Supporting Information

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Bioinspired Synthesis of (–)-PF-1018

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SUPPORTING INFORMATION

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Materials and Methods

Unless otherwise stated, reactions were carried out under nitrogen atmosphere utilizing standard Schlenk-technique using oven-dried glassware and stir bars (160 ºC) or heat gun-dried (>550 ºC) while under vacuum glassware and stir bars. Heating over room temperature was achieved with aluminium heating blocks or oil baths. Low temperature reactions were performed with acetone/dry ice baths (–78 ºC, –50 ºC, –30 ºC) or ice baths (0 ºC). Dry solvents were used from the following sources: tetrahydrofuran (THF), dichloromethane (DCM), benzene and diethyl ether (Et_2O) were Fisher certified ACS reagents dried and degassed with an Innovative Technology PS-MD-6 solvent system. Chloroform ($CHCl_3$), toluene (PhMe), pyridine and *N*,*N*-dimethylformamide (DMF) were purchased as extra dry and stabilized from Acros Organics.

n-Buthyllithium and *s*-Buthyllithium were purchased from Acros Organics and titrated using *N*-benzylbenzamide. All reagents used were purchased from commercial vendors and directly used unless otherwise stated.

Reactions were monitored by thin layer chromatography (TLC) on glass plates precoated with silica gel (0.25 mm, 60Å pore size, F_{254}) from MilliporeSigma and visualized under UV light (254 nm) or stained with ceric ammonium molybdate. Flash column chromatography was performed either by hand or on Teledyne ISCO Combiflash Rf+ system with manually packed Universal RediSep cartridges using Geduran® Si 60 silicagel (40-60 µm particle size) from MilliporeSigma or when specifically stated with spherical 20-40 µm particle size silica from RediSep Rf. HPLC purifications were performed on an Agilent 1260 Infininty Prep Pump system with 1260 Infinity II Diode Array Detector WR connected to a Gemini 5 µm, C18, 110Å semipreparative column.

^1H and ^{13}C spectra were measured with a Bruker Avance III HD 400 MHz spectrometer equipped with a CryoProbe™ operating at 400 MHz for ^1H and 100 MHz for ^{13}C spectra. Signals were calibrated from residual protium in NMR solvents ($CHCl_3$: δ 7.26) for ^1H and solvent resonance ($CDCl_3$: δ 77.00) for ^{13}C. NMR data are reported as: chemical shift (δ ppm), multiplicity expressed as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, coupling constant (Hz), and integration. ^{13}C NMR shifts expressed with the exact same number are distinguishable as two peaks on the correspondent spectrum. All raw FID files were processed and the spectra analyzed using the program Mnova 11.0.3 from Mestrelab Research S. L.

High-resolution mass spectra (HRMS) were recorded on an Agilent Technologies 6224 time-of-flight (TOF) spectrometer with either atmospheric pressure chemical ionization (APCI) or electrospray ionization (ESI) sources. Infrared (IR) spectra were recorded on a ThermoScientific Nicolet-6700 Fourier Transform Infrared Spectrometer (FTIR) and reported as frequency of absorption (cm^{-1}) with intensity of absorption (s = strong, m = medium, w = weak, br = broad). Optical rotations were measured on a Jasco P-2000 polarimeter using a 100 mm path-length Jasco CG3-100/10 Cylindrical Glass Cell at the Sodium D-line (589 nm) at the given temperature in (ºC) and concentration expressed in g/100 mL. Melting points were measured on a Stanford Research Systems OptiMelt MPA100 automated melting point system in open glass capillaries and are uncorrected.

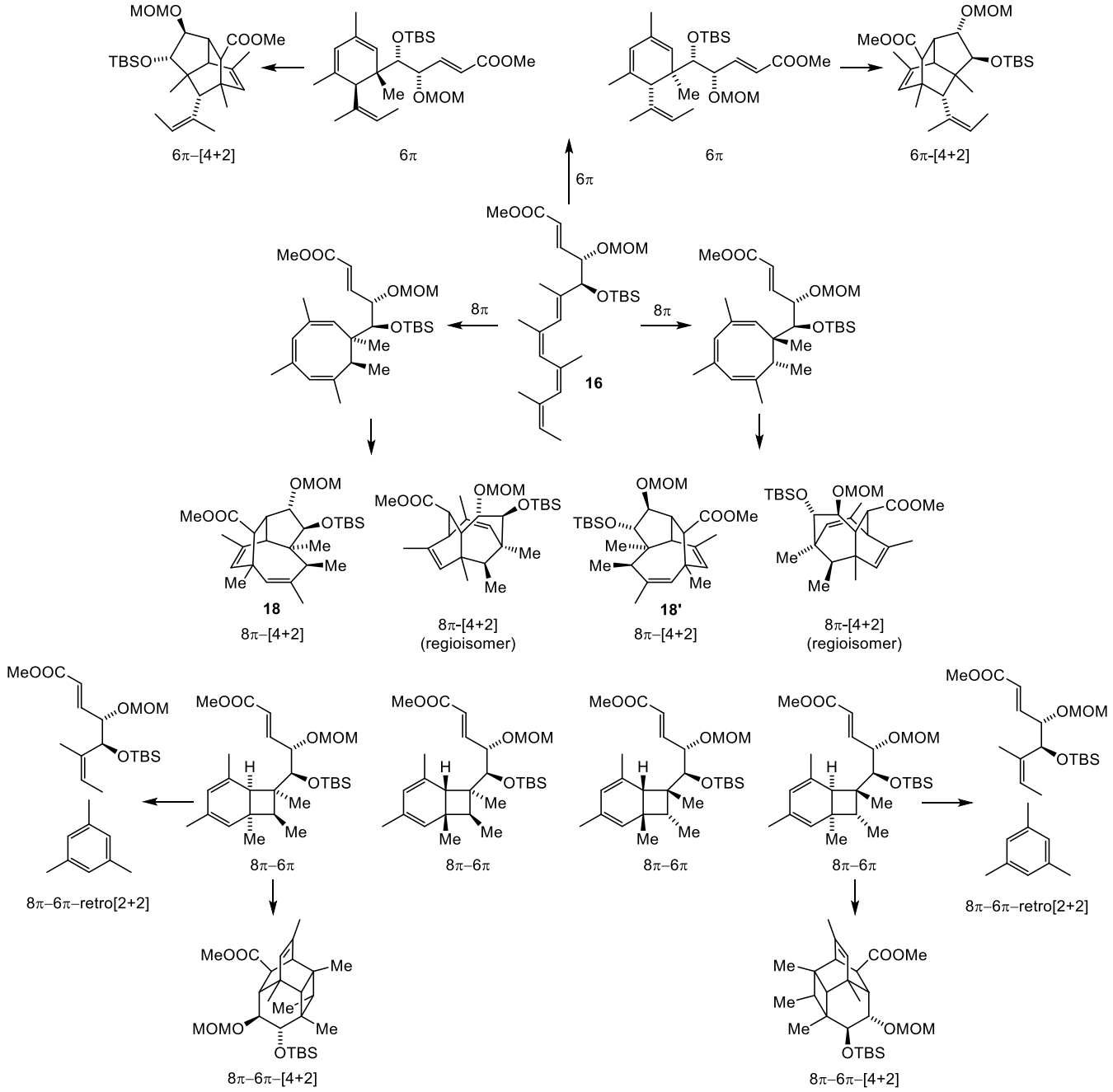
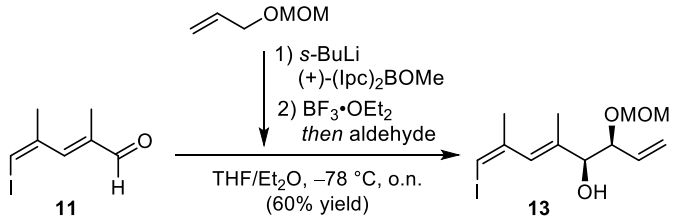


Figure S1. Potential products that could arise from cascade reaction **16** → **18**.

Experimental Procedures and Characterization Data



Vinyl iodide 13.
To a solution of allyl methoxymethyl ether (1.30 g, 12.7 mmol, 2.26 equiv.) in dry THF (12 mL) at −78 °C was added *s*-butyllithium (1.4 M in cyclohexane, 8.53 mL, 11.9 mmol, 2.12 equiv.) over 20 min. The reaction mixture was stirred at −78 °C for 30 min after which a solution of (+)-B-methoxydiisopinocampheylborane (3.74 g, 11.8 mmol, 2.10 equiv.) in dry diethyl ether (22 mL) was added over 20 min. The reaction was further stirred at −78 °C for 1 h before boron trifluoride diethyl etherate (1.61 mL, 12.7 mmol, 2.26 equiv.) was added dropwise, followed by immediate addition of a solution of aldehyde **11** (1.33 g, 5.63 mmol, 1.00 equiv.) in dry THF (30 mL) in the dark and in contact with the flask's inner wall to ensure pre-cooling. The reaction mixture was stirred for an additional 3 h at −78 °C, then slowly warmed to room temperature and stirred overnight.

The solvent was exchanged to diethyl ether (45 mL) and an aqueous solution of NaOH (2.5 M, 8 mL) was added followed by careful addition of H_2O_2 in water (30% w/w, 23 mL) causing intense gas evolution. The mixture was stirred under reflux for 3 h or until no more gas evolution was observed at room temperature. The layers were separated, and the aqueous phase was extracted three times with diethyl ether. The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure.

The crude residue was purified by flash column chromatography on silica gel, (EtOAc/Hex, gradient, 0 to 12%) yielding **13** as a colourless oil (1.14 g, 3.37 mmol, 60% yield, *d.r.*>20:1, 96% *ee*, Mosher's ester analysis, see below).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.05 (s, 1H), 5.94 (s, 1H), 5.74 (ddd, *J* = 17.5, 10.3, 7.3 Hz, 1H), 5.36–5.26 (m, 2H), 4.76 (d, *J* = 6.7 Hz, 1H), 4.64 (d, *J* = 6.7 Hz, 1H), 4.07 (t, *J* = 7.4 Hz, 1H), 4.01 (dd, *J* = 7.5, 2.1 Hz, 1H), 3.43 (s, 3H), 2.90 (d, *J* = 2.4 Hz, 1H), 1.97 (s, 3H), 1.71 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 137.2, 134.3, 130.5, 119.4, 94.5, 80.1, 79.4, 77.30, 55.9, 24.6, 14.1

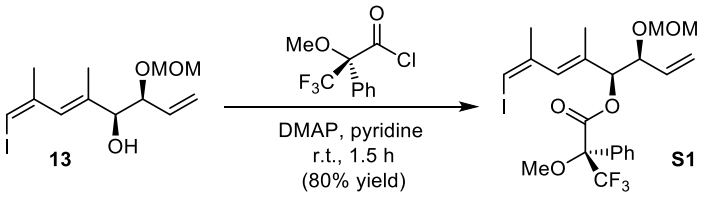
IR (ATR): 3465 (br), 2924 (s), 2851 (m), 2363 (w), 1261 (w), 1151 (m), 1081 (m), 1031 (s), 922 (m), 768 (w)

HRMS (+ESI): calc. for $C_{12}H_{19}INaO_3$ $[M+Na]^+$ 361.0271 found 361.0275

$[\alpha]_D^{23}$ +70.6° (*c* 0.67, $CHCl_3$)

R_F = 0.42 (25% EtOAc in hexanes)

Procedure for Mosher's ester analysis



Mosher's ester S1.
To a solution of triene **13**, (5.0 mg, 15 µmol, 1.0 equiv.) and DMAP (6.4 mg, 52 µmol. 3.5 equiv.) in pyridine (0.50 mL) was added (*R*)-(−)-α-Methoxy-α-(trifluoromethyl)phenylacetyl chloride (Mosher's acyl chloride, 2.8 µL, 15 µmol, 1.0 equiv.). The reaction mixture was stirred for 1.5 h.

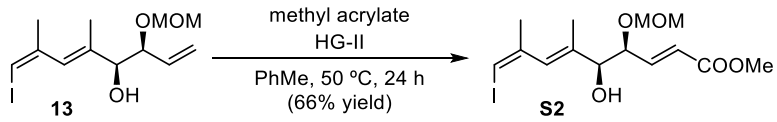
The solvent was evaporated and the residue was filtered through a pad of silica eluting with 30% EtOAc/hexanes affording ester **S1** as a colourless oil (6.6 mg, 12 µmol, 80% yield, *d.r.* 1:0.02).

(*S*)-diastereomer:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.55 (m, 2H), 7.43–7.34 (m, 3H), 6.08 (br, 1H), 5.96 (s, 1H), 5.69 (ddd, *J* = 18.0, 10.3, 7.8 Hz, 1H), 5.41–5.31 (m, 3H), 4.69 (d, *J* = 6.7 Hz, 1H), 4.57 (d, *J* = 6.7 Hz, 1H), 4.27 (t, *J* = 8.2 Hz, 1H), 3.59–3.57 (br, 3H), 3.29 (s, 3H), 1.89 (s, 3H), 1.56 (d, *J* = 1.3 Hz, 3H)

(*R*)-diastereomer:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59–7.50 (m, 2H), 7.42–7.34 (m, 3H), 6.10 (app quintet, *J* = 1.5 Hz, 1H), 6.03 (br, 1H), 5.66 (ddd, *J* = 17.2, 10.3, 7.7 Hz, 1H), 5.45 (d, *J* = 8.7 Hz, 1H), 5.37–5.27 (m, 2H), 4.50 (d, *J* = 6.8 Hz, 1H), 4.37 (d, *J* = 6.8 Hz, 1H), 4.22 (t, *J* = 8.1 Hz, 1H), 3.58 (d, *J* = 1.4 Hz, 3H), 3.10 (s, 3H), 1.90 (dd, *J* = 1.5, 0.7 Hz, 3H), 1.69 (d, *J* = 1.3 Hz, 3H)



Conjugated ester S2.
A Schlenk tube was charged with vinyl iodide **13** (1.00 g, 2.96 mmol, 1.00 equiv.), methyl acrylate (0.80 mL, 8.9 mmol, 3.0 equiv.) and dry degassed toluene (freeze-pump-thaw, 3x10 min, 5.0 mL). A solution of 2nd generation Hoveyda–Grubbs catalyst (186 mg, 0.300 mmol, 0.10 equiv.) in dry degassed toluene (freeze-pump-thaw, 3x10 min, 6.6 mL) was loaded in a syringe. 0.55 mL of the solution were added in one portion every hour while the reaction mixture was stirred at 50 ºC. After the addition was complete the suspension was stirred for an additional 12 h at the same temperature.

The solvents were evaporated at 28 ºC and the crude product was submitted to flash column chromatography on silica gel (EtOAc/Hex, gradient, 0 to 30%) affording ester **S2** (776 mg, 1.96 mmol, 66% yield) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 (dd, *J* = 15.8, 6.4 Hz, 1H), 6.10–6.04 (m, 2H), 5.91 (s, 1H), 4.70 (s, 2H), 4.24 (ddd, *J* = 7.4, 6.4, 1.3 Hz, 1H), 4.03 (dd, *J* = 7.4, 2.7 Hz, 1H), 3.72 (s, 3H), 3.43 (s, 3H), 2.96–2.94 (m, 1H), 1.94 (d, *J* = 1.3 Hz, 3H), 1.71 (d, *J* = 1.3 Hz, 3H)

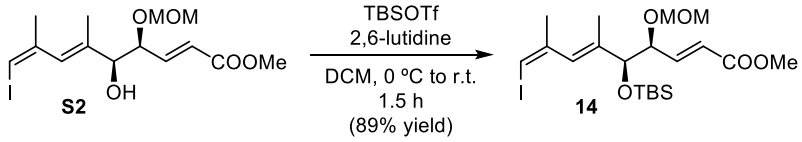
^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 144.2, 144.0, 136.2, 131.0, 123.4, 95.5, 78.9, 78.5, 77.4, 56.1, 51.7, 24.6, 14.0

IR (ATR): 3560 (br), 2950 (m), 1721 (s), 1660 (w), 1436 (m), 1277 (s), 1150 (m), 1023 (s), 916 (s), 730 (s)

HRMS (+APCI): calc. for $C_{14}H_{20}IO_4$ $[M-OH]^+$ 379.0401, found 379.0434

$[\alpha]_D^{23}$ +56.9º (*c* 0.93, $CHCl_3$)

R_F = 0.16 (20% EtOAc in hexanes)



Silyl ether 14.
To vinyl iodide **S2** (1.04 g, 2.63 mmol, 1.00 equiv.) in dry DCM (22 mL) was added 2,6-lutidine (0.76 mL, 6.6 mmol, 2.5 equiv.). The solution was cooled down to 0 ºC and TBSOTf (0.91 ml, 3.9 mmol, 1.5 equiv.) was added dropwise. The reaction mixture was allowed to warm up to room temperature and was stirred for 1.5 h.

An aqueous saturated $NaHCO_3$ solution was added and the layers were separated. The aqueous phase was extracted three times with DCM and the organic layers were combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude material (yellow oil, 1.50 g) was purified by flash column chromatography on silica gel (EtOAc/hexanes, gradient, 0 to 15%) affording silyl ether **14** as a yellow oil (1.20 g, 2.35 mmol, 89% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (dd, *J* = 15.7, 6.0 Hz, 1H), 6.09–6.03 (m, 2H), 5.82 (br s, 1H), 4.75 (d, *J* = 6.7 Hz, 1H), 4.65 (d, *J* = 6.7 Hz, 1H), 4.23 (ddd, *J* = 7.3, 6.0, 1.5 Hz, 1H), 4.08 (dd, *J* = 6.9, 0.9 Hz, 1H), 3.71 (s, 3H), 3.37 (s, 3H), 1.91 (dd, *J* = 1.5, 0.7 Hz, 3H), 1.66 (d, *J* = 1.3 Hz, 3H), 0.91 (s, 9H), 0.10 (s, 3H), 0.08 (s, 3H)

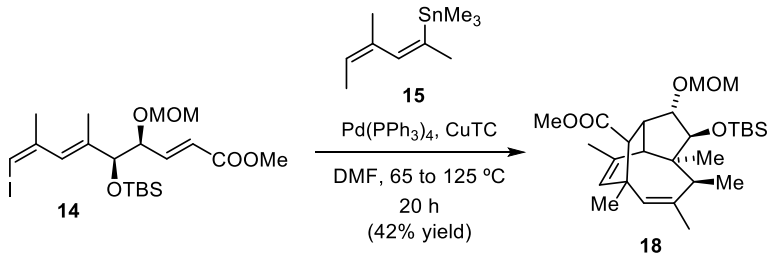
^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 145.2, 144.3, 138.0, 130.0, 122.1, 96.0, 80.4, 78.5, 77.1, 55.8, 51.5, 25.8, 24.4, 18.2, 14.2, −4.6, −4.9

IR (ATR): 2951 (m), 2928 (m), 2888 (w), 2856 (m), 2361 (w), 1726 (s), 1661 (w), 1435 (m), 1251 (m), 1152 (m), 1092 (s), 1028 (s), 912 (m), 872 (m), 837 (s), 775 (s)

HRMS (+APCI): calc. for $C_{18}H_{30}IO_3Si$ $[M-OMOM]^+$ 449.1003, found 449.1009

$[\alpha]_D^{23}$ +1.50° (*c* 1.07, $CHCl_3$)

R_F = 0.58 (20% EtOAc in hexanes)



Cascade product 18.
$Pd(PPh_3)_4$ (25.8 mg, 22.3 µmol, 0.100 equiv.) and copper(I) thiophene-2-carboxylate (CuTC, 46.8 mg, 0.246 mmol, 1.10 equiv.) were charged into a dried flask under N_2 that was wrapped in aluminum foil to shield it from light. A solution of vinyl stannane **15** (81.0 mg, 0.313 mmol, 1.40 equiv.) in benzene (1.2 mL) and vinyl iodide **14** (114 mg, 0.223 mmol, 1.00 equiv.) were combined and concentrated (rotary evaporator bath temperature 30 °C, pressure 35 mbar, darkness) to azeotropically remove traces of water. The iodide/stannane mixture was redissolved in dry DMF (2.2 mL) and added to the Pd/Cu solid mixture avoiding light. The result was immediately heated to 65 °C (external aluminium block temperature) and stirred for 50 min. The temperature was then increased to 125 °C and the mixture further stirred in the dark for 20 h.

After cooling, the solvent was evaporated at 60 ºC and 10 mbar. The resulting black gum was dissolved in a small amount of DCM and loaded on a pad of silica pre-equilibrated with hexanes. The DCM was evaporated under a flow of nitrogen and the remaining residue was eluted with 7:3 hexanes/Et_2O (4x3.8 mL) yielding 95 mg of a slightly yellow which was purified by flash column chromatography on silica gel, (EtOAc/Hex, gradient, 0 to 3%) providing tricycle **18** as a white crystalline solid (45.0 mg, 94.0 µmol, 42% yield). The same procedure performed on 831 mg of vinyl iodide **14** afforded **18** (309 mg, 0.645 mmol, 40% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.34 (s, 1H), 5.00 (s, 1H), 4.63–4.57 (m, 2H), 3.93–3.84 (m, 2H), 3.59 (s, 3H), 3.25 (s, 3H), 2.88 (q, *J* = 7.6 Hz, 1H), 2.71 (s, 1H), 2.65 (d, *J* = 11.3 Hz, 1H), 2.32 (dd, *J* = 11.4, 4.9 Hz, 1H), 1.86 (s, 3H), 1.82 (s, 3H), 1.19 (s, 3H), 1.12 (s, 3H), 1.07 (d, *J* = 7.5 Hz, 3H), 0.91 (s, 9H), 0.11 (s, 3H), 0.06 (s. 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 140.6, 138.0, 133.1, 125.0, 97.8, 92.9, 87.8, 55.3, 55.2, 53.9, 51.2, 50.9, 44.3, 40.5, 34.4, 29.3, 29.0, 26.0, 25.0, 24.2, 18.2, 15.8, –4.24, –4.39

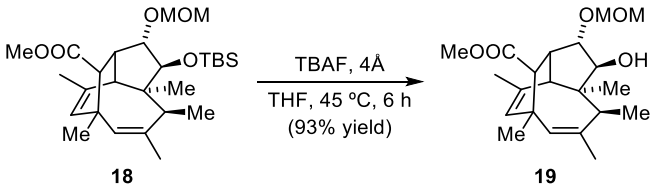
IR (ATR): 2929 (m), 2856 (w), 1731 (m), 1460 (m), 1252 (m), 1197 (m), 1173 (m), 1124 (s), 1109 (s), 1041 (s), 876 (s), 837 (s), 774 (s)

HRMS (+APCI): calc. for $C_{27}H_{47}O_5Si$ $[M+H]^+$ 479.3187, found 479.3191

$[\alpha]_D^{23}$ +15.1° (*c* 2.33, $CHCl_3$)

R_F = 0.29 (12% Et_2O in hexanes), 0.36 (10% EtOAc in hexanes)

Mp: 84-86 ºC



18 **19**

Alcohol 19.
To a solution of silyl ether **18** (120 mg, 0.251 mmol, 1.00 equiv.) in dry THF (4.0 mL) at room temperature were added 4Å molecular sieves followed by a solution of TBAF (1.0 M in THF, 0.45 mL, 0.45 mmol, 1.8 equiv.). The mixture was stirred for 4 h at 45 ºC after which additional TBAF (1.0 M, 0.10 mL, 0.10 mmol, 0.4 equiv.) was added, and the reaction was further stirred for 2 h.

The mixture was filtered over a plug of silica gel, eluting with 3:1 hexanes/EtOAc. Alcohol **19** was obtained as a colourless oil (85.0 mg, 0.233 mmol, 93% yield) which solidified upon standing and could be used for the next step without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.34 (d, *J* = 1.2 Hz 1H), 4.98 (s, 1H), 4.66 (q, *J* = 7.1 Hz, 2H), 3.98 (dd, *J* = 7.9, 6.2 Hz, 1H), 3.79 (dd, *J* = 7.9, 1.5 Hz, 1H), 3.58 (s, 3H), 3.40 (s, 3H), 2.88 (q, *J* = 7.3 Hz, 1H), 2.69 (d, *J* = 11.3 Hz, 1H), 2.50 (s, 1H), 2.41 (dd, *J* = 11.3, 6.1 Hz, 1H), 1.88 (s, 3H), 1.82 (d, *J* = 1.5 Hz, 3H), 1.28 (s, 3H), 1.13 (s, 3H), 1.10 (d, *J* = 7.5 Hz, 3H)

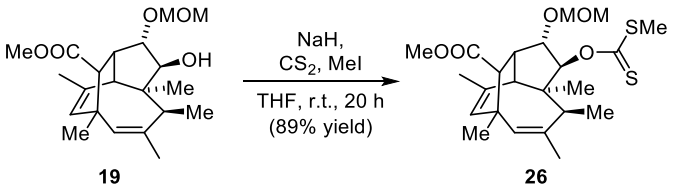
^{13}C NMR (100 MHz, $CDCl_3$) δ 174.8, 141.5, 137.9, 132.7, 124.9, 97.9, 95.5, 87.4, 56.6, 55.6, 54.5, 51.4, 51.1, 44.1, 40.6, 34.7, 29.7, 29.0, 25.1, 24.1, 15.7

IR (ATR): 3473 (br), 2933 (m), 1731 (m), 1459 (m), 1376 (w), 1174 (m), 1148 (m), 1107 (s), 1039 (s), 912 (m)

HRMS (+ESI): calc. for $C_{21}H_{33}O_5$ $[M+H]^+$ 365.2323, found 365.2340

$[\alpha]_D^{23}$ +95.3º (*c* 1.73, $CHCl_3$)

R_F = 0.20 (20% EtOAc in hexanes)



19 **26**

Methyl xanthate 26.
To alcohol **19** (130 mg, 0.357 mmol, 1.00 equiv.) dissolved in dry THF (6.0 mL) was added NaH (60% w/w in paraffin oil, 42.8 mg, 1.07 mmol, 3.00 equiv.) followed by CS_2, (64 µL, 1.1 mmol, 3.0 equiv.). After vigorously stirring for 50 minutes, methyl iodide (68 µL, 1.1 mmol, 3.0 equiv.) was added and the mixture was stirred for an additional 20 h.

The reaction was quenched by the addition of aqueous saturated NH_4Cl. The phases were separated and the aqueous layer was extracted three times with diethyl ether. The organic layers were combined, dried over Na_2SO_3, filtered and concentrated under reduced pressure. The crude material (168 mg) was purified by flash column chromatography on silica gel, (10% EtOAc/Hexanes). Methyl xanthate **26** was obtained as a dark yellow oil (145 mg, 0.319 mmol, 89% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.36 (d, *J* = 8.2 Hz, 1H), 5.39 (s, 1H), 5.12 (s, 1H), 4.56 (q, *J* = 6.9 Hz, 2H), 4.37 (dd, *J* = 8.1, 6.0 Hz, 1H), 3.60 (s, 3H), 3.26 (s, 3H), 2.96 (q, *J* = 7.4 Hz, 1H), 2.90 (d, *J* = 11.3 Hz, 1H), 2.66 (s, 1H), 2.62 (s, 3H), 2.51 (dd, *J* = 11.3, 5.8 Hz, 1H), 1.94 (s, 3H), 1.83 (s, 3H), 1.27 (s, 3H), 1.15 (s, 3H), 1.00 (d, *J* = 7.5 Hz, 3H)

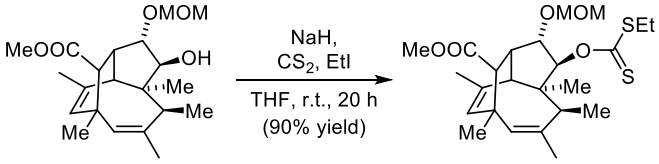
^{13}C NMR (100 MHz, $CDCl_3$) δ 217.2, 174.7, 139.8, 137.2, 133.7, 125.7, 96.4, 94.6, 88.4, 57.1, 55.3, 54.0, 51.4, 51.1, 44.4, 40.5, 34.8, 29.3, 29.0, 25.1, 24.1, 19.7, 15.6

IR (ATR): 2919 (m), 2849 (w), 1731 (m), 1456 (m), 1380 (w), 1213 (s), 1106 (m), 1061 (s), 1036 (m), 914 (w), 754 (m)

HRMS (+ESI): calc. for $C_{23}H_{34}O_5S_2Na$ $[M+Na]^+$ 477.1740, found 477.1762

$[\alpha]_D^{23}$ +63.1° (*c* 2.14, $CHCl_3$)

R_F = 0.59 (20% EtOAc in hexanes)



19 **27**

Ethyl xanthate 27.
The same procedure as for methyl xanthate **26** (see above) was followed changing the reagent ratio: **19**, (15.0 mg, 41.2 µmol, 1.00 equiv.), NaH, (60% w/w in paraffin oil, 6.6 mg, 0.16 mmol, 4.0 equiv.), CS_2, (10 µL, 0.16 mmol, 4.0 equiv.) and ethyl iodide, (20 µL, 0.25 mmol, 6.0 equiv.). The crude material (20 mg) was purified by flash column chromatography on silica gel (10% EtOAc/Hexanes) yielding xanthate **27** as a dark yellow oil (17.3 mg, 0.369 mmol, 90% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.36 (d, *J* = 8.2 Hz, 1H), 5.39 (s, 1H), 5.11 (s, 1H), 4.56 (q, *J* = 6.9 Hz, 2H), 4.36 (dd, *J* = 8.3, 5.9 Hz, 1H), 3.60 (s, 3H), 3.26 (s, 3H), 3.20 (q, *J* = 7.4 Hz, 2H), 2.96 (q, *J* = 7.7 Hz, 1H), 2.90 (d, *J* = 11.3 Hz, 1H), 2.66 (s, 1H), 2.51 (dd, *J* = 11.3, 5.8 Hz, 1H), 1.94 (s, 3H), 1.83 (s, 3H), 1.36 (t, *J* = 7.4 Hz, 3H), 1.26 (s, 3H), 1.15 (s, 3H), 1.00 (d, *J* = 7.5 Hz, 3H)

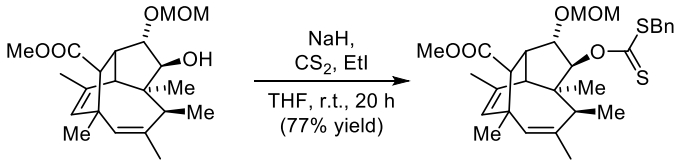
^{13}C NMR (100 MHz, $CDCl_3$) δ 216.2, 174.7, 139.9, 137.2, 133.7, 125.7, 96.4, 94.1, 88.4, 57.1, 55.3, 54.1, 51.4, 51.1, 44.4, 40.5, 34.8, 31.0, 29.3, 29.0, 25.1, 24.1, 15.5, 13.0

IR (ATR): 2923 (m), 2851 (w), 1732 (m), 1457 (m), 1379 (w), 1211 (s), 1172 (m), 1107 (m), 1065 (s), 1032 (s), 915 (m)

HRMS (+ESI): calc. for $C_{24}H_{36}NaO_5S_2$ $[M+Na]^+$ 491.1896, found 491.1909

$[\alpha]_D^{23}$ +53.0° (*c* 0.4, $CHCl_3$)

R_F = 0.59 (20% EtOAc in hexanes)



19 **20**

Benzyl xanthate 20.
The same procedure as for methyl xanthate **26** (see above) was followed changing the reagent ratio: **19** (40.0 mg, 0.110 mmol, 1.00 equiv.), NaH (60% w/w in paraffin oil,17.6 mg, 0.439 mmol, 4.00 equiv.), CS_2, (26 µL, 0.439 mmol, 4.00 equiv.) and freshly distilled BnBr, (65 µL, 0.549 mmol, 5.00 equiv.).

The crude product (120 mg) was purified by flash column chromatography on silica gel, (Et_2O/Hexanes, gradient, 0 to 10%) giving benzyl xanthate **20** as a yellow oil (45.0 mg, 84.8 µmol, 77 % yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.27 (m, 5H), 6.36 (d, *J* = 8.2 Hz, 1H), 5.39 (s, 1H), 5.10 (s, 1H), 4.56 (dd, *J* = 9.6, 6.9, 2H), 4.46 (s, 2H), 4.36 (dd, *J* = 8.3, 5.9 Hz, 1H), 3.60 (s, 3H), 3.25 (s, 3H), 2.96 (q, *J* = 7.6 Hz, 1H), 2.90 (d, *J* = 11.2 Hz, 1H), 2.66 (s, 1H), 2.51 (dd, *J* = 11.4, 5.8 Hz, 1H), 1.91 (s, 3H), 1.83 (s, 3H), 1.28 (s, 3H), 1.15 (s, 3H), 1.00 (d, *J* = 7.5 Hz, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 215.5, 174.7, 139.8, 137.2, 135.0, 133.7, 129.2, 128.6, 127.7, 125.7, 96.5, 94.6, 88.5, 57.1, 55.3, 54.0, 51.4, 51.11, 44.4, 41.6, 40.5, 34.7, 29.3, 29.0, 25.1, 24.1, 15.6

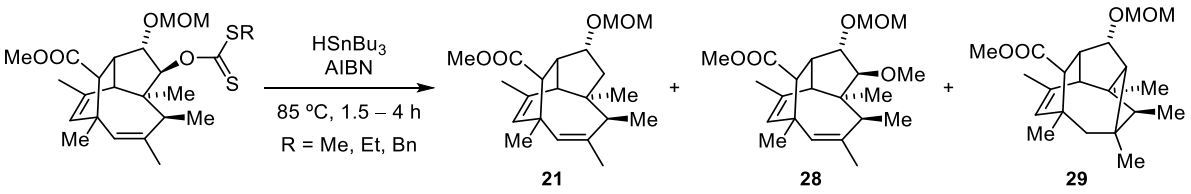
IR (ATR): 2924 (m), 2850 (w), 1730 (m), 1454 (m), 1380 (w), 1216 (s), 1107 (m), 1195 (m), 1058 (s), 1039 (s), 914 (w)

HRMS (+APCI): calc. for $C_{27}H_{33}O_3S_2$ $[M-OMOM]^+$ 469.1866, found 469.1882

$[\alpha]_D^{23}$ +53.4º (*c* 0.20, $CHCl_3$)

R_F = 0.46 (15% EtOAc in hexanes)

General procedure for Barton-McCombie Deoxygenation



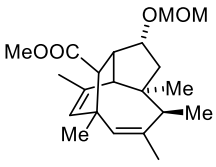
Entry	Xanthate		$HSnBu_3$ [eq.]	yield [%]		
1*	**26**	R = Me	4.8	21	6	46
2	**26**	R = Me	50	41	29	10
3	**27**	R = Et	50	49	19	2
4	**20**	R = Bn	40	76	12	6

* Reaction was run in PhMe (11.6 mL), with 580 mg of **27** and 97 mg of AIBN.

A vial was charged with the corresponding xanthate (45.0 µmol, 1.00 equiv.) and AIBN (1.9 mg, 9.7 µmol, 0.25 equiv.). The vial was evacuated and flushed with nitrogen three times and tributyltin hydride (0.59 ml, 2.2 mmol, 50 equiv., entries 2-3) or (0.47 ml, 2.8 mmol, 40 equiv., entry 4) was added. The mixture was stirred at 85 ºC for 1.5 to 4 h (monitored by ^{1}H NMR).

The reaction mixture was then cooled down to room temperature and submitted to flash column chromatography on silica gel (Et_2O/Hexanes, gradient, 0 to 12%).

Results for entry 4 are shown below.



21

Deoxygenated tricycle 21.
Tricycle **21** was obtained together with methyl ether **28** as a white solid, 14 mg. NMR shows a **21** to **28** molar ratio of 1:0.15 (12.0 mg, 34.4 µmol, 76% yield). Elution at 6% Et_2O in hexanes.

An additional run using benzyl xanthate **20** (92 mg) allowed for isolation of fractions with clean tricycle **21** after a second separation on spherical 20-40 µm particle size silica.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.31 (s, 1H), 5.01 (s, 1H), 4.61–4.56 (m, 2H), 4.05–3.96 (m, 1H), 3.58 (s, 3H), 3.29 (s, 2H), 2.82 (q, *J* = 7.0, 1H), 2.79 (d, *J* = 11.9, 1H), 2.59 (s, 1H), 2.57 (dd, *J* = 11.7, 4.9 Hz, 1H), 2.20 (dd, *J* = 13.7, 7.7 Hz, 1H), 1.83 (d, *J* = 1.3 Hz, 3H), 1.71 (s, 3H), 1.42 (dd, *J* = 13.7, 9 Hz, 1H), 1.41 (d, *J* = 13.5 Hz, 1H), 1.12 (s, 3H), 1.10 (s, 3H), 0.90 (d, *J* = 7.3 Hz, 3H)

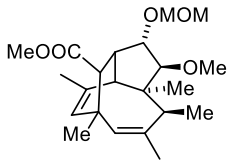
^{13}C NMR (100 MHz, $CDCl_3$) δ 174.9, 139.4, 138.3, 134.2, 124.3, 96.4, 88.2, 56.7, 56.4, 55.3, 55.0, 51.0, 50.0, 42.6, 40.8, 34.8, 30.7, 28.7, 25.4, 24.1, 14.7

IR (ATR): 2929 (s), 2851 (w), 1734 (s), 1461 (m), 1442 (m), 1378 (w), 1244 (w), 1195 (m), 1152 (s), 1102 (s), 1043 (s), 915 (w)

HRMS (+APCI): calc. for $C_{21}H_{33}O_4$ $[M+H]^+$ 349.2373, found 349.2372

$[\alpha]_D^{23}$ +26.0º (*c* 0.25, $CHCl_3$)

R_F = 0.28 (20% Et_2O in hexanes)



28

Methyl ether 28.
Methyl ether **28** was obtained together with tricycle **21** as a white solid, 14 mg. NMR shows a **21** to **28** molar ratio of 1:0.15 (2.0 mg, 5.3 µmol, 12% yield). Elution at 6% Et_2O in hexanes.

An additional run using benzyl xanthate **20** (92 mg) allowed for isolation of fractions with clean **28** after a second separation on spherical 20-40 µm particle size silica.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.34 (s, 1H), 5.00 (s, 1H), 4.67 (dd, *J* = 18.1, 6.8 Hz, 2H), 4.06–4.01 (m, 1H), 3.59 (s, 3H), 3.52 (d, *J* = 7.9 Hz, 1H), 3.48 (s, 3H), 3.29 (s, 3H), 2.85 (q, *J* = 7.4 Hz, 1H), 2.71 (d, *J* = 11.3 Hz, 1H), 2.66 (s, 1H), 2.36 (dd, *J* = 11.3, 5.6 Hz, 1H), 1.82 (s, 3H), 1.81 (s, 3H), 1.27 (s, 3H), 1.12 (s, 3H), 1.04 (d, *J* = 7.4 Hz, 3H)

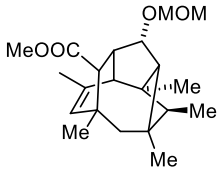
^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 140.8, 137.8, 132.8, 125.1, 96.7, 96.6, 91.5, 60.0, 55.7, 55.4, 54.6, 51.5, 51.0, 44.8, 40.5, 34.7, 29.9, 29.0, 24.9, 24.2, 15.6

IR (ATR): 2930 (s), 2851 (w), 2362 (w), 2337 (w), 1733 (s), 1460 (m), 1376 (w), 1198 (w), 1174 (m), 1124 (m), 1107 (s), 1142 (s), 977 (w), 917 (w)

HRMS (+APCI): calc. for $C_{22}H_{35}O_5$ $[M+H]^+$ 379.2479, found 379.2474

$[\alpha]_D^{23}$ +33.7º (*c* 0.33, $CHCl_3$)

R_F = 0.27 (20% Et_2O in hexanes)



29

Tetracycle 29.
Tetracycle **29** was obtained as a colourless oil (1.0 mg, 2.9 µmol, 6% yield). Elution at 5.5% Et_2O in hexanes.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.33 (s, 1H), 4.62 (q, *J* = 6.7 Hz, 2H), 3.74 (s, 1H), 3.59 (s, 3H), 3.34 (s, 3H), 2.86 (d, *J* = 9.3 Hz, 1H), 2.68 (d, *J* = 9.3 Hz, 1H), 2.21 (d, *J* = 8.9 Hz, 2H), 2.01 (q, *J* = 7.5 Hz, 1H), 1.60 (s, 3H), 1.20 (d, *J* = 14.7 Hz, 1H), 1.13 (s, 3H), 1.13 (d, *J* = 14.8 Hz, 1H), 1.01 (s, 3H), 0.95 (d, *J* = 7.6 Hz, 3H), 0.87 (s, 3H)

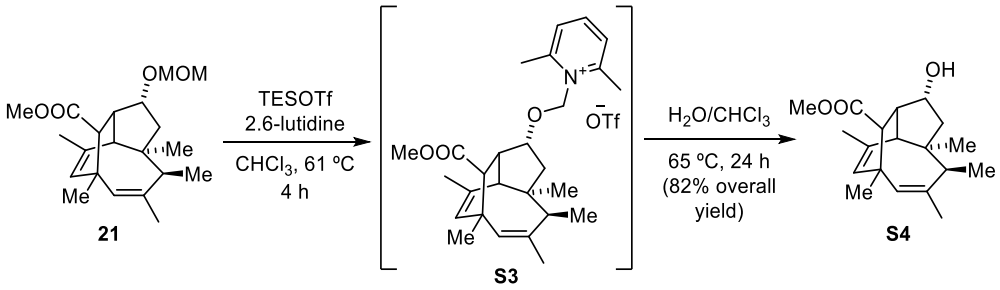
^{13}C NMR (100 MHz, $CDCl_3$) δ 206.9, 175.3, 138.0, 125.7, 94.6, 87.6, 58.5, 55.5, 53.3, 51.7, 51.1, 50.9, 46.9, 38.18, 37.5, 30.9, 30.4, 26.5, 24.2, 23.5, 13.9

IR (ATR): 2956 (s), 2924 (s), 1739 (s), 1457 (m), 1374 (m), 1206 (w), 1150 (s), 1097 (m), 1038 (s), 922 (w)

HRMS (+APCI): calc. for $C_{21}H_{33}O_4$ $[M+H]^+$ 349.2373, found 349.2373

$[\alpha]_D^{23}$ +37.1º (*c* 0.20, $CHCl_3$)

R_F = 0.36 (20% Et_2O in hexanes)



Tricyclic alcohol S4.
To a solution of acetal **21** (28.0 mg, 80.3 µmol, 1.00 equiv.) in dry chloroform (0.62 mL) were added 2,6-lutidine (56 µL, 0.48 mmol, 6.0 equiv.) and TESOTf (68 µL, 0.32 mmol, 4.0 equiv.). After stirring under reflux for 4 h, the solution was allowed to cool down and water (0.67 mL) was added. The mixture was heated to 65 ºC and stirred vigorously for 24 h.

The phases were separated and the aqueous layer was extracted three times with DCM. The organic layers were combined, dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude material was purified by flash column chromatography on silica gel (35% EtOAc/Hexanes) affording alcohol **S4** (20.0 mg, 65.8 µmol, 82% yield) as a white fluffy solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.32 (s, 1H), 5.01 (s, 1H), 4.27 (ddd, *J* = 8.2, 5.1 Hz, 1H), 3.59 (s, 3H), 2.84 (d, *J* = 11.4 Hz, 1H), 2.82 (q, *J* = 7.3 Hz, 1H), 2.56 (s, 1H), 2.47 (dd, *J* = 11.5, 4.9 Hz, 1H), 2.23 (dd, *J* = 13.6, 7.6 Hz, 1H), 1.83 (d, *J* = 1.5 Hz, 3H), 1.71 (s, 3H), 1.37 (ddd, *J* = 13.6, 8.8, 1.1 Hz, 1H), 1.14 (s, 3H), 1.12 (s, 3H), 0.92 (d, *J* = 7.4 Hz, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.7, 139.6, 138.3, 134.0, 124.3, 81.7, 57.3, 56.6, 55.2, 52.7, 51.1, 45.2, 40.8, 34.8, 30.8, 28.7, 25.5, 24.0, 14.7

IR (ATR): 3517 (m), 2923 (s), 2851 (w), 1709 (s), 1437 (m), 1373 w), 1355 (w), 1238 (w), 1201 (m), 1178 (m), 1021 (w)

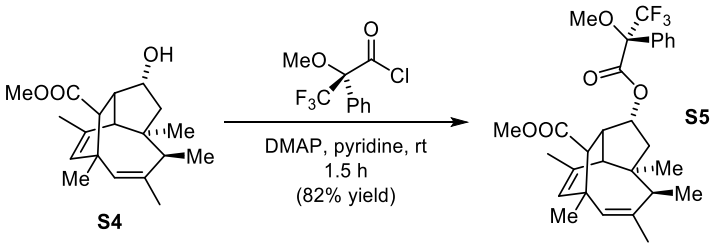
HRMS (+APCI): calc. for $C_{19}H_{27}O_2$ $[M-OH]^+$ 287.2006, found 287.2003

$[\alpha]_D^{23}$ +28.0º (*c* 1.00, $CHCl_3$)

Mp: 158-160 ºC

R_F = 0.20 (30% EtOAc in hexanes)

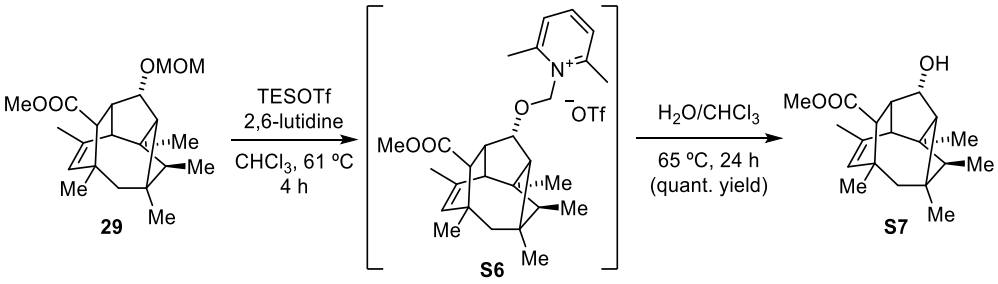
Procedure for Mosher's ester analysis



Mosher's ester S5.
To a solution of tricycle **S4**, (3.5 mg, 12 µmol, 1.0 equiv) and DMAP (4.9 mg, 40 µmol. 3.5 equiv.) in pyridine (0.40 mL) was added (*R*)-(−)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (Mosher's acyl chloride, 3.0 µL, 12 µmol, 1.0 equiv.). The reaction mixture was stirred for 1.5 h.

The solvent was evaporated, and the residue was filtered through a pad of silica eluting with 30% EtOAc/Hexanes. Ester **S5** was obtained as a colourless oil (4.9 mg, 9.4 µmol, 82% yield, *d.r.* 1:0.02).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.44 (m, 2H), 7.42–7.34 (m, 3H), 5.42 (td, *J* = 8.4, 4.9 Hz, 1H), 5.36 (s, 1H), 5.15 (s, 1H), 3.58 (s, 3H), 3.55 (d, *J* = 0.8 Hz, 3H), 2.89 (q, *J* = 7.3 Hz, 1H), 2.85 (s, 1H), 2.79 (d, *J* = 11.6 Hz, 1H), 2.53 (dd, *J* = 11.6, 4.8 Hz, 1H), 2.33 (dd, *J* = 13.8, 7.9 Hz, 1H), 1.82–1.77 (m, 6H), 1.56 (ddd, *J* = 13.8, 8.8, 1.0 Hz, 1H), 1.15 (d, *J* = 2.7 Hz, 6H), 0.94 (d, *J* = 7.4 Hz, 3H)



Tetracyclic alcohol S7.
The same procedure as for alcohol **S4** was followed (see above). **29** (16.2 mg, 46.2 µmol, 1.00 equiv.), TESOTf (40 µL, 0.19 mmol, 4.0 equiv.), 2,6-lutidine (32 µL, 0.28 mmol, 6.0 equiv.). Alcohol **S7** was obtained as a white solid (14.1 mg, 46.3 µmol, quantitative yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.34 (s, 1H), 3.93 (s, 1H), 3.59 (s, 3H), 2.77 (s, 2H), 2.24 (s, 1H), 2.12 (s, 1H), 2.02 (q, *J* = 7.6 Hz, 1H), 1.62 (s, 3H), 1.25 (br s, 1H), 1.20 (s, 3H), 1.17 (q, *J* = 14.7 Hz, 2H), 1.02 (s, 3H), 0.96 (d, *J* = 7.6 Hz, 3H), 0.88 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 175.2, 137.9, 125.8, 83.5, 61.5, 55.2, 54.0, 53.2, 51.6, 51.1, 47.0, 38.1, 37.7, 37.4, 30.4, 26.5, 24.9, 23.5, 13.8

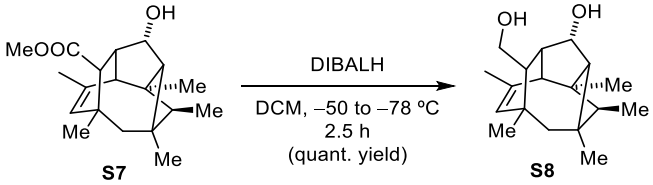
IR (ATR)**:** 3418 (w, br), 2959 (s), 2922 (s), 2873 (m), 2358 (w), 1724 (s), 1457 (m), 1434 (m), 1374 (m), 1206 (m), 1158 (m), 1025 (m)

HRMS (+APCI): calc. for $C_{19}H_{29}O_3$ $[M+H]^+$ 305.2111, found 305.2108

$[\alpha]_D^{23}$ +19.1° (*c* 0.42, $CHCl_3$)

Mp: 103-104 °C

R_F = 0.29 (30% EtOAc in hexanes)



Tetracyclic diol S8.
To alcohol **S7** (49.2 mg, 0.162 mmol, 1.00 equiv.) dissolved in DCM (2.7 mL) at −78 °C was added dropwise a solution of DIBALH (1.5 M in toluene, 0.43 mL, 0.65 mmol, 4.0 equiv.). The mixture was warmed to −50 °C and stirred at the same temperature for 2.5 h.

The reaction was quenched with saturated aqueous Rochelle's salt (1.5 mL), then warmed to room temperature and stirred for 30 min. The mixture was diluted with water/diethyl ether and extracted three times with diethyl ether. The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure to afford pure diol **S8** (44.8 mg, 0.162 mmol, quantitative yield) as a white fluffy solid. It was used for the next step without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.42 (s, 1H), 3.95 (s, 1H), 3.68 (dt, *J* = 9.8, 4.6 Hz, 1H), 3.47–3.38 (m, 1H), 2.74 (d, *J* = 9.3 Hz, 1H), 2.68 (d, *J* = 9.3 Hz, 1H), 2.13 (s, 1H), 1.93 (q, *J* = 7.5 Hz, 1H), 1.56 (s, 3H), 1.45 (br s, 1H), 1.33 (dd, *J* = 7.1, 3.9 Hz, 2H), 1.20 (s, 3H), 1.14 (d, *J* = 2.2 Hz, 2H), 1.01 (s, 3H), 0.97 (d, *J* = 7.6 Hz, 3H), 0.88 (s, 3H)

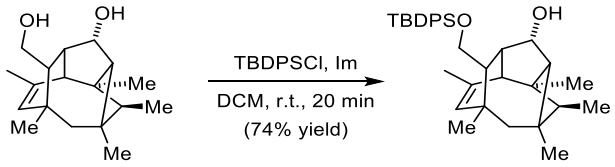
^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 128.6, 84.3, 65.0, 61.0, 53.1, 53.0, 52.7, 52.3, 47.6, 37.5, 37.4, 37.3, 29.6, 26.5, 24.9, 23.4, 13.9

IR (ATR)**:** 3263 (m, br), 2957 (m), 2922 (s), 2868 (m), 1724 (w), 1453 (m), 1371 (w), 1022 (s), 981 (w), 814 (w)

HRMS (+APCI): calc. for $C_{18}H_{29}O_2$ $[M+H]^+$ 277.2162, found 277.2167

$[\alpha]_D^{23}$ −14.1° (*c* 1.00, $CHCl_3$)

R_F = 0.10 (40% EtOAc in hexanes)



TBDPS-protected alcohol S9.
To a solution of diol **S8** (45.0 mg, 0.163 mmol, 1.00 equiv.) in DCM (3.3 mL) was added imidazole (22.7 mg, 0.334 mmol, 2.05 equiv.) followed by TBDPSCl (63 µL, 0.24 mmol, 1.5 equiv.). The resulting mixture was stirred at room temperature for 20 min after which an aqueous saturated $NaHCO_3$ solution (4.0 mL) was added. The mixture was vigorously stirred for 5 min, after which the aqueous phase was separated and extracted three times with DCM. The organic layers were combined, dried over $MgSO_4$ and concentrated under reduced pressure yielding a colourless oil, 113 mg.

Purification by flash column chromatography on silica gel (EtOAc/Hexanes, gradient, 0 to 20%) yielded 95 mg of a colourless oil containing alcohol **S9** (62.4 mg, 0.121 mmol, 74% yield). Despite our efforts, separation of product from TBDPSOH was not possible by either flash chromatography or HPLC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 6.9 Hz, 4H), 7.47–7.34 (m, 6H), 5.21 (s, 1H), 3.87 (s, 1H), 3.73 (dd, *J* = 10.0, 4.2 Hz, 1H), 3.29 (t, *J* = 9.8 Hz, 1H), 2.80 (d, *J* = 9.3 Hz, 1H), 2.47 (d, *J* = 9.3 Hz, 1H), 1.89 (q, *J* = 7.6 Hz, 1H), 1.43 (s, 3H), 1.37 (dd, *J* = 9.7, 4.3 Hz, 1H),1.16 (s, 3H), 1.10–1.00 (m, 12H), 0.93 (d, *J* = 7.6 Hz, 3H), 0.85 (s, 3H), 0.78 (s, 3H)

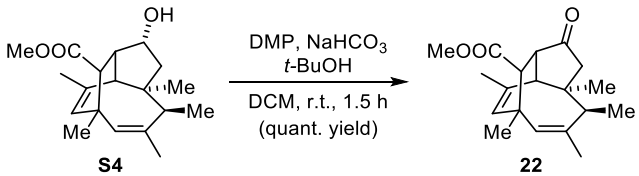
^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 135.7, 134.9, 134.2, 134.1, 129.5, 128.2, 127.6, 127.6, 84.5, 65.5, 61.0, 52.9, 52.7, 52.5, 52.2, 47.5, 37.4, 37.2, 29.5, 27.0, 26.6, 24.9, 23.3, 19.3, 13.9

IR (ATR)**:** 3392 (w, br), 2958 (m), 2928 (m), 2857 (m), 2361 (s), 2340 (m), 1472 (w), 1428 (m), 1111 (s), 1061 (m), 822 (m), 739 (m)

HRMS (+ESI): calc. for $C_{34}H_{47}O_2Si$ $[M+H]^+$ 515.3340, found 515.3360

$[\alpha]_D^{23}$ +6.9° (*c* 1.00, $CHCl_3$)

R_F = 0.29 (10% Et_2O in hexanes)



Tricyclic ketone 22.
Alcohol **S4** (38.0 mg, 0.125 mmol, 1.00 equiv.) was dissolved in DCM (2.6 mL) and $NaHCO_3$ (52.4 mg, 0.624 mmol, 5.00 equiv.) was added followed by 1 small drop of *t*-BuOH. Dess–Martin periodinane (132 mg, 0.312 mmol, 2.50 equiv.) was added and the reaction mixture was stirred at room temperature for 90 min.

A 1:1 solution of saturated aqueous $Na_2S_2O_3$/$NaHCO_3$ (3.5 mL each) was added and the result was vigorously stirred for 15 min, after which the mixture was diluted with water and DCM. The phases were separated, and the aqueous layer was extracted three times with DCM. The organic layers were combined, dried over Na_2SO_4 and concentrated under reduced pressure yielding a slightly yellow solid, 51 mg.

Purification by flash column chromatography on silica gel (Et_2O/Hexanes, gradient, 0 to 20%) allowed for isolation of ketone **22** as a white crystalline solid (37.8 mg, 0.125 mmol, quantitative yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.37 (s, 1H), 4.92 (s, 1H), 3.60 (s, 3H), 3.07 (s, 1H), 3.04 (q, *J* = 7.3 Hz, 1H), 2.97 (d, *J* = 11.8 Hz, 1H), 2.82 (d, *J* = 11.8 Hz, 1H), 2.36 (d, *J* = 17.2 Hz, 1H), 2.08 (dd, *J* = 17.2, 0.9 Hz, 1H), 1.88 (d, *J* = 1.5 Hz, 3H), 1.58 (s, 3H), 1.26 (s, 3H), 1.17 (s, 3H), 0.91 (d, *J* = 7.4 Hz, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 216.4, 173.1, 137.7, 137.5, 124.9, 55.8, 52.7, 51.3, 50.0, 49.3, 48.0, 41.6, 34.4, 28.9, 27.7, 24.7, 24.2, 14.6

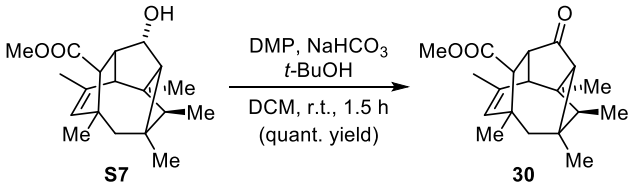
IR (ATR): 2923 (m), 2851 (w), 1733 (s), 1459 (m), 1234 (m), 1174 (m), 1019 (w)

HRMS (+APCI): calc. for $C_{19}H_{27}O_3$ $[M+H]^+$ 303.1955, found 303.1955

$[\alpha]_D^{23}$ +97.3º (*c* 0.53, $CHCl_3$)

Mp: 110-112 ºC

R_F = 0.40 (20% EtOAc in hexanes)



Tetracyclic ketone 30.
The same procedure as for ketone **22** (see above) was followed: **S7** (11.9 mg, 39.1 µmol, 1.00 equiv), $NaHCO_3$ (16.4 mg, 0.195 mmol, 5.00 equiv.), Dess–Martin periodinane (41.4 mg, 98.5 µmol, 2.50 equiv.). Ketone **30** was obtained as a white crystalline solid (11.8 mg, 39.0 µmol, quantitative yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.40 (s, 1H), 3.61 (s, 3H), 3.03 (dd, *J* = 10.1, 2.0 Hz, 1H), 2.80 (d, *J* = 10.1 Hz, 1H), 2.44 (s, 1H), 2.41 (s, 1H), 2.39 (q, *J* = 7.5 Hz, 1H), 1.65 (s, 3H), 1.39 (d, *J* = 15.3 Hz, 1H), 1.27 (d, *J* = 16.0 Hz, 1H), 1.12 (s, 6H), 1.02 (d, *J* = 7.5 Hz, 3H), 0.96 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 137.6, 125.7, 62.2, 53.7, 53.1, 51.6, 51.5, 50.2, 40.6, 39.9, 38.7, 37.7, 30.2, 26.0, 23.9, 23.3, 14.0

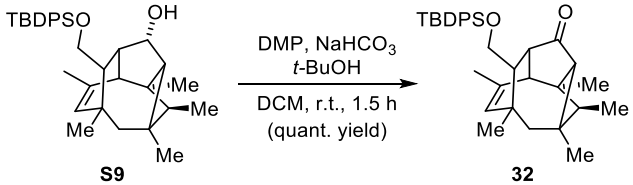
IR (ATR): 2960 (m), 2923 (m), 2851 (m), 2357 (W), 1743 (m), 1454 (w), 1376 (w), 1106 (s), 814 (m)

HRMS (+APCI): calc. for $C_{19}H_{27}O_3$ $[M+H]^+$ 303.1955, found 303.1947

$[\alpha]_D^{23}$ +76.7º (*c* 0.3, $CHCl_3$)

R_F = (20% Et_2O in hexanes)

Mp: 147-150 ºC



Tetracyclic ketone 32.

The same procedure as for ketone **22** (see above) was followed. **S9** (81.1 mg, 0.158 mmol, 1.00 equiv.), $NaHCO_3$ (66.2 mg, 0.788 mmol, 5.00 equiv.), Dess–Martin periodinane (167 mg, 0.393 mmol, 2.50 equiv.). Purification by flash column chromatography on silica gel (Et_2O/Hexanes, gradient, 0 to 30%) yielded ketone **32** as a colourless oil (81.0 mg, 0.158 mmol, quantitative yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (td, *J* = 7.5, 1.8 Hz, 4H), 7.44–7.35 (m, 6H), 5.29 (s, 1H), 3.74 (dd, *J* = 9.9, 4.7 Hz, 1H), 3.35 (t, *J* = 9.8 Hz, 1H), 3.16 (dd, *J* = 10.2, 2.1 Hz, 1H), 2.45 (d, *J* = 10.2 Hz, 1H), 2.40 (br s, 1H), 2.26 (q, *J* = 7.5 Hz, 1H), 1.68 (dd, *J* = 9.8, 4.7 Hz, 1H), 1.48 (d, *J* = 1.5 Hz, 3H), 1.25 (d, *J* = 14.6 Hz, 1H), 1.19 (d, J = 14.3 Hz, 1H), 1.07 (s, 12H), 0.99 (d, *J* = 7.6 Hz, 3H), 0.94 (s, 3H), 0.82 (s, 3H)

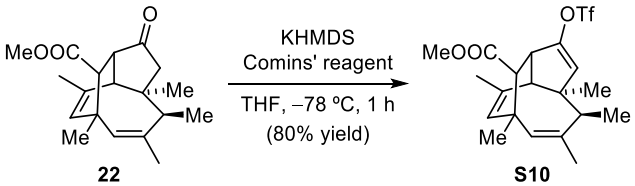
^{13}C NMR (100 MHz, $CDCl_3$) δ 175.2, 136.1, 135.8, 135.6, 134.0, 133.8, 129.5, 129.5, 128.1, 127.6, 127.6, 64.0, 62.1, 52.3, 52.2, 50.8, 49.8, 40.4, 39.2, 37.7, 37.7, 29.1, 27.0, 26.1, 23.9, 23.1, 19.2, 14.1

IR (ATR): 2957 (m), 2928 (s), 2856 (m), 2360 (m), 2340 (w), 1724 (s), 1455 (m), 1428 (w), 1112 (s), 1087 (s), 823 (w)

HRMS (+APCI): calc. for $C_{34}H_{45}O_2Si$ $[M+H]^+$ 513.3183, found 513.3179

$[\alpha]_D^{23}$ +47.6° (*c* 0.6, $CHCl_3$)

R_F = 0.36 (20% Et_2O in hexanes)



22 S10

Enol triflate S10.
A flame-dried vial charged with ketone **22** (15.0 mg, 49.6 µmol, 1.00 equiv.) and dry THF (1.4 mL) was cooled to −78 °C. To the stirred mixture was added a solution of KHMDS (1.2 M in toluene, 46 µL, 55 µmol, 1.1 equiv.) in a dropwise manner. The reaction was stirred at the same temperature for 35 min after which a solution of Comins' reagent (25.3 mg, 64.5 µmol, 1.3 equiv.) in THF (0.40 mL) was added dropwise.

After stirring for 60 min at −78 °C, diethyl ether (0.7 mL) was added to the reaction mixture followed by an aqueous saturated solution of NH_4Cl (1.2 mL). Upon warming to room temperature, the mixture was extracted three times with diethyl ether and the combined extracts were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure yielding a yellow oil, 48 mg.

Purification by flash column chromatography on silica gel, (EtOAc/Hexanes, 0%, then 4%) afforded enol triflate **S10** as a colourless oil (12.0 mg, 39.7 µmol, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.38 (s, 2H), 5.06 (s, 1H), 3.61 (s, 3H), 3.19 (d, *J* = 9.8 Hz, 1H), 2.97 (q, *J* = 7.3 Hz, 1H), 2.81 (d, *J* = 9.8 Hz, 1H), 2.63 (s, 1H), 1.83 (s, 3H), 1.47 (s, 3H), 1.31 (s, 3H), 1.12 (s, 3H), 0.94 (d, *J* = 7.5 Hz, 3H)

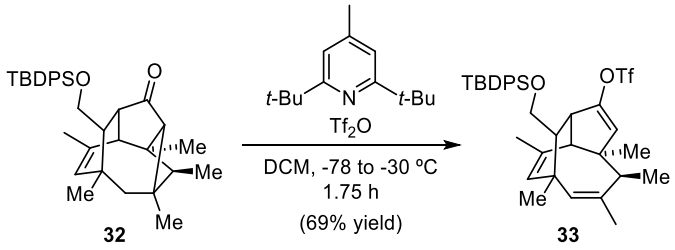
^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 149.5, 138.7, 137.1, 132.1, 125.5, 120.0, 118.4 (q, *J* = 320.2 Hz), 57.3, 52.2, 51.5, 51.4, 46.4, 40.4, 37.3, 29.0, 27.5, 24.9, 24.1, 15.0

IR (ATR): 2925 (m), 2361 (m), 2340 (m), 1736 (m), 1423 (m), 1214 (s), 1142 (m), 827 (w)

HRMS (+APCI): calc. for $C_{20}H_{26}F_3O_5S$ $[M+H]^+$ 435.1448, found 435.1453

$[\alpha]_D^{23}$ +17.1° (*c* 0.5, $CHCl_3$)

R_F = 0.59 (10% Et_2O in hexanes)



Enol triflate 33.
To ketone **32** (18.5 mg, 36.1 µmol, 1.00 equiv.) and 2.6-di-tertbutyl-4-methylpyridine (14.8 mg, 72.2 µmol, 2.0 equiv.) dissolved in DCM (0.95 mL) at −78 ºC was added Tf_2O (11.5 µL, 68.5 µmol, 1.90 equiv.) and the mixture was stirred at −78º C for 45 min, then warmed to −30 ºC and stirred for 1 h.

A saturated aqueous solution of $NaHCO_3$ was added and the cold solution was warmed to room temperature. The phases were separated, and the aqueous phase was extracted twice with diethyl ether. The organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. Crude product was a yellow oil, 39 mg.

Purification by flash column chromatography on silica gel (EtOAc/Hexanes, 0%, then 0.5%) allowed for isolation of enol triflate **33** as a colourless oil, (16.0 mg, 24.8 µmol, 69% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (ddd, *J* = 9.4, 7.8, 1.7 Hz, 4H), 7.40 (dd, *J* = 11.0, 7.0 Hz, 6H), 5.33 (d, *J* = 1.9 Hz, 1H), 5.27 (s, 1H), 4.99 (s, 1H), 3.66 (dd, *J* = 9.9, 4.6 Hz, 1H), 3.34 (d, *J* = 10.1 Hz, 1H), 3.19 (t, *J* = 9.9 Hz, 1H), 2.89 (q, *J* = 7.6 Hz, 1H), 2.55 (d, *J* = 10.1 Hz, 1H), 1.90 (dd, *J* = 10.1, 4.6 Hz, 1H), 1.67 (d, *J* = 1.7 Hz, 3H), 1.45 (s, 3H), 1.28 (s, 3H), 1.04 (s, 9H), 0.92 (d, *J* = 7.7 Hz, 3H), 0.91 (s, 3H)

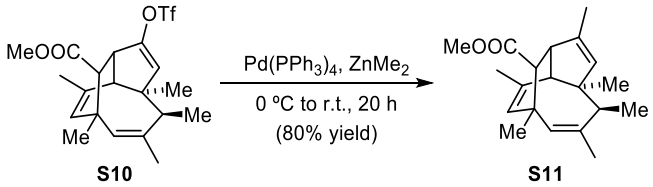
^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 136.8, 135.9, 135.6, 135.6, 133.9, 133.5, 129.6, 129.5, 127.9, 127.6, 116.6, 62.9, 56.6, 51.6, 49.0, 44.4, 39.6, 37.4, 34.7, 31.6, 26.8, 22.7, 19.1, 15.0, 14.1, 11.4

IR (ATR): 2956 (m), 2930 (m), 2856 (m), 2359 (w), 1565 (w), 1640 (s), 1423 (m), 1249 (w), 1432 (m), 1212 (s), 1143 (m), 1112 (m), 835 (m)

HRMS (+ESI): calc. for $C_{35}H_{44}F_3O_4SSi$ $[M+H]^+$ 645.2676, found 645.2670

$[\alpha]_D^{23}$ +8.6º (*c* 0.47, $CHCl_3$)

R_F = 0.70 (5% Et_2O in hexanes)



Triene ester S11.
To a solution of triflate **S10** (4.0 mg, 8.3 µmol, 1.0 equiv.) in THF (0.35 mL) at 0 ºC was added $Pd(PPh_3)_4$ (1.9 mg, 1.7 µmol, 0.20 equiv.) and the mixture was stirred for 30 min at the same temperature. Then, a solution of dimethylzinc (1.2 M in toluene, 17.3 µL, 20.7 µmol, 2.50 equiv.) was added at 0 ºC, and the reaction was stirred at room temperature for 20 h.

The reaction mixture was quenched with water (0.8 mL) and extracted four times with diethyl ether. The combined extracts were dried over $MgSO_4$ yielding a brown residue, 5 mg, which was purified by flash column chromatography on silica gel (Et_2O/Hexanes, 0%, then 0.5%, then 1% then 2%) affording triene **S11** as a slightly yellow solid (2.0 mg, 6.7 µmol, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.35 (s, 1H), 5.04 (s, 1H), 4.91 (s, 1H), 3.59 (s, 3H), 2.86 (q, *J* = 7.4 Hz, 1H), 2.80 (d, *J* = 9.6 Hz, 1H), 2.69 (d, *J* = 9.6 Hz, 1H), 2.44 (s, 1H), 1.82 (d, *J* = 1.5 Hz, 3H), 1.70 (s, 3H), 1.42 (s, 3H), 1.22 (s, 3H), 1.08 (s, 3H), 0.91 (d, *J* = 7.5 Hz, 3H)

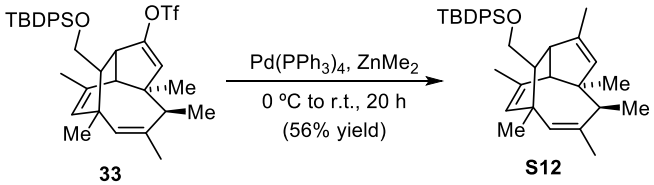
^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 141.0, 139.4, 139.0, 131.6, 129.0, 124.6, 60.8, 55.7, 53.2, 52.1, 51.0, 40.4, 37.3, 29.7, 29.1, 27.8, 24.9, 24.2, 15.3, 14.6

IR (ATR)**:** 2961 (m), 2926 (s), 2854 (m), 2361 (s), 2340 (m), 1738 (s), 1434 (m), 1375 (w), 1170 (m), 1147 (s), 1015 (w), 841 (m)

HRMS (+APCI): calc. for $C_{20}H_{29}O_2$ $[M+H]^+$ 301.2162, found 301.2168

$[\alpha]_D^{23}$ +40.4° (*c* 0.2, $CHCl_3$)

R_F = 0.53 (10% Et_2O in hexanes)



Triene TBDPS-alcohol S12.
Tricycle **S12** was synthesized following the same procedure as for triene **S11** (see above). **33** (15.0 mg, 20.9 µmol, 1.00 equiv.), $Pd(PPh_3)_4$ (4.8 mg, 4.2 µmol, 0.20 equiv.), dimethylzinc (1.2 M in toluene, 47 µL, 57 µmol, 2.5 equiv). Purification by flash column chromatography on silica gel (Et_2O/Hexanes, 0%, then 1%) afforded tricycle **S12** as a colourless oil, (6.0 mg, 12 µmol, 56% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70–7.60 (m, 4H), 7.44–7.34 (m, 6H), 5.20 (s, 1H), 4.99 (s, 1H), 4.84 (s, 1H), 3.69 (dd, *J* = 9.7, 4.5 Hz, 1H), 3.21 (t, *J* = 9.8 Hz, 1H), 3.01 (d, *J* = 9.8 Hz, 1H), 2.77 (q, *J* = 7.6 Hz, 1H), 2.49 (d, *J* = 9.9 Hz, 1H), 1.74 (s, 3H), 1.71 (dd, *J* = 10.2, 4.4 Hz, 1H), 1.66 (s, 3H), 1.40 (s, 3H), 1.20 (s, 3H), 1.05 (s, 9H), 0.92–0.87 (m, 6H)

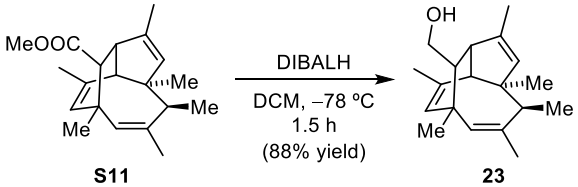
^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 138.1, 137.4, 135.6, 134.1, 133.2, 129.5, 127.6, 127.1, 126.8, 64.1, 59.8, 55.3, 50.3, 49.5, 39.8, 37.4, 28.4, 27.6, 26.9, 24.8, 24.1, 19.2, 15.3, 14.8

IR (ATR): 2958 (m), 2927 (m), 2855 (m), 1428 (w), 1105 (s), 1055 (m), 821 (m), 777 (s), 757 (m)

$[\alpha]_D^{23}$ +12.0° (*c* 0.25, $CHCl_3$)

HRMS (+ESI): calc. for $C_{35}H_{46}OSi$ $[M+H]^+$ 511.3391, found 511.3395

R_F = 0.26 (1% Et_2O in hexanes)



Triene alcohol 23.
Ester **S11** (5.0 mg, 16.6 µmol, 1.00 equiv.) was dissolved in DCM (0.80 mL) and cooled to −78 °C. A solution of DIBALH (1.2M in toluene, 55 µL, 66 µmol 4.0 equiv.) was added dropwise and the resulting mixture was stirred for 1.5 h.

The reaction was quenched with a saturated aqueous solution of Rochelle's salt (0.5 mL), then warmed to room temperature and stirred for 30 min. The mixture was diluted with water/DCM and extracted three times with DCM. The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (5% EtOAc/Hexanes) afforded alcohol **23** (4.0 mg, 15 µmol, 88% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.45 (s, 1H), 5.00 (s, 1H), 4.87 (s, 1H), 3.62–349 (m, 2H), 2.84–274 (m, 1H), 2.64 (d, *J* = 9.7 Hz, 1H), 1.75 (s, 3H), 1.70 (s, 3H), 1.44 (br s, 1H), 1.40 (s, 3H), 1.25 (br s, 1H), 1.21 (s, 3H), 1.12 (s, 3H), 0.90 (d, *J* = 7.5 Hz, 3H)

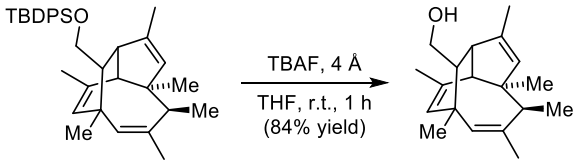
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 140.1, 137.6, 132.8, 127.7, 127.5, 65.4, 60.0, 55.7, 51.4, 49.8, 39.7, 37.2, 28.5, 27.7, 24.9, 24.1, 15.3, 14.6

IR (ATR)**:** 3286 (m, br), 2958 (s), 2919 (s), 2850 (m), 1728 (w, br), 1657 (w), 1455 (m), 1441 (m), 1033 (s), 1005 (s), 840 (s)

HRMS (+APCI): calc. for $C_{19}H_{29}O$ $[M+H]^+$ 273.2213, found 273.2219

$[\alpha]_D^{23}$ +8.5º (*c* 0.30, $CHCl_3$)

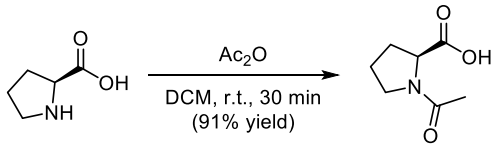
R_F = 0.35 (10% Et_2O in hexanes)



S12 **23**

Triene alcohol 23.
To a solution of silyl ether **S12** (10.0 mg, 19.6 µmol, 1.00 equiv.) in dry THF (0.76 mL) were added 4 Å molecular sieves followed by a solution of TBAF (1 M in THF, 35 µL, 35 µmol 1.8 equiv.). The mixture was stirred at room temperature for 3 h, after which additional TBAF (1 M, 10 µL, 10 µmol 0.50 equiv.) was added, and the reaction was further stirred for 1 h.

The mixture was filtered through a pad of silica, eluting with 25% EtOAc in hexanes. A colourless oil, 9 mg, was obtained and submitted to flash column chromatography on silica gel (EtOAc/Hexanes, 2%, then 3% then 3.75%) affording alcohol **23** as a colourless gum (4.5 mg, 16.5 µmol, 85% yield).



S13

L-Proline was acetylated following the procedure by Budiša et al.[1]

N-acetyl-L-proline (13).
L-Proline (500 mg, 4.34 mmol, 1.00 equiv.) was stirred in DCM (9.0 mL) and acetic anhydride (0.41 mL, 4.3 mmol, 1.0 equiv.) until a clear solution was obtained (30 min). DCM was removed under reduced pressure and the residue was dissolved in water (4.5 mL) and freeze-dried. The resulting solid contained approx. 1/10 of unreacted proline, therefore it was dissolved in water (5.6 mL) and filtered through a short ion-exchange column (Dowex® 50WX8, 50-100 mesh). Acidic fractions were collected and freeze-dried to give N-acetyl-L-proline (**S13**) as a white solid (620 mg, 3.95 mmol, 91% yield).

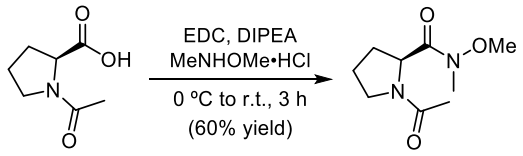
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.60 (dd, *J* = 8.0, 2.5 Hz, 1H), 3.59 (ddd, *J* = 10.6, 7.4, 3.4 Hz, 1H), 3.52–3.43 (m, 1H), 2.56–2.48 (m, 1H), 2.17 (s, 3H), 2.13–1.90 (m, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.4, 171.2, 60.2, 48.8, 27.1, 24.8, 22.1

HRMS (+ESI): calc. for $C_7H_{12}NO_3$ $[M+H]^+$ 158.0812, found 158.0815

$[\alpha]_D^{27}$ –177.0º (*c* 0.51, $CHCl_3$)

1. N. Budisa et al. *New J. Chem.* **2016**, *40*, 5209-5220



S13 **24**

Weinreb amide 24 was synthesized following the procedure by Stallforth et al.[2]

Weinreb amide 24.
N-acetyl proline (**S13**) (1.11 g, 7.09 mmol, 1.00 equiv.) was dissolved in DCM (20.6 mL) and cooled down to 0 ºC. To the solution was added EDC (1.60 g, 8.36 mmol, 1.18 equiv.) followed by DIPEA (2.40 mL, 13.9 mmol, 1.96 equiv.). The mixture was stirred for 15 min at 0 ºC and then N,O-dimethylhydroxylamine hydrochloride (691 mg, 7.09 mmol, 1.00 equiv.) was added. The resulting mixture was further stirred for 1 h at 0 ºC and another 2 h at room temperature.

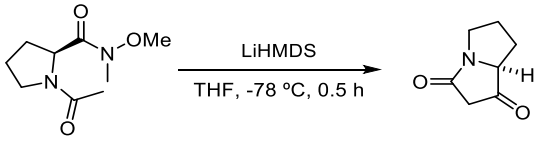
Water was added, the aqueous phase was extracted with DCM and the combined organic layers were dried over sodium Na_2SO_3. The solvent was evaporated, and the crude product purified by flash column chromatography on silica gel (5% MeOH/DCM) affording amide **24** as a slightly yellow oil (857 mg, 4.28 mmol, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.96–4.86 (m, 1H), 3.83 (s, 3H), 3.70 (ddd, *J* = 9.9, 7.4, 4.9 Hz, 1H), 3.52 (dt, *J* = 9.7, 7.0 Hz, 1H), 3.20 (s, 3H), 2.21–2.11 (m, 2H), 2.09 (s, 3H), 2.02–1.86 (m, 2H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 169.3, 61.2, 58.3, 56.1, 48.0, 29.1, 24.7, 22.3

HRMS (+ESI): calc. for $C_9H_{17}N_2O_3$ $[M+H]^+$ 201.1234, found 201.1237

$[\alpha]_D^{27}$ –22.0º (*c* 0.43, $CHCl_3$)



24 **S14**

S14 was synthesized following the procedure by Stallforth et al.[2]

Pyrrolizidine dione S14.
A solution of LiHMDS (1 M in THF, 3.60 mmol, 3.60 mL, 2.00 equiv.) diluted in dry THF (17.7 mL) at –78 ºC was added over 0.5 h to a solution of **S14** (360 mg, 1.80 mmol) in THF (21 mL).

After 2 h the reaction was allowed to warm to –30 ºC and acidified with 1M HCl. The aqueous phase was extracted with DCM, dried over Na_2SO_4 and concentrated under reduced pressure. A slightly yellow gum 230 mg containing **S14** was obtained.

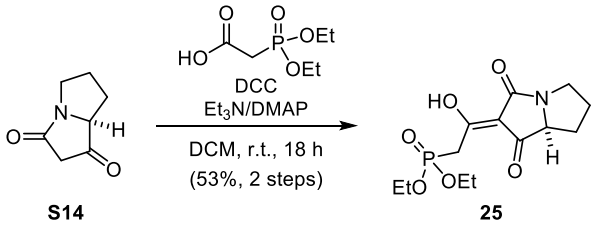
Due to thermal instability it was directly used for the next step.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.31–4.23 (m, 1H), 3.88 (dt, *J* = 11.6, 7.9 Hz, 1H), 3.45 (dd, *J* = 21.6, 2.0, Hz, 1H), 3.31–3.22 (m, 1H), 3.10 (dd, *J* = 21.6, 1.5 Hz, 1H), 2.20–2.05 (m, 3H), 1.72–1.62 (m, 1H)

IR (ATR): 2890 (w), 2579 (br), 1765 (m), 1688 (s), 1586 (s), 1369 (s), 1308 (s), 1258 (m), 1222 (m), 1074 (w), 809 (m), 750 (s)

$[\alpha]_D^{24}$ –61.3º (*c* 0.1, $CHCl_3$)

2. Klapper, M., Götze, S., Barnett, R., Willing, K., P. Stallforth, P., *Angew. Chem. Int.* **2016**, *55*, 8944-8947



S14 **25**

Synthesis of phosphonate ester 25 was accomplished by a modification of the procedure by Yoshii et al.[3]

Phosphonate ester 25.
To a solution of pyrrolizidinedione **S14** (230 mg, 1.65 mmol, 1.00 equiv.), DMAP (263 mg, 2.15 mmol, 1.30 equiv.) and DCC (375 mg, 1.82 equiv.) in DCM (11.3 mL) at room temperature was added dropwise diethyl phosphonacetic acid (292 µL, 1.82 mmol, 1.10 equiv). The reaction mixture was stirred at room temperature for 18 h.

The suspension was filtered, and the solvents evaporated to yield a brown gum which was purified by flash column chromatography on silica gel (MeOH/DCM, gradient, 0 to 6%). The obtained fractions were washed with a saturated aqueous solution of NH_4Cl followed by a 1M aqueous solution of HCl. Phosphonate ester **25** was obtained as an orange gum (300 mg, 0.946 mmol, 53% yield from **24**), which turned solid upon standing for 2 days.

^{1}H NMR spectrum showed broaden peaks, most likely caused by an increased isomer exchange rate in the presence of residual water. By using chloroform stored over 4Å mol. sieves, both isomers could be distinguished.

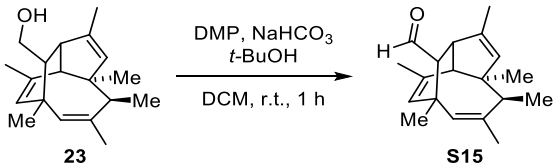
^{1}H NMR (400 MHz, $CDCl_3$, * denotes minor isomer) δ 4.17 (app quintet, *J* = 7.2 Hz, 4H+4H*), 3.99 (dd, *J* = 10.4 Hz, 6.7 1H), 3.89 (dd, *J* = 23.0 Hz, 13.6, 1H*), 3.78–3.67 (m, 1H+1H*), 3.61 (d, *J* = 23.4 Hz, 1H*), 3.57 (d, *J* = 23.8 Hz, 1H), 3.51 (d, *J* = 23.4, 1H), 3.48 (d, *J* = 23.1, 1H*), 3.29 (ddd, *J* = 11.9, 9.0, 3.8 Hz, 1H), 3.21 (ddd, *J* = 8.4, 4.4, 3.7 Hz, 1H*), 2.25–2.02 (m, 3H+3H*), 1.60–1.47 (m, 1H+1H*), 1.32 (t, *J* = 7.1 Hz, 6H+6H*)

^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 177.7 (d, *J* = 9.4 Hz), 176.0, 104.1 (d, *J* = 6.6 Hz), 69.0, 62.8 (d, *J* = 6.2 Hz), 62.8 (d, *J* = 6.1 Hz), 42.8, 31.6 (d, *J* = 130.3 Hz), 26.6 (d, *J* = 20.7 Hz), 16.2 (d, *J* = 6.4 Hz)

IR (ATR)**:** 3399 (w, br), 2977 (w), 2926 (w), 1672 (m), 1609 (s), 1544 (m), 1441 (s), 1231 (s), 1033 (s), 968 (s), 753 (m)

HRMS (+APCI): calc. for $C_{13}H_{21}NO_6P$ $[M+H]^+$ 318.1101, found 318.1099

$[\alpha]_D^{23}$ –19.5º (*c* 0.53, $CHCl_3$)



23 **S15**

Tricyclic aldehyde S15.
To alcohol **23** (4.0 mg, 15 µmol, 1.0 equiv.) dissolved in DCM (1.6 mL) were added $NaHCO_3$ (6.2 mg, 73 µmol, 5.0 equiv.), 1 small drop of *t*-BuOH and Dess–Martin periodinane (15.6 mg, 37.0 µmol, 2.50 equiv.). The mixture was stirred for 60 min at room temperature.

A 1:1 mixture of saturated aqueous $Na_2S_2O_3$/$NaHCO_3$ (0.5 mL each) was added. The resulting mixture was stirred for 20 min at room temperature, the layers were separated and the aq. phase was extracted three times with DCM. 3.2 mg of a colourless oil containing aldehyde **S15** were obtained. Given its instability it was immediately used for the next step.

3. E. Yoshii et al. *Chem. Pharm. Bull*. **1987**, *35*, 4368-4371

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.49 (d, *J* = 4.5 Hz, 1H), 5.49 (s, 1H), 5.07 (s, 1H), 4.88 (s, 1H), 2.89–2.81 (m, 2H), 2.69 (d, *J* = 9.6 Hz, 1H), 2.22–2.17 (m, 1H), 1.80 (d, *J* = 1.5 Hz, 3H), 1.68 (s, 3H), 1.44 (d, *J* = 0.7 Hz, 3H), 1.23 (s, 3H), 1.18 (s, 3H), 0.92 (d, *J* = 7.5 Hz, 3H)

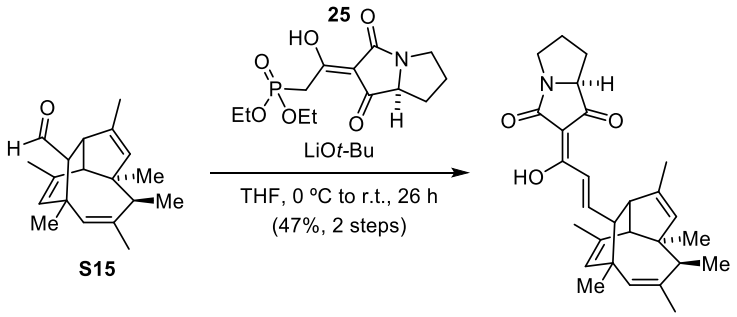
^{13}C NMR (100 MHz, $CDCl_3$) δ 205.4, 140.2, 140.1, 139.7, 131.0, 129.1, 126.4, 61.0, 60.8, 55.5, 49.2, 39.6, 37.1, 28.4, 27.7, 24.8, 24.2, 15.3, 14.4

IR (ATR): 2957 (m), 2922 (s), 2851 (m), 2366 (w), 1719 (m), 1457 (w), 1019 (w)

HRMS (+APCI): calc. for $C_{19}H_{27}O$ $[M+H]^+$ 271.2056, found 271.2058

$[\alpha]_D^{23}$ +10.6° (*c* 0.26, $CHCl_3$)

R_F = 0.68 (10% Et_2O in hexanes)



(–)-PF-1018.
To phosphonate **25** (9.4 mg, 30 µmol, 2.5 equiv.) dissolved in THF (0.50 mL) at 0 °C was added LiO*t*-Bu (4.7 mg, 59 µmol, 5.0 equiv.). The reaction was stirred at 0 °C for 30 min after which a solution of aldehyde **S15** (3.2 mg, 12 µmol, 1.0 equiv.) in THF (0.16 mL) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 26 h.

To the resulting suspension was added an aqueous saturated solution of NH_4Cl followed by DCM. The phases were separated, and the aqueous layer was extracted five times with DCM. The organic layers were combined, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The resulting yellow gum, 5.2 mg, was submitted to flash column chromatography on spherical 20-40 µm particle size, 60Å pore size silica (MeOH/DCM, 0.1%, then 0.2% then 0.5%). **(–)-PF1018** was obtained as a slightly yellow solid, (2.4 mg, 5.5 µmol, 47% yield from alcohol **23**). ^{1}H NMR shows two isomers in ratio 3.45:1.

^{1}H NMR (400 MHz, $CDCl_3$, * denotes minor isomer) δ 13.72 (br, 1H+1H*) 7.12 (d, *J* = 15.7 Hz, 1H*), 7.04 (dd, *J* = 15.6, 10.1 Hz,1H*), 7.01–6.98 (m, 2H), 5.37 (s, 1H+1H*) 5.03 (s, 1H+1H*), 4.91 (s, 1H+1H*), 4.05 (dd, *J* = 9.9, 6.9 Hz, 1H*), 3.96 (dd, *J* = 10.0, 6.9 Hz, 1H), 3.78 (ddd, *J* = 11.6, 7.9, 7.9, 1H*) 3.76 (ddd, *J* = 11.4, 7.9, 7.9 1H), 3.27 (ddd, *J* = 11.2, 9.2, 3.8 Hz, 1H), 3.24-3.18 (m, 1H*), 2.83 (q, *J* = 7.3 Hz, 1H+1H*), 2.63 (d, *J* = 9.7 Hz, 1H+1H*), 2.51 (d, *J* = 9.6 Hz, 1H+1H*), 2.43 (d, *J* = 10.0 Hz, 1H*), 2.43–2.38 (m, 1H) 2.00–2.23 (m, 3H + 3H*) 1.82 (br, s, 3H+3H*), 1.73 (br, s, 3H+3H*), 1.48-1.67 (m, 1H + 1H*), 1.43 (br, s, 3H+3H*) 1.22 (br, s, 3H+3H*), 0.95 (br, s, 3H+3H*), 0.92 (d, *J* = 7.5 Hz, 3H+3H*)

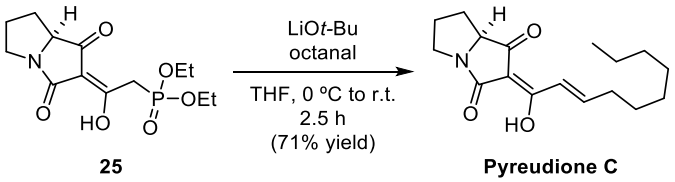
^{13}C NMR (100 MHz, $CDCl_3$, * denotes minor isomer) δ 203.8, 195.0, 177.6, 175.7*, 174.3, 155.7*, 154.7, 140.7, 140.7*, 139.5*, 139.4, 139.0, 139.0*, 132.1, 132.0*, 128.6, 126.4, 120.1, 119.6*, 103.7*, 101.3, 68.7, 66.4*, 60.8*, 60.8, 55.3, 55.3*, 54.3, 54.2*, 53.5*, 53.3, 43.3*, 43.1, 41.1, 37.4, 29.8 (q), 29.7* (q), 27.7, 27.1*, 27.0*, 26.9, 24.8, 24.7*, 24.2, 15.3, 14.6, 14.6*

IR (ATR): 2959 (m), 2922 (s), 2852 (m), 1706 (m), 1640 (s), 1578 (s), 1432 (m)

HRMS (+APCI): calc. for $C_{28}H_{36}NO_3$ $[M+H]^+$ 434.2690, found 434.2686

$[\alpha]_D^{23}$ −76.6° (*c* 0.04, $CHCl_3$)

R_F = 0.30 (4% MeOH in DCM)



25 **Pyreudione C**

Pyreudione C.

To a solution of phosphonate **25** (12.4 mg, 39.0 µmol, 1.50 equiv.) in THF (0.9 mL) at 0 ºC was added Li*O*t-Bu (6.2 mg, 78 µmol, 3.0 equiv.). The orange suspension was stirred at 0 ºC for 30 min after which octanal (4.0 µL, 26 µmol, 1.0 equiv.) in THF (0.18 mL) was added dropwise. The reaction was stirred at room temperature for 2.5 h.

A saturated aqueous solution of NH_4Cl (0.5 mL) was added and all solvents were evaporated under reduced pressure. To the remaining residue was added acetone (1.0 mL) and the resulting suspension was stirred for 20 min at room temperature. The mixture was filtered through a pad of celite and the filtrate was concentrated under reduced pressure and submitted to HPLC purification (H_2O/ACN, gradient, 66 to 100%) yielding **pyreudione C** (5.4 mg, 18 µmol, 71% yield) as yellow oil, ^{1}H NMR shows two isomers in ratio 1:0.22.

^{1}H NMR (400 MHz, $CDCl_3$, * denotes minor isomer) δ 7.25–7.07 (m, 2H+2H*), 4.06 (dd, *J* = 9.9, 6.8 Hz, 1H*), 3.96 (dd, *J* = 10.1, 6.8 Hz, 1H), 3.75 (dt, *J* = 11.3, 8.2 Hz, 1H+1H*), 3.27 (ddd, *J* = 11.9, 8.8, 4.0 Hz, 1H), 3.22 (ddd, 11.7, 8.6, 4.0 Hz, 1H*), 2.32 (app. q, *J* = 7.1 Hz, 2H+2H*), 2.24–2.00 (m, 3H+3H*), 1.60–1.44 (m, 3H+3H*), 1.37–1.19 (m, 8H+8H*), 0.88 (t, *J* = 6.7 Hz, 3H+3H*)

^{13}C NMR (100 MHz, $CDCl_3$, * denotes minor isomer) δ 203.9*, 195.1, 177.5, 175.6*, 174.3, 170.7*, 152.1*, 151.2, 121.3, 120.8*, 103.6*, 101.2, 68.7, 66.4*, 43.4*, 43.1, 33.5*, 33.3, 31.7, 29.7*, 29.2, 29.0, 28.2, 28.1*, 27.1*, 27.0*, 26.9, 26.8, 22.6, 14.1

IR (ATR): 2925 (m), 2854 (w), 1704 (m), 1641 (s), 1575 (s), 1425 (m), 1532 (m), 1352 (m), 1242 (m), 1036 (w), 982 (w), 944 (w), 881 (w), 771 (w)

HRMS (+ESI): calc. for $C_{17}H_{26}NO_3$ $[M+H]^+$ 292.1907, found 292.1910

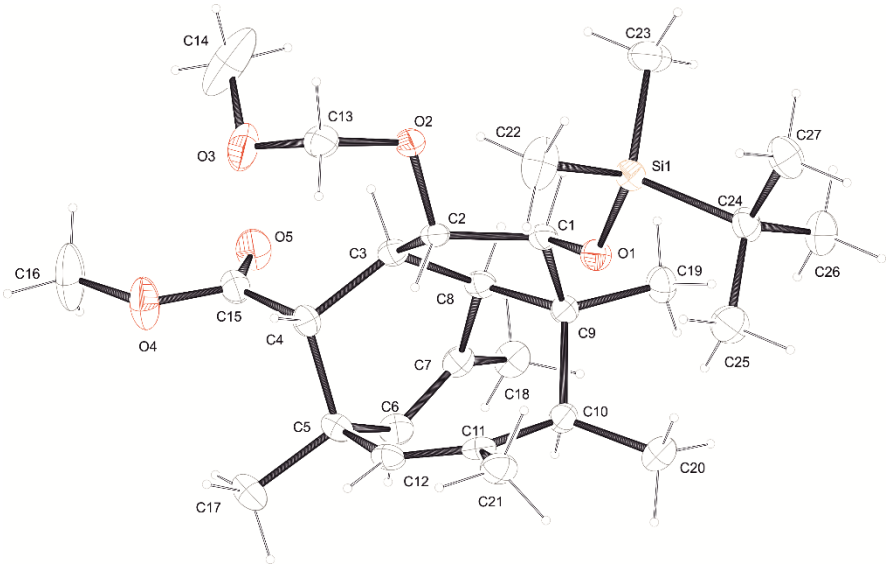
$[\alpha]_D^{27}$ −24.2º (*c* 0.33, $CHCl_3$); $[\alpha]_D^{24}$ –29.6º (*c* 0.42, MeOH)

R_F = 0.21 (1% MeOH in DCM)

Crystallographic Data

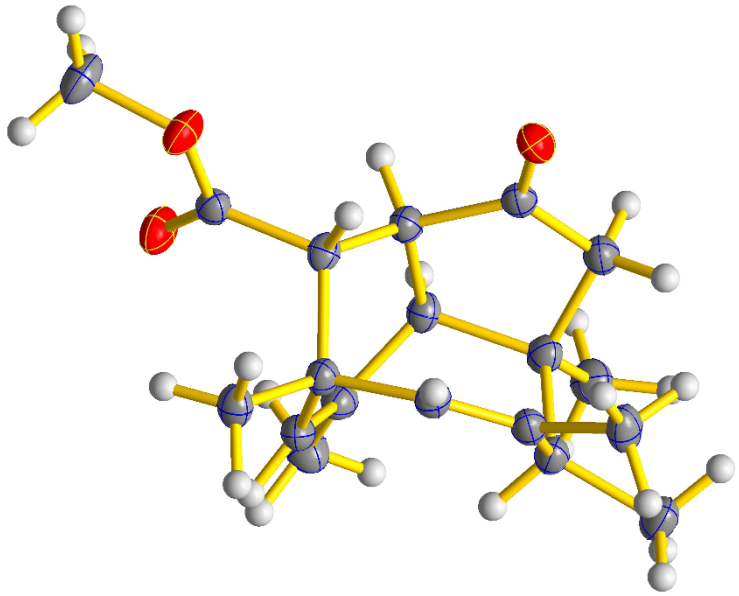
The single-crystal X-ray analyses published here were performed by Dr. Peter Mayer (compound **18**) in the Analytic Department of the Faculty for Chemistry and Pharmacy of the Ludwig-Maximilians Universität Munich, and by Dr. Hu (compounds **22** and **30**) at the Department of Chemistry of New York University, with support from the X-ray facility from the Materials Research Science and Engineering Center (MRSEC) program of the National Science Foundation (NSF) under Award Numbers DMR-0820341 and DMR-1420073.

Cascade product **18**



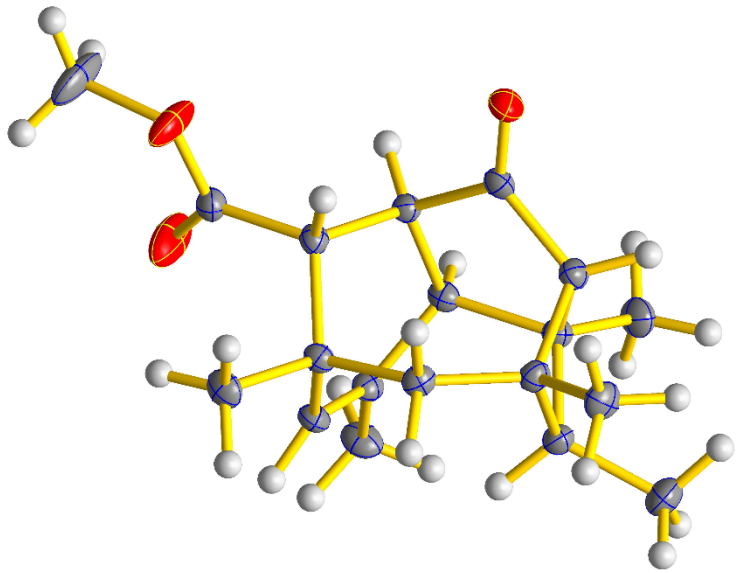
net formula	$C_{27}H_{46}O_5Si$	**transmission factor range**	0.8915–0.9705
M_r/g mol^{-1}	478.73	**refls. measured**	10273
crystal size/mm	0.090 × 0.060 × 0.050	**R_{int}**	0.0272
T/K	100.(2)	**mean $\sigma(I)/I$**	0.0561
radiation	MoKα	**θ range**	3.192–27.472
diffractometer	'Bruker D8 Venture TXS'	**observed refls.**	5200
crystal system	monoclinic	**x, y (weighting scheme)**	0.0253, 0.4855
space group	'P 1 21 1'	**hydrogen refinement**	constr
a/Å	9.6241(3)	**Flack parameter**	0.12(7)
b/Å	12.7646(4)	**refls in refinement**	6052
c/Å	11.3130(4)	**parameters**	310
α/°	90	**restraints**	1
β/°	95.6180(10)	**$R(F_{obs})$**	0.0443
γ/°	90	**$R_w(F^2)$**	0.0916
V/Å^3	1383.10(8)	**S**	1.055
Z	2	**shift/error$_{max}$**	0.001
calc. density/g cm^{-3}	1.150	**max electron density/e Å^{-3}**	0.296
μ/mm^{-1}	0.117	**min electron density/e Å^{-3}**	−0.280
absorption correction	Multi-Scan		

Tricycle **22**



Identification code	18dtr9h
Chemical formula	C19H26O3
Formula weight	302.40 g/mol
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal size	0.160 x 0.190 x 0.530 mm
Crystal habit	colorless rod
Crystal system	monoclinic
Space group	P 1 21 1
Unit cell dimensions	a = 8.7775(10) Å b = 7.8110(9) Å c = 12.1927(14) Å α = 90° β = 99.3488(15)° γ = 90°
Volume	824.84(16) Å3
Z	2
Density (calculated)	1.218 g/cm3
Absorption coefficient	0.081 mm-1
F(000)	328
Diffractometer	Bruker APEX-II CCD
Radiation source	sealed tube, Mo
Theta range for data collection	1.69 to 28.28°
Index ranges	-11<=h<=11, -10<=k<=10, -16<=l<=16
Reflections collected	11424
Independent reflections	4102 [R(int) = 0.0245]
Cov. of independent reflections	99.8%
Absorption correction	multi-scan
Max. and min. transmission	0.7457 and 0.6166
Structure solution technique	direct methods
Structure solution program	SHELXT (Sheldrick 2015)
Refinement method	Full-matrix least-squares on F2
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)
Function minimized	Σ w(Fo2 - Fc2)2
Data / restraints / parameters	4102 / 1 / 205
Goodness-of-fit on F2	1.061
Final R indices	3765 data; I>2σ(I) R1 = 0.0412, wR2 = 0.1026 all data R1 = 0.0456, wR2 = 0.1054
Weighting scheme	w=1/[σ2(Fo2)+(0.0698P)2+0.0163P] where P=(Fo2+2Fc2)/3
Absolute structure parameter	0.6(4)
Largest diff. peak and hole	0.285 and -0.167 eÅ-3
R.M.S. deviation from mean	0.046 eÅ-3

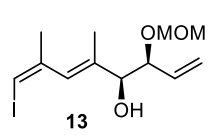
Tetracycle **30**



Identification code	18dtr10h
Chemical formula	C19H26O3
Formula weight	302.40 g/mol
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal size	0.160 x 0.540 x 0.560 mm
Crystal habit	colorless plate
Crystal system	monoclinic
Space group	P 1 21 1
Unit cell dimensions	a = 8.7382(6) Å b = 8.1682(6) Å c = 11.6148(8) Å α = 90° β = 99.9432(10)° γ = 90°
Volume	816.56(10) Å3
Z	2
Density (calculated)	1.230 g/cm3
Absorption coefficient	0.081 mm-1
F(000)	328
Diffractometer	Bruker APEX-II CCD
Radiation source	sealed tube, Mo
Theta range for data collection	1.78 to 28.29°
Index ranges	-11<=h<=11, -10<=k<=10, -15<=l<=15
Reflections collected	12719
Independent reflections	4033 [R(int) = 0.0226]
Cov. of independent reflections	100.0%
Absorption correction	multi-scan
Max. and min. transmission	0.7457 and 0.6835
Structure solution technique	direct methods
Structure solution program	SHELXS-97 (Sheldrick 2008)
Refinement method	Full-matrix least-squares on F2
Refinement program	SHELXL-2014 (Sheldrick 2014)
Function minimized	Σ w(Fo2 - Fc2)2
Data / restraints / parameters	4033 / 1 / 205
Goodness-of-fit on F2	1.037
Final R indices	3883 data; I>2σ(I) R1 = 0.0366, wR2 = 0.0958 all data R1 = 0.0380, wR2 = 0.0971
Weighting scheme	w=1/[σ2(Fo2)+(0.0631P)2+0.0998P] where P=(Fo2+2Fc2)/3
Absolute structure parameter	0.4(3)
Largest diff. peak and hole	0.259 and -0.183 eÅ-3
R.M.S. deviation from mean	0.041 eÅ-3

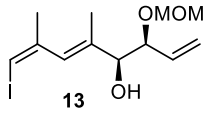
NMR spectra

^{1}H NMR ($CDCl_3$, 400 MHz)



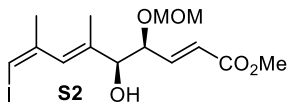
13

^{13}C NMR ($CDCl_3$, 100 MHz)

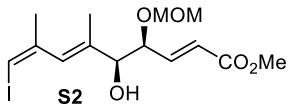


13

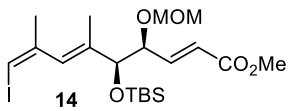
^{1}H NMR ($CDCl_3$, 400 MHz)



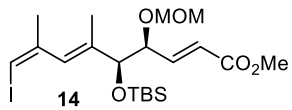
^{13}C NMR ($CDCl_3$, 100 MHz)



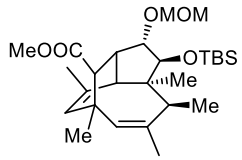
^{1}H NMR ($CDCl_3$, 400 MHz)



^{13}C NMR ($CDCl_3$, 100 MHz)

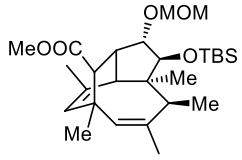


^{1}H NMR ($CDCl_3$, 400 MHz)



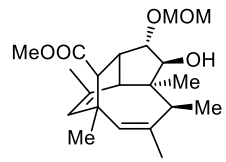
18

^{13}C NMR ($CDCl_3$, 100 MHz)



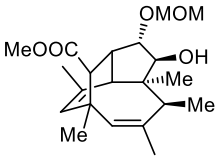
18

^{1}H NMR ($CDCl_3$, 400 MHz)



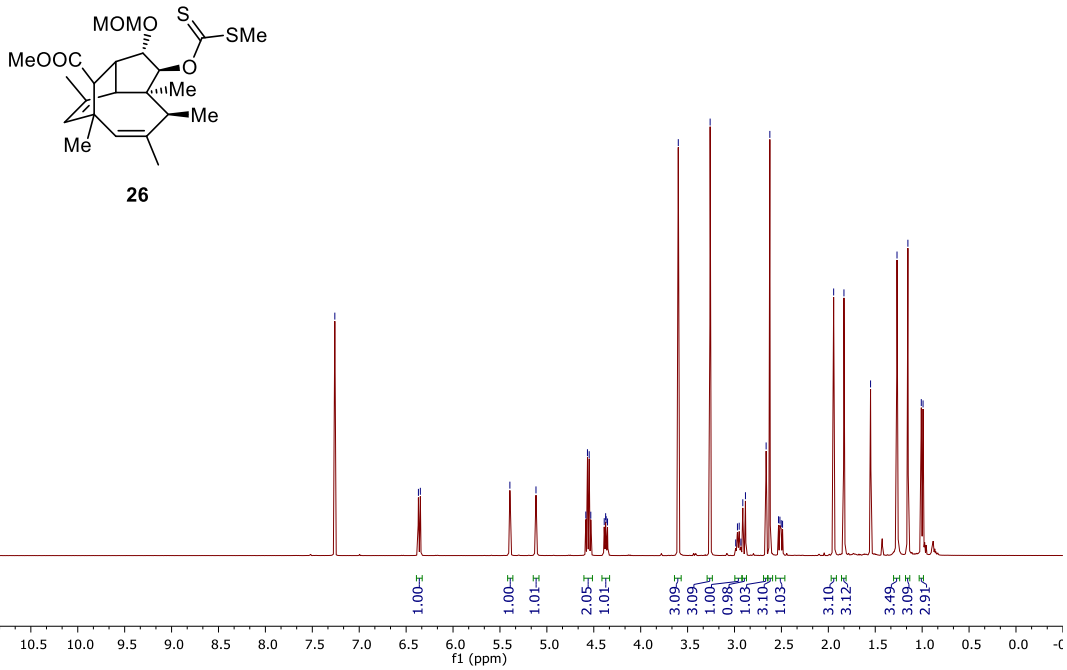
19

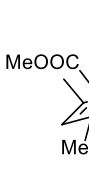
^{13}C NMR ($CDCl_3$, 100 MHz)



19

^{1}H NMR ($CDCl_3$, 400 MHz)



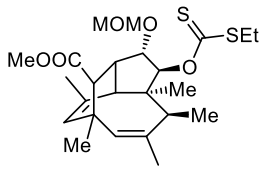


26

^{13}C NMR ($CDCl_3$, 100 MHz)

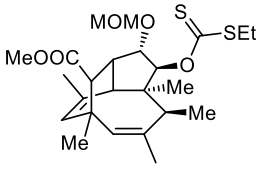
26

^{1}H NMR ($CDCl_3$, 400 MHz)



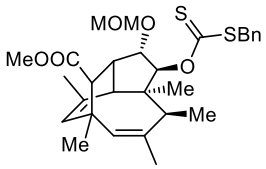
27

^{13}C NMR ($CDCl_3$, 100 MHz)



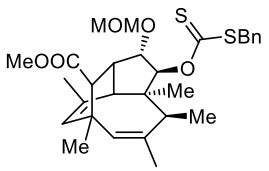
27

^{1}H NMR ($CDCl_3$, 400 MHz)



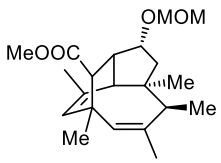
20

^{13}C NMR ($CDCl_3$, 100 MHz)



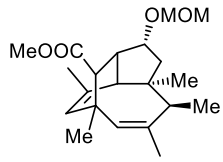
20

^{1}H NMR ($CDCl_3$, 400 MHz)



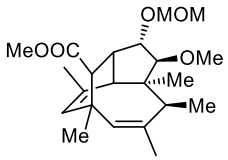
21

^{13}C NMR ($CDCl_3$, 100 MHz)



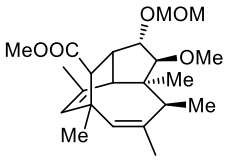
21

^{1}H NMR ($CDCl_3$, 400 MHz)



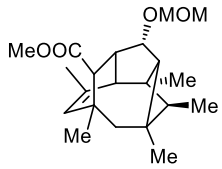
28

^{13}C NMR ($CDCl_3$, 100 MHz)



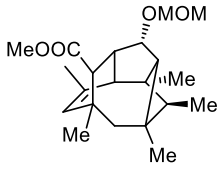
28

^{1}H NMR ($CDCl_3$, 400 MHz)



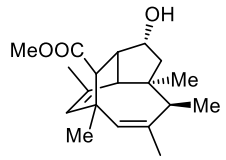
29

^{13}C NMR ($CDCl_3$, 100 MHz)



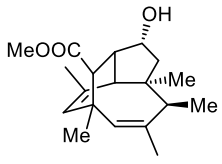
29

^{1}H NMR ($CDCl_3$, 400 MHz)



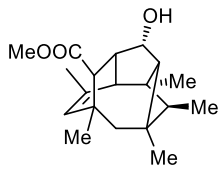
S4

^{13}C NMR ($CDCl_3$, 100 MHz)



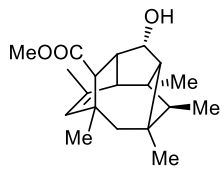
S4

^{1}H NMR ($CDCl_3$, 400 MHz)



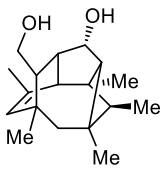
S7

^{13}C NMR ($CDCl_3$, 100 MHz)



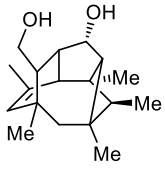
S7

^{1}H NMR ($CDCl_3$, 400 MHz)



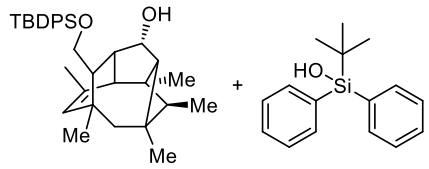
S8

^{13}C NMR ($CDCl_3$, 100 MHz)



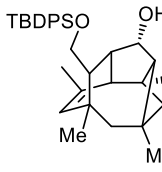
S8

^{1}H NMR ($CDCl_3$, 400 MHz)



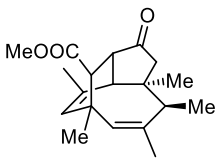
S9

^{13}C NMR ($CDCl_3$, 100 MHz)



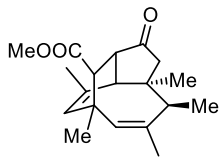
S9

^{1}H NMR ($CDCl_3$, 400 MHz)



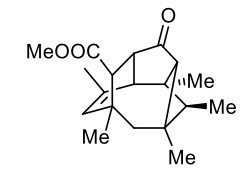
22

^{13}C NMR ($CDCl_3$, 100 MHz)



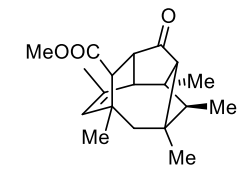
22

^{1}H NMR ($CDCl_3$, 400 MHz)



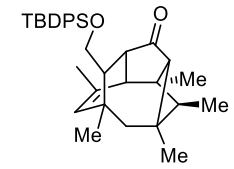
30

^{13}C NMR ($CDCl_3$, 100 MHz)



30

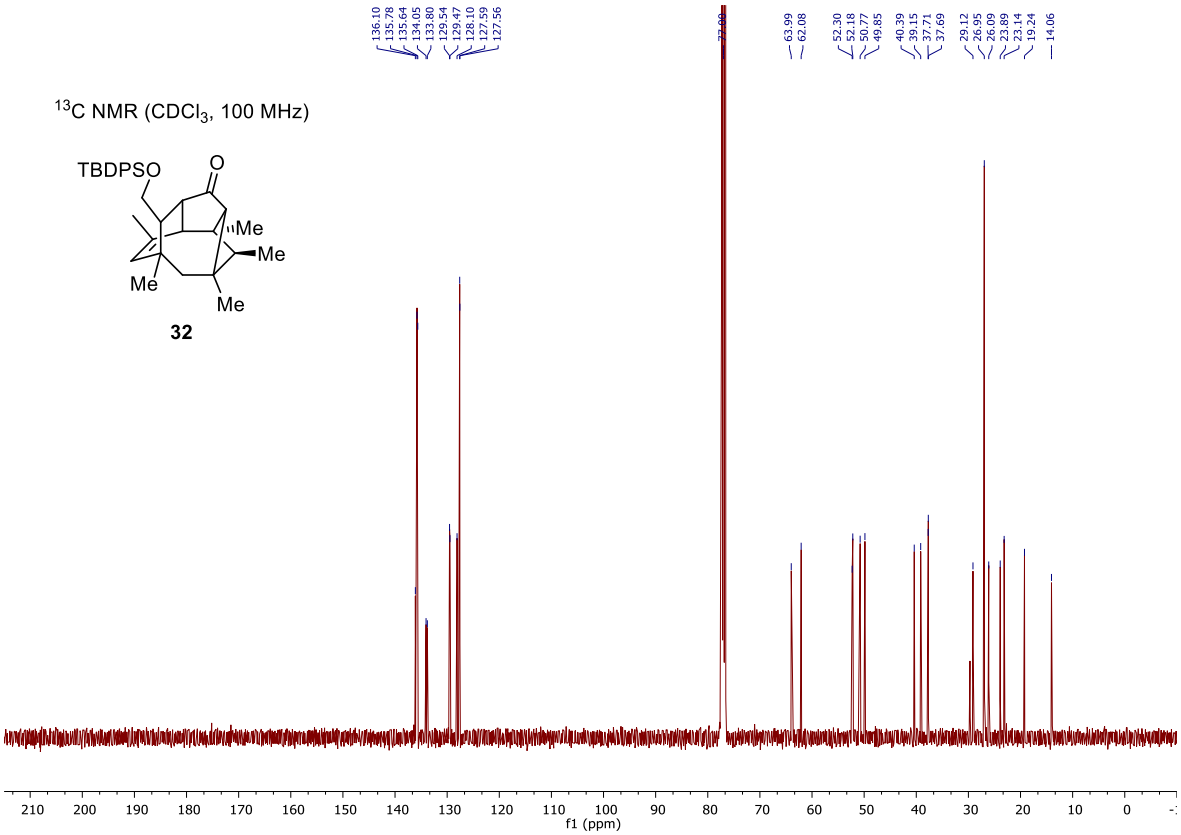
^{1}H NMR ($CDCl_3$, 400 MHz)



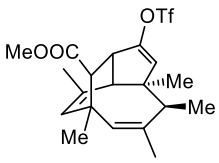
32

^{13}C NMR ($CDCl_3$, 100 MHz)

32

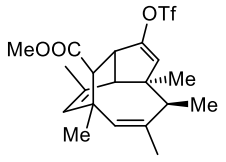


^{1}H NMR ($CDCl_3$, 400 MHz)



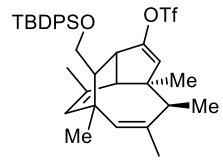
S10

^{13}C NMR ($CDCl_3$, 100 MHz)



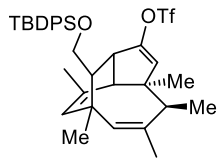
S10

^{1}H NMR ($CDCl_3$, 400 MHz)



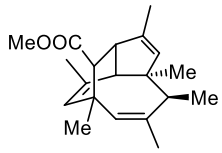
33

^{13}C NMR ($CDCl_3$, 100 MHz)



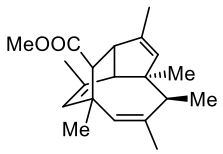
33

^{1}H NMR ($CDCl_3$, 400 MHz)



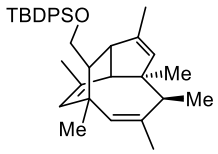
S11

^{13}C NMR ($CDCl_3$, 100 MHz)



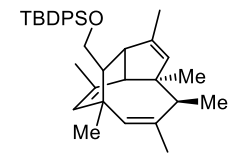
S11

^{1}H NMR ($CDCl_3$, 400 MHz)



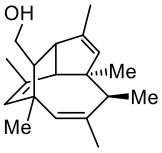
S12

^{13}C NMR ($CDCl_3$, 100 MHz)



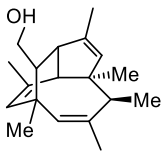
S12

^{1}H NMR ($CDCl_3$, 400 MHz)



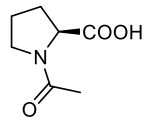
23

^{13}C NMR ($CDCl_3$, 100 MHz)



23

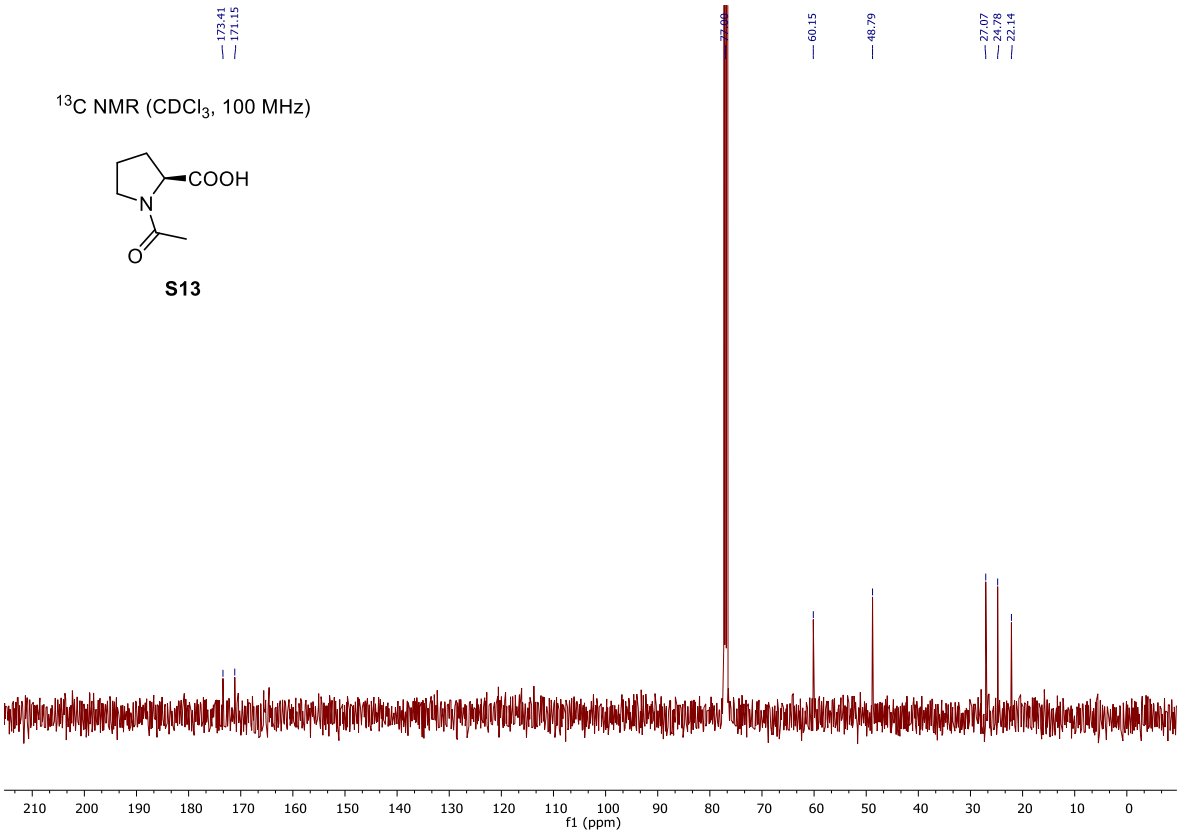
^{1}H NMR ($CDCl_3$, 400 MHz)



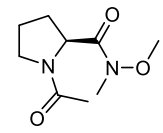
S13

^{13}C NMR ($CDCl_3$, 100 MHz)

S13



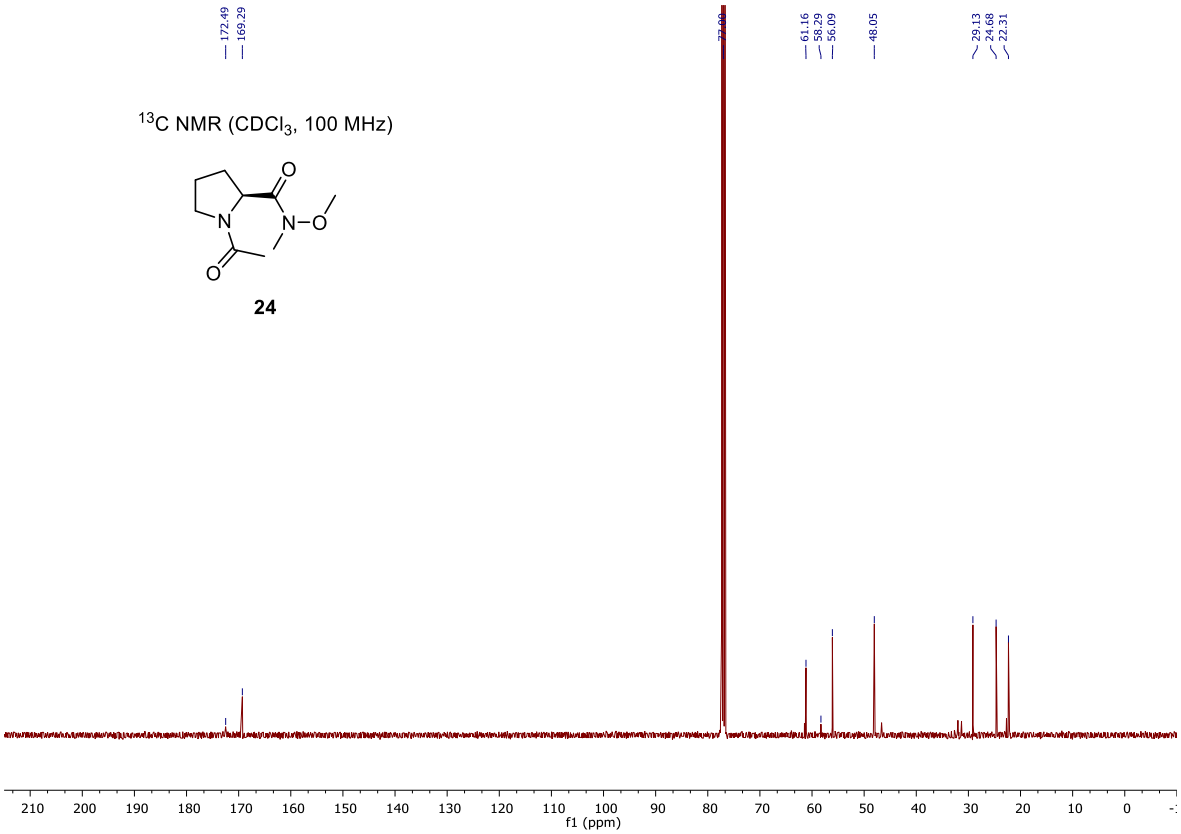
^{1}H NMR ($CDCl_3$, 400 MHz)



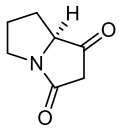
24

^{13}C NMR ($CDCl_3$, 100 MHz)

24

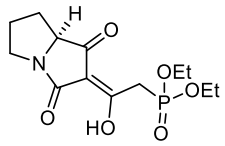


^{1}H NMR ($CDCl_3$, 400 MHz)



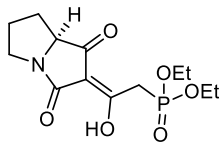
S14

^{1}H NMR ($CDCl_3$, 400 MHz)



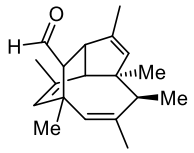
25

^{13}C NMR ($CDCl_3$, 100 MHz)



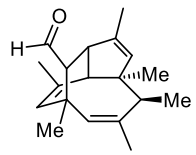
25

^{1}H NMR ($CDCl_3$, 400 MHz)

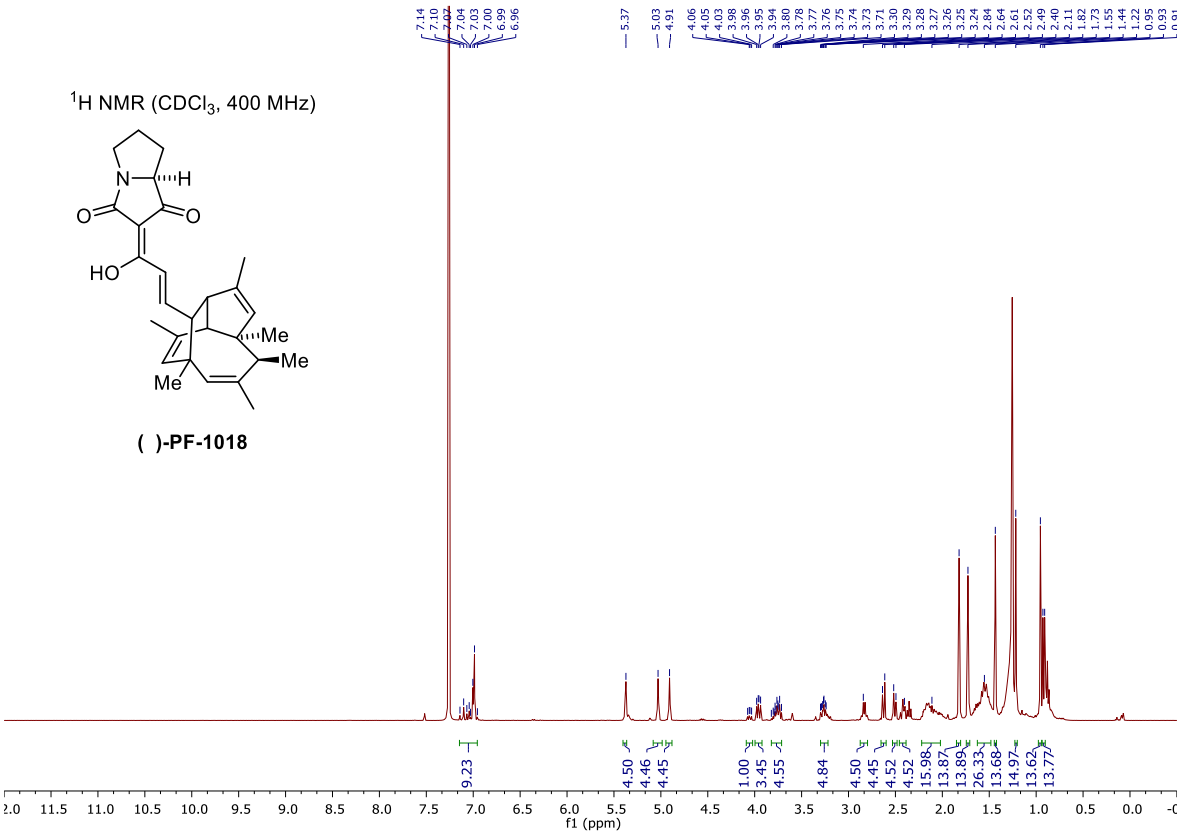


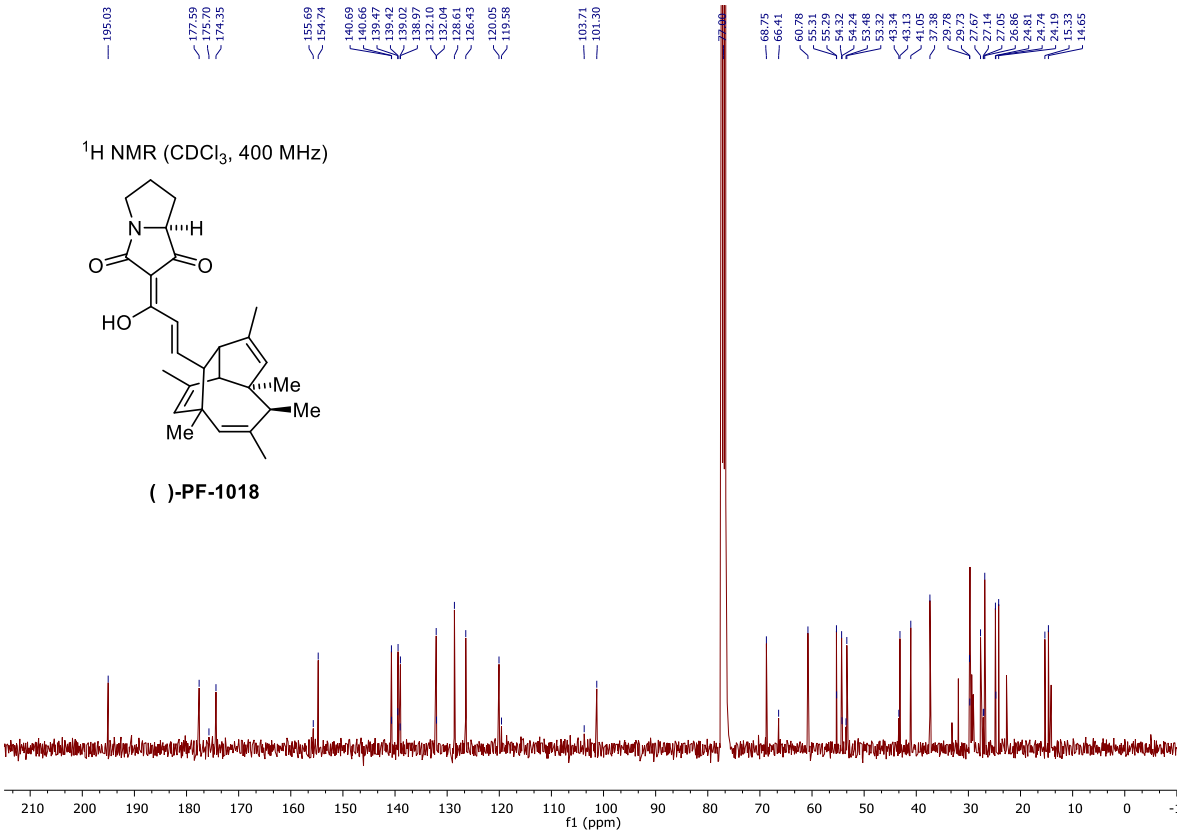
S15

^{13}C NMR ($CDCl_3$, 100 MHz)

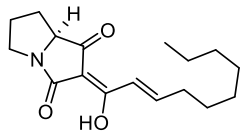


S15


^{1}H NMR ($CDCl_3$, 400 MHz)
N
H
O
O
HO
Me
Me
Me
( )-PF-1018
f1 (ppm)

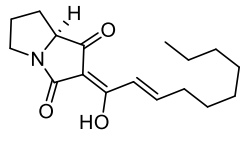

^{1}H NMR ($CDCl_3$, 400 MHz)
N
H
O
O
HO
Me
Me
Me
( )-PF-1018
f1 (ppm)

^{1}H NMR ($CDCl_3$, 400 MHz)

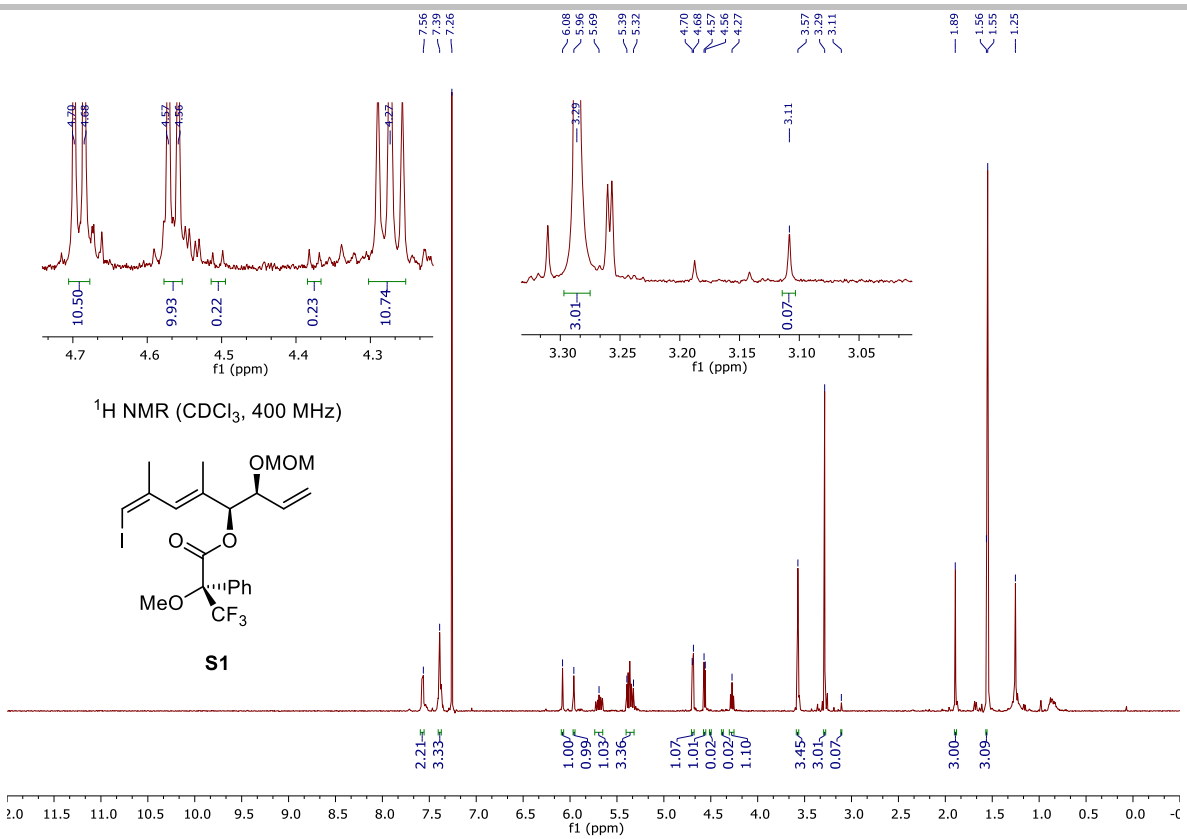


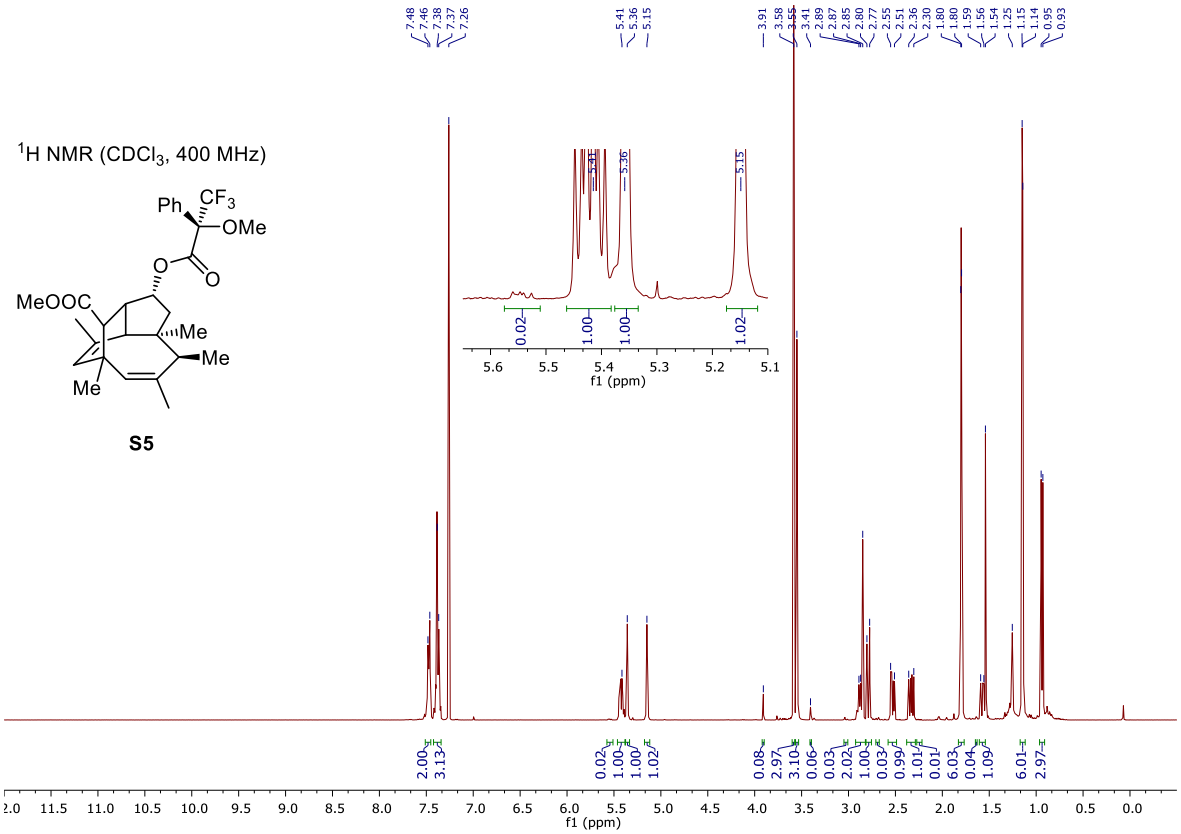
Pyreudione C

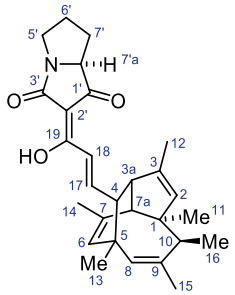
^{13}C NMR ($CDCl_3$, 100 MHz)



Pyreudione C


^{1}H NMR ($CDCl_3$, 400 MHz)
OMOM
I
O
O
MeO
Ph
CF_3
S1
f1 (ppm)

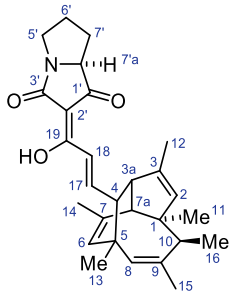

^{1}H NMR ($CDCl_3$, 400 MHz)
Ph
CF_3
OMe
O
O
MeOOC
Me
Me
Me
S5
f1 (ppm)



( )-PF-1018

Proton	Major Isomer		Minor Isomer	
	Natural	Synthetic	Natural	Synthetic
2	5.03 (br, s)	5.03 (br, s)	5.03 (br, s)	5.03 (br, s)
3a	2.50 (br, d, 9.7)	2.51 (br, d, 9.6)	2.50 (br, d, 9.7)	2.51 (br, d, 9.6)
4	2.41 (m)	2.38–2.43 (m)	2.43 (br, d, 10.1)	2.43 (br, d, 10.1)
6	5.37 (br, s)	5.37 (br, s)	5.37 (br, s)	5.37 (br, s)
7a	2.62 (d, 9.7)	2.63 (d, 9.7)	2.62 (d, 9.7)	2.63 (d, 9.7)
8	4.91 (br, s)	4.91 (br, s)	4.91 (br, s)	4.91 (br, s)
10	2.83 (br, q, 7.5)	2.83 (br, q, 7.3)	2.83 (br, q, 7.5)	2.83 (br, q, 7.3)
11	1.22 (br, s)	1.22 (br, s)	1.22 (br, s)	1.22 (br, s)
12	1.73 (br, s)	1.73 (br, s)	1.72 (br, s)	1.73 (br, s)
13	0.95 (br, s)	0.95 (br, s)	0.95 (br, s)	0.95 (br, s)
14	1.82 (br, d, 1.5)	1.82 (br, s)	1.83 (br, d, 1.5)	1.82 (br, s)
15	1.43 (br, d, 0.8)	1.44 (br, s)	1.43 (br, d, 0.8)	1.44 (br, s)
16	0.92 (d, 7.5)	0.92 (d, 7.5)	0.92 (d, 7.4)	0.92 (d, 7.5)
17	7.01 (m)	7.01–6.98 (m)	7.04 (dd, 15.6, 10.1)	7.04 (dd, 15.6, 10.1)
18	7.00 (m)	7.01–6.98 (m)	7.12 (d, 15.6)	7.12 (d, 15.7)
19-OH	12.35 (br)	13.72 (br)	12.35 (br)	13.72 (br)
5’	3.27(ddd, 11.5, 8.7, 3.8) 3.75 (ddd, 11.5, 7.8, 7.8)	3.27 (ddd, 11.2, 9.2, 3.8) 3.76 (ddd, 11.4, 7.9, 7.9)	3.22 (ddd, 11.5, 8.5, 4.1) 3.79 (ddd, 11.5, 8.0, 8.0)	3.24–3.18 (m) 3.78 (ddd, 11.6, 7.9, 7.9)
6’	2.04–2.22 (m)	2.00–2.23 (m)	2.04–2.22 (m)	2.00–2.23 (m)
7’	1.55 (dddd, 12.1, 10.3, 10.3, 8.2)	1.48–1.67 (m)	1.55 (dddd, 12.1, 10.3, 10.0, 8.2)	1.48–1.67 (m)
7’a	3.96 (dd, 10.3, 6.9)	3.96 (dd, 10.0, 6.9)	4.06 (dd, 10.0, 6.9)	4.05 (dd, 9.9, 6.9)

4. S. Gomi, K. Imamura, T. Yaguchi, Y. Kodama, N. Minowa, M. Koyama *J. Antibiot.* **1994**, *47*, 571-580

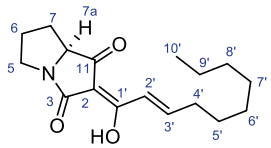


( )-PF-1018

Carbon	Major Isomer		Minor Isomer	
	Natural	Synthetic	Natural	Synthetic
1	60.8	60.8	60.8	60.8
2	128.6	128.6	128.6	128.6
3	140.7	140.7	140.6	140.7
3a	54.4	54.3	54.3	54.2
4	53.3	53.3	53.5	53.5
5	41.1	41.1	41.1	41.1
6	126.4	126.4	126.4	126.4
7	138.9	139.0	138.9	138.9
7a	55.3	55.3	55.3	55.3
8	132.1	132.1	132.0	132.0
9	139.4	139.4	139.4	139.5
10	37.4	37.4	37.4	37.4
11	27.6	27.7	27.6	27.7
12	14.6	14.6	14.6	14.6
13	29.8	29.8	29.7	29.7
14	24.1	24.2	24.1	24.2
15	24.8	24.8	24.8	24.7
16	15.3	15.3	15.3	15.3
17	154.7	154.7	155.6	155.7
18	120.1	120.1	119.6	119.6
19	174.3	174.3	175.7	175.7
2’	101.3	101.3	103.7	103.7
3’	177.6	177.6	170.8	[b]
5’	43.1	43.1	43.3	43.3
6’	26.8[a]	26.9	27.1[a]	27.1
7’	26.8[a]	26.9	27.0[a]	27.0
7’a	68.7	68.7	66.4	66.4
1’	195.0	195.0	203.7	203.8

[a] Interchangeable according to the isolation paper [b] Indistinguishable from noise

4. S. Gomi, K. Imamura, T. Yaguchi, Y. Kodama, N. Minowa, M. Koyama *J. Antibiot.* **1994**, *47*, 571-580



Pyreudione C

Proton	Major Isomer		Minor Isomer	
	Natural	Synthetic	Natural	Synthetic
5	3.25 (ddd, 11.5, 8.9, 4.0) 3.73 (dt, 11.5, 7.9)	3.27 (ddd, 11.9, 8.8, 4.0) 3.75 (dt, 11.3, 8.2)	3.20 (ddd, 11.6, 8.8, 4.2) 3.76 (dt, 11.4, 7.9)	3.22 (ddd, 11.7, 8.6, 4.0) 3.75 (dt, 11.3, 8.2)
6	2.05 (m), 2.14 (m)	2.24–2.00 (m) 1.60–1.44 (m)	2.05 (m), 2.14 (m)	2.24–2.00 (m) 1.60–1.44 (m)
7	1.52 (m), 2.14 (m)		1.52 (m), 2.14 (m)	
7a	3.94 (dd, 10.0, 6.9)	3.96 (dd, 10.1, 6.8)	4.04 (dd, 9.9, 7.0)	4.06 (dd, 9.9, 6.8)
2’	7.08 (dt, 15.7, 1.3)	7.25–7.07 (m)	7.19	7.25–7.07 (m)
3’	7.18 (dt, 15.8, 7.0)		7.20	
4’	2.30 (m)	2.32 (app q, 7.1)	2.30 (m)	2.32 (app q, 7.1)
5’	1.48 (m)	1.60–1.44 (m)	1.48 (m)	1.60–1.44 (m)
6’	1.30 (m)	1.37–1.19 (m)	1.30 (m)	1.37–1.19 (m)
7’	1.27 (m)		1.27 (m)	
8’	1.27 (m)		1.27 (m)	
9’	1.27 (m)		1.27 (m)	
10’	0.86 (t, 7.1)	0.88 (t, 6.7)	0.86 (t, 7.1)	0.88 (t, 6.7)

*The 0.02 ppm deviation is owed to the different reference taken (Stallforth δ $CHCl_3$ = 7.24, Trauner δ $CHCl_3$ = 7.26)

Carbon	Major Isomer		Minor Isomer	
	Natural	Synthetic	Natural	Synthetic
1	195.1	195.1	203.8	203.9
2	101.2	101.2	101.2	103.6
3	177.5	177.5	170.7	170.7
5	43.1	43.1	43.4	43.4
6	26.9	26.9	27.1	27.1
7	26.8	26.8	27.0	27.0
7a	68.7	68.7	66.4	66.4
1’	174.3	174.3	175.6	175.6
2’	121.3	121.3	120.8	120.8
3’	151.1	151.2	152.1	152.1
4’	33.3	33.3	33.4	33.5
5’	28.2	28.2	28.1	28.1
6’	29.2	29.2	29.7	29.7
7’	29.0	29.0	29.0	29.0
8’	31.7	31.7	31.7	31.7
9’	22.6	22.6	22.6	22.6
10’	14.0	14.1	14.0	14.1

2. Klapper, M., Götze, S., Barnett, R., Willing, K., Stallforth, P., *Angew. Chem. Int.*, **2016**, *55*, 8944-8947

Computational Methods

Initial conformational searches were completed using the CREST conformer-rotamer ensemble sampling tool,[5] version 2.7.1 with xtb version 6.2 RC2 (SAW190805).[6] These inital conformer geometries were recalculated in Gaussian 16 Rev. A.03 (sse4)[7] with at the SMD(DMF)-ωB97X-D/6-311+G(d,p)[8] level of theory. This functional was chosen for its ability to reproduce CCSD geometries of asynchronous Diels–Alder reactions as well as its ability to accurately reproduce experimental reaction barriers.[9] Following Head-Gordon's suggested basis set for energetics,[10] single point energies at the SMD(DMF)-ωB97X-D/def2-QZVPP level of theory were computed.[11] Thermochemistry was calculated using the program GoodVibes version 3.0.1,[12] using quasiharmonic approximations to entropy[13] and enthalpy[14] and corrected for 398.15 K. All reported energies are quasiharmonic corrected. All reported structures are stationary points on the energy surface and characterized as transition states or minima by frequency calculations.

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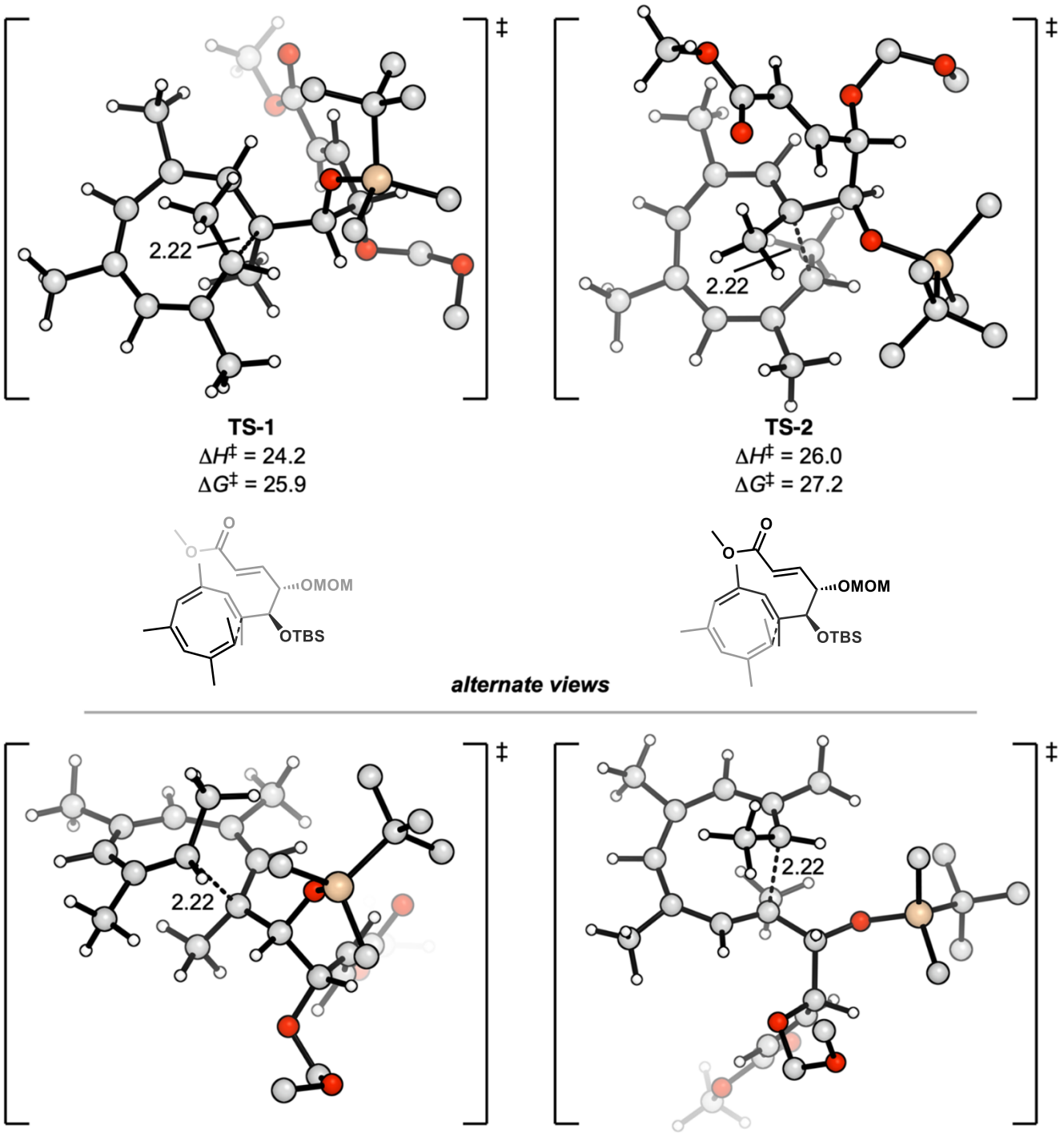


Figure S2. Calculated TS-1 and TS-2 shown in two alternate angles. Hs on protecting groups are omitted for clarity. Silicon is shown in wheat colour.

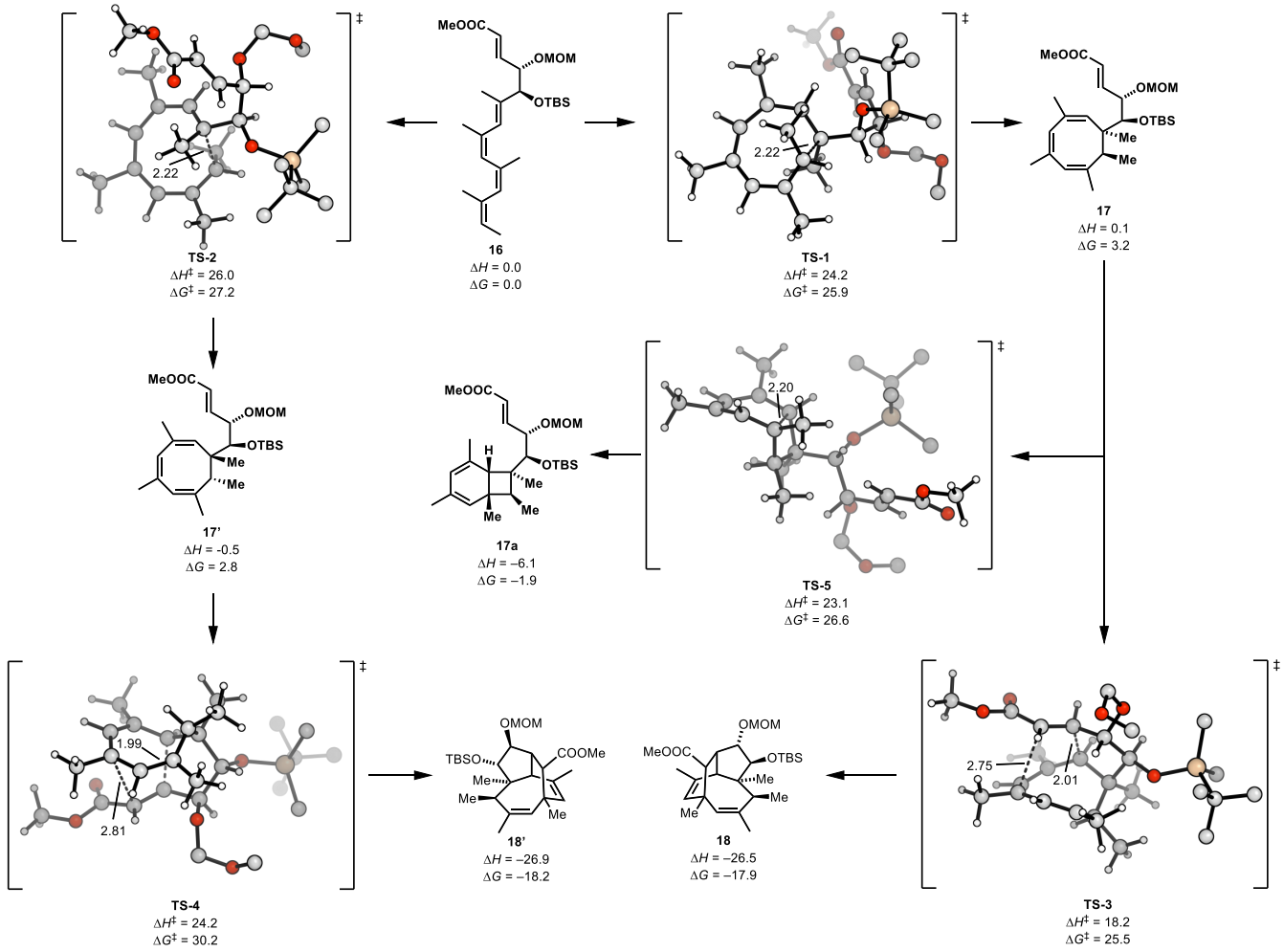


Figure S3. Calculated cascade energy surface starting from **16** and leading to **18**.

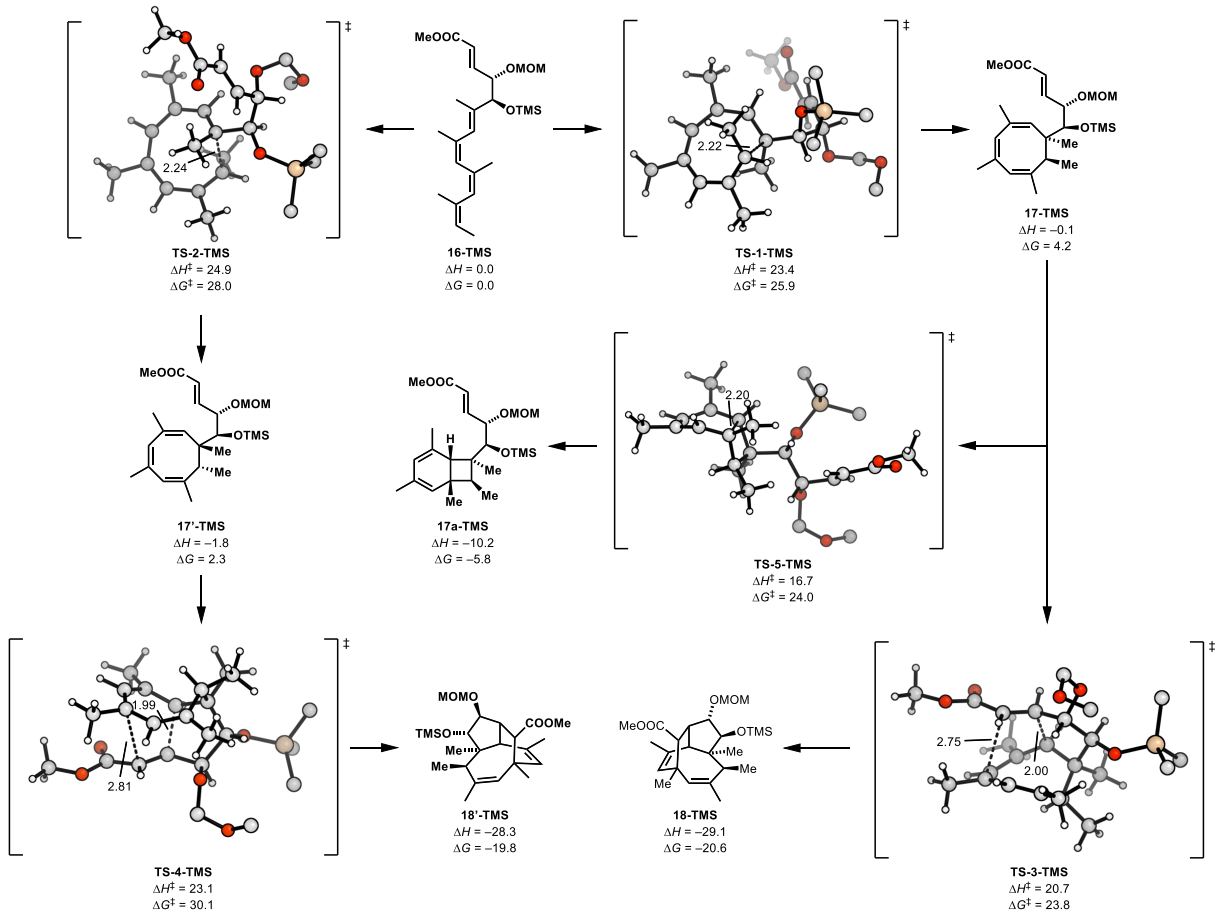
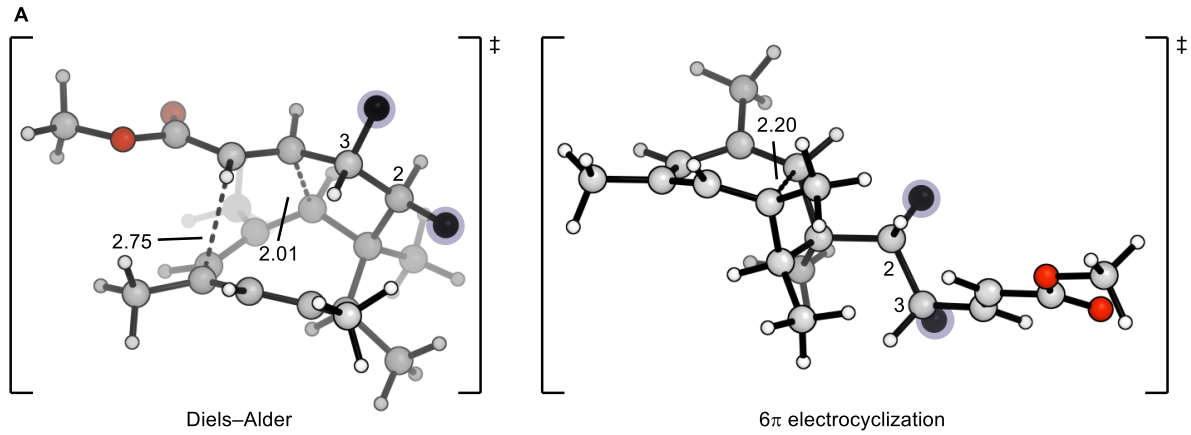


Figure S4. Calculated cascade energy surface starting from **16-TMS** and leading to **18-TMS**.



Barriers for Diels–Alder and 6π electrocylization transition states, reported as $\Delta G^{‡}$ relative to 8π-cycloadduct

C2 substituent	C3 substituent	D.A. to **18**	D.A. to **18'**	6π electrocyclization
OTBS	OMOM	22.3	27.4	23.4
OTMS	OMOM	19.6	27.7	19.8
H	OMOM	28.1	–	23.5

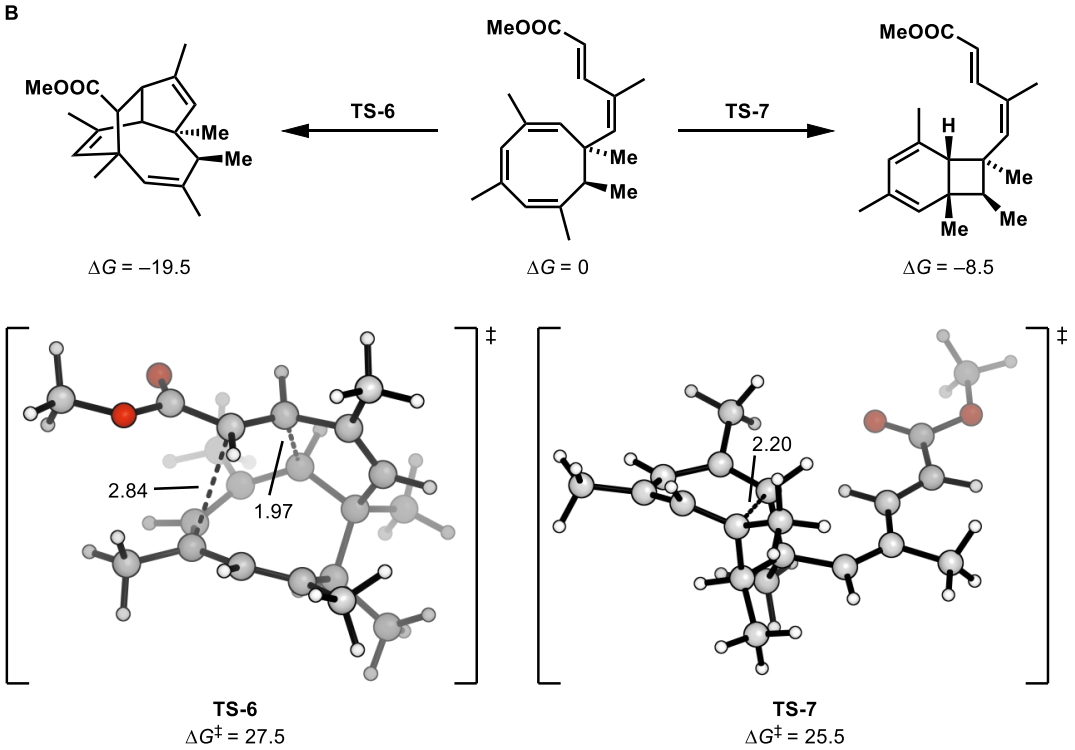


Figure S5. (A) barriers for Diels–Alder and 6-π electrocyclization for OTBS, OTMS, and H substituent at the 2 position. (**B**) biomimetic reaction model for competing Diels–Alder and 6-π electrocyclization.

Cartesian Coordinates of Calculated Structures

Energies reported below are at the ωB97X-D/6-311+G(d,p) level of theory. Frequencies for transition states abbreviated as F.

16-TBS.out

ZPE	0.686264
DE	0.728321
DH	0.729265
DG	0.610870
E	-1722.146990
H	-1721.417726
G	-1721.536120

Cartesian coordinates

C	-0.989261	0.190021	-2.866645
C	-4.482147	-1.181718	-1.787092
C	-2.225246	-0.629351	-2.649815
C	-3.324300	-0.236090	-1.992309
C	-3.953464	3.010275	0.078977
C	-3.443521	1.151854	-1.486073
C	-3.851648	1.549610	-0.273446
C	-3.949182	-1.066574	2.586948
C	-4.216451	0.623167	0.823026
C	-3.380637	-0.173462	1.515643
C	-1.942279	-0.155939	1.215940
C	-0.994784	-2.059469	2.647323
C	-0.934594	-0.910353	1.674514
C	0.468027	-0.650650	1.151193
C	0.994610	-1.843992	0.324550
C	2.381614	-1.527291	-0.146525
C	3.484866	-1.946533	0.467960
C	4.841744	-1.492262	0.108111
H	-0.440733	-0.154175	-3.747543
H	-1.208591	1.253762	-2.995335
H	-0.325942	0.088523	-2.001174
H	-5.421386	-0.723361	-2.113981
H	-4.333902	-2.105077	-2.351937
H	-4.605233	-1.444529	-0.732622
H	-2.192102	-1.656002	-3.010052
H	-4.963113	3.255311	0.427523
H	-3.267571	3.250252	0.899317
H	-3.714134	3.650212	-0.773574
H	-3.152132	1.934876	-2.185529
H	-3.737262	-2.118603	2.374842
H	-3.526519	-0.839248	3.569618
H	-5.032499	-0.944222	2.648220
H	-5.267490	0.635090	1.111602
H	-1.650991	0.593136	0.487634
H	-0.003976	-2.253565	3.067780
H	-1.670539	-1.871979	3.478884
H	-1.317299	-2.978595	2.148086
H	2.445287	-0.855772	-0.996865
H	3.441452	-2.605823	1.329018
O	5.832210	-1.777081	0.747369
O	4.872941	-0.715977	-0.981217
C	6.149057	-0.181093	-1.345483
H	5.971995	0.417018	-2.236792
H	6.543047	0.446230	-0.544045
H	6.855410	-0.983255	-1.565088
H	1.001096	-2.727582	0.970415
H	1.133559	-0.593270	2.027424
O	0.573450	0.512612	0.371292
O	0.147250	-2.052582	-0.793628
C	-0.071770	-3.394009	-1.126978
H	-0.470189	-3.379819	-2.147738
H	0.858437	-3.970311	-1.089176
O	-0.959931	-4.040378	-0.257947
C	-2.293203	-3.563728	-0.368958
H	-2.354047	-2.497275	-0.136834
H	-2.680554	-3.734209	-1.381290
H	-2.896057	-4.128588	0.342828
Si	1.271162	1.936697	0.935135
C	0.364395	2.484418	2.476616
H	-0.695720	2.661035	2.271187
H	0.434445	1.720141	3.258049
H	0.795027	3.408247	2.876802
C	3.077765	1.636662	1.324258
H	3.195886	0.837932	2.063753
H	3.640056	1.354859	0.429007
H	3.531232	2.542556	1.740460
C	1.059326	3.160364	-0.487565
C	1.705829	4.501333	-0.107503
H	2.781330	4.399081	0.072327
H	1.575534	5.226067	-0.921509
H	1.252879	4.932814	0.791642
C	1.740596	2.610532	-1.750042
H	2.817767	2.477925	-1.602712
H	1.321728	1.646237	-2.050039
H	1.605599	3.309439	-2.585896
C	-0.437640	3.375179	-0.756995
H	-0.949761	2.433784	-0.971058
H	-0.936217	3.840965	0.099033
H	-0.577660	4.037853	-1.621285

16-TMS.out

ZPE	0.600600
DE	0.638975
DH	0.639919
DG	0.528669
E	-1604.208888
H	-1603.568969
G	-1603.680219

Cartesian coordinates

C	-0.840755	-0.327794	2.943558
C	-4.156793	1.369473	1.768905
C	-1.976304	0.607418	2.663217
C	-3.117432	0.305909	2.028301
C	-4.149145	-2.963822	0.164642
C	-3.405171	-1.086040	1.606919
C	-3.882539	-1.504266	0.426020
C	-3.743141	0.945973	-2.579361
C	-4.166373	-0.611588	-0.721588
C	-3.263429	0.069617	-1.452961
C	-1.837516	-0.057077	-1.130553
C	-0.660626	1.542118	-2.751159
C	-0.746470	0.520461	-1.649168
C	0.608478	0.151875	-1.064242
C	1.302232	1.363957	-0.408834
C	2.655417	0.944008	0.082069
C	3.781812	1.137331	-0.599753
C	5.094603	0.606192	-0.184353
H	-0.342893	-0.065533	3.881667
H	-1.161932	-1.370612	3.005253

H	-0.102755	-0.257304	2.137104
H	-5.141064	1.044586	2.122359
H	-3.895718	2.298379	2.281424
H	-4.256968	1.586946	0.702119
H	-1.823058	1.644170	2.958490
H	-5.175877	-3.114861	-0.186854
H	-3.486080	-3.333498	-0.626105
H	-3.995581	-3.570526	1.060097
H	-3.191904	-1.856210	2.347315
H	-3.368505	0.601948	-3.547478
H	-4.834341	0.949265	-2.621986
H	-3.403269	1.977196	-2.445431
H	-5.213988	-0.552719	-1.016683
H	-1.636192	-0.742173	-0.315965
H	-1.393276	1.377613	-3.537907
H	-0.805081	2.552633	-2.354954
H	0.330647	1.517653	-3.213669
H	2.665910	0.402765	1.022595
H	3.788890	1.668220	-1.546437
O	6.097329	0.706967	-0.859235
O	5.071957	-0.008224	1.003417
C	6.305546	-0.582912	1.445839
H	6.088960	-1.032983	2.412293
H	6.646074	-1.345791	0.743801
H	7.072411	0.185988	1.552678
H	1.398162	2.151954	-1.162344
H	1.257843	-0.135049	-1.907277
O	0.540980	-0.874914	-0.111734
O	0.523015	1.815081	0.688468
C	0.427774	3.205619	0.817645
H	0.081808	3.380694	1.842724
H	1.397364	3.687651	0.655770
O	-0.450123	3.787507	-0.105307
C	-1.808323	3.442186	0.126826
H	-1.957620	2.361686	0.063249
H	-2.132703	3.794813	1.114273
H	-2.401639	3.939391	-0.641212
Si	0.903429	-2.488532	-0.402455
C	2.761725	-2.663858	-0.516564
H	3.159575	-2.062099	-1.340914
H	3.247051	-2.331286	0.406381
H	3.047881	-3.705910	-0.695568
C	0.182883	-3.389109	1.060069
H	-0.898383	-3.220096	1.111735
H	0.354001	-4.467532	0.976732
H	0.628875	-3.047323	1.998730
C	0.093894	-3.031729	-1.997623
H	-0.996619	-2.978569	-1.920390
H	0.406581	-2.403647	-2.838352
H	0.368058	-4.065368	-2.234876

17-TBS.out

ZPE	0.689975
DE	0.730508
DH	0.731452
DG	0.616971
E	-1722.151182
H	-1721.419730
G	-1721.534211

Cartesian coordinates

C	1.611618	-3.174854	-0.393728
C	1.822441	-1.285300	-2.677509
C	2.358812	-1.853424	-0.163730
C	2.754174	-1.216550	-1.493406
C	6.364898	-1.174327	-1.030369
C	3.979804	-0.702648	-1.668426
C	5.027568	-0.600437	-0.644131
C	4.057413	2.149054	1.475919
C	4.837295	-0.008148	0.544024
C	3.665662	0.763228	1.005840
C	2.376669	0.406992	1.071896
C	1.655456	-1.579140	2.241275
C	1.643622	-0.901788	0.850025
C	0.182392	-0.581450	0.328220
C	-0.961541	-1.391704	0.972963
C	-2.199000	-1.193091	0.144213
C	-2.542669	-1.983567	-0.869965
H	2.200615	-3.822202	-1.049540
H	1.461191	-3.710307	0.545663
H	0.634307	-3.038452	-0.863912
H	0.905263	-0.711431	-2.520924
H	1.517474	-2.313738	-2.890431
H	2.308876	-0.884213	-3.569185
H	3.298260	-2.117351	0.328638
H	6.719160	-0.723120	-1.963787
H	7.116964	-1.005256	-0.256641
H	6.285931	-2.251956	-1.210353
H	4.271279	-0.381538	-2.668555
H	3.192732	2.712069	1.835473
H	4.794711	2.093145	2.284893
H	4.523618	2.715461	0.661747
H	5.698386	0.055566	1.210443
H	1.716870	1.164200	1.481904
H	1.267848	-0.904584	3.005194
H	1.062224	-2.495124	2.277445
H	2.688176	-1.834153	2.497251
H	-2.777114	-0.300635	0.360545
H	-1.969523	-2.870417	-1.121793
C	-3.654764	-1.683147	-1.787639
H	-0.691665	-2.454247	0.978177
H	0.157643	-0.869645	-0.724384
O	-0.171637	0.774757	0.445711
Si	-0.373617	1.923637	-0.755358
C	-1.166314	3.354836	0.191232
C	-0.192272	3.858625	1.267320
H	0.074058	3.063221	1.970592
H	0.733984	4.244850	0.829028
H	-0.650821	4.674195	1.841882
C	-1.499272	4.499822	-0.775888
H	-0.603631	4.883115	-1.276840
H	-2.208494	4.185071	-1.549035
H	-1.955485	5.336688	-0.231305
C	-2.454652	2.859016	0.866438
H	-2.248898	2.035734	1.557493
H	-2.922236	3.672975	1.435973
H	-3.188673	2.507390	0.133153
C	1.270637	2.407558	-1.506569
H	1.953830	2.820672	-0.759285
H	1.760014	1.543109	-1.966740
H	1.119646	3.161095	-2.287467
C	-1.496999	1.286661	-2.112413
H	-1.141613	0.331182	-2.511760
H	-2.523287	1.144255	-1.763380
H	-1.513900	2.003688	-2.940414
O	-1.155879	-0.934642	2.299437
C	-1.851478	-1.818906	3.128943
H	-1.476628	-2.841854	3.015149
H	-1.681030	-1.458515	4.150047
O	-3.224738	-1.882596	2.853254
C	-3.909807	-0.676009	3.142626
H	-3.791023	-0.403822	4.199335
H	-3.551742	0.152160	2.521856

H	-4.965606	-0.848626	2.933143
O	-3.860989	-2.294334	-2.815314
O	-4.411370	-0.652248	-1.388601
C	-5.451962	-0.243242	-2.280386
H	-6.170230	-1.050499	-2.432634
H	-5.936202	0.602595	-1.796896
H	-5.034093	0.062464	-3.241290

17-biomimetic.out

ZPE	0.435464
DE	0.459884
DH	0.460828
DG	0.382047
E	-929.329089
H	-928.868261
G	-928.947042

Cartesian coordinates

C	-2.909441	1.731959	-1.563751
C	-0.356961	0.685935	-2.517482
C	-2.243588	0.636939	-0.721111
C	-1.174827	-0.091263	-1.517665
C	-2.440038	-3.484931	-1.354368
C	-1.023582	-1.419811	-1.431598
C	-1.832320	-2.327266	-0.605998
C	-0.807925	-1.989007	2.854076
C	-2.026026	-2.180110	0.713203
C	-1.364782	-1.252713	1.653216
C	-1.203176	0.075096	1.585858
C	-2.940743	1.754908	1.445692
C	-1.742523	1.157091	0.667689
C	-0.739119	2.287456	0.491293
C	1.351051	3.570754	0.190291
C	0.601475	2.277595	0.379603
C	1.377335	1.040411	0.348333
C	2.692506	0.959021	0.105449
H	-3.797025	2.127029	-1.067120
H	-2.235021	2.567624	-1.768914
H	-3.231097	1.319310	-2.523699
H	-0.971532	0.966938	-3.379300
H	0.480439	0.087491	-2.882252
H	0.035880	1.613185	-2.096056
H	-3.018002	-0.096255	-0.477958
H	-1.659895	-4.058980	-1.866296
H	-2.984132	-4.157746	-0.688139
H	-3.128148	-3.126862	-2.127776
H	-0.310452	-1.903954	-2.098812
H	-0.333505	-1.307649	3.563250
H	-1.603374	-2.531966	3.376456
H	-0.068187	-2.733785	2.540576
H	-2.628878	-2.942132	1.207725
H	-0.667676	0.513785	2.427425
H	-2.634463	2.021306	2.461373
H	-3.326655	2.658724	0.968649
H	-3.748566	1.020884	1.513892
H	-1.207482	3.268083	0.429787
H	2.123695	3.696410	0.955268
H	1.854785	3.590009	-0.782101
H	0.675369	4.425816	0.241694
H	0.844828	0.108345	0.498571
H	3.317637	1.825255	-0.075656
C	3.346173	-0.359560	0.055526
O	2.810494	-1.429711	0.250119
O	4.651272	-0.240749	-0.245320
C	5.394625	-1.460195	-0.331410
H	4.986268	-2.105357	-1.111281
H	6.412094	-1.167635	-0.582482
H	5.380269	-1.988043	0.623700

17-TMS.out

ZPE	0.605684
DE	0.641969
DH	0.642913
DG	0.537815
E	-1604.214691
H	-1603.571778
G	-1603.676876

Cartesian coordinates

C	-1.086794	0.917664	-2.713454
C	-1.497498	-1.941638	-2.052262
C	-1.998001	0.587640	-1.522514
C	-2.450451	-0.868968	-1.585878
C	-6.040051	-0.315787	-1.818626
C	-3.730583	-1.198494	-1.363497
C	-4.800765	-0.275255	-0.964605
C	-4.256688	0.395498	2.529476
C	-4.712133	0.532311	0.102351
C	-3.665725	0.557521	1.144254
C	-2.340497	0.709050	1.025497
C	-1.398657	2.604941	-0.130506
C	-1.435188	1.058190	-0.139964
C	-0.012039	0.406757	0.099570
C	1.196384	1.283029	-0.298012
C	2.413354	0.407875	-0.398394
C	2.779518	-0.212355	-1.517708
H	-1.592095	0.649003	-3.645454
H	-0.864666	1.985633	-2.758346
H	-0.138362	0.375327	-2.690902
H	-0.639341	-2.061090	-1.385660
H	-1.095314	-1.715790	-3.044083
H	-2.006496	-2.906397	-2.105865
H	-2.902857	1.184986	-1.659697
H	-6.435380	-1.336243	-1.870432
H	-6.822101	0.339213	-1.428559
H	-5.811571	-0.012883	-2.846225
H	-4.043878	-2.225413	-1.551513
H	-3.490399	0.454283	3.305563
H	-5.006146	1.170657	2.725603
H	-4.768532	-0.569255	2.620951
H	-5.583797	1.144774	0.335920
H	-1.797298	0.716082	1.964425
H	-1.087287	2.980815	0.845025
H	-0.722787	3.023328	-0.878866
H	-2.404793	2.980013	-0.339310
H	2.957385	0.237938	0.525141
H	2.238515	-0.071353	-2.448238
C	3.871272	-1.198613	-1.584756
H	0.998929	1.734628	-1.275500
H	0.045566	-0.453445	-0.570269
O	0.208320	-0.026441	1.425562
Si	0.270523	-1.623627	1.944579
C	0.791346	-1.501742	3.729643
C	-1.401465	-2.449246	1.794394
H	-2.150365	-1.963001	2.426373
H	-1.768678	-2.433096	0.763809
H	-1.321336	-3.496981	2.106304
C	1.516918	-2.593673	0.939275
H	1.280157	-2.576519	-0.129376
H	2.533335	-2.210729	1.067011
H	1.505704	-3.640344	1.263986
O	1.383129	2.299973	0.671220

C	1.998615	3.459597	0.186639
H	1.529822	3.790785	-0.746305
H	1.863611	4.211938	0.972182
O	3.358191	3.294047	-0.110742
C	4.163920	3.085485	1.036361
H	4.071513	3.926154	1.735899
H	3.896228	2.160256	1.556661
H	5.196680	3.015676	0.694493
O	4.093173	-1.885626	-2.560025
O	4.590292	-1.278703	-0.458055
C	5.620122	-2.271069	-0.429949
H	6.362818	-2.078890	-1.205923
H	6.077561	-2.190952	0.553922
H	5.196140	-3.267400	-0.566847
H	0.066774	-0.922383	4.310447
H	0.862302	-2.498172	4.178351
H	1.768790	-1.018672	3.823500

17-MOM.out

ZPE	0.498443
DE	0.526626
DH	0.527570
DG	0.438802
E	-1120.286954
H	-1119.759384
G	-1119.848151

Cartesian coordinates

C	1.368100	-2.211021	2.068964
C	1.513923	-3.206262	-0.709384
C	1.994389	-1.300150	1.004379
C	2.407481	-2.094342	-0.223659
C	5.997179	-1.506945	-0.188843
C	3.599303	-1.901022	-0.807143
C	4.617825	-0.932366	-0.381651
C	3.531289	2.390069	-1.333298
C	4.380195	0.374656	-0.188148
C	3.174094	1.158824	-0.523398
C	1.884516	0.950456	-0.218374
C	0.857254	0.720845	1.992352
C	1.148860	-0.030836	0.677219
C	-0.183041	-0.427804	-0.017661
C	-1.342611	0.566144	0.021500
C	-2.578964	-0.091336	-0.524757
C	-3.680125	-0.308736	0.189340
H	2.016508	-3.074167	2.244108
H	1.264475	-1.685171	3.019665
H	0.383847	-2.592968	1.786434
H	0.497393	-2.860134	-0.908746
H	1.433885	-3.997722	0.042560
H	1.910594	-3.650331	-1.624865
H	2.914648	-0.907751	1.445611
H	5.995235	-2.260567	0.606103
H	6.331413	-2.011698	-1.101990
H	6.726016	-0.734519	0.065699
H	3.897690	-2.571768	-1.613017
H	4.035150	2.113027	-2.265751
H	2.647084	2.981896	-1.579923
H	4.226529	3.027624	-0.775507
H	5.233580	0.989443	0.099654
H	1.198913	1.692197	-0.617494
H	0.451884	1.715816	1.794642
H	0.134530	0.185747	2.614652
H	1.781407	0.844159	2.564786
H	-2.540764	-0.400216	-1.567764
H	-3.752733	-0.005154	1.228456
C	-4.857252	-0.978482	-0.403465
H	-1.529336	0.886622	1.050613
H	0.011482	-0.681086	-1.064984
O	-4.946069	-1.381090	-1.541697
O	-5.847058	-1.088705	0.494730
C	-7.050285	-1.718081	0.039777
H	-6.850404	-2.742759	-0.277758
H	-7.724292	-1.714463	0.893665
H	-7.487164	-1.156316	-0.787493
H	-0.567606	-1.333092	0.459340
O	-1.036386	1.710428	-0.781902
C	-1.830111	2.836571	-0.504947
H	-1.699862	3.506247	-1.361763
H	-2.883239	2.560833	-0.395630
O	-1.472961	3.478087	0.687048
C	-0.255243	4.199172	0.597555
H	-0.086078	4.665971	1.568084
H	0.590653	3.544333	0.365386
H	-0.322297	4.980090	-0.170345

17a-TBS.out

ZPE	0.690780
DE	0.730685
DH	0.731629
DG	0.619380
E	-1722.161976
H	-1721.430347
G	-1721.542596

Cartesian coordinates

C	0.988455	-2.515901	1.521120
C	-1.736008	-1.802194	2.453516
C	-0.130811	-2.417635	0.498644
C	-1.592880	-2.360314	1.038789
C	-3.828214	-5.283901	-0.235264
C	-2.311313	-3.671260	0.920198
C	-3.138765	-3.956729	-0.091239
C	-3.283162	-0.676824	-2.128282
C	-3.422312	-2.944092	-1.122677
C	-2.891990	-1.713709	-1.117817
C	-1.928561	-1.298730	-0.042458
C	-0.066229	-1.429360	-1.892043
C	-0.405094	-1.169122	-0.427109
C	0.143536	0.195733	0.057565
C	1.560004	0.547569	-0.439906
C	2.638709	-0.433767	-0.092081
C	3.399701	-1.053890	-0.990078
C	4.478338	-2.000568	-0.644605
H	-2.288989	-0.365126	0.390695
H	1.956770	-2.695577	1.051577
H	1.069846	-1.624732	2.148780
H	0.786623	-3.365193	2.182699
H	-1.349920	-2.501831	3.201722
H	-1.204718	-0.852795	2.569228
H	-2.793133	-1.620695	2.673086
H	-0.054132	-3.282338	-0.168164
H	-3.568942	-5.961237	0.581375
H	-4.916433	-5.158343	-0.248182
H	-3.553666	-5.762808	-1.181680
H	-2.110269	-4.415542	1.689646
H	-3.844006	-1.117453	-2.956116
H	-3.912840	0.086597	-1.659121
H	-2.410454	-0.154774	-2.527514
H	-4.129767	-3.216822	-1.903292
H	-0.261254	-0.554942	-2.518468
H	0.985554	-1.700667	-2.005566

H	-0.661116	-2.261011	-2.278885
H	2.821455	-0.573513	0.967672
H	3.249385	-0.911861	-2.055200
H	0.173894	0.195722	1.154316
H	1.510032	0.691720	-1.525608
O	5.145662	-2.581099	-1.473954
O	4.644085	-2.162268	0.672745
C	5.662847	-3.082505	1.078804
H	5.448365	-4.083108	0.700058
H	6.640572	-2.755766	0.721013
H	5.641910	-3.080649	2.166475
O	-0.726544	1.217620	-0.394836
O	1.897112	1.780778	0.190873
C	2.842020	2.524247	-0.524420
H	2.399891	2.897778	-1.463426
H	3.729538	1.915682	-0.762627
O	3.189657	3.587896	0.312261
C	3.966363	4.552043	-0.371241
H	3.405965	4.993987	-1.205332
H	4.214019	5.333341	0.346799
H	4.895623	4.116345	-0.760047
Si	-1.034951	2.701285	0.344804
C	-2.897365	3.055275	0.150459
C	-0.597434	2.596486	2.160932
H	-0.867755	3.527670	2.669521
H	-1.130126	1.778002	2.656370
H	0.476264	2.438660	2.288060
C	-0.101789	4.068930	-0.537057
H	0.058578	3.801949	-1.586512
H	-0.658696	5.010367	-0.517012
H	0.873684	4.241053	-0.076955
C	-3.219708	4.400504	0.825811
H	-2.650094	5.231917	0.400023
H	-4.284253	4.634246	0.694379
H	-3.022238	4.373615	1.902572
C	-3.761700	1.977282	0.818233
H	-3.498685	1.835341	1.872041
H	-4.820052	2.267897	0.779426
H	-3.672699	1.012489	0.317153
C	-3.253916	3.149150	-1.340729
H	-3.008389	2.226874	-1.874893
H	-4.329667	3.331541	-1.466065
H	-2.722478	3.972258	-1.830362

17a-TMS.out

ZPE	0.604816
DE	0.641030
DH	0.641975
DG	0.536792
E	-1604.229942
H	-1603.587967
G	-1603.693150

Cartesian coordinates

C	0.594756	2.261582	1.489349
C	2.564870	0.291908	2.476927
C	1.488299	1.564734	0.477081
C	2.700869	0.748396	1.026125
C	6.136441	1.868625	-0.429322
C	4.012617	1.443570	0.812597
C	4.841521	1.143632	-0.193924
C	3.123252	-1.849020	-1.937040
C	4.513077	0.050041	-1.125334
C	3.392220	-0.678338	-1.040364
C	2.372481	-0.389070	0.022562
C	0.923169	0.693808	-1.887153
C	1.041021	0.339660	-0.408390
C	-0.168686	-0.488338	0.075945
C	-1.557825	-0.035442	-0.407664
C	-1.959502	1.368034	-0.074497
C	-2.260613	2.286095	-0.989638
C	-2.675253	3.666461	-0.670965
H	2.149311	-1.332478	0.529405
H	-0.135828	2.911254	1.004969
H	0.057226	1.563356	2.136019
H	1.214399	2.894530	2.133398
H	2.651828	1.132409	3.172846
H	1.602257	-0.198220	2.652467
H	3.354960	-0.427951	2.714023
H	1.872407	2.325325	-0.209774
H	6.300031	2.649946	0.316096
H	6.983507	1.174760	-0.394844
H	6.146610	2.331112	-1.422506
H	4.263826	2.243924	1.507492
H	3.836648	-1.894816	-2.763409
H	3.198098	-2.780486	-1.365321
H	2.107840	-1.817687	-2.339904
H	5.246387	-0.183193	-1.894752
H	0.628684	-0.168507	-2.490955
H	0.181459	1.482933	-2.035381
H	1.877837	1.064750	-2.269618
H	-2.048379	1.597131	0.981989
H	-2.195477	2.069223	-2.050740
H	-0.182238	-0.481999	1.172948
H	-1.595168	-0.191510	-1.491758
O	-2.935971	4.495558	-1.516488
O	-2.729298	3.917351	0.641699
C	-3.114948	5.242728	1.021479
H	-2.408775	5.975109	0.627227
H	-4.119242	5.468828	0.659580
H	-3.097309	5.252210	2.109168
O	-0.008254	-1.809069	-0.402676
O	-2.486740	-0.907069	0.236012
C	-3.602076	-1.194673	-0.557115
H	-3.302582	-1.804332	-1.426834
H	-4.083178	-0.269019	-0.915351
O	-4.472240	-1.912276	0.267113
C	-5.537837	-2.478509	-0.470521
H	-5.167783	-3.195547	-1.214794
H	-6.179469	-2.999233	0.239781
H	-6.125594	-1.706694	-0.983636
Si	-0.275722	-3.236693	0.438492
C	1.232088	-4.300834	0.133422
C	-0.448406	-2.878913	2.265126
H	-0.560415	-3.818798	2.816698
H	0.435226	-2.365281	2.658697
H	-1.327310	-2.260594	2.467345
C	-1.782132	-4.121236	-0.225514
H	-1.775149	-4.138909	-1.320349
H	-1.786646	-5.160590	0.121970
H	-2.707432	-3.645493	0.108978
H	1.389039	-4.469106	-0.936688
H	2.136281	-3.838801	0.541518
H	1.107821	-5.279219	0.610814

17a-biomimetic.out

ZPE	0.435696
DE	0.459619
DH	0.460563
DG	0.383241
E	-929.344254
H	-928.883690
G	-928.961013

Cartesian coordinates

C	0.135353	-0.388993	2.235216
C	-2.773943	-0.585569	2.560950
C	-0.662127	-0.652441	0.968395
C	-2.219343	-0.604404	1.138384
C	-4.558411	-2.486835	-1.352145
C	-2.936562	-1.678102	0.363648
C	-3.800697	-1.413573	-0.623481
C	-3.451734	2.408510	-1.108411
C	-4.024890	-0.025301	-1.066405
C	-3.298781	1.004407	-0.612529
C	-2.230703	0.758721	0.408750
C	-0.678008	0.027056	-1.527871
C	-0.757727	0.526686	-0.079653
C	0.124076	1.736038	0.094518
C	2.167585	3.135487	0.236806
C	1.466735	1.812835	0.074508
C	2.290674	0.619160	-0.097063
C	3.629865	0.604105	-0.148857
H	-2.233351	1.573092	1.142020
H	1.209964	-0.399167	2.039727
H	-0.109712	0.579149	2.680566
H	-0.070831	-1.164600	2.978638
H	-2.630730	-1.551647	3.056124
H	-2.299828	0.187147	3.171714
H	-3.848696	-0.378705	2.531810
H	-0.310727	-1.580839	0.504925
H	-4.325783	-3.479162	-0.959822
H	-5.638550	-2.325534	-1.266988
H	-4.319312	-2.472570	-2.421323
H	-2.772116	-2.705059	0.686589
H	-4.234220	2.491116	-1.866229
H	-3.688285	3.088659	-0.282681
H	-2.508680	2.760004	-1.544056
H	-4.790759	0.141806	-1.820824
H	-0.952371	0.822158	-2.227746
H	0.337633	-0.294677	-1.769456
H	-1.348042	-0.819124	-1.691624
H	-0.415268	2.673135	0.228459
H	2.827427	3.127519	1.110425
H	2.790389	3.361899	-0.634627
H	1.445790	3.944440	0.360133
H	1.784568	-0.337052	-0.186020
H	4.230737	1.502245	-0.070858
C	4.349868	-0.669335	-0.313834
O	3.845153	-1.767767	-0.408650
O	5.678750	-0.471331	-0.346656
C	6.489739	-1.640262	-0.499950
H	6.259481	-2.148086	-1.438051
H	7.518277	-1.285733	-0.508591
H	6.335959	-2.326776	0.334358

17'-TBS.out

ZPE	0.689667
DE	0.730075
DH	0.731020
DG	0.617626
E	-1722.152436
H	-1721.421417
G	-1721.534810

Cartesian coordinates

C	1.524096	-1.411696	-2.558022
C	2.756948	-2.876649	-0.286563
C	2.325537	-0.585812	-1.541492
C	3.194334	-1.480709	-0.653838
C	6.347974	0.156967	-1.372478
C	4.430795	-1.088865	-0.316679
C	5.044596	0.215025	-0.621919
C	3.654731	2.243110	1.953768
C	4.512935	1.377285	-0.219711
C	3.331902	1.547088	0.652104
C	2.079953	1.155383	0.395622
C	1.414523	1.717436	-1.900757
C	1.479481	0.568477	-0.868142
H	2.202656	-2.053006	-3.127402
H	1.012905	-0.761961	-3.272249
H	0.773527	-2.057746	-2.096262
H	2.371793	-3.424038	-1.150643
H	3.600041	-3.439961	0.120173
H	1.975216	-2.880284	0.476923
H	3.056397	-0.031351	-2.134533
H	6.201596	-0.282889	-2.365065
H	7.065200	-0.482307	-0.845953
H	6.790122	1.148457	-1.493387
H	5.084226	-1.802072	0.186120
H	4.355419	1.645144	2.548041
H	2.756423	2.416760	2.550910
H	4.139847	3.208601	1.770378
H	5.068337	2.292060	-0.430713
H	1.341089	1.380322	1.157179
H	0.896977	2.582076	-1.486783
H	0.890958	1.409194	-2.811884
H	2.427606	2.025892	-2.171404
C	0.002330	0.155737	-0.586774
C	-0.203895	-0.989547	0.425706
O	-0.737334	1.272329	-0.150873
C	-1.603348	-1.521231	0.310718
H	0.496921	-1.788275	0.182360
O	0.034686	-0.505485	1.738741
Si	-2.138029	1.965430	-0.751887
C	-1.926521	-2.588777	-0.414843
H	-2.376019	-0.955847	0.821756
C	0.067256	-1.491916	2.732561
C	-3.013022	2.646490	0.783239
C	-1.718263	3.348512	-1.941287
C	-3.200901	0.708394	-1.646062
H	-1.172850	-3.173517	-0.933085
C	-3.315483	-3.035450	-0.634615
H	0.043868	-0.944580	3.681480
H	-0.794572	-2.163883	2.660588
O	1.197171	-2.314813	2.660333
C	-2.147338	3.738275	1.429538
C	-4.370464	3.242317	0.381079
C	-3.234275	1.515371	1.798038
H	-1.021738	4.067856	-1.501189
H	-1.266835	2.955350	-2.857453
H	-2.628802	3.888245	-2.223663
H	-3.700310	0.017668	-0.962006
H	-3.972585	1.235467	-2.217682
H	-2.612942	0.117917	-2.356465
O	-3.615300	-3.947223	-1.375708
O	-4.216844	-2.327330	0.055747
C	2.407677	-1.627331	2.941145
H	-1.164183	3.352528	1.717850
H	-1.992645	4.586841	0.755023
H	-2.634731	4.121491	2.335698
H	-4.261283	4.061512	-0.337672
H	-5.028965	2.488897	-0.064618
H	-4.882658	3.646121	1.264092
H	-3.727058	1.906331	2.698020

H	-3.875458	0.725026	1.391845
H	-2.285880	1.060337	2.100115
C	-5.591033	-2.671665	-0.146200
H	3.217549	-2.350481	2.842056
H	2.572411	-0.804535	2.239376
H	2.398459	-1.232995	3.965395
H	-5.778533	-3.702054	0.160073
H	-6.159024	-1.985610	0.478548
H	-5.868065	-2.543483	-1.193881
H	-0.404205	-0.212366	-1.534340

17'-TMS.out

ZPE	0.605174
DE	0.641625
DH	0.642569
DG	0.537132
E	-1604.217524
H	-1603.574955
G	-1603.680392

Cartesian coordinates

C	0.950051	-0.223766	-2.775762
C	2.111334	-2.572778	-1.397627
C	1.893463	0.053154	-1.596195
C	2.695555	-1.194500	-1.222276
C	5.985466	0.296794	-1.544434
C	3.987229	-1.084578	-0.881984
C	4.737785	0.170987	-0.711719
C	3.746113	1.156643	2.567252
C	4.370627	1.122984	0.156814
C	3.268086	1.045246	1.137845
C	1.964746	0.898367	0.878965
C	1.215520	2.369935	-0.936057
C	1.221939	0.902290	-0.443529
H	1.521560	-0.628345	-3.615723
H	0.471183	0.696196	-3.119524
H	0.162637	-0.943368	-2.538365
H	1.667077	-2.701301	-2.388202
H	2.889106	-3.330226	-1.276607
H	1.335331	-2.792231	-0.661001
H	2.651198	0.736333	-1.986554
H	5.737943	0.301068	-2.611583
H	6.646017	-0.560994	-1.376550
H	6.537330	1.210346	-1.311855
H	4.574422	-1.995750	-0.766095
H	4.409216	0.320963	2.819194
H	2.911196	1.159147	3.271874
H	4.325366	2.075330	2.714476
H	5.021478	1.991775	0.263652
H	1.305590	0.880821	1.740101
H	0.836481	3.037163	-0.162194
H	0.593895	2.492919	-1.829204
H	2.235234	2.679157	-1.179110
C	-0.271690	0.525714	-0.206415
C	-0.575584	-0.884527	0.330841
O	-0.886769	1.468937	0.647137
C	-2.062098	-1.108444	0.268879
H	-0.077002	-1.607160	-0.317663
O	-0.112929	-1.010056	1.665344
Si	-2.204630	2.452523	0.306888
C	-2.692878	-1.538793	-0.820995
H	-2.623911	-0.832194	1.156028
C	-0.156719	-2.312011	2.182718
C	-1.696860	4.207884	0.694801
C	-2.687777	2.280788	-1.492158
H	-2.147642	-1.817451	-1.717557
C	-4.160816	-1.608984	-0.947059
H	-0.030084	-2.197727	3.265031
H	-1.112295	-2.799587	1.962008
O	0.830541	-3.150517	1.653403
H	-1.288247	4.282933	1.707745
H	-0.938827	4.570997	-0.005459
H	-2.561499	4.877540	0.633022
H	-3.033396	1.268171	-1.724281
H	-3.508963	2.971413	-1.713554
H	-1.857288	2.523954	-2.162500
O	-4.729507	-1.934301	-1.967377
O	-4.806946	-1.262286	0.172080
C	2.144044	-2.773455	2.039004
C	-6.236787	-1.256898	0.111353
H	2.832411	-3.469658	1.559553
H	2.378473	-1.755092	1.715602
H	2.260486	-2.842508	3.128261
H	-6.616120	-2.255454	-0.111141
H	-6.569847	-0.940414	1.097572
H	-6.585268	-0.553440	-0.646613
H	-0.751591	0.559064	-1.188199
C	-3.632046	1.956537	1.407685
H	-3.315035	1.875403	2.452469
H	-4.423647	2.712512	1.357295
H	-4.065483	0.998625	1.104845

18-TBS.out

ZPE	0.695861
DE	0.733707
DH	0.734651
DG	0.628868
E	-1722.201046
H	-1721.466394
G	-1721.572178

Cartesian coordinates

C	-1.213997	-3.560059	0.159319
C	-0.565555	-2.529876	-2.395935
C	-0.012162	-2.602954	0.137965
C	0.448079	-2.313302	-1.294541
C	4.101750	-1.549926	-1.712877
C	1.654146	-1.854158	-1.654980
C	2.841968	-1.327268	-0.863390
C	2.592330	-2.169390	2.925118
C	3.055941	-1.949672	0.495030
C	2.333910	-1.609336	1.558328
C	1.183126	-0.657789	1.389842
C	-0.866664	-1.777026	2.376250
C	-0.191015	-1.349620	1.068088
C	-0.970114	-0.160743	0.449328
C	0.043184	0.622547	-0.386468
C	1.400363	0.447376	0.315268
C	2.555097	0.205632	-0.670423
C	3.793949	0.952355	-0.228597
H	-1.400288	-3.925203	1.169679
H	-2.129216	-3.094326	-0.208707
H	-1.003856	-4.437602	-0.457293
H	-0.872303	-3.576321	-2.478556
H	-0.163510	-2.219527	-3.362632
H	-1.465120	-1.943362	-2.187946
H	0.801382	-3.159475	0.609369
H	4.034122	-1.022025	-2.667540
H	5.001186	-1.205238	-1.194829
H	4.221889	-2.617915	-1.917451
H	1.795708	-1.693833	-2.724250
H	1.736208	-2.745508	3.289983

H	3.469282	-2.821108	2.929281
H	2.756933	-1.359677	3.644660
H	3.870976	-2.663561	0.590482
H	1.034368	-0.140968	2.342886
H	-0.854865	-0.949268	3.091325
H	-1.906590	-2.061716	2.216248
H	-0.357977	-2.628730	2.835143
H	1.634168	1.364101	0.850509
H	2.285435	0.610083	-1.649682
O	4.166526	1.097339	0.912185
O	4.458834	1.464163	-1.276041
C	5.680623	2.145025	-0.976750
H	6.393351	1.464878	-0.506449
H	6.068339	2.490116	-1.933051
H	5.496759	2.994674	-0.317067
H	0.061521	0.179758	-1.379928
O	-0.351800	1.973286	-0.646484
C	-0.163386	2.910159	0.354905
H	-0.958457	3.660279	0.255978
H	-0.217849	2.462624	1.360483
O	1.095131	3.527137	0.176375
C	1.439190	4.338639	1.280019
H	2.400974	4.800681	1.056920
H	0.695401	5.128732	1.448934
H	1.532973	3.742953	2.198489
H	-1.288955	0.476059	1.288225
O	-2.077570	-0.536168	-0.331792
Si	-3.722288	-0.324549	-0.109492
C	-4.470457	-1.394018	-1.445201
H	-5.561653	-1.419828	-1.363859
H	-4.214521	-1.022579	-2.442239
H	-4.102827	-2.421664	-1.361256
C	-4.252493	-0.910866	1.587597
H	-4.127112	-1.993311	1.687512
H	-3.680032	-0.424780	2.383079
H	-5.310980	-0.679329	1.748555
C	-4.237218	1.490210	-0.333252
C	-3.802311	2.325724	0.880491
H	-2.723035	2.278747	1.049689
H	-4.064377	3.380963	0.726927
H	-4.298428	1.993259	1.798093
C	-5.768617	1.559588	-0.457043
H	-6.089977	2.606167	-0.539395
H	-6.128737	1.034579	-1.347622
H	-6.274224	1.130165	0.414828
C	-3.604058	2.067798	-1.606828
H	-2.512845	2.073356	-1.541015
H	-3.891747	1.496072	-2.496276
H	-3.942076	3.101943	-1.758879

18-TMS.out

ZPE	0.609918
DE	0.644122
DH	0.645067
DG	0.546177
E	-1604.266477
H	-1603.621411
G	-1603.720301

Cartesian coordinates

C	-2.205980	-3.091403	0.187824
C	-1.286502	-2.331283	-2.375197
C	-0.857122	-2.354839	0.182296
C	-0.295576	-2.224280	-1.237643
C	3.448074	-2.075688	-1.513847
C	0.982411	-1.984975	-1.561537
C	2.206619	-1.607194	-0.741050
C	1.661214	-2.179795	3.066654
C	2.260735	-2.175874	0.655934
C	1.559796	-1.663372	1.662667
C	0.586935	-0.551780	1.389199
C	-1.666781	-1.268369	2.325132
C	-0.866021	-1.038039	1.037736
C	-1.412974	0.217536	0.322297
C	-0.263708	0.779051	-0.511909
C	1.019788	0.440990	0.267698
C	2.162049	-0.039130	-0.642743
C	3.486234	0.526521	-0.179510
H	-2.489903	-3.368659	1.203539
H	-3.010032	-2.489286	-0.238415
H	-2.128674	-4.020834	-0.381814
H	-1.757726	-3.316823	-2.425226
H	-0.800899	-2.140844	-3.334484
H	-2.085049	-1.596177	-2.236273
H	-0.170047	-3.011636	0.721295
H	3.505466	-1.601174	-2.496800
H	4.369030	-1.847253	-0.969960
H	3.403842	-3.159430	-1.656619
H	1.189705	-1.909595	-2.629543
H	0.705189	-2.584689	3.413307
H	2.415224	-2.966213	3.148969
H	1.927552	-1.368811	3.753562
H	2.942705	-3.005658	0.827340
H	0.484743	0.037154	2.305865
H	-1.535097	-0.420715	3.003935
H	-2.734010	-1.363665	2.116483
H	-1.348578	-2.173772	2.848251
H	1.370315	1.344062	0.762168
H	2.002130	0.343334	-1.654454
O	3.832577	0.676846	0.968859
O	4.264917	0.865379	-1.218915
C	5.568304	1.359495	-0.898059
H	6.142870	0.604067	-0.358571
H	6.043439	1.579735	-1.851875
H	5.499348	2.266120	-0.294528
H	-0.273874	0.278223	-1.477268
O	-0.441545	2.154142	-0.864920
C	-0.200470	3.106182	0.112123
H	-0.884841	3.944676	-0.067724
H	-0.373726	2.716412	1.127852
O	1.136327	3.551380	-0.000702
C	1.501491	4.378868	1.084003
H	2.527546	4.705302	0.913880
H	0.853902	5.263113	1.154332
H	1.453440	3.832451	2.036073
H	-1.640170	0.948061	1.114731
O	-2.555751	-0.017025	-0.464111
Si	-4.022532	0.776867	-0.309355
C	-4.993827	0.213845	-1.796763
H	-6.002618	0.639519	-1.791700
H	-4.502330	0.518678	-2.725770
H	-5.089057	-0.876764	-1.804290
C	-4.866461	0.263485	1.279406
H	-5.021657	-0.819414	1.315673
H	-4.275412	0.553403	2.154103
H	-5.845423	0.748497	1.363822
C	-3.752499	2.626600	-0.292757
H	-3.222477	2.958225	-1.189693
H	-4.712779	3.151584	-0.242244
H	-3.163207	2.927575	0.579623

18-biomimetic.out

ZPE	0.440461

DE	0.462326
DH	0.463270
DG	0.392605
E	-929.375010
H	-928.911740
G	-928.982405

Cartesian coordinates

C	3.938487	0.037797	-0.889744
C	2.381380	-2.125059	-1.828777
C	2.426664	0.194518	-0.682586
C	1.629880	-0.874373	-1.434082
C	-1.874899	0.039772	-2.390388
C	0.316615	-0.846299	-1.694243
C	-0.800405	0.105243	-1.293674
C	0.674716	3.382801	0.189650
C	-0.382224	1.542264	-1.107105
C	0.240021	1.962541	-0.010438
C	0.612131	0.965601	1.047235
C	3.083277	1.033575	1.650425
C	2.021633	0.280717	0.837233
C	1.771771	-1.089029	1.418353
C	-0.095468	-2.642174	2.130728
C	0.484678	-1.366898	1.611448
C	-0.401853	-0.191694	1.253519
C	-1.356878	-0.458721	0.065141
H	4.470317	0.909211	-0.505537
H	4.344633	-0.848920	-0.394524
H	4.172788	-0.034076	-1.954469
H	3.199681	-1.920217	-2.524324
H	1.714225	-2.852755	-2.294781
H	2.827832	-2.593986	-0.944518
H	2.165763	1.162866	-1.114904
H	-2.273820	-0.972351	-2.495572
H	-2.708068	0.716221	-2.178009
H	-1.438924	0.338825	-3.348039
H	-0.081807	-1.724331	-2.203687
H	1.766483	3.446819	0.259888
H	0.346156	4.024148	-0.631665
H	0.274598	3.782309	1.127980
H	-0.620710	2.237730	-1.908664
H	0.685288	1.494582	2.001480
H	2.737742	1.159851	2.680241
H	4.029285	0.488028	1.684382
H	3.279805	2.026865	1.235303
H	2.584361	-1.785795	1.607398
H	-0.685671	-2.458978	3.035454
H	-0.772212	-3.095601	1.398451
H	0.685366	-3.368673	2.366530
H	-1.030223	0.046527	2.116878
H	-1.485244	-1.534565	-0.072516
C	-2.733469	0.099882	0.352413
O	-2.975799	1.165604	0.868818
O	-3.697715	-0.746789	-0.042641
C	-5.044162	-0.288449	0.111572
H	-5.211336	0.614159	-0.479323
H	-5.674845	-1.096533	-0.253494
H	-5.264714	-0.083968	1.160539

18'.out

ZPE	0.695653
DE	0.733442
DH	0.734386
DG	0.629042
E	-1722.201106
H	-1721.466720
G	-1721.572064

Cartesian coordinates

C	1.345657	-3.607535	0.398089
C	0.744383	-2.739398	-2.214834
C	0.072521	-2.758438	0.288484
C	-0.313174	-2.475709	-1.166599
C	-3.861683	-1.471200	-1.841971
C	-1.467026	-1.939073	-1.585752
C	-2.687520	-1.396699	-0.850210
C	-2.685725	-2.866068	2.755091
C	-3.043040	-2.193392	0.380370
C	-2.414986	-2.031616	1.540756
C	-1.326472	-1.004409	1.636290
C	0.961178	-1.663983	2.429537
C	0.118857	-1.455277	1.166483
C	0.641329	-0.219339	0.373968
C	-0.264637	0.932832	0.784300
C	-1.656002	0.295458	0.883311
C	-2.361916	0.106094	-0.479955
C	-3.626466	0.938059	-0.502797
H	1.484585	-3.954291	1.422790
H	2.245846	-3.062320	0.105437
H	1.267983	-4.497546	-0.230232
H	0.995513	-3.801308	-2.289744
H	0.414467	-2.399545	-3.198325
H	1.672942	-2.213586	-1.967594
H	-0.722000	-3.376720	0.712116
H	-3.668211	-0.867973	-2.732745
H	-4.795227	-1.129502	-1.386247
H	-4.005732	-2.507860	-2.159014
H	-1.539867	-1.761887	-2.658823
H	-1.780625	-3.410200	3.050110
H	-3.483448	-3.591676	2.579759
H	-2.964760	-2.235265	3.606158
H	-3.815005	-2.951797	0.270003
H	-1.224065	-0.730015	2.689788
H	0.943210	-0.758930	3.042686
H	2.003923	-1.881262	2.200102
H	0.549002	-2.483713	3.026861
H	-2.307606	0.895955	1.518223
H	-1.727022	0.495020	-1.277493
O	-4.467013	0.970398	0.366339
O	-3.723626	1.656157	-1.630199
C	-4.911847	2.440401	-1.779821
H	-5.794532	1.798468	-1.787414
H	-4.810284	2.949906	-2.735711
H	-4.995745	3.169054	-0.971813
O	2.009536	0.024706	0.588130
Si	3.035328	0.902234	-0.408370
C	2.348771	0.979729	-2.147672
C	3.255289	2.621633	0.292295
C	4.684711	-0.035687	-0.378937
H	3.092736	1.413518	-2.824726
H	2.087387	-0.012303	-2.528225
H	1.452117	1.604509	-2.174927
H	2.278219	3.088868	0.448368
H	3.779231	2.593355	1.253543
H	3.836826	3.252119	-0.388650
C	5.045858	-0.410071	1.065634
C	5.790932	0.855117	-0.964991
C	4.574325	-1.316081	-1.218515
H	4.290929	-1.068134	1.506715
H	6.010118	-0.934948	1.092507
H	5.135091	0.474271	1.706164
H	6.741193	0.306193	-0.997990

H	5.561402	1.173487	-1.988147
H	5.950971	1.754448	-0.361634
H	3.775232	-1.969704	-0.855214
H	4.373686	-1.095561	-2.271996
H	5.512821	-1.884252	-1.171979
O	-0.137244	1.985283	-0.160084
C	-0.757157	3.171566	0.197115
H	-0.754668	3.809102	-0.695251
H	-1.797180	3.009004	0.524880
O	-0.033905	3.782058	1.240551
C	-0.688439	4.936512	1.725130
H	-0.066958	5.354176	2.517183
H	-0.812025	5.688839	0.935014
H	-1.676838	4.691919	2.136158
H	0.034757	1.294708	1.774403
H	0.468702	-0.377276	-0.694568

18'-TMS.out

ZPE	0.610070
DE	0.644291
DH	0.645235
DG	0.546095
E	-1604.265283
H	-1603.620048
G	-1603.719188

Cartesian coordinates

C	1.656764	-3.707139	0.232921
C	0.913299	-2.858501	-2.335989
C	0.410355	-2.810601	0.209590
C	-0.042780	-2.493275	-1.221719
C	-3.531912	-1.216660	-1.721813
C	-1.171663	-1.865843	-1.579088
C	-2.311238	-1.238739	-0.785130
C	-2.244183	-2.756892	2.798190
C	-2.665488	-2.025886	0.451468
C	-1.972713	-1.926492	1.581191
C	-0.812083	-0.978445	1.635468
C	1.443624	-1.814691	2.332611
C	0.574601	-1.527760	1.102922
C	1.154908	-0.326717	0.300764
C	0.353020	0.885993	0.748558
C	-1.076689	0.351444	0.908673
C	-1.859883	0.231620	-0.418919
C	-3.061224	1.151970	-0.371391
H	1.836717	-4.082744	1.240702
H	2.558306	-3.182206	-0.094935
H	1.517209	-4.579222	-0.409107
H	1.036317	-3.941229	-2.432098
H	0.561779	-2.473247	-3.294747
H	1.908859	-2.444507	-2.148324
H	-0.385258	-3.400555	0.672300
H	-3.336332	-0.618211	-2.615282
H	-4.416463	-0.814339	-1.220160
H	-3.765209	-2.236470	-2.040382
H	-1.289699	-1.688417	-2.648047
H	-1.365101	-3.362608	3.047963
H	-3.094756	-3.426570	2.651018
H	-2.444335	-2.119925	3.666736
H	-3.493346	-2.726695	0.368932
H	-0.646015	-0.723564	2.685656
H	1.506361	-0.921332	2.959779
H	2.460857	-2.098025	2.066704
H	0.996126	-2.615073	2.930944
H	-1.649914	0.992342	1.578787
H	-1.238658	0.583340	-1.244068
O	-3.848503	1.239293	0.542707
O	-3.170280	1.879043	-1.491914
C	-4.310594	2.740099	-1.578506
H	-5.232538	2.156989	-1.541991
H	-4.225157	3.246852	-2.537422
H	-4.305393	3.468288	-0.765848
O	2.545276	-0.182648	0.462298
Si	3.595283	0.553782	-0.619090
C	2.831284	0.640553	-2.324104
C	4.013299	2.267364	-0.004130
H	3.550670	1.075148	-3.026993
H	2.553586	-0.348569	-2.700753
H	1.937759	1.270668	-2.316433
H	3.102961	2.865482	0.100475
H	4.506194	2.224123	0.972889
H	4.690197	2.777330	-0.698598
O	0.517335	1.926051	-0.203891
C	0.027727	3.161513	0.187197
H	0.015301	3.793919	-0.708731
H	-0.993979	3.086884	0.593907
O	0.876249	3.713462	1.167120
C	0.357111	4.920109	1.687219
H	1.069343	5.289183	2.425115
H	0.235173	5.676465	0.900637
H	-0.613609	4.759903	2.174910
H	0.720726	1.223841	1.723995
H	0.929324	-0.465482	-0.760684
C	5.121564	-0.524184	-0.633904
H	5.897264	-0.096046	-1.277979
H	5.540689	-0.626778	0.372309
H	4.886842	-1.526546	-1.006937

TS-1.out

ZPE	0.686447
DE	0.727508
DH	0.728452
DG	0.611182
E	-1722.108355
H	-1721.379903
G	-1721.497172
F	-501.214

Cartesian coordinates

C	1.471133	-3.180691	1.247136
C	0.488626	-2.752164	0.366650
C	2.845344	-3.299358	0.964773
C	3.710790	-2.705421	0.043241
C	0.844717	-0.568643	0.511289
C	1.352683	-0.399140	-0.770180
C	2.613038	-0.714110	-1.297246
C	3.578131	-1.637597	-0.881415
H	-0.512612	-2.719192	0.787894
C	0.494145	-3.076948	-1.099820
H	1.491221	-3.064602	-1.537586
H	-0.145016	-2.391693	-1.657835
H	0.087746	-4.088363	-1.224480
H	4.486378	-1.544999	-1.476124
H	3.365408	-3.930890	1.684718
H	0.653576	0.006579	-1.497433
C	1.734332	-0.406375	1.715004
H	2.674001	-0.944135	1.610078
H	1.237191	-0.734269	2.629794
H	1.965766	0.656378	1.833931
C	1.058819	-3.514348	2.666425
H	0.049920	-3.149975	2.874293
H	1.739378	-3.082731	3.405145

H	1.053340	-4.599848	2.818702
C	5.125842	-3.279553	0.046277
H	5.243719	-4.069750	0.789527
H	5.871604	-2.505716	0.251900
H	5.367316	-3.707902	-0.931960
C	2.916244	0.015957	-2.599042
H	2.268074	-0.353742	-3.401555
H	3.950323	-0.129798	-2.916566
H	2.734159	1.090455	-2.505046
C	-0.591046	-0.093366	0.735508
H	-0.993624	-0.613513	1.615191
C	-0.710971	1.426651	1.060432
H	-1.783509	1.642311	1.003243
O	-1.361938	-0.334981	-0.411928
O	-0.256866	1.664909	2.378518
Si	-2.961654	-0.841445	-0.492323
C	-4.019147	0.155899	0.685642
H	-5.048813	-0.217082	0.669286
H	-3.652757	0.065241	1.713734
H	-4.040058	1.218099	0.426150
C	-3.414556	-0.531177	-2.300350
C	-2.458287	-1.310595	-3.215545
H	-1.421594	-0.987935	-3.077713
H	-2.503326	-2.389023	-3.030301
H	-2.724315	-1.144185	-4.267578
C	-4.857245	-0.992899	-2.555443
H	-4.979507	-2.066082	-2.374780
H	-5.574267	-0.460352	-1.921189
H	-5.135639	-0.800958	-3.599584
C	-3.295779	0.968844	-2.608747
H	-3.533391	1.157781	-3.663642
H	-3.986730	1.564820	-2.003495
H	-2.281549	1.337427	-2.423902
C	-3.093468	-2.650643	-0.038725
H	-2.801605	-2.816361	1.003482
H	-4.130375	-2.987232	-0.145188
H	-2.464507	-3.279026	-0.675437
C	-1.005158	2.630770	3.073297
H	-0.456504	2.801072	4.006055
H	-1.086509	3.559043	2.499434
O	-2.319458	2.225457	3.327946
C	-2.409229	1.079496	4.157789
H	-3.465951	0.925488	4.376085
H	-2.011911	0.188818	3.659762
H	-1.864761	1.233519	5.098130
C	-0.013607	2.262108	0.037073
H	-0.373635	2.143711	-0.981573
C	1.005508	3.082703	0.276449
H	1.406985	3.223782	1.273092
C	1.663071	3.792763	-0.836721
O	1.329506	3.756231	-2.000848
O	2.719174	4.497818	-0.400348
C	3.458076	5.212252	-1.396656
H	4.264513	5.711156	-0.863401
H	3.866978	4.523608	-2.138017
H	2.822662	5.948329	-1.892004

TS-1-TMS.out

ZPE	0.601357
DE	0.638495
DH	0.639439
DG	0.531575
E	-1604.172479
H	-1603.533040
G	-1603.640904
F	-500.847

Cartesian coordinates

C	-1.580302	-2.944468	-1.135382
C	-0.795386	-2.676757	-0.023759
C	-2.964488	-2.714956	-1.253746
C	-3.870446	-1.850413	-0.636530
C	-0.539907	-0.492925	-0.298638
C	-1.326289	-0.090980	0.772393
C	-2.721336	-0.048176	0.912633
C	-3.733123	-0.757394	0.258158
H	0.256378	-2.916210	-0.150570
C	-1.269383	-2.853964	1.390570
H	-2.300992	-2.537800	1.539996
H	-0.629851	-2.311103	2.088693
H	-1.207927	-3.920599	1.639536
H	-4.716553	-0.397930	0.559068
H	-3.410818	-3.276353	-2.074405
H	-0.780074	0.206594	1.663815
C	-0.987286	-0.241709	-1.714270
H	-2.022192	-0.534454	-1.877845
H	-0.352826	-0.761011	-2.434850
H	-0.904621	0.829768	-1.920272
C	-0.898114	-3.495079	-2.371319
H	0.188406	-3.422600	-2.281652
H	-1.204641	-2.969103	-3.279509
H	-1.146664	-4.554180	-2.505518
C	-5.327825	-2.077198	-1.032029
H	-5.432100	-2.887235	-1.755524
H	-5.769884	-1.175110	-1.465760
H	-5.926746	-2.339288	-0.153786
C	-3.179227	0.866010	2.041476
H	-4.265883	0.962688	2.074082
H	-2.748347	1.866648	1.941248
H	-2.852061	0.468634	3.008665
C	0.972670	-0.383778	-0.102176
H	1.461176	-1.061914	-0.814671
C	1.546348	1.030480	-0.422269
H	2.567565	1.018989	-0.026716
O	1.315040	-0.695394	1.226483
O	1.590703	1.206067	-1.825470
Si	2.662523	-1.578266	1.714079
C	2.609128	-3.300494	0.989860
H	1.741732	-3.862983	1.347942
H	2.581059	-3.279944	-0.104545
H	3.511040	-3.848159	1.285110
C	4.228456	-0.726885	1.149091
C	2.525190	-1.620939	3.569793
H	1.590597	-2.099310	3.878935
H	3.354645	-2.188036	4.004914
H	2.548417	-0.611555	3.991527
C	2.721787	1.905282	-2.280234
H	2.544185	2.070116	-3.348577
H	2.836992	2.859463	-1.756905
O	3.917502	1.210271	-2.069549
C	3.982657	-0.029330	-2.754865
H	4.994160	-0.413735	-2.623711
H	3.268033	-0.752536	-2.347771
H	3.782710	0.103343	-3.825725
C	0.787827	2.108911	0.280402
H	0.769413	2.034061	1.364236
C	0.128287	3.099280	-0.314089
H	0.107725	3.209246	-1.391918
C	-0.650416	4.060486	0.489296
O	-0.720556	4.086261	1.698500
O	-1.306799	4.925566	-0.300208
H	4.283906	-0.670898	0.056980
H	4.302987	0.290172	1.546417

H	5.102712	-1.288653	1.496258
C	-2.122043	5.896228	0.364791
H	-1.514046	6.528107	1.014369
H	-2.571914	6.493405	-0.425510
H	-2.898797	5.405645	0.953854

TS-2.out

ZPE	0.686227
DE	0.727420
DH	0.728365
DG	0.610361
E	-1722.105340
H	-1721.376976
G	-1721.494979
F	-502.648

Cartesian coordinates

C	0.876128	-3.323691	-0.507474
C	0.454404	-2.740493	0.678102
C	2.207302	-3.590395	-0.880630
C	3.450263	-3.063608	-0.524708
C	0.890882	-0.611710	0.203224
C	1.958330	-0.461063	1.081329
C	3.283760	-0.910561	0.993907
C	3.857244	-1.954373	0.259001
H	-0.620204	-2.608330	0.755236
C	1.109103	-2.985544	2.007140
H	2.195557	-3.035807	1.951840
H	0.831097	-2.217780	2.733731
H	0.748561	-3.946926	2.392797
H	4.942043	-1.949970	0.362179
H	2.272986	-4.310494	-1.696056
H	1.730305	0.063187	2.005655
C	1.113642	-0.612879	-1.286502
H	1.952891	-1.241850	-1.574809
H	0.220195	-0.935121	-1.820037
H	1.346168	0.407657	-1.608389
C	-0.173723	-3.677968	-1.540385
H	-1.152623	-3.292360	-1.253310
H	0.073988	-3.282093	-2.529388
H	-0.259570	-4.766472	-1.636150
C	4.643817	-3.794734	-1.135001
H	4.332770	-4.637376	-1.754401
H	5.249449	-3.124489	-1.752634
H	5.297048	-4.185740	-0.348329
C	4.226632	-0.216585	1.968839
H	5.271481	-0.350681	1.681743
H	4.025876	0.855340	2.032675
H	4.107458	-0.633948	2.975322
C	-0.434676	0.004723	0.664807
H	-0.659588	-0.377226	1.669672
C	-0.417005	1.555201	0.820107
O	-1.452667	-0.321744	-0.246537
H	-1.466448	1.829715	0.973295
O	0.325815	1.901540	1.973925
C	0.057553	2.261951	-0.405693
Si	-3.068534	-0.644574	0.088502
C	-0.233596	2.950834	2.723964
H	-0.495497	2.041986	-1.315406
C	1.083688	3.107811	-0.448190
C	-3.780605	0.640120	1.248488
C	-3.881452	-0.583207	-1.616199
C	-3.249296	-2.321046	0.898467
H	0.521246	3.195351	3.479204
H	-0.444488	3.820401	2.094017
O	-1.451561	2.609087	3.320008
H	1.663168	3.348687	0.435041
C	1.486948	3.727293	-1.724154
H	-4.816793	0.379917	1.490180
H	-3.222980	0.676524	2.190328
H	-3.777983	1.643900	0.814260
C	-5.379401	-0.894864	-1.479051
C	-3.703960	0.819150	-2.217450
C	-3.227831	-1.616594	-2.545441
H	-4.303176	-2.501970	1.136233
H	-2.902496	-3.135565	0.256850
H	-2.690025	-2.363706	1.839194
C	-1.347362	1.552734	4.259891
O	0.955399	3.553284	-2.798910
O	2.551722	4.527586	-1.555102
H	-5.550967	-1.896312	-1.070296
H	-5.888343	-0.173958	-0.830207
H	-5.864998	-0.852731	-2.462400
H	-4.158880	0.862587	-3.215504
H	-4.182884	1.589090	-1.603603
H	-2.645968	1.080516	-2.320992
H	-2.157922	-1.423859	-2.670516
H	-3.343664	-2.637000	-2.165418
H	-3.694978	-1.578562	-3.538211
H	-2.321662	1.453881	4.738397
H	-1.088029	0.605865	3.774748
H	-0.591570	1.779688	5.022504
C	3.046731	5.180255	-2.728893
H	2.279239	5.822395	-3.164135
H	3.892803	5.778848	-2.397983
H	3.372101	4.446257	-3.468000

TS-2-TMS.out

ZPE	0.601868
DE	0.638852
DH	0.639796
DG	0.532356
E	-1604.170494
H	-1603.530698
G	-1603.638138
F	-494.733

Cartesian coordinates

C	-3.098976	-0.829442	-1.080238
C	-2.715101	-0.030021	-0.015117
C	-3.305470	-2.221976	-1.053874
C	-2.848853	-3.266874	-0.248724
C	-0.526371	-0.498996	-0.011817
C	-0.509727	-1.240852	1.163184
C	-0.942845	-2.548047	1.429852
C	-1.871931	-3.362885	0.774627
H	-2.596107	1.020847	-0.268305
C	-3.151923	-0.243180	1.404510
H	-3.187665	-1.292787	1.693214
H	-2.500624	0.290817	2.101991
H	-4.161418	0.170418	1.518888
H	-1.888591	-4.360385	1.212524
H	-3.887480	-2.572083	-1.905601
H	-0.125155	-0.721102	2.036765
C	-0.297137	-1.164630	-1.342846
H	-0.878884	-2.077938	-1.448454
H	-0.527582	-0.493232	-2.169197
H	0.759314	-1.442449	-1.420017
C	-3.273717	-0.151684	-2.424690
H	-2.572160	0.680064	-2.516825
H	-3.100767	-0.836774	-3.257533
H	-4.283941	0.260324	-2.529161

C	-3.486332	-4.620968	-0.551518
H	-4.222980	-4.554669	-1.353587
H	-2.733976	-5.360898	-0.841201
H	-3.996631	-5.010528	0.335206
C	-0.392355	-3.112947	2.733090
H	-0.551947	-4.190430	2.805748
H	0.677881	-2.918620	2.837319
H	-0.893865	-2.647551	3.589333
C	-0.020022	0.939225	0.116574
H	-0.549371	1.400846	0.955766
C	1.493903	1.086506	0.471224
O	-0.270364	1.647526	-1.073954
H	1.717750	2.151520	0.324745
O	1.739639	0.740172	1.820851
C	2.377482	0.317845	-0.450394
Si	-0.664538	3.285050	-1.166990
C	1.957191	1.834599	2.675407
H	2.232969	0.517606	-1.508689
C	3.284938	-0.576396	-0.067396
C	0.888652	4.281207	-1.467205
C	-1.830178	3.445726	-2.612409
C	-1.472723	3.810646	0.434514
H	2.291846	1.399508	3.622915
H	2.724619	2.497035	2.263238
O	0.823530	2.631669	2.860087
H	3.452472	-0.805330	0.977559
C	4.079136	-1.308975	-1.071147
H	0.635785	5.327986	-1.668500
H	1.556292	4.261779	-0.599961
H	1.441021	3.897727	-2.331078
H	-0.763159	3.775097	1.267092
H	-1.834320	4.840693	0.343501
H	-2.329610	3.175982	0.684331
C	-0.185476	2.021275	3.648563
O	4.000538	-1.180951	-2.273420
O	4.923771	-2.169492	-0.480407
H	0.186627	1.807903	4.657919
H	-1.013643	2.727269	3.711896
H	-0.545903	1.090200	3.199071
C	5.745694	-2.951394	-1.353260
H	6.352553	-3.578006	-0.703019
H	5.130041	-3.572535	-2.006061
H	6.385556	-2.306767	-1.958212
H	-2.799270	2.987035	-2.395443
H	-2.001525	4.502697	-2.842898
H	-1.418679	2.970070	-3.508131

TS-3.out

ZPE	0.690798
DE	0.729355
DH	0.730300
DG	0.623980
E	-1722.125332
H	-1721.395033
G	-1721.501352
F	-450.791

Cartesian coordinates

C	1.009276	-2.910385	1.411527
C	0.553899	-0.350810	2.669415
C	-0.192499	-2.098040	0.910271
C	-0.552191	-0.996359	1.876155
C	-4.248678	-0.701467	2.369858
C	-1.813971	-0.576457	2.063960
C	-3.070807	-1.018068	1.478089
C	-3.472920	-2.459590	-2.033619
C	-3.343823	-1.774297	0.347289
C	-2.674027	-1.897624	-0.880900
C	-1.430861	-1.342667	-1.217365
C	0.563857	-2.753255	-1.405880
C	-0.064779	-1.620777	-0.573679
C	0.728090	-0.322211	-0.841854
C	-0.151327	0.886384	-0.534657
C	-1.580602	0.644833	-0.985154
C	-2.601841	1.130812	-0.166132
C	-3.962562	1.138743	-0.617656
H	1.100602	-3.849734	0.864831
H	1.944437	-2.361455	1.306360
H	0.872442	-3.164304	2.466051
H	0.971969	-1.048959	3.402042
H	0.190123	0.527558	3.206833
H	1.373157	-0.053019	2.010016
H	-1.041318	-2.789497	0.893057
H	-4.313291	0.380803	2.518021
H	-5.192969	-1.041054	1.942870
H	-4.120959	-1.157429	3.357650
H	-1.951937	0.208209	2.805774
H	-2.993307	-3.362205	-2.427364
H	-4.495708	-2.709061	-1.745646
H	-3.517170	-1.729292	-2.846580
H	-1.289974	-1.357764	-2.298869
H	0.544764	-2.498267	-2.468914
H	1.604209	-2.921563	-1.122777
H	0.013655	-3.688888	-1.269175
H	-1.747540	0.738294	-2.056085
H	-2.387865	1.537599	0.811610
H	-0.144450	1.074289	0.539565
H	0.901678	-0.294991	-1.929179
O	-4.373424	0.638685	-1.655772
O	-4.802935	1.748819	0.264571
C	-6.190885	1.655128	-0.032732
H	-6.510473	0.611099	-0.080719
H	-6.706118	2.160904	0.782791
H	-6.427723	2.145155	-0.979931
O	1.956703	-0.252615	-0.156020
Si	3.468264	-0.022766	-0.853921
C	3.843154	-1.444183	-2.013915
C	3.525548	1.572564	-1.827088
C	4.695096	0.013760	0.591766
H	3.920605	-2.397137	-1.482414
H	3.059387	-1.541691	-2.772038
H	4.788932	-1.267776	-2.536840
H	2.795388	1.551130	-2.640866
H	3.297876	2.438801	-1.201692
H	4.520199	1.708635	-2.265631
C	4.453834	1.231916	1.495075
C	6.115141	0.097863	0.005506
C	4.578344	-1.258146	1.442956
H	5.216116	1.268375	2.284445
H	3.476612	1.180841	1.984545
H	4.507191	2.174921	0.941098
H	6.852273	0.138334	0.817487
H	6.354502	-0.773765	-0.612422
H	6.253638	0.994404	-0.608123
H	3.615381	-1.302827	1.959135
H	4.686585	-2.169595	0.845624
H	5.364701	-1.270117	2.209126
O	0.432760	2.000182	-1.200940
C	0.009539	3.257050	-0.744600
H	0.588473	3.977982	-1.334103
H	-1.063619	3.403342	-0.904363
O	0.212842	3.453359	0.627762
C	1.567127	3.305203	1.019768

H	1.912822	2.282416	0.854350
H	2.215890	3.996206	0.465476
H	1.619729	3.537015	2.083926
H	-4.368974	-2.134151	0.310703

TS-3-TMS.out

ZPE	0.605046
DE	0.639972
DH	0.640916
DG	0.541575
E	-1604.189391
H	-1603.548474
G	-1603.647815
F	-448.263

Cartesian coordinates

C	1.429985	-2.818008	1.662794
C	0.835126	-0.258097	2.834156
C	0.245325	-2.049378	1.057558
C	-0.199451	-0.931766	1.970243
C	-3.924604	-0.650591	2.194089
C	-1.475317	-0.521659	2.059546
C	-2.685306	-0.980470	1.395393
C	-2.831855	-2.489936	-2.106792
C	-2.875614	-1.759802	0.263193
C	-2.120580	-1.901166	-0.911273
C	-0.858444	-1.344323	-1.168523
C	1.136725	-2.768636	-1.190278
C	0.460504	-1.613616	-0.429571
C	1.271330	-0.324920	-0.675218
C	0.376817	0.887445	-0.443230
C	-1.017890	0.640793	-0.989791
C	-2.093572	1.144168	-0.252514
C	-3.419241	1.142732	-0.796757
H	1.597411	-3.757851	1.135577
H	2.353514	-2.237695	1.632722
H	1.212742	-3.069291	2.704423
H	1.195302	-0.935187	3.615596
H	0.422707	0.629461	3.318474
H	1.704174	0.031466	2.237939
H	-0.586455	-2.760513	1.005294
H	-4.005898	0.434701	2.308579
H	-4.834415	-1.008427	1.710947
H	-3.863771	-1.079564	3.200133
H	-1.670904	0.274566	2.775587
H	-2.320862	-3.397334	-2.446491
H	-3.871769	-2.739365	-1.888686
H	-2.819230	-1.776161	-2.935395
H	-3.894063	-2.126476	0.162108
H	-0.642203	-1.380840	-2.237014
H	1.180097	-2.544414	-2.259534
H	2.158393	-2.927825	-0.841977
H	0.579476	-3.701032	-1.059374
H	-1.109197	0.718155	-2.071119
H	-1.948972	1.564600	0.732229
H	0.308901	1.081741	0.627253
H	1.521606	-0.317186	-1.747915
O	-3.757870	0.623014	-1.851498
O	-4.318548	1.768118	0.014333
C	-5.683111	1.665155	-0.373618
H	-5.996903	0.619501	-0.425046
H	-6.252769	2.183012	0.396955
H	-5.857219	2.138471	-1.342707
O	2.441344	-0.240406	0.097821
Si	4.018163	-0.055696	-0.442708
C	4.147915	1.358959	-1.654877
C	4.969844	0.287350	1.123684
C	4.603309	-1.632844	-1.259443
H	5.189091	1.486399	-1.972091
H	3.544612	1.171454	-2.548036
H	3.801267	2.293957	-1.207492
H	4.816279	-0.513449	1.854166
H	4.648283	1.229742	1.578851
H	6.043817	0.358655	0.922384
O	1.011512	1.997206	-1.069017
C	0.629213	3.252025	-0.572700
H	1.224049	3.973765	-1.144886
H	-0.440554	3.433791	-0.719496
O	0.847246	3.403007	0.803272
C	2.200091	3.224339	1.189315
H	2.270503	3.506336	2.240255
H	2.509648	2.181895	1.074226
H	2.866799	3.865383	0.598115
H	4.007251	-1.865485	-2.147655
H	5.646978	-1.529527	-1.576740
H	4.541338	-2.483733	-0.573868

TS-3-MOM.out

ZPE	0.499267
DE	0.525507
DH	0.526451
DG	0.445052
E	-1120.251677
H	-1119.725226
G	-1119.806625
F	-451.692

Cartesian coordinates

C	2.451797	-3.104992	1.003365
C	2.245901	-0.580984	2.353742
C	1.230993	-2.244765	0.650348
C	1.030603	-1.143799	1.663171
C	-2.571861	-0.609938	2.518109
C	-0.173782	-0.642269	1.979443
C	-1.509330	-0.976108	1.508949
C	-2.322265	-2.219088	-2.006524
C	-1.940182	-1.652076	0.379018
C	-1.387089	-1.771853	-0.907694
C	-0.133823	-1.302120	-1.326491
C	1.707831	-2.867155	-1.749226
C	1.255910	-1.723276	-0.820915
C	2.151941	-0.502804	-1.074444
C	1.415022	0.777143	-0.706977
C	-0.071963	0.668635	-1.033577
C	-0.973005	1.220158	-0.119527
C	-2.362776	1.347461	-0.442018
H	3.394501	-2.581181	0.820348
H	2.422673	-3.385395	2.059162
H	2.460621	-4.028454	0.423724
H	3.019154	-0.296087	1.633596
H	2.700822	-1.317583	3.023066
H	1.987687	0.300290	2.943846
H	0.355459	-2.900575	0.705637
H	-2.569523	0.474240	2.669886
H	-3.569942	-0.902972	2.190377
H	-2.365797	-1.074408	3.488266
H	-0.183516	0.131632	2.745044
H	-1.953895	-3.140954	-2.469602
H	-3.335589	-2.396616	-1.641875
H	-2.370577	-1.455225	-2.787697
H	-2.990746	-1.928978	0.419487
H	-0.083002	-1.285360	-2.416023

H	1.585034	-2.573744	-2.795104
H	2.762409	-3.108995	-1.596678
H	1.117578	-3.772526	-1.577018
H	-0.320435	0.813283	-2.083369
H	-0.643876	1.565488	0.850141
H	1.513357	0.985021	0.359673
H	2.361623	-0.454636	-2.148978
O	-2.904668	0.917110	-1.451319
O	-3.070708	1.985531	0.533410
C	-4.483429	1.996189	0.369207
H	-4.879040	0.978155	0.326907
H	-4.882466	2.509945	1.242891
H	-4.773982	2.530394	-0.538347
H	3.115409	-0.574057	-0.563043
O	2.035964	1.842644	-1.428903
C	1.756231	3.127382	-0.937499
H	2.271918	3.811411	-1.621468
H	0.680760	3.329516	-0.930687
O	2.183202	3.325694	0.382619
C	3.580486	3.167659	0.555584
H	3.887964	2.124980	0.421240
H	3.813311	3.478846	1.574207
H	4.138513	3.796310	-0.150325

TS-4.out

ZPE	0.691282
DE	0.729582
DH	0.730527
DG	0.624997
E	-1722.095035
H	-1721.364508
G	-1721.470038
F	-587.374

Cartesian coordinates

C	4.587250	-2.473328	-0.341138
H	5.318398	-1.659834	-0.383861
H	4.583352	-2.979485	-1.308688
H	4.943762	-3.186570	0.408973
C	3.207260	-1.960573	0.017401
C	2.181670	-2.205914	-0.882652
C	3.180950	-0.994297	1.044946
C	0.869475	-1.751701	-0.732267
C	1.279866	0.417188	-0.754461
C	2.560906	0.734040	-0.302190
H	2.700988	1.395325	0.540149
H	1.201653	0.294140	-1.825731
C	3.679120	0.641389	-1.238890
O	3.643119	0.111888	-2.332064
O	4.804207	1.205938	-0.746502
C	5.960450	1.126418	-1.579434
H	6.228726	0.085907	-1.774960
H	5.793286	1.640587	-2.528110
H	6.758603	1.618007	-1.026040
C	0.004217	-1.801778	-1.977302
H	-0.341806	-2.821240	-2.171975
H	-0.876619	-1.167844	-1.874200
H	0.576945	-1.477230	-2.848907
C	0.214239	-2.109945	0.611408
H	0.987235	-2.622612	1.187424
C	-0.221421	-0.940892	1.527319
C	0.963991	-0.421465	2.300038
H	0.658628	0.113438	3.197427
C	2.295314	-0.480920	2.125848
H	4.205343	-0.765366	1.338499
C	0.064420	1.080419	-0.111513
H	-0.557274	1.463182	-0.925808
C	-0.878394	0.224609	0.761146
H	-1.257112	0.927353	1.513366
C	-0.867884	-3.175144	0.366263
H	-0.454782	-3.991357	-0.232656
H	-1.201751	-3.606420	1.310946
H	-1.734998	-2.766151	-0.150848
C	-1.241661	-1.413673	2.581797
H	-2.184395	-1.711841	2.120914
H	-0.850181	-2.260098	3.153373
H	-1.450845	-0.601412	3.284131
C	3.142518	0.225164	3.171583
H	2.534549	0.636824	3.978342
H	3.879432	-0.456725	3.608336
H	3.702687	1.048227	2.711876
O	0.445862	2.183757	0.717393
C	0.689688	3.373728	0.022966
H	1.170307	4.041619	0.747128
H	1.343859	3.212600	-0.839587
O	-0.478089	3.958693	-0.488940
C	-1.392378	4.352258	0.519894
H	-2.212227	4.874039	0.025688
H	-1.791380	3.487441	1.060505
H	-0.914021	5.030433	1.238321
O	-1.953328	-0.276938	-0.009049
Si	-3.458524	0.450058	-0.163666
C	-4.000902	1.109460	1.501906
C	-3.371589	1.841464	-1.412230
C	-4.607638	-0.925851	-0.770450
H	-3.409369	1.979923	1.802161
H	-5.049295	1.423155	1.459021
H	-3.906445	0.347818	2.281633
H	-3.126086	1.461432	-2.409150
H	-4.330883	2.365674	-1.476570
H	-2.608364	2.574880	-1.136063
C	-4.019129	-1.593450	-2.022094
C	-5.975534	-0.318313	-1.120859
C	-4.791971	-1.980863	0.330314
H	-3.059117	-2.072727	-1.811108
H	-4.704481	-2.366511	-2.393801
H	-3.864094	-0.874194	-2.833449
H	-6.665604	-1.108304	-1.444014
H	-6.433279	0.185524	-0.262499
H	-5.901305	0.407590	-1.937148
H	-3.839254	-2.432360	0.623339
H	-5.252873	-1.554618	1.227495
H	-5.446604	-2.787284	-0.025473
H	2.484867	-2.580628	-1.857875

TS-4-TMS.out

ZPE	0.605029
DE	0.639922
DH	0.640866
DG	0.540483
E	-1604.178638
H	-1603.537772
G	-1603.638154
F	-451.557

Cartesian coordinates

C	-1.115201	-1.749933	2.992983
C	-0.202679	0.949518	3.114161
C	-0.032680	-1.369387	1.971520
C	0.604909	-0.047000	2.325326
C	4.296856	-0.013369	1.736481
C	1.873336	0.263258	2.014609

C	2.918022	-0.497948	1.351750
C	2.342361	-3.124877	-1.356400
C	2.869572	-1.626394	0.549825
C	1.889928	-2.105144	-0.338012
C	0.603232	-1.584536	-0.529584
C	-1.306838	-2.808435	0.364532
C	-0.532192	-1.480273	0.493388
C	-1.417881	-0.294673	0.016095
C	-0.550084	0.837477	-0.580060
C	0.771613	0.304301	-1.139218
C	1.957044	0.976382	-0.840692
C	3.158609	0.666518	-1.553695
H	-1.385013	-2.802280	2.907830
H	-2.026511	-1.156702	2.871702
H	-0.745827	-1.594160	4.009050
H	-0.338003	0.611999	4.147351
H	0.292277	1.921173	3.132252
H	-1.197202	1.088566	2.685792
H	0.753451	-2.129213	2.047435
H	4.422903	1.021518	1.402807
H	5.086760	-0.612597	1.282058
H	4.425074	-0.022261	2.824066
H	2.219322	1.238784	2.350965
H	1.787986	-4.061392	-1.229199
H	3.409461	-3.342113	-1.283029
H	2.138151	-2.757490	-2.366014
H	3.843626	-2.083996	0.395633
H	0.167735	-1.986369	-1.444631
H	-1.527940	-3.028601	-0.678941
H	-2.254570	-2.780515	0.903834
H	-0.703099	-3.625789	0.770745
H	0.702092	-0.053359	-2.163113
H	2.000653	1.728979	-0.068997
O	3.293208	-0.222460	-2.384695
O	4.204440	1.464803	-1.188512
C	5.473490	1.105894	-1.719638
H	5.750737	0.092046	-1.419078
H	6.184531	1.819468	-1.304867
H	5.480805	1.168888	-2.810326
O	-2.282224	-0.735649	-1.019390
Si	-3.945544	-0.510153	-0.989280
C	-4.705150	-1.549647	0.368315
C	-4.326538	1.289634	-0.657492
C	-4.529828	-1.054142	-2.672197
H	-5.778786	-1.345473	0.446602
H	-4.577168	-2.619295	0.177664
H	-4.251776	-1.319143	1.338521
H	-3.748079	1.956046	-1.303673
H	-5.391251	1.487814	-0.823009
H	-4.100861	1.548348	0.381008
O	-0.354683	1.855496	0.383502
C	-0.367179	3.157674	-0.122081
H	0.141897	3.772700	0.629945
H	0.154629	3.222140	-1.081323
O	-1.663698	3.637262	-0.353296
C	-2.401193	3.811390	0.843485
H	-3.397371	4.154469	0.564218
H	-2.487249	2.873039	1.400771
H	-1.925612	4.564313	1.485783
H	-1.127753	1.250829	-1.412443
H	-1.998277	0.113936	0.851896
H	-4.249243	-2.093790	-2.867098
H	-5.619991	-0.981188	-2.742509
H	-4.098420	-0.430528	-3.461046

TS-5.out

ZPE	0.687960
DE	0.728160
DH	0.729104
DG	0.615128
E	-1722.112161
H	-1721.383057
G	-1721.497034
F	-538.730

Cartesian coordinates

C	4.989179	-1.428178	-0.347412
C	3.995440	-1.889077	-1.214156
C	4.835893	-0.218967	0.351342
C	3.787580	0.691301	0.157170
H	5.754296	0.184079	0.774257
C	2.457395	0.353222	-0.135732
C	2.632451	-1.643702	-1.033876
H	4.328458	-2.345730	-2.146528
C	2.062185	-1.891379	0.369976
C	1.549120	-0.501989	0.779734
H	1.913894	1.153043	-0.635987
H	2.926893	-2.075515	1.012769
C	1.775959	-0.205048	2.262728
H	1.423589	0.795489	2.523394
H	2.841198	-0.274248	2.497857
H	1.246364	-0.927252	2.890852
C	1.186786	-3.138340	0.462639
H	0.902887	-3.339017	1.499534
H	1.754766	-4.003501	0.106442
H	0.276747	-3.074169	-0.138195
C	1.733120	-1.871475	-2.230365
H	1.367780	-2.904312	-2.252800
H	0.856648	-1.221763	-2.230109
H	2.277997	-1.685646	-3.158564
C	6.352591	-2.072505	-0.382543
H	7.150970	-1.361974	-0.155655
H	6.548006	-2.516886	-1.362737
H	6.410204	-2.882479	0.352609
C	4.165267	2.157714	0.087155
H	5.246579	2.306486	0.120201
H	3.792072	2.592362	-0.846004
H	3.711706	2.728758	0.903773
C	0.076819	-0.221819	0.379277
H	-0.056506	-0.607074	-0.633847
C	-0.995378	-0.930089	1.248017
H	-0.619292	-1.914930	1.536677
O	-0.173457	1.164315	0.394641
O	-1.234440	-0.172367	2.421934
Si	-1.071658	2.061856	-0.700857
C	-2.909646	1.979190	-0.339023
H	-3.405779	2.869810	-0.740546
H	-3.382644	1.104206	-0.792014
H	-3.097492	1.949098	0.738648
C	-0.724064	1.424335	-2.426573
H	-1.271691	2.014267	-3.168813
H	0.341879	1.475228	-2.669574
H	-1.048881	0.383592	-2.530356
C	-0.470224	3.843398	-0.464291
C	1.061162	3.898736	-0.518052
H	1.452603	3.503715	-1.461949
H	1.408185	4.936470	-0.424791
H	1.505467	3.320511	0.295272
C	-0.943881	4.371489	0.898611
H	-0.570561	3.754268	1.722273
H	-0.576431	5.394088	1.056161
H	-2.036222	4.400191	0.967097
C	-1.047966	4.728538	-1.579749

H	-2.142909	4.706060	-1.600505
H	-0.686651	4.423637	-2.567404
H	-0.744715	5.772168	-1.425515
C	-1.518529	-0.937218	3.558168
H	-0.804758	-1.761673	3.663617
H	-1.435611	-0.247851	4.405823
O	-2.786723	-1.535537	3.529748
C	-3.846995	-0.605803	3.673704
H	-3.780088	-0.085253	4.637370
H	-3.847000	0.138902	2.870359
H	-4.778306	-1.170920	3.634983
C	-2.272945	-1.131463	0.474619
H	-3.177207	-0.731261	0.921642
C	-2.363322	-1.740412	-0.706743
H	-1.504087	-2.162115	-1.217366
C	-3.661182	-1.831403	-1.399692
O	-4.718010	-1.400285	-0.992988
O	-3.530842	-2.455069	-2.581671
C	-4.722746	-2.588766	-3.362982
H	-4.423177	-3.111262	-4.268983
H	-5.472559	-3.170258	-2.823990
H	-5.130029	-1.607528	-3.612398

TS-5-TMS.out

ZPE	0.601972
DE	0.638614
DH	0.639558
DG	0.531368
E	-1604.177340
H	-1603.537782
G	-1603.645973
F	-540.738

Cartesian coordinates

C	-4.957460	0.027121	-1.081900
C	-3.983953	-0.601339	-1.865655
C	-4.772905	0.208159	0.298436
C	-3.698209	-0.312670	1.033348
H	-5.678538	0.438968	0.856326
C	-2.383625	-0.431392	0.568336
C	-2.612812	-0.525626	-1.620968
H	-4.343042	-1.300051	-2.622129
C	-2.019113	0.863393	-1.349791
C	-1.502669	0.749287	0.094181
H	-1.820839	-1.195166	1.100953
H	-2.870660	1.547056	-1.296068
C	-1.765752	2.024540	0.897061
H	-1.400918	1.932219	1.922089
H	-2.839263	2.228768	0.923165
H	-1.270313	2.883171	0.436452
C	-1.125340	1.371421	-2.477581
H	-1.691088	1.376890	-3.414362
H	-0.238668	0.751111	-2.631616
H	-0.800430	2.397685	-2.284368
C	-1.736398	-1.557492	-2.296684
H	-1.528344	-1.265720	-3.332561
H	-0.773066	-1.680481	-1.800376
H	-2.229790	-2.531477	-2.313502
C	-6.335417	0.239135	-1.657971
H	-7.113962	0.194063	-0.892723
H	-6.555103	-0.508571	-2.425635
H	-6.399938	1.220299	-2.140524
C	-4.017300	-0.964253	2.364287
H	-5.085867	-0.941002	2.588613
H	-3.701430	-2.013541	2.344906
H	-3.478208	-0.485086	3.187648
C	-0.023495	0.291452	0.221881
H	0.125604	-0.509247	-0.508349
C	1.065613	1.337517	-0.106931
H	0.807425	1.831116	-1.046412
O	0.225898	-0.194365	1.523377
O	1.152326	2.305604	0.924544
Si	0.854037	-1.683609	1.973873
C	-0.180118	-2.235028	3.427729
H	0.184695	-3.187470	3.826672
H	-0.141931	-1.496791	4.235308
H	-1.227947	-2.366050	3.139318
C	2.641343	-1.503899	2.491820
H	2.968400	-2.407806	3.018223
H	3.306163	-1.357423	1.635118
H	2.769603	-0.656982	3.173756
C	0.711744	-2.890497	0.551121
C	1.484374	3.589906	0.480172
H	0.859489	3.881776	-0.370980
H	1.303655	4.253015	1.333622
O	2.808954	3.704196	0.034570
C	3.762175	3.635986	1.081472
H	3.605808	4.447438	1.803481
H	3.717639	2.678539	1.610523
H	4.747105	3.745508	0.627417
C	2.384430	0.631353	-0.271686
H	3.098543	0.744090	0.538648
C	2.685175	-0.156199	-1.301617
H	1.999986	-0.307728	-2.129742
C	3.954831	-0.903960	-1.327058
O	4.822803	-0.858994	-0.482504
O	4.036896	-1.677812	-2.420647
C	5.220889	-2.472703	-2.546611
H	5.305714	-3.169090	-1.710636
H	5.109716	-3.019894	-3.480252
H	6.107376	-1.837611	-2.585790
H	1.331972	-2.588264	-0.299025
H	1.054696	-3.878881	0.876446
H	-0.321833	-2.991138	0.205074

TS-5-MOM.out

ZPE	0.495766
DE	0.523977
DH	0.524922
DG	0.434279
E	-1120.245916
H	-1119.720995
G	-1119.811638
F	-544.982

Cartesian coordinates

C	4.330226	-0.984500	0.828102
C	4.216260	-0.592080	-0.508074
C	3.379525	-0.594315	1.788490
C	2.327213	0.298078	1.550765
H	3.700794	-0.704672	2.822619
C	1.617719	0.389964	0.345837
C	3.001948	-0.390099	-1.169129
H	5.138109	-0.292573	-1.008201
C	1.933451	-1.486121	-1.039514
C	0.813935	-0.767778	-0.282516
H	1.147395	1.365007	0.202649
H	2.345376	-2.233174	-0.355149
C	0.154748	-1.675691	0.759171
H	-0.535184	-1.126311	1.405492
H	0.911595	-2.137092	1.399102
H	-0.408641	-2.473946	0.263133

C	1.584081	-2.202618	-2.338744
H	0.823127	-2.966976	-2.153911
H	2.466783	-2.702108	-2.749135
H	1.198528	-1.522294	-3.102072
C	3.039836	0.420535	-2.444962
H	3.769746	1.229046	-2.367627
H	3.321481	-0.211694	-3.294951
H	2.071730	0.863437	-2.682867
C	5.634664	-1.570356	1.309377
H	5.843840	-1.313190	2.350499
H	6.467986	-1.227260	0.689481
H	5.610714	-2.662955	1.235787
C	2.035272	1.343791	2.606613
H	1.056921	1.176140	3.069929
H	2.790992	1.365948	3.394649
H	1.996128	2.335088	2.141314
C	-0.261450	-0.183355	-1.215298
H	-0.746994	-1.000823	-1.756806
C	-1.323146	0.668934	-0.503840
H	-0.981667	0.940699	0.499443
C	-2.649198	-0.027833	-0.408312
H	-3.104376	-0.313491	-1.353550
C	-3.266304	-0.286337	0.742474
H	-2.823637	-0.004676	1.692548
C	-4.569646	-0.970883	0.857474
O	-5.115798	-1.185488	1.918453
O	-5.092252	-1.331269	-0.320321
C	-6.359783	-1.995502	-0.276351
H	-6.613868	-2.210032	-1.312125
H	-6.287620	-2.923340	0.293345
H	-7.116760	-1.348791	0.170257
H	0.201427	0.461517	-1.964456
O	-1.497136	1.873339	-1.264573
C	-1.949685	2.963692	-0.503610
H	-2.225436	3.733626	-1.232514
H	-2.814294	2.692765	0.110520
O	-0.980984	3.441391	0.388886
C	0.139271	4.022946	-0.256183
H	0.657611	3.301178	-0.895829
H	-0.165946	4.882524	-0.866710
H	0.819870	4.361793	0.524941

TS-6.out

ZPE	0.434588
DE	0.457718
DH	0.458662
DG	0.385032
E	-929.290232
H	-928.831569
G	-928.905200
F	-443.945

Cartesian coordinates

C	-3.742929	-1.466312	0.195424
C	-2.304947	-1.370549	-2.291800
C	-2.270955	-1.043050	0.267898
C	-1.533032	-1.385576	-1.000844
C	1.906982	-2.685619	-0.356986
C	-0.221571	-1.666104	-1.039549
C	0.764877	-1.774388	0.024308
C	0.750706	0.295715	3.226010
C	0.773780	-1.288462	1.319966
C	0.179582	-0.154114	1.902325
C	-0.705104	0.746618	1.292177
C	-3.133132	0.913161	1.661021
C	-2.069909	0.470393	0.636163
C	-2.123960	1.390820	-0.555174
C	-0.853154	2.892759	-2.114968
C	-0.985419	1.952919	-0.953640
C	0.262194	1.601434	-0.192825
C	1.263150	0.876742	-0.849935
H	-4.216614	-1.399707	1.175605
H	-4.319070	-0.851296	-0.501463
H	-3.817794	-2.506329	-0.132736
H	-3.061789	-2.160712	-2.315315
H	-1.641692	-1.507668	-3.147842
H	-2.836613	-0.422087	-2.416775
H	-1.815914	-1.608175	1.087408
H	2.434443	-2.263249	-1.218295
H	2.625202	-2.809278	0.454337
H	1.534715	-3.671130	-0.656321
H	0.190493	-1.905016	-2.018176
H	-0.034782	0.347066	3.986974
H	1.539478	-0.367785	3.584288
H	1.172590	1.300369	3.122640
H	1.559309	-1.720141	1.934623
H	-0.818054	1.639139	1.907858
H	-2.941667	1.941997	1.977387
H	-4.137035	0.880570	1.232225
H	-3.115606	0.272506	2.548186
H	-3.071570	1.584577	-1.051303
H	-0.387608	3.833588	-1.802650
H	-0.209925	2.461036	-2.888617
H	-1.826963	3.115688	-2.556946
H	0.645443	2.382293	0.464059
H	1.080188	0.389365	-1.796624
C	2.569440	0.770640	-0.273816
O	2.904496	1.183690	0.829309
O	3.448457	0.113060	-1.085613
C	4.722197	-0.171668	-0.520483
H	4.623476	-0.784939	0.378825
H	5.271451	-0.722676	-1.283009
H	5.259526	0.745839	-0.269529

TS-7.out

ZPE	0.433075
DE	0.457376
DH	0.458320
DG	0.379735
E	-929.285916
H	-928.827596
G	-928.906181
F	-527.558

Cartesian coordinates

C	-3.670133	-1.584158	-0.103696
C	-3.673182	-0.445478	-0.917618
C	-2.471560	-2.119537	0.397137
C	-1.187429	-1.694950	0.022692
H	-2.550580	-3.130148	0.793031
C	-0.825606	-0.376262	-0.280431
C	-2.740251	0.582735	-0.803337
H	-4.357609	-0.446732	-1.766498
C	-2.416982	1.101076	0.600832
C	-0.917923	0.806997	0.715246
H	0.026876	-0.308876	-0.956133
H	-2.907971	0.421994	1.301926
C	-0.545317	0.434107	2.161346
H	0.498535	0.128750	2.258511
H	-1.177989	-0.386617	2.510945
H	-0.705900	1.295272	2.818435
C	-2.929210	2.504312	0.906261

H	-2.600330	2.816610	1.902418
H	-4.023010	2.514090	0.895564
H	-2.587057	3.253228	0.188466
C	-2.591562	1.554201	-1.949409
H	-3.373261	2.321426	-1.909919
H	-1.629895	2.071990	-1.915815
H	-2.668369	1.040162	-2.909507
C	-4.926350	-2.412671	0.000305
H	-4.710692	-3.469362	0.174377
H	-5.526805	-2.323510	-0.909698
H	-5.548583	-2.058636	0.829229
C	-0.155596	-2.767434	-0.263762
H	-0.556924	-3.773447	-0.123937
H	0.183545	-2.681829	-1.302623
H	0.731250	-2.652336	0.367777
C	-0.044938	1.962790	0.265144
H	-0.549218	2.920434	0.173636
C	1.275362	1.975056	0.002976
C	1.953668	3.250546	-0.425128
H	2.764423	3.516599	0.260652
H	2.396173	3.145804	-1.421107
H	1.243572	4.078530	-0.453904
C	2.105371	0.776595	0.117363
H	1.639422	-0.138209	0.467322
C	3.411807	0.707389	-0.173013
H	3.983215	1.554696	-0.532616
C	4.132365	-0.567870	-0.015314
O	3.656752	-1.611582	0.377424
O	5.421773	-0.440552	-0.371137
C	6.227242	-1.618724	-0.266358
H	5.841941	-2.406620	-0.915889
H	7.224019	-1.323059	-0.586967
H	6.254363	-1.975444	0.764614