Origins of Stereoselectivities of Dihydroxylations of *cis*-Bicyclo[3.3.0]octenes

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Supporting Information – Table of Contents

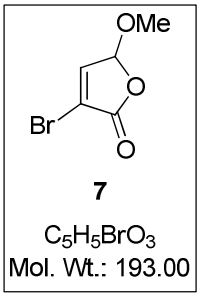
Full reference 7:

Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

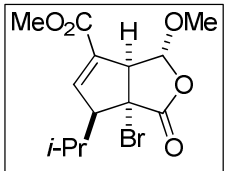
A. Experimental Procedures

Chemical Materials and Methods

Unless stated otherwise, reactions were conducted in oven-dried glassware under an atmosphere of nitrogen or argon using anhydrous solvents (either freshly distilled or passed through activated alumina columns). All other commercially obtained reagents were used as received. Reaction temperatures were controlled using an IKAmag temperature modulator. Thin-layer chromatography (TLC) was conducted with E. Merck silica gel 60 F254 pre-coated plates, (0.25 mm) and visualized by exposure to UV light (254 nm) or stained with anisaldehyde, ceric ammonium molybdate, potassium permanganate and iodine. Flash column chromatography (CC) was performed using normal phase silica gel (60 Å, 230–240 mesh, Merck KGA). ^{1}H NMR spectra were recorded on Bruker spectrometers (at 500 or 600 MHz) and are reported relative to deuterated solvent signals. Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. ^{13}C NMR spectra were recorded on Bruker Spectrometers (at 125 MHz). Data for ^{13}C NMR spectra are reported in terms of chemical shift. IR spectra were recorded on a Varian 640-IR spectrometer and are reported in terms of frequency of absorption (cm^{-1}). High resolution mass spectra were obtained from the UC Irvine Mass Spectrometry Facility with a Micromass LCT spectrometer. See *JOC Standard Abbreviations and Acronyms* for abbreviations (available at http://pubs.acs.org/userimages/ContentEditor/1218717864819/joceah_abbreviations.pdf).



3-Bromo-5-methoxyfuran-2(5*H*)-one (7)[1]: Compound **7** was prepared as follows: To a solution of 5-methoxyfuran-2(5*H*)-one[2] (413 mg, 3.62 mmol) in PhH (3 mL) at 0 °C, bromine (0.19 mL, 3.7 mmol) in PhH (3 mL) was added and the mixture stirred at 0 °C for 5 h. Pyridine (0.31 mL, 3.9 mmol) was added and the mixture kept at 0 °C for 30 min. The resulting yellow suspension was filtered, rinsed with PhH, and the filtrate concentrated. Purification of the residue by CC (SiO_2; hexanes/EtOAc 75:25) afforded **7** (591 mg, 85%) as a pale yellow oil. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.28 (dd, J = 1.4, 0.8 Hz, 1H), 5.80 (dd, J = 1.4, 0.8 Hz, 1H), 3.56 (d, J = 0.9 Hz, 3H).

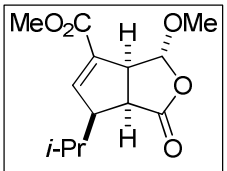


8

$C_{13}H_{17}BrO_5$

Mol. Wt.: 333.1751

(±)-(3*R*,3a*S*,6*S*,6a*R*)-Methyl 6a-bromo-6-isopropyl-3-methoxy -1-oxo-3,3a,6,6a-tetrahydro-1*H*-cyclopenta[*c*]furan-4-carboxy late (8): Compound **6**[3] (1.46 g, 10.4 mmol) and Ph_3P (2.73 g, 10.4 mmol) were added to a solution of **7** (1.00 g, 5.20 mmol) in PhH (21 mL). The initially orange mixture was stirred at rt for 45 min, during which time it turned dark brown, and was concentrated. Purification of the residue by CC (SiO_2; hexanes/EtOAc 95:5 → 60:40) gave **8** (397 mg, 23%) as a pale yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.84 (t, J = 1.7 Hz, 1H), 5.45 (s, 1H), 4.02 (s, 1H), 3.81 (s, 3H), 3.58 (s, 3H), 3.37 (dt, J = 6.6, 1.8 Hz, 1H), 2.34 (oct, J = 6.7 Hz, 1H), 1.27 (d, J = 6.7 Hz, 3H), 0.89 (d, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 172.2, 163.3, 146.0, 131.5, 105.2, 66.8, 64.1, 57.6, 53.5, 52.3, 27.5, 23.5, 20.6; IR (film) 2960, 2873, 1787, 1718, 1639, 1439, 1353, 1272, 1248, 1223, 1174, 1111, 1033, 946 cm^{-1}; HRMS (ESI) calculated for $C_{13}H_{17}O_5{}^{79}Br$ (M+Na) 355.0157, observed 355.0149, calculated for $C_{13}H_{17}O_5{}^{81}Br$ (M+Na) 357.0138, observed 357.0128.

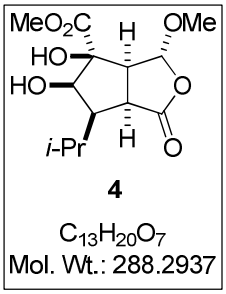


3

$C_{13}H_{18}O_5$

Mol. Wt.: 254.2790

(±)-(3*R*,3a*S*,6*S*,6a*S*)-Methyl 6-isopropyl-3-methoxy-1-oxo-3,3a, 6,6a-tetrahydro-1*H*-cyclopenta[*c*]furan-4-carboxylate (3): To a solution of **8** (354 mg, 1.06 mmol) in AcOH (10 mL), Zn dust (1.42 g, 21.7 mmol) was added and the mixture stirred at rt for 2 h. Filtration through a plug of Celite (rinse with Et_2O) and purification of the residue by CC (SiO_2; hexanes/EtOAc 92:8 → 50:50) yielded **3** (238 mg, 88%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.92 (t, J = 1.8 Hz, 1H), 5.45 (s, 1H), 3.78 (s, 3H), 3.63 (dt, J = 7.4, 2.5 Hz, 1H), 3.51 (s, 3H), 3.38 (t, J = 8.0 Hz, 1H), 2.81 (tt, J = 8.8, 2.3 Hz, 1H), 2.23–2.13 (m, 1H), 1.16 (d, J = 6.4 Hz, 3H), 0.98 (d, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 175.7, 164.3, 148.2, 132.7, 104.8, 56.8, 56.1, 53.5, 52.0, 42.9, 27.2, 23.2, 21.4; IR (film) 2959, 2871, 1779, 1717, 1631, 1439, 1352, 1275, 1198, 1154, 1108, 953 cm^{-1}; HRMS (ESI) calculated for $C_{13}H_{18}O_5$ (M+Na) 277.1052, observed 277.1056.



(±)-(3*R*,3a*S*,4*S*,5*R*,6*R*,6a*S*)-Methyl 4,5-dihydroxy-6-isopropyl -3-methoxy-1-oxohexahydro-1*H*-cyclopenta[*c*]furan-4-carboxylate (4): To a solution of **3** (60 mg, 0.24 mmol) in 1:1 *t*-BuOH/H_2O (2.4 mL), NMO (65 mg, 0.48 mmol), and OsO_4 (0.15 mL, 0.012 mmol; 2.5 wt% in *t*BuOH) were added. After stirring at rt for 90 min, the mixture was filtered through a plug of SiO_2 (rinsed with Et_2O) and concentrated. Purification of the residue by CC (SiO_2; hexanes/EtOAc 75:25 → 50:50) provided a 92:8 mixture of **4** and **5** (59 mg, 87%) as a colorless solid. An analytical sample of **4** was obtained by recrystallization from CH_2Cl_2. Data for **4**: mp 146–147 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.53 (s, 1H), 3.88 (s, 3H), 3.83 (d, J = 3.1 Hz, 1H), 3.77 (s, 1H), 3.46 (s, 3H), 3.23 (t, J = 8.4 Hz, 1H), 3.04 (d, J = 8.8 Hz, 1H), 2.70 (s, 1H), 2.47–2.37 (m, 1H), 2.06 (br t, J = 9.6 Hz, 1H), 1.15 (d, J = 6.5 Hz, 3H), 0.99 (d, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 176.1, 174.8, 103.0, 81.1, 76.3, 56.8, 54.2, 53.6, 51.9, 43.8, 23.9, 22.2, 21.7; IR (film) 3466 (br), 2961, 2917, 2871, 1736 (br), 1439, 1360, 1256, 1178, 1113, 1008, 953 cm^{-1}; HRMS (ESI) calculated for $C_{13}H_{20}O_7$ (M+Na) 311.1107, observed 311.1116. A crystal suitable for X-ray structure elucidation was grown by slow evaporation of an EtOAc solution (colorless needle).

NMR Table for 4

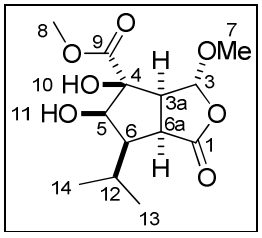


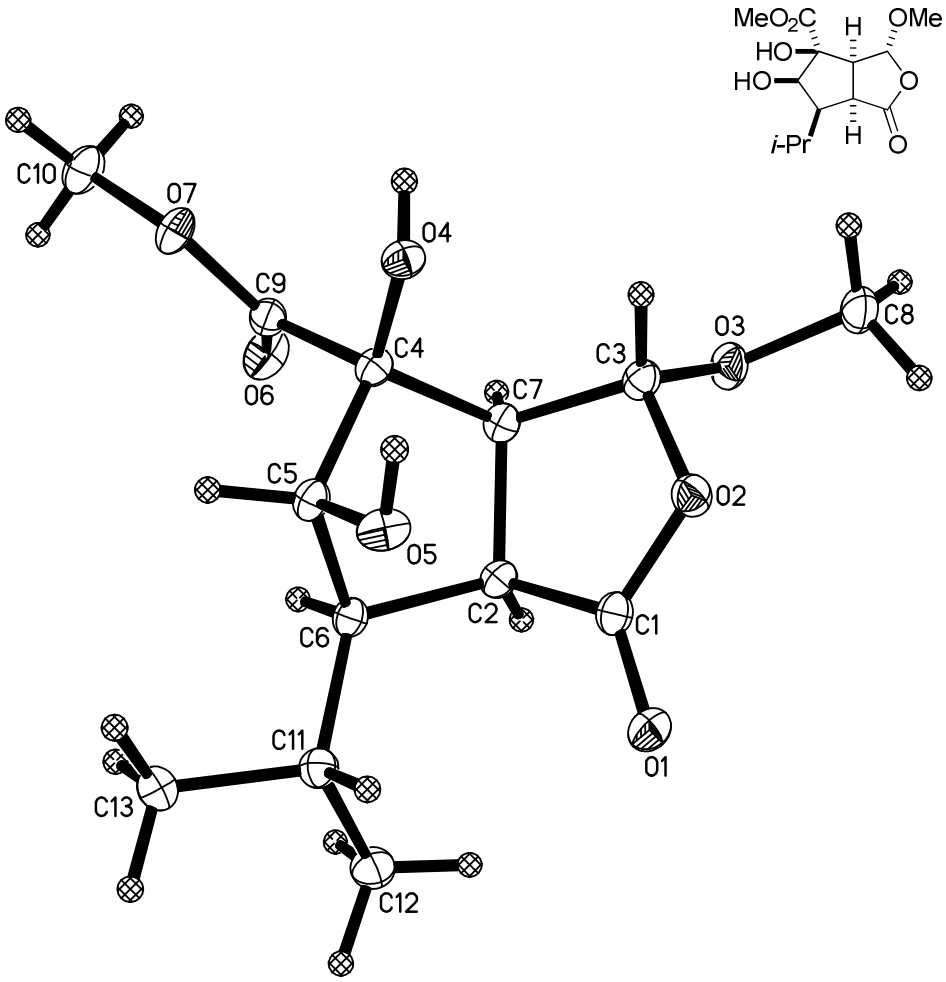
Table S1. ^{1}H (500 MHz), ^{13}C (125 MHz), HMBC, COSY, and NOESY NMR data for **4**, $CDCl_3$.

atom	^{13}C (mult)	^{1}H mult, J (Hz)	HMBC[a]	COSY[b]	NOESY[b]
1	176.1 (C)				
3	103.0 (CH)	5.53 (s, 1H)	1, 4, 6a, 7	3a	3a[c], 7[c], 10[c], 11[c]

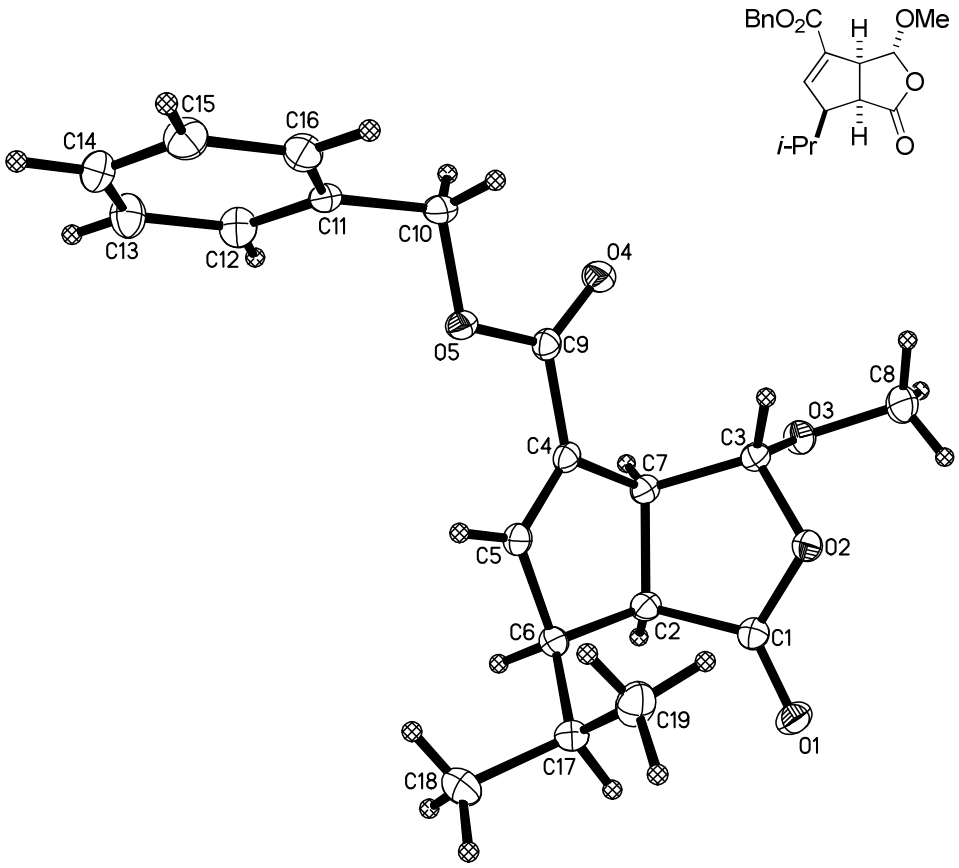
3a	51.9 (CH)	3.04 (d, 8.8, 1H)	1, 3, 4, 5, 9	3, 6a	3, 6a
4	81.1 (C)				
5	76.3 (CH)	3.83 (d, 3.1, 1H)	3a, 4, 6, 6a, 9	6, 11	6, 11, 14
6	53.6 (CH)	2.06 (br. t, 9.6, 1H)		5, 6a, 11, 12	5[c], 6a[c], 13[c], 14[c]
6a	43.8 (CH)	3.23 (t, 8.4, 1H)	1, 4, 5, 6	3a, 6	3a, 6, 13
7	56.8 (CH_3)	3.46 (s, 3H)	3		3
8	54.2 (CH_3)	3.88 (s, 3H)	4, 9		
9	174.8 (C)				
10		3.77 (s, 1H)	3a, 4, 5, 9		3, 11
11		2.70 (s, 1H)	4, 5, 6	5, 6	3, 5, 10
12	23.9 (CH)	2.47–2.37 (m, 1H)		6, 13, 14	13, 14
13	22.2 (CH_3)	1.15 (d, 6.5, 3H)	6, 12, 14	12, 14	6, 6a, 12, 14
14	21.7 (CH_3)	0.99 (d, 6.6, 3H)	6, 12, 13	12, 13	6, 12, 13

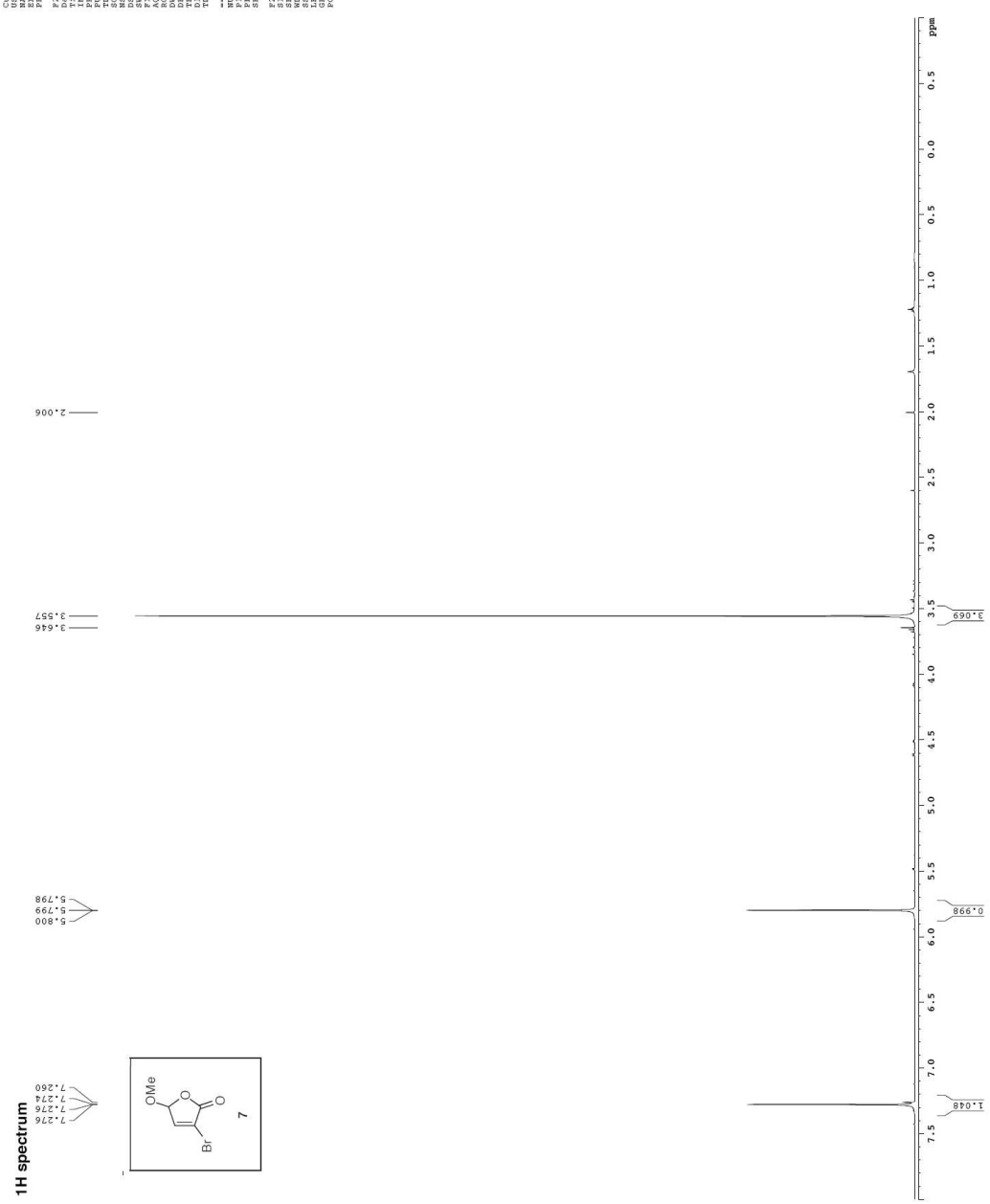
[a]Carbons that correlate to the proton resonance. Optimized for 10 Hz coupling. [b]Protons that correlate to the proton resonance. [c]1-D NOE observed by irradiation with 2 second delay.

Single-Crystal X-ray Structure of 4[5]



Single-Crystal Structure of the Benzyl Ester Analogue of 3[5]

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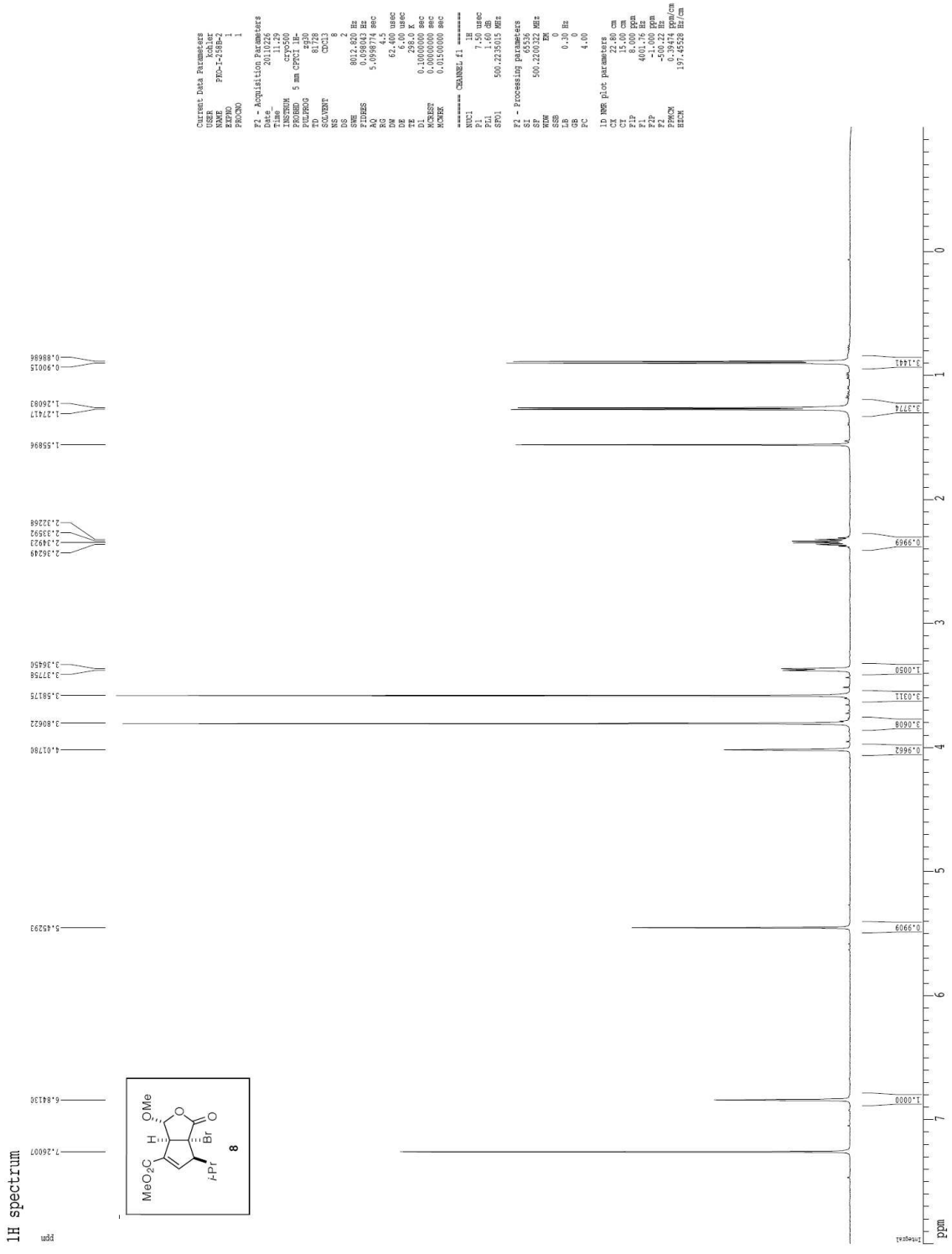
O
O
Br
7
ppm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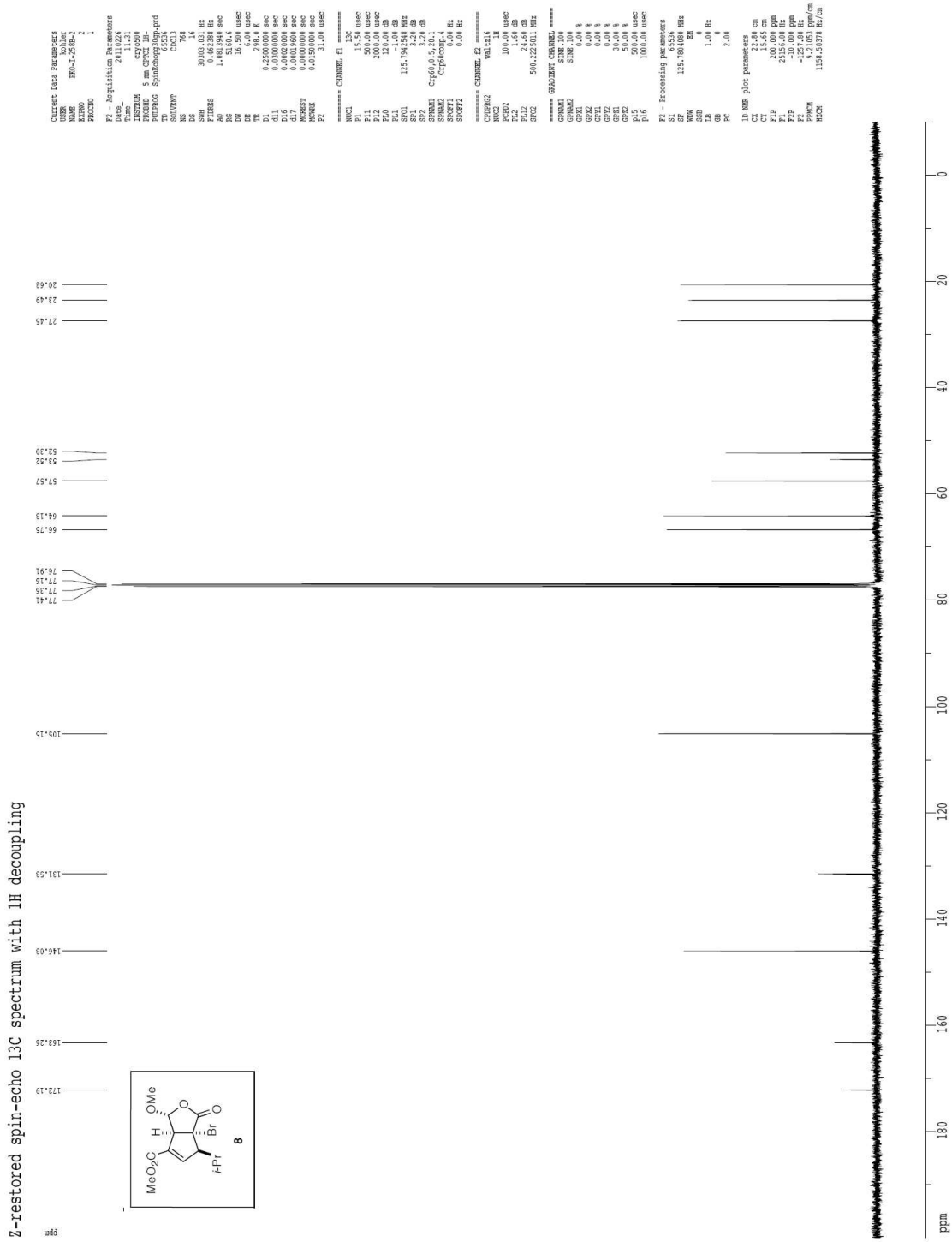
OMe
H
O
Br
i-Pr
8
ppm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OMe
H
Br
O
i-Pr
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d11 0.03000000 sec
D15 0.00201600 sec
d12 0.00001000 sec
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MCWBK 0.01500000 sec
P2 31.00 usec
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P1 15.50 usec
P11 5000.00 usec
P12 2000.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7941548 MHz
SI 32768
SF02 3.20 dB
SFRQM1 Cpd0,0.5,20.1
SFRQM2 CrpHcomp,4
SFRQF1 0.00 Hz
SFOFF2 0.00 Hz
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PCPD2 100.00 usec
PL2 1.60 dB
PL12 12.60 dB
SFO2 500.2229911 MHz
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GPNAM2 SINE.100
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GPZ2 0.00 %
GPZ11 0.00 %
GPZ12 0.00 %
GPZ21 30.00 %
GPZ22 50.00 %
p15 500.00 usec
p16 1000.00 usec
F2 - Processing parameters
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WDW 0
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PC 2.00
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F2P -1257.80 Hz
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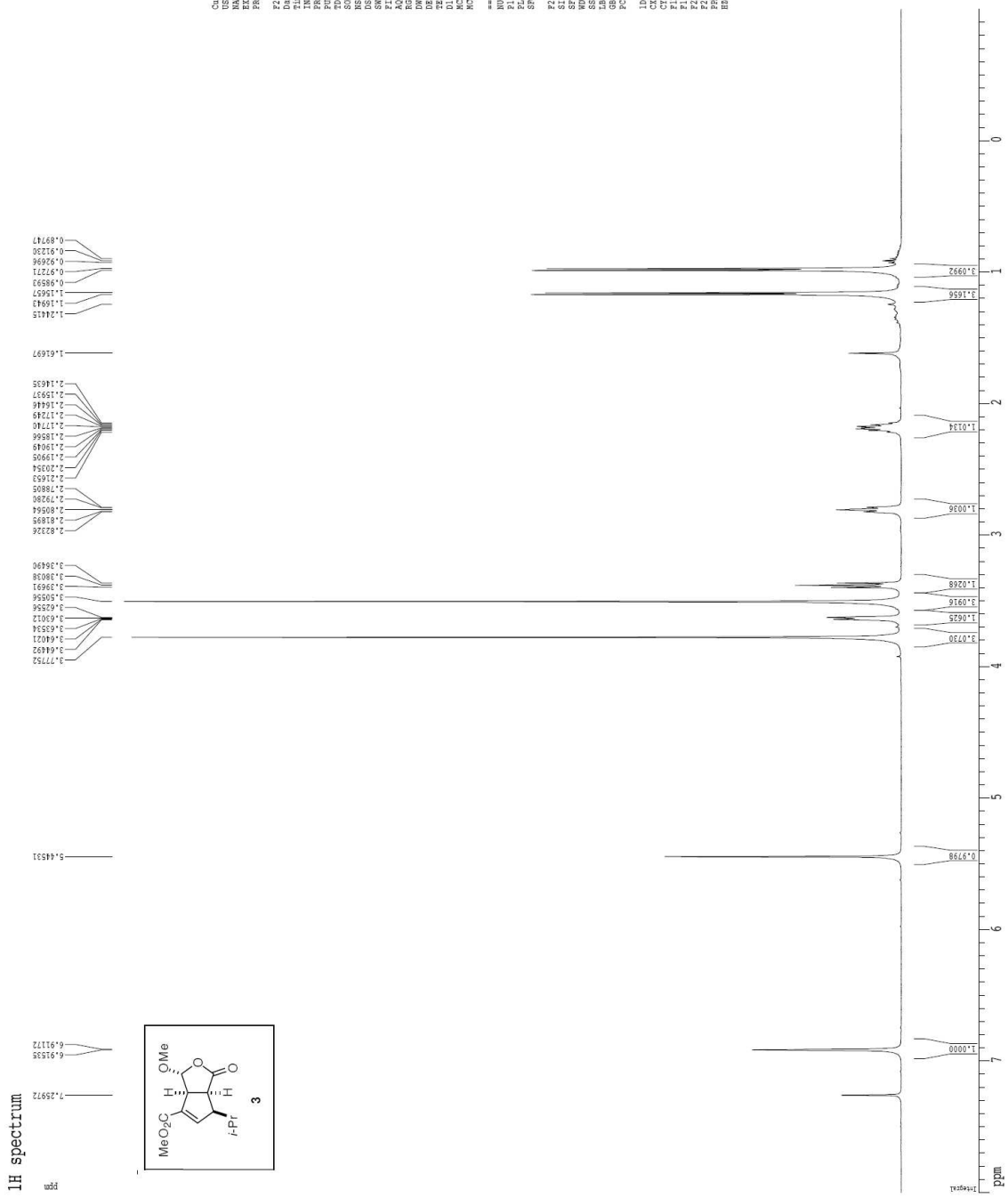
180
ppm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OMe
i-Pr
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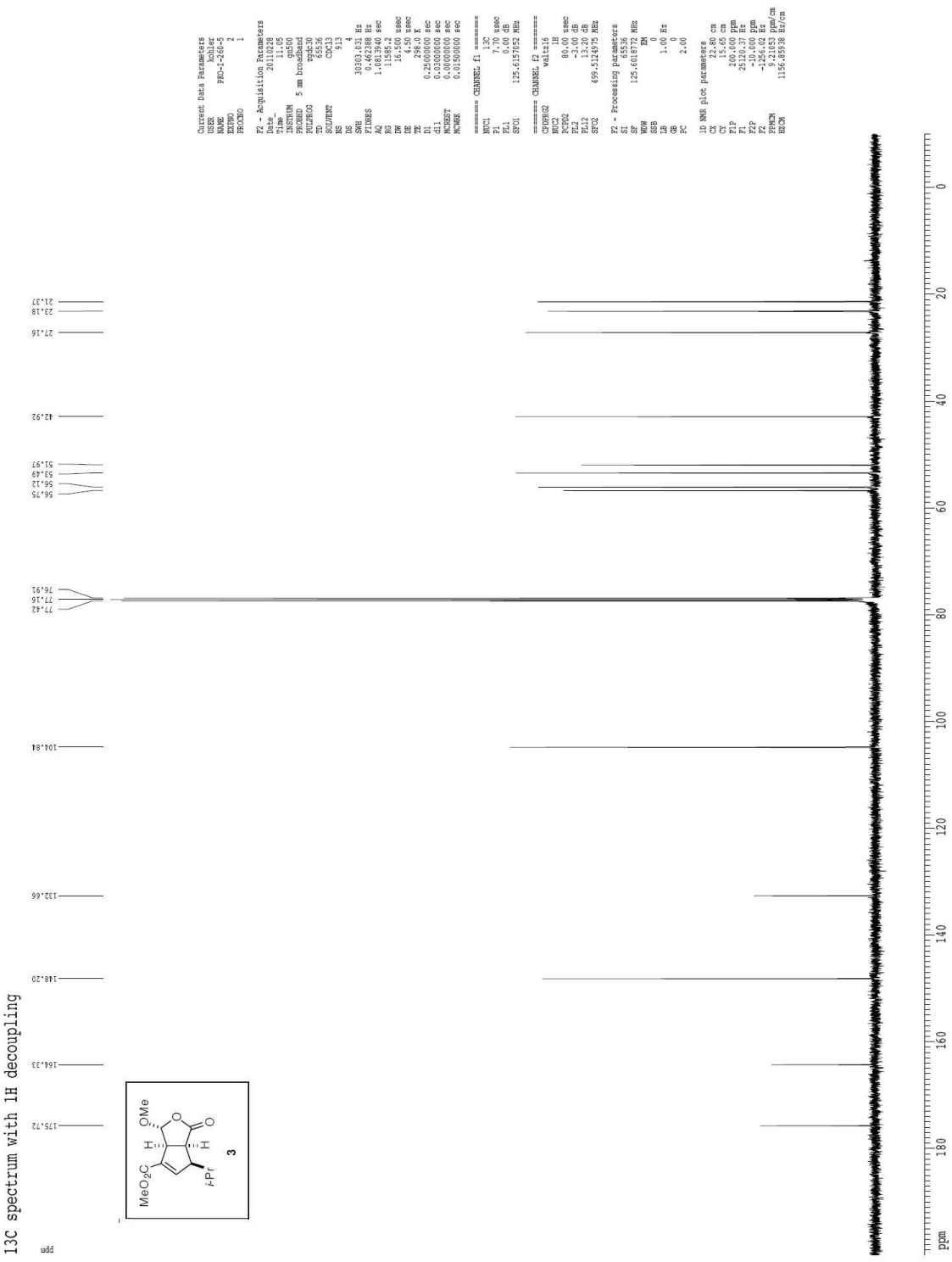
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PL12 13.20 dB
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51.97
53.49
56.12
56.75
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77.16
77.42
104.84
132.66
148.20
164.33
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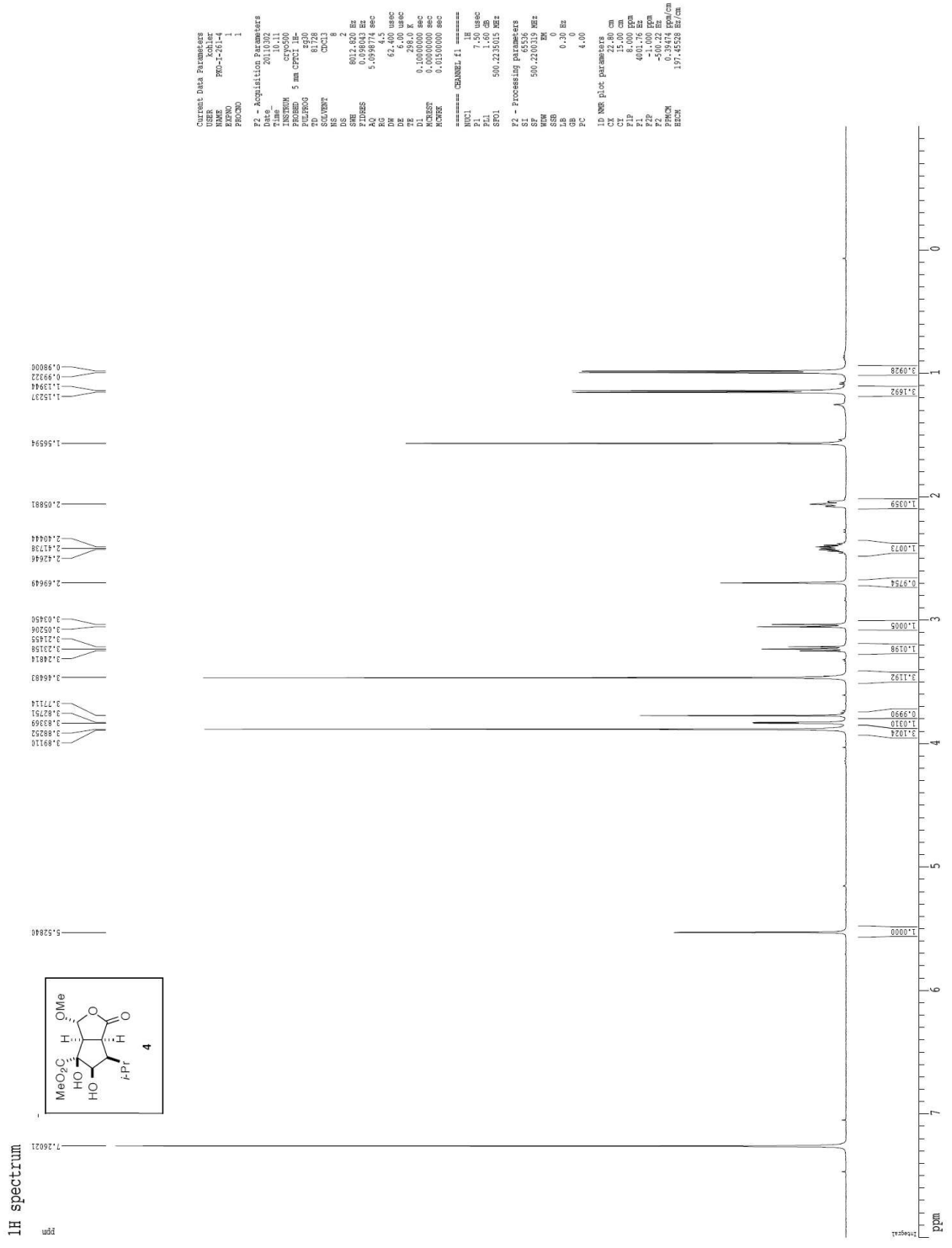
180
ppm
MeO2C
OMe
i-Pr
3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i-Pr
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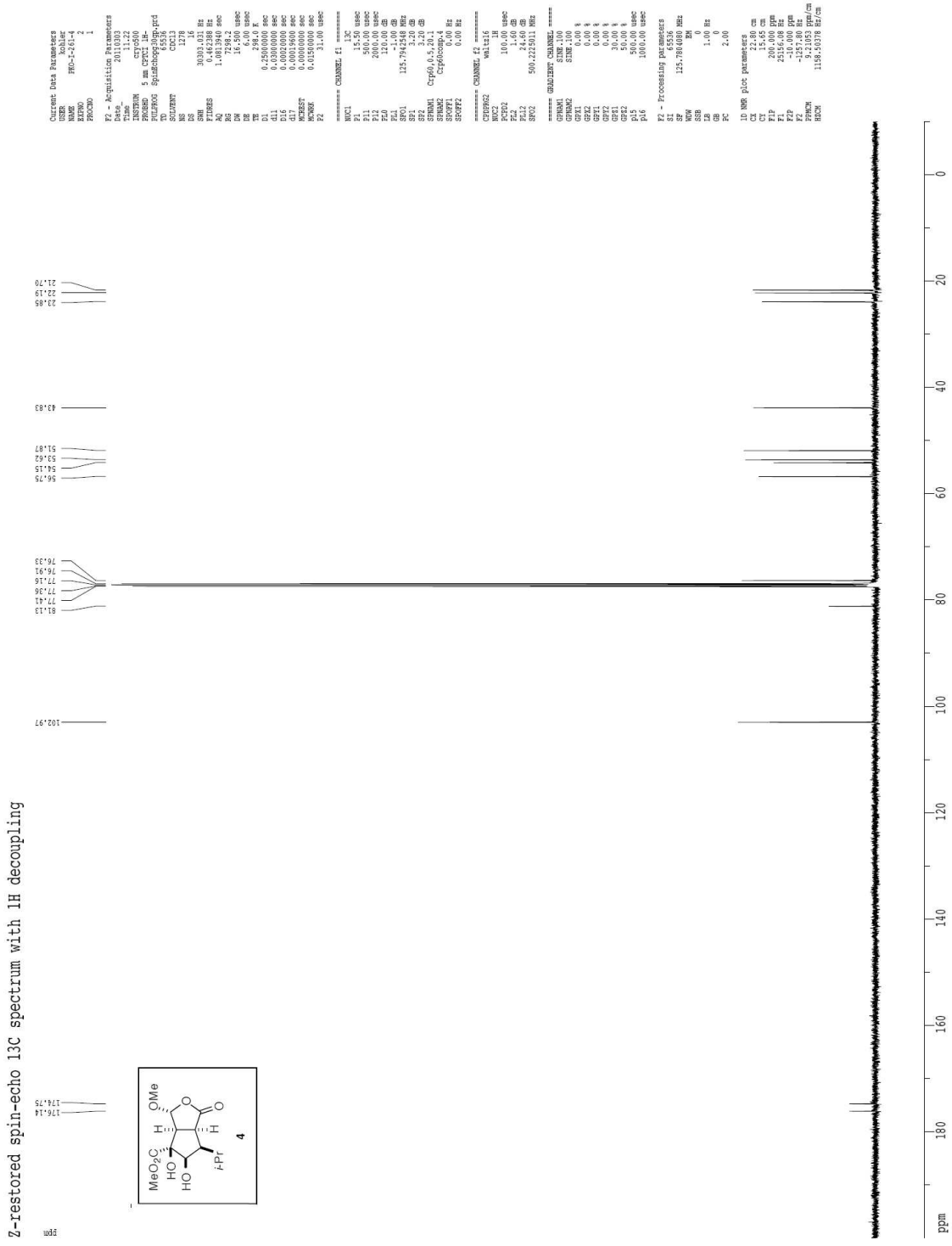
ppm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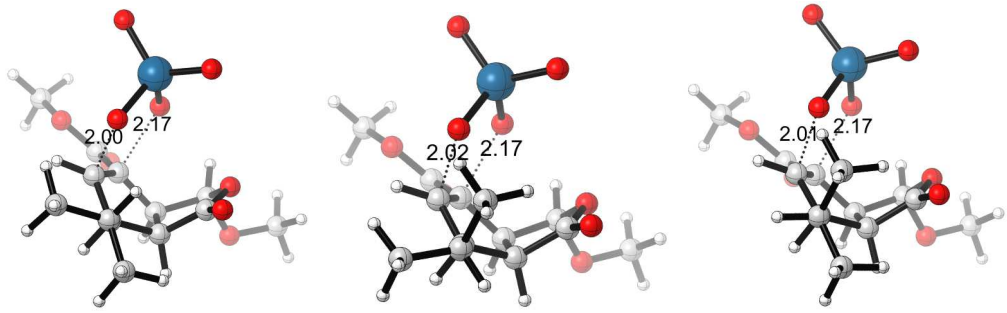
ppm
MeO2C
HO
HO
OMe
H
O
O
H
i-Pr
4

B. Computational Data

1. Cartesian coordinates of stationary points: TS3β, TS3α

The transition state for the β-attack of OsO_4 on compound **3** was obtained at the B3LYP/6-31G* level. The other conformers of the transition states were generated by manually rotating the isopropyl group by 60°. Out of 6 structures thus generated, 3 transition state conformers were produced (Figure S1). Transition state structures for the α-attack of OsO_4 on compound **3** were obtained in the same manner, which also gave 3 TS structures (Figure S2).



TS 3β $\Delta G^{\neq}$ = 0.0 kcal/mol

TS 3β-1 $\Delta G^{\neq}$ = 6.0 kcal/mol

TS 3β-2 $\Delta G^{\neq}$ = 6.2 kcal/mol

Figure S1. Transition state structures for the β-attack of OsO_4 on compound **3.**

TS3β

O	-0.37091987	-0.22255193	0.00000000
O	0.19583413	1.95289307	-0.06222000
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O	1.99812713	4.51507807	3.36139200
O	3.48416513	2.92864307	4.00794700
C	-0.21308887	0.81902507	0.58284100
C	-0.42408387	1.11785807	2.07208500
C	0.15207413	3.10328007	0.81484800
C	1.56859213	2.23639707	2.82451900
C	1.66003513	0.90351307	3.24565000
C	0.32646513	0.19496907	3.07739100
C	0.19967613	2.51822607	2.23347700
C	-1.21446687	4.42285307	-0.58831400
C	2.35183913	3.35398507	3.41055200
C	4.31168313	3.96435207	4.56696700
C	0.32669313	-1.33052393	2.82497100
C	-1.11208787	-1.86758293	2.77203400
C	1.13883413	-2.06353593	3.90475000
H	-1.50277987	1.10968607	2.25184400
H	1.00932713	3.72364107	0.54193600

H	2.34969513	0.61575407	4.02823500
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H	3.76620213	4.51513807	5.33760300
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H	0.79309913	-1.51664693	1.85355800
H	-1.66862087	-1.43517993	1.93607200
H	-1.65280487	-1.65719693	3.70513800
H	-1.10469787	-2.95455393	2.63364400
H	0.73812713	-1.86850693	4.90912100
H	2.19423413	-1.77292393	3.89295800
H	1.09531513	-3.14587193	3.73971400
H	5.17147013	3.44933807	4.99506500
O	2.94178013	2.38979007	1.14961300
O	2.85825313	-0.04899093	1.96340200
Os	3.73917713	0.87727207	0.74019600
O	5.41510813	0.93638207	1.09268800
O	3.33808513	0.37156607	-0.84461600

Sum of electronic and zero-point Energies= -1273.921559

Sum of electronic and thermal Energies= -1273.897653

Sum of electronic and thermal Enthalpies= -1273.896709

Sum of electronic and thermal Free Energies= -1273.976299

Imaginary frequency: -328.36 cm^{-1}

TS3β-1

O	-0.35608307	-0.26706231	0.00000000
O	-0.68166907	-2.49186131	0.00952800
O	0.80110093	-4.09259431	0.82893200
O	-2.14380107	-5.21785831	3.46850100
O	-3.88387307	-3.87665331	4.03186200
C	-0.43892207	-1.29372931	0.62220100
C	-0.25518907	-1.51250331	2.12841900
C	-0.49317607	-3.59787031	0.92218000
C	-2.06650407	-2.90969231	2.88877200
C	-2.36635107	-1.60254231	3.29548000
C	-1.13897907	-0.71890931	3.13565600
C	-0.66061407	-2.98787931	2.32021800
C	1.09119193	-4.73408831	-0.41079500
C	-2.67862307	-4.12728231	3.47927300

C	-4.55351007	-5.01899231	4.59501100
C	-1.23178707	0.83274669	3.07126000
C	-1.63798607	1.37956769	4.45334800
C	-2.11571807	1.46973769	1.98628200
H	0.80502993	-1.33402731	2.33482700
H	-1.24043807	-4.34684431	0.65017500
H	-3.08530207	-1.41252631	4.08152300
H	-0.62071007	-0.89521831	4.09608600
H	-0.02336207	-3.54374131	3.01521600
H	2.09917193	-5.14317131	-0.31841500
H	1.05621293	-4.02397831	-1.24447500
H	0.38272493	-5.55247931	-0.60286700
H	-3.95343007	-5.45609431	5.39725100
H	-4.72790107	-5.77426331	3.82463800
H	-0.19884907	1.15802369	2.88092400
H	-0.96528407	1.03502969	5.24880200
H	-2.65893407	1.07501769	4.71767800
H	-1.61819407	2.47480069	4.45114700
H	-3.17757307	1.30965269	2.19177800
H	-1.88736407	1.09078669	0.99023200
H	-1.93611007	2.55184269	1.98014900
H	-5.49890607	-4.63930431	4.98195100
O	-3.32971407	-3.31214631	1.17651300
O	-3.80961007	-0.94178031	2.05138700
Os	-4.44965907	-2.01148931	0.79968500
O	-6.06910207	-2.46637931	1.12808800
O	-4.16595007	-1.37408731	-0.76360000

Sum of electronic and zero-point Energies= -1273.911459
Sum of electronic and thermal Energies= -1273.887540
Sum of electronic and thermal Enthalpies= -1273.886596
Sum of electronic and thermal Free Energies= -1273.966773
Imaginary frequency: -317.62 cm^{-1}

TS3β-2

O	-0.19287833	-0.20771513	0.00000000
O	0.65178167	1.84093987	-0.37442800
O	-0.41993133	3.86831387	0.04521300
O	2.65584367	4.75683787	2.65718200
O	4.01722367	3.16912087	3.53500500
C	0.11786867	0.87323387	0.42973600
C	-0.04103833	1.41544887	1.85386100
C	0.71669067	3.11566787	0.30805500

C	2.04603067	2.46422987	2.45725900
C	2.01754267	1.21360287	3.09006700
C	0.60949867	0.64226987	3.03865800
C	0.70947467	2.76254187	1.80143200
C	-0.52543633	4.31175687	-1.30575600
C	2.91719167	3.59115687	2.87708100
C	4.92966867	4.20585487	3.93849200
C	0.32533967	-0.86465313	3.30202900
C	1.02448767	-1.91393013	2.42230100
C	-1.19694333	-1.09830913	3.29564900
H	-1.11542033	1.53993087	2.01755800
H	1.62605767	3.60428187	-0.04919900
H	2.66856867	0.99210887	3.92663800
H	0.15080167	1.12691087	3.92066100
H	0.21572567	3.57478287	2.34406900
H	-1.41214233	4.94680187	-1.35387000
H	-0.63867433	3.46705587	-1.99431000
H	0.35820867	4.89837187	-1.59491200
H	4.43744967	4.90390887	4.62054600
H	5.29205867	4.75302387	3.06464100
H	0.67687467	-1.02786713	4.33259100
H	2.11082467	-1.86859913	2.51865300
H	0.76045167	-1.79878713	1.36948300
H	0.70017067	-2.91147813	2.74389600
H	-1.59394933	-1.02004013	2.27774600
H	-1.72856533	-0.37977313	3.93309200
H	-1.42734333	-2.10317813	3.66580900
H	5.75072167	3.69149387	4.43750000
O	3.42660767	2.28221087	0.78969900
O	3.23269367	0.02720287	2.01255300
Os	4.17131267	0.69471387	0.67174100
O	5.84219867	0.75690887	1.04731200
O	3.77759467	-0.07199313	-0.80728900

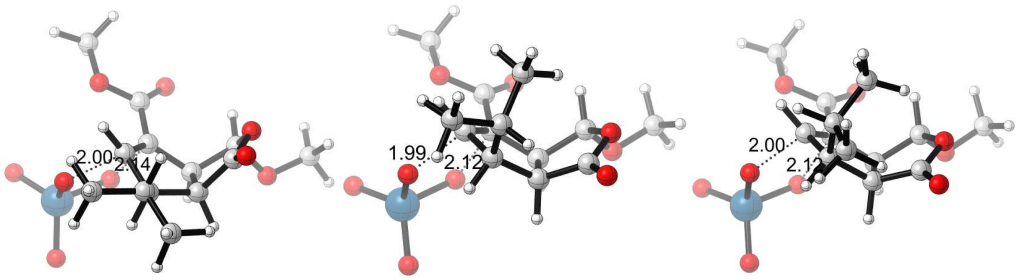
Sum of electronic and zero-point Energies= -1273.911596

Sum of electronic and thermal Energies= -1273.887794

Sum of electronic and thermal Enthalpies= -1273.886850

Sum of electronic and thermal Free Energies= -1273.966464

Imaginary frequency: -315.89 cm^{-1}



TS 3α $\Delta G^{\neq}$ = 2.2 kcal/mol

TS 3α-1 $\Delta G^{\neq}$ = 3.6 kcal/mol

TS 3α-2 $\Delta G^{\neq}$ = 4.7 kcal/mol

Figure S2. Transition state structures for the α-attack of OsO_4 on compound **3.**

TS3α

O	0.16320474	-0.31157270	0.00000000
O	0.60017274	-2.47639270	-0.39906900
O	0.98674274	-3.44332570	-2.48613200
O	3.60024074	-4.76188670	0.34073400
O	4.96307774	-3.41766770	1.54487300
C	0.88417674	-1.14512770	-0.48637200
C	2.19611274	-0.93815170	-1.26123300
C	1.50816974	-3.25413570	-1.21157300
C	3.76399174	-2.42735370	-0.20969700
C	4.00498574	-1.14124570	0.29474300
C	3.27924074	-0.08697170	-0.52897500
C	2.76250874	-2.37607270	-1.35847100
C	-0.16210626	-4.28655070	-2.52423600
C	4.07229774	-3.66410270	0.56144600
C	5.34040874	-4.55827870	2.33822400
C	2.83521874	1.18436630	0.23133400
C	2.10721474	2.15661730	-0.71050000
C	4.04234674	1.88356730	0.87969400
H	1.93909974	-0.51401470	-2.23640500
H	1.65999074	-4.19666870	-0.68408100
H	4.27173374	-0.98747470	1.33146400
H	3.97810274	0.24975830	-1.30996200
H	3.23885974	-2.61057770	-2.31343400
H	-0.41831426	-4.41191570	-3.57808900
H	-1.00626226	-3.83413970	-1.99165700
H	0.05818474	-5.26925570	-2.08377800
H	5.79564374	-5.32516870	1.70702100
H	4.46547074	-4.97809970	2.84099400
H	2.13315174	0.88978530	1.02020000

H	1.18284874	1.72226830	-1.09868100
H	2.74957274	2.44188530	-1.55477700
H	1.84055474	3.07458930	-0.17485700
H	4.77136074	2.19638330	0.12150400
H	4.56899774	1.24448630	1.59643400
H	3.71334674	2.78010530	1.41690900
H	6.05941574	-4.17966270	3.06425300
O	5.48707274	-2.84889870	-1.40444300
O	5.92773774	-0.70206970	-0.06162000
Os	6.82371574	-1.72555070	-1.19017200
O	7.14446474	-0.87078370	-2.64149200
O	8.16518774	-2.48259670	-0.44069700

Sum of electronic and zero-point Energies= -1273.917892
Sum of electronic and thermal Energies= -1273.894039
Sum of electronic and thermal Enthalpies= -1273.893095
Sum of electronic and thermal Free Energies= -1273.972826
Imaginary frequency: -347.50 cm^{-1}

TS3α-1

O	0.32640948	0.04451039	0.00000000
O	0.46620848	-2.08609961	0.70845100
O	1.30611248	-4.09055461	-0.11210600
O	3.40876648	-4.68475561	2.57108500
O	4.88572048	-3.38673061	3.69540300
C	1.00584048	-0.89848961	0.31475300
C	2.52763348	-0.96745461	0.37661400
C	1.46051548	-3.12929761	0.86869100
C	3.76863648	-2.42674661	1.86447500
C	3.99314748	-1.11614361	2.30724300
C	3.19720948	-0.09887761	1.51452800
C	2.84265048	-2.45199261	0.66680900
C	0.13791948	-4.89438361	0.03235500
C	3.98205448	-3.62476561	2.72236000
C	5.17237248	-4.50267561	4.55824400
C	2.26846948	0.78234439	2.40472600
C	3.09770348	1.84552339	3.14323500
C	1.40383148	-0.01195861	3.39934400
H	2.90576248	-0.63794361	-0.59413800
H	1.29891848	-3.54704561	1.86649100
H	4.29610248	-0.92036061	3.32725100
H	3.89468548	0.59603339	1.03428100

H	3.30964748	-2.96704761	-0.17600400
H	0.18326148	-5.64740461	-0.75665000
H	-0.77291952	-4.29583161	-0.08254800
H	0.12714448	-5.39397861	1.01114800
H	5.56878048	-5.33858861	3.97676600
H	4.26713948	-4.82445061	5.07954100
H	1.59527748	1.30080839	1.71310000
H	3.66010848	2.47395139	2.44313400
H	3.81807848	1.39315339	3.83685000
H	2.44450348	2.49960839	3.73169800
H	2.01702448	-0.49262961	4.17231400
H	0.80144548	-0.78674461	2.91604500
H	0.70964648	0.66356439	3.91095800
H	5.91715048	-4.13801861	5.26524300
O	5.54242748	-2.97126461	0.82907900
O	5.85511948	-0.61734361	1.79614200
Os	6.82565748	-1.76759761	0.86680700
O	7.14111748	-1.16200061	-0.70613200
O	8.18358948	-2.31914561	1.75314600

Sum of electronic and zero-point Energies= -1273.916213

Sum of electronic and thermal Energies= -1273.892327

Sum of electronic and thermal Enthalpies= -1273.890383

Sum of electronic and thermal Free Energies= -1273.970491

Imaginary frequency: -332.00 cm^{-1}

TS 3α-2

O	-0.29673589	-0.25222552	0.00000000
O	-0.50208689	1.93620248	0.44835100
O	-1.42546689	3.84159848	-0.50060300
O	-3.57209989	4.73980848	1.85527000
O	-5.05158789	3.63037748	3.16407500
C	-1.00564589	0.68684248	0.25890600
C	-2.52486989	0.70172648	0.41673500
C	-1.53073489	2.95259548	0.54938400
C	-3.83624389	2.37592648	1.59290800
C	-3.98694189	1.17580648	2.29659800
C	-3.13926789	0.05482848	1.72640400
C	-2.88540889	2.20698148	0.43076600
C	-0.30694189	4.72078148	-0.41669400
C	-4.12009589	3.70975448	2.19141600
C	-5.39935789	4.87892348	3.79048400
C	-2.23553489	-0.58026052	2.83128000

C	-1.15981989	0.35250148	3.41161700
C	-1.65100689	-1.93429452	2.39646000
H	-2.93725389	0.18539048	-0.45343100
H	-1.37041289	3.45029648	1.51124800
H	-4.27851289	1.17111848	3.33956000
H	-3.80712089	-0.75471052	1.41102800
H	-3.33570489	2.54865648	-0.50452800
H	-0.39047689	5.40623748	-1.26208100
H	0.63793711	4.16918948	-0.48298700
H	-0.33285089	5.29509948	0.51979300
H	-5.79487489	5.57741348	3.04912400
H	-4.52300689	5.32205548	4.27056800
H	-2.94277689	-0.79196252	3.64792700
H	-1.57611689	1.32150748	3.71525100
H	-0.34321789	0.53885448	2.70904100
H	-0.71779889	-0.10553952	4.30356800
H	-0.95827289	-1.82694952	1.55861500
H	-2.44887189	-2.62439352	2.09555200
H	-1.11107289	-2.39586252	3.23148700
H	-6.16053889	4.62962948	4.52935300
O	-5.60557789	2.57445548	0.44622000
O	-5.83372889	0.49346748	1.92802600
Os	-6.83843289	1.35729948	0.75732800
O	-7.10952189	0.39204148	-0.63379800
O	-8.22878889	2.03858048	1.48960500

Sum of electronic and zero-point Energies= -1273.913350

Sum of electronic and thermal Energies= -1273.889407

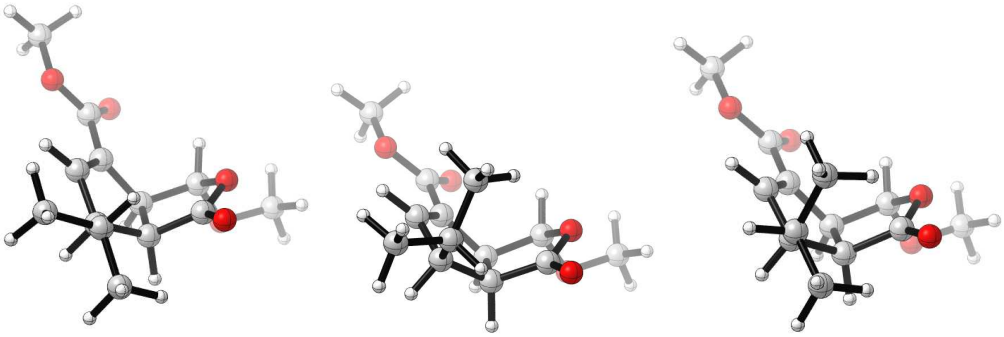
Sum of electronic and thermal Enthalpies= -1273.888463

Sum of electronic and thermal Free Energies= -1273.968883

Imaginary frequency: -331.25 cm^{-1}

2. Optimized structures and energies of compound 3

Geometry of compound **3** was optimized at the B3LYP/6-31G* level. There was only one envelope conformation obtained for the cyclopentene ring after minimization, while the isopropyl group can adopt a variety of different conformations. The other conformers were generated by manually rotating the isopropyl by 60°. Out of 6 structures thus generated, 3 different conformers were produced (Figure S3).



3	**3-1**	**3-2**
$\Delta G^{\neq}$ = 0.0 kcal/mol	$\Delta G^{\neq}$ = 1.1 kcal/mol	$\Delta G^{\neq}$ = 2.5 kcal/mol

Figure S3. Optimized structures of compound **3**.

3

C	0.14836795	-0.60830860	0.00000000
C	0.26617795	0.14796840	1.33240600
C	-1.94604905	0.40567640	0.68558300
C	-1.38233805	-0.72334460	-0.18527500
H	0.63385595	0.00242240	-0.76676800
H	-1.72892905	-0.57825260	-1.21352400
C	-1.66367605	-2.13057860	0.30596000
C	0.69518795	-2.07390860	0.01135900
H	0.90140795	-2.34138560	-1.04068700
C	-0.53657705	-2.85034860	0.41995600
H	-0.51633905	-3.89474160	0.70930500
O	-0.95778105	0.61241340	1.71942000
O	1.25281695	0.35130040	1.99338600
C	2.00442195	-2.36673160	0.78439300
C	3.16735295	-1.53721660	0.21779200
C	2.34942395	-3.86452560	0.73530500
H	1.86267195	-2.07733960	1.83157500
H	2.98567695	-0.46619260	0.33452600
H	4.09764595	-1.77339860	0.74679800
H	3.32689695	-1.75738060	-0.84676600
H	1.59536995	-4.48694760	1.22914800
H	2.45138295	-4.21666660	-0.30003500
H	3.30411195	-4.04913160	1.24040700
C	-3.04295905	-2.61118160	0.52365300
O	-4.03631205	-1.93064960	0.33645400
O	-3.09008605	-3.89172860	0.95501600
C	-4.40849805	-4.41159960	1.18948600
H	-4.99750505	-4.39677760	0.26854900

H	-4.26056105	-5.43542560	1.53400000
H	-4.92504405	-3.82049460	1.95041600
H	-2.88041505	0.16443640	1.20038900
O	-2.07446605	1.54261540	-0.10468700
C	-2.64297305	2.65977140	0.57319700
H	-1.99360105	3.00723340	1.38472700
H	-2.75345405	3.45050340	-0.17166500
H	-3.63105105	2.40767640	0.98436900

Sum of electronic and zero-point Energies= -882.044509
Sum of electronic and thermal Energies= -882.026241
Sum of electronic and thermal Enthalpies= -882.025297
Sum of electronic and thermal Free Energies= -882.091339

3-1

C	0.35608307	-0.19287834	0.00000000
C	0.75695607	0.75827966	1.12672900
C	-1.56653793	0.82062766	1.12065400
C	-1.18537693	-0.27393034	0.10517700
H	0.70303707	0.26098566	-0.93219500
H	-1.70783793	-0.05018534	-0.82981800
C	-1.43935793	-1.69915334	0.54725400
C	0.90363907	-1.66524134	0.11829500
H	1.16966207	-1.98374434	-0.90149700
C	-0.32106293	-2.43846234	0.53673100
H	-0.29323893	-3.49518134	0.78111300
O	-0.34778593	1.15202066	1.82608400
O	1.86292207	1.14190166	1.41022600
C	2.16727107	-1.91528534	0.99376300
C	2.88061707	-3.19973134	0.54176000
C	1.86864807	-1.97421234	2.50163700
H	2.84292807	-1.07047134	0.81915200
H	3.18027407	-3.14494334	-0.51172500
H	3.78426507	-3.37065534	1.13774900
H	2.23915107	-4.08297534	0.66130900
H	1.32211207	-1.09752734	2.85947000
H	1.27985807	-2.86413134	2.75713400
H	2.80577807	-2.02547234	3.06699700
C	-2.80248093	-2.16093334	0.87808000
O	-3.78073693	-1.43498134	0.88054800
O	-2.85181593	-3.47738334	1.18461200
C	-4.15389893	-3.97806634	1.52701200
H	-4.84910093	-3.84371634	0.69405400

H	-4.01149393	-5.03767734	1.74102000
H	-4.54744093	-3.45798334	2.40451900
H	-2.28119893	0.50199666	1.88587200
O	-2.03120293	1.92439666	0.41784100
C	-2.49431593	2.98967466	1.24300300
H	-1.67899693	3.41864366	1.83640800
H	-2.89666493	3.74945466	0.56988500
H	-3.29087993	2.64465766	1.91780500

Sum of electronic and zero-point Energies= -882.042088
Sum of electronic and thermal Energies= -882.023727
Sum of electronic and thermal Enthalpies= -882.022783
Sum of electronic and thermal Free Energies= -882.089635

3-2

C	-0.34124628	-0.54896142	0.00000000
C	0.09955672	0.20479358	1.26145800
C	-2.10109028	0.86215658	0.92882700
C	-1.87231828	-0.30990042	-0.03602600
H	0.18499172	-0.07931542	-0.83634200
H	-2.25686528	-0.02027342	-1.01924200
C	-2.44249328	-1.64308442	0.40495800
C	-0.15339528	-2.10936042	-0.03862100
H	-0.06388828	-2.35766942	-1.11003700
C	-1.50864128	-2.60521742	0.40183600
H	-1.70388928	-3.64755442	0.63340800
O	-0.96067128	0.85801558	1.81649700
O	1.20450672	0.28687358	1.73624500
C	1.05130472	-2.82813142	0.63014400
C	1.01354872	-2.88281342	2.16663800
C	2.39544072	-2.29696142	0.10998100
H	0.95524872	-3.86788642	0.27883200
H	0.05155172	-3.25901542	2.53548100
H	1.79236872	-3.56421442	2.52895700
H	1.19544372	-1.90434842	2.61506900
H	2.43172472	-2.30853842	-0.98702000
H	2.56818772	-1.27385142	0.45470800
H	3.21924372	-2.92152442	0.47460100
C	-3.88145128	-1.80523942	0.69285000
O	-4.69296128	-0.89873842	0.62553900
O	-4.20719828	-3.07019542	1.04230700
C	-5.59587028	-3.28530442	1.34025700

H	-6.21633728	-3.05533642	0.46998200
H	-5.67736728	-4.34066742	1.60168900
H	-5.91145528	-2.65628042	2.17694900
H	-2.98396428	0.76292258	1.56695000
O	-2.13441828	2.03762558	0.18820600
C	-2.39972228	3.20540358	0.96084800
H	-1.59162928	3.40447758	1.67371600
H	-2.47644328	4.03348958	0.25331100
H	-3.34828128	3.10614858	1.50781000

Sum of electronic and zero-point Energies= -882.040738
Sum of electronic and thermal Energies= -882.022545
Sum of electronic and thermal Enthalpies= -882.021601
Sum of electronic and thermal Free Energies= -882.087383

3. Cartesian coordinates of stationary points: R9, R11, R11', R13, R13'

R9

C	0.22255192	-0.62314539	0.00000000
C	-1.29574608	1.22712661	-0.43735800
C	0.17437692	0.93258861	-0.11133800
H	0.18864392	-0.99672639	1.02753100
H	0.48667292	1.42065861	0.82032800
C	1.15339392	1.21273961	-1.23174100
C	1.47036692	-1.08635639	-0.77669800
H	2.28098692	-1.36978039	-0.09025000
C	1.84168892	0.12812961	-1.59497200
H	2.60133292	0.10135561	-2.37088400
H	-1.44657408	2.01184061	-1.18306300
H	1.24026292	-1.97125539	-1.38123800
H	1.26350992	2.20290861	-1.66559300
H	-1.87340408	1.50545061	0.45256400
C	-1.84311308	-0.09707339	-0.95952900
O	-0.96580208	-1.10018439	-0.66892900
O	-2.88503008	-0.29900139	-1.52542700

Sum of electronic and zero-point Energies= -421.860021
Sum of electronic and thermal Energies= -421.853099
Sum of electronic and thermal Enthalpies= -421.852155
Sum of electronic and thermal Free Energies= -421.891727

R11

C	-0.40059346	0.22255193	0.00000000

C	0.31494054	-1.15834407	0.03817100
H	-0.38528446	0.71312093	0.97912000
H	0.41691254	-1.59596007	1.04196400
C	-0.56361346	-2.02772707	-0.83989900
C	-1.84478746	-0.06720907	-0.48228800
H	-2.55914946	-0.09358707	0.35371700
C	-1.72457146	-1.43165507	-1.12451500
H	-2.21143646	0.70160293	-1.17610600
H	-0.25177746	-3.01595307	-1.16368800
C	0.43030954	1.05549793	-1.01617700
H	0.06371754	0.85624393	-2.03101300
H	0.33531454	2.13190693	-0.84172800
H	-2.51825846	-1.87156207	-1.72259100
C	1.72586254	-0.93338307	-0.53144200
O	2.56594654	-1.79424507	-0.67472800
C	1.87321354	0.54644893	-0.88669600
H	2.50028954	0.68201393	-1.77254200
H	2.38919554	1.03273593	-0.04492500

Sum of electronic and zero-point Energies= -385.911661
Sum of electronic and thermal Energies= -385.904338
Sum of electronic and thermal Enthalpies= -385.903394
Sum of electronic and thermal Free Energies= -385.943645

R11'

C	-0.28189910	-0.01483680	0.00000000
C	-0.99544210	-1.39901980	-0.07418700
H	0.07560690	0.29632920	-0.98582200
H	-1.23495210	-1.73450980	-1.09126600
C	-0.06193110	-2.34908380	0.64290100
C	0.93916690	-0.22369380	0.95051200
H	1.87286990	0.14342920	0.50394600
C	0.97147990	-1.71200680	1.19907700
H	0.82041990	0.33094220	1.89397900
H	-0.26850110	-3.41270580	0.71278900
C	-1.35367310	0.97848320	0.52242500
C	-2.29869410	0.13465820	1.39291200
H	-0.91124310	1.82287020	1.06120700
H	-1.91401910	1.39522020	-0.32382500
H	1.75202890	-2.19036780	1.78504400
H	-3.31077310	0.53241020	1.50637700
H	-1.88641210	-0.00570080	2.40316700
C	-2.31545310	-1.23365780	0.70935700

O	-3.20180110	-2.05649080	0.76788300

Sum of electronic and zero-point Energies= -385.910669
Sum of electronic and thermal Energies= -385.903268
Sum of electronic and thermal Enthalpies= -385.902324
Sum of electronic and thermal Free Energies= -385.942976

R13

C	-0.48961422	-0.01483680	0.00000000
C	-0.31184222	-1.56458080	0.02344800
H	-0.45946122	0.40483520	1.00909400
H	-0.45423422	-2.01792080	1.01060800
C	-1.31143022	-2.05952580	-0.98922000
C	-1.85763222	0.22909820	-0.68812000
H	-2.63905022	0.46790520	0.04710400
C	-2.14698022	-1.08954280	-1.36906200
H	-2.96999422	-1.21581380	-2.06743900
H	-1.83016622	1.07272820	-1.38994300
H	-1.33511822	-3.09286280	-1.32026100
C	1.69324878	-0.74529080	-0.81852800
O	2.83756178	-0.76804780	-1.18893900
C	0.73526878	0.44207020	-0.80701900
H	0.48204278	0.66952820	-1.84999300
H	1.24271178	1.32053020	-0.40038500
O	1.05692878	-1.85389880	-0.34467100

Sum of electronic and zero-point Energies= -421.858473
Sum of electronic and thermal Energies= -421.851512
Sum of electronic and thermal Enthalpies= -421.850567
Sum of electronic and thermal Free Energies= -421.890353

R13'

C	0.51928781	0.19287834	0.00000000
C	-0.60441919	-1.84100066	-0.71210700
C	-1.21860519	-0.83110366	-1.33234500
C	-0.57146119	0.50555634	-1.06471700
C	0.57304781	-1.36434466	0.09164100
H	0.22318081	0.61490934	0.96365100
H	-2.08165419	-0.93639066	-1.98455700
H	-1.29145519	1.24961734	-0.70081800
H	0.59150181	-1.74824966	1.11733800
H	-0.14273419	0.92248434	-1.98748200

H	-0.87331019	-2.89007366	-0.78097200
C	2.61554681	-0.71873266	-0.83610200
O	3.67945281	-0.84610466	-1.38384000
C	1.95680181	0.57722034	-0.36534300
H	2.04037381	1.33780934	-1.14626600
H	2.52508081	0.94171734	0.49866700
O	1.82418081	-1.78077366	-0.52033600

Sum of electronic and zero-point Energies= -421.858026
Sum of electronic and thermal Energies= -421.850978
Sum of electronic and thermal Enthalpies= -421.850034
Sum of electronic and thermal Free Energies= -421.890407

4. Cartesian coordinates of stationary points: TS9β, TS11β, TS13β

TS9β

C	0.10385756	-0.04451039	0.00000000
C	0.34341356	1.49053661	1.85088400
C	1.59342856	-0.81375139	1.72657900
C	1.89558356	-1.54095839	0.58151400
C	0.90740956	-1.24391939	-0.52384600
C	0.31817856	-0.00840739	1.53764100
H	-0.94952644	-0.07914939	-0.29600300
H	1.03886656	1.78720561	2.63631500
H	2.47040756	-2.45826539	0.59864000
H	0.24147456	-2.10615939	-0.66934700
H	-0.49303544	-0.52185139	2.06991400
O	3.10309456	0.67284261	1.83897600
O	3.62692456	-0.73367039	-0.24829100
Os	4.35075256	0.63208661	0.59407100
O	5.87807656	0.21188361	1.25149800
O	4.32632156	2.04511961	-0.37078900
H	1.38209656	-1.03311239	-1.48695100
H	1.93596356	-1.09284139	2.71547600
H	-0.65400744	1.85951061	2.11940100
C	0.75144756	2.12999261	0.52588100
O	0.65219556	1.19969561	-0.47939900
O	1.10253956	3.25914561	0.32023900

Sum of electronic and zero-point Energies= -813.746072
Sum of electronic and thermal Energies= -813.733861
Sum of electronic and thermal Enthalpies= -813.732917
Sum of electronic and thermal Free Energies= -813.786468
Imaginary frequency: -325.47 cm^{-1}

TS11β

C	-0.26706230	-0.51928783	0.00000000
C	-0.39527230	-1.23533383	1.37122700
H	0.78049770	-0.29731083	-0.22764200
H	0.45870470	-1.07688383	2.04412800
C	-1.62534130	-0.62121783	2.00314500
C	-1.09567230	0.78234517	0.13881100
H	-0.45013730	1.63760517	0.38599200
C	-2.01568330	0.51594817	1.30831900
H	-1.63860030	1.05172317	-0.77432800
H	-1.89052530	-0.82394583	3.03273200
C	-0.81465330	-1.53756883	-1.04208200
C	-0.56230430	-2.93472083	-0.45104900
H	-1.88686630	-1.38124583	-1.19743700
H	-0.33869530	-1.40377783	-2.01844800
H	-2.61249630	1.30208117	1.75483800
H	0.40236570	-3.34746183	-0.77843500
H	-1.32638930	-3.67699983	-0.70176000
O	-3.15944130	-2.07265183	1.60592400
O	-3.80806830	0.04589617	0.29741000
Os	-4.47806630	-1.56054483	0.56051900
O	-4.47748730	-2.47016183	-0.89598200
O	-5.96590630	-1.48449683	1.41030000
C	-0.47375330	-2.74970983	1.06644200
O	-0.41339730	-3.62732983	1.89356500

Sum of electronic and zero-point Energies= -777.799982

Sum of electronic and thermal Energies= -777.787182

Sum of electronic and thermal Enthalpies= -777.786237

Sum of electronic and thermal Free Energies= -777.841192

Imaginary frequency: -288.22 cm^{-1}

TS13β

C	0.25222551	-0.19287834	0.00000000
C	-1.27939249	0.33272366	1.82148700
C	-1.61020749	1.16246966	0.75764900
C	-0.63167749	1.01659966	-0.38828600
C	0.02527351	-0.38825234	1.52909200
H	1.30651851	0.00739066	-0.20877500
H	-2.21904749	2.05141366	0.86860700
H	-0.02606649	1.93040566	-0.46227700
H	0.82117451	0.04843366	2.14393200

O	-2.68667849	-1.22380434	1.80417400
O	-3.33620249	0.35911066	-0.11285200
Os	-3.97045449	-1.11782034	0.60609500
O	-5.49924149	-0.85177734	1.33411900
O	-3.87586449	-2.41976834	-0.50591600
H	-1.13567949	0.89782566	-1.35374700
H	-1.60990349	0.50070666	2.83883000
C	-0.06659449	-2.51923834	0.63659200
O	-0.09363649	-3.71919034	0.63555800
O	0.04022851	-1.79392634	1.79470600
C	-0.13194749	-1.56994234	-0.56037100
H	-1.14973749	-1.60159834	-0.96628400
H	0.53334951	-1.93338434	-1.34750900

Sum of electronic and zero-point Energies= -813.742092

Sum of electronic and thermal Energies= -813.729848

Sum of electronic and thermal Enthalpies= -813.728904

Sum of electronic and thermal Free Energies= -813.782831

Imaginary frequency: -323.63 cm^{-1}

5. Cartesian coordinates of stationary points: TS9α, TS11α, TS13α

TS9α

C	-0.75667653	-0.19287834	0.00000000
C	0.07029547	-2.41780034	-0.53719800
C	-2.07850453	-1.46564234	-1.57401200
C	-2.28488653	-0.12334534	-1.86655900
C	-1.61901953	0.76844466	-0.84105200
C	-1.23668553	-1.64269834	-0.32357200
H	-0.76264353	0.04584966	1.06713900
H	0.05068147	-3.12379134	-1.37154800
H	-2.54956953	0.23244966	-2.85413000
H	-2.36013553	1.29208066	-0.22573600
H	-1.83302553	-2.07235334	0.48700300
O	-3.90508453	-2.20520734	-0.84019200
O	-4.29945853	0.26884766	-1.40864800
Os	-5.24036153	-1.06164334	-0.74246500
O	-5.66134853	-0.75209834	0.89164100
O	-6.52710353	-1.50529734	-1.78443800
H	-0.98781353	1.53333166	-1.30554900
H	-2.16803753	-2.25487134	-2.31077000
H	0.36254347	-2.98115634	0.35668600
O	0.61159347	-0.12121734	-0.45193500

C	1.12277447	-1.34254734	-0.78588200
O	2.24485147	-1.48077434	-1.19332400

Sum of electronic and zero-point Energies= -813.746464
Sum of electronic and thermal Energies= -813.734040
Sum of electronic and thermal Enthalpies= -813.733096
Sum of electronic and thermal Free Energies= -813.787930
Imaginary frequency: -313.03 cm^{-1}

TS11α

C	0.08902077	0.01483680	0.00000000
C	0.14468777	1.56265080	0.07994000
H	0.79338977	-0.44708020	0.69803800
H	0.48649677	1.95598280	1.04540400
C	1.03136877	1.99049880	-1.05894600
C	0.52310377	-0.30925720	-1.45912900
H	1.13288777	-1.21567920	-1.53117600
C	1.25952677	0.92749780	-1.91742100
H	-0.35055723	-0.46821120	-2.11055700
H	1.15474477	3.03241780	-1.32627300
C	-1.37115423	-0.36525520	0.34724000
C	-2.22821123	0.79785280	-0.18020200
H	-1.65860223	-1.33415220	-0.07370400
H	-1.48072823	-0.44246020	1.43554700
H	1.60961677	1.04816780	-2.93579100
H	-3.15812123	0.97257080	0.36901000
H	-2.50706623	0.65333980	-1.23403600
O	2.86088777	2.26507180	0.05420700
O	3.24887177	0.24474380	-1.50010100
Os	4.14645377	1.11403180	-0.26617100
O	5.52908577	1.88797080	-0.92355600
O	4.42761777	0.11680780	1.10294900
C	-1.32193723	2.03095880	-0.11946000
O	-1.67119823	3.18413280	-0.21981100

Sum of electronic and zero-point Energies= -777.802374
Sum of electronic and thermal Energies= -777.789579
Sum of electronic and thermal Enthalpies= -777.788635
Sum of electronic and thermal Free Energies= -777.843762
Imaginary frequency: -258.65 cm^{-1}

TS13α

C	0.45994063	-0.08902077	0.00000000

C	1.49561263	-2.15254877	0.75726400
C	1.66088063	-1.22460877	1.77203700
C	0.87981563	0.03651523	1.49122400
C	0.57772563	-1.60728277	-0.30765200
H	1.13465863	0.49094923	-0.63485000
H	1.99268363	-1.48385877	2.77004200
H	1.45555063	0.94467323	1.69591800
H	0.89509963	-1.84803877	-1.32554300
O	3.24337463	-2.06673077	-0.45000600
O	3.63362463	-0.45803477	1.52403600
Os	4.52578363	-1.00546777	0.11297200
O	4.77971163	0.28757723	-0.98547600
O	5.92307763	-1.89101677	0.56114400
H	-0.00021737	0.06462123	2.15095300
H	1.68037063	-3.21427777	0.86167100
C	-1.69900037	-1.15576277	-0.09725800
O	-2.86952337	-1.38816077	0.04180800
C	-1.01483037	0.19799123	-0.28452600
H	-1.47349237	0.94722023	0.36539200
H	-1.17927537	0.51856123	-1.32084300
O	-0.75552637	-2.14776977	-0.12317000

Sum of electronic and zero-point Energies= -813.747277

Sum of electronic and thermal Energies= -813.734918

Sum of electronic and thermal Enthalpies= -813.733974

Sum of electronic and thermal Free Energies= -813.788270

Imaginary frequency: -277.80 cm^{-1}

C. Literature Search

Searches in SciFinder were performed on 8/25/2011. Structure searches are summarized in Table S1, reaction searches in Table S2. The hits were screened manually to remove duplicates and extract the 24 relevant examples. A control search (Table S3), in which the bridgehead hydrogens were omitted, revealed another 2 relevant examples not found in the previous searches.

Table S1: SciFinder substructure searches. Bold bonds indicate the "lock ring fusion tool", squares around atoms indicate the "lock atoms tool".

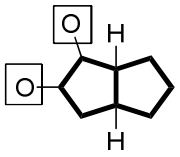
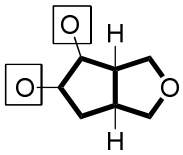
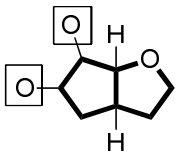
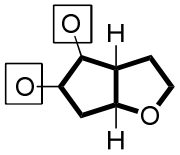
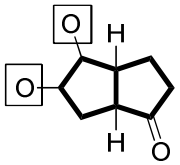
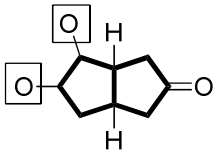
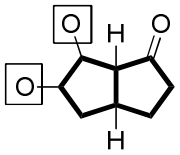
Entry	Search pattern	Hits	Relevant hits
1		44	13
2		16	1
3		34	6
4		23	2
5		2	0
6		6	0
7		0	0

Table S2: SciFinder reaction (substructure) searches. Bold bonds indicate the "lock ring fusion tool".

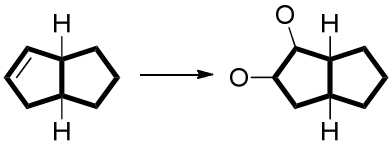
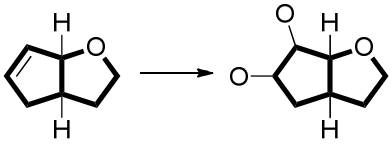
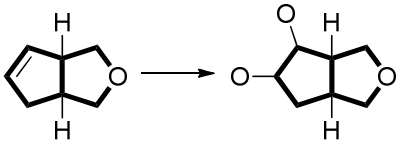
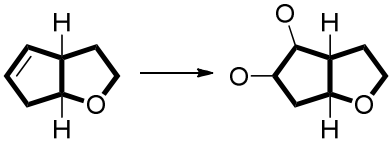
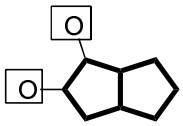
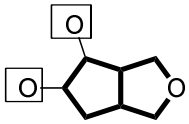
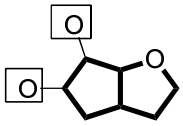
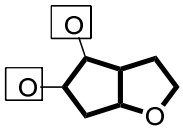
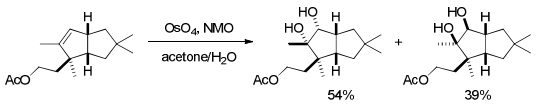
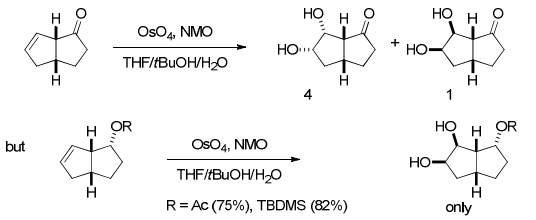
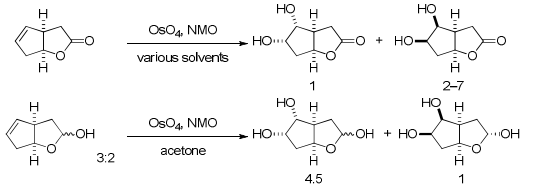
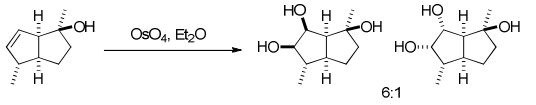
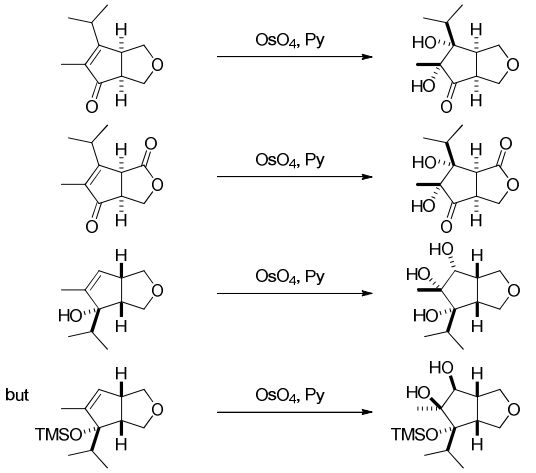
Entry	Search pattern	Hits	Relevant hits not covered in Table S1
1		22	2
2		9	0
3		0	0
4		13	0

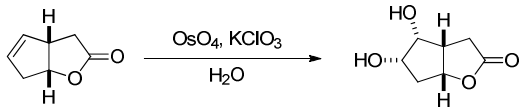
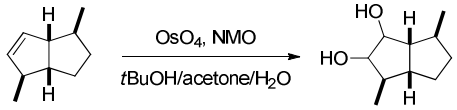
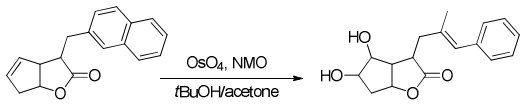
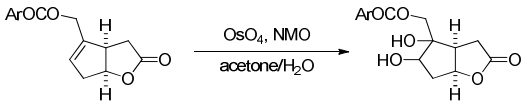
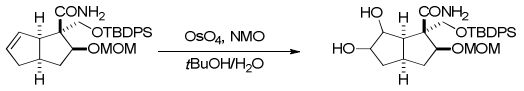
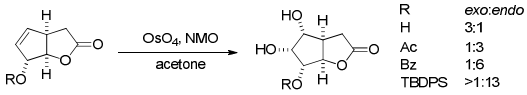
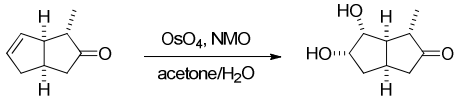
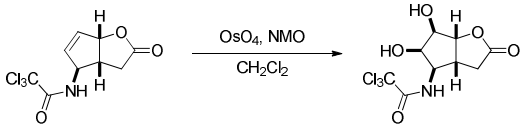
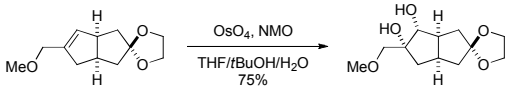
Table S3: SciFinder control substructure searches. Bold bonds indicate the "lock ring fusion tool", squares around atoms indicate the "lock atoms tool".

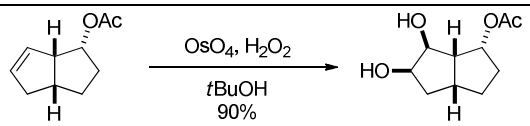
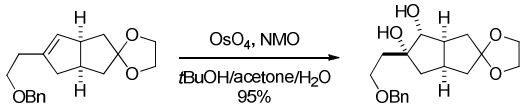
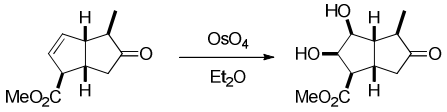
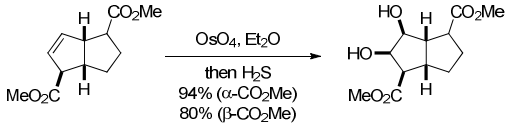
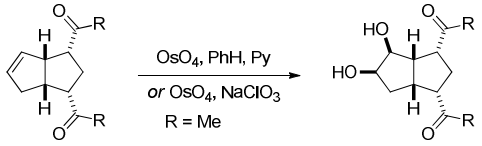
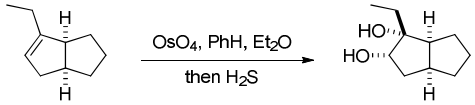
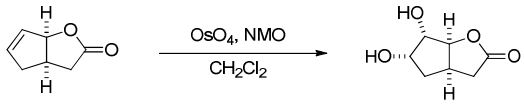
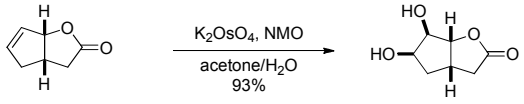
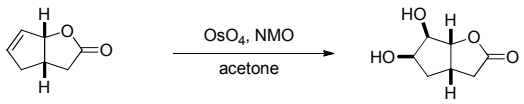
Entry	Search pattern	Hits	Relevant hits not covered in Tables S1 or S2
1		45	0
2		16	0
3		36	0
4		28	2

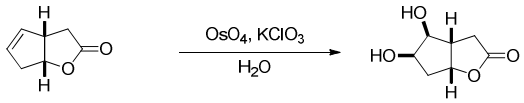
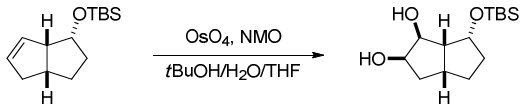
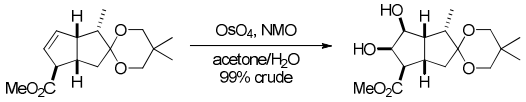
The 26 relevant examples are given in Table S4. Entries 1–6 signify cases where dihydroxylation occurred from the concave face or both faces, and good evidence for the structural assignment is given. In entries 7–12, diastereomeric mixtures are reported without evidence for the assignment, or the products were not assigned. The dihydroxylation product of Entry 13 is assigned by NOE analysis of a later synthetic intermediate. For Entries 14–26, no evidence is given for the assignment. One of the examples (Entry 24) was refuted by a later publication (Entry 6), where an X-ray crystal structure of the product was obtained. Entries 2, 3, 6, 21–23, and 24 were investigated by computational studies and are discussed in the main text.

Table S4: Relevant literature examples from the SciFinder literature searches (Tables S1–S3).

Entry	Reaction(s)	Comment	Reference
1		Assignment based on coupling constants.	6
2		"... the carbonyl group may be directing the reaction." Assignment based on NOE.	7
3		"... may be a directing effect from the carbonyl group." Strong solvent effect observed. Assignment based on coupling constants, chemical correlation, and a crystal structure.	8
4		Chemical evidence for assignment.	9
5		Crystallographic evidence and chemical correlation.	10

Entry	Reaction(s)	Comment	Reference
6		Crystal structure.	11
7		Unassigned 3:1 mixture.	12
8		Unassigned 1:5:5:1 mixture.	13
9		Unspecified mixture.	14
10		Not assigned.	15
11	 R *exo:endo* H 3:1 Ac 1:3 Bz 1:6 TBDPS >1:13	No direct evidence for assignment reported.	16
12		5.5:1 exo:endo reported, no evidence for assignment given.	17
13		NOE assignment of a later intermediate.	18
14		No evidence for assignment reported.	19

Entry	Reaction(s)	Comment	Reference
15		No evidence for assignment reported.	20
16		No evidence for assignment reported.	21
17		No evidence for assignment reported.	22
18		No evidence for assignment reported.	23
19		No evidence for assignment reported.	24
20		Discussion of the preferred conformation of the product (through coupling constants). No direct evidence for assignment reported.	25
21		No evidence for assignment reported.	26
22		No evidence for assignment reported.	27
23		No evidence for assignment reported.	28

Entry	Reaction(s)	Comment	Reference
24		No evidence for assignment reported. Refuted by Entry 6.	29
25		No evidence for assignment reported.	30
26		No evidence for assignment reported.	31

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