

Kinetics and Thermodynamics of Reversible Thiol Additions to Mono- and Diactivated Michael Acceptors: Implications for the Design of Drugs that Bind Covalently to Cysteines

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SUPPORTING INFORMATION

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Computational Details

Choice of functional

The performance of a range of density functional theory methods for modeling the additions of thiols to Michael acceptors was evaluated by comparing the computed and experimental values of ΔG for thiol additions to α -cyano substituted Michael acceptors **3** and **14–18**. Spectroscopic measurements of ΔG for addition of β -mercaptoethanol to the Michael acceptors in PBS containing 1–2% DMSO were reported by Taunton and coworkers.¹ In the calculations, β -mercaptoethanol was modeled as MeSH. The combinations of functional and basis set initially examined were as follows. An aqueous environment was simulated using the CPCM² continuum solvent model.

Method A	B3LYP ³ /6-31+G(d)
Method B	M06-2X ⁴ /6-311G(2d,p)//B3LYP/6-31+G(d)
Method C	ω B97X-D ⁵ /aug-cc-pVTZ//B3LYP/6-31+G(d)
Method D	M06-2X/6-31+G(d)
Method E	M06-2X/6-311+G(d,p)

Our previous calculations^{6,7} on thiol additions to α,β -unsaturated ketones showed that a computational procedure comprising B3LYP geometry optimizations followed by M06-2X/6-311G(2d,p) single-point energy calculations provided good agreement with CBS-QB3 energetics or with experiment. Method B is similar to this computational procedure. Method A examines the effect of omitting the M06-2X single-point correction to the potential energy.

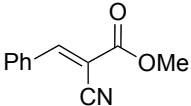
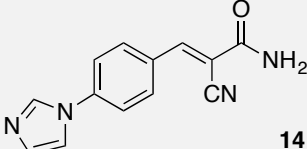
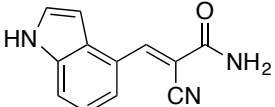
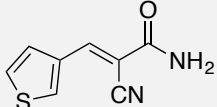
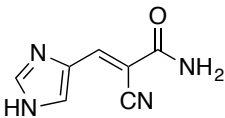
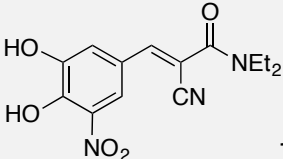
Rowley et al.⁸ reported computations on MeS[−] and MeSH additions to simple Michael acceptors in the gas phase, and showed that the range-separated functional ω B97X-D in conjunction with the aug-cc-pVTZ basis set gave energetics in close agreement with CCSD(T)//MP2. In Method C we explore the performance of this functional and basis set, using the same B3LYP geometries employed in Methods A and B.

Wang and coworkers⁹ recently used M06-2X/6-31G(d) calculations with SMD implicit solvent to predict values of ΔG for thiol additions to β -aryl substituted enones, and reported that the theoretical and experimental values agreed to within 1 kcal/mol. Method D employs the same functional, with a double-zeta basis set and an alternative continuum solvent model. Method E employs the same M06-2X functional and the larger 6-311+G(d,p) basis set.

The results of computations with Methods A–E are shown in Table S1. Also shown in the table are the experimental ΔG values derived from the K_d values reported by Taunton and coworkers.¹

1. Serafimova, I. M.; Pufall, M. A.; Krishnan, S.; Duda, K.; Cohen, M. S.; Maglathlin, R. L.; McFarland, J. M.; Miller, R. M.; Frödin, M.; Taunton, J. *Nat. Chem. Biol.* **2012**, *8*, 471–476.
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3. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372–1377. (c) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652. (d) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623–11627.
4. Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215–241. (b) Zhao, Y.; Truhlar, D. G. *Acc. Chem. Res.* **2008**, *41*, 157–167.
5. Chai, J.-D.; Head-Gordon, M. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615–6620.
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8. Smith, J. M.; Jami Alahmadi, Y.; Rowley, C. N. *J. Chem. Theory Comput.* **2013**, *9*, 4860–4865.
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Table S1. Computed and Experimental Thermodynamics of Thiol Additions to Michael Acceptors.^a

Michael acceptor		Calc ΔG					Expt ^b ΔG
		Method A	Method B	Method C	Method D	Method E	
	3	9.1	-1.0	0.7	-3.5	-2.9	-2.8
	14	7.8	-2.1		-4.7	-3.8	-3.9
	15	9.8	-1.3	0.3	-3.8	-2.6	-3.0
	16	8.7	-1.1	0.5	-3.6	-2.8	-2.6
	17	10.6	-0.2	1.8	-2.6	-1.3	-2.0
	18^c	4.7	-4.6	-3.1	-7.1	-5.7	-3.2

^a ΔG in kcal/mol. ^b ΔG for Michael additions of β -mercaptoethanol in PBS containing 1–2% DMSO; data from ref. 1. ^c NEt_2 was modeled as NMe_2 .

Calculations with Method A predict that thiol addition to each Michael acceptor is substantially unfavorable in thermodynamic terms, contrary to experiment. The computed ΔG values show errors of up to 13 kcal/mol compared to experiment.

Calculations with Method B yield values of ΔG in good qualitative agreement with experiment, being in most cases 3.1–3.8 kcal/mol less negative than the experimental values. Method B captures the general trend of relative reactivities of the Michael acceptors. The computed ΔG values predict that thiol addition is thermodynamically favorable.

Method C yields ΔG values that are 1.5–3.1 kcal/mol less negative than the experimental values. In four of the five cases examined, the calculations predict that thiol addition is thermodynamically unfavorable. We also tested the more computationally expensive procedure of performing geometry optimizations with $\omega\text{B97X-D/aug-cc-pVTZ}$, by calculating the additions of MeSH to the smaller

Michael acceptors **19–21**; the resulting values of ΔG were 0.6–2.5 kcal/mol less negative than the values computed with Method E.

Computations with Method D give ΔG values that are 0.7–1.0 kcal/mol more negative than experiment in most cases. This method provides qualitatively correct predictions of the relative reactivities of the Michael acceptors.

Out of the five methods, Method E leads to the closest agreement with the experimental ΔG values. For five out of the six Michael acceptors, the agreement between theory and experiment is within 0.1–0.7 kcal/mol; in three of these cases the agreement is even better, within 0.2 kcal/mol. Overall, the reaction that is modeled least accurately by most of the methods is the addition to entacapone (**18**). This may reflect the partial ionization of the Michael acceptor nitrocatechol group as mentioned in the paper.

Calculation of entropy

The free energies of reaction reported in Table S1 were computed using only a single conformer of each species (i.e., the lowest-lying conformer). In order to determine the effect of the entropic contributions of other low-lying conformers, we performed torsional sampling calculations in MacroModel 10.2,¹⁰ using the MCMM conformational search mode in conjunction with the MMFF94s force field in water. The approach was similar to that previously described.¹¹ The computed conformational entropy corrections S_{conf} for individual thiols, Michael acceptors and MeSH adducts are shown in Table S2. Also shown is the overall change in ΔG for addition to each Michael acceptor that results from incorporation of conformational entropy (i.e., $-T\Delta S_{\text{conf}}$).

The conformational entropy corrections for individual species are in the range $S_{\text{conf}} = 1\text{--}5$ e.u. Including these conformational entropy corrections in the calculation of the overall free energy for thiol addition has only a small effect on ΔG , the exact values of the correction being in the range -0.5 to $+0.2$ kcal/mol. When the conformational entropy corrections are used in conjunction with the best-performing functional (Method E), the agreement between the experimental and theoretical ΔG values improves in five out of the six cases considered in Table S1. However, because the agreement between experiment and theory with Method E is already very good, we did not routinely perform S_{conf} calculations for the reactions considered in this paper.

Solvent model

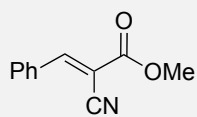
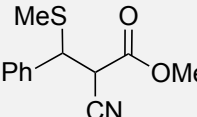
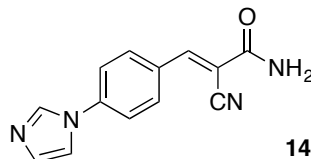
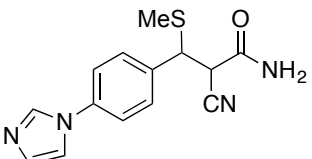
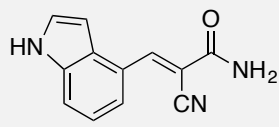
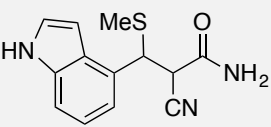
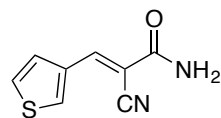
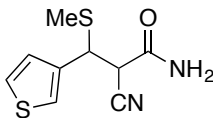
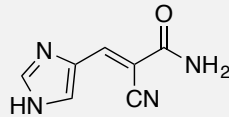
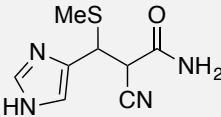
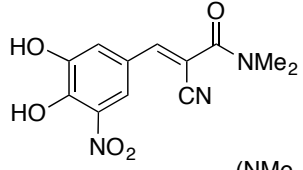
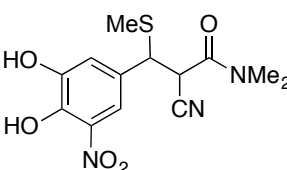
The calculations described throughout this paper utilized the CPCM continuum solvent model² to simulate an aqueous medium. We also briefly explored the use of SMD¹² as an alternative solvent model. Thus, for the addition of MeSH to **3**, computations with M06-2X/6-311+G(d,p) in SMD implicit water predict a ΔG value of -5.1 kcal/mol. Calculations with the same functional and basis set but using CPCM implicit water (Method E) predict a ΔG value of -2.9 kcal/mol, which is in closer agreement with the experimental value of (-2.8 kcal/mol) .

10. (a) MacroModel, version 10.2, Schrödinger, LLC, New York, NY, 2013. (b) Maestro, version 9.6, Schrödinger, LLC, New York, NY, 2013.

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12. Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* **2009**, *113*, 6378–6396.

Table S2. Computed Conformational Entropies.

Compound	S_{conf} (e.u.)	Compound	S_{conf} (e.u.)	$-T\Delta S_{\text{conf}}$ for MeSH addition (kcal/mol)
MeSH	0			
 3	1.3		3.0	-0.5
 14	3.8		4.2	-0.1
 15	3.3		3.6	-0.1
 16	4.8		4.6	0.1
 17	2.7		3.9	-0.4
 18 (NMe ₂ analogue)	5.4		4.6	0.2

Computed Activation Barriers for Thiolate Additions to β -Alkyl Substituted Michael Acceptors

Transition states and activation energies were computed for the additions of MeSH to β -alkyl substituted Michael acceptors **24–28**, catalyzed by DBU. The mechanism is the same as that in Figure 2 of the paper, and involves the initial deprotonation of the thiol by the base followed by rate-limiting addition of the thiolate anion to the Michael acceptor. Computed values of $\Delta G^\ddagger$ are shown in Table S3. Also shown for comparison is the computed ΔG for the β -Ph substituted Michael acceptor **1**.

Table S3. Computed Activation Barriers for Thiol Additions to Michael Acceptors.^a

Michael acceptor		$\Delta G^\ddagger$
	1	17.0
	24	17.1
	25	16.0
	26	17.2
	27	18.7
	28	18.4

^a $\Delta G^\ddagger$ computed at the M06-2X/6-311+G(d,p) level of theory in CPCM water (kcal/mol). DBU was used as a model base catalyst (B).

Cartesian Coordinates and Energies

Computed Cartesian coordinates and energies of the species discussed in the paper are given below. The data are arranged in sections following the sequence discussed in the paper. Underneath the coordinates for each species are listed the relevant energies, which are denoted by symbols described at the beginning of each respective section. All energies are reported in Hartree.

Compounds related to Table 1 (Thermodynamics of thiol additions)

Geometries in this section were optimized with M06-2X/6-311+G(d,p) in CPCM water. Underneath the coordinates of each species are listed the following energies:

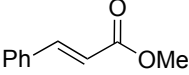
- M06-2X/6-311+G(d,p) solution-phase potential energy (E)
- M06-2X/6-311+G(d,p) solution-phase enthalpy at 298.15 K (H)
- M06-2X/6-311+G(d,p) solution-phase Gibbs free energy at 298.15 K and 1 mol/L (G)

MeSH

H	1.281617	-0.835875	0.000000
S	-0.048357	-0.666049	0.000000
C	-0.048357	1.157319	0.000000
H	-1.092394	1.463448	0.000000
H	0.437318	1.542651	0.893017
H	0.437318	1.542651	-0.893017

0 imaginary frequencies
E = -438.678982
H = -438.628150
G = -438.654641

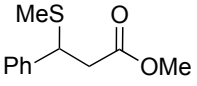
1



C	0.000000	0.536041	0.000000
C	-1.103799	-0.218943	0.000000
C	-2.434114	0.423197	0.000000
O	-2.646951	1.614309	0.000000
O	-3.411524	-0.491251	0.000000
C	-4.749428	0.019509	0.000000
H	-1.088672	-1.301506	0.000000
C	1.389592	0.066531	0.000000
H	-0.135551	1.615285	0.000000
H	-5.397343	-0.851904	0.000000
H	-4.921317	0.623856	0.890255
H	-4.921317	0.623856	-0.890255
C	2.414925	1.019424	0.000000
C	3.750056	0.629669	0.000000
C	4.077495	-0.722252	0.000000
C	3.064371	-1.681804	0.000000
C	1.732673	-1.293035	0.000000
H	2.158448	2.073373	0.000000
H	4.531584	1.379819	0.000000
H	5.116156	-1.030550	0.000000
H	3.316482	-2.735454	0.000000
H	0.958703	-2.051260	0.000000

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 H = -537.266275
 G = -537.313863

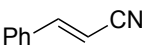
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C	1.390450	-0.251049	0.155598
C	2.240870	-0.200333	1.259130
C	3.565882	-0.621214	1.154950
C	4.051628	-1.097522	-0.057412
C	3.208341	-1.147261	-1.167247
C	1.889600	-0.722660	-1.062058
H	1.245278	-0.746551	-1.934759
H	3.581796	-1.513970	-2.116165
H	5.080848	-1.425614	-0.141306
H	4.215116	-0.574284	2.021296
H	1.864323	0.170874	2.206775
C	-0.042479	0.206019	0.287134
H	-0.239131	0.481853	1.325317
S	-0.382862	1.696418	-0.732191
C	-1.043166	-0.874526	-0.122594
C	0.773759	2.850870	0.050969
H	0.543244	2.957543	1.110986
H	1.799801	2.506227	-0.077228
H	0.649813	3.812941	-0.443786
C	-2.449302	-0.553824	0.329345
H	-0.768142	-1.817206	0.362024
H	-1.035700	-1.051119	-1.199220
O	-2.729547	0.032506	1.345167
O	-3.361466	-1.035963	-0.514806
C	-4.732254	-0.841179	-0.138839
H	-4.950400	0.223279	-0.060538
H	-5.321234	-1.294794	-0.930186
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2

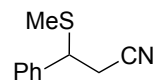


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C	-0.520531	-2.039007	0.000000
C	-1.491436	-3.085840	0.000000
N	-2.262121	-3.942631	0.000000
H	0.514345	-2.357928	0.000000
C	0.000000	0.408140	0.000000
H	-1.958448	-0.525130	0.000000
C	-0.570851	1.686202	0.000000
C	0.231239	2.822275	0.000000
C	1.616086	2.692948	0.000000
C	2.195975	1.423718	0.000000
C	1.397027	0.290038	0.000000
H	-1.650843	1.785991	0.000000
H	-0.224814	3.804748	0.000000
H	2.244598	3.575397	0.000000

H	3.274304	1.320675	0.000000
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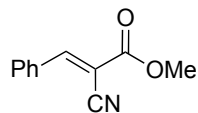
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C	-0.591617	-0.194794	0.160333
C	-1.415959	-0.232575	1.284364
C	-2.778141	-0.488997	1.152646
C	-3.326938	-0.712980	-0.106140
C	-2.508619	-0.679762	-1.233047
C	-1.148484	-0.422291	-1.100927
H	-0.518854	-0.403992	-1.984501
H	-2.929629	-0.854690	-2.215920
H	-4.386843	-0.912018	-0.210000
H	-3.408679	-0.512383	2.033426
H	-0.990183	-0.057515	2.266622
C	0.884141	0.089580	0.315483
H	1.101224	0.287932	1.367070
S	1.807589	-1.420301	-0.153497
C	1.345161	1.297464	-0.522861
C	3.488131	-0.949609	0.347034
H	4.085697	-1.859607	0.318098
H	3.481390	-0.562258	1.365882
H	3.923730	-0.220941	-0.334650
C	0.590577	2.498454	-0.161758
H	1.204111	1.106355	-1.588523
H	2.403968	1.503451	-0.357592
N	-0.016693	3.426219	0.140755

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 G = -840.395316

3

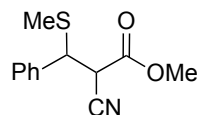


C	2.412320	-1.434488	-0.000139
C	1.522613	-0.347701	0.000003
C	2.047644	0.955519	0.000135
C	3.420485	1.153131	0.000133
C	4.291429	0.064129	-0.000022
C	3.785152	-1.232254	-0.000165
C	0.103424	-0.674052	0.000065
C	-0.998840	0.105152	0.000062
C	-0.995207	1.534578	-0.000046
N	-1.010344	2.685808	-0.000136
C	-2.334125	-0.568086	0.000101
O	-2.486105	-1.763560	0.000201
O	-3.328099	0.312758	-0.000004
C	-4.655386	-0.235040	-0.000154
H	-0.119784	-1.738222	0.000122
H	1.395373	1.817057	0.000258

H	3.815250	2.161618	0.000243
H	5.362311	0.228386	-0.000014
H	4.456752	-2.081672	-0.000284
H	2.014739	-2.443199	-0.000235
H	-4.806635	-0.841298	0.891896
H	-4.805834	-0.842854	-0.891271
H	-5.323186	0.620615	-0.001178

0 imaginary frequencies
E = -629.694950
H = -629.504084
G = -629.555783

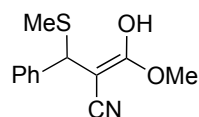
P3



C	0.910517	-0.818308	0.303819
C	0.009867	0.242492	-0.381277
H	0.825500	-0.745964	1.390061
C	0.485869	-2.158194	-0.107031
N	0.141412	-3.201400	-0.440825
C	2.367220	-0.599738	-0.112989
S	0.617343	1.892490	0.141576
C	-1.452139	0.024227	-0.072243
H	0.171991	0.162443	-1.459095
O	2.767026	-0.777920	-1.231722
O	3.093984	-0.164474	0.901419
C	4.460066	0.168451	0.595267
H	4.894986	0.502074	1.531755
H	4.483956	0.964241	-0.148339
H	4.979015	-0.711290	0.218249
C	-1.930495	0.100078	1.238057
C	-3.275155	-0.122185	1.506966
C	-4.158174	-0.413917	0.467943
C	-3.688941	-0.482951	-0.838846
C	-2.338991	-0.265188	-1.107444
H	-1.973113	-0.321469	-2.127325
H	-4.370012	-0.704895	-1.651643
H	-5.207288	-0.583152	0.678915
H	-3.636894	-0.063322	2.526540
H	-1.251829	0.346749	2.048139
C	-0.487225	2.903467	-0.879190
H	-0.356435	2.660065	-1.933213
H	-1.523942	2.752832	-0.579928
H	-0.205902	3.941403	-0.709328

0 imaginary frequencies
E = -1068.400816
H = -1068.154043
G = -1068.214976

Enol tautomer of P3

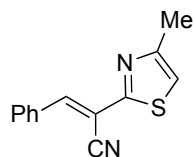


C	1.998925	-0.438738	-0.985071
C	1.455154	-0.027729	0.234168
C	2.223251	-0.130598	1.391937
C	3.518017	-0.644290	1.337192

C	4.051241	-1.057393	0.121892
C	3.287504	-0.953755	-1.040604
C	0.050869	0.522871	0.316485
C	-1.031555	-0.501761	0.037200
C	-2.350654	-0.204776	0.241761
O	-3.275043	-1.142769	0.163995
C	-4.659007	-0.748788	0.194470
S	-0.191295	1.963230	-0.822320
C	0.919957	3.147126	-0.016472
C	-0.712093	-1.820780	-0.362373
N	-0.449227	-2.898329	-0.686438
O	-2.796225	1.001737	0.555564
H	-0.100438	0.925442	1.322690
H	0.846426	4.082299	-0.568951
H	0.617015	3.309978	1.017361
H	1.944659	2.778779	-0.058941
H	-5.214228	-1.671223	0.056799
H	-4.902407	-0.297741	1.154578
H	-4.869687	-0.051933	-0.615258
H	1.808992	0.192078	2.341339
H	4.106691	-0.716458	2.243914
H	5.058125	-1.454988	0.076432
H	3.699687	-1.271714	-1.990897
H	1.410028	-0.348918	-1.891891
H	-2.139075	1.680946	0.295036

0 imaginary frequencies
E = -1068.378298
H = -1068.131883
G = -1068.191848

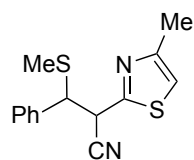
4



C	-2.916327	0.662771	0.514593
C	-2.203222	-0.455598	0.058010
C	-2.918016	-1.574548	-0.395767
C	-4.305528	-1.561331	-0.437101
C	-5.002164	-0.437777	0.000236
C	-4.304480	0.666932	0.484517
C	-0.745286	-0.544064	0.048148
C	0.172444	0.444158	-0.004342
C	-0.177596	1.829318	-0.129314
N	-0.403280	2.951913	-0.249258
C	1.615540	0.144345	0.006151
N	2.101799	-1.053301	0.142064
C	3.476801	-1.047975	0.103410
C	4.034220	0.185529	-0.061669
S	2.812599	1.389808	-0.176748
C	4.221518	-2.337874	0.243399
H	-0.332223	-1.548949	0.055402
H	-2.374395	-2.452938	-0.725657
H	-4.842531	-2.428446	-0.801574
H	-6.085257	-0.427313	-0.022656
H	-4.844582	1.532408	0.848554
H	-2.394999	1.518691	0.922301
H	5.079510	0.446133	-0.118572
H	5.296821	-2.170458	0.196525

H 3.938094 -3.027240 -0.554395
H 3.980921 -2.812418 1.196767
0 imaginary frequencies
E = -1008.979066
H = -1008.766641
G = -1008.821954

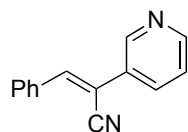
P4



N	2.318765	-0.537218	0.794355
C	1.742325	-0.427685	-0.360096
S	2.775227	0.073248	-1.649009
C	4.078309	0.146157	-0.528014
C	3.657230	-0.211785	0.717753
C	0.265789	-0.675576	-0.565937
C	-0.049425	-2.064454	-0.204317
N	-0.297639	-3.146064	0.092139
C	4.502048	-0.276090	1.950479
C	-0.601855	0.286103	0.288401
C	-2.074168	-0.022846	0.160156
C	-2.798438	-0.410305	1.285948
C	-4.155291	-0.710712	1.183460
C	-4.795471	-0.626847	-0.047842
C	-4.076273	-0.237577	-1.177216
C	-2.724567	0.066417	-1.073155
H	-0.289855	0.170850	1.329100
H	-2.299340	-0.477391	2.246977
H	-4.708471	-1.008430	2.066191
H	-5.850401	-0.859746	-0.129689
H	-4.571446	-0.166407	-2.138282
H	-2.175666	0.390116	-1.951649
H	5.068394	0.439200	-0.840709
H	4.108024	0.395941	2.715406
H	4.497989	-1.288235	2.359853
H	5.530017	0.008477	1.729501
S	-0.186065	1.997682	-0.226943
C	-1.340281	2.889625	0.849546
H	-1.147633	3.950545	0.697853
H	-2.370978	2.662667	0.579640
H	-1.156892	2.634854	1.893164
H	0.012203	-0.550891	-1.622590

0 imaginary frequencies
E = -1447.686598
H = -1447.417962
G = -1447.482287

5

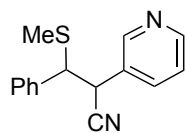


C	2.888540	0.826073	0.616899
C	1.949768	0.013175	-0.019208
C	2.420057	-1.129876	-0.674258
N	3.697727	-1.501630	-0.687340

C	4.577797	-0.725468	-0.050247
C	4.222853	0.449185	0.604365
C	0.503371	0.337014	-0.012857
C	0.185708	1.737895	0.032982
N	-0.008954	2.871115	0.096496
C	-0.458493	-0.607431	0.015799
C	-1.913077	-0.433533	-0.008655
C	-2.697732	-1.404666	0.629116
C	-4.081266	-1.290032	0.658351
C	-4.703081	-0.215327	0.027558
C	-3.935031	0.737798	-0.637362
C	-2.549986	0.632564	-0.657886
H	-0.118145	-1.634988	0.110511
H	-2.213314	-2.246946	1.110872
H	-4.673858	-2.041770	1.165306
H	-5.782849	-0.127947	0.041633
H	-4.416784	1.561248	-1.150460
H	-1.970175	1.364930	-1.204875
H	1.729949	-1.759261	-1.228178
H	5.612547	-1.050439	-0.072964
H	4.977227	1.050138	1.095033
H	2.577416	1.734419	1.121436

0 imaginary frequencies
E = -648.889643
H = -648.672642
G = -648.724172

P5

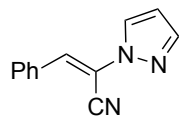


C	-2.626064	-0.800051	0.965006
C	-2.026980	-0.470163	-0.247501
C	-2.816811	0.116377	-1.232675
N	-4.112390	0.389104	-1.075299
C	-4.671093	0.074832	0.094276
C	-3.972929	-0.521370	1.140880
C	-0.546894	-0.693041	-0.492155
C	-0.181040	-2.081001	-0.177080
N	0.097970	-3.162519	0.092750
C	0.355130	0.262124	0.337628
C	1.822529	-0.014735	0.110749
C	2.623288	-0.415350	1.178517
C	3.976035	-0.687557	0.983979
C	4.536024	-0.561101	-0.282197
C	3.740297	-0.157890	-1.353885
C	2.392521	0.116996	-1.158054
H	0.121142	0.118964	1.396096
H	2.187347	-0.515088	2.167068
H	4.588564	-0.996552	1.822556
H	5.587666	-0.771491	-0.435843
H	4.172746	-0.053242	-2.341800
H	1.783794	0.452021	-1.991741
H	-2.378903	0.380278	-2.191768
H	-5.725982	0.304708	0.201834
H	-4.478567	-0.761537	2.066956
H	-2.051889	-1.270790	1.757061
S	-0.117053	1.980758	-0.102389
C	1.129870	2.865771	0.871936

H	0.906097	3.926441	0.768549
H	1.058917	2.583034	1.922115
H	2.130971	2.664047	0.492919
H	-0.331423	-0.542070	-1.554471

0 imaginary frequencies
E = -1087.598418
H = -1087.325348
G = -1087.386247

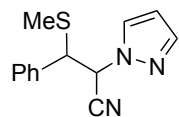
6



N	-3.097715	0.570112	-0.657767
N	-2.178078	-0.117518	0.048669
C	-2.726551	-1.151699	0.743281
C	-4.070642	-1.139535	0.465196
C	-4.242727	-0.042732	-0.410189
C	-0.812438	0.242322	-0.024049
C	-0.585161	1.653959	-0.161860
N	-0.410445	2.782877	-0.294813
C	0.166639	-0.675250	0.004542
C	1.611857	-0.440042	0.035251
C	2.442052	-1.402786	-0.555180
C	3.819310	-1.228640	-0.578568
C	4.388126	-0.100950	0.008511
C	3.573783	0.845590	0.625470
C	2.194514	0.679649	0.642733
H	-0.149339	-1.714077	-0.023796
H	1.999047	-2.284781	-1.004398
H	4.448707	-1.974962	-1.047661
H	5.463139	0.032780	-0.001771
H	4.014554	1.710917	1.105329
H	1.577696	1.406905	1.155366
H	-5.153326	0.321345	-0.861271
H	-4.822095	-1.806936	0.851689
H	-2.127289	-1.778801	1.383075

0 imaginary frequencies
E = -626.807048
H = -626.608652
G = -626.658504

P6

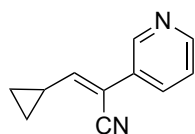


N	-2.708647	-0.554420	-0.988727
N	-2.190866	-0.501550	0.247956
C	-3.095473	-0.107074	1.178205
C	-4.277729	0.101373	0.506865
C	-3.975421	-0.195535	-0.839882
C	-0.776075	-0.741376	0.442564
C	-0.438651	-2.113501	0.016049
N	-0.165355	-3.174244	-0.326581
C	0.099822	0.271616	-0.328320
C	1.568036	-0.000846	-0.104009
C	2.375711	-0.356392	-1.182711
C	3.729663	-0.623308	-0.991953

C	4.283144	-0.537204	0.280680
C	3.480413	-0.179488	1.362878
C	2.131051	0.091097	1.171377
H	-0.137913	0.172524	-1.389820
H	1.944021	-0.424165	-2.175685
H	4.348563	-0.896059	-1.838294
H	5.336051	-0.743547	0.430985
H	3.908192	-0.106231	2.355538
H	1.517190	0.393397	2.013862
H	-4.628735	-0.164908	-1.698673
H	-5.218780	0.416252	0.924814
H	-2.824836	-0.010595	2.217721
S	-0.418110	1.949327	0.203806
C	0.796033	2.908744	-0.740955
H	0.551470	3.957726	-0.581656
H	1.805824	2.709818	-0.384329
H	0.715996	2.676463	-1.802708
H	-0.576345	-0.667051	1.514083

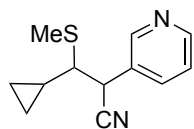
0 imaginary frequencies
E = -1065.519420
H = -1065.264602
G = -1065.323611

7



C	-2.787421	-0.062083	0.022675
C	-3.738722	-0.808953	0.941887
C	-3.746825	-1.110561	-0.514969
H	-3.314885	-2.046241	-0.845108
H	-4.566403	-0.739986	-1.115152
H	-3.301329	-1.537881	1.611467
H	-4.553215	-0.229424	1.354186
H	-3.032440	0.970749	-0.190601
C	-1.369980	-0.402725	0.083368
H	-1.136465	-1.444473	0.292418
C	-0.337778	0.447843	-0.079758
C	-0.606852	1.842087	-0.297712
N	-0.803713	2.964265	-0.468668
C	1.087739	0.049335	-0.026921
C	1.494207	-1.219206	-0.454617
H	0.767703	-1.907558	-0.876073
N	2.751582	-1.651626	-0.400477
C	3.677931	-0.814939	0.074062
H	4.695074	-1.190577	0.109107
C	3.389133	0.478183	0.495626
H	4.178434	1.122372	0.860631
C	2.074298	0.917037	0.442181
H	1.814062	1.918439	0.768213

0 imaginary frequencies
E = -534.558566
H = -534.361690
G = -534.409166

P7

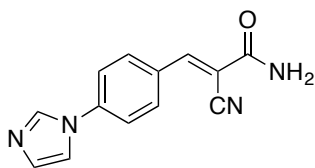
C	0.856662	1.532132	0.441079
C	1.123869	0.257645	-0.318462
C	0.272038	-0.935979	0.200647
H	0.858525	0.396537	-1.371197
C	-1.208350	-0.686751	-0.019838
C	0.575599	-1.207250	1.610692
C	1.164530	2.847992	-0.216280
H	1.037756	1.471453	1.509985
C	-0.263299	2.435861	-0.001365
H	1.570342	3.636413	0.402691
H	1.551250	2.810893	-1.227557
H	-0.836068	2.129169	-0.868589
H	-0.834212	2.935936	0.769923
N	0.804257	-1.407169	2.718896
C	-2.023413	-0.122324	0.959532
N	-3.305896	0.183868	0.767284
C	-3.829134	-0.068254	-0.434915
C	-3.106275	-0.636714	-1.478014
C	-1.771376	-0.951360	-1.264196
H	-1.618912	0.096830	1.944279
H	-4.873678	0.192192	-0.570096
H	-3.581018	-0.827620	-2.431583
H	-1.173152	-1.393378	-2.054580
S	2.917384	-0.088416	-0.248762
C	3.032278	-1.510118	-1.372292
H	4.089255	-1.642476	-1.598607
H	2.656024	-2.423215	-0.912986
H	2.495361	-1.300583	-2.297875
H	0.553080	-1.833664	-0.356401

0 imaginary frequencies

E = -973.266249

H = -973.013247

G = -973.069232

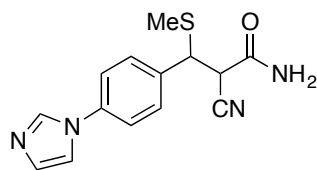
14

C	0.698535	-0.502188	0.045100
C	-0.151785	-1.572325	-0.269897
C	-1.526291	-1.409025	-0.313709
C	-2.075750	-0.168038	0.001473
C	-1.250743	0.902260	0.348419
C	0.123646	0.738391	0.360698
H	0.739054	1.577442	0.654026
H	-1.686304	1.852311	0.630875
N	-3.480078	0.006108	-0.016687
H	-2.165150	-2.233999	-0.602159
H	0.275359	-2.539787	-0.506792
C	2.131182	-0.769728	0.037758
H	2.412552	-1.819859	0.032060
C	3.181367	0.073569	0.011355

C	3.064988	1.495913	-0.057210
N	3.038300	2.645886	-0.123562
C	4.572240	-0.517999	0.010579
O	4.735448	-1.726607	0.047162
N	5.587658	0.363847	-0.032764
H	5.450862	1.362032	-0.062749
H	6.532470	0.010086	-0.035812
C	-4.169220	1.151891	-0.364279
C	-5.489753	0.844838	-0.213855
N	-5.635050	-0.453141	0.226804
C	-4.419647	-0.924862	0.331749
H	-3.665596	2.039779	-0.706982
H	-6.340840	1.479364	-0.402843
H	-4.144417	-1.909599	0.677460

0 imaginary frequencies
E = -795.540735
H = -795.311710
G = -795.369576

P14

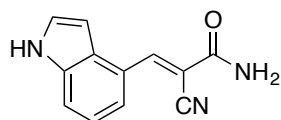


C	0.268035	0.364107	-1.008782
C	-0.366983	0.204293	0.224900
C	0.407032	-0.040561	1.356544
C	1.792799	-0.122526	1.267710
C	2.407406	0.018759	0.028788
C	1.646247	0.259562	-1.114509
C	-1.869356	0.287874	0.345831
S	-2.537723	1.898654	-0.219561
C	-1.656810	2.971280	0.946003
C	-2.583874	-0.813459	-0.473587
C	-4.099223	-0.792344	-0.173943
N	-4.891237	-0.618086	-1.240735
C	-2.060790	-2.127533	-0.091707
N	-1.646265	-3.151866	0.221450
O	-4.493949	-0.923371	0.968970
H	-2.385457	-0.675092	-1.539650
H	-2.162609	0.157445	1.390014
H	-0.317888	0.572806	-1.897511
H	2.131042	0.353250	-2.078551
N	3.820637	-0.080772	-0.074820
H	2.389788	-0.276543	2.158182
H	-0.072136	-0.154283	2.322719
H	-1.896274	2.691915	1.971663
H	-0.581841	2.915058	0.777555
H	-2.002000	3.986499	0.757481
H	-5.891573	-0.577379	-1.107152
H	-4.527575	-0.512982	-2.174351
C	4.624177	-0.950854	0.603752
C	4.645154	0.666071	-0.890723
N	5.885125	-0.805421	0.279636
H	4.221003	-1.674351	1.296145
C	5.909287	0.207464	-0.653143
H	4.263349	1.450327	-1.522325
H	6.830911	0.552040	-1.094528

0 imaginary frequencies

E = -1234.248298
H = -1233.963090
G = -1234.030228

15

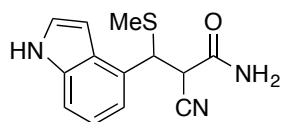


C	-1.630240	-0.485584	-0.005316
C	-0.449376	0.270421	-0.211549
C	-0.576861	1.646483	-0.409489
C	-1.828586	2.275877	-0.394214
C	-2.995468	1.558549	-0.176355
C	-2.879985	0.182730	0.016013
C	-1.897942	-1.874170	0.221643
C	-3.255320	-1.994171	0.362035
N	-3.847416	-0.764948	0.240709
C	0.818320	-0.438323	-0.247111
C	2.069398	0.012360	-0.017936
C	2.366332	1.347910	0.393299
N	2.671990	2.403305	0.741064
C	3.218487	-0.956134	-0.146172
N	4.441655	-0.460979	0.122443
O	3.025638	-2.116341	-0.474260
H	4.600970	0.496938	0.392706
H	5.236994	-1.077140	0.049409
H	0.769764	-1.500278	-0.475236
H	0.298764	2.246897	-0.617565
H	-1.883510	3.343596	-0.565451
H	-3.962666	2.046734	-0.165410
H	-4.837502	-0.586498	0.308779
H	-3.854558	-2.872312	0.544145
H	-1.189523	-2.684546	0.284096

0 imaginary frequencies

E = -702.103050
H = -701.898380
G = -701.951274

P15

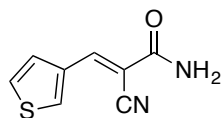


C	2.571950	0.429525	-2.370140
N	3.487127	-0.033813	-1.460040
C	2.862227	-0.253434	-0.257955
C	1.494468	0.079720	-0.421839
C	1.339278	0.517959	-1.783078
C	3.392976	-0.707593	0.953845
C	2.523540	-0.827994	2.020098
C	1.157372	-0.512641	1.882496
C	0.625824	-0.069129	0.682337
C	-0.850421	0.213542	0.591205
S	-1.239269	1.949580	0.129776
C	-0.312775	2.785478	1.443699
C	-1.567089	-0.704631	-0.430602
C	-3.092994	-0.486749	-0.353403
N	-3.666770	-0.061401	-1.487850

C	-1.287281	-2.105558	-0.108104
N	-1.068060	-3.201850	0.155550
O	-3.686776	-0.689264	0.688922
H	-1.188349	-0.518370	-1.438039
H	-1.311930	0.029552	1.564149
H	0.502007	-0.626413	2.739365
H	2.892977	-1.172521	2.978231
H	4.444458	-0.950772	1.048384
H	-0.654765	2.447129	2.421691
H	0.755129	2.601724	1.331491
H	-0.514659	3.850238	1.337929
H	-4.659088	0.126439	-1.495928
H	-3.141596	0.094717	-2.333242
H	0.446335	0.881070	-2.264806
H	2.876343	0.668100	-3.377008
H	4.467133	-0.181590	-1.644985

0 imaginary frequencies
E = -1140.809735
H = -1140.548549
G = -1140.610070

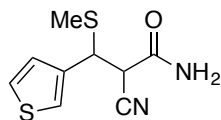
16



C	1.505393	0.020976	0.000237
C	1.531135	1.448041	0.000219
C	0.367289	-0.704659	0.000148
N	1.613064	2.597644	0.000222
H	0.524727	-1.780111	0.000151
C	2.823107	-0.710045	0.000352
C	-1.011267	-0.271338	0.000061
O	2.861667	-1.930549	-0.000290
N	3.926840	0.061546	-0.000165
H	4.829369	-0.388996	-0.000571
H	3.894795	1.069017	-0.000096
C	-2.019194	-1.211999	-0.000106
S	-3.568125	-0.503373	-0.000243
C	-2.896021	1.087415	0.000000
C	-1.538997	1.067827	0.000127
H	-1.907226	-2.286419	-0.000183
H	-3.550269	1.945564	0.000017
H	-0.942726	1.967675	0.000274

0 imaginary frequencies
E = -891.310518
H = -891.171439
G = -891.218989

P16

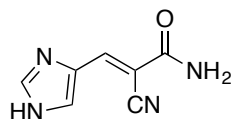


C	-2.966252	-0.304018	1.249840
C	-1.636299	-0.019212	1.282988
C	-1.050450	0.011147	-0.024292
C	-1.962815	-0.247246	-1.005213
S	-3.532317	-0.533992	-0.361802

C	0.393889	0.299259	-0.303268
C	1.335159	-0.724755	0.375007
C	0.957472	-2.081760	-0.026413
N	0.656707	-3.141146	-0.352727
S	0.897654	1.962258	0.291222
C	-0.278229	2.953454	-0.667047
C	2.792551	-0.476647	-0.071171
O	3.080205	-0.506718	-1.252650
N	3.660105	-0.229925	0.919958
H	1.233199	-0.659397	1.461488
H	0.580921	0.258826	-1.378622
H	-1.089820	0.174693	2.197129
H	-3.652689	-0.389584	2.078313
H	-1.794636	-0.283575	-2.071622
H	-0.150345	2.764775	-1.732639
H	-1.300168	2.730302	-0.362674
H	-0.052057	3.997026	-0.454205
H	4.625784	-0.042132	0.691162
H	3.384937	-0.213279	1.888944

0 imaginary frequencies
E = -1330.015416
H = -1329.820188
G = -1329.878046

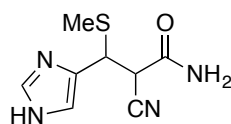
17



C	-1.118395	0.012316	-0.000034
C	-1.069802	1.440007	-0.000131
C	-0.024384	-0.778818	0.000051
H	-0.226354	-1.846081	0.000129
N	-1.148578	2.589953	-0.000187
C	-2.472883	-0.643419	-0.000028
C	1.356816	-0.395627	0.000032
O	-2.581502	-1.860879	0.000118
N	-3.533997	0.186801	-0.000102
H	-3.445129	1.190780	0.000319
H	-4.459379	-0.214265	0.000297
C	2.422748	-1.275617	0.000137
N	3.531594	-0.496176	0.000179
C	3.123309	0.807551	-0.000118
N	1.822405	0.905611	-0.000105
H	2.463062	-2.352337	0.000263
H	4.489375	-0.818892	0.000305
H	3.826019	1.626160	-0.000205

0 imaginary frequencies
E = -564.542046
H = -564.398507
G = -564.444331

P17

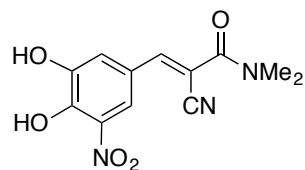


N	3.116428	-0.837462	0.400513
C	2.760911	-0.962390	-0.900454

N	1.549051	-0.503709	-1.113734
C	1.103248	-0.062618	0.112730
C	2.063421	-0.265030	1.066546
C	-0.252531	0.535444	0.283794
S	-0.360205	2.229913	-0.428146
C	0.899803	3.036350	0.593435
C	-1.312655	-0.349979	-0.416723
C	-1.312405	-1.754291	0.224490
N	-0.591832	-2.670947	-0.440656
C	-2.658227	0.214250	-0.295905
N	-3.719343	0.643550	-0.203140
O	-1.925748	-1.967777	1.253833
H	-1.064217	-0.413642	-1.479381
H	-0.495141	0.607208	1.346483
H	3.416381	-1.395118	-1.639973
H	2.086643	-0.056957	2.123129
H	0.648540	2.942391	1.649857
H	1.882900	2.609966	0.398818
H	0.897335	4.089139	0.315063
H	-0.459486	-3.578650	-0.017714
H	0.027972	-2.395038	-1.189848
H	3.998820	-1.116135	0.804874

0 imaginary frequencies
E = -1003.245846
H = -1003.045928
G = -1003.100998

18 (with NEt₂ modeled as NMe₂)

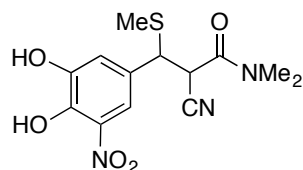


C	2.108867	-0.022268	-0.214646
C	0.938381	-0.638814	0.031428
C	2.226291	1.342966	-0.620779
H	1.023929	-1.703163	0.231793
N	2.364819	2.428562	-0.980868
C	3.371429	-0.861960	-0.213744
C	-0.424568	-0.117109	0.049340
O	3.327760	-2.004586	-0.653429
N	4.500080	-0.285784	0.244329
C	4.549617	0.893644	1.103916
H	3.564929	1.134346	1.497635
H	5.200268	0.670328	1.951182
H	4.949330	1.755749	0.565714
C	5.754005	-1.016227	0.106132
H	5.717273	-1.639573	-0.783482
H	5.935775	-1.647994	0.980215
H	6.565121	-0.293849	0.014582
C	-1.451350	-1.051892	0.056674
C	-2.777400	-0.627072	0.050188
C	-3.117683	0.729941	0.054508
C	-2.062178	1.667889	0.072213
C	-0.749989	1.254538	0.070029
H	0.011950	2.021228	0.103022
H	-1.243332	-2.113353	0.060362
N	-3.821874	-1.641154	0.048486
O	-3.504962	-2.805576	0.049323

O	-4.990099	-1.262262	0.045710
O	-4.343346	1.254307	0.055287
H	-5.002806	0.537662	0.053843
O	-2.352436	2.985492	0.097921
H	-3.311491	3.106442	0.111456

0 imaginary frequencies
E = -1004.071350
H = -1003.822435
G = -1003.889328

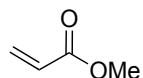
P18 (with NEt_2 modeled as NMe_2)



C	2.167135	1.805419	0.017485
C	0.870045	1.398057	0.235838
C	0.536247	0.033917	0.258485
C	1.523938	-0.909928	0.073526
C	2.843081	-0.493440	-0.140567
C	3.195034	0.857258	-0.175233
C	-0.888673	-0.407552	0.480661
C	-1.848158	0.110781	-0.615264
C	-1.317586	-0.206229	-1.943601
N	-0.899803	-0.466324	-2.981744
S	-1.562277	0.180773	2.080524
C	-0.395463	-0.653578	3.188156
C	-3.224772	-0.587590	-0.470203
O	-3.241350	-1.800673	-0.314706
N	-4.315069	0.192117	-0.519760
H	-1.922073	1.196501	-0.542231
H	-0.941636	-1.497346	0.475909
H	0.114913	2.158825	0.402055
O	2.470403	3.121257	-0.006728
O	4.414404	1.373615	-0.368533
N	3.860321	-1.514308	-0.327094
H	1.304506	-1.969132	0.088062
H	-0.432626	-1.731530	3.033837
H	0.615520	-0.280377	3.027042
H	-0.710269	-0.421736	4.204294
C	-5.628105	-0.405946	-0.296573
C	-4.296913	1.627729	-0.805925
H	-5.305909	1.919915	-1.089867
H	-4.002300	2.208899	0.070878
H	-3.640931	1.858750	-1.644277
H	-6.170593	0.191276	0.437555
H	-6.196252	-0.427116	-1.229222
H	-5.503696	-1.418060	0.075917
H	3.417703	3.229868	-0.166384
H	5.053795	0.650292	-0.491350
O	3.537096	-2.677534	-0.283894
O	5.017356	-1.148563	-0.523780

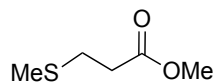
0 imaginary frequencies
E = -1442.782284
H = -1442.476950
G = -1442.553100

19



C	0.000000	0.118443	0.000000
C	1.460151	-0.152145	0.000000
C	2.331318	0.850429	0.000000
H	1.765456	-1.191232	0.000000
H	3.398727	0.668669	0.000000
H	1.988620	1.879328	0.000000
O	-0.702289	-1.017855	0.000000
O	-0.510850	1.213343	0.000000
C	-2.128223	-0.876311	0.000000
H	-2.524487	-1.887180	0.000000
H	-2.451341	-0.337996	0.890455
H	-2.451341	-0.337996	-0.890455
0 imaginary frequencies			
E = -306.433528			
H = -306.329955			
G = -306.364782			

P19



C	3.156726	-2.017655	0.000000
S	2.552782	-0.308369	0.000000
C	0.765477	-0.651021	0.000000
C	0.000000	0.661898	0.000000
C	-1.491842	0.441785	0.000000
H	4.244829	-1.977223	0.000000
H	2.816908	-2.541555	0.893055
H	2.816908	-2.541555	-0.893055
H	0.517630	-1.237438	0.886040
H	0.517630	-1.237438	-0.886040
H	0.247387	1.266836	0.876722
H	0.247387	1.266836	-0.876722
O	-2.152827	1.601058	0.000000
O	-2.038988	-0.633020	0.000000
C	-3.584001	1.511835	0.000000
H	-3.942609	2.536759	0.000000
H	-3.927110	0.986660	-0.890741
H	-3.927110	0.986660	0.890741
0 imaginary frequencies			
E = -745.150330			
H = -744.990021			
G = -745.035483			

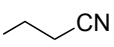
20



C	-0.584372	-0.525866	0.000000
C	0.000000	0.784639	0.000000
C	1.319393	0.959377	0.000000
H	-0.696655	1.613909	0.000000
H	1.736854	1.958012	0.000000
H	2.005137	0.121048	0.000000
N	-1.065066	-1.571696	0.000000
0 imaginary frequencies			
E = -170.810976			

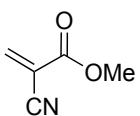
H = -170.754656
G = -170.782545

P20



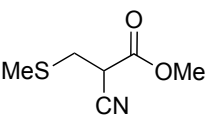
 C -2.742556 0.507060 0.000000
 S -1.452869 -0.767157 0.000000
 C 0.000000 0.327205 0.000000
 C 1.267229 -0.533001 0.000000
 C 2.466531 0.303372 0.000000
 N 3.397927 0.976617 0.000000
 H -3.701342 -0.008801 0.000000
 H -2.667326 1.125632 0.893728
 H -2.667326 1.125632 -0.893728
 H -0.026824 0.959118 0.888606
 H -0.026824 0.959118 -0.888606
 H 1.301418 -1.175157 0.882697
 H 1.301418 -1.175157 -0.882697
 0 imaginary frequencies
 E = -609.528473
 H = -609.415240
 G = -609.453669

21



 C 2.289349 -0.172482 0.000000
 C 0.978565 -0.415758 0.000000
 C 0.468401 -1.758790 0.000000
 N 0.071250 -2.837889 0.000000
 C 0.000000 0.720850 0.000000
 H 2.637394 0.853394 0.000000
 H 3.015902 -0.974208 0.000000
 O -1.252182 0.287794 0.000000
 O 0.329325 1.877674 0.000000
 C -2.270238 1.302176 0.000000
 H -3.214199 0.766817 0.000000
 H -2.175730 1.919752 0.891975
 H -2.175730 1.919752 -0.891975
 0 imaginary frequencies
 E = -398.672174
 H = -398.567982
 G = -398.607270

P21

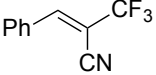


 S -1.661221 -0.382422 -0.624153
 C -2.974477 -1.488709 -0.042158
 H -3.510747 -1.836220 -0.923406
 H -2.546504 -2.342624 0.481298
 H -3.661926 -0.950505 0.609117
 C -0.957542 0.056301 0.996462
 H -0.707570 -0.855235 1.538705

H	-1.678160	0.636234	1.573129
C	0.332296	0.872311	0.814480
H	0.759302	1.056645	1.805099
C	0.071188	2.171953	0.190420
N	-0.152596	3.194278	-0.281162
C	1.374053	0.104346	-0.000620
O	1.883786	0.500802	-1.013223
O	1.630000	-1.058387	0.577181
C	2.571439	-1.905901	-0.103531
H	2.647668	-2.802180	0.503592
H	3.535451	-1.404780	-0.176148
H	2.198174	-2.143639	-1.098789

0 imaginary frequencies
E = -837.385624
H = -837.224768
G = -837.274223

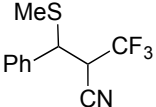
22



C	3.267132	1.121880	-0.335723
C	4.135325	0.091398	0.019986
C	3.633910	-1.175868	0.304134
C	2.267159	-1.408749	0.236286
C	1.382403	-0.370783	-0.089135
C	1.898486	0.897885	-0.389119
C	-0.042092	-0.693939	-0.115509
C	-1.097431	0.127981	0.009350
C	-2.507400	-0.396087	-0.051920
F	-3.177422	-0.129595	1.079975
C	-1.027045	1.535285	0.254274
N	-1.019685	2.666077	0.467046
F	-2.550029	-1.714266	-0.242678
F	-3.198681	0.178665	-1.048632
H	-0.275259	-1.748654	-0.226775
H	1.243319	1.703244	-0.693356
H	3.659009	2.101676	-0.579201
H	5.202321	0.274023	0.062775
H	4.306371	-1.982466	0.568354
H	1.874539	-2.397622	0.445150

0 imaginary frequencies
E = -738.877640
H = -738.726286
G = -738.776041

P22

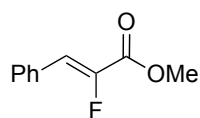


C	2.142218	-0.383223	1.170830
C	1.335429	-0.034537	0.090179
C	1.863444	-0.076835	-1.202044
C	3.178971	-0.473377	-1.407794
C	3.982414	-0.823506	-0.323569
C	3.463043	-0.776207	0.965167
C	-0.097802	0.386341	0.332629
S	-0.423913	2.098269	-0.250587
C	0.902341	2.931377	0.661712

C	-1.071847	-0.600521	-0.359415
C	-2.551901	-0.310549	-0.095476
C	-0.774116	-1.962556	0.101260
N	-0.528555	-3.017633	0.479350
H	-0.937412	-0.575645	-1.445278
H	-0.301620	0.359435	1.405413
H	1.737451	-0.348053	2.176794
H	4.082656	-1.042866	1.812879
H	5.009307	-1.128550	-0.485259
H	3.580133	-0.504319	-2.413674
H	1.251061	0.216679	-2.048566
H	0.809472	2.734600	1.729657
H	1.879376	2.613730	0.300307
H	0.773045	3.997183	0.479581
F	-3.313988	-1.354734	-0.439417
F	-2.782633	-0.051386	1.195008
F	-2.973840	0.736173	-0.806568

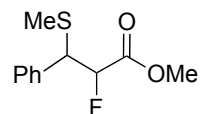
0 imaginary frequencies
E = -1177.587795
H = -1177.380324
G = -1177.438010

23



C	-3.525890	-1.368540	-0.000341
C	-2.138138	-1.420821	-0.000289
C	-1.371978	-0.245934	0.000060
C	-2.036449	0.990909	0.000405
C	-3.424805	1.038115	0.000372
C	-4.173884	-0.136573	-0.000016
C	0.084383	-0.395944	0.000072
C	1.028015	0.545139	-0.000098
C	2.494759	0.304440	-0.000071
O	2.797200	-0.989327	0.000400
C	4.198051	-1.302697	0.000216
F	0.745745	1.857495	-0.000262
O	3.304502	1.197375	-0.000453
H	0.465148	-1.410688	0.000222
H	-1.474486	1.913842	0.000735
H	-3.925090	1.999107	0.000651
H	-5.256347	-0.090891	-0.000049
H	-4.099976	-2.287148	-0.000626
H	-1.634968	-2.381505	-0.000523
H	4.671344	-0.893225	0.891698
H	4.671132	-0.893179	-0.891356
H	4.253538	-2.386707	0.000189

0 imaginary frequencies
E = -636.692681
H = -636.509515
G = -636.558980

P23

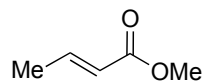
S	2.076975	-1.783994	-0.086795
C	0.498248	-0.901222	-0.365543
H	0.207300	-1.082303	-1.402873
C	0.573726	0.591252	-0.124298
C	0.053838	1.463410	-1.081565
H	-0.356000	1.063824	-2.003773
C	0.057026	2.839040	-0.861231
H	-0.346153	3.505753	-1.614206
C	0.581597	3.352448	0.320019
H	0.587225	4.422023	0.493120
C	1.106204	2.486426	1.277942
H	1.519661	2.882410	2.197991
C	1.105076	1.113860	1.057266
H	1.523068	0.441393	1.797275
C	-0.579863	-1.564733	0.496807
F	-0.217831	-1.542787	1.827228
C	-1.898367	-0.814175	0.359662
H	-0.717848	-2.607221	0.200482
O	-2.318846	-0.856997	-0.897922
O	-2.458338	-0.249822	1.258659
C	-3.517433	-0.118455	-1.187579
H	-3.705118	-0.268692	-2.245973
H	-4.343857	-0.501396	-0.590799
H	-3.358026	0.937523	-0.970331
C	3.048448	-0.961786	-1.377925
H	4.042465	-1.405659	-1.357102
H	3.124377	0.105519	-1.170761
H	2.598250	-1.126032	-2.356615

0 imaginary frequencies

E = -1075.404892

H = -1075.165520

G = -1075.223206

24

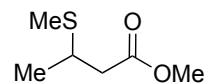
C	0.690851	-3.202144	0.000000
C	0.809340	-1.715371	0.000000
C	-0.221542	-0.870433	0.000000
C	0.000000	0.590929	0.000000
O	1.074807	1.146730	0.000000
O	-1.161752	1.257235	0.000000
C	-1.067108	2.685980	0.000000
H	1.812251	-1.294129	0.000000
H	-1.249780	-1.213813	0.000000
H	-0.350518	-3.523715	0.000000
H	1.192593	-3.619843	0.876881
H	1.192593	-3.619843	-0.876881
H	-2.090496	3.049256	0.000000
H	-0.540161	3.028300	0.890206
H	-0.540161	3.028300	-0.890206

0 imaginary frequencies

E = -345.743997

H = -345.610696
G = -345.649119

P24



O	2.334777	0.078898	-0.656925
C	3.446156	-0.724923	-0.237619
C	1.435174	0.369301	0.283775
O	1.525839	-0.011241	1.425464
C	0.316382	1.237244	-0.239320
C	-1.052612	0.739388	0.221433
C	-2.146000	1.750327	-0.096459
H	-1.009273	0.547122	1.296091
H	0.368118	1.298982	-1.327856
H	-3.128034	1.380138	0.200618
H	-1.960325	2.682930	0.443133
H	-2.167367	1.966138	-1.167031
H	4.064903	-0.855077	-1.120344
H	4.002037	-0.215509	0.548770
H	3.092706	-1.688462	0.128200
S	-1.342560	-0.881937	-0.587185
C	-2.703525	-1.509205	0.434170
H	-2.915091	-2.521680	0.093476
H	-2.405355	-1.539558	1.481906
H	-3.599521	-0.901917	0.315090
H	0.479792	2.243826	0.158716

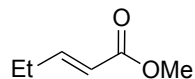
0 imaginary frequencies

E = -784.457013

H = -784.267156

G = -784.315809

25



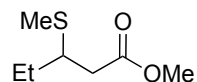
O	2.097912	-0.731432	0.116685
C	3.417184	-0.187096	0.231200
H	3.681907	0.352582	-0.677707
H	3.472943	0.487544	1.085152
H	4.076314	-1.038198	0.374627
C	1.111037	0.154408	-0.069369
O	1.304405	1.346711	-0.140110
C	-0.200861	-0.519642	-0.170718
H	-0.207145	-1.600746	-0.089816
C	-1.317212	0.185080	-0.353712
H	-1.233939	1.268972	-0.420742
C	-2.690331	-0.395638	-0.452189
H	-3.107866	-0.134201	-1.430267
H	-2.638931	-1.485326	-0.398474
C	-3.609570	0.154297	0.645099
H	-4.617352	-0.249410	0.538397
H	-3.671639	1.243371	0.590151
H	-3.234308	-0.115269	1.634221

0 imaginary frequencies

E = -385.046871

H = -384.883530

G = -384.925834

P25

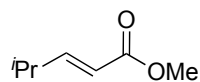
O	-2.526861	-0.312073	-0.647537
C	-3.766759	0.163314	-0.105750
C	-1.534204	-0.482368	0.226893
O	-1.646681	-0.255080	1.406867
C	-0.279158	-1.009520	-0.424354
C	0.962600	-0.258466	0.055096
C	2.261138	-0.922226	-0.404336
H	0.936033	-0.201748	1.147239
H	-0.373098	-0.960919	-1.510901
H	3.094913	-0.253680	-0.175721
C	2.513301	-2.274732	0.263333
H	2.235410	-1.032261	-1.493046
H	-4.447185	0.237241	-0.948707
H	-4.147444	-0.540260	0.633829
H	-3.622081	1.139212	0.356683
S	0.818962	1.466231	-0.557872
C	1.939841	2.306643	0.593939
H	1.909794	3.367457	0.349372
H	1.600892	2.165501	1.619857
H	2.962014	1.947589	0.482745
H	-0.202004	-2.064059	-0.144099
H	3.496266	-2.658064	-0.015594
H	2.485742	-2.181287	1.352030
H	1.775136	-3.023057	-0.031299

0 imaginary frequencies

E = -823.759992

H = -823.540112

G = -823.592111

26

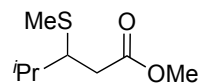
C	-0.340258	-2.332750	0.000000
C	0.208744	-0.939750	0.000000
C	-0.522859	0.174246	0.000000
H	1.295147	-0.845474	0.000000
C	0.122057	1.504771	0.000000
H	-1.606821	0.151882	0.000000
C	0.122057	-3.074125	1.260786
H	-1.432976	-2.276692	0.000000
C	0.122057	-3.074125	-1.260786
O	-0.790333	2.485058	0.000000
O	1.313129	1.717158	0.000000
C	-0.277108	3.821878	0.000000
H	-1.147234	4.471642	0.000000
H	0.327553	3.992990	0.890205
H	0.327553	3.992990	-0.890205
H	-0.270305	-4.093403	1.263339
H	1.213956	-3.130312	1.291060
H	-0.220518	-2.569253	2.165960
H	-0.270305	-4.093403	-1.263339
H	-0.220518	-2.569253	-2.165960
H	1.213956	-3.130312	-1.291060

0 imaginary frequencies

E = -424.352387

H = -424.159563
G = -424.205001

P26



C	-4.003170	-0.150116	-0.239882
O	-2.689202	-0.551137	-0.651362
C	-1.727727	-0.435731	0.266402
O	-1.925155	-0.012015	1.378900
C	-0.394540	-0.925810	-0.244729
C	0.754950	-0.046448	0.245522
C	2.140369	-0.695962	0.080546
C	2.355081	-1.788237	1.132011
S	0.613918	1.563368	-0.628240
C	1.470764	2.635098	0.557763
C	2.374346	-1.242841	-1.327365
H	-0.272153	-1.946369	0.133378
H	2.879589	0.089668	0.268914
H	-4.643625	-0.312012	-1.101681
H	-4.333958	-0.756486	0.602659
H	-4.001315	0.901822	0.043740
H	1.442353	3.645832	0.153141
H	0.959203	2.618345	1.519811
H	2.510217	2.333077	0.679831
H	-0.423547	-0.985066	-1.333801
H	3.370454	-2.184520	1.060308
H	2.212033	-1.400201	2.143276
H	1.666870	-2.625660	0.986780
H	3.412519	-1.561985	-1.439993
H	1.739391	-2.112388	-1.520566
H	2.165602	-0.487868	-2.088794
H	0.588100	0.175417	1.302932

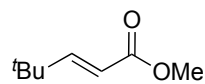
0 imaginary frequencies

E = -863.065331

H = -862.815981

G = -862.870552

27

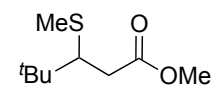


C	-1.418873	-1.561701	0.000000
C	-0.139216	-0.771265	0.000000
C	-0.015898	0.556062	0.000000
C	1.324130	1.182338	0.000000
O	1.231955	2.518582	0.000000
C	2.471509	3.235050	0.000000
O	2.383748	0.598242	0.000000
H	0.776585	-1.362757	0.000000
H	-0.865040	1.228080	0.000000
C	-2.660064	-0.670068	0.000000
C	-1.418873	-2.454457	1.253113
C	-1.418873	-2.454457	-1.253113
H	2.203993	4.287622	0.000000
H	3.049258	2.987961	0.890288
H	3.049258	2.987961	-0.890288
H	-3.558581	-1.291526	0.000000
H	-2.690288	-0.031959	0.886980

H	-2.690288	-0.031959	-0.886980
H	-2.310717	-3.086478	1.256151
H	-0.539564	-3.103307	1.272363
H	-1.421508	-1.848727	2.162519
H	-2.310717	-3.086478	-1.256151
H	-1.421508	-1.848727	-2.162519
H	-0.539564	-3.103307	-1.272363

0 imaginary frequencies
E = -463.659169
H = -463.437118
G = -463.484527

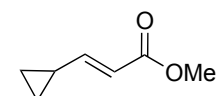
P27



C	-4.176276	-0.388331	-0.194666
O	-2.859188	-0.832677	-0.546469
C	-1.878156	-0.473575	0.283974
C	-0.542552	-1.031424	-0.144597
C	0.590830	-0.063860	0.195660
S	0.328535	1.458812	-0.816778
C	0.395581	2.725373	0.481524
O	-2.062624	0.194062	1.272599
C	2.011349	-0.666744	0.058288
H	0.458355	0.259221	1.231800
H	-0.578022	-1.259585	-1.210710
C	3.048553	0.383067	0.474866
C	2.141038	-1.866889	1.010326
C	2.295134	-1.124471	-1.375715
H	-4.833534	-0.773856	-0.968347
H	-4.458684	-0.784391	0.780224
H	-4.209877	0.700449	-0.171744
H	0.191666	3.683550	0.005048
H	-0.367836	2.523304	1.232547
H	1.382439	2.756094	0.942022
H	-0.419326	-1.978658	0.389746
H	4.051627	-0.048670	0.433179
H	3.024571	1.250664	-0.187961
H	2.869263	0.722522	1.499854
H	3.313447	-1.515966	-1.444484
H	1.612965	-1.919703	-1.687221
H	2.203980	-0.292843	-2.079043
H	3.182430	-2.196791	1.042665
H	1.841253	-1.597368	2.027538
H	1.540208	-2.718910	0.686341

0 imaginary frequencies
E = -902.370770
H = -902.092332
G = -902.148936

28

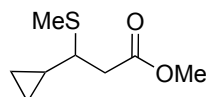


C	-0.002954	-2.358460	0.000000
C	0.294852	-0.926184	0.000000
C	-0.619693	0.048989	0.000000
H	1.347188	-0.644544	0.000000

C	-0.203033	1.462265	0.000000
H	-1.683618	-0.156140	0.000000
C	0.937831	-3.286187	0.745187
H	-1.051649	-2.628963	0.000000
C	0.937831	-3.286187	-0.745187
O	-1.263665	2.282430	0.000000
O	0.937831	1.869003	0.000000
C	-0.974041	3.684039	0.000000
H	-1.937884	4.184679	0.000000
H	-0.405170	3.951890	0.890101
H	-0.405170	3.951890	-0.890101
H	0.482790	-4.121234	1.260159
H	1.776327	-2.828732	1.254255
H	0.482790	-4.121234	-1.260159
H	1.776327	-2.828732	-1.254255

0 imaginary frequencies
E = -423.122244
H = -422.952539
G = -422.995525

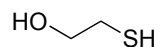
P28



C	-1.964531	-0.789883	-0.534562
C	-0.687495	-0.198903	0.004877
C	0.539003	-0.949531	-0.516149
H	-0.690545	-0.248509	1.098351
C	1.798567	-0.533078	0.203894
H	0.658053	-0.813672	-1.592247
C	-3.220490	-0.739309	0.287940
H	-2.081824	-0.708127	-1.610140
C	-2.495443	-2.044342	0.105460
O	2.812675	-0.309246	-0.632688
O	1.893828	-0.427215	1.402380
C	4.056503	0.067894	-0.025994
H	4.754504	0.204791	-0.846376
H	3.933423	0.995784	0.531648
H	4.401121	-0.719537	0.643411
H	-4.160735	-0.598218	-0.228464
H	-3.157923	-0.270459	1.262587
H	-2.938279	-2.792269	-0.538324
H	-1.951069	-2.435283	0.957289
S	-0.473305	1.564646	-0.457143
C	-1.845613	2.319862	0.456961
H	-1.737638	3.398396	0.350876
H	-2.804122	2.009494	0.045800
H	-1.786026	2.056800	1.513260
H	0.398915	-2.018102	-0.325492

0 imaginary frequencies
E = -861.833329
H = -861.607171
G = -861.659303

β-Mercaptoethanol

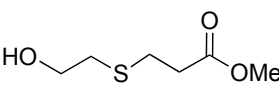


C	-0.032795	0.603584	0.062317
S	-1.720849	-0.069295	-0.074341

C	1.026556	-0.474088	-0.066742
O	2.290477	0.169354	0.030552
H	-1.696491	-0.789815	1.057924
H	0.062680	1.323001	-0.751697
H	0.074630	1.136764	1.006365
H	0.905608	-1.213044	0.732703
H	0.919456	-0.984981	-1.028664
H	2.981320	-0.495014	-0.045050

0 imaginary frequencies
E = -553.203715
H = -553.116256
G = -553.148536

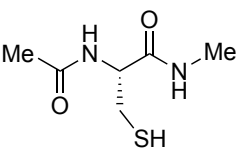
Adduct of β -Mercaptoethanol and methyl acrylate



C	4.923702	0.133222	-0.000009
O	3.672715	-0.567851	0.000000
C	2.574676	0.190182	-0.000005
O	2.601170	1.395872	-0.000017
C	1.325530	-0.655039	0.000009
C	0.068799	0.199844	0.000002
S	-1.394584	-0.882482	0.000016
C	-2.678026	0.408266	-0.000002
C	-4.051612	-0.236919	0.000004
O	-5.001876	0.819952	-0.000012
H	-2.560572	1.029436	0.889867
H	-2.560569	1.029412	-0.889888
H	0.039311	0.834968	0.886198
H	0.039307	0.834948	-0.886208
H	1.363994	-1.307122	0.876864
H	1.363989	-1.307142	-0.876831
H	5.691202	-0.634879	0.000005
H	5.005101	0.755252	-0.890770
H	5.005097	0.755281	0.890731
H	-4.171652	-0.865409	-0.888471
H	-4.171655	-0.865385	0.888496
H	-5.884699	0.439226	-0.000007

0 imaginary frequencies
E = -859.672638
H = -859.475767
G = -859.529431

2-acetamido-3-mercapto-N-methylpropionamide

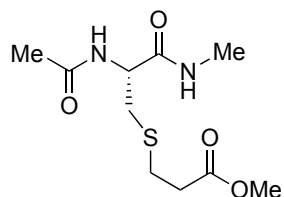


C	-3.948003	-0.404613	0.415609
N	-2.560271	-0.059698	0.681720
C	-1.601352	-0.276464	-0.229002
C	-0.198668	0.215170	0.141790
C	-0.039923	1.641198	-0.405489
S	1.561772	2.400934	0.006282
O	-1.813664	-0.787917	-1.322259
N	0.772057	-0.688349	-0.433273
C	1.745858	-1.296305	0.290829
C	2.609500	-2.274214	-0.468109

O	1.930909	-1.062079	1.477988
H	-0.052607	0.214054	1.222191
H	-0.794401	2.293524	0.035880
H	-0.176869	1.642386	-1.487604
H	0.591899	-0.997353	-1.379320
H	-4.543225	-0.142662	1.286598
H	-4.316979	0.144162	-0.451996
H	-4.044440	-1.473619	0.220621
H	3.638579	-1.913123	-0.444357
H	2.578797	-3.234132	0.048113
H	2.298892	-2.407514	-1.503047
H	2.320086	1.533877	-0.683495
H	-2.313021	0.333116	1.577182

0 imaginary frequencies
E = -893.990148
H = -893.788186
G = -893.842418

Adduct of 2-acetamido-3-mercapto-*N*-methylpropionamide with methyl acrylate



C	-5.126105	-0.121127	-1.573900
O	-4.571905	-0.706931	-0.386901
C	-3.367797	-0.271166	-0.024504
O	-2.750257	0.559670	-0.647502
C	-2.909554	-0.919320	1.260067
C	-1.441432	-0.670040	1.566386
S	-0.411543	-1.595221	0.373000
C	1.260365	-0.997013	0.770453
C	1.787215	0.105304	-0.173249
N	3.221800	0.230360	-0.035556
C	4.073796	-0.647922	-0.607944
O	3.673517	-1.605371	-1.263192
C	1.182257	1.472551	0.153167
N	-0.050632	1.702668	-0.313585
C	-0.771369	2.911016	0.053207
O	1.809348	2.288555	0.823452
C	5.544546	-0.384213	-0.399088
H	1.552058	-0.174998	-1.202521
H	1.289615	-0.666370	1.810974
H	1.921471	-1.856771	0.666619
H	-1.216653	0.393771	1.494202
H	-1.208396	-1.019457	2.571480
H	-3.142488	-1.985705	1.217783
H	-3.527394	-0.500167	2.060159
H	-6.094788	-0.592591	-1.708648
H	-5.237883	0.954530	-1.442861
H	-4.479377	-0.322798	-2.426948
H	3.559057	1.025840	0.490606
H	-1.736283	2.894099	-0.445979
H	-0.924869	2.961345	1.134449
H	-0.209950	3.792164	-0.258391
H	-0.574942	0.952995	-0.750471
H	6.011313	-0.242209	-1.374650
H	5.736743	0.487986	0.223538

```
H      5.992128   -1.265122    0.062215
0 imaginary frequencies
E = -1200.465911
H = -1200.154610
G = -1200.224134
```

Compounds related to Figure 1 (Thiol addition to bardoxolone methyl)

Geometries in this section were optimized with M06-2X/6-31+G(d) in CPCM water. Single-point energy calculations were subsequently performed with M06-2X/6-311+G(d,p) in CPCM water on the 6-31+G(d) geometries. Underneath the coordinates of each species are listed the following energies:

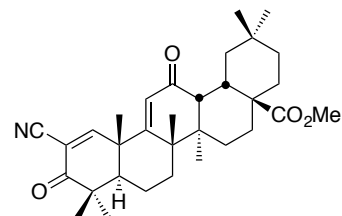
- M06-2X/6-31+G(d) solution-phase potential energy (E)
- M06-2X/6-31+G(d) solution-phase enthalpy at 298.15 K (H)
- M06-2X/6-31+G(d) solution-phase Gibbs free energy at 298.15 K and 1 mol/L (G)
- M06-2X/6-311+G(d,p) solution-phase potential energy (E_{LBS})

MeSH

H	1.282078	-0.836658	0.000000
S	-0.048399	-0.666673	0.000000
C	-0.048399	1.157218	0.000000
H	-1.094044	1.467269	0.000000
H	0.438375	1.546422	0.894198
H	0.438375	1.546422	-0.894198

0 imaginary frequencies
E = -438.633413
H = -438.582224
G = -438.608570
 E_{LBS} = -438.678967

Bardoxolone methyl 12

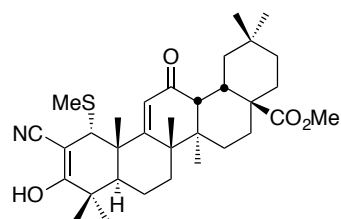


C	4.836541	1.525576	-0.285263
C	5.695395	0.387363	0.156404
C	5.003253	-0.846150	0.731912
C	3.455331	-0.749154	0.623302
C	2.930232	-0.028233	-0.650538
C	3.558688	1.344182	-0.664745
C	2.756315	-2.090493	0.827034
C	1.274540	-1.859415	1.101691
C	0.551512	-1.075061	-0.015090
C	1.392139	0.049420	-0.641828
C	-0.767860	-0.414179	0.553974
C	-1.555478	0.150879	-0.652301
C	-0.709840	1.145219	-1.422306
C	0.760127	1.026246	-1.319815
C	-1.645044	-1.457797	1.280054
C	-3.068515	-0.962021	1.563675
C	-3.795351	-0.508057	0.284926
C	-2.998609	0.632053	-0.392338
C	-5.251867	-0.061913	0.581374
C	-5.338103	1.277709	1.313970
C	-4.578100	2.406500	0.599019
C	-3.123486	1.947125	0.393195
O	6.907627	0.479736	0.098851
C	5.468429	2.813019	-0.389101
N	5.989110	3.844541	-0.462050

C	3.355511	-0.710472	-1.982175
C	0.276673	-2.100530	-1.152312
C	-3.946155	-1.680218	-0.684138
O	-3.822357	-1.616272	-1.891136
O	-4.307868	-2.808359	-0.062454
C	-4.534493	-3.946894	-0.902364
C	-4.580007	3.653474	1.488304
C	-5.245910	2.764782	-0.735536
C	-0.389358	0.711763	1.556680
H	3.136631	-0.103036	1.456882
C	5.390483	-0.832359	2.229319
C	5.602689	-2.114218	0.098891
O	-1.205890	2.001291	-2.144617
H	3.003059	2.199418	-1.036055
H	3.193020	-2.615145	1.683468
H	2.907954	-2.743746	-0.040507
H	0.763978	-2.821680	1.223196
H	1.189118	-1.342906	2.063685
H	-1.674029	-0.677688	-1.365162
H	1.291673	1.791672	-1.878230
H	-1.170116	-1.738142	2.227307
H	-1.717489	-2.377221	0.685287
H	-3.045254	-0.125278	2.269591
H	-3.640059	-1.759292	2.048244
H	-3.434440	0.799319	-1.383629
H	-5.797239	0.009984	-0.368917
H	-5.746642	-0.844170	1.168747
H	-4.934097	1.170555	2.330169
H	-6.394618	1.555031	1.427196
H	-2.565691	2.731249	-0.134020
H	-2.668858	1.851955	1.384705
H	2.923532	-0.166468	-2.826832
H	3.006573	-1.744758	-2.029642
H	4.442141	-0.701024	-2.096921
H	0.029357	-1.626559	-2.104962
H	-0.534716	-2.781947	-0.879787
H	1.162341	-2.718552	-1.321173
H	-4.816286	-4.755121	-0.230522
H	-3.621222	-4.199339	-1.445218
H	-5.337918	-3.737848	-1.611280
H	-4.033001	4.474877	1.009883
H	-4.105702	3.447147	2.455184
H	-5.604904	3.994401	1.678551
H	-4.683402	3.560087	-1.239573
H	-6.266048	3.128641	-0.563536
H	-5.309232	1.917149	-1.424310
H	-1.093122	0.754465	2.392068
H	-0.374272	1.700871	1.091350
H	0.603446	0.555051	1.987750
H	4.883298	-1.648736	2.752431
H	5.103584	0.110478	2.707287
H	6.469805	-0.966510	2.340558
H	5.297105	-2.994375	0.671638
H	6.693561	-2.052884	0.129382
H	5.294214	-2.261780	-0.938356

0 imaginary frequencies
E = -1600.333015
H = -1599.591371
G = -1599.687323
E_{LBS} = -1600.735397

Enol 32



C	-4.615941	-1.313607	-0.777721
C	-3.075921	-1.102740	-0.668915
C	-2.594011	-0.379693	0.618038
C	-3.293532	1.009111	0.670701
C	-4.785530	0.838305	0.549573
C	-5.371881	-0.203196	-0.090641
C	-2.293674	-2.392446	-0.914435
C	-0.826649	-2.072142	-1.173846
C	-0.153061	-1.294105	-0.023567
C	-1.060729	-0.236375	0.623202
C	1.135790	-0.547951	-0.556273
C	1.877292	0.023679	0.675873
C	0.968657	0.952321	1.457667
C	-0.488365	0.756885	1.331155
C	2.075769	-1.520655	-1.301925
C	3.474455	-0.942658	-1.551461
C	4.160488	-0.488262	-0.250563
C	3.295708	0.587786	0.448299
C	5.594413	0.043183	-0.514844
C	5.617208	1.406337	-1.207899
C	4.788998	2.471913	-0.471842
C	3.359111	1.929577	-0.298483
C	4.362897	-1.677483	0.687717
O	4.231226	-1.651518	1.895329
C	4.734789	3.742091	-1.325956
C	5.421244	2.826933	0.880788
C	0.710474	0.585873	-1.531051
O	1.411285	1.818806	2.204041
C	0.165954	-2.341627	1.081004
C	-2.966855	-1.129293	1.921322
S	-2.598969	2.145795	-0.629927
C	-3.924441	3.371012	-0.809604
C	-5.639794	1.782900	1.194689
N	-6.367839	2.523782	1.715291
O	-6.703447	-0.357454	-0.179889
C	-5.009257	-1.260682	-2.270924
C	-5.093833	-2.664864	-0.202442
O	4.781619	-2.770433	0.039074
C	5.057974	-3.918552	0.850372
H	-2.813117	-0.423887	-1.492900
H	-3.095823	1.481208	1.637986
H	-2.694911	-2.912735	-1.790992
H	-2.405846	-3.084919	-0.071930
H	-0.265629	-3.001156	-1.329526
H	-0.765577	-1.514812	-2.114699
H	2.030305	-0.816848	1.367865
H	-1.075297	1.494835	1.871391
H	1.627408	-1.795246	-2.263865
H	2.189933	-2.453472	-0.735455
H	3.416002	-0.087821	-2.233415
H	4.093609	-1.694207	-2.050534
H	3.711121	0.749868	1.449213

H	6.124131	0.116291	0.444164
H	6.137316	-0.693995	-1.117920
H	5.231758	1.307231	-2.232088
H	6.658616	1.742737	-1.299131
H	2.753330	2.666994	0.242756
H	2.922103	1.838090	-1.298146
H	-2.524925	-0.611891	2.778257
H	-2.590431	-2.154901	1.920096
H	-4.048398	-1.164437	2.069007
H	0.377620	-1.886142	2.051300
H	1.015773	-2.969693	0.797014
H	-0.687130	-3.010686	1.220147
H	5.380608	-4.694798	0.159435
H	4.155179	-4.227812	1.381270
H	5.847491	-3.690855	1.569097
H	4.139953	4.519741	-0.831720
H	4.282606	3.538603	-2.303988
H	5.742299	4.141595	-1.494000
H	4.810969	3.576046	1.399803
H	6.422175	3.249794	0.732270
H	5.522417	1.964251	1.545923
H	1.423710	0.692116	-2.352836
H	0.630870	1.557944	-1.036448
H	-0.267034	0.390448	-1.980791
H	-4.430633	-1.999961	-2.833282
H	-4.805027	-0.270445	-2.692516
H	-6.071006	-1.485270	-2.401458
H	-4.680590	-3.485080	-0.795152
H	-6.183061	-2.728640	-0.256567
H	-4.790926	-2.809868	0.837361
H	-3.558130	4.094798	-1.541084
H	-4.843335	2.919698	-1.189722
H	-4.120595	3.890945	0.130743
H	-7.183435	0.372499	0.250356

0 imaginary frequencies

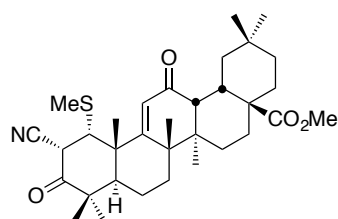
E = -2038.992963

H = -2038.194457

G = -2038.297514

E_{LBS} = -2039.442779

Ketone 33



C	4.894039	0.634218	-0.845934
C	5.389235	-0.085748	0.415860
C	4.609518	-1.322300	0.864554
C	3.074830	-1.200498	0.592544
C	2.629818	-0.478949	-0.711456
C	3.368854	0.883287	-0.774501
C	2.324216	-2.524036	0.745669
C	0.851271	-2.227516	1.013343
C	0.180697	-1.368205	-0.082636
C	1.100393	-0.294596	-0.697063
C	-1.077306	-0.615412	0.513128
C	-1.832116	0.022394	-0.678533

C	-0.921285	0.961319	-1.444936
C	0.533984	0.734106	-1.355790
C	-2.023254	-1.595998	1.241307
C	-3.401792	-0.995936	1.545449
C	-4.105268	-0.475007	0.279458
C	-3.231690	0.608212	-0.396958
C	-5.519887	0.078060	0.597444
C	-5.494031	1.412183	1.344833
C	-4.657853	2.487646	0.632425
C	-3.245612	1.920600	0.402444
O	6.385865	0.296889	0.987236
C	5.636261	1.883271	-1.043425
N	6.203402	2.875611	-1.215575
C	2.927849	-1.258162	-2.018305
C	-0.199860	-2.355772	-1.224681
C	-4.355356	-1.621438	-0.699853
O	-4.249701	-1.550151	-1.908206
O	-4.783544	-2.730141	-0.085146
C	-5.103358	-3.838970	-0.934325
C	-5.312243	2.911479	-0.689493
C	-4.553842	3.720431	1.535304
C	-0.602180	0.463675	1.525097
H	2.705690	-0.555047	1.406170
C	5.283006	-2.526438	0.164014
C	4.825816	-1.475629	2.379227
O	-1.361099	1.864869	-2.147426
S	2.983417	1.961444	0.668655
C	2.737914	3.554950	-0.168671
H	5.121475	-0.005593	-1.708488
H	3.082420	1.432850	-1.674454
H	2.720156	-3.100428	1.587203
H	2.455739	-3.151646	-0.144108
H	0.786465	-1.737963	1.991011
H	0.288589	-3.164226	1.100769
H	-2.018686	-0.786211	-1.399840
H	1.119020	1.481513	-1.883978
H	-1.560298	-1.918622	2.181102
H	-2.173029	-2.503281	0.642852
H	-3.308481	-0.170521	2.258952
H	-4.027407	-1.752409	2.028707
H	-3.665627	0.818167	-1.380939
H	-6.066875	-0.670088	1.183073
H	-6.068663	0.201955	-0.345471
H	-5.087439	1.262675	2.354689
H	-6.524649	1.768512	1.474495
H	-2.785865	1.779310	1.385925
H	-2.636180	2.665001	-0.124992
H	2.305321	-2.148965	-2.103788
H	3.962874	-1.587500	-2.104007
H	2.700928	-0.617512	-2.877021
H	-0.361601	-1.858204	-2.184132
H	-1.101329	-2.921167	-0.970784
H	0.596049	-3.091545	-1.367337
H	-5.426124	-4.635537	-0.267000
H	-5.904542	-3.566518	-1.623958
H	-4.220097	-4.144848	-1.498918
H	-4.697595	3.668775	-1.191175
H	-6.300373	3.348220	-0.500899
H	-5.446254	2.079371	-1.386976
H	-5.547441	4.135808	1.743021
H	-4.084584	3.467083	2.493422

H	-3.951954	4.503666	1.058749
H	-1.302672	0.563037	2.358411
H	-0.491141	1.450304	1.067192
H	0.372230	0.214540	1.954839
H	4.793274	-3.453121	0.476538
H	5.251643	-2.479928	-0.926069
H	6.332894	-2.579720	0.467582
H	4.445028	-0.602014	2.918849
H	5.888832	-1.580988	2.605733
H	4.308864	-2.363981	2.751125
H	2.551743	4.290028	0.616766
H	3.626657	3.849490	-0.729137
H	1.867774	3.511856	-0.828087

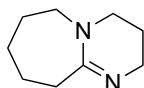
0 imaginary frequencies
E = -2038.995375
H = -2038.197258
G = -2038.301351
E_{LBS} = -2039.441851

Compounds related to Figure 2 and Table S3 (Kinetics of thiol additions)

Certain species in Figure 2 are also included in Table 1 and their coordinates and energies are listed in the relevant section above. Geometries of the remaining species in Figure 2 reported below were optimized with M06-2X/6-311+G(d,p) in CPCM water. Underneath the coordinates of each species are listed the following energies:

- M06-2X/6-311+G(d,p) solution-phase potential energy (E)
- M06-2X/6-311+G(d,p) solution-phase enthalpy at 298.15 K (H)
- M06-2X/6-311+G(d,p) solution-phase Gibbs free energy at 298.15 K and 1 mol/L (G)

DBU

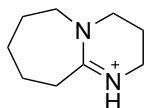


N	-1.478286	-1.451500	-0.136520
C	-2.698253	-0.665815	0.010249
C	-2.437162	0.620338	0.786994
C	-1.413042	1.438845	0.021303
N	-0.325299	0.583243	-0.462029
C	-0.400570	-0.781282	-0.367734
C	0.893409	-1.549675	-0.506151
C	1.897316	-1.245324	0.620485
C	2.747675	0.006193	0.394668
C	1.954962	1.308878	0.293452
C	0.905386	1.283726	-0.820785
H	-3.449829	-1.279149	0.510549
H	-3.098635	-0.411881	-0.981376
H	-3.349978	1.202405	0.923695
H	-2.046461	0.363669	1.776136
H	-0.979651	2.211568	0.664262
H	-1.882618	1.943702	-0.830589
H	0.610480	2.302550	-1.079168
H	1.452109	1.526116	1.242826
H	1.330916	0.846866	-1.728588

H	2.648230	2.133046	0.102149
H	3.320392	-0.125344	-0.531518
H	3.478608	0.091015	1.203683
H	2.567720	-2.102767	0.719802
H	1.352903	-1.162327	1.568306
H	0.616541	-2.602687	-0.485870
H	1.356050	-1.354292	-1.479344

0 imaginary frequencies
E = -462.014806
H = -461.756609
G = -461.798977

DBUH⁺



C	-0.332158	0.694953	-0.373925
N	-1.466998	1.333766	-0.138075
C	-2.743766	0.660255	0.096124
C	-2.456119	-0.677967	0.754673
C	-1.457792	-1.452443	-0.087389
N	-0.283207	-0.622130	-0.412235
C	0.956715	-1.343472	-0.753250
C	2.003265	-1.293982	0.358130
C	2.788020	0.017031	0.390274
C	1.934959	1.271786	0.576879
C	0.913424	1.512761	-0.551428
H	-3.347022	1.302462	0.734611
H	-3.262651	0.527545	-0.856180
H	-3.374212	-1.256100	0.850356
H	-2.047837	-0.512233	1.754086
H	-1.906096	-1.797765	-1.022684
H	-1.091112	-2.322112	0.458467
H	1.356454	-0.943688	-1.687903
H	0.653903	-2.370331	-0.951764
H	1.507353	-1.473915	1.317717
H	2.699591	-2.120296	0.197393
H	3.349995	0.112159	-0.545814
H	3.525438	-0.028147	1.195039
H	2.592962	2.141896	0.609684
H	1.409154	1.237565	1.536466
H	0.622236	2.562539	-0.575200
H	1.356648	1.283636	-1.524514
H	-1.432654	2.341794	-0.098120

0 imaginary frequencies
E = -462.487638
H = -462.214494
G = -462.257039

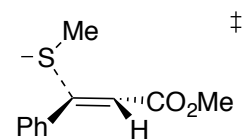
MeS⁻

C	0.000000	0.000000	-1.132869
S	0.000000	0.000000	0.710683
H	0.000000	1.018813	-1.524570
H	0.882318	-0.509406	-1.524570
H	-0.882318	-0.509406	-1.524570

0 imaginary frequencies

E = -438.209580
H = -438.168690
G = -438.192235

TS1

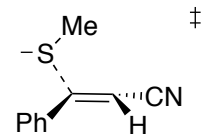


C	3.315714	-1.071636	-1.214963
C	1.968628	-0.779866	-1.036900
C	1.497200	-0.297866	0.189398
C	2.414661	-0.114100	1.227755
C	3.765119	-0.406066	1.052619
C	4.221554	-0.886894	-0.170697
C	0.062452	0.024232	0.422425
C	-0.960095	-0.642522	-0.271091
C	-2.272954	-0.654667	0.265233
O	-2.661737	-0.145219	1.318396
O	-3.163416	-1.337184	-0.530529
C	-4.502307	-1.395880	-0.056836
S	0.172663	2.232603	-0.089653
C	-1.490504	2.446663	-0.770882
H	-0.163026	0.221202	1.464536
H	-0.805012	-1.092323	-1.242290
H	-1.457693	3.057877	-1.672874
H	-1.872366	1.453562	-1.042564
H	-2.172843	2.902221	-0.052505
H	-5.060514	-1.955389	-0.804637
H	-4.556857	-1.907293	0.905619
H	-4.924608	-0.395345	0.050068
H	2.062795	0.262719	2.183019
H	4.458709	-0.259617	1.872660
H	5.271254	-1.115836	-0.311508
H	3.662365	-1.443707	-2.172340
H	1.279616	-0.918875	-1.862053

1 imaginary frequency

E = -975.658451
H = -975.427742
G = -975.483391

TS2

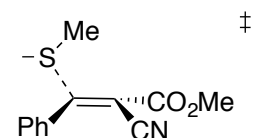


C	3.682892	-0.171810	-0.140721
C	2.867191	-0.549684	-1.206361
C	1.487125	-0.608243	-1.049168
C	0.894529	-0.290693	0.177083
C	1.721010	0.090433	1.237575
C	3.103625	0.148471	1.083307
C	-0.580797	-0.338938	0.387934
C	-1.383762	-1.224278	-0.358484
C	-2.627110	-1.634362	0.130754
N	-3.654550	-1.991247	0.551804
S	-0.982655	1.831725	-0.036197
C	-2.730124	1.674174	-0.488586

H	-0.850322	-0.258534	1.435765
H	-1.125255	-1.534722	-1.361677
H	-2.998944	2.445434	-1.210630
H	-2.876476	0.695712	-0.958750
H	-3.387499	1.753085	0.378479
H	1.272742	0.343769	2.193108
H	3.726808	0.441599	1.920321
H	4.758415	-0.128918	-0.264969
H	3.308921	-0.799830	-2.164108
H	0.868465	-0.896890	-1.891009

1 imaginary frequency
E = -840.036321
H = -839.852784
G = -839.902907

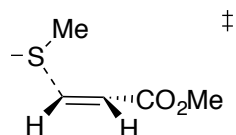
TS3



C	4.417666	-0.500076	0.059263
C	3.533161	-0.816014	-0.970969
C	2.165184	-0.653138	-0.797289
C	1.659334	-0.166322	0.415351
C	2.558550	0.169787	1.435344
C	3.926717	-0.004112	1.263529
C	0.231457	0.017700	0.690219
C	-0.822927	-0.691228	0.195915
C	-0.716170	-1.688446	-0.816264
N	-0.641586	-2.509734	-1.623061
C	-2.173252	-0.379148	0.710477
O	-2.402697	0.423791	1.584897
O	-3.127497	-1.082825	0.090936
C	-4.471120	-0.812844	0.507160
S	-0.054498	2.591235	-0.593474
C	-1.613209	2.041802	-1.370530
H	-0.007739	0.661111	1.526861
H	-1.754083	2.511691	-2.345518
H	-2.478970	2.275508	-0.747162
H	-1.598286	0.957694	-1.531752
H	-4.591035	-1.041216	1.565665
H	-4.714247	0.234272	0.327619
H	-5.100794	-1.459652	-0.096545
H	2.176662	0.567035	2.369607
H	4.607962	0.253146	2.065594
H	5.484038	-0.630325	-0.081428
H	3.912593	-1.183159	-1.917074
H	1.496178	-0.873224	-1.618759

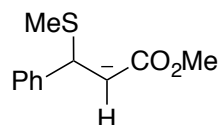
1 imaginary frequency
E = -1067.911800
H = -1067.679806
G = -1067.740843

TS19



C	1.003138	-1.503820	-0.075694
C	-0.144350	-1.027176	-0.689638
C	-1.162968	-0.394636	0.086775
S	2.671173	0.146987	0.163146
C	1.646213	1.572178	-0.284595
H	1.662213	-2.155581	-0.633415
H	0.969915	-1.682633	0.990851
H	-0.257774	-1.030009	-1.766012
H	2.126979	2.179319	-1.052068
H	1.429167	2.201512	0.579568
H	0.694865	1.199050	-0.689782
O	-2.220155	0.026201	-0.675316
O	-1.168718	-0.213089	1.301839
C	-3.275676	0.672780	0.026147
H	-4.016006	0.938423	-0.725154
H	-3.719250	0.005407	0.766490
H	-2.916037	1.571865	0.529025
1 imaginary frequency			
E = -744.638859			
H = -744.494123			
G = -744.539004			

Int1

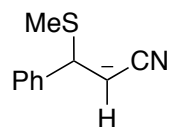


C	1.382307	2.820800	0.270618
S	0.017566	2.059854	-0.658908
C	-0.103398	0.378200	0.185676
C	-1.215598	-0.409907	-0.396445
C	-2.484876	-0.328897	0.147034
O	-2.878524	0.342396	1.127606
O	-3.420812	-1.132477	-0.517428
C	-4.726540	-1.143695	0.029525
C	1.243404	-0.300731	0.117837
H	-0.329647	0.622868	1.225858
H	-1.041757	-1.027399	-1.267419
H	1.483004	3.852943	-0.064068
H	1.160079	2.813521	1.338965
H	2.317015	2.289144	0.089050
H	-5.312742	-1.810828	-0.601573
H	-4.729611	-1.518413	1.055898
H	-5.175469	-0.148129	0.022418
C	1.987922	-0.512619	1.278202
C	3.228222	-1.149277	1.227878
C	3.742569	-1.578600	0.009819
C	3.009318	-1.364935	-1.158308
C	1.775254	-0.729039	-1.103234
H	1.593298	-0.176429	2.231881
H	3.791154	-1.304389	2.141236
H	4.706566	-2.071664	-0.033674

H	3.404705	-1.692728	-2.113070
H	1.215540	-0.553313	-2.016005

0 imaginary frequencies
E = -975.662927
H = -975.431455
G = -975.488301

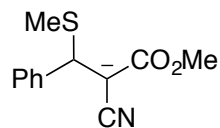
Int2



C	2.894260	-0.086354	-1.227975
C	1.508730	-0.067122	-1.112492
C	0.894713	-0.162625	0.140191
C	1.701975	-0.264723	1.273748
C	3.091094	-0.285834	1.161810
C	3.691908	-0.197787	-0.089804
C	-0.608913	-0.144698	0.268704
S	-1.053900	1.715811	-0.037949
C	-2.852095	1.593027	0.136837
C	-1.320026	-1.117944	-0.577249
C	-2.506474	-1.681601	-0.155348
N	-3.500910	-2.181071	0.225758
H	-0.880169	-0.280609	1.317153
H	-1.041680	-1.237358	-1.616552
H	-3.279778	2.570389	-0.084733
H	-3.236507	0.857331	-0.569655
H	-3.125233	1.302621	1.152528
H	1.238824	-0.331562	2.253040
H	3.701723	-0.370416	2.053437
H	4.771661	-0.213442	-0.179876
H	3.354147	-0.013285	-2.206887
H	0.894746	0.024821	-2.002116

0 imaginary frequencies
E = -840.038869
H = -839.854469
G = -839.905265

Int3

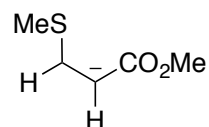


C	-1.520431	2.981550	-0.067921
S	-0.124995	2.153894	0.747289
C	-0.028311	0.598393	-0.259356
C	1.129277	-0.228409	0.217399
C	1.008582	-1.026871	1.359115
N	0.880910	-1.686519	2.309928
C	2.371576	-0.118298	-0.452060
O	2.613115	0.586685	-1.433992
O	3.357285	-0.901955	0.089778
C	4.625538	-0.835598	-0.551483
C	-1.350858	-0.139645	-0.292445
H	0.212311	0.922959	-1.272806
H	-1.624486	3.969197	0.379957
H	-1.322360	3.091921	-1.134820
H	-2.441785	2.418030	0.081077

H	5.275924	-1.505462	0.006787
H	4.556961	-1.163675	-1.589596
H	5.025111	0.179055	-0.524723
C	-1.852908	-0.581401	-1.517768
C	-3.048316	-1.293433	-1.585709
C	-3.761315	-1.570091	-0.423291
C	-3.271355	-1.127787	0.804064
C	-2.077898	-0.415755	0.868071
H	-1.301873	-0.365061	-2.427552
H	-3.423704	-1.625249	-2.546877
H	-4.694034	-2.119516	-0.472534
H	-3.823758	-1.333756	1.713714
H	-1.709429	-0.058867	1.823278

0 imaginary frequencies
E = -1067.937219
H = -1067.704059
G = -1067.764232

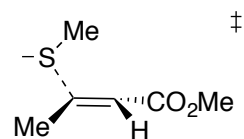
Int19



C	1.179592	-1.112473	0.499447
C	-0.098026	-1.075661	-0.233851
C	-1.134793	-0.257662	0.178563
O	-1.199868	0.502070	1.172112
O	-2.258403	-0.330741	-0.661312
C	-3.386961	0.417103	-0.250450
S	2.582541	-0.084520	-0.233558
C	1.784329	1.541508	-0.214911
H	1.632881	-2.105580	0.534377
H	1.060117	-0.750969	1.521897
H	-0.214167	-1.652765	-1.142538
H	2.374346	2.218960	-0.830989
H	1.722217	1.933608	0.800331
H	0.780937	1.443304	-0.631625
H	-4.152554	0.251276	-1.007892
H	-3.759649	0.082754	0.720881
H	-3.163465	1.484204	-0.186701

0 imaginary frequencies
E = -744.645545
H = -744.499855
G = -744.544440

TS24

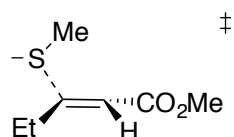


C	-2.081331	2.030730	-0.194244
C	-1.033395	1.052782	0.273767
C	0.159784	0.925974	-0.432795
C	1.301691	0.335065	0.176824
O	1.402266	-0.096000	1.325265
O	2.380938	0.276592	-0.670696
C	3.561097	-0.310014	-0.137101

S	-2.319298	-0.893772	0.131607
C	-1.032837	-2.035793	-0.439113
H	0.220033	1.192016	-1.481715
H	-0.948051	0.951485	1.349742
H	-2.213274	1.969443	-1.276249
H	-1.762317	3.048883	0.053444
H	-3.045618	1.851145	0.282862
H	-0.676581	-2.684671	0.362173
H	-1.397700	-2.654709	-1.259314
H	-0.188476	-1.439702	-0.809954
H	4.300425	-0.274422	-0.934415
H	3.920957	0.248984	0.728080
H	3.383693	-1.345308	0.159050

1 imaginary frequency
E = -783.945524
H = -783.771334
G = -783.818400

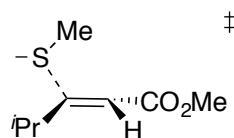
TS25



C	-1.404602	-0.373521	0.164112
O	-1.604250	-0.014808	1.324203
O	-2.469432	-0.574101	-0.679826
C	-3.756246	-0.335822	-0.123807
H	-3.946330	-0.997193	0.723026
H	-3.853347	0.699473	0.207254
H	-4.469297	-0.538976	-0.919961
C	-0.153599	-0.630346	-0.463966
H	-0.153455	-0.879786	-1.519124
C	1.039486	-0.469466	0.233757
H	0.944974	-0.422562	1.314150
C	2.296733	-1.145641	-0.261304
H	2.392564	-0.983422	-1.338737
H	3.171780	-0.692692	0.210546
C	2.274173	-2.648298	0.041128
H	2.145651	-2.826345	1.112211
H	3.209247	-3.120064	-0.269301
H	1.450773	-3.138152	-0.481913
S	1.791451	1.748791	0.139194
C	0.249314	2.534143	-0.398933
H	-0.416710	1.749001	-0.781205
H	-0.254896	3.049764	0.419665
H	0.433722	3.245265	-1.204648

1 imaginary frequency
E = -823.248900
H = -823.044788
G = -823.096940

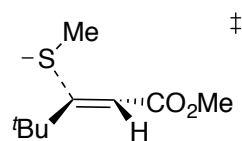
TS26



C	1.596868	-0.442594	-0.184990
O	1.926786	-0.062040	-1.309107
O	2.567135	-0.788605	0.726751
C	3.911498	-0.670539	0.280802
H	4.097600	-1.313453	-0.581059
H	4.145801	0.360421	0.010059
H	4.533535	-0.983681	1.116792
C	0.282831	-0.587589	0.336210
H	0.185721	-0.861811	1.378641
C	-0.826868	-0.262387	-0.447176
H	-0.625611	-0.202217	-1.512088
C	-2.201257	-0.827097	-0.129119
H	-2.941834	-0.203697	-0.639782
C	-2.523386	-0.834317	1.363083
H	-2.370812	0.155885	1.797092
H	-3.562510	-1.130552	1.526393
H	-1.889010	-1.548539	1.895265
C	-2.309688	-2.245521	-0.707406
H	-2.094334	-2.256166	-1.778853
H	-3.318063	-2.641037	-0.558607
H	-1.602382	-2.914981	-0.210966
S	-1.303130	2.001347	-0.353138
C	0.200615	2.582140	0.472756
H	0.739926	1.701554	0.847709
H	0.855992	3.126579	-0.208521
H	-0.038993	3.222721	1.322030

l imaginary frequency
 E = -862.554011
 H = -862.320424
 G = -862.374239

TS27

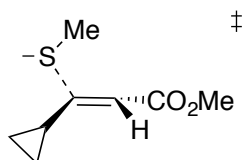


C	4.144591	-0.730533	0.124798
O	2.825262	-0.839272	0.641370
C	1.810907	-0.460541	-0.209731
C	0.527624	-0.586878	0.381665
C	-0.617682	-0.230029	-0.336659
C	-1.984243	-0.811536	0.029359
C	-1.930954	-2.310186	-0.330229
O	2.086355	-0.067277	-1.344934
C	-2.304082	-0.668454	1.518801
S	-0.967363	2.065695	-0.204464
C	0.617124	2.548793	0.527156
H	4.276412	-1.361719	-0.755575
H	4.377419	0.301666	-0.142741
H	4.807222	-1.064084	0.920840
H	0.482018	-0.882607	1.421928
H	-0.470500	-0.164307	-1.411229
C	-3.102300	-0.170891	-0.801320
H	-2.298904	0.384489	1.807673
H	-3.293820	-1.084978	1.727888
H	-1.580937	-1.205053	2.137591
H	-1.684961	-2.449136	-1.387278
H	-2.904388	-2.773400	-0.143370
H	-1.176788	-2.826059	0.266807

H	1.112092	1.643770	0.902684
H	1.274086	3.026803	-0.200882
H	0.464524	3.227706	1.366792
H	-4.034834	-0.724978	-0.661179
H	-3.276214	0.865053	-0.506148
H	-2.853480	-0.190354	-1.866912

1 imaginary frequency
E = -901.858926
H = -901.596273
G = -901.651262

TS28



C	-1.637865	-0.522278	0.129293
O	-1.795229	-0.273747	1.325187
O	-2.732235	-0.757212	-0.667876
C	-3.997833	-0.681109	-0.024444
H	-4.078249	-1.421547	0.772989
H	-4.738601	-0.884940	-0.794758
H	-4.163305	0.311857	0.396975
C	-0.412256	-0.611448	-0.583806
H	-0.449818	-0.776622	-1.653800
C	0.798913	-0.376197	0.066975
H	0.767299	-0.424090	1.151379
S	1.296929	1.904338	0.108212
C	-0.341708	2.567399	-0.294283
H	-0.846377	2.973970	0.583355
H	-0.270493	3.346323	-1.054089
H	-0.950641	1.748910	-0.700437
C	2.072850	-0.866291	-0.525472
H	2.150068	-0.764887	-1.602404
C	3.346088	-0.759258	0.257588
C	2.696593	-2.104205	0.077105
H	4.262881	-0.558666	-0.281193
H	3.276163	-0.296581	1.235189
H	3.162974	-2.813418	-0.594382
H	2.198266	-2.541710	0.933564

1 imaginary frequency
E = -861.321780
H = -861.111458
G = -861.162841

Compounds related to Figure 3 (Isodesmic reactions)

Calculations in this section were performed with CBS-QB3. Underneath the coordinates of each species are listed the following energies:

- CBS-QB3 total electronic energy at 0 K including zero-point energy (E)
- CBS-QB3 enthalpy at 298.15 K (H)

Ethane

C	0.000000	0.000000	0.765136
C	0.000000	0.000000	-0.765136
H	0.881988	0.509216	-1.163447
H	-0.881988	0.509216	-1.163447
H	0.000000	-1.018432	-1.163447
H	0.000000	1.018432	1.163447
H	0.881988	-0.509216	1.163447
H	-0.881988	-0.509216	1.163447

0 imaginary frequencies
E = -79.630570
H = -79.626126

Acrylonitrile

C	-0.578384	-0.534990	0.000000
C	0.000000	0.770093	0.000000
C	1.317079	0.984285	0.000000
H	-0.703387	1.596344	0.000000
H	1.712031	1.992514	0.000000
H	2.027253	0.166418	0.000000
N	-1.066867	-1.581658	0.000000

0 imaginary frequencies
E = -170.538705
H = -170.533604

Cyanoethane

C	0.000000	0.808350	0.000000
C	-1.518507	0.563388	0.000000
H	-1.823672	0.000979	-0.884090
H	-2.046409	1.519000	0.000000
H	-1.823672	0.000979	0.884090
H	0.294350	1.391595	-0.877731
C	0.773378	-0.432523	0.000000
H	0.294350	1.391595	0.877731
N	1.367975	-1.419920	0.000000

0 imaginary frequencies
E = -171.751156
H = -171.745511

Ethylene

C	0.000000	0.000000	0.663610
C	0.000000	0.000000	-0.663610
H	0.000000	0.922662	1.234557
H	0.000000	-0.922662	1.234557
H	0.000000	0.922662	-1.234557

H 0.000000 -0.922662 -1.234557
 0 imaginary frequencies
 E = -78.416649
 H = -78.412655

1,1-Dicyanoethylene

C 0.000000 0.000000 1.745478
 C 0.000000 0.000000 0.403186
 H 0.000000 0.930365 2.297884
 H 0.000000 -0.930365 2.297884
 C 0.000000 1.222226 -0.348946
 C 0.000000 -1.222226 -0.348946
 N 0.000000 -2.206946 -0.950029
 N 0.000000 2.206946 -0.950029
 0 imaginary frequencies
 E = -262.651700
 H = -262.645160

1,1-Dicyanoethane

C -0.246491 0.486010 0.000000
 C 0.959825 1.457628 0.000000
 H 0.919966 2.087858 0.888831
 H 0.919966 2.087858 -0.888831
 H 1.897304 0.901944 0.000000
 H -1.174296 1.070123 0.000000
 C -0.263190 -0.349420 1.209562
 C -0.263190 -0.349420 -1.209562
 N -0.263190 -0.972612 2.177715
 N -0.263190 -0.972612 -2.177715
 0 imaginary frequencies
 E = -263.859653
 H = -263.852463

Styrene

C 0.000000 0.558994 0.000000
 C -1.006446 -0.421075 0.000000
 C -0.685926 -1.772327 0.000000
 C 0.648375 -2.182339 0.000000
 C 1.658606 -1.224901 0.000000
 C 1.335351 0.129081 0.000000
 H -2.048977 -0.125080 0.000000
 H -1.479156 -2.511793 0.000000
 H 0.894733 -3.238045 0.000000
 H 2.698876 -1.530865 0.000000
 H 2.127816 0.870529 0.000000
 C -0.281412 2.003662 0.000000
 C -1.474688 2.602967 0.000000
 H 0.604894 2.634582 0.000000
 H -1.552479 3.683407 0.000000
 H -2.408867 2.052894 0.000000
 0 imaginary frequencies
 E = -309.039042
 H = -309.031180

Phenylethane

C 0.518786 1.928631 0.000000
 C 2.038518 2.104431 0.000000
 H 2.296160 3.166385 0.000000
 H 2.497775 1.653740 -0.884184

H	2.497775	1.653740	0.884184
H	0.100166	2.444816	-0.871991
H	0.100166	2.444816	0.871991
C	0.000000	0.499533	0.000000
C	-1.384762	0.280363	0.000000
C	-1.912485	-1.005758	0.000000
C	-1.061288	-2.111174	0.000000
C	0.314648	-1.910319	0.000000
C	0.839545	-0.616748	0.000000
H	-2.056299	1.134134	0.000000
H	-2.987874	-1.147280	0.000000
H	-1.468497	-3.115993	0.000000
H	0.987705	-2.760961	0.000000
H	1.915149	-0.487141	0.000000

0 imaginary frequencies
E = -310.244641
H = -310.236285