 ppm
27 H Isotropic =  31.0620 ppm; relative to TMS:   1.2183 ppm
28 H Isotropic =  31.4735 ppm; relative to TMS:   0.8068 ppm
29 H Isotropic =  30.8660 ppm; relative to TMS:   1.4143 ppm
30 H Isotropic =  30.0022 ppm; relative to TMS:   2.2781 ppm
```

Table 35S: Absolute energy and coordinates of compound epi-**10**, conformer II

Level of theory: B3LYP/6-311G(d)
Point group: C1
Number of negative eigenvalues in the Hessian matrix: 0
E(RB+HF-LYP) = -691.639492697 a.u.



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.637809	-0.788831	-0.035438
2	8	0	-0.749683	-1.822876	0.413274
3	8	0	0.564140	-1.251676	0.668599
4	6	0	1.021336	-0.581060	-0.525167
5	6	0	-0.042386	0.461427	-0.903726
6	6	0	-0.655703	1.288183	0.265301
7	8	0	-1.602399	0.317576	0.814647
8	8	0	-1.191917	-0.319752	-1.290400
9	6	0	-3.000942	-1.426745	-0.116800
10	1	0	-3.697043	-0.711614	-0.554605
11	1	0	-2.961018	-2.321685	-0.737496
12	1	0	-3.337394	-1.694290	0.884291
13	6	0	0.265681	1.735606	1.392139
14	6	0	-1.460690	2.464440	-0.292814
15	1	0	0.248502	1.066544	-1.761315
16	1	0	1.023801	-1.323806	-1.335444
17	6	0	2.451114	-0.147829	-0.281803
18	6	0	2.927651	1.017806	-0.718080
19	6	0	3.326700	-1.176627	0.386972
20	1	0	2.980261	-1.392128	1.400441
21	1	0	4.362767	-0.837393	0.437187
22	1	0	3.299471	-2.127528	-0.156086
23	1	0	3.977847	1.267337	-0.606777
24	1	0	2.313749	1.764912	-1.208116
25	1	0	-0.800058	3.260494	-0.649363
26	1	0	-2.096245	2.142096	-1.119310
27	1	0	-2.099529	2.877669	0.490592
28	1	0	1.012753	2.447685	1.035905
29	1	0	-0.333190	2.228632	2.161812
30	1	0	0.774489	0.888677	1.845823

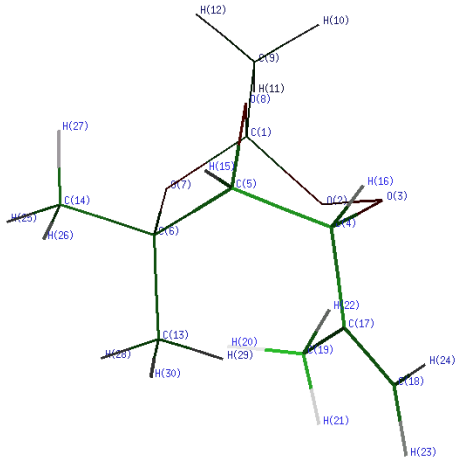
Table 36S: GIAO-B3LYP/6-311G(d) NMR absolute isotropic shielding tensor elements (σ, ppm) of epi-10, conformer II, and relative chemical shifts with respect to TMS (ppm).

1 C Isotropic = 55.0702 ppm; relative to TMS: 129.3964 ppm
2 O Isotropic = -30.4433 ppm; relative to TMS: ---
3 O Isotropic = 24.2835 ppm; relative to TMS: ---

```
 4 C Isotropic =  94.5210 ppm; relative to TMS:  89.9456 ppm
 5 C Isotropic = 100.7718 ppm; relative to TMS:  83.6948 ppm
 6 C Isotropic =  94.6908 ppm; relative to TMS:  89.7758 ppm
 7 O Isotropic = 161.2999 ppm; relative to TMS:    ---
 8 O Isotropic = 179.9915 ppm; relative to TMS:    ---
 9 C Isotropic = 163.4740 ppm; relative to TMS:  20.9926 ppm
10 H Isotropic =  31.0660 ppm; relative to TMS:   1.2143 ppm
11 H Isotropic =  30.8594 ppm; relative to TMS:   1.4209 ppm
12 H Isotropic =  30.7632 ppm; relative to TMS:   1.5171 ppm
13 C Isotropic = 159.7672 ppm; relative to TMS:  24.6994 ppm
14 C Isotropic = 155.0407 ppm; relative to TMS:  29.4259 ppm
15 H Isotropic =  28.2795 ppm; relative to TMS:   4.0008 ppm
16 H Isotropic =  27.2411 ppm; relative to TMS:   5.0392 ppm
17 C Isotropic =  31.7001 ppm; relative to TMS: 152.7665 ppm
18 C Isotropic =  70.1888 ppm; relative to TMS: 114.2778 ppm
19 C Isotropic = 161.6163 ppm; relative to TMS:  22.8503 ppm
20 H Isotropic =  30.0763 ppm; relative to TMS:   2.2040 ppm
21 H Isotropic =  30.6853 ppm; relative to TMS:   1.5950 ppm
22 H Isotropic =  30.4691 ppm; relative to TMS:   1.8112 ppm
23 H Isotropic =  27.3274 ppm; relative to TMS:   4.9529 ppm
24 H Isotropic =  27.7543 ppm; relative to TMS:   4.5260 ppm
25 H Isotropic =  31.2552 ppm; relative to TMS:   1.0251 ppm
26 H Isotropic =  30.5946 ppm; relative to TMS:   1.6857 ppm
27 H Isotropic =  30.9850 ppm; relative to TMS:   1.2953 ppm
28 H Isotropic =  31.3401 ppm; relative to TMS:   0.9402 ppm
29 H Isotropic =  30.7934 ppm; relative to TMS:   1.4869 ppm
30 H Isotropic =  30.3568 ppm; relative to TMS:   1.9235 ppm
```

Table 37S: Absolute energy and coordinates of compound epi-**10**, conformer III

Level of theory: B3LYP/6-311G(d)
Point group: C1
Number of negative eigenvalues in the Hessian matrix: 0
E(RB+HF-LYP) = -691.628054551 a.u.



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.692349	-0.597565	0.034163
2	8	0	-0.676526	-1.409646	0.737964
3	8	0	0.328838	-1.876494	-0.197319
4	6	0	1.022727	-0.741322	-0.730594
5	6	0	-0.019828	0.400562	-0.935583
6	6	0	-0.525355	1.334418	0.232976
7	8	0	-1.701061	0.612183	0.715562
8	8	0	-1.228983	-0.312449	-1.251151
9	6	0	-3.023452	-1.290747	0.045912
10	1	0	-2.941256	-2.238074	-0.486799
11	1	0	-3.318782	-1.486378	1.076882
12	1	0	-3.775758	-0.662390	-0.432475
13	6	0	0.395657	1.587225	1.418646
14	6	0	-1.036297	2.644821	-0.369247
15	1	0	0.257024	0.998768	-1.802807
16	1	0	1.257694	-1.079296	-1.750501
17	6	0	2.336921	-0.425956	-0.047783
18	6	0	2.755092	-1.109716	1.013969
19	6	0	3.176597	0.622860	-0.733880
20	1	0	2.687826	1.603310	-0.754078
21	1	0	4.140057	0.745282	-0.236542
22	1	0	3.372172	0.351446	-1.778341
23	1	0	3.722095	-0.912638	1.466075
24	1	0	2.143690	-1.885134	1.458331
25	1	0	-1.607790	3.197913	0.378790
26	1	0	-0.206698	3.276242	-0.701487
27	1	0	-1.691084	2.448069	-1.220528
28	1	0	-0.131541	2.215550	2.140954
29	1	0	0.670002	0.657679	1.909096
30	1	0	1.305922	2.113416	1.121520

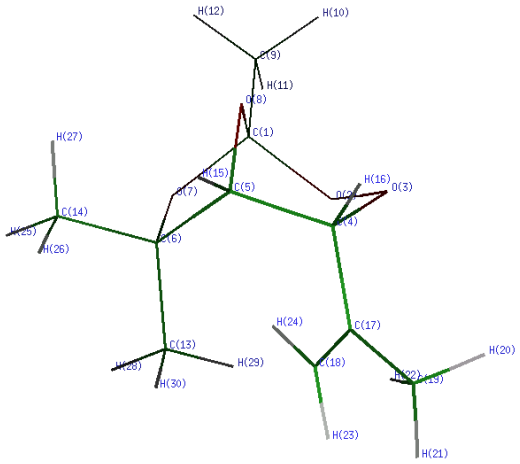
Table 38S: GIAO-B3LYP/6-311G(d) NMR absolute isotropic shielding tensor elements (σ, ppm) of epi-10, conformer III, and relative chemical shifts with respect to TMS (ppm).

1 C Isotropic = 50.8995 ppm; relative to TMS: 133.5671 ppm
2 O Isotropic = -13.9545 ppm; relative to TMS: ---
3 O Isotropic = 38.5680 ppm; relative to TMS: ---

```
 4 C Isotropic =  91.2767 ppm; relative to TMS:  93.1899 ppm
 5 C Isotropic =  99.5909 ppm; relative to TMS:  84.8757 ppm
 6 C Isotropic =  95.9100 ppm; relative to TMS:  88.5566 ppm
 7 O Isotropic = 155.9331 ppm; relative to TMS:    ---
 8 O Isotropic = 188.9993 ppm; relative to TMS:    ---
 9 C Isotropic = 163.4310 ppm; relative to TMS:  21.0356 ppm
10 H Isotropic =  30.5792 ppm; relative to TMS:   1.7011 ppm
11 H Isotropic =  30.6985 ppm; relative to TMS:   1.5818 ppm
12 H Isotropic =  30.8988 ppm; relative to TMS:   1.3815 ppm
13 C Isotropic = 159.1226 ppm; relative to TMS:  25.3440 ppm
14 C Isotropic = 153.7470 ppm; relative to TMS:  30.7196 ppm
15 H Isotropic =  28.2258 ppm; relative to TMS:   4.0545 ppm
16 H Isotropic =  27.4106 ppm; relative to TMS:   4.8697 ppm
17 C Isotropic =  35.4523 ppm; relative to TMS: 149.0143 ppm
18 C Isotropic =  65.6111 ppm; relative to TMS: 118.8555 ppm
19 C Isotropic = 162.2695 ppm; relative to TMS:  22.1971 ppm
20 H Isotropic =  30.7593 ppm; relative to TMS:   1.5210 ppm
21 H Isotropic =  30.3165 ppm; relative to TMS:   1.9638 ppm
22 H Isotropic =  30.6213 ppm; relative to TMS:   1.6590 ppm
23 H Isotropic =  27.1128 ppm; relative to TMS:   5.1675 ppm
24 H Isotropic =  26.6245 ppm; relative to TMS:   5.6558 ppm
25 H Isotropic =  30.9504 ppm; relative to TMS:   1.3299 ppm
26 H Isotropic =  31.2005 ppm; relative to TMS:   1.0798 ppm
27 H Isotropic =  30.7863 ppm; relative to TMS:   1.4940 ppm
28 H Isotropic =  30.9907 ppm; relative to TMS:   1.2896 ppm
29 H Isotropic =  30.1293 ppm; relative to TMS:   2.1510 ppm
30 H Isotropic =  31.3609 ppm; relative to TMS:   0.9194 ppm
```

Table 39S: Absolute energy and coordinates of compound epi-**10**, conformer IV

Level of theory: B3LYP/6-311G(d)
Point group: C1
Number of negative eigenvalues in the Hessian matrix: 0
E(RB+HF-LYP) = -691.626421543 a.u.



Standard orientation:

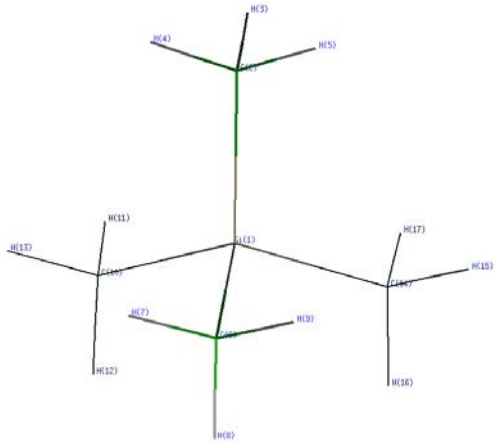
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.620070	-0.685288	0.079246
2	8	0	-0.501751	-1.437998	0.691948
3	8	0	0.458860	-1.810818	-0.329998
4	6	0	1.040344	-0.610809	-0.858830
5	6	0	-0.096959	0.449568	-0.981784
6	6	0	-0.598036	1.334406	0.223900
7	8	0	-1.665854	0.508066	0.786814
8	8	0	-1.269637	-0.347330	-1.228695
9	6	0	-2.894004	-1.473872	0.167518
10	1	0	-2.781525	-2.403606	-0.390072
11	1	0	-3.102103	-1.707709	1.211767
12	1	0	-3.721068	-0.894409	-0.244619
13	6	0	0.373538	1.683351	1.341671
14	6	0	-1.267685	2.590503	-0.339025
15	1	0	0.081573	1.073674	-1.855942
16	1	0	1.261363	-0.914733	-1.888612
17	6	0	2.350838	-0.210304	-0.191091
18	6	0	3.097279	0.760113	-0.719060
19	6	0	2.789559	-1.022078	0.997268
20	1	0	2.982482	-2.058151	0.702960
21	1	0	3.701458	-0.611737	1.435134
22	1	0	2.015574	-1.070433	1.766394
23	1	0	4.048960	1.046061	-0.283143
24	1	0	2.797586	1.304647	-1.610794
25	1	0	-1.836959	3.090050	0.447371
26	1	0	-0.522769	3.293840	-0.722470
27	1	0	-1.956549	2.331622	-1.145428
28	1	0	-0.163321	2.255989	2.102297
29	1	0	0.767715	0.788139	1.816562
30	1	0	1.205813	2.287843	0.979165

Table 40S: GIAO-B3LYP/6-311G(d) NMR absolute isotropic shielding tensor elements (σ, ppm) of epi-10, conformer IV, and relative chemical shifts with respect to TMS (ppm).

1 C Isotropic = 51.0417 ppm; relative to TMS: 133.4249 ppm
2 O Isotropic = -15.2373 ppm; relative to TMS: ---
3 O Isotropic = 33.7449 ppm; relative to TMS: ---

```
 4 C Isotropic =  93.5075 ppm; relative to TMS:  90.9591 ppm
 5 C Isotropic =  98.2788 ppm; relative to TMS:  86.1878 ppm
 6 C Isotropic =  96.2420 ppm; relative to TMS:  88.2246 ppm
 7 O Isotropic = 156.7434 ppm; relative to TMS:    ---
 8 O Isotropic = 186.9892 ppm; relative to TMS:    ---
 9 C Isotropic = 163.2595 ppm; relative to TMS:  21.2071 ppm
10 H Isotropic =  30.6154 ppm; relative to TMS:   1.6649 ppm
11 H Isotropic =  30.7241 ppm; relative to TMS:   1.5562 ppm
12 H Isotropic =  30.9295 ppm; relative to TMS:   1.3508 ppm
13 C Isotropic = 157.8290 ppm; relative to TMS:  26.6376 ppm
14 C Isotropic = 153.2857 ppm; relative to TMS:  31.1809 ppm
15 H Isotropic =  28.1397 ppm; relative to TMS:   4.1406 ppm
16 H Isotropic =  27.0497 ppm; relative to TMS:   5.2306 ppm
17 C Isotropic =  25.5449 ppm; relative to TMS: 158.9217 ppm
18 C Isotropic =  72.2790 ppm; relative to TMS: 112.1876 ppm
19 C Isotropic = 159.7700 ppm; relative to TMS:  24.6966 ppm
20 H Isotropic =  29.9464 ppm; relative to TMS:   2.3339 ppm
21 H Isotropic =  30.5850 ppm; relative to TMS:   1.6953 ppm
22 H Isotropic =  29.9777 ppm; relative to TMS:   2.3026 ppm
23 H Isotropic =  27.3143 ppm; relative to TMS:   4.9660 ppm
24 H Isotropic =  27.6837 ppm; relative to TMS:   4.5966 ppm
25 H Isotropic =  30.9134 ppm; relative to TMS:   1.3669 ppm
26 H Isotropic =  31.1822 ppm; relative to TMS:   1.0981 ppm
27 H Isotropic =  30.7309 ppm; relative to TMS:   1.5494 ppm
28 H Isotropic =  30.9200 ppm; relative to TMS:   1.3603 ppm
29 H Isotropic =  30.7696 ppm; relative to TMS:   1.5107 ppm
30 H Isotropic =  30.9367 ppm; relative to TMS:   1.3436 ppm
```

Table 41S: Absolute energy and coordinates of TMS
Level of theory: B3LYP/6-311G(d)
Point group: TD
Number of negative eigenvalues in the Hessian matrix: 0
E(RB+HF-LYP) = -449.253001174 a.u.



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	14	0	0.000000	0.000000	0.000000
2	6	0	1.091833	1.091833	1.091833
3	1	0	1.739858	1.739858	0.492846
4	1	0	0.492846	1.739858	1.739858
5	1	0	1.739858	0.492846	1.739858
6	6	0	-1.091833	-1.091833	1.091833
7	1	0	-1.739858	-0.492846	1.739858
8	1	0	-1.739858	-1.739858	0.492846
9	1	0	-0.492846	-1.739858	1.739858
10	6	0	-1.091833	1.091833	-1.091833
11	1	0	-0.492846	1.739858	-1.739858
12	1	0	-1.739858	0.492846	-1.739858
13	1	0	-1.739858	1.739858	-0.492846
14	6	0	1.091833	-1.091833	-1.091833
15	1	0	1.739858	-1.739858	-0.492846
16	1	0	0.492846	-1.739858	-1.739858
17	1	0	1.739858	-0.492846	-1.739858

Table 42S: GIAO-B3LYP/6-311G(d) NMR absolute isotropic shielding tensor elements (σ, ppm) of TMS and relative chemical shifts of TMS with respect to TMS (ppm)

```
 1 Si Isotropic = 339.1634 ppm; relative to TMS: ---
 2 C  Isotropic = 184.4666 ppm; relative to TMS: 0 ppm
 3 H  Isotropic =  32.2803 ppm; relative to TMS: 0 ppm
 4 H  Isotropic =  32.2803 ppm; relative to TMS: 0 ppm
 5 H  Isotropic =  32.2803 ppm; relative to TMS: 0 ppm
 6 C  Isotropic = 184.4666 ppm; relative to TMS: 0 ppm
 7 H  Isotropic =  32.2803 ppm; relative to TMS: 0 ppm
 8 H  Isotropic =  32.2803 ppm; relative to TMS: 0 ppm
 9 H  Isotropic =  32.2803 ppm; relative to TMS: 0 ppm
10 C  Isotropic = 184.4666 ppm; relative to TMS: 0 ppm
11 H  Isotropic =  32.2803 ppm; relative to TMS: 0 ppm
12 H  Isotropic =  32.2803 ppm; relative to TMS: 0 ppm
13 H  Isotropic =  32.2803 ppm; relative to TMS: 0 ppm
14 C  Isotropic = 184.4666 ppm; relative to TMS: 0 ppm
15 H  Isotropic =  32.2803 ppm; relative to TMS: 0 ppm
16 H  Isotropic =  32.2803 ppm; relative to TMS: 0 ppm
17 H  Isotropic =  32.2803 ppm; relative to TMS: 0 ppm
```