Electronic supplementary information (ESI)

Sulfuric acid and Amberlyst-H$^+$ catalyzed condensation reactions of renewable keto acids with paraformaldehyde: Synthesis of a new dispiro *bis*-lactone ring system 2,9,13-trioxadispiro[4.1.4.3]tetradecane-3,6,10-trione

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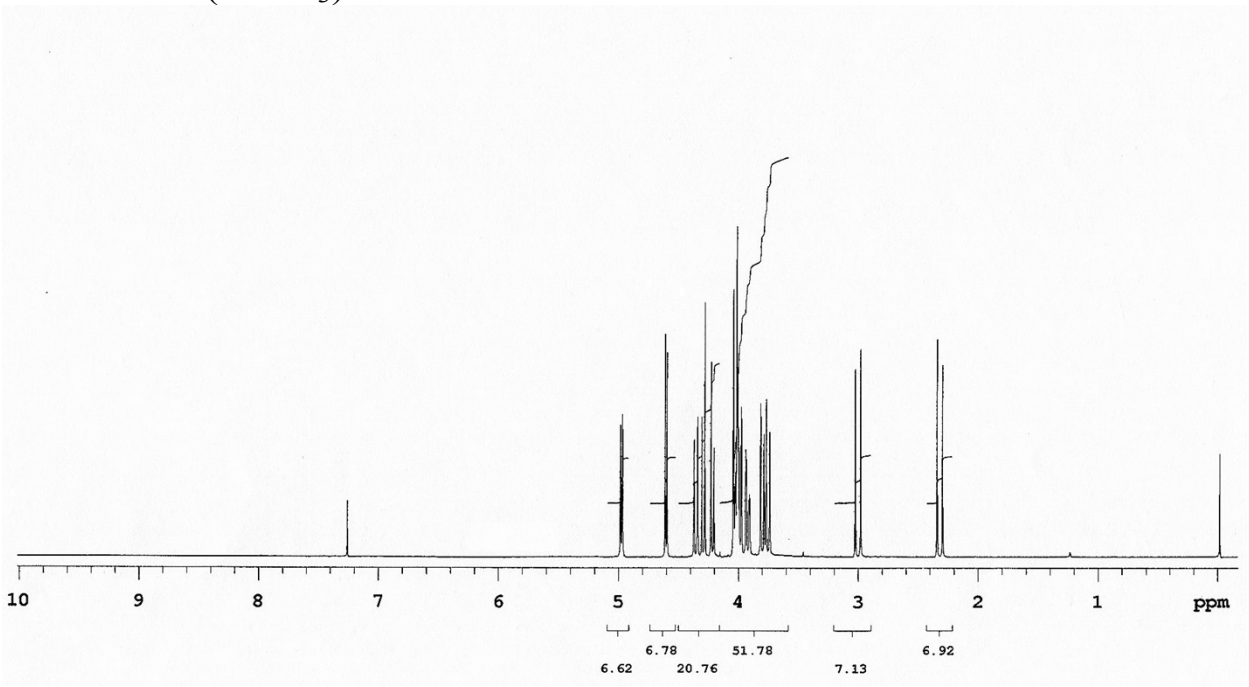
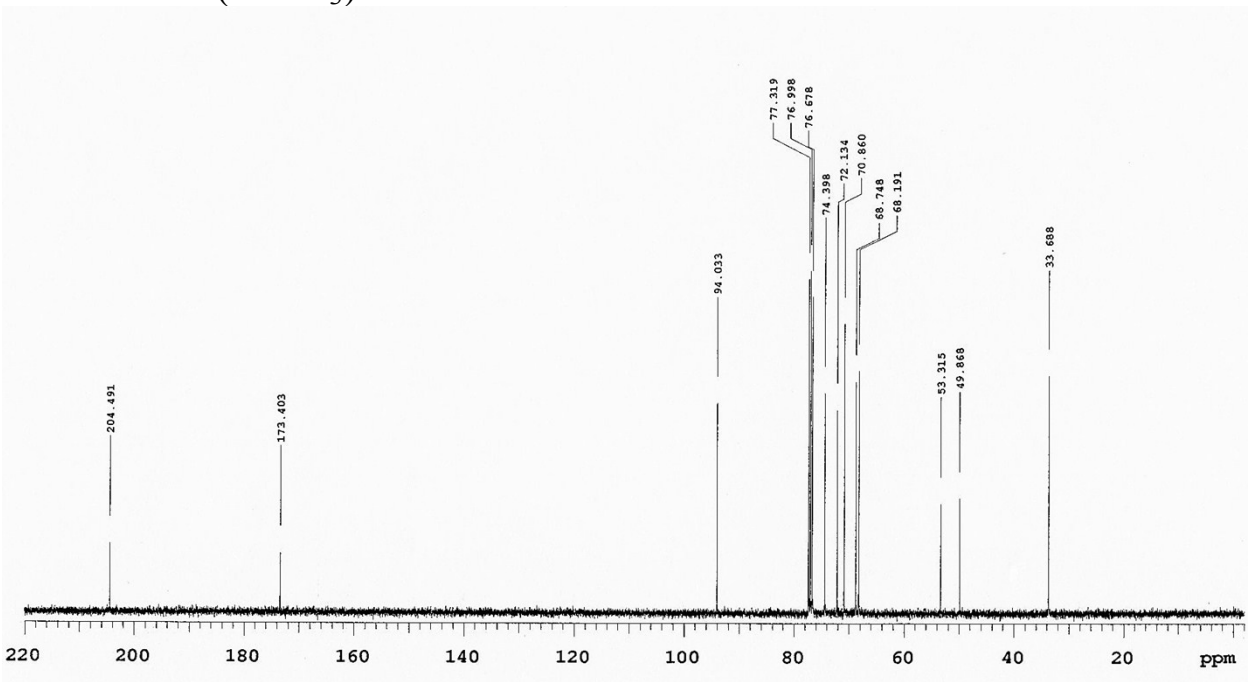
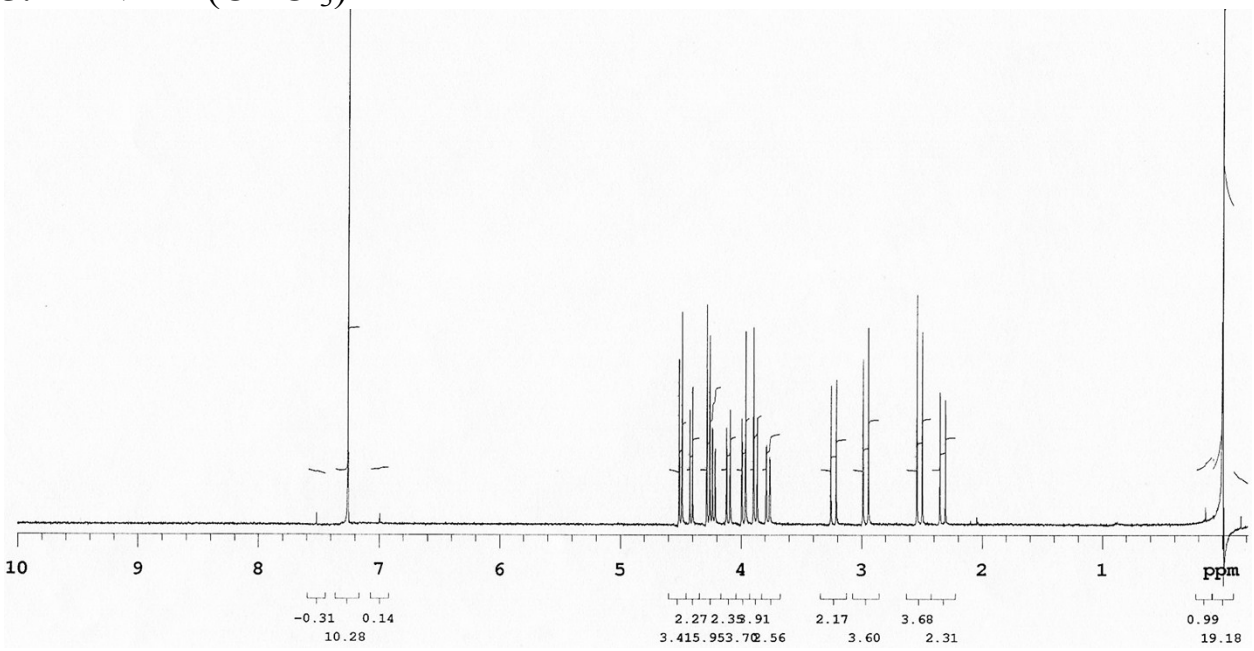
3. ^{1}H NMR ($CDCl_3$)



3. ^{13}C NMR ($CDCl_3$)



5. ^{1}H NMR ($CDCl_3$)



5. ^{13}C NMR ($CDCl_3$)

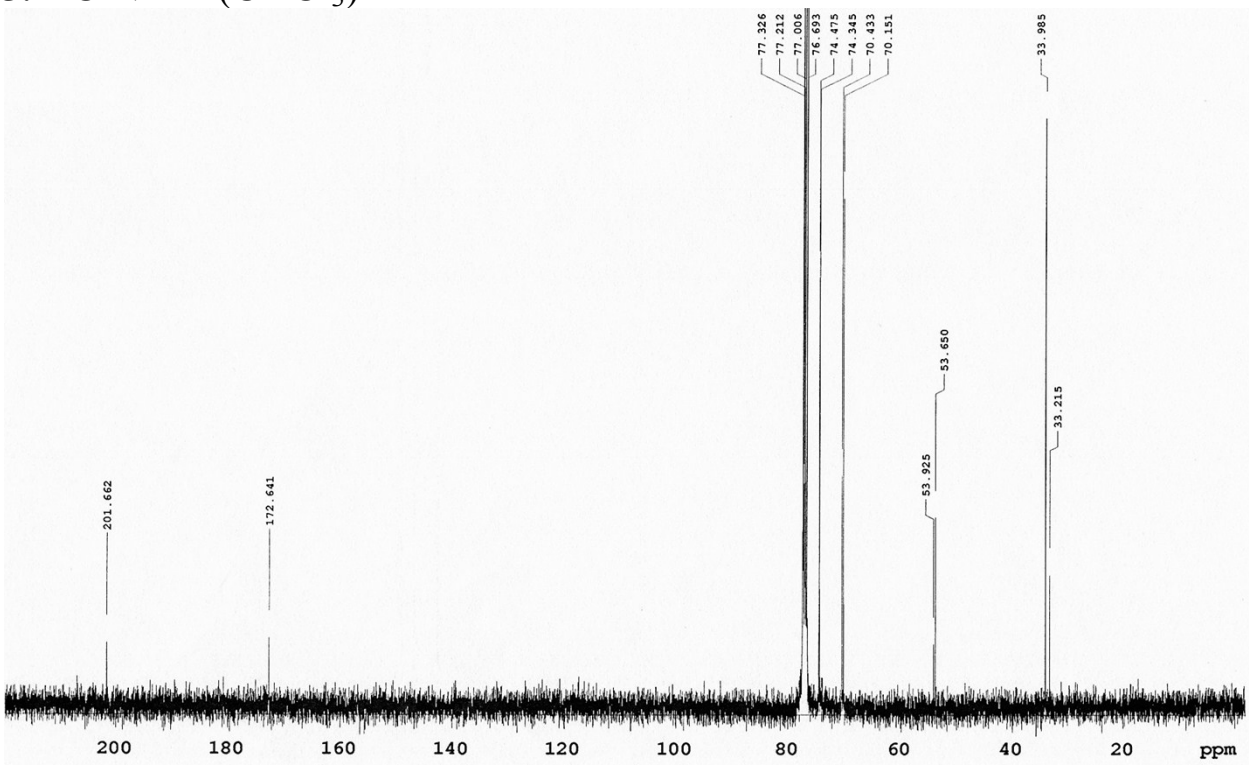
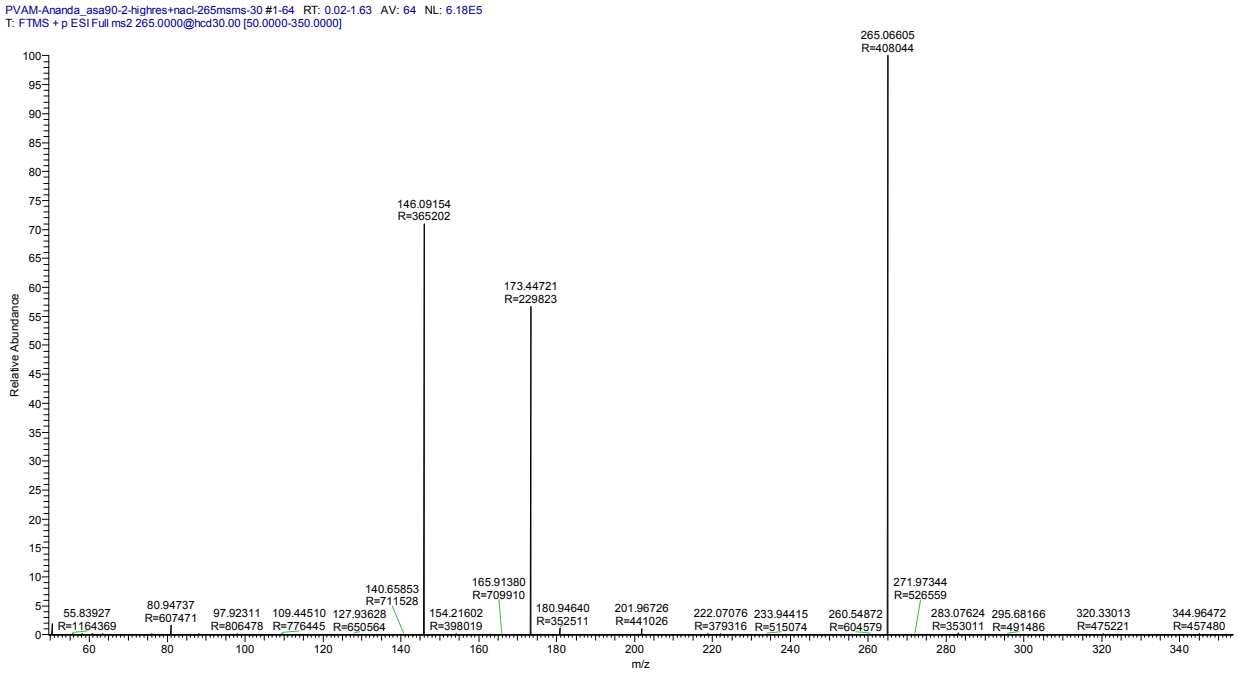


Fig. 1. ^{1}H and ^{13}C NMR of 3 and 5

3. HRMS $(M + Na)^+ = 265.06605$



5. HRMS $(M + Na)^+ = 263.05039$

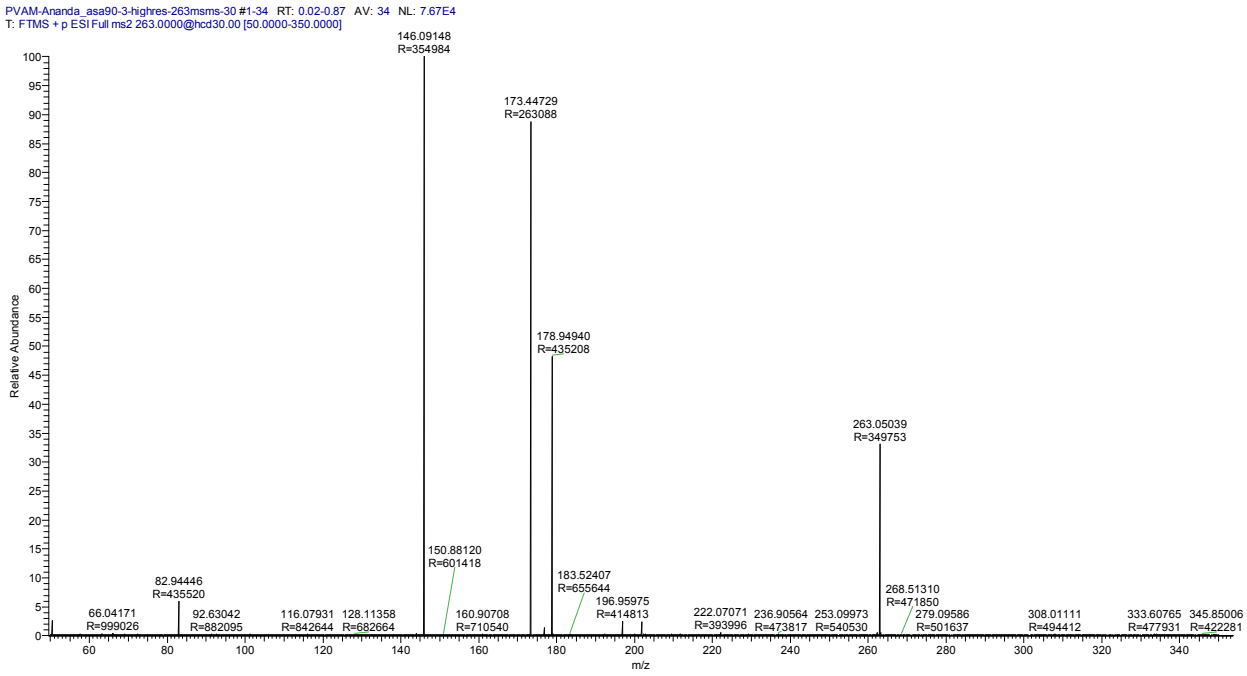


Fig. 2. Mass Spectra data of 3 and 5

Compound 3, X-Ray crystallography data

Table 1. Bond lengths [Å] and angles [°] for 3

O(1)-C(2)	1.203(2)
C(2)-O(3)	1.358(3)
C(2)-C(6)	1.514(3)
O(3)-C(4)	1.442(2)
O(1')-C(2')	1.196(6)
C(2')-O(3')	1.363(5)
C(2')-C(4)	1.517(6)
O(3')-C(6)	1.424(5)
C(4)-C(5)	1.537(2)
C(5)-C(11)	1.530(2)
C(5)-C(6)	1.538(2)
C(5)-C(7)	1.539(2)
C(7)-O(8)	1.419(2)
O(8)-C(9)	1.420(2)
C(9)-C(10)	1.537(2)
C(10)-C(11)	1.520(2)
C(10)-C(17)	1.533(2)
C(10)-C(13)	1.541(2)
C(11)-O(12)	1.2123(19)
C(13)-O(14)	1.427(2)
O(14)-C(15)	1.411(2)
C(15)-O(16)	1.406(2)
O(16)-C(17)	1.424(2)

O(1)-C(2)-O(3)	119.6(2)
O(1)-C(2)-C(6)	129.3(2)
O(3)-C(2)-C(6)	111.01(16)
C(2)-O(3)-C(4)	109.48(17)
O(1')-C(2')-O(3')	113.9(8)
O(1')-C(2')-C(4)	131.3(10)

O(3')-C(2')-C(4)	112.3(6)
C(2')-O(3')-C(6)	108.2(5)
O(3)-C(4)-C(5)	107.07(15)
C(2')-C(4)-C(5)	102.4(4)
C(11)-C(5)-C(4)	112.13(13)
C(11)-C(5)-C(6)	113.33(14)
C(4)-C(5)-C(6)	101.66(14)
C(11)-C(5)-C(7)	108.48(14)
C(4)-C(5)-C(7)	110.45(15)
C(6)-C(5)-C(7)	110.70(14)
O(3')-C(6)-C(5)	108.7(5)
C(2)-C(6)-C(5)	103.57(16)
O(8)-C(7)-C(5)	111.64(14)
C(7)-O(8)-C(9)	110.42(13)
O(8)-C(9)-C(10)	111.28(14)
C(11)-C(10)-C(17)	110.55(13)
C(11)-C(10)-C(9)	107.47(14)
C(17)-C(10)-C(9)	110.75(14)
C(11)-C(10)-C(13)	110.83(13)
C(17)-C(10)-C(13)	107.21(14)
C(9)-C(10)-C(13)	110.05(14)
O(12)-C(11)-C(10)	121.93(15)
O(12)-C(11)-C(5)	121.77(15)
C(10)-C(11)-C(5)	116.23(13)
O(14)-C(13)-C(10)	110.19(13)
C(15)-O(14)-C(13)	110.55(14)
O(16)-C(15)-O(14)	111.50(16)
C(15)-O(16)-C(17)	110.24(14)
O(16)-C(17)-C(10)	109.71(14)

Symmetry transformations used to generate equivalent atoms:

Table 2. Torsion angles [°] for 3

O(1)-C(2)-O(3)-C(4)	-177.7(2)
C(6)-C(2)-O(3)-C(4)	3.0(3)

O(1')-C(2')-O(3')-C(6)	164(3)
C(4)-C(2')-O(3')-C(6)	0(4)
C(2)-O(3)-C(4)-C(5)	-19.2(3)
O(1')-C(2')-C(4)-C(5)	-177(3)
O(3')-C(2')-C(4)-C(5)	-16(3)
O(3)-C(4)-C(5)-C(11)	147.91(17)
C(2')-C(4)-C(5)-C(11)	144.9(14)
O(3)-C(4)-C(5)-C(6)	26.5(2)
C(2')-C(4)-C(5)-C(6)	23.5(14)
O(3)-C(4)-C(5)-C(7)	-91.0(2)
C(2')-C(4)-C(5)-C(7)	-94.0(14)
C(2')-O(3')-C(6)-C(5)	17(3)
O(1)-C(2)-C(6)-C(5)	-165.1(3)
O(3)-C(2)-C(6)-C(5)	14.1(3)
C(11)-C(5)-C(6)-O(3')	-146.0(14)
C(4)-C(5)-C(6)-O(3')	-25.5(14)
C(7)-C(5)-C(6)-O(3')	91.9(14)
C(11)-C(5)-C(6)-C(2)	-144.27(17)
C(4)-C(5)-C(6)-C(2)	-23.7(2)
C(7)-C(5)-C(6)-C(2)	93.60(19)
C(11)-C(5)-C(7)-O(8)	-52.37(18)
C(4)-C(5)-C(7)-O(8)	-175.64(13)
C(6)-C(5)-C(7)-O(8)	72.56(19)
C(5)-C(7)-O(8)-C(9)	64.84(18)
C(7)-O(8)-C(9)-C(10)	-66.90(18)
O(8)-C(9)-C(10)-C(11)	55.86(17)
O(8)-C(9)-C(10)-C(17)	176.71(14)
O(8)-C(9)-C(10)-C(13)	-64.92(19)
C(17)-C(10)-C(11)-O(12)	8.7(2)
C(9)-C(10)-C(11)-O(12)	129.68(17)
C(13)-C(10)-C(11)-O(12)	-110.03(17)
C(17)-C(10)-C(11)-C(5)	-168.19(14)
C(9)-C(10)-C(11)-C(5)	-47.21(17)
C(13)-C(10)-C(11)-C(5)	73.08(18)
C(4)-C(5)-C(11)-O(12)	-8.8(2)
C(6)-C(5)-C(11)-O(12)	105.54(18)

C(7)-C(5)-C(11)-O(12)	-131.09(16)
C(4)-C(5)-C(11)-C(10)	168.05(14)
C(6)-C(5)-C(11)-C(10)	-77.56(18)
C(7)-C(5)-C(11)-C(10)	45.80(17)
C(11)-C(10)-C(13)-O(14)	174.46(14)
C(17)-C(10)-C(13)-O(14)	53.73(18)
C(9)-C(10)-C(13)-O(14)	-66.80(18)
C(10)-C(13)-O(14)-C(15)	-57.84(19)
C(13)-O(14)-C(15)-O(16)	62.7(2)
O(14)-C(15)-O(16)-C(17)	-63.9(2)
C(15)-O(16)-C(17)-C(10)	60.3(2)
C(11)-C(10)-C(17)-O(16)	-175.69(13)
C(9)-C(10)-C(17)-O(16)	65.31(19)
C(13)-C(10)-C(17)-O(16)	-54.78(18)

Symmetry transformations used to generate equivalent atoms:

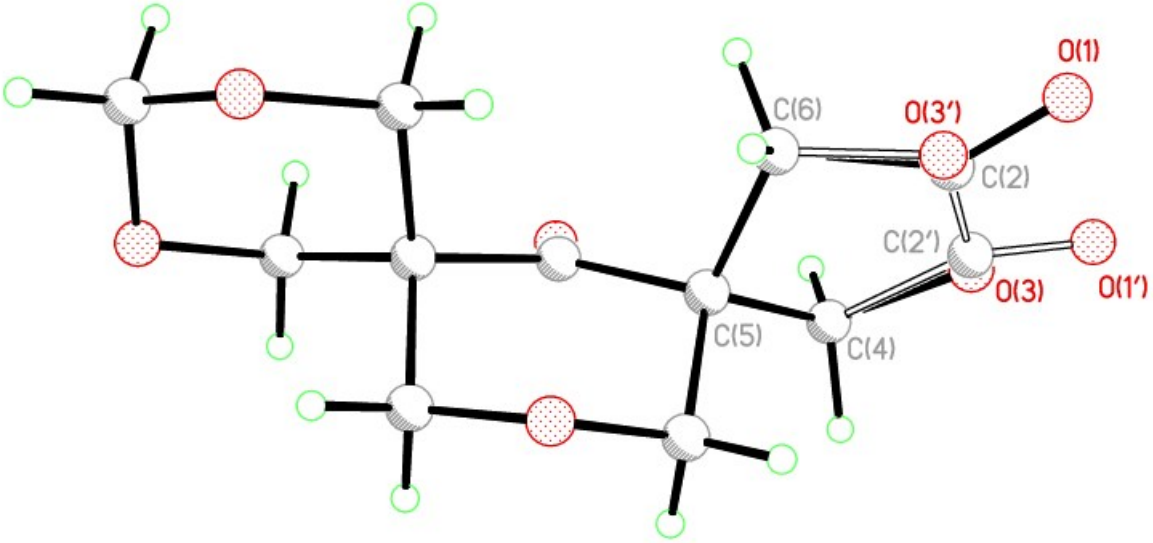


Figure 3. Mode of disordering in 3.

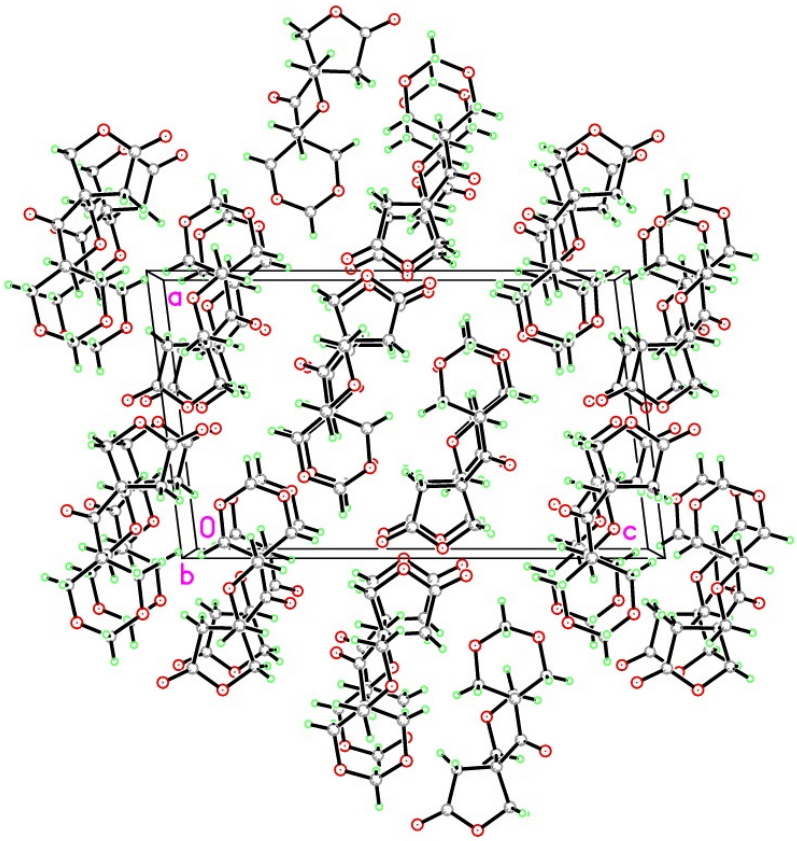


Fig. 4. Crystal packing in 3.

Computational Studies of 3

Geometrical optimizations and vibrational analysis were carried out employing density functional theory Becke three-parameter hybrid functional combined with Lee-Yang-Parr correlation functional method (B3LYP) in conjunction with 6-31G* basis set [1].
All calculations were performed using *Gaussian03* suite of programs [2] implemented on dual core Opteron 240 personal computer under Linux operating system. Harmonic vibration frequencies were calculated for all localized stationary structures to verify whether they are true minima.

Table 3. Cartesian coordinates of optimized structures obtained at the B3LYP/6-31G* level of theory. The number of imaginary frequencies (NImag) is given in parenthesis.

Structure 3b out,down (NImag = 0)

0 1

C	1.30324900	0.23973500	0.10706800
C	-1.11020700	-0.11424600	1.70088300
C	1.21318600	-0.28439800	1.55963900
H	-0.97491900	0.75429500	2.36742900
H	-1.98716400	-0.67097200	2.04659800
H	1.30608600	0.55578000	2.26748200
H	2.02699400	-0.98522800	1.74938300
C	0.00027600	0.92577600	-0.31513700
O	-0.00026900	-0.98277400	1.79848200
O	0.00576800	1.85053000	-1.11021500
C	2.48960000	1.21751600	-0.04986800
H	2.46993700	1.66201700	-1.05393500
H	2.43897100	2.02643500	0.68446200
C	1.58998900	-0.95523400	-0.85493600
H	1.51898700	-0.61009100	-1.89914100
H	0.88193800	-1.77106700	-0.69639800
C	-2.47069800	1.39400900	0.15462100
H	-2.61243700	1.96595300	1.07590400
H	-2.31653300	2.08274800	-0.67973200
C	-3.38271400	-0.60603500	-0.55636300
O	-4.22897700	-1.39888000	-0.86910200
O	-3.67222800	0.63243100	-0.06904600
C	-1.31676200	0.37205000	0.24881200
C	-1.86567200	-0.77673000	-0.63148500
H	-1.57437200	-1.77201800	-0.28913200
H	-1.56870700	-0.67598100	-1.68289300
C	3.88586000	-0.51624700	-0.73364100
H	4.83328200	-1.00299400	-0.50025200
H	3.89007200	-0.12558300	-1.76838100

O	2.87829100	-1.49467200	-0.60103000
O	3.72382000	0.54205700	0.17604100

Structure 3c in,up (NImag = 0)

0 1

C	1.21767100	0.00245800	-0.25327800
C	-0.86719600	2.03054700	-0.48984500
C	1.40951000	1.51627100	-0.50398500
H	-0.80359400	2.18485200	-1.58009500
H	-1.57180400	2.76558200	-0.08636100
H	1.42754600	1.72110200	-1.58705600
H	2.35797400	1.84396800	-0.07647600
C	-0.24041200	-0.41726000	-0.48959100
O	0.38646400	2.28451600	0.11396300
O	-0.51431100	-1.53944000	-0.87689600
C	2.14482800	-0.82955000	-1.17035400
H	1.91278400	-1.89669000	-1.05578400
H	2.00957600	-0.55996700	-2.22160500
C	1.63972400	-0.32686900	1.21233300
H	1.36571700	-1.36725800	1.45001900
H	1.15565700	0.34704400	1.92249300
C	-1.35663500	0.60331400	-0.19309200
C	-1.80470500	0.43949200	1.29561300
H	-2.17192100	1.39592800	1.68979200
H	-1.02945700	0.06698000	1.96697200
C	3.78603200	-0.90889400	0.47717700
H	4.83701300	-0.68293700	0.66008600
H	3.57989500	-1.98170000	0.64908300
O	3.03538900	-0.13073700	1.38312800
O	3.51214200	-0.57696200	-0.85999400
C	-3.41612400	-0.65501300	0.05256800
C	-2.64978300	0.22491000	-0.92751000
H	-3.25978200	1.11296400	-1.14051800
H	-2.49100800	-0.31640900	-1.86094900
O	-2.86974900	-0.51466100	1.30034100
O	-4.36194100	-1.36145300	-0.15926800

Structure 3e in,down;**1,3-dioxane boat** (NImag = 0)

0 1

C	-1.21808800	0.14844600	0.19871900
C	0.90393400	2.01749800	-0.54942600
C	-1.37960700	1.55808900	-0.42170400
H	0.77558000	2.76010600	0.25732700
H	1.65840600	2.40073500	-1.24397500

H	-1.46111000	2.31051500	0.37993300
H	-2.28784800	1.61423700	-1.02525600
C	0.18537900	0.01847200	0.80560400
O	-0.29824900	1.88295500	-1.28107300
O	0.36501200	-0.57259600	1.85413800
C	-2.29564000	-0.06820900	1.28087700
H	-2.15899200	-1.04187200	1.76108200
H	-2.24175500	0.70442700	2.05213700
C	2.59043400	0.84684600	0.97188800
H	3.13972200	1.76636700	0.73218600
H	2.31600200	0.84865300	2.02717500
C	3.12494200	-0.96054700	-0.36752000
O	3.72967100	-1.92623000	-0.74815900
O	3.46501700	-0.26862400	0.75213800
C	1.36260300	0.67108800	0.04413500
C	1.91878900	-0.29696400	-1.02783700
H	2.26859600	0.25378700	-1.91023100
H	1.23077600	-1.06210700	-1.38771800
O	-2.69274600	-1.64923000	-0.64865800
O	-3.58786000	0.06029000	0.69410900
C	-1.46871600	-0.96428100	-0.88515300
H	-0.71261000	-1.75085000	-0.84453100
H	-1.45795300	-0.51810100	-1.89109100
C	-3.77657300	-0.79003500	-0.43430200
H	-3.95243700	-0.15154200	-1.31802800
H	-4.64786200	-1.42929700	-0.26067100

Structure 3a up,out (NImag = 0)

0 1

C	1.31521300	0.13657500	-0.23796100
C	-0.02985500	0.86779900	-0.20295400
O	0.07208400	-1.92389400	-0.74180600
O	-0.08223100	2.08110500	-0.09918500
C	1.73835000	-0.21654000	1.22229600
H	1.67135100	0.68654000	1.85018200
H	1.10081700	-0.99677700	1.64454100
C	2.41464600	1.07028800	-0.79288800
H	2.38786800	2.02939300	-0.25847300
H	2.27005600	1.26668900	-1.85899200
C	-1.72354100	-0.39592400	1.21017000
H	-1.33253600	-1.37801300	1.48442300
H	-1.41218800	0.34507000	1.95589800
C	-3.68574900	0.24984900	0.17143800
O	-4.86946200	0.36687100	0.00944000
O	-3.15562400	-0.47006600	1.20948800

C	-1.31494300	0.02278900	-0.23621800
C	-2.54993600	0.82074900	-0.66608300
H	-2.78879700	0.74676900	-1.73071400
H	-2.42110700	1.88190600	-0.42375200
C	3.98009100	0.17619700	0.68215000
H	4.95909400	-0.30281700	0.71414600
H	3.98130600	1.11162200	1.27218700
O	3.69622300	0.45990700	-0.66394000
O	3.05915700	-0.73458400	1.24235100
C	-1.11117400	-1.23915100	-1.10271000
H	-1.08277800	-0.95927100	-2.16883800
H	-1.94109900	-1.93811500	-0.95730900
C	1.22370700	-1.16245200	-1.07310100
H	2.09151700	-1.79139800	-0.87110800
H	1.21447200	-0.91738800	-2.14782200

Structure 3f out,down;1,3-dioxane boat (NImag = 0)

0 1

C	1.30911800	0.11590200	0.36653800
C	-1.24036200	-0.39870100	1.68102400
C	1.08511200	-0.63985600	1.69752300
H	-1.15155600	0.34187400	2.49374000
H	-2.15700500	-0.97369000	1.84663500
H	1.15746900	0.05959600	2.54745200
H	1.85943600	-1.40335000	1.81275600
C	0.07304400	0.96158900	0.02958700
O	-0.16330900	-1.31314300	1.73218600
O	0.16895500	2.07634700	-0.45043200
C	-2.43612800	1.37473900	0.29250900
H	-2.66101100	1.79067800	1.27855100
H	-2.20526500	2.19071800	-0.39675900
C	-3.27683400	-0.45950400	-0.83056300
O	-4.08976100	-1.17443300	-1.35098300
O	-3.61231100	0.67902600	-0.16230800
C	-1.29830900	0.33237400	0.31818500
C	-1.75872800	-0.63659000	-0.79567600
H	-1.50165400	-1.68130800	-0.60970800
H	-1.36484200	-0.35880000	-1.78136600
O	2.91251600	-1.37960800	-0.64674100
O	3.34263200	0.92215800	-0.74890500
C	2.59261800	0.98793000	0.45821700
H	3.21116500	0.65445100	1.30715500
H	2.33971000	2.03949100	0.59420100
C	3.84715200	-0.36624400	-0.98620600
H	4.74218900	-0.57578600	-0.38117900

H	4.09458700	-0.39758000	-2.05592900
C	1.57494800	-0.92107400	-0.76927100
H	1.39896500	-0.47275800	-1.75657800
H	0.93825000	-1.79968100	-0.65271400

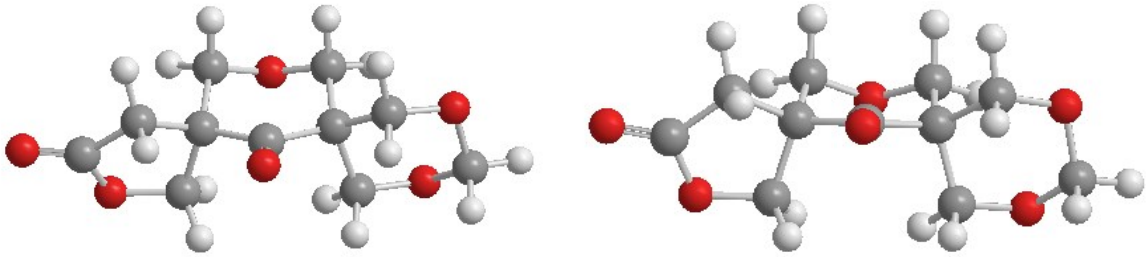
Structure 3d out,downTS (NImag = 1)

0 1

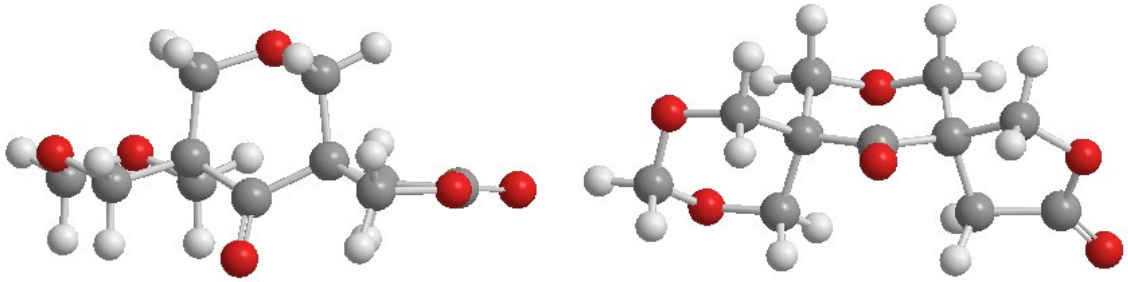
C	-1.28089600	-0.25012400	-0.10725800
C	1.00746400	-1.21475400	1.41569100
C	-1.30813000	-0.96542300	1.26452000
H	0.87979700	-2.29683200	1.24113500
H	1.83685300	-1.08186600	2.11850800
H	-1.40268900	-2.05441900	1.12093900
H	-2.16520800	-0.61782300	1.84222400
C	0.06570600	-0.47389400	-0.80465100
O	-0.14573600	-0.68053800	2.02978800
O	0.13600700	-0.59085200	-2.01557600
C	-2.42935400	-0.75093400	-1.01236000
H	-2.33008000	-0.30370100	-2.01049200
H	-2.40881300	-1.83878100	-1.12082000
C	-1.52729500	1.27390900	0.11213400
H	-1.37594900	1.81396900	-0.83669300
H	-0.85241100	1.67721800	0.86960800
C	1.32756700	-0.50768700	0.07875400
C	1.84779800	0.93281600	0.31405000
H	1.73706100	1.25703900	1.35270000
H	1.35948800	1.68823400	-0.31208700
C	-3.81650900	0.96816300	-0.27637200
H	-4.78829100	1.15686200	0.18071100
H	-3.74043800	1.47050100	-1.25876800
O	-2.84281000	1.49446300	0.59864800
O	-3.69215600	-0.42196700	-0.43928600
C	2.51819900	-1.19606100	-0.64219800
H	2.82081400	-2.11897300	-0.13664100
H	2.28035700	-1.41332500	-1.68528400
C	3.32541600	0.90425500	-0.06794400
O	4.12413000	1.79323200	0.05652100
O	3.64177900	-0.30180100	-0.60649900

B3LYP/6-31G* Optimized structures of 3 (top and side-views)

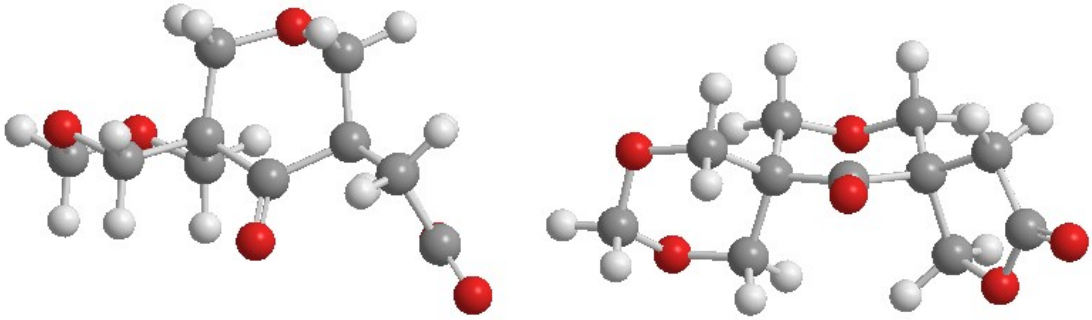
(relative energies are given in kcalmol^{-1}) Grey = C, Red = O, White = H



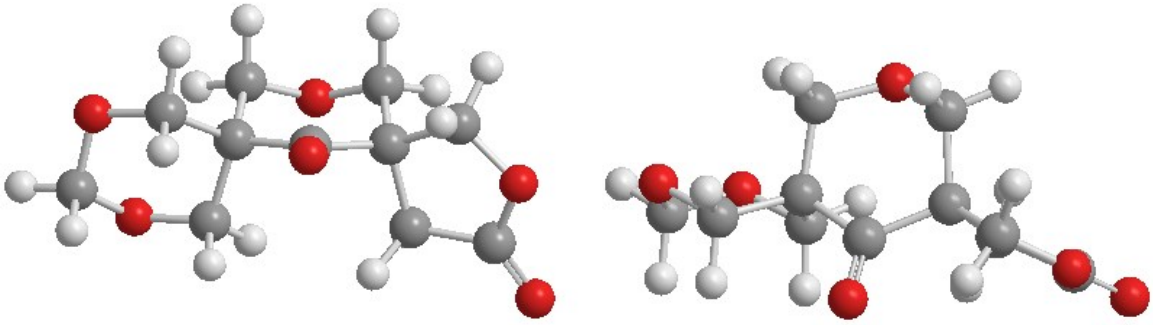
3a up,out E_{rel} = 0 kcalmol^{-1}



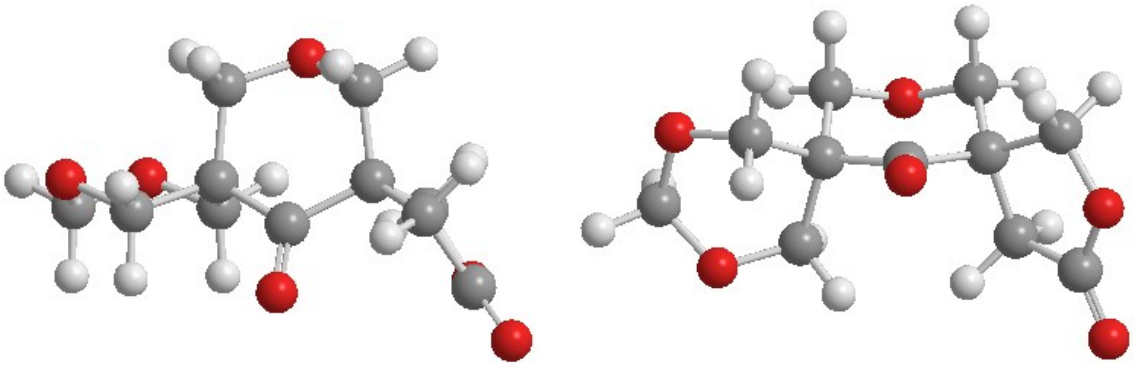
3b down,out E_{rel} = 0.4 kcalmol^{-1}



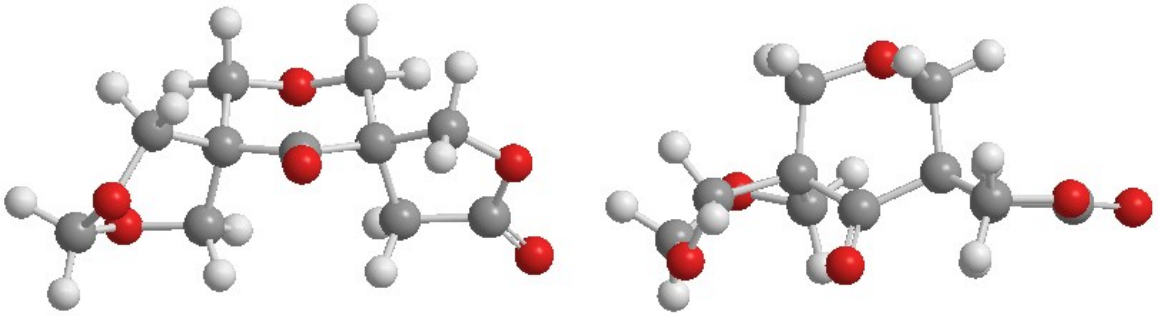
3c up,in E_{rel} = 1.6 kcalmol^{-1}



3d down,outTS = TS E_{rel} = 1.3 kcalmol^{-1}



3e down,in;1,3-dioxane boat E_{rel} = 9.3 kcalmol^{-1}



3f down,out;1,3-dioxane boat E_{rel} = 5.1 kcalmol^{-1}

References

[1]. P.J. Stephens, F.J. Devlin, C.F. Chabalowski, M.J. Frisch, *Ab Initio* Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields. J. Phys. Chem. 98 (1994) 11623-11627.

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