Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

The reaction of potassium xanthates with five-membered cyclic carbonates: selectivity of the underlying cascade reactions and mechanistic insights

Misha Rumyantsev[a,*], Ilia A. Korablev[a,b], Sergey Rumyantsev[a]

[a]Nizhny Novgorod State Technical University n.a. R.E. Alekseev, 24 Minin St., 603950 Nizhny Novgorod, Russia

[b]Lobachevsky State University of Nizhny Novgorod, 23 Prospekt Gagarina (Gagarin Avenue), 603950 Nizhny Novgorod, Russia

*Corresponding author. 606026, Dzerzhinsk, Nizhny Novgorod region, Gaidar st., 49 Tel./fax: +7 8313 344730, E-mail address: rumih@mail2k.ru

Contents:

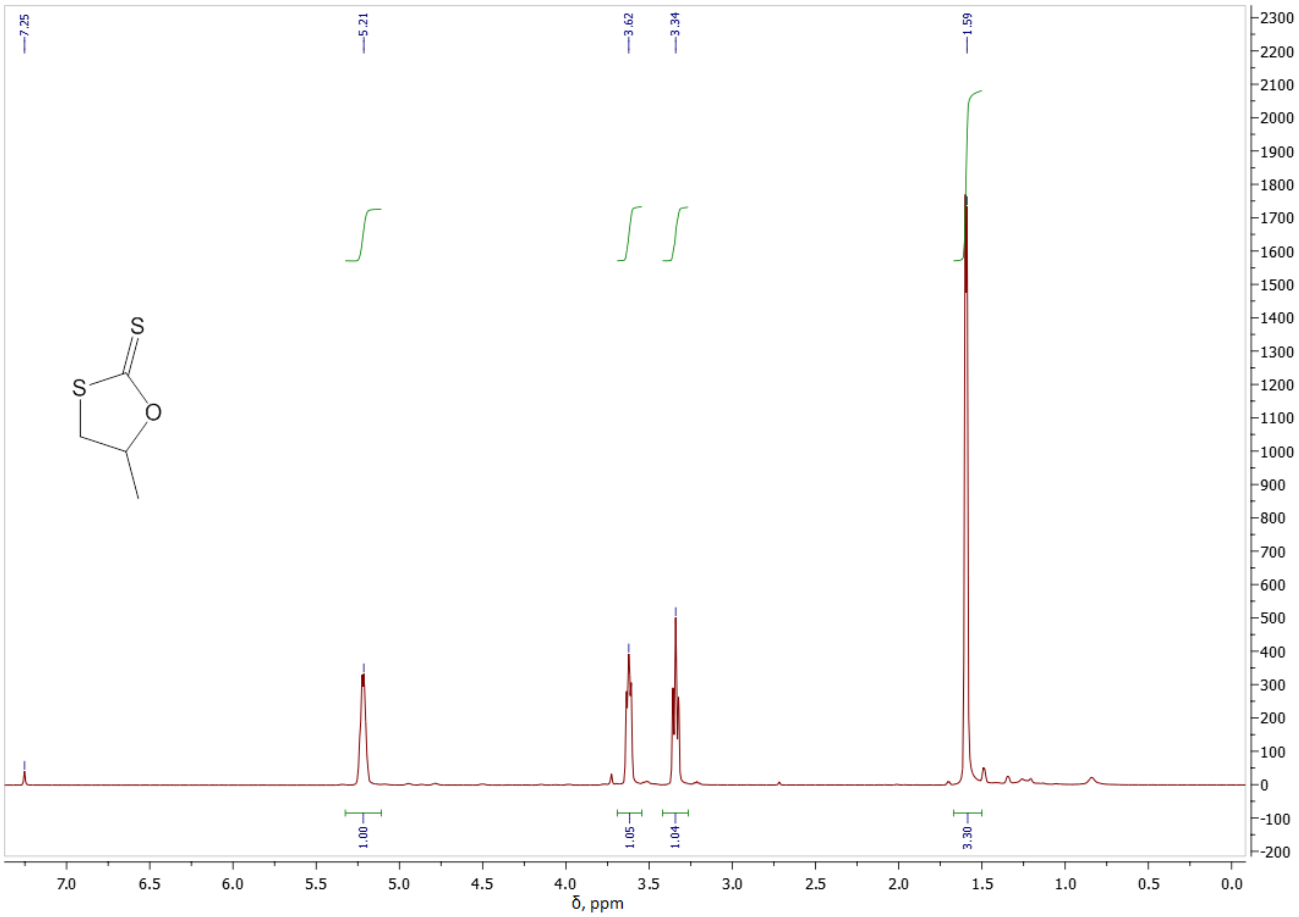


Figure S1. 1H NMR spectra of 5-methyl-1,3-oxathiolane-2-thione (dithiocarbonate **IV**) ($cdcl_3$, 25°C).

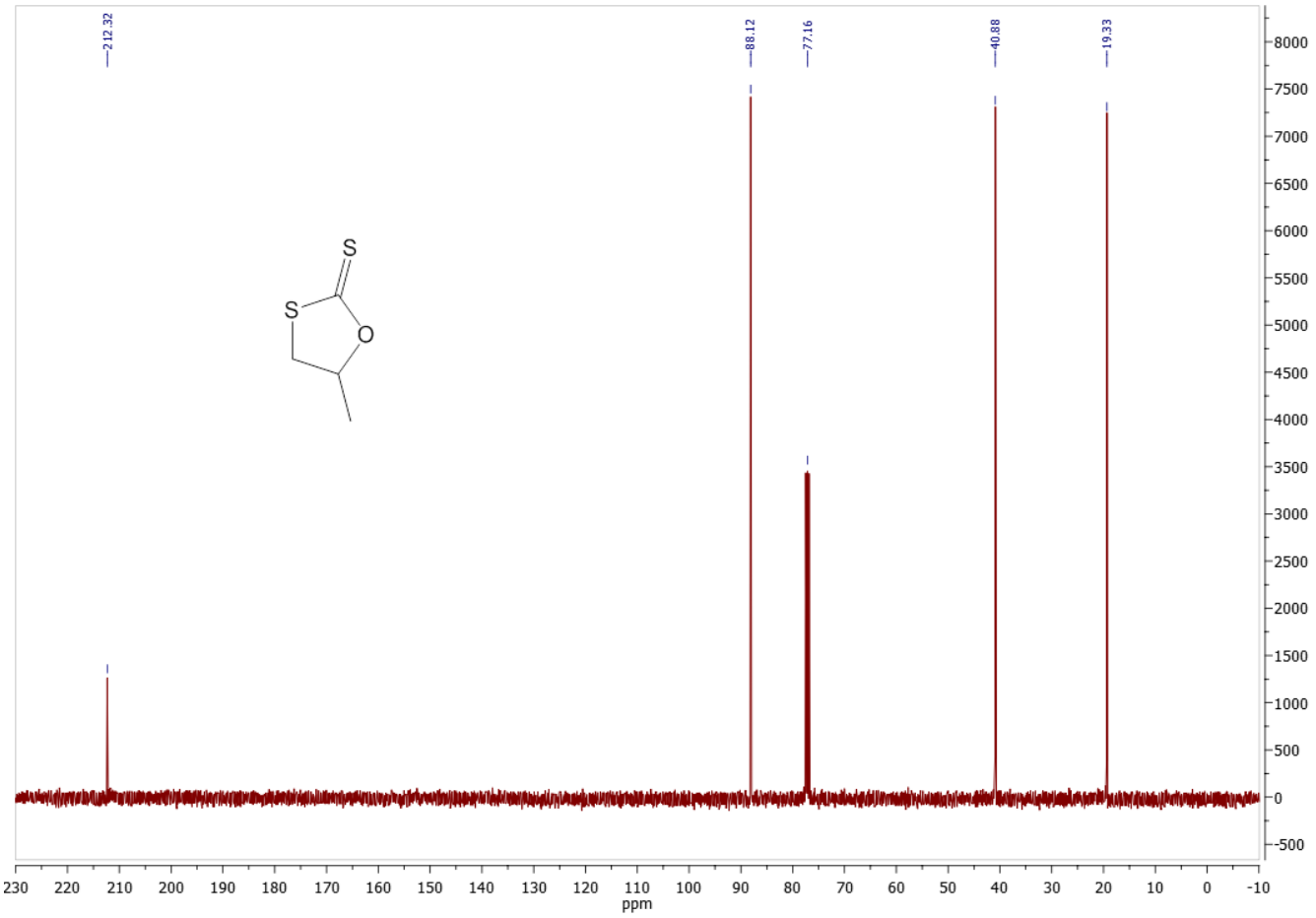


Figure S2. 13C NMR spectra of 5-methyl-1,3-oxathiolane-2-thione (dithiocarbonate **IV**) ($cdcl_3$, 25°C).

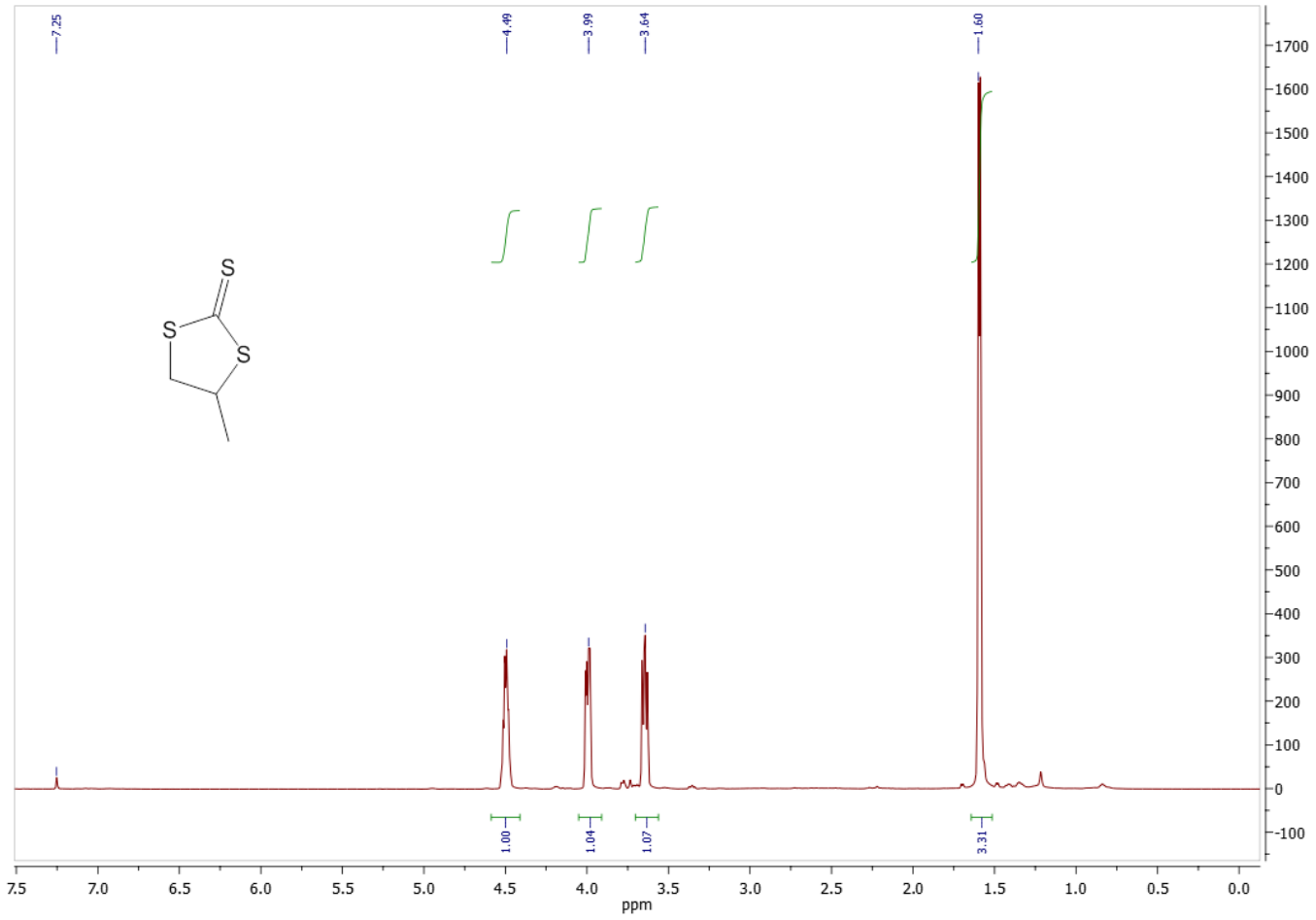


Figure S3. 1H NMR spectra of 4-methyl-1,3-dithiolane-2-thione (trithiocarbonate) ($cdcl_3$, 25°C).

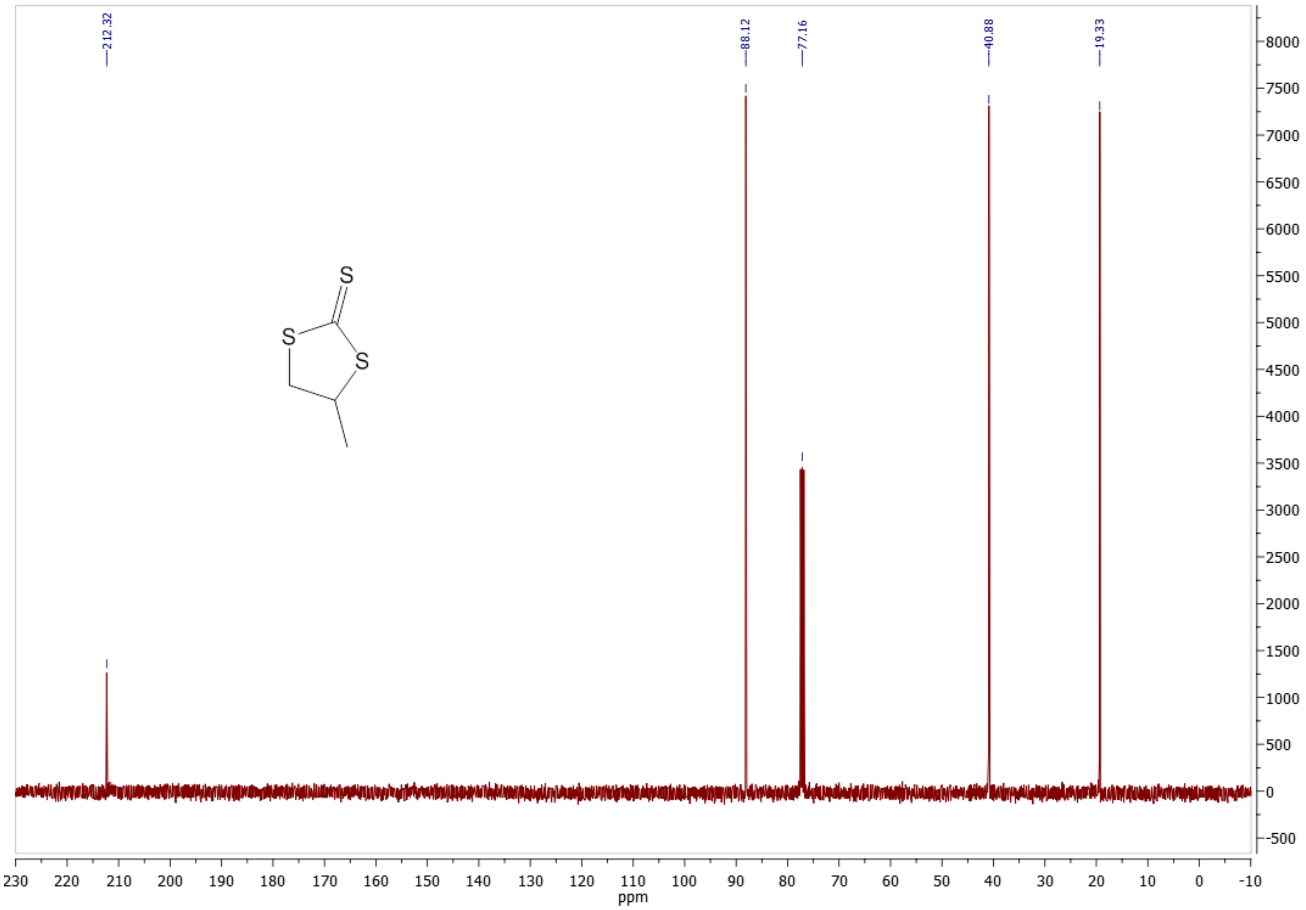
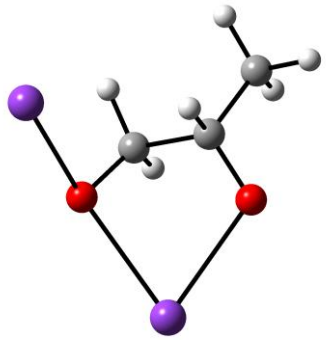


Figure S4. 13C NMR spectra of 4-methyl-1,3-dithiolane-2-thione (trithiocarbonate) ($cdcl_3$, 25°C).

Calculated atomic coordinates, frequencies and energies

Potassium propane-1,2-bis(olate) (Figure 7)



atomic coordinates:

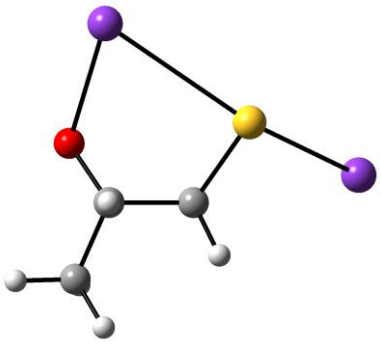
K2C3H6O2

C	0.000000000	0.000000000	0.000000000
H	0.000000000	0.000000000	1.131015000
C	1.502154000	0.000000000	-0.390702000
H	1.930791000	-0.974905000	-0.027553000
H	1.515141000	-0.095727000	-1.506872000
C	-0.627573000	-1.344559000	-0.414172000
H	-0.128848000	-2.207753000	0.047340000
H	-1.685425000	-1.364671000	-0.131880000
H	-0.571432000	-1.455972000	-1.505140000
O	-0.689363000	1.071697000	-0.501144000
K	0.914057000	2.906153000	-1.213176000
K	2.548843000	0.306384000	2.438992000
O	2.226229000	1.088685000	0.057311000

Zero-point correction= 0.088405 (Hartree/Particle)
Thermal correction to Energy= 0.097873
Thermal correction to Enthalpy= 0.098817
Thermal correction to Gibbs Free Energy= 0.051324
Sum of electronic and zero-point Energies= -1468.044083
Sum of electronic and thermal Energies= -1468.034615
Sum of electronic and thermal Enthalpies= -1468.033671
Sum of electronic and thermal Free Energies= -1468.081164

Number of imaginary frequencies = 0
Lowest frequency = 42.0332

Potassium 1-sulfidopropan-2-olate (Figure 7)



atomic coordinates:

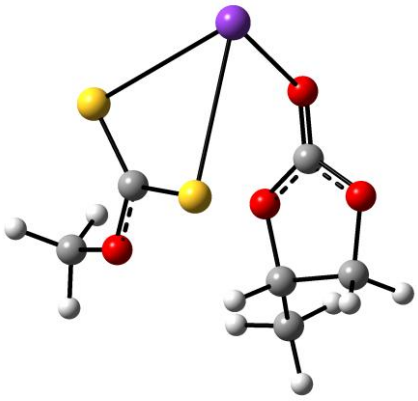
K2C3H6SO

C	0.239005000	0.048982000	-0.189075000
H	-0.135397000	0.341936000	0.831149000
C	1.714145000	-0.359097000	0.041277000
H	1.750160000	-1.155366000	0.794854000
H	2.086629000	-0.810284000	-0.893674000
C	-0.562610000	-1.208315000	-0.567854000
H	-0.480297000	-2.001272000	0.185807000
H	-1.619899000	-0.952144000	-0.690326000
H	-0.197715000	-1.600370000	-1.525951000
O	0.078142000	1.059141000	-1.108216000
S	2.841541000	1.005418000	0.569211000
K	0.324271000	2.919329000	0.671326000
K	2.212480000	1.478438000	-2.471453000

Zero-point correction= 0.088030 (Hartree/Particle)
Thermal correction to Energy= 0.097674
Thermal correction to Enthalpy= 0.098618
Thermal correction to Gibbs Free Energy= 0.051712
Sum of electronic and zero-point Energies= -1791.046894
Sum of electronic and thermal Energies= -1791.037250
Sum of electronic and thermal Enthalpies= -1791.036306
Sum of electronic and thermal Free Energies= -1791.083212

Number of imaginary frequencies = 0
Lowest frequency = 70.2560

Initial structure used for the scan depicted in Figure 7



atomic coordinates:

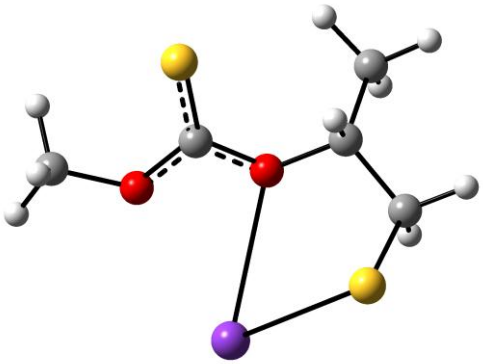
KC6H9S2O4

C	-0.236412000	-0.102408000	0.053041000
K	-1.128359000	-0.299754000	3.456476000
H	5.033578000	1.021937000	0.691583000
C	4.428778000	0.572849000	-0.101166000
H	4.070267000	1.359926000	-0.768179000
H	4.700982000	-1.194231000	1.827141000
O	2.440347000	0.699587000	1.271111000
H	5.057804000	-0.109224000	-0.679992000
C	2.149254000	0.146800000	2.446244000
C	3.266746000	-0.193697000	0.486059000
C	3.657505000	-1.271375000	1.511615000
H	3.433608000	-2.280791000	1.167974000
H	2.615703000	-0.604282000	-0.288608000
S	-0.014332000	-1.642990000	0.756676000
O	2.825626000	-0.987339000	2.646642000
O	1.387150000	0.621650000	3.255472000
S	-1.291051000	1.105911000	0.598454000
O	0.534612000	0.099954000	-1.026246000
C	0.562220000	1.374609000	-1.671178000
H	0.887060000	2.144099000	-0.967085000
H	1.280466000	1.264272000	-2.482903000
H	-0.424748000	1.629774000	-2.061471000

Zero-point correction= 0.156902 (Hartree/Particle)
Thermal correction to Energy= 0.172551
Thermal correction to Enthalpy= 0.173495
Thermal correction to Gibbs Free Energy= 0.110921
Sum of electronic and zero-point Energies= -1930.922311
Sum of electronic and thermal Energies= -1930.906662
Sum of electronic and thermal Enthalpies= -1930.905718
Sum of electronic and thermal Free Energies= -1930.968292

Number of imaginary frequencies = 0
Lowest frequency = 35.7688

Initial structure used for the scan depicted in Figure 8



atomic coordinates:

KC5H9S2O2

C	0.014033000	-0.002494000	0.016507000
S	0.013347000	-0.070298000	1.666817000
O	1.097978000	0.021821000	-0.758305000
C	2.394965000	-0.056493000	-0.150317000
H	2.485799000	-0.987474000	0.410512000
H	2.547859000	0.795181000	0.513486000
H	3.096550000	-0.034256000	-0.981280000
C	-2.388219000	0.155051000	-0.280592000
H	-2.341728000	0.760288000	0.628526000
O	-1.022337000	0.049967000	-0.792034000
C	-2.901141000	-1.245636000	0.006705000
H	-2.278259000	-1.749492000	0.749166000
H	-3.920000000	-1.183319000	0.397858000
H	-2.917218000	-1.839418000	-0.912128000
C	-3.183046000	0.877561000	-1.356207000
H	-4.221493000	0.895101000	-1.008637000
H	-3.167614000	0.257541000	-2.262528000
S	-2.612544000	2.583114000	-1.710932000
K	-0.020095000	1.482453000	-3.002343000

Zero-point correction= 0.141726 (Hartree/Particle)
Thermal correction to Energy= 0.154411
Thermal correction to Enthalpy= 0.155356
Thermal correction to Gibbs Free Energy= 0.100811
Sum of electronic and zero-point Energies= -1742.398373
Sum of electronic and thermal Energies= -1742.385688
Sum of electronic and thermal Enthalpies= -1742.384743
Sum of electronic and thermal Free Energies= -1742.439289

Number of imaginary frequencies = 0
Lowest frequency = 37.5732