Model Studies of β-Scission Ring-opening Reactions of Cyclohexyloxy Radicals: Application to Thermal Rearrangements of dispiro-1,2,4-Trioxanes.

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Supporting Information

Contents:

General

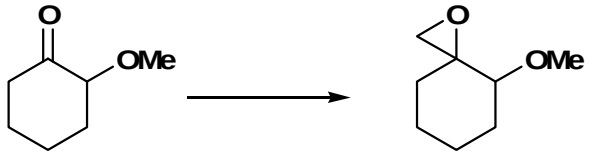
^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-400 (400MHz ^{1}H, 100 MHz ^{13}C) and Bruker AC200 (200MHz ^{1}H, 50 MHz ^{13}C) spectrometer at either room temperature or -50°C as indicated. Chemical shifts (δ) are reported in ppm, using residual solvent as internal standard and coupling constants (*J*) are given in hertz.

All starting materials and reagents were obtained from commercial suppliers and used without further purification.

Caution

Hydrogen peroxide was purchased from fisher chemicals as a 60% solution. Caution should be taken during the initial drying of hydrogen peroxide. The procedure should take place in thick glass walled flat bottom container containing no sharp or ground glass edges. Constant monitoring of temperature is essential during the addition of phosphorus pentoxide. Once dry the ethereal solution is used straight away and is not stored.

Preparation of 4-methoxy-1-oxa-*spiro*-octane



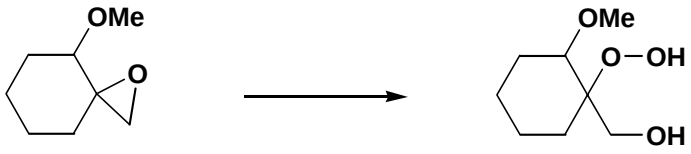
4-Methoxy-1-oxa-*spiro*-octane. Dried dimethyl sulfoxide (150 mL) was added with stirring to sodium hydride (60 % oil dispersion, 6.13 g; 153 mmol), which had been washed with petrol ether b.p. 40-60°C (2 x 100 mL). Under a constant flow of nitrogen trimethylsulfoxonium iodide (34.40 g; 156 mmol) was added slowly over 15 minutes with constant stirring. The mixture was then stirred continuously for an additional 30 minutes until all the hydrogen gas had evolved. 1-methoxycyclohexanone (10.04g; 79 mmol) was added drop wise over *ca*. 5 minutes. The reaction was left to stir for *ca*. 45 minutes. The reaction mixture was poured into water (500 mL) and the product extracted using diethyl ether (3 x 100 mL). The organic extract was washed with water (50 ml) and sat. sodium chloride (50 mL) and dried over magnesium sulphate. The solvent was distilled off before 4-methoxy-1-oxa*spiro*octane was collected by distillation under reduced pressure as a clear, colourless liquid (10.00 g; 71 mmol; 90 % yield) (b.p. 40°C at 80mm Hg)

[δ_H(200 MHz $CDCl_3$); 1.1-2.0 (12H, m), 3.30 (minor), 3.35 (major) (s OCH_3)] δ_C(50 MHz, $CDCl_3$); 20.8, 21.9, 24.0, 24.9, 29.5, 30.0, 30.2, 30.8 ($\underline{C}H_2$), 50.4, 51.8 ($\underline{C}H_2O$), 56.8,57.2 ($O\underline{C}H_3$), 59.7, 60.2 ($\underline{q}C$) 78.9, 79.7 ($\underline{C}H$)]

Drying of hydrogen peroxide

Hydrogen peroxide (60 %; 12.1 mL; 0.214 mmol) was added with stirring to dry diethyl ether (50 mL), at *ca.* -78°C in a thick walled, flat bottomed vessel. Anhydrous calcium chloride (*ca.* 4 g) was added and the reaction mixture stirred for 10 minutes. Phosphorus pentoxide (*ca.* 4 g) was then added in small portions over 15 minutes with careful monitoring of reaction temperature in order to minimise reaction temperature. The ethereal solution of hydrogen peroxide was decanted into a pre-cooled reaction vessel (-78°C) and use immediately.

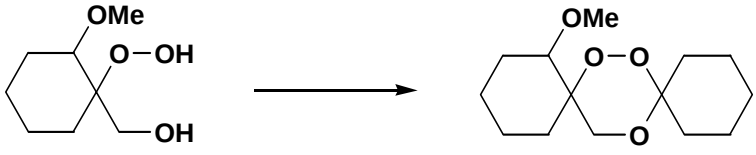
Preparation of 1-hydroperoxy-1-hydroxymethyl-2-methoxycyclohexanone



1-hydroperoxy-1-hydroxymethyl-2-methoxycyclohexanone. A solution of 4-methoxy-1-oxa*spiro*octane (6.04 g; 43 mmol) in dry diethyl ether (5 mL) was added drop wise to a pre-dried ethereal solution (*ca.* 50 mL) at 0°C and stirred for 4 hours. The reaction mixture was poured into water (50 mL) and extracted using diethyl ether (3 x 20 mL). The organic extracts were washed with sat. sodium bicarbonate (10 mL) and water (10 mL). The solvent was removed under reduced pressure to yield a yellow oil which was purified collected by flash column chromatography on silica gel eluting with 5:3 petrol ether b.p. 40-60°C/ ethyl acetate at R_f = 0.28 as a viscous oil (0.59g; 3.4 mmol; 8% yield).

[δ_H(200 MHz $CDCl_3$); 1.10-1.75 (8H, m), 3.30 s, 3H, OCH_3), 3.44 (m, 1H, CH), 3.70, (d, 1H, *J*=12.0, OCH_2), 3.86 (d, 1H, *J*=12.0 OCH_2) δ_C(50 MHz, $CDCl_3$); 20.4, 20.4, 24.7, 26.9 ($\underline{C}H_2$), 56.7 ($\underline{C}H_3$), 62.6 (CH_2OH), 78.0 (CH), 84.0 ($\underline{C}OOH$)]

Preparation of *Dispiro*-1,2,4-trioxane 10

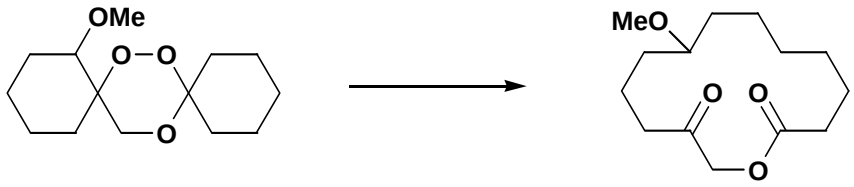


10

2-(Methoxy)cyclohexane-1-*spiro*-3'-(1',2',4'-trioxane)-6'-*spiro*-1''-2''-cyclohexane.

Cyclohexanone (0.98 g; 10 mmol) was added to a cooled (-5°C) solution of 1-hydroperoxy-1-hydroxymethyl-2-methoxycyclohexane oxide (0.88 g; 5 mmol) in dry DCM (30 mL) along with 2 drops of conc. sulphuric acid (*ca.* 50mg). The mixture was allowed to warm up to room temperature and left to stir for *ca*. 4 days. The solution was washed in turn with sat. sodium bicarbonate (30 mL) and water (30 mL) before being extracted into DCM. The extracts were combined and dried over anhydrous magnesium sulphate before the solvent was removed under vacuum. Excess cyclohexanone was then removed under high vacuum. 2-(Methoxy)Cyclohexane-1-*spiro*-3'-(1',2',4'-trioxane)-6'-*spiro*-1''-cyclohexane was isolated through flash column chromatography on silica gel eluting with 1:25 ,ethyl acetate/petrol ether 40-60°C Rf = 0.25, as a yellow viscous oil (0.35 g; 1.4 mmol; 28% yield). [$C_{14}H_{24}O_4$ requires C 65.6% H 9.4%, found C 65.3% H 9.6%, m/z 256 (M^+), accurate mass $C_{14}H_{24}O_4$ requires 256.16728, found 256.16746, δ_H(400 MHz, -50°C CD_2Cl_2) 1.15-1.95 (m 18H), 3.30 (s, 3H, OCH_3), 3.55 (m, 1H) , 3.86 (d, 1H, J = 12.4)], 4.08 (s, 1H, CH) δ_C(100.6 MHz, -50°C, $CDCl_3$); 18.5, 19.3, 21.9, 23.7, 24.7, 25.0, 27.4, 27.8 (CH_2), 56.8 (CH_3), 61.7 (CH_2O), 72.6 (CH), 78.0 (spiro-C), 102.0 (spiro-acetal C)

Thermal decomposition of cyclohexane-1-*spiro*-3'-(1'-2'-4'-trioxane)-6'-*spiro*-1''-2''-methoxycyclohexane (10).

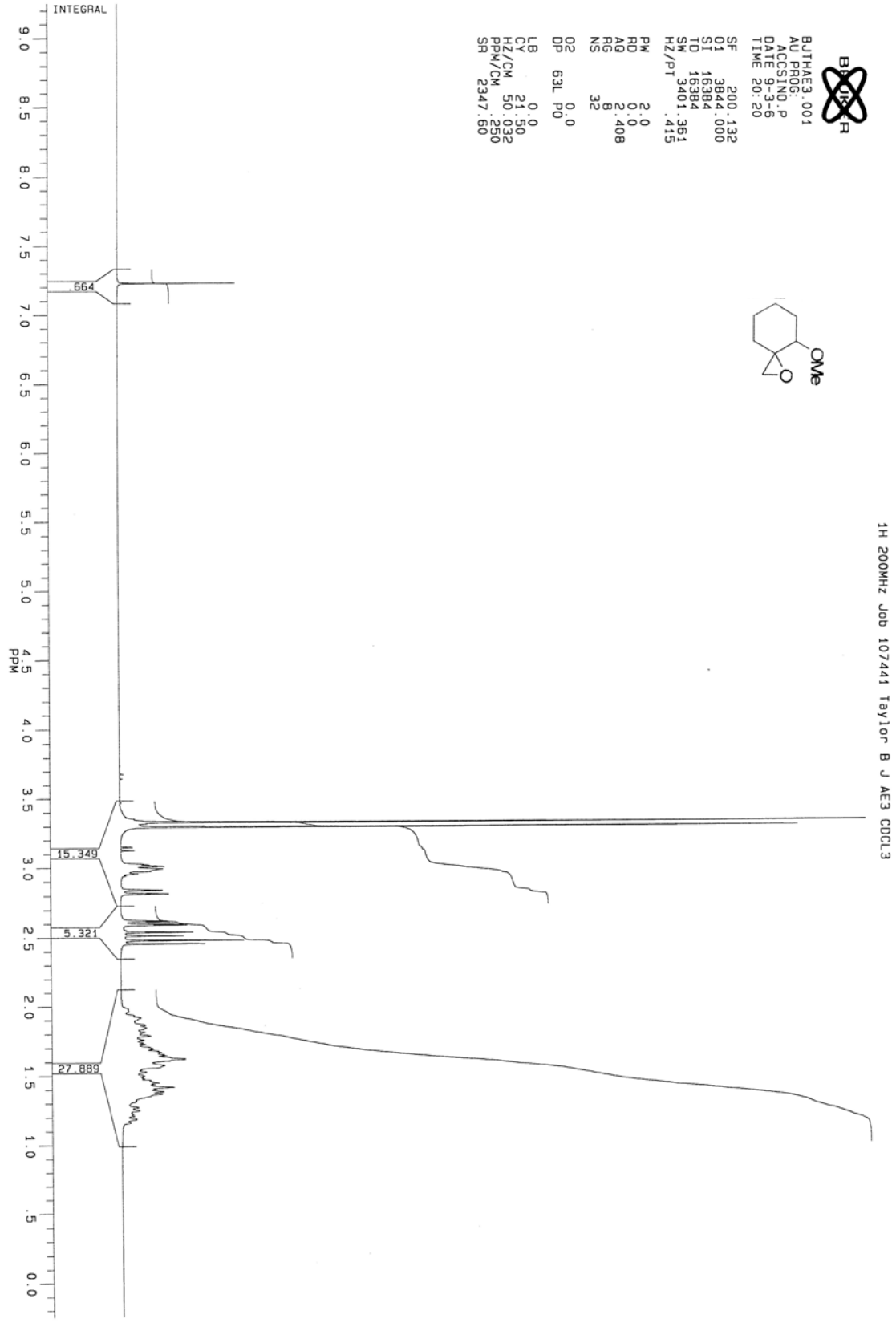


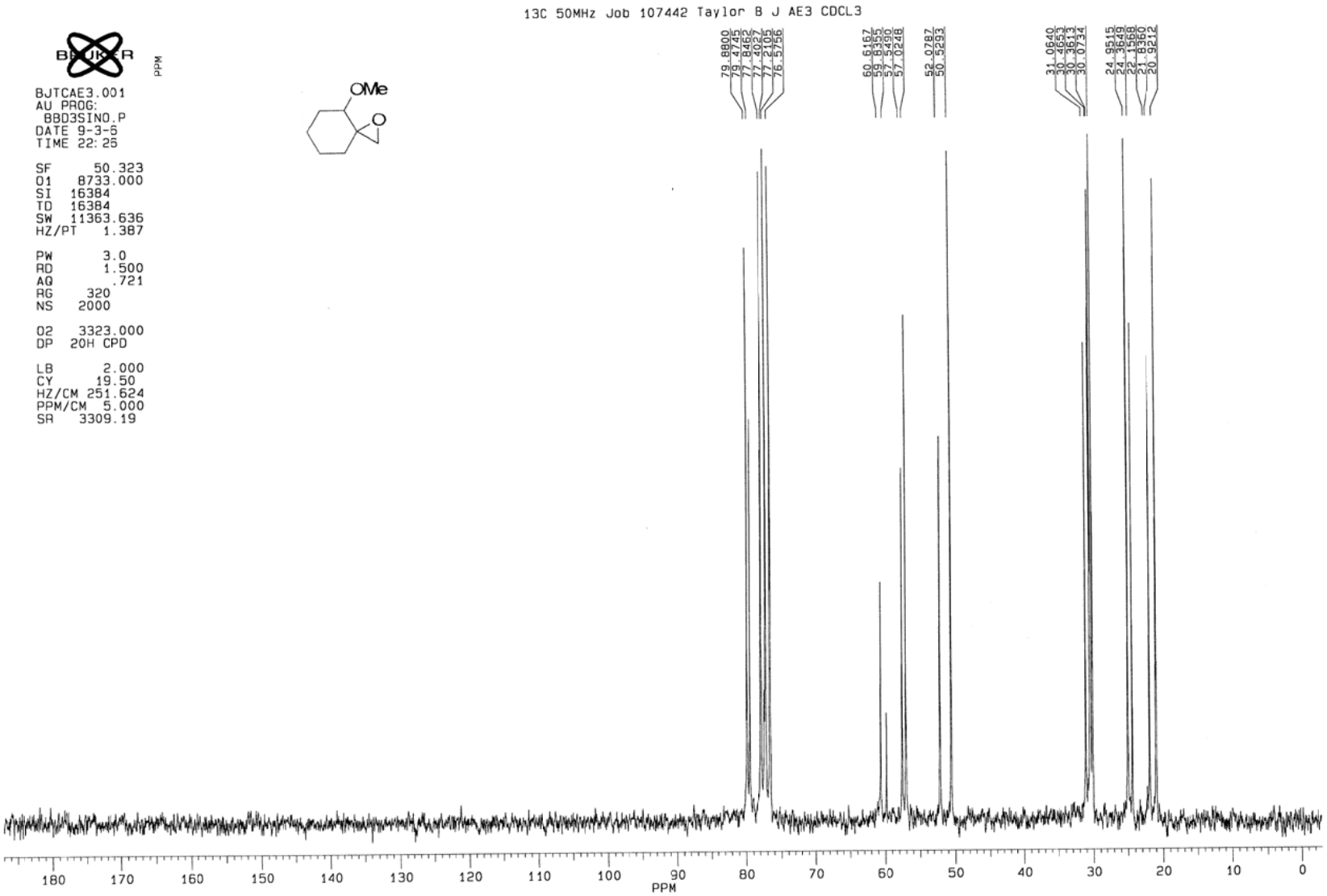
10 **11**

Cyclohexane-1-*spiro*-3'-(1'-2'-4'-trioxane)-6'-*spiro*-1''-2''-methoxycyclohexane (300mg; 117 mmol) was divided into 3 equal portions, each portion was dissolved in decane (10 mL) and pipetted into a thermolysis tube. The solutions were then degassed and the tubes sealed, as stated, before placing in a silicon oil bath for 16 hours. Quantative GC analysis indicated one major product and two minor products. The two minor products were identified as cyclohexanone and 2-methoxycyclohexanone by comparison of the retention times with those of authentic samples. The product was isolated using column chromatography on 'flash' silica eluting with ethyl acetate / Petroleum ether 40-60°C (1:3) rf 0.46 (200mg; 77.8 mmol; Mp 57°C; 66.6% yield).

[$C_{14}H_{24}O_4$, requires C 65.6%, H 9.4%, found C 65.3%, H 9.7%, m/z 256 (M^+), accurate mass $C_{14}H_{24}O_4$ requires 256.1672§ actual 256.16746 δ_H (400MHz, $CDCl_3$); **Bט**$_{CO}$ 1715.4cm^{-1} **Bט**$_{CO}$ 1738.7cm^{-1}, δ_H(400 MHz, $CDCl_3$) 1.25-1.70 (13H, m), 1.77 (1H, m), 2.21 (1H, m), 2.40 (1H, m), 2.52 (1H, m), 2.69 (1H, m), 3.12 (1H, m, CH), 3.31 (3H, s, CH_3), 4.28 (1H, d, *J* 16.0, CH_2O), 4.28 (1H, d, *J* 16.0, CH_2O) δ_c (400MHz, $CDCl_3$); 21.9, 23.4, 23.5, 24.2, 26.7, 30.0, 30.8, 32.9, 37.4 (CH_2), 56.3 (OCH_3), 68.4 (CH_2), 78.1 (CH), 172.8, 207.4 (CO)]

Spectral data

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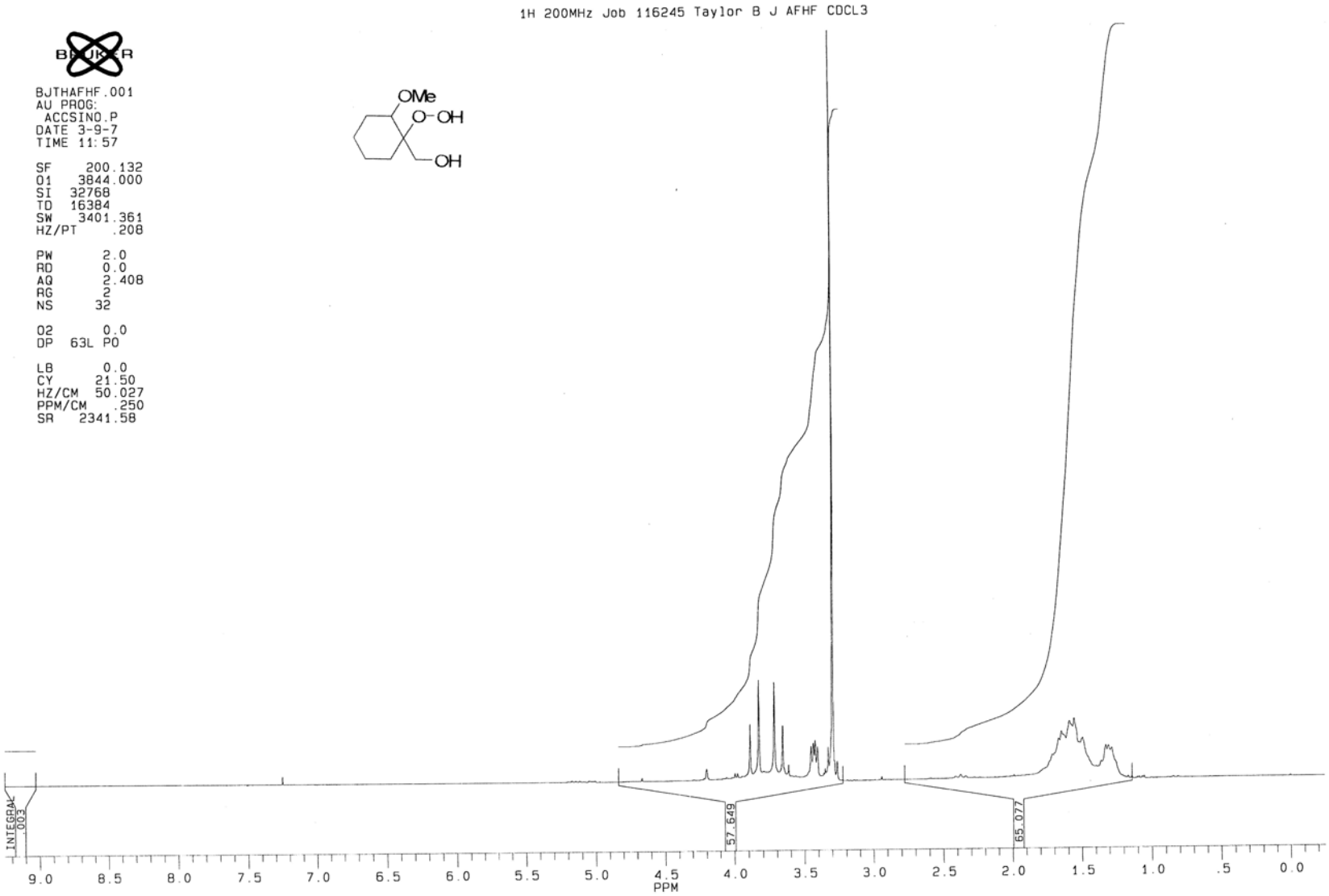
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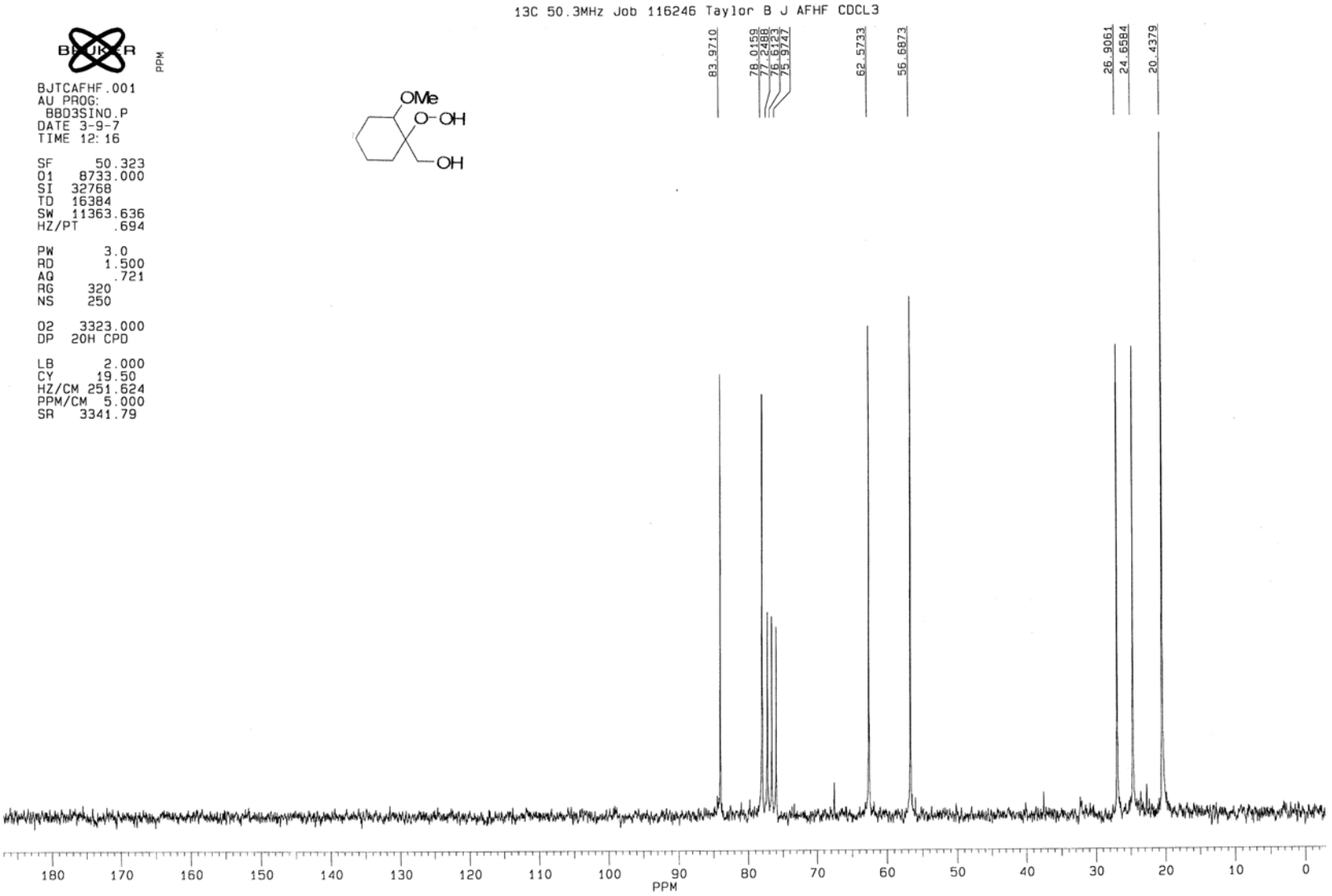
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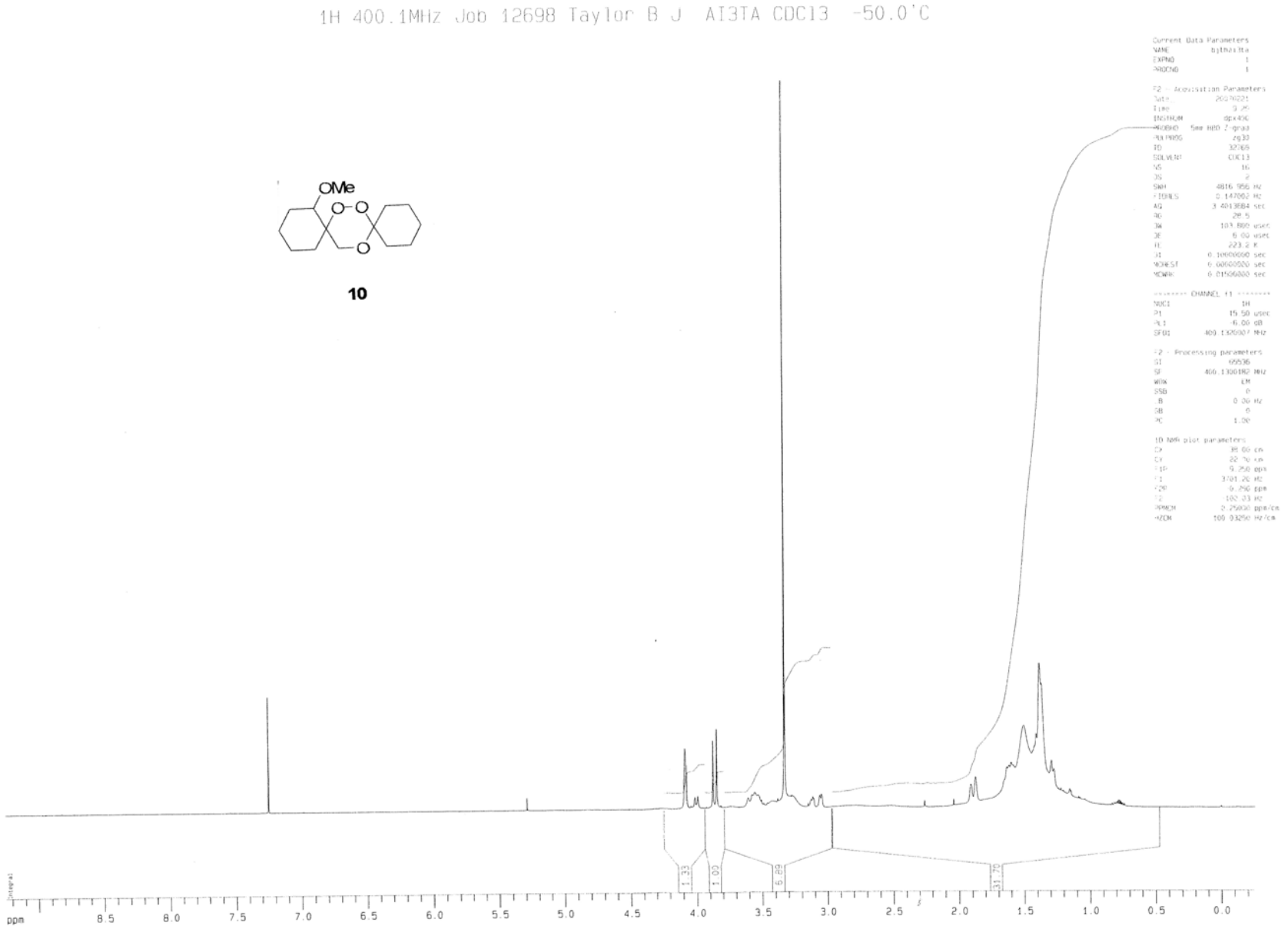
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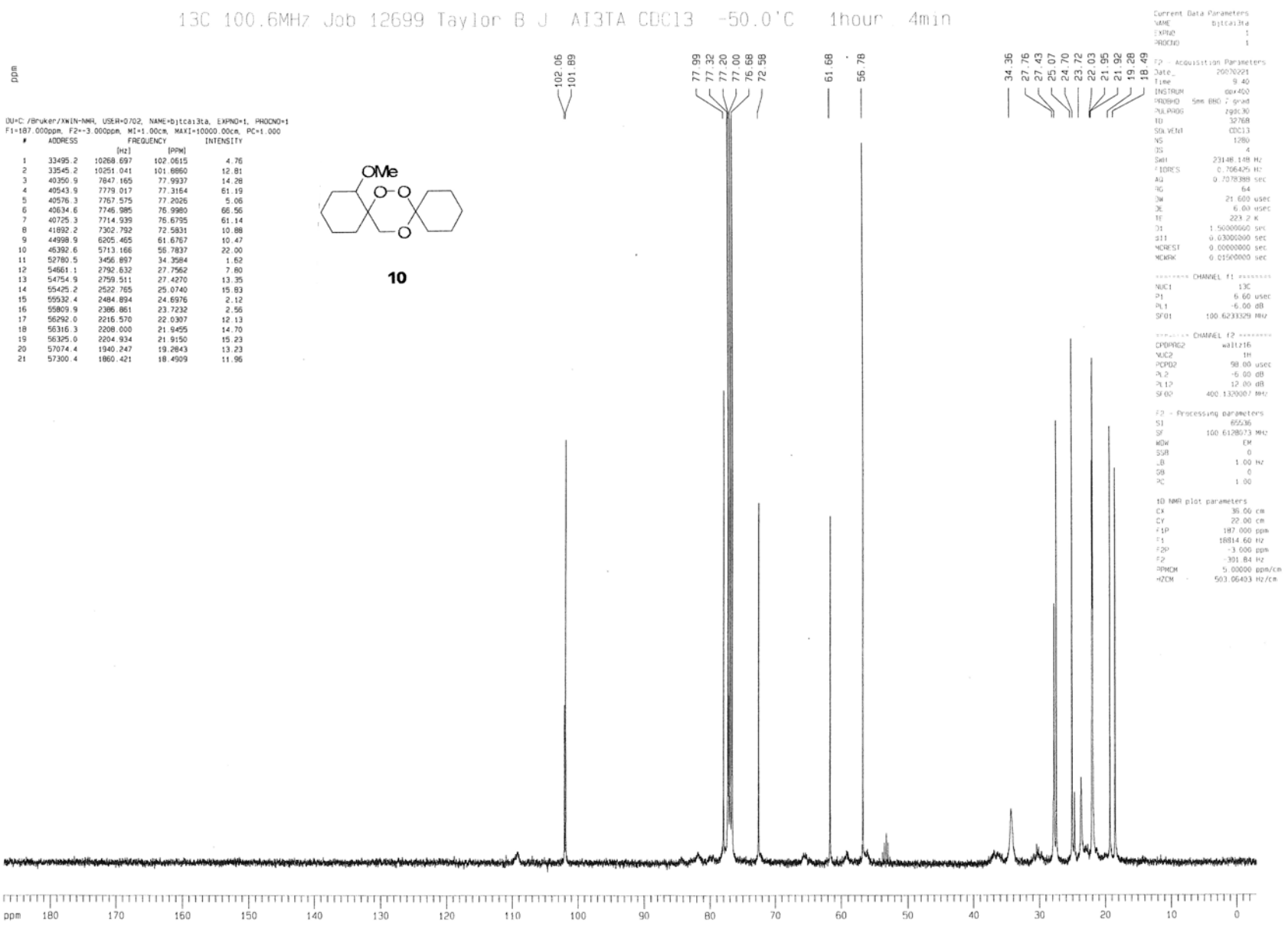

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6	40634.6	7746.985	76.9980	66.56
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15	55532.4	2484.894	24.6976	2.12
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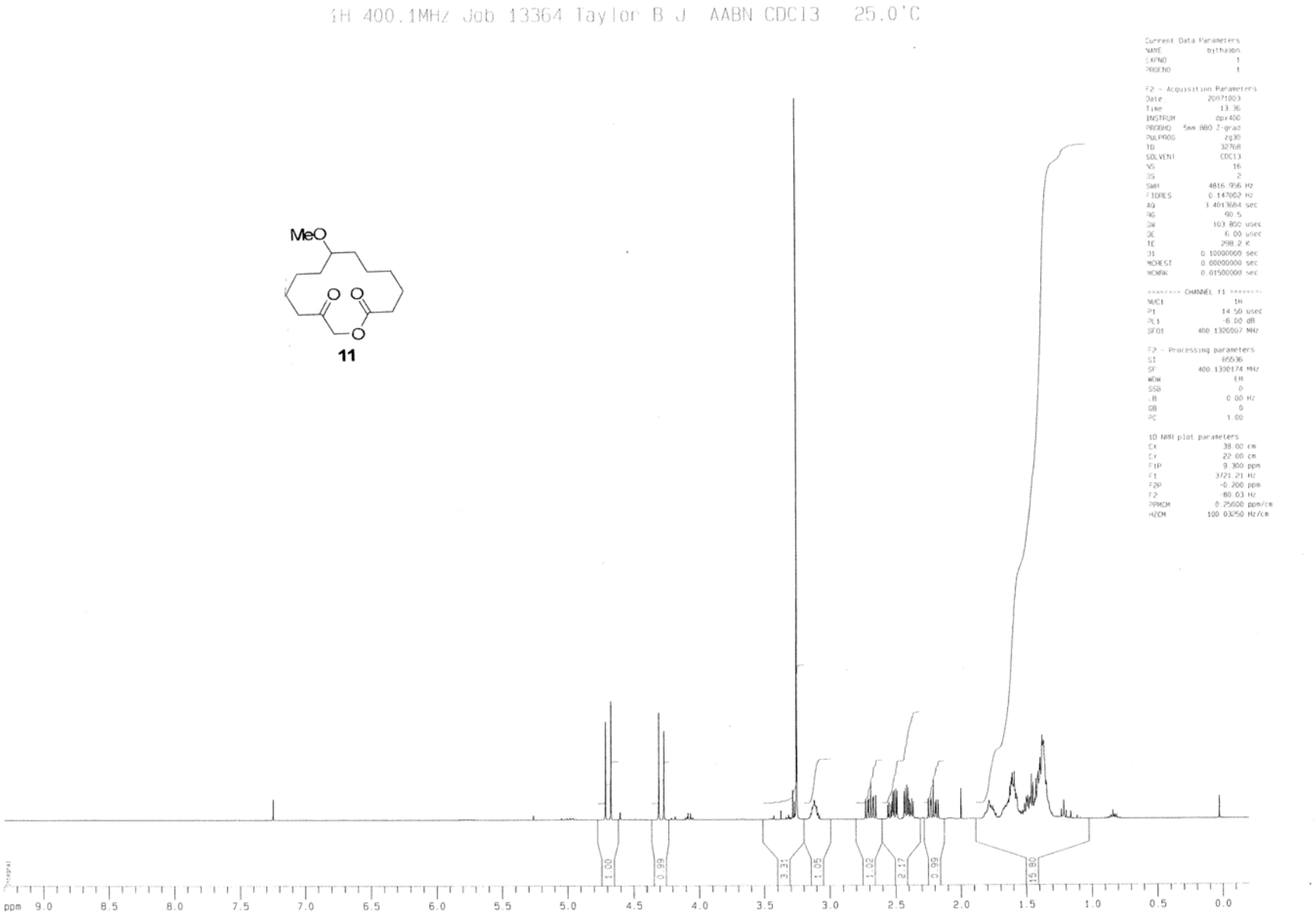
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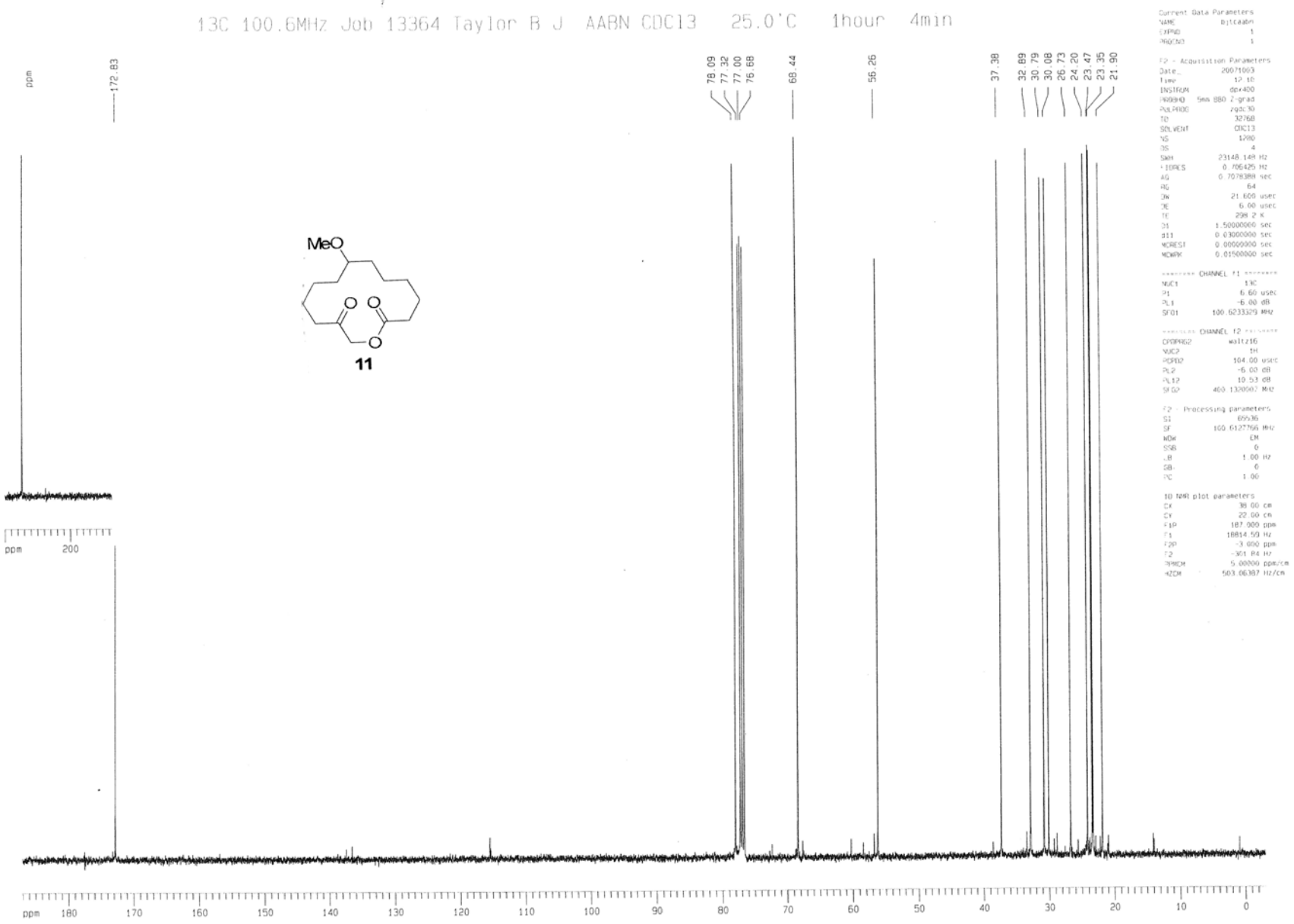
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X-ray crystallographic data for macrocyclic keto lactone 11

Table 1. Crystal data and structure refinement for kjmbjt1.

Identification code	kjmbjt1	
Empirical formula	C14 H24 O4	
Formula weight	256.33	
Temperature	273(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 5.9569(12) Å	α= 90°.
	b = 27.197(5) Å	β= 100.74(3)°.
	c = 8.9521(18) Å	γ = 90°.
Volume	1424.9(5) $Å^3$	
Z	4	
Density (calculated)	1.195 Mg/m^3	
Absorption coefficient	0.086 mm^{-1}	
F(000)	560	
Crystal size	0.55 x 0.35 x 0.15 mm^3	
Theta range for data collection	1.50 to 30.48°.	
Index ranges	-8<=h<=8, 0<=k<=38, 0<=l<=12	
Reflections collected	6617	
Independent reflections	6617 [R(int) = 0.0000]	
Completeness to theta = 30.48°	92.3 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6617 / 1 / 328	
Goodness-of-fit on F^2	0.807	
Final R indices [I>2sigma(I)]	R1 = 0.0574, wR2 = 0.1181	
R indices (all data)	R1 = 0.1751, wR2 = 0.1656	
Absolute structure parameter	0(2)	
Largest diff. peak and hole	0.254 and -0.282 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for kjmbjt1. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	5398(7)	9343(2)	4171(4)	28(1)
O(2)	1819(7)	10306(1)	3116(4)	24(1)
O(3)	7389(6)	10010(1)	5174(3)	22(1)
O(4)	6299(7)	9226(1)	-2252(3)	26(1)
C(1)	7237(10)	9529(2)	4726(5)	19(1)
C(2)	9544(10)	9281(2)	4954(5)	25(1)
C(3)	9524(11)	8771(2)	4246(5)	30(1)
C(4)	8758(11)	8763(2)	2508(5)	28(1)
C(5)	10267(10)	9063(2)	1639(5)	24(1)
C(6)	9458(11)	9049(2)	-99(5)	28(1)
C(7)	7202(10)	9330(2)	-662(5)	19(1)
C(8)	7477(10)	9886(2)	-561(5)	22(1)
C(9)	5264(10)	10181(2)	-749(5)	24(1)
C(10)	3969(10)	10132(2)	587(5)	25(1)
C(11)	5243(10)	10353(2)	2083(5)	20(1)
C(12)	3922(11)	10295(2)	3387(5)	17(1)
C(13)	5181(11)	10249(2)	5002(5)	22(1)
C(14)	5110(12)	8774(2)	-2490(6)	31(2)
O(5)	473(7)	7122(1)	4459(3)	22(1)
O(6)	-3142(7)	6172(2)	3350(3)	24(1)
O(7)	2416(6)	6448(1)	5452(3)	20(1)
O(8)	1520(7)	7297(1)	-1972(3)	25(1)
C(15)	2256(10)	6926(2)	5020(5)	19(1)
C(16)	4590(10)	7164(2)	5280(5)	21(1)
C(17)	4602(11)	7684(2)	4606(5)	27(1)
C(18)	3864(11)	7729(2)	2864(5)	25(1)
C(19)	5365(10)	7440(2)	1954(5)	24(1)
C(20)	4568(10)	7467(2)	218(5)	24(1)
C(21)	2358(9)	7189(2)	-380(5)	21(1)
C(22)	2588(9)	6631(2)	-282(5)	20(1)
C(23)	313(10)	6344(2)	-497(5)	25(1)
C(24)	-928(9)	6386(2)	838(5)	19(1)
C(25)	309(10)	6143(2)	2322(5)	20(1)
C(26)	-1068(10)	6185(2)	3584(5)	19(1)
C(27)	196(11)	6199(2)	5245(5)	22(1)
C(28)	282(12)	7747(2)	-2236(6)	29(1)

Table 3. Bond lengths [Å] and angles [°] for kjmbjt1.

Molecule 1		**Molecule 2**	
Bond lengths [Å]		Bond lengths [Å]	
O(1)-C(1)	1.224(7)	O(5)-C(15)	1.210(6)
O(2)-C(12)	1.231(7)	O(6)-C(26)	1.214(7)
O(3)-C(1)	1.368(7)	O(7)-C(15)	1.356(7)
O(3)-C(13)	1.449(7)	O(7)-C(27)	1.466(7)
O(4)-C(14)	1.415(7)	O(8)-C(28)	1.427(7)
O(4)-C(7)	1.452(6)	O(8)-C(21)	1.449(5)
C(1)-C(2)	1.510(8)	C(15)-C(16)	1.511(8)
C(2)-C(3)	1.525(8)	C(16)-C(17)	1.539(8)
C(3)-C(4)	1.538(7)	C(17)-C(18)	1.544(7)
C(4)-C(5)	1.531(8)	C(18)-C(19)	1.535(8)
C(5)-C(6)	1.541(7)	C(19)-C(20)	1.540(7)
C(6)-C(7)	1.545(8)	C(20)-C(21)	1.526(8)
C(7)-C(8)	1.523(7)	C(21)-C(22)	1.526(8)
C(8)-C(9)	1.525(8)	C(22)-C(23)	1.544(8)
C(9)-C(10)	1.545(7)	C(23)-C(24)	1.521(7)
C(10)-C(11)	1.532(7)	C(24)-C(25)	1.543(7)
C(11)-C(12)	1.533(7)	C(25)-C(26)	1.519(7)
C(12)-C(13)	1.504(7)	C(26)-C(27)	1.537(8)
Bond angles [°]		Bond angles [°]	
C(1)-O(3)-C(13)	112.8(4)	C(15)-O(7)-C(27)	113.1(4)
C(14)-O(4)-C(7)	113.6(4)	C(28)-O(8)-C(21)	114.1(4)
O(1)-C(1)-O(3)	121.3(5)	O(5)-C(15)-O(7)	123.4(5)
O(1)-C(1)-C(2)	126.4(5)	O(5)-C(15)-C(16)	125.9(5)
O(3)-C(1)-C(2)	112.2(5)	O(7)-C(15)-C(16)	110.7(5)
C(1)-C(2)-C(3)	114.4(5)	C(15)-C(16)-C(17)	113.8(5)
C(2)-C(3)-C(4)	114.3(5)	C(16)-C(17)-C(18)	116.6(5)
C(5)-C(4)-C(3)	114.5(5)	C(19)-C(18)-C(17)	114.3(5)
C(4)-C(5)-C(6)	113.4(5)	C(18)-C(19)-C(20)	114.3(5)
C(5)-C(6)-C(7)	114.0(4)	C(21)-C(20)-C(19)	114.4(4)
O(4)-C(7)-C(8)	105.5(4)	O(8)-C(21)-C(22)	105.6(4)
O(4)-C(7)-C(6)	111.4(4)	O(8)-C(21)-C(20)	111.2(4)
C(8)-C(7)-C(6)	113.2(5)	C(22)-C(21)-C(20)	114.2(5)
C(7)-C(8)-C(9)	115.8(5)	C(21)-C(22)-C(23)	115.3(5)
C(8)-C(9)-C(10)	114.5(4)	C(24)-C(23)-C(22)	114.1(4)
C(11)-C(10)-C(9)	113.9(5)	C(23)-C(24)-C(25)	114.9(5)
C(10)-C(11)-C(12)	112.6(5)	C(26)-C(25)-C(24)	111.8(5)

O(2)-C(12)-C(13)	119.9(5)	O(6)-C(26)-C(25)	122.9(5)
O(2)-C(12)-C(11)	119.7(5)	O(6)-C(26)-C(27)	117.8(4)
C(13)-C(12)-C(11)	120.4(5)	C(25)-C(26)-C(27)	119.1(5)
O(3)-C(13)-C(12)	114.8(4)	O(7)-C(27)-C(26)	113.7(4)

Computational Details

Gaussian 03, Revision C.02[1] and employed the B3LYP[2] hybrid functional throughout. 6-31G** basis sets were used for all atoms.[3] Geometry optimizations were run as spin-unrestricted calculations in the doublet spin state with no symmetry constraints. All stationary points were confirmed as either local minima or transition states via analytical frequency calculations. Transition states were also further characterized via IRC calculations and shown to link to the expected adjacent minima. Natural population analyses were performed using the NBO program version 3.0[4] implemented within Gaussian 03. The value of the total spin expectation operator, $\langle S^2 \rangle$, was checked in all cases was less than 0.76, indicating minimal spin contamination.

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R = H

8a
SCF Energy= -464.276511017
+Zero Point Energy= -464.054159
Enthalpy (298 K)= -464.042692
Free Energy (298 K)= -464.090462

C 0.362031 1.167549 -0.229931
C -0.094655 -0.262435 0.174102
C 0.921973 -1.312935 -0.416009
C 2.376670 -1.008811 -0.042751
C 2.778147 0.421464 -0.429593
C 1.812436 1.450794 0.172961
O -0.019052 -0.434997 1.533439
C -1.507575 -0.582855 -0.345337
H 0.791396 -1.279207 -1.505549
H 2.508059 -1.148101 1.035866
H 3.029456 -1.736357 -0.540369
H 3.805076 0.623245 -0.103530
H 2.774098 0.515583 -1.525486
H 1.887459 1.424864 1.266167
H 2.090020 2.463393 -0.142692
H -0.325158 1.883511 0.227867
H 0.243494 1.262810 -1.318067
H 0.628323 -2.311750 -0.077874
O -2.396033 0.402597 0.141998
H -1.519895 -0.601666 -1.449469
H -1.798239 -1.583094 0.015256
C -3.732509 0.183454 -0.254027
H -4.333390 0.991241 0.170281
H -3.842421 0.196511 -1.350400
H -4.116703 -0.779133 0.118009

TS 8a
SCF Energy= -464.255688412
+Zero Point Energy= -464.036675
Enthalpy (298 K)= -464.024962
Free Energy (298 K)= -464.073379
Nimag=1 (-381.93 cm^{-1})

C 1.831542 1.502205 0.209074
C 0.426645 1.387274 -0.290197
C -0.155876 -0.602610 0.274703
C 0.940928 -1.345360 -0.513741
C 2.354224 -0.996651 -0.032378
C 2.774126 0.438823 -0.380352
O -0.061684 -0.494590 1.512341
C -1.546596 -0.614515 -0.382817
O -2.378383 0.344384 0.222783
C -3.702676 0.306326 -0.264520
H 0.835304 -1.163255 -1.590269
H 2.385836 -1.136050 1.053783
H 3.070592 -1.700893 -0.470908
H 3.793342 0.618661 -0.018857
H 2.808214 0.554566 -1.473569
H 1.829990 1.439274 1.302854
H 2.213528 2.505496 -0.046208
H -0.367597 1.897586 0.243544
H 0.279806 1.311903 -1.367569
H 0.753748 -2.418191 -0.359442
H -1.466667 -0.448226 -1.470155
H -1.956664 -1.632868 -0.243559
H -4.263471 1.079973 0.264918
H -3.750497 0.509600 -1.346573
H -4.178836 -0.668887 -0.077623

P 8a
SCF Energy= -464.264010282
+Zero Point Energy= -464.047021
Enthalpy (298 K)= -464.033408
Free Energy (298 K)= -464.087129

C 2.268633 1.324618 0.398356
C 1.135709 1.923532 -0.364695
C -0.372696 -0.696097 0.226040
C 0.715341 -1.293939 -0.664729
C 2.125050 -1.245937 -0.058754
C 2.897173 0.070600 -0.249465
O -0.253690 -0.588613 1.428483
C -1.654998 -0.305665 -0.503531
O -2.636100 0.106854 0.405153
C -3.838318 0.488302 -0.229821
H 0.684094 -0.826955 -1.657175
H 2.037924 -1.467229 1.010708
H 2.720460 -2.052951 -0.501616
H 3.900003 -0.071446 0.172043
H 3.044859 0.258356 -1.322869
H 1.948387 1.090790 1.419970
H 3.069204 2.081018 0.498720
H 0.313326 2.413942 0.145010
H 1.222231 2.073831 -1.438165
H 0.419193 -2.342625 -0.821439
H -1.398975 0.492112 -1.224461
H -1.990235 -1.170445 -1.107869
H -4.533736 0.791558 0.555786
H -3.688965 1.334472 -0.919329
H -4.284816 -0.342848 -0.798817

P 8a (straight-chain)
SCF Energy= -464.266139620
+Zero Point Energy= -464.049927
Enthalpy (298 K)= -464.035593
Free Energy (298 K)= -464.092319

C 5.234016 -0.373495 -0.012703
H 5.646549 -0.984920 0.783615
H 5.685278 -0.464089 -0.995699
C 3.960478 0.378264 0.179303
H 3.938789 1.257495 -0.479031
C 2.690027 -0.465715 -0.101087
H 3.898583 0.757862 1.208401
C 1.395506 0.329559 0.100020
H 2.735105 -0.849216 -1.129189
H 2.695435 -1.347157 0.554182
C 0.137692 -0.500275 -0.164580
H 1.356628 0.724065 1.123256
H 1.382827 1.206039 -0.556976
C -1.155463 0.302437 -0.065785

```
H  0.170807 -0.930178 -1.177723
H  0.080455 -1.364354 0.512486
C  -2.425715 -0.536189 0.064893
O  -1.180832 1.513916 -0.089919
O  -3.562986 0.268083 -0.058786
H  -2.402102 -1.340613 -0.694178
H  -2.387583 -1.046247 1.047147
C  -4.763824 -0.459287 0.096990
H  -5.585350 0.251101 -0.016586
H  -4.868205 -1.249264 -0.663714
H  -4.832970 -0.928311 1.091334
```

9
SCF Energy= -424.977963955
+Zero Point Energy= -424.784785
Enthalpy (298 K)= -424.774546
Free Energy (298 K)= -424.820082

C -0.232857 1.272016 -0.389043
C -1.654071 1.281642 0.171650
H -0.229909 1.263186 -1.483678
C -2.434537 0.022453 -0.231267
H -1.608360 1.354659 1.263950
H -2.172484 2.178920 -0.188749
C -1.688105 -1.254417 0.180058
H -3.432685 0.037336 0.220915
H -2.584004 0.020968 -1.320503
C -0.266852 -1.288370 -0.380501
H -1.643971 -1.320538 1.272917
H -2.231088 -2.139830 -0.173186
C 0.572907 -0.020509 0.052351
H 0.285713 -2.169329 -0.042385
H -0.264238 -1.290050 -1.475311
O 0.731200 -0.009817 1.358263
O 1.767659 -0.041932 -0.734697
C 2.975948 0.023338 0.002901
H 3.781808 0.022084 -0.734092
H 3.036825 0.933992 0.613282
H 3.092275 -0.833551 0.678704
H 0.344651 2.139230 -0.057278

TS 9
SCF Energy= -424.969841529
+Zero Point Energy= -424.778398
Enthalpy (298 K)= -424.768198
Free Energy (298 K)= -424.812774
Nimag=1 (-457.94 cm^{-1})

C -0.242128 1.361066 -0.440442
C -1.614118 1.354357 0.168949
H -0.183910 1.225722 -1.520022
C -2.431571 0.114350 -0.224712
H -1.521057 1.415495 1.258738
H -2.145821 2.264115 -0.154814
C -1.737754 -1.193310 0.181811
H -3.424112 0.167777 0.237093
H -2.592737 0.118888 -1.312289
C -0.337271 -1.335416 -0.417769
H -1.654202 -1.242308 1.273382
H -2.349863 -2.046507 -0.133083
C 0.657844 -0.299979 0.142839
H 0.088804 -2.314531 -0.165961
H -0.355701 -1.268283 -1.509996
O 0.749666 -0.094090 1.373408
O 1.788209 -0.274237 -0.671665
C 2.964788 0.236144 -0.048214
H 3.757155 0.159080 -0.794433
H 2.841207 1.283549 0.250752
H 3.222347 -0.343107 0.843471
H 0.456155 2.103450 -0.061556

P 9
SCF Energy= -424.986973174
+Zero Point Energy= -424.797317
Enthalpy (298 K)= -424.785107
Free Energy (298 K)= -424.835187

C -0.911824 1.862339 -0.474885
C -1.924688 1.189728 0.388182
H -1.019890 1.856165 -1.556152
C -2.426723 -0.171697 -0.139591
H -1.528569 1.069862 1.403514
H -2.806292 1.850667 0.488454
C -1.491306 -1.373380 0.080339
H -3.380111 -0.403492 0.351129
H -2.654001 -0.076644 -1.211158
C -0.126052 -1.306000 -0.617684
H -1.319369 -1.512816 1.153464
H -2.011266 -2.271114 -0.274355
C 0.919297 -0.518735 0.150110
H 0.286263 -2.319482 -0.721125
H -0.198601 -0.906086 -1.633579
O 0.911143 -0.307766 1.345034
O 1.928254 -0.132286 -0.664212
C 3.005294 0.563913 -0.018083
H 3.728848 0.782570 -0.803379
H 2.645641 1.489429 0.438534
H 3.458102 -0.057268 0.758746
H -0.179928 2.541609 -0.050989

P 9 (straight-chain)
SCF Energy= -424.988494327
+Zero Point Energy= -424.799096
Enthalpy (298 K)= -424.786295
Free Energy (298 K)= -424.839314

C -4.548789 -0.233378 0.015364
C -3.158730 -0.534471 -0.433013
H -4.970421 -0.719193 0.889535
H -5.104277 0.595606 -0.411529
H -3.065403 -0.358278 -1.513470
C -2.076338 0.309076 0.289280
H -2.931613 -1.596718 -0.268586
C -0.656485 -0.017547 -0.187652
H -2.286027 1.374646 0.129973
H -2.151247 0.138738 1.371312
C 0.415377 0.823296 0.531677
H -0.444442 -1.080603 -0.026215
H -0.584369 0.156341 -1.269345
C 1.819453 0.521647 0.051150
H 0.244166 1.890591 0.370677
H 0.368150 0.627685 1.609768
O 2.544218 1.289950 -0.543014
O 2.177850 -0.749094 0.358661
C 3.490199 -1.138497 -0.077599
H 3.611465 -2.174350 0.238820
H 3.576272 -1.056472 -1.163921
H 4.253086 -0.505593 0.382564

R = Me

8a (R = Me, equatorial)
SCF Energy= -503.590262205
+Zero Point Energy= -503.339797
Enthalpy (298 K)= -503.326915
Free Energy (298 K)= -503.377675

C 2.383259 -1.289942 0.098551
C 2.880741 0.049351 -0.452795
C 1.974698 1.193166 0.010871
C 0.499655 1.003892 -0.387610
C -0.055863 -0.355616 0.161509
C 0.919253 -1.531641 -0.268457
C -0.327500 2.212992 0.075502
O -0.043223 -0.400791 1.528970
C -1.447372 -0.752320 -0.387454
O -2.448869 0.101957 0.125781
C -3.748206 -0.294464 -0.259155
H -1.650545 -1.791739 -0.082167
H 0.809173 -1.622476 -1.357311
H 2.491768 -1.303808 1.188865
H 2.986518 -2.118356 -0.292829
H 3.914652 0.229143 -0.135927
H 2.892631 0.010283 -1.551879
H 2.028080 1.279711 1.103692
H 2.329855 2.146732 -0.398309
H 0.445180 0.938822 -1.485327
H 0.548252 -2.456927 0.181673
H -1.438066 -0.722795 -1.491453
H -4.448995 0.414102 0.188046
H -3.875560 -0.279116 -1.353460
H -3.987129 -1.307601 0.100220
H -1.362510 2.155103 -0.261114
H -0.336295 2.268364 1.169137
H 0.117731 3.138728 -0.305637

8a TS (R = Me, equatorial, substituted C-C(R) bond cleavage)
SCF Energy= -503.576857359
+Zero Point Energy= -503.329313
Enthalpy (298 K)= -503.316183
Free Energy (298 K)= -503.367584
Nimag=1 (-391.83 cm^{-1})

C 2.366704 -1.290043 0.103177
C 2.889811 0.054457 -0.413769
C 2.017355 1.233855 0.033560
C 0.590420 1.181281 -0.446173
C -0.117309 -0.649496 0.284434
C 0.937218 -1.575704 -0.361305
C -0.328917 2.253667 0.063379
O -0.059592 -0.410367 1.515075
C -1.491342 -0.774950 -0.405960
O -2.462037 0.017509 0.230316
C -3.757878 -0.187757 -0.291882
H -1.769351 -1.844792 -0.346189
H 0.866958 -1.529916 -1.456074
H 2.378045 -1.294559 1.198932
H 3.027561 -2.098048 -0.231452
H 3.917075 0.211888 -0.064626
H 2.936303 0.031374 -1.512365
H 2.015809 1.304506 1.127829
H 2.457367 2.175578 -0.336107
H 0.473273 0.932107 -1.504229
H 0.652246 -2.598348 -0.075531
H -1.413330 -0.533944 -1.479971
H -4.437399 0.459568 0.267127
H -3.818799 0.070833 -1.361409
H -4.083937 -1.232947 -0.173334
H -1.360869 2.097894 -0.251515
H -0.311986 2.287578 1.155823
H 0.007697 3.232221 -0.312797

P 8a (R = Me, equatorial, substituted C-C(R) bond cleavage)
SCF Energy= -503.587928221
+Zero Point Energy= -503.342147
Enthalpy (298 K)= -503.327258
Free Energy (298 K)= -503.383750

C 2.176763 -1.473829 0.015873
C 2.878732 -0.140728 -0.296031
C 2.205771 1.128466 0.266429
C 1.045666 1.637707 -0.528528
C -0.331558 -0.969867 0.268026
C 0.763268 -1.640104 -0.558829
C 0.004099 2.508739 0.093430
O -0.211741 -0.737841 1.453638
C -1.624340 -0.677564 -0.487564
O -2.583311 -0.128287 0.371773
C -3.799185 0.162889 -0.285456
H -1.976881 -1.620027 -0.949393
H 0.707907 -1.298510 -1.600106
H 2.116674 -1.609978 1.101294
H 2.803822 -2.285863 -0.370748
H 3.896460 -0.204882 0.108333
H 2.994570 -0.032774 -1.384406
H 1.893686 0.951542 1.303870
H 2.974228 1.923389 0.320802
H 1.133551 1.617473 -1.614640
H 0.501552 -2.709313 -0.582565
H -1.382397 0.003638 -1.322712
H -4.472928 0.589287 0.460808
H -3.662126 0.891704 -1.099974
H -4.263806 -0.741791 -0.708861
H -0.749574 2.829116 -0.632245
H -0.512176 1.989670 0.912169
H 0.442558 3.422094 0.530989

8a TS (R = Me, equatorial, unsubstituted C-C bond cleavage)
SCF Energy= -503.571083960
+Zero Point Energy= -503.323703
Enthalpy (298 K)= -503.310502
Free Energy (298 K)= -503.362167
Nimag=1 (-369.65 cm^{-1})

```
C  2.476187 -1.302640 0.053209
C  2.864452 0.080088 -0.492064
C  1.940261 1.197967 0.005719
C  0.458774 1.021862 -0.368410
C  -0.177733 -0.177718 0.376526
C  1.108580 -1.730701 -0.369882
C  -0.335552 2.299479 -0.021741
O  0.027053 -0.318752 1.601749
C  -1.469531 -0.780734 -0.214765
O  -2.543501 0.098092 0.080446
C  -3.789907 -0.411291 -0.347622
H  -1.637593 -1.759978 0.258036
H  0.868966 -1.666876 -1.430846
H  2.533515 -1.307263 1.147327
H  3.201904 -2.053894 -0.302239
H  3.897796 0.304809 -0.203068
H  2.850219 0.050948 -1.591345
H  2.004899 1.268287 1.098111
H  2.289978 2.156408 -0.396863
H  0.374559 0.846527 -1.450153
H  0.655849 -2.570598 0.149572
H  -1.387210 -0.926205 -1.304554
H  -4.550588 0.323521 -0.074343
H  -3.817711 -0.565312 -1.438224
H  -4.026568 -1.368947 0.141389
H  -1.389175 2.200932 -0.287709
H  -0.276505 2.494811 1.053674
H  0.086062 3.160245 -0.552144
```

P 8a (R = Me, equatorial, unsubstituted C-C(R) bond cleavage)

```
SCF Energy= -503.583427515
+Zero Point Energy= -503.337909
Enthalpy (298 K)= -503.322905
Free Energy (298 K)= -503.379416

C  2.382606 -1.426109 0.030570
C  2.610833 -0.125234 -0.766819
C  1.837222 1.114775 -0.284953
C  0.303365 1.024385 -0.347615
C  -0.280494 0.307476 0.867756
C  1.101713 -2.128566 -0.266481
C  -0.348827 2.427469 -0.401579
O  0.274912 0.271853 1.951836
C  -1.683948 -0.296356 0.764452
O  -2.169047 -0.283443 -0.560142
C  -3.467826 -0.830520 -0.671730
H  -2.341787 0.281778 1.436346
H  0.698924 -2.141633 -1.275290
H  2.452958 -1.219768 1.105877
H  3.223987 -2.108798 -0.193956
H  3.680047 0.117994 -0.732247
H  2.378804 -0.312432 -1.825285
H  2.125508 1.351202 0.745757
H  2.154007 1.964330 -0.902893
H  -0.015988 0.481957 -1.243284
H  0.672079 -2.821643 0.449926
H  -1.634337 -1.318869 1.169441
H  -3.753685 -0.774910 -1.724367
H  -3.495013 -1.882650 -0.349162
H  -4.199894 -0.267515 -0.072292
H  -1.438972 2.357071 -0.451666
H  -0.075458 3.018145 0.479283
H  -0.005970 2.964542 -1.291347
```

8a (R = Me, axial)
SCF Energy= -503.589790112
+Zero Point Energy= -503.339550
Enthalpy (298 K)= -503.326605
Free Energy (298 K)= -503.377299

C 2.792439 0.307967 -0.093219
C 1.822903 1.000026 0.876212
C 0.357370 0.973396 0.401210
C -0.096203 -0.528117 0.102397
C 0.914031 -1.199586 -0.878496
C 2.357597 -1.137305 -0.369513
C 0.093896 1.900558 -0.794832
O -0.031967 -1.154122 1.318472
C -1.525709 -0.601308 -0.470579
O -2.391141 0.189416 0.317089
C -3.751598 0.024005 -0.021755
H 0.832639 -0.702524 -1.852770
H 2.434317 -1.723968 0.552390
H 3.023524 -1.604320 -1.104850
H 3.806201 0.323865 0.323762
H 2.841305 0.864103 -1.039326
H 1.884932 0.507662 1.852067
H 2.121185 2.045320 1.026603
H -0.284294 1.307928 1.221022
H 0.602794 -2.240193 -1.028346
H -1.546257 -0.270326 -1.522366
H -1.840431 -1.657710 -0.450239
H -4.332104 0.669971 0.641055
H -3.954085 0.312011 -1.065686
H -4.080892 -1.017325 0.117401
H -0.973988 1.968690 -1.012423
H 0.445757 2.908332 -0.547045
H 0.615903 1.588314 -1.704295

8a TS (R = Me, axial, substituted C-C(R) bond cleavage)
SCF Energy= -503.575319454
+Zero Point Energy= -503.327502
Enthalpy (298 K)= -503.314466
Free Energy (298 K)= -503.365581
Nimag=1 (-365.94 cm^{-1})
C 2.775820 0.301154 -0.074352
C 1.832790 1.033818 0.897521
C 0.408773 1.182384 0.420214
C -0.158269 -0.828730 0.104524
C 0.920554 -1.234086 -0.919606
C 2.338625 -1.144383 -0.347651
C 0.132542 1.996050 -0.813875
O -0.056700 -1.228789 1.289670
C -1.566546 -0.651084 -0.491677
O -2.369467 0.129727 0.363768
C -3.730468 0.135568 -0.012949
H 0.829309 -0.639865 -1.836610
H 2.367445 -1.719071 0.584493
H 3.043435 -1.615602 -1.042606
H 3.787768 0.304329 0.347388
H 2.839790 0.852622 -1.022329
H 1.825893 0.508910 1.857314
H 2.230423 2.044888 1.088180
H -0.323367 1.323062 1.210328
H 0.699360 -2.273650 -1.203257
H -1.518406 -0.212544 -1.501591
H -1.988406 -1.666767 -0.599509
H -4.261885 0.762876 0.706460
H -3.878469 0.549855 -1.023176
H -4.162685 -0.876697 0.009562
H -0.934250 2.017704 -1.046442
H 0.446499 3.036859 -0.634519
H 0.683951 1.651438 -1.694098

P 8a (R = Me, axial, substituted C-C(R) bond cleavage)
SCF Energy= -503.585712437
+Zero Point Energy= -503.340149
Enthalpy (298 K)= -503.325014
Free Energy (298 K)= -503.383252

C 2.736692 -0.386972 -0.110075
C 2.188292 0.641313 0.913976
C 1.083460 1.528348 0.423042
C -0.579483 -1.011738 0.046265
C 0.497589 -1.421284 -0.955584
C 1.882988 -1.646777 -0.332808
C 1.340060 2.596609 -0.589861
O -0.514391 -1.281232 1.227506
C -1.785885 -0.297618 -0.557478
O -2.707193 0.039862 0.440587
C -3.848305 0.696334 -0.070669
H 0.538425 -0.696759 -1.778501
H 1.743245 -2.169661 0.619883
H 2.446998 -2.323803 -0.985293
H 3.723950 -0.716367 0.237581
H 2.910772 0.112296 -1.073430
H 1.860532 0.104309 1.809815
H 3.040190 1.273728 1.220374
H 0.159878 1.572979 0.993414
H 0.140658 -2.361472 -1.403549
H -1.421504 0.593642 -1.099013
H -2.231345 -0.962219 -1.323171
H -4.497182 0.919635 0.778931
H -3.588314 1.639265 -0.577627
H -4.400876 0.064284 -0.783965
H 0.413556 2.970930 -1.038251
H 1.848110 3.468888 -0.141078
H 1.993136 2.251992 -1.401709

8a TS (R = Me, axial, unsubstituted C-C bond cleavage)
SCF Energy= -503.568442693
+Zero Point Energy= -503.321090
Enthalpy (298 K)= -503.307976
Free Energy (298 K)= -503.359226
Nimag=1 (-378.38 cm^{-1})

C 2.783054 0.371676 -0.181122
C 1.841324 1.028948 0.839273
C 0.351123 1.027451 0.444027
C -0.218930 -0.414641 0.445518
C 1.087267 -1.319024 -1.016954

```
C  2.450488 -1.108545 -0.436965
C  0.040235 1.864981 -0.804615
O  0.062768 -1.169377 1.401824
C  -1.547871 -0.657814 -0.294852
O  -2.514220 0.194036 0.302918
C  -3.813341 -0.010520 -0.214908
H  0.822174 -0.748724 -1.905628
H  2.534545 -1.677409 0.495182
H  3.193786 -1.532973 -1.133290
H  3.813668 0.446692 0.185036
H  2.758201 0.919251 -1.132731
H  1.934882 0.506814 1.796929
H  2.157877 2.066004 1.005565
H  -0.197934 1.494997 1.274522
H  0.668608 -2.321015 -0.980657
H  -1.477535 -0.448604 -1.373522
H  -1.814609 -1.715537 -0.156957
H  -4.479445 0.687445 0.297579
H  -3.857660 0.184167 -1.298319
H  -4.165336 -1.037711 -0.034705
H  -1.038074 1.930385 -0.968345
H  0.416280 2.885033 -0.670848
H  0.502104 1.468840 -1.714154
```

P 8a (R = Me, axial, unsubstituted C-C bond cleavage)

```
SCF Energy= -503.578781413
+Zero Point Energy= -503.333174
Enthalpy (298 K)=  -503.318140
Free Energy (298 K)= -503.374671
C  -2.717303 0.786197 -0.155323
C  -1.465759 1.130171 -0.987932
C  -0.064643 0.914327 -0.375601
C  0.458627 -0.505322 -0.567685
C  -2.234289 -1.258331 1.336428
C  -2.973962 -0.712073 0.161298
C  0.065128 1.396271 1.084301
O  -0.171441 -1.390923 -1.117782
C  1.865272 -0.837397 -0.058234
O  2.715608 0.289368 -0.117569
C  4.022720 0.010603 0.347082
H  -2.416098 -0.858071 2.330505
H  -2.751913 -1.307765 -0.728346
H  -4.056438 -0.812604 0.350478
H  -3.577250 1.155930 -0.728546
H  -2.719583 1.358986 0.781048
H  -1.512951 0.583455 -1.936185
H  -1.537892 2.196042 -1.240716
H  0.644898 1.521768 -0.959310
H  -1.589161 -2.124778 1.251456
H  1.768075 -1.205443 0.979959
H  2.247214 -1.670509 -0.665697
H  4.600025 0.933476 0.259793
H  4.019803 -0.312512 1.399549
H  4.508105 -0.773151 -0.253799
H  1.109330 1.390286 1.402351
H  -0.306943 2.422396 1.170377
H  -0.517296 0.768256 1.763891
```

R = OMe

8a (R = Me, axial)
SCF Energy= -578.796852177
+Zero Point Energy= -578.541836
Enthalpy (298 K)= -578.527784
Free Energy (298 K)= -578.581344

C 1.827859 0.744062 1.061184
C 0.386997 0.701215 0.555483
C 0.016427 -0.791898 0.038226
C 1.061130 -1.174625 -1.050672
C 2.496692 -1.118814 -0.519965
C 2.840582 0.282200 0.003940
O 0.123020 -1.567149 1.138677
C -1.409754 -0.810854 -0.546645
O -2.318833 -0.267213 0.392864
C -3.669993 -0.514559 0.061369
H 0.940081 -0.482304 -1.891673
H 2.606200 -1.851830 0.286922
H 3.193196 -1.407143 -1.316057
H 3.850130 0.293046 0.430399
H 2.838543 0.996893 -0.828170
H 1.889687 0.102005 1.946803
H 2.044271 1.771775 1.376963
H -0.320998 0.929838 1.356716
O 0.222073 1.589636 -0.529585
H 0.820898 -2.181429 -1.412591
H -1.444432 -0.247697 -1.492141
H -1.666859 -1.859822 -0.764832
H -4.284093 -0.065888 0.845778
H -3.946226 -0.067544 -0.906569
H -3.882536 -1.593342 0.015443
C -0.817555 2.549615 -0.373507
H -0.867453 3.112955 -1.308192
H -1.780414 2.065339 -0.178705
H -0.594382 3.244898 0.447778

8a TS (R = OMe, axial, substituted C-C(R) bond cleavage)
SCF Energy= -578.792807874
+Zero Point Energy= -578.538918
Enthalpy (298 K)= -578.525024
Free Energy (298 K)= -578.578050
Nimag=1 (-249.71 cm^{-1})

C -1.747835 0.471247 -1.254346
C -0.432569 0.864506 -0.635681
C 0.194778 -0.908940 0.214964
C -0.981545 -1.143500 1.182825
C -2.314012 -1.340432 0.454254
C -2.783823 -0.060766 -0.250166
O 0.292629 -1.618101 -0.826176
C 1.485050 -0.439124 0.917523
O 2.456059 0.119820 0.054024
C 3.253567 -0.835512 -0.640012
H -1.049773 -0.310501 1.892756
H -2.189612 -2.143001 -0.281408
H -3.079236 -1.667951 1.167576
H -3.723874 -0.251294 -0.780688
H -2.994535 0.717529 0.493993
H -1.532841 -0.289920 -2.009789
H -2.153241 1.354302 -1.771223
H 0.423567 0.971873 -1.300452
O -0.536394 1.826088 0.323037
H -0.737086 -2.042522 1.767257
H 1.247803 0.322791 1.666490
H 1.899070 -1.310047 1.455052
H 3.971402 -0.267208 -1.237103
H 3.808445 -1.468951 0.069071
H 2.642937 -1.468914 -1.287957
C 0.549066 2.761027 0.413372
H 0.456725 3.256021 1.381480
H 1.515553 2.255967 0.335613
H 0.460285 3.508329 -0.384143

8a TS (R = OMe, axial, substituted C-C(R) bond cleavage, no H-bonding)
SCF Energy= -578.785540973
+Zero Point Energy= -578.532424
Enthalpy (298 K)= -578.518200
Free Energy (298 K)= -578.572784
Nimag=1 (-289.54 cm^{-1})

C 2.347165 0.032184 0.711601
C 1.093076 0.860059 0.594296
C -0.353325 -0.603449 0.425779
C 0.136947 -1.275027 -0.869608
C 1.517033 -1.916794 -0.714598
C 2.621075 -0.872975 -0.501334
H 0.729923 1.320662 1.515548
O -0.177807 -1.178296 1.536069
C -1.623582 0.245943 0.254576
O -2.669984 -0.645881 -0.098113
C -3.902461 0.011135 -0.297347
H 0.137605 -0.542181 -1.685580
H 1.486847 -2.601687 0.140088
H 1.747824 -2.515866 -1.603281
H 3.585896 -1.372187 -0.355114
H 2.722319 -0.249530 -1.398549
H 2.249757 -0.573211 1.617155
H 3.190095 0.724825 0.856303
O 1.082032 1.687052 -0.494006
H -0.617219 -2.030316 -1.122457
H -1.846614 0.752034 1.207371
H -1.499885 1.002465 -0.536634
H -4.636312 -0.751231 -0.569831
H -4.245546 0.524198 0.614956
H -3.845048 0.755235 -1.108633
C 0.487823 2.973288 -0.314952
H 0.499295 3.461589 -1.290407
H -0.545559 2.896806 0.039100
H 1.070192 3.569206 0.397883

P 8a (R = OMe, axial, substituted C-C(R) bond cleavage)
SCF Energy= -578.797448937
+Zero Point Energy= -578.545296
Enthalpy (298 K)= -578.529599

Free Energy (298 K)= -578.588346

C 2.002877 0.320417 1.154821
C 0.825142 1.095855 0.666499
C -0.546183 -1.145021 -0.215819
C 0.633158 -1.537829 -1.104530
C 1.933425 -1.814549 -0.336263
C 2.707471 -0.560460 0.099841
O -0.702569 -1.612484 0.901689
C -1.616847 -0.275711 -0.886185
O -2.449993 0.430262 -0.000105
C -3.474130 -0.350682 0.605420
H 0.791669 -0.777907 -1.878560
H 1.690289 -2.426514 0.540058
H 2.589708 -2.418673 -0.973692
H 3.669704 -0.881969 0.517043
H 2.943627 0.054173 -0.778159
H 1.663111 -0.306509 1.986498
H 2.752082 1.017925 1.569092
H -0.028205 1.297217 1.308978
O 1.069899 1.999003 -0.328546
H 0.318867 -2.453038 -1.629902
H -1.125258 0.465665 -1.522957
H -2.206103 -0.933301 -1.554301
H -4.091831 0.340952 1.183459
H -4.105159 -0.832059 -0.158307
H -3.058939 -1.115752 1.266669
C 0.089013 3.025548 -0.470073
H 0.307697 3.549648 -1.402275
H -0.922945 2.606473 -0.506337
H 0.149435 3.734014 0.366125

8a TS (R = OMe, axial, unsubstituted C-C bond cleavage)
SCF Energy= -578.774649264
+Zero Point Energy= -578.523080
Enthalpy (298 K)= -578.508566
Free Energy (298 K)= -578.564373
Nimag=1 (-323.60 cm^{-1})

C 1.796976 0.697841 1.049034
C 0.327732 0.650175 0.613057
C -0.179902 -0.794841 0.400310
C 1.182399 -1.281267 -1.239944
C 2.524269 -1.132892 -0.597679
C 2.779945 0.284131 -0.056009
O 0.150135 -1.674433 1.216472
C -1.503523 -0.929760 -0.368738
O -2.475779 -0.223853 0.391612
C -3.759460 -0.269105 -0.195893
H 0.861752 -0.507268 -1.932646
H 2.627495 -1.872387 0.204372
H 3.297177 -1.375966 -1.347171
H 3.802726 0.343624 0.333291
H 2.712982 1.001397 -0.882641
H 1.900446 0.037292 1.916264
H 2.036237 1.713417 1.386625
H -0.305361 1.036355 1.427227
O 0.085414 1.413099 -0.568202
H 0.814711 -2.283933 -1.440749
H -1.440300 -0.509095 -1.380569
H -1.749877 -1.999926 -0.430306
H -4.431522 0.302264 0.449059
H -3.764379 0.177946 -1.202605
H -4.135549 -1.300823 -0.275688
C -0.330287 2.744139 -0.323193
H -0.475020 3.218953 -1.296949
H -1.279272 2.769096 0.230893
H 0.420701 3.320021 0.236865

P 8a (R = OMe, axial, unsubstituted C-C bond cleavage)
SCF Energy= -578.780429868
+Zero Point Energy= -578.530630
Enthalpy (298 K)= -578.514418
Free Energy (298 K)= -578.574128

C -1.701610 0.756384 -1.120729
C -0.222810 0.614206 -0.726550
C 0.260109 -0.843465 -0.663623
C -1.694958 -1.146921 1.612826
C -2.783764 -0.855879 0.636682
C -2.730752 0.548940 0.003446
O -0.277057 -1.727647 -1.302618
C 1.527926 -1.109135 0.146947
O 2.529685 -0.202457 -0.284838
C 3.731455 -0.337712 0.447883
H -1.251307 -0.348315 2.198041
H -2.794292 -1.621801 -0.150135
H -3.759061 -0.954572 1.149972
H -3.717000 0.777003 -0.418836
H -2.554256 1.289631 0.792382
H -1.888054 0.052321 -1.938783
H -1.847035 1.763603 -1.530222
H 0.393450 1.048378 -1.532148
O 0.081118 1.267980 0.500952
H -1.468077 -2.170891 1.893188
H 1.305036 -0.968938 1.215387
H 1.826777 -2.152946 -0.023845
H 4.439926 0.389071 0.043725
H 3.579515 -0.133511 1.518902
H 4.159418 -1.346580 0.345093
C 0.679013 2.544004 0.351779
H 0.824159 2.946800 1.357359
H 1.653969 2.467168 -0.147615
H 0.039207 3.238044 -0.212405

8a (R = Me, equatorial)
SCF Energy= -578.793694092
+Zero Point Energy= -578.538797
Enthalpy (298 K)= -578.524905
Free Energy (298 K)= -578.578042

C 1.912190 1.137576 -0.173711
C 0.523821 0.699665 -0.646143
C 0.032192 -0.629762 0.181450
C 1.120687 -1.711441 -0.134448
C 2.524130 -1.277507 0.294052
C 2.948221 0.026242 -0.394390
O -0.447501 1.697789 -0.664734
C -0.702706 2.370345 0.560978
O 0.031914 -0.318023 1.485553
C -1.344879 -1.102096 -0.342437
H -1.490625 -2.150795 -0.027077
H 1.094506 -1.931005 -1.210423
H 2.529058 -1.136757 1.380022
H 3.239906 -2.076394 0.067844
H 3.927086 0.351781 -0.024771
H 3.066318 -0.150398 -1.473125
H 1.876885 1.400252 0.887442
H 2.188097 2.039141 -0.734160
H 0.577815 0.349650 -1.684880
H 0.828691 -2.629416 0.387172
O -2.371829 -0.293378 0.179866
H -1.354784 -1.092582 -1.446491
H -1.592159 2.980782 0.395024
H -0.896939 1.639934 1.358625
H 0.132556 3.018654 0.854260
C -3.650029 -0.677778 -0.273827
H -4.375725 -0.009442 0.195797
H -3.742871 -0.590270 -1.368296
H -3.890242 -1.715710 0.008417

8a TS (R = OMe, equatorial, substituted C-C(R) bond cleavage)
SCF Energy= -578.787757117
+Zero Point Energy -578.534381
Enthalpy (298 K)= -578.520437
Free Energy (298 K)= -578.573740
Nimag=1 (-276.16 cm^{-1})

C 1.899967 1.187808 -0.087826
C 0.569884 0.875751 -0.725579
C 0.002106 -0.849806 0.290616
C 1.140380 -1.751965 -0.236747
C 2.518748 -1.279292 0.235037
C 2.925424 0.076187 -0.362240
O -0.455578 1.755200 -0.658746
C -0.710957 2.405979 0.593709
O 0.041929 -0.472469 1.491394
C -1.362706 -1.138440 -0.357927
H -1.572724 -2.214663 -0.201510
H 1.101642 -1.829130 -1.331386
H 2.492217 -1.202989 1.327183
H 3.274004 -2.031175 -0.021084
H 3.897603 0.379474 0.042560
H 3.063398 -0.026011 -1.448370
H 1.771199 1.311994 0.991791
H 2.265198 2.145212 -0.491864
H 0.615316 0.478756 -1.741749
H 0.943972 -2.761084 0.152730
O -2.363911 -0.351723 0.236448
H -1.321373 -0.981485 -1.448987
H -1.628560 2.976177 0.446531
H -0.849440 1.653448 1.374135
H 0.104607 3.088865 0.856322
C -3.641739 -0.601930 -0.304862
H -4.349668 0.040037 0.224946
H -3.687413 -0.369088 -1.380882
H -3.946149 -1.652158 -0.168231

P 8a (R = OMe, equatorial, substituted C-C(R) bond cleavage)
SCF Energy= -578.793925028
+Zero Point Energy= -578.541758
Enthalpy (298 K)= -578.526189
Free Energy (298 K)= -578.584407

C 2.086479 1.047512 0.117500
C 0.940655 1.287043 -0.818911
C -0.240280 -1.191404 0.316238
C 0.902842 -1.883205 -0.422839
C 2.291059 -1.557864 0.147367
C 2.894242 -0.206584 -0.275601
O -0.008594 2.245630 -0.608054
C -0.425160 2.499639 0.736282
O -0.151588 -0.856674 1.482354
C -1.537424 -1.039731 -0.471531
H -1.851507 -2.045607 -0.812565
H 0.843118 -1.665911 -1.496018
H 2.221161 -1.599729 1.239764
H 2.985821 -2.349536 -0.156587
H 3.890546 -0.133026 0.176085
H 3.058232 -0.202197 -1.362913
H 1.733558 0.938189 1.149334
H 2.765854 1.920801 0.114965
H 1.121537 1.180332 -1.888001
H 0.712710 -2.963245 -0.322420
O -2.521412 -0.431005 0.319532
H -1.322115 -0.453265 -1.379940
H -1.202957 3.262324 0.666675
H -0.833874 1.595712 1.196899
H 0.398358 2.888002 1.346955
C -3.727715 -0.217661 -0.384976
H -4.421729 0.265005 0.306581
H -3.581518 0.435889 -1.258895
H -4.172624 -1.163812 -0.731747

8a TS (R = OMe, equatorial, unsubstituted C-C bond cleavage)
SCF Energy= -578.768834961
+Zero Point Energy= -578.517160
Enthalpy (298 K)= -578.502675
Free Energy (298 K)= -578.557707
Nimag=1 (-307.07 cm^{-1})

C 1.908857 1.114903 -0.131116

```
C  0.507921 0.714618 -0.599020
C  -0.128463 -0.375265 0.309535
C  1.358711 -1.927263 -0.216307
C  2.640566 -1.314794 0.249114
C  2.957712 0.031143 -0.423954
O  -0.402296 1.808910 -0.702498
C  -0.723448 2.501218 0.498539
O  0.038046 -0.325966 1.541325
C  -1.379027 -1.086290 -0.236528
H  -1.444461 -2.087555 0.217816
H  1.180600 -2.001448 -1.288374
H  2.602782 -1.191400 1.337137
H  3.461058 -2.023430 0.043979
H  3.941882 0.376906 -0.088397
H  3.036736 -0.118843 -1.510214
H  1.886208 1.319391 0.944098
H  2.181938 2.042764 -0.645929
H  0.561664 0.341221 -1.628164
H  0.925812 -2.725739 0.379206
O  -2.501939 -0.305677 0.126350
H  -1.322538 -1.205112 -1.331172
H  -1.436253 3.277020 0.209353
H  -1.191631 1.844638 1.240009
H  0.155735 2.980466 0.948575
C  -3.717866 -0.864352 -0.323000
H  -4.519758 -0.201701 0.010549
H  -3.753178 -0.940450 -1.421396
H  -3.886845 -1.868378 0.097920
C  -3.951684 -0.667537 -0.243881
H  -4.669356 -0.986913 0.514926
H  -4.314679 0.262550 -0.708985
H  -3.892332 -1.441466 -1.025696
```

P 8a (R = OMe, equatorial, unsubstituted C-C bond cleavage)

```
SCF Energy= -578.777377331
+Zero Point Energy=    -578.527362
Enthalpy (298 K)=      -578.511172
Free Energy (298 K)=   -578.571033

C  2.139652 0.509428 0.021762
C  0.747175 0.734084 -0.572115
C  -0.399078 0.159412 0.287573
C  0.818860 -2.513896 -0.397315
C  2.031197 -2.081004 0.354648
C  2.768580 -0.868172 -0.255802
O  0.432493 2.121655 -0.796101
C  0.516324 2.976880 0.340068
O  -0.298816 0.012165 1.489093
C  -1.703720 -0.059805 -0.465439
H  -1.515187 -0.799571 -1.264792
H  0.864399 -2.635817 -1.476936
H  1.767224 -1.866718 1.396385
H  2.749000 -2.920929 0.390029
H  3.790306 -0.846977 0.141561
H  2.868559 -1.016559 -1.340338
H  2.098896 0.675133 1.103504
H  2.793618 1.277720 -0.407632
H  0.696817 0.299802 -1.577382
H  -0.046602 -2.918540 0.116097
O  -2.713093 -0.480960 0.408974
H  -1.956920 0.888410 -0.972476
H  0.166150 3.955472 0.004104
H  -0.114579 2.635950 1.170344
H  1.546180 3.079234 0.704574
```