Supporting Information

Amine Induced Retardation of the Radical-Mediated Thiol-Ene Reaction *via* the Formation of Metastable Disulfide Radical Anions

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Table of Contents

Sections **Page No.**

1: General Experimental Procedures For FTIR Kinetic Studies

Reaction formulations were prepared with stoichiometric concentrations of thiol and alkene functional groups (3 M) in ethylene glycol diacetate: methanol (1:1) with the photoinitiator 2,2-dimethoxy-2-phenylacetophenone (0.03 M). Formulations were then laminated between NaCl plates separated by a 0.051 mm plastic spacer. Thiol (2570 cm^{-1}, S—H stretch) and alkene (3050 cm^{-1}, C=C—H stretch) conversions were monitored in real-time in the mid IR (Nicolet Magna-IR 750 series II FTIR spectrometer) at a collection rate of ~1 scan per second and a resolution of 1 cm^{-1}. Samples were then irradiated with 365-nm light at an intensity of 2.5 mW cm^{-2} (Acticure 4000 light source) until the functional group absorption peak was no longer decreasing; irradiation intensities were measured with a NIST Traceable Radiometer Photometer, model IL1400A. A representative IR spectrum before and after irradiation of the butyl 3-mercaptopropionate (**MP**) with trimethylolpropane diallyl ether (**E1**) reaction is shown in **Figure S1.**

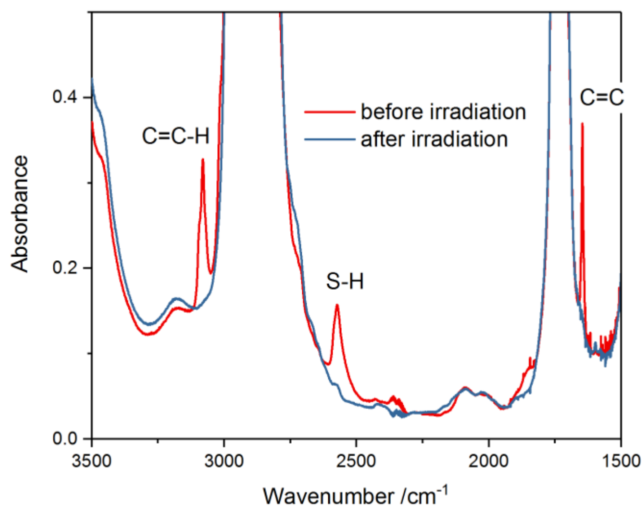


Figure S1. FTIR spectrum of the TEC reaction between **MP** (3 M) and **E1** (1.5 M) before and after irradiation for 5 min with 2.5 mW cm^{-2} UV-light (365 nm). The reaction was formulated with DMPA (0.03 M) and diluted with ethylene glycol diacetate: methanol (1:1).

2: Effect Of Amines On Thioacetic Acid Thiol-Ene Reactions

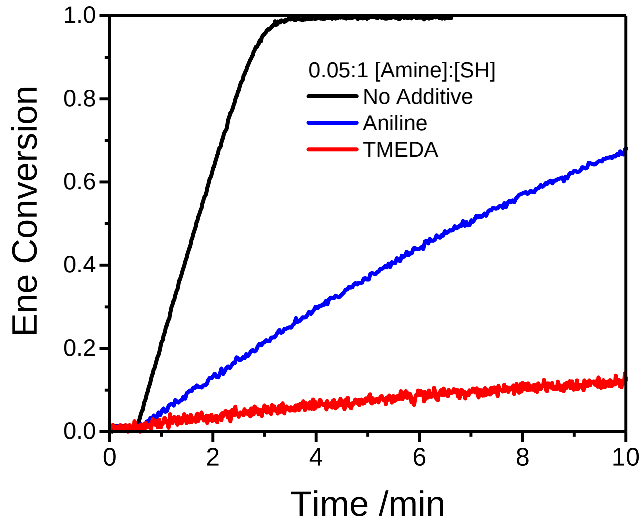
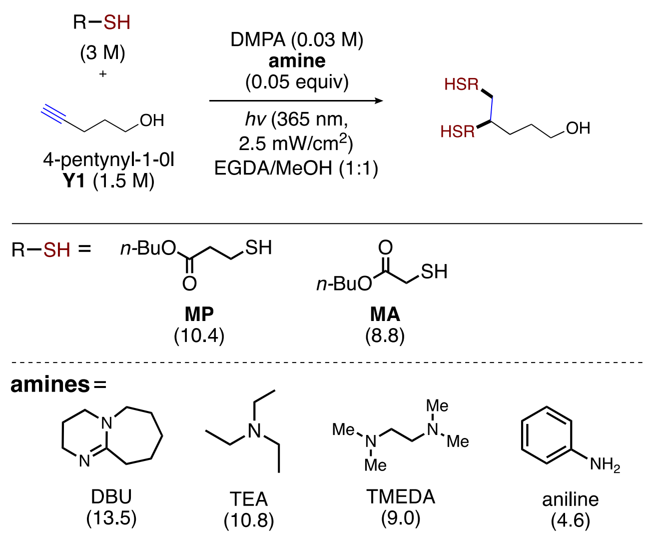


Figure S2. Ene conversion versus time for the TEC reaction between **TA** and **E1** (1:1 [SH]:[C=C]) in the presence of amines with varying basicity. The reactions were formulated with **TA** (3 M), **E1** (1.5 M), DMPA (0.03 M) with no amine, aniline, or TMEDA (0.05:1 [Amine]:[SH]). Samples were irradiated for 10 min with 2.5 mW cm^{-2} UV-light (365 nm) and conversions were determined from the depletion of the peak centered at 3050 cm^{-1} corresponding to the alkene functional group.

3: Amine Effects On Thiol-Yne Reactions

Scheme S1. Thiol-Yne Reactions in the Presence of Amines



General procedure for thiol-yne reactions: Reaction formulations were prepared with the thiols **MP** or **MA** (3 M) and **Y1** (1.5 M) in ethylene glycol diacetate: methanol (1:1) with DMPA (0.03 M) (see **Scheme S1**). Formulations were then laminated between NaCl plates separated by a 0.051 mm plastic spacer. Thiol (2570 cm^{-1}, S—H stretch) and alkyne (3330 cm^{-1}, C≡C—H stretch) conversions were monitored in real-time in the mid IR (Nicolet Magna-IR 750 series II FTIR spectrometer) at a collection rate of ~1 scan per second and a resolution of 1 cm^{-1}. Samples were irradiated with 365-nm light at an intensity of 10 mW cm^{-2} (Acticure 4000 light source) until the functional group absorption peak was no longer decreasing; irradiation intensities were measured with a NIST Traceable Radiometer Photometer, model IL1400A. A representative IR spectrum before and after irradiation of the **MP/Y1** reaction is shown in **Figure S3.** Conversion profiles for thiol-yne reactions in the presence of amines are shown in **Figure S4** for **MP/Y1** reactions and **Figure S5** for **MA/Y1** reactions.

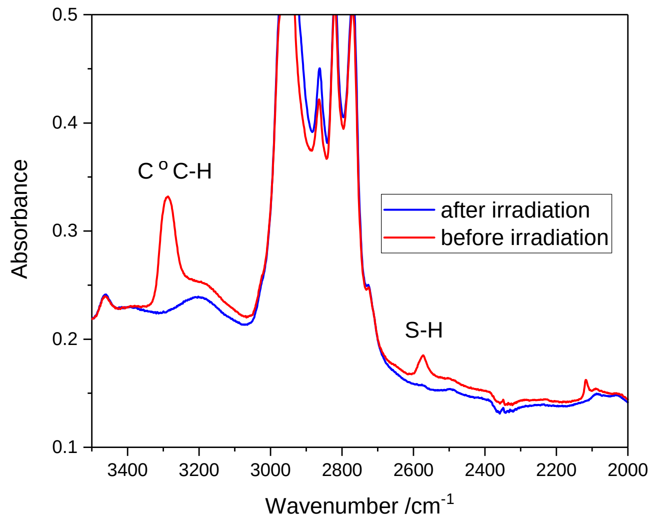


Figure S3. FTIR spectrum of the thiol-yne reaction between **MP** (3 M) and **Y1** (1.5 M) before and after irradiation for 5 min with 10 mW cm^{-2} UV-light (365 nm). The reaction was formulated with DMPA (0.03 M) and diluted with ethylene glycol diacetate.

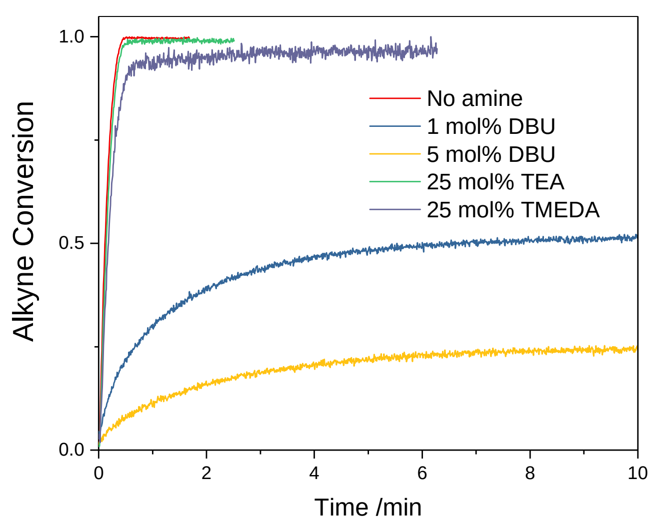


Figure S4. Ene conversion versus time for the thiol-yne reaction between **MP** and **Y1** in the presence of amines with varying basicity. The reactions were formulated with **MP** (3 M), **Y1** (1.5 M), DMPA (0.03 M) with no amine, 1 mol% DBU, 5 mol% DBU, 25 mol% TEA, and 25 mol% TMEDA with respect to **MP**. Samples were irradiated for 10 min with 10 mW cm^{-2} UV-light (365 nm) and conversions were determined from the depletion of the peak centered at 3330 cm^{-1} corresponding to the alkyne functional group.

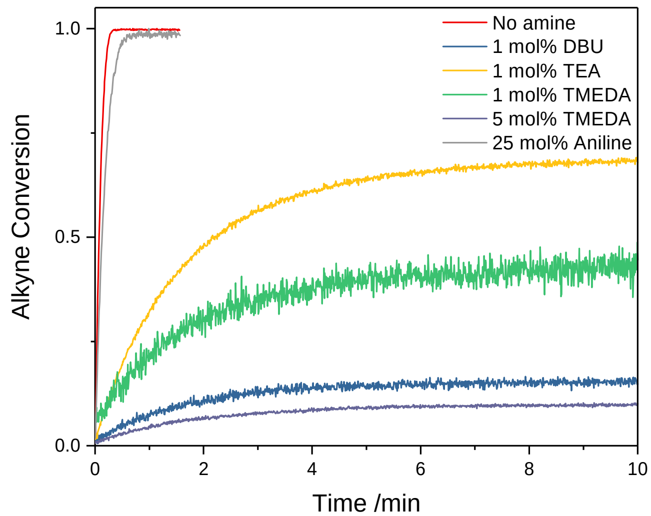


Figure S5. Ene conversion versus time for the thiol-yne reaction between **MA** and **Y1** in the presence of amines with varying basicity. The reactions were formulated with **MA** (3 M), **Y1** (1.5 M), DMPA (0.03 M) with no amine, 1 mol% DBU, 1 mol% TEA, 1 mol% TMEDA, 5 mol% TMEDA, and 25 mol% aniline with respect to **MA**. Samples were irradiated for 10 min with 10 mW cm^{-2} UV-light (365 nm) and conversions were determined from the depletion of the peak centered at 3330 cm^{-1} corresponding to the alkyne functional group.

4: Anion Effects On MP/E1 TEC Kinetics

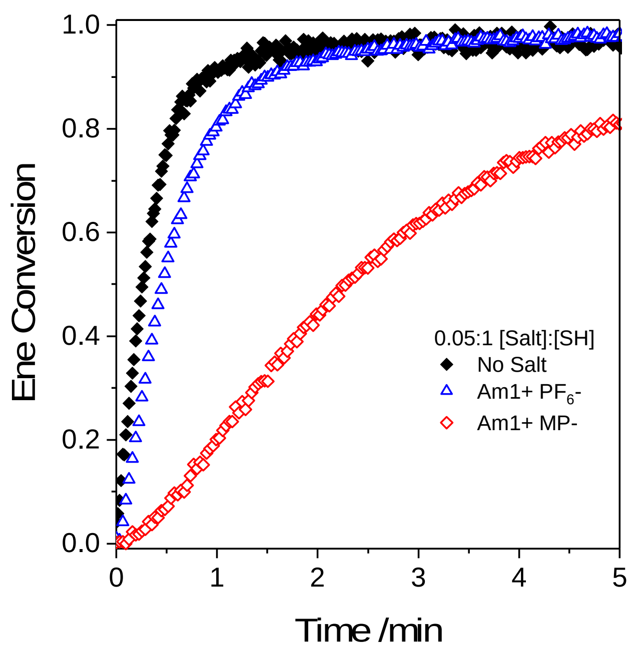


Figure S6. Ene conversion versus time for the TEC reaction between **MP** and **E1** (1:1 [SH]:[C=C]) in the presence of salt additives. The reaction samples were formulated with no salt, [**Am1**$^+$ PF_6^-], and [**Am1**$^+$ **MP**$^-$] (0.05:1 [additive]:[SH]).

5: Amine And Thiolate Effects On Thiol-Norbornene Kinetics

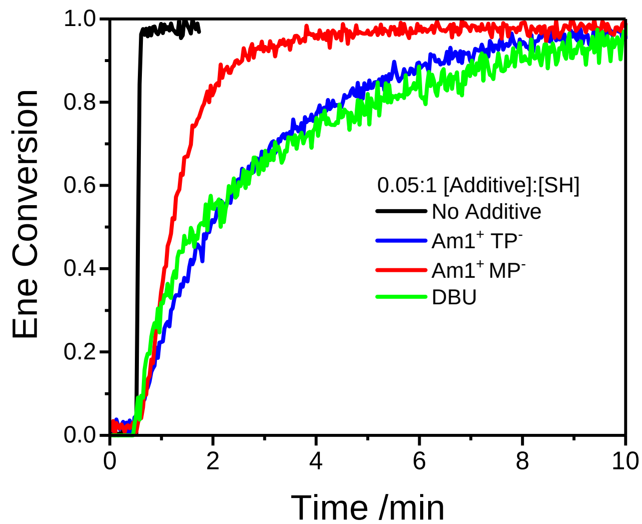


Figure S7. Ene conversion versus time plot for the TEC reaction between **MP** and **E2** (1:1 [SH]:[C=C]) in the presence of amines with varying basicity. The reactions were formulated with **MP** (3 M), **E2** (3 M), with no amine, DBU, or TEA (0.05:1 [Amine]:[SH]). Samples were irradiated for 10 min with 2.5 mW cm^{-2} UV-light (365 nm) and conversions were determined from the depletion of the peak centered at 3050 cm^{-1} corresponding to the alkene functional group.

6: Amine And Thiolate Effects On Thiol-Vinyl Siloxane Kinetics

At reaction steady-state (i.e. when conversion increases linearly with time), the quasi-steady state approximation for reactive intermediates is applicable for both carbon and thiyl radicals in radical-mediated thiol-ene reactions. Under these conditions the overall thiol-ene reaction may be described by the following set of kinetic equations:[1]

$$R_i = -\frac{d[I]}{dt} = \frac{2.303 f \epsilon [I] I_0 \lambda}{N_{AV} hc} \quad (1)$$

$$\frac{d[SH]}{dt} = -k_{CT}[SH][C\cdot] \quad (2)$$

$$\frac{d[C=C]}{dt} = -k_p[C=C][S\cdot] \quad (3)$$

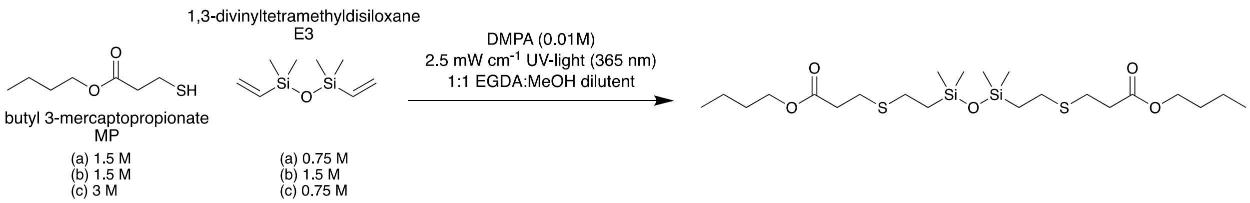
$$\frac{d[S\cdot]}{dt} = R_i - R_t(S\cdot) + k_{CT}[SH][C\cdot] - k_p[C=C][S\cdot] \quad (4)$$

$$\frac{d[C\cdot]}{dt} = R_i - R_t(C\cdot) - k_{CT}[SH][C\cdot] + k_p[C=C][S\cdot] \quad (5)$$

$$R_t(S\cdot) = 2k_{t1}[S\cdot]^2 + k_{t2}[S\cdot][C\cdot] \quad (6)$$

$$R_t(C\cdot) = k_{t2}[S\cdot][C\cdot] + 2k_{t3}[C\cdot]^2 \quad (7)$$

Where [S·] and [C·] are the thiyl radical and carbon radical, respectively, [I] is the concentration of photoinitiator, [SH] and [C=C] are the concentrations of thiol and alkene functional groups, respectively, R_i and R_t is the rate of radical generation from initiation and radical termination, respectively, f is the initiator efficiency (assumed to be 0.3), ε is the molar absorptivity 150 L mol^{-1} cm^{-1} of DMPA for 365 nm light, I_0 is the light intensity 2.5 mW cm^{-2}, λ is the wavelength 365 nm, N_{AV} is Avogadro's number, *h* is Plank's constant, *c* is the speed of light, and k_{t1}, k_{t2}, and k_{t3} are the termination rate constants for the three combinations possible for radical-radical recombination. Combining equations (2) and (3) affords the relation k_p/k_{CT} = [C·]/[S·], which allows for us to estimate the relative fraction of thiol-ene radicals that are thiyl radicals during the steady-state kinetic regime. For mercaptopropionate-type thiols reacting with allyl ether-type and norbornene-type alkenes, this ratio was determined to be [C·]/[S·] = 10 and 1.0, respectively.[1] In order to determine this ratio for the TEC reaction between butyl 3-mercaptopropionate and 1,3-divinylsiloxane, reactions with varying concentrations of thiol and alkene functional groups were carried out and the reaction kinetics were fit to a model simulation generated by solving equations (1-7) as a function of time.



Kinetic data for the determination of the k_P/k_{CT} ratio for the MP/E3 TEC reaction were obtained by FTIR. Samples were formulated with either 1.5 M or 3 M **MP** and 0.75 M or 1.5 M **E3** in ethylene glycol diacetate: methanol (1:1) and 0.01 M photoinitiator. Reactions were then irradiated with 365 nm UV-light at an intensity of 2.5 mW cm^{-2} (see the above scheme for details). The reaction kinetics were then simulated using the ODE45 differential equation solver in MATLAB R2016a and fit to the conversion data. Simulation and reaction conversion data are shown in **Figure S8**.

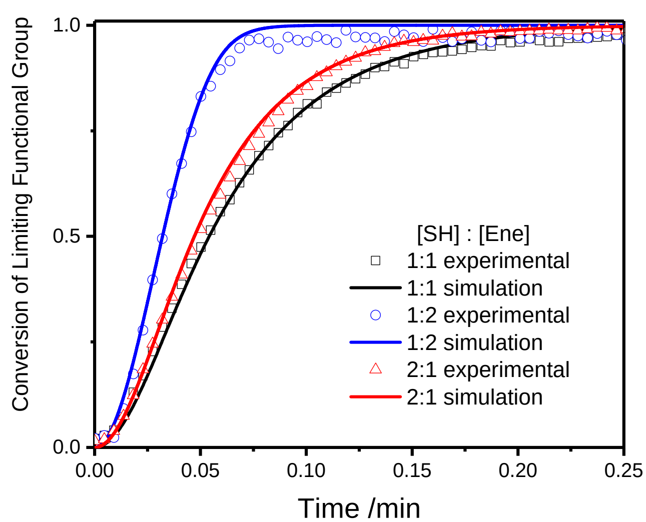


Figure S8. Model predictions and experimental data for functional group conversion versus time of **MP** and **E3** TEC reactions. Conversions of the limiting functional group for 1:1 (1.5 M), 2:1 (3:1.5 M), and 1:2 (1.5:3 M) ratios of thiol to vinyl functional groups. Samples contain 0.015 M DMPA and were irradiated at 1.0 mW cm^{-2}. Optimized kinetic parameters used for modeling are k_p = 1.68 x 10^6 M^{-1} sec^{-1} [95% CI 1.55-1.83 x 10^6] and k_{CT} = 6.76 x 10^6 M^{-1} sec^{-1} [95% CI 6.50-6.84 x 10^6] and k_{t1}, k_{t2}, k_{t3} = 1 x 10^6 M^{-1} sec^{-1}, which were taken from reference 1.

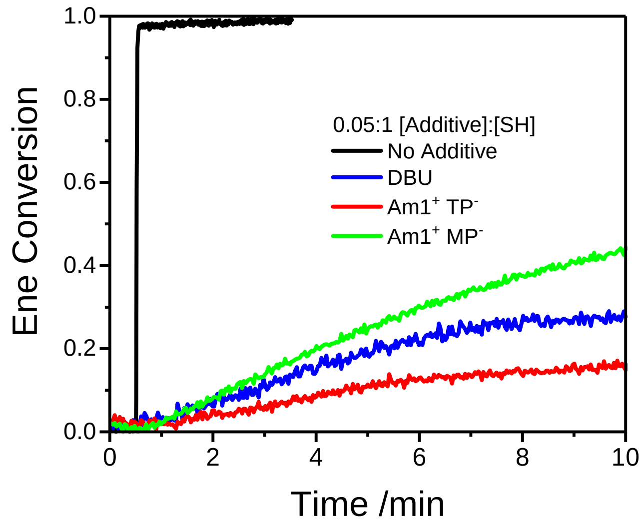


Figure S9. Ene conversion versus time plot for the thiol-ene coupling reaction between **MP** and **E3** (1:1 [SH]:[C=C]) in the presence of amines with varying basicity. The reactions were formulated with **MP** (3 M), **E3** (1.5 M), with no amine, DBU, or TEA (0.05:1 [Amine]:[SH]). Samples were irradiated for 10 min with 2.5 mW cm^{-2} UV-light (365 nm) and conversions were determined from the depletion of the peak centered at 3050 cm^{-1} corresponding to the alkene functional group.

7: Amine Effects On MA/E1 TEC Reaction With No Initiator

Interaction between amine and/or thiolate anion with the photoinitiator was considered as a potential cause of retardation if these species react with 2,2-dimethoxy-2-phenylacetophenone to reduce the effective initiator concentration or react with the initiators excited state or its radical fragments more rapidly than the reactants leading to reductions in steady-state thiol-ene radicals. Previous work in our group has shown that radical TEC reactions can be carried out by direct irradiation of the thiol-ene formulation.[2,3] UV-light centered around 254-nm induces the homolytic cleavage of the S—H bond resulting in a thiyl radical while UV-light around 365-nm activates the alkene functional group through a currently unknown mechanism. To determine if retardation persists without an initiator, the reaction between **MA** (3 M) and **E1** (1.5 M) in ethylene glycol diacetate: methanol (1:1) was irradiated with UV-light (no filter) in the presence of no additive, TEA, and TMEDA (0.05 equiv.) The runs with no amine reached a conversion ~55% after 20 minutes of irradiation, while trials with either amine present did not show any reaction. Thus we concluded that the retardation event is independent of the initiation method. Conversion profiles are shown in **Figure S10.**

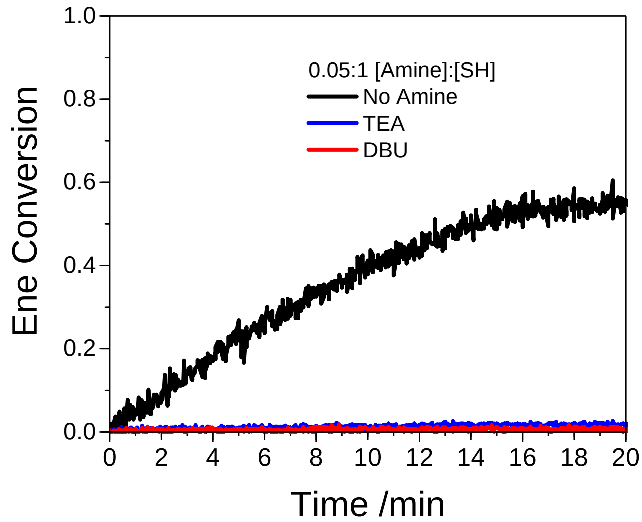


Figure S10. Ene conversion versus time for the TEC reaction between **MA** and **E1** (1:1 [SH]:[C=C]) in the presence of amines with varying basicity. The reactions were formulated with **MA** (3 M), **E1** (1.5 M), with no amine, DBU, or TEA (0.05:1 [Amine]:[SH]). Samples were irradiated for 20 min with 50 mW cm^{-2} UV-light (no filter) and conversions were determined from the depletion of the peak centered at 3050 cm^{-1} corresponding to the alkene functional group.

8: Detailed Computational Methods

Electronic structure calculations were performed using the GAUSSIAN 09 computational software package.[4] We defined the reference state for the reaction enthalpies, entropies, and Gibbs free energies (ΔG°) for the various reactions examined within this study as the separated reactants in solution as is appropriate for solution-phase bimolecular reactions.[5] We computed reactant and product geometries for the thermodynamic analysis of disulfide radical anion (DRA) formation, electron densities for the population analysis of DRAs, and reorganization energies (λ) for the associative electron transfer (ET) reactions of thiolate anions and thiyl radicals using DFT based on the LC-*w*PBE density functional,[6] 6-31+G** basis set[7] and the ethyl acetate (EtOAc) conductor-like polarized continuum solvation model (CPCM).[8] We chose the LC-*w*PBE functional because it was shown to predict intersulfur distances, adiabatic electron affinities and UV/Vis spectra of DRA molecules accurately[9,10] relative to over 50 tested functionals.[11] Therefore, it should provide a reliable description of the molecular structures and energetics computed in this study. To further improve the reported energies, we performed LC-*w*PBE/aug-cc-PVTZ single-point energy calculations at the LC-*w*PBE/6-31+G** geometries.[12,13]

An adequate treatment of solvent is essential for describing reactions involving anionic species and ET. We employed the CPCM to treat the solute-solvent electrostatic and non-electrostatic interactions.[8] We modeled the resin state with EtOAc in place of ethylene glycol diacetate because of the structural similarity between the two solvent molecules. We calculated λ_{total} using computed equilibrium and non-equilibrium Gibbs free energies in solution as described by Cossi and Barone.[14,15] Vibrational frequencies were calculated at the LC-*w*PBE/6-31+G** level of theory to verify that the optimized reactant and product geometries have only real vibrational modes and to compute zero-point energies (ZPE), thermal corrections and entropies at 298 K. Thermal corrections to Gibbs free energies were calculated at the LC-*w*PBE/6-31+G** level of theory and the electronic energies at the LC-*w*PBE/aug-cc-PVTZ level of theory to obtain accurate ΔG°s for the reactions studied.

The commonly employed rigid rotor, harmonic oscillator, and ideal gas approximations for calculating entropies typically overestimate the entropies of solution-phase reactions because the ideal gas partition functions do not explicitly account for hindered translation, rotation, and vibration of the solvated species.[16] Translational entropies are quenched in solution to a greater degree than rotational, and vibrational entropies, and are therefore the largest source of error in the ideal gas partition function. Our approach to correct these errors involves subtracting the translational entropy contributions ($-TS^{\circ}_{Trans}$) from the free energies of the reactants and products in solution, as recommended by Tanaka and coworkers[17] to provide a better prediction of the free energies. This approach is particularly important in DRA formation as the number of species changes from two molecules to one. Otherwise, translational entropies would be significantly overestimated.

Atomic polar tensor population analysis was used to analyze electron density distributions because it is independent of the basis set and exhibits good performance for diverse classes of molecules.[18,19] The bond dissociation energy (BDE) is defined to be the standard enthalpy change for the gas phase homolytic dissociation of disulfide molecules into two thiyl radicals. For the BDE study, we optimized reactant and product geometries based on the B3P86 density functional[20] and 6-31G* basis set in gas phase because this level of theory was shown to reproduce the BDEs of disulfide molecules within experimental error.

8.1: The general description of dissociative electron transfer model by Savéant[22,23]

This model attempts to elucidate the kinetics of electron transfer in the liquid phase which involves the dissociation or formation of bonds. It was developed from the conventional Marcus theory of electron transfer,[24] hence preserving a quadratic driving force-free energy relationship. $\boldsymbol{\Delta G^{\ddagger}}$ is the free energy of activation for the forward reaction that is dissociative by convention. $\boldsymbol{\Delta G_0^{\ddagger}}$ is the free energy of activation at zero driving force. $\boldsymbol{\Delta G^{0}}$ is the free energy of the reaction. $\boldsymbol{BDE}$ is the energy required for homolytic bond dissociation of a molecule in the gas phase before the electron transfer. The reorganization energy ($\boldsymbol{\lambda_{tot}}$) is the sum of the thermally induced reorganization of the solvent molecules and the internal reorganization involving the changes in bond lengths and angles accompanying the electron transfer.

$$RS\text{-}SR' + e^{-} \leftrightarrow [RSSR']^{\bullet -} \leftrightarrow RS\bullet + R'S^{-}$$

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger}\left(1 + \frac{\Delta G^{0}}{4\Delta G_0^{\ddagger}}\right)^{2} \qquad \Delta G_0^{\ddagger} = \frac{BDE + \lambda_{tot}}{4}$$

Table S1. Comparison of the geometric relaxations of **TP** and **TA** upon ET

	TP⁻	**TP•**	**|Δ(TP⁻- TP•|**	**TA⁻**	**TA•**	**|Δ(TA⁻- TA•|**
D(C-S)	1.75619	1.756	0.00019	1.73181	1.76276	0.03095
D(C=O)				1.23451	1.21222	0.02229
D($C_α$-$C_β$)	1.39521	1.40548	0.01027	1.51859	1.49759	0.021
D($C_β$-H)	1.08595	1.08686	0.00091	1.09177	1.09004	0.00173
D($C_β$-$C_γ$)	1.38844	1.38883	0.00039			
A(S-C=O)				124.504	118.476	6.028
A(S-$C_α$-$C_β$)	120.072	121.734	1.662			
Dihed(S-$C_α$-$C_β$-H)	0	0	0	179.887	168.171	11.716

D = distance between two nuclei in angstroms, A = angle formed between three consecutive nuclei in degrees, Dihed = dihedral angel formed by four nuclei in degrees.

9: SI references

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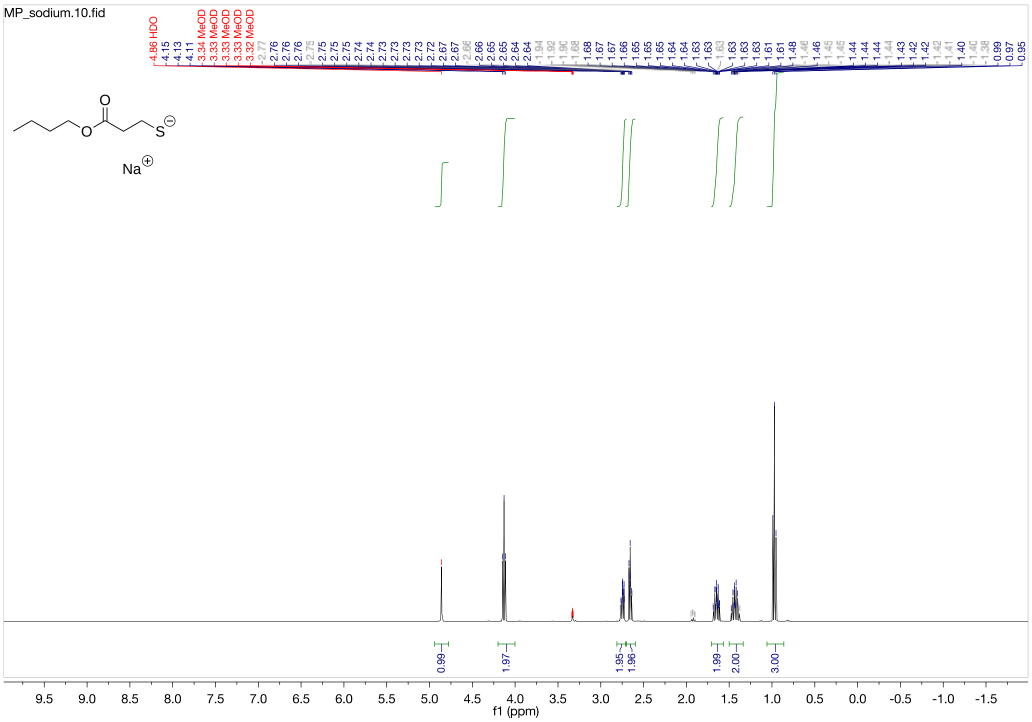
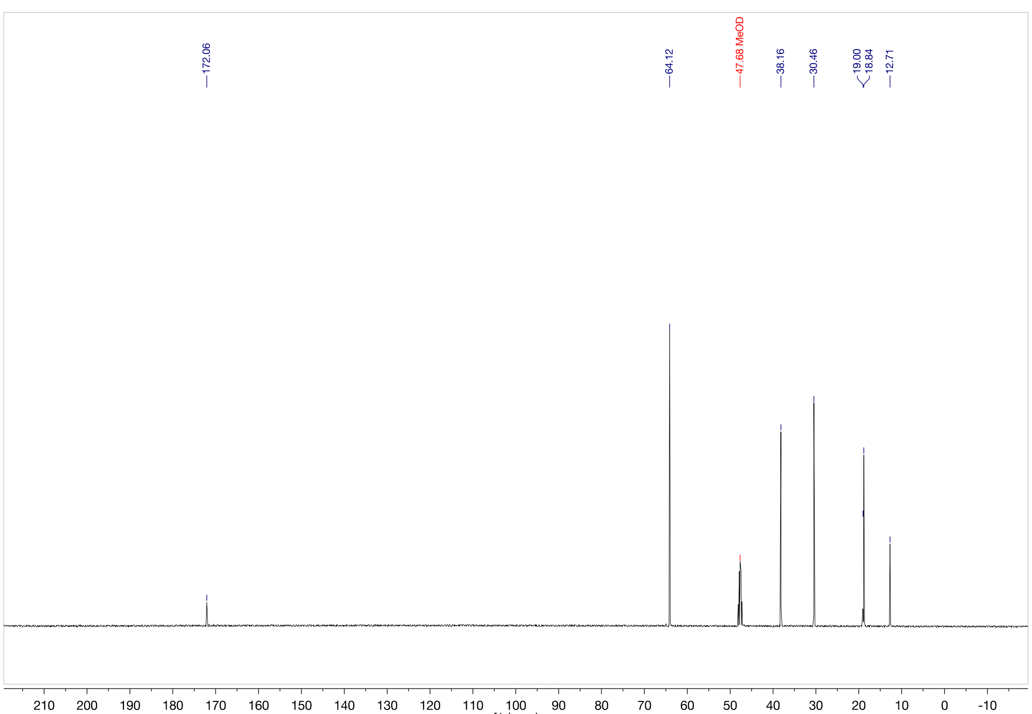
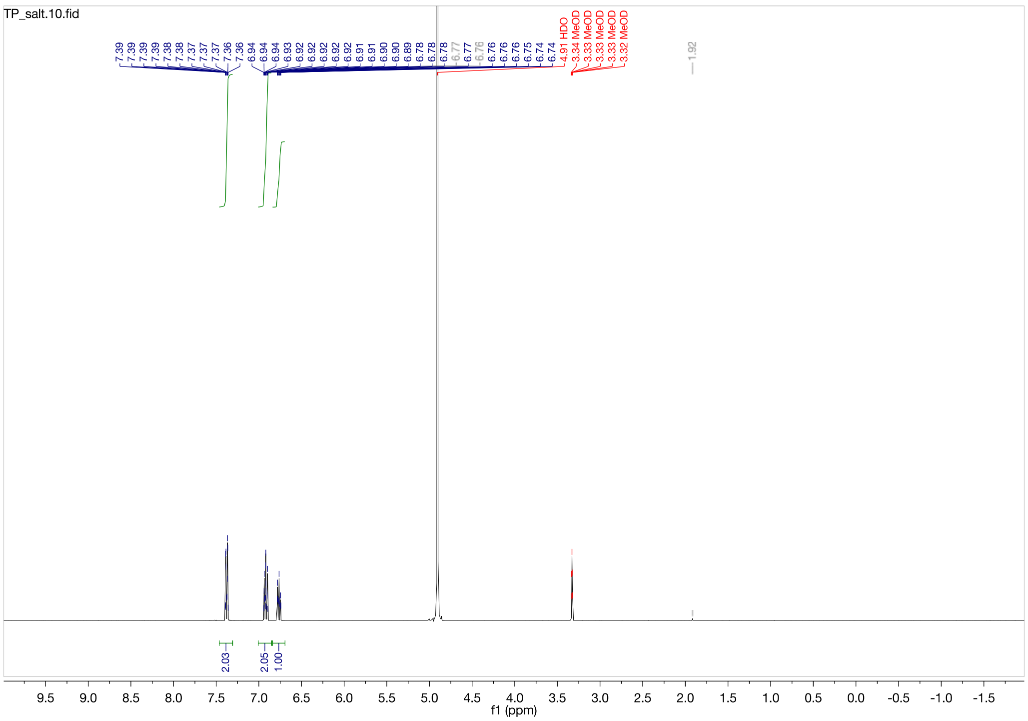
10: NMR of Compounds

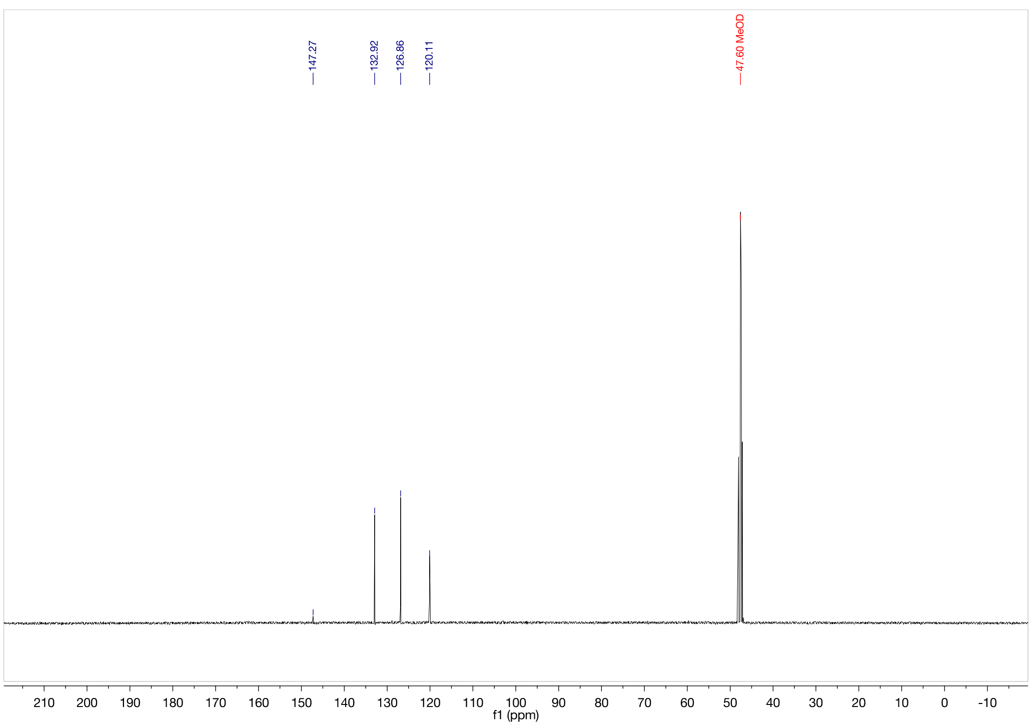
Sodium/butyl 3-mercaptopropionate thiolate [Na+ MP-]



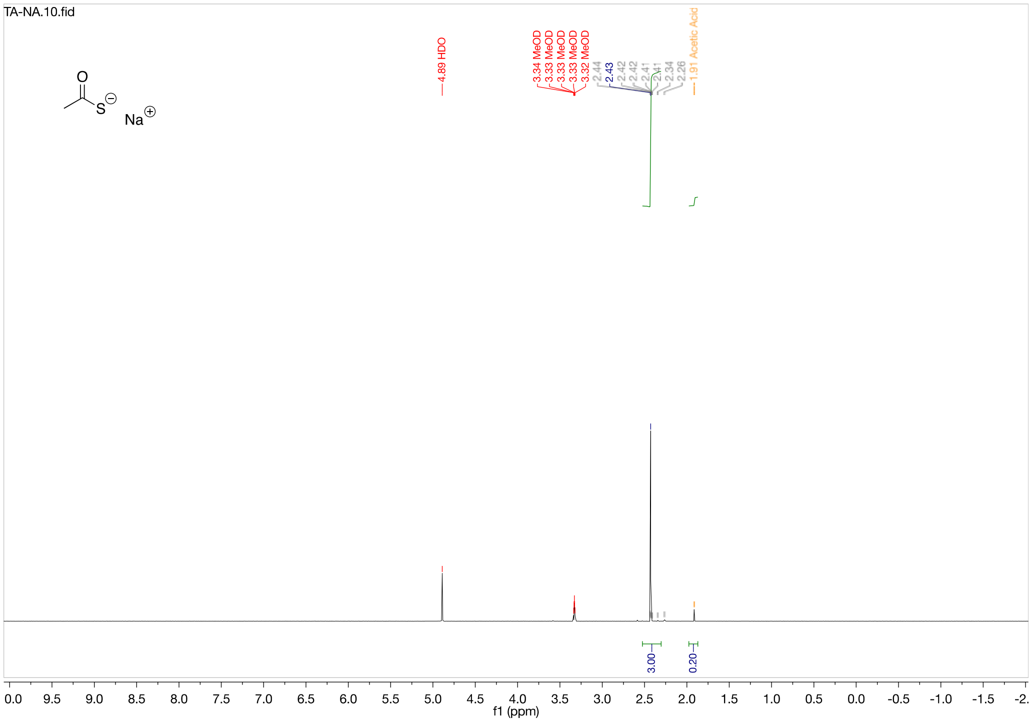


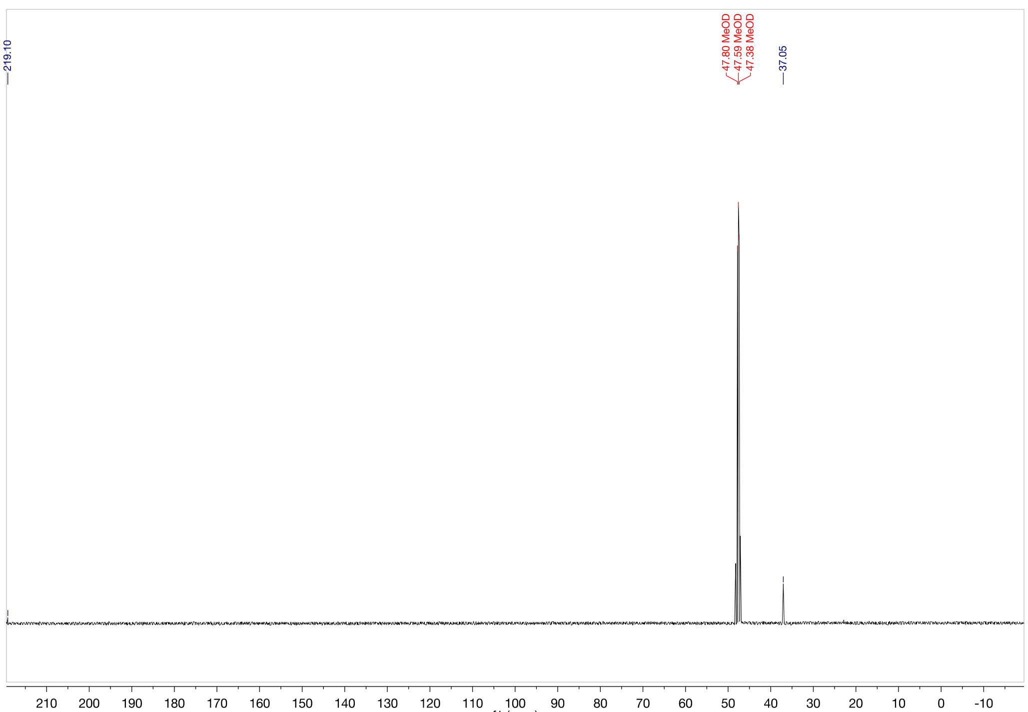
Sodium/thiophenolate [Na$^+$ TP$^-$]



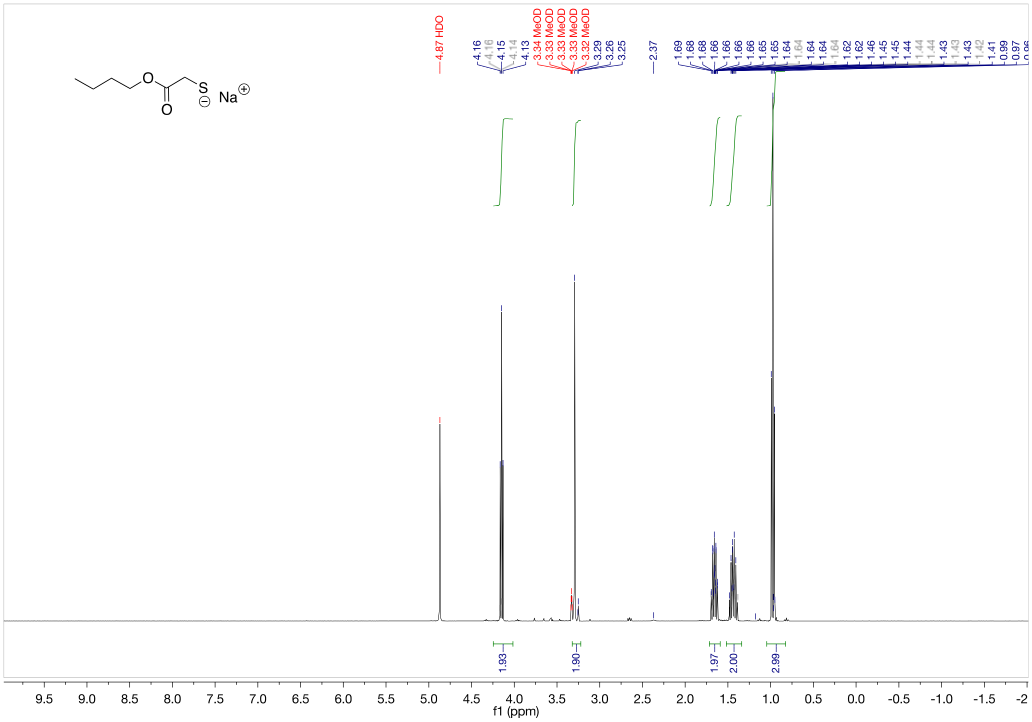


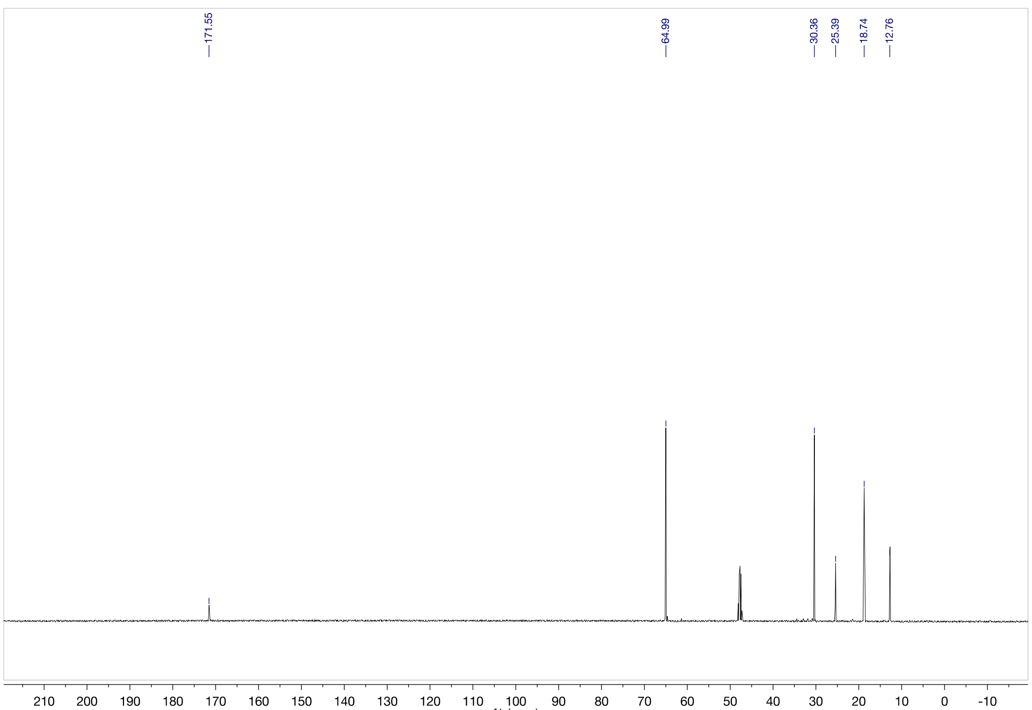
Sodium/thioacetate [Na⁺ TA⁻]



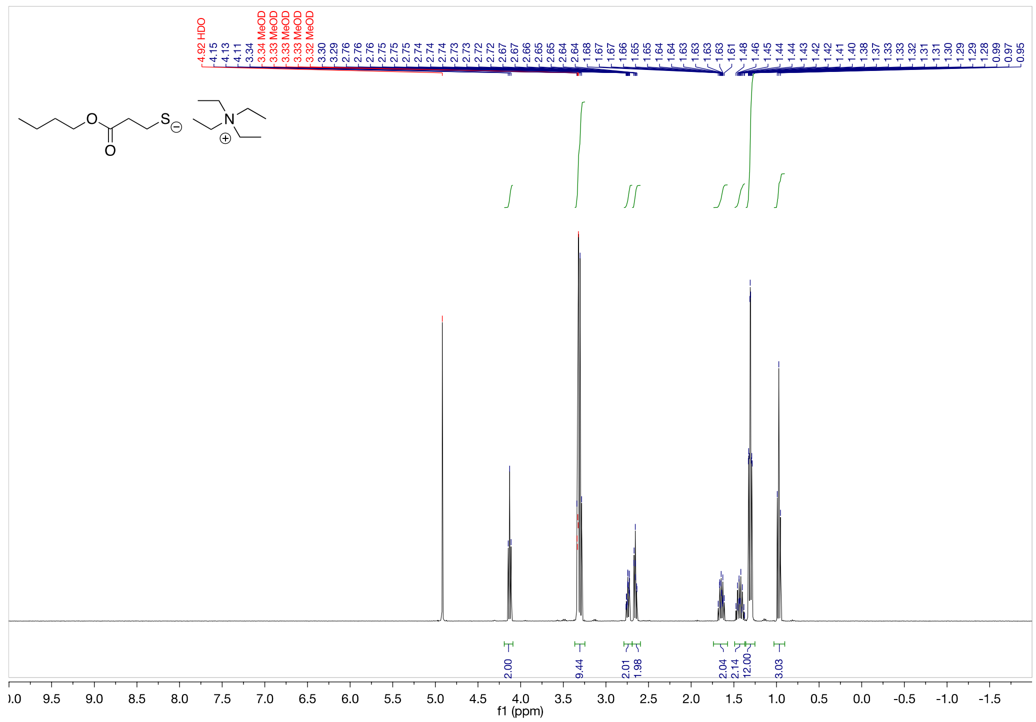


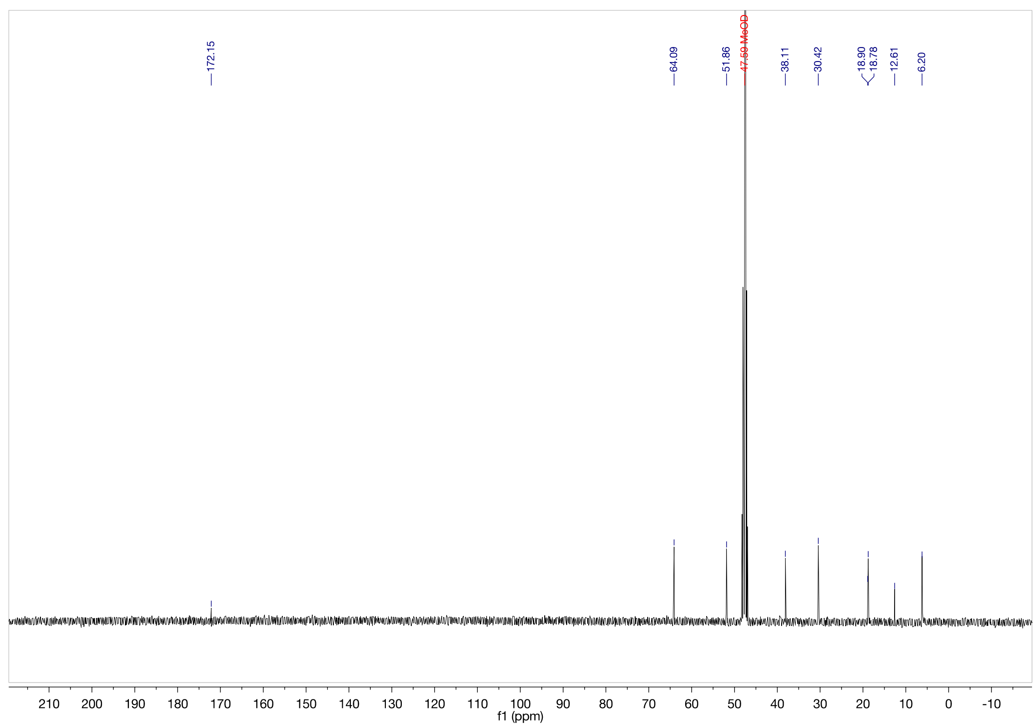
Sodium/butyl 3-mercaptoacetate thiolate [Na$^+$ MA$^-$]



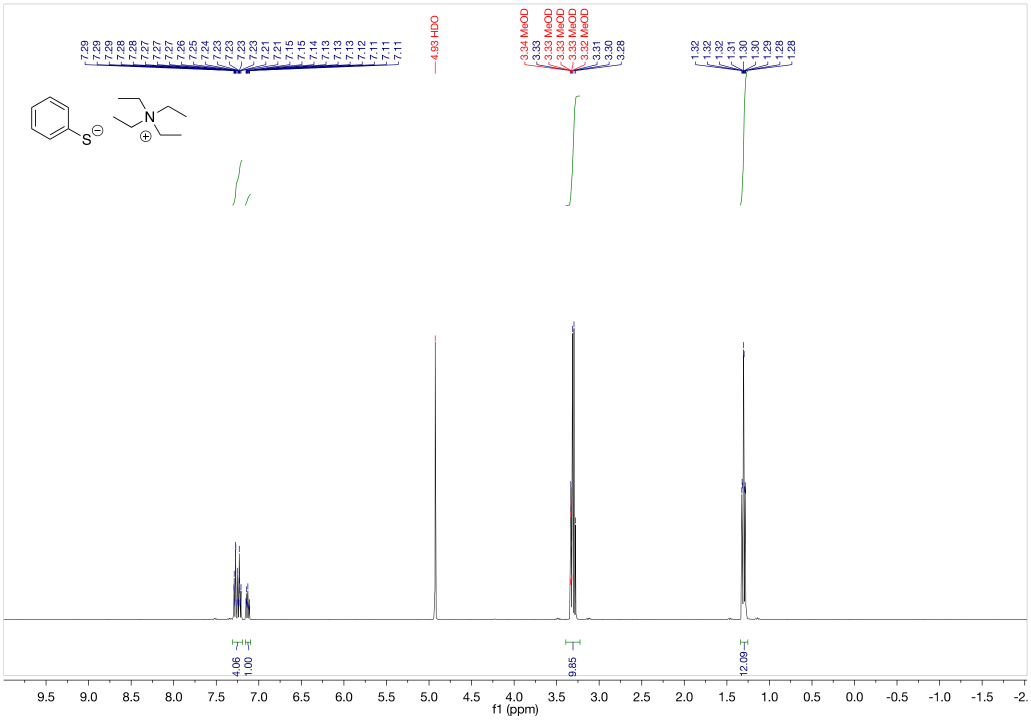


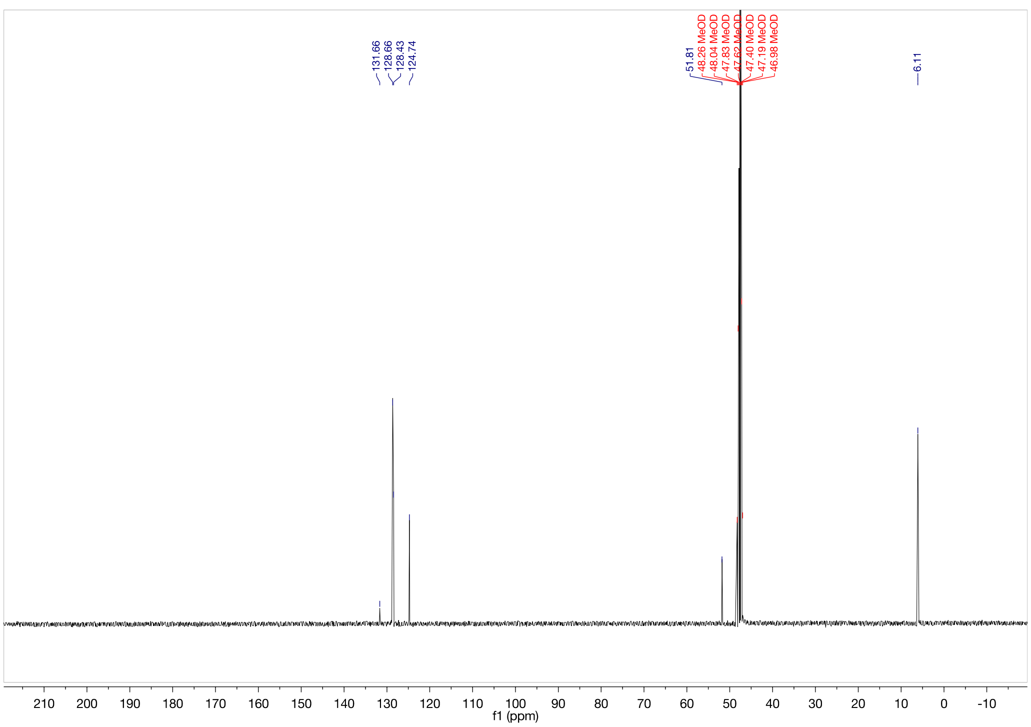
Tetraethylammonium/butyl 3-mercaptopropionate thiolate [Am1+ MP-]



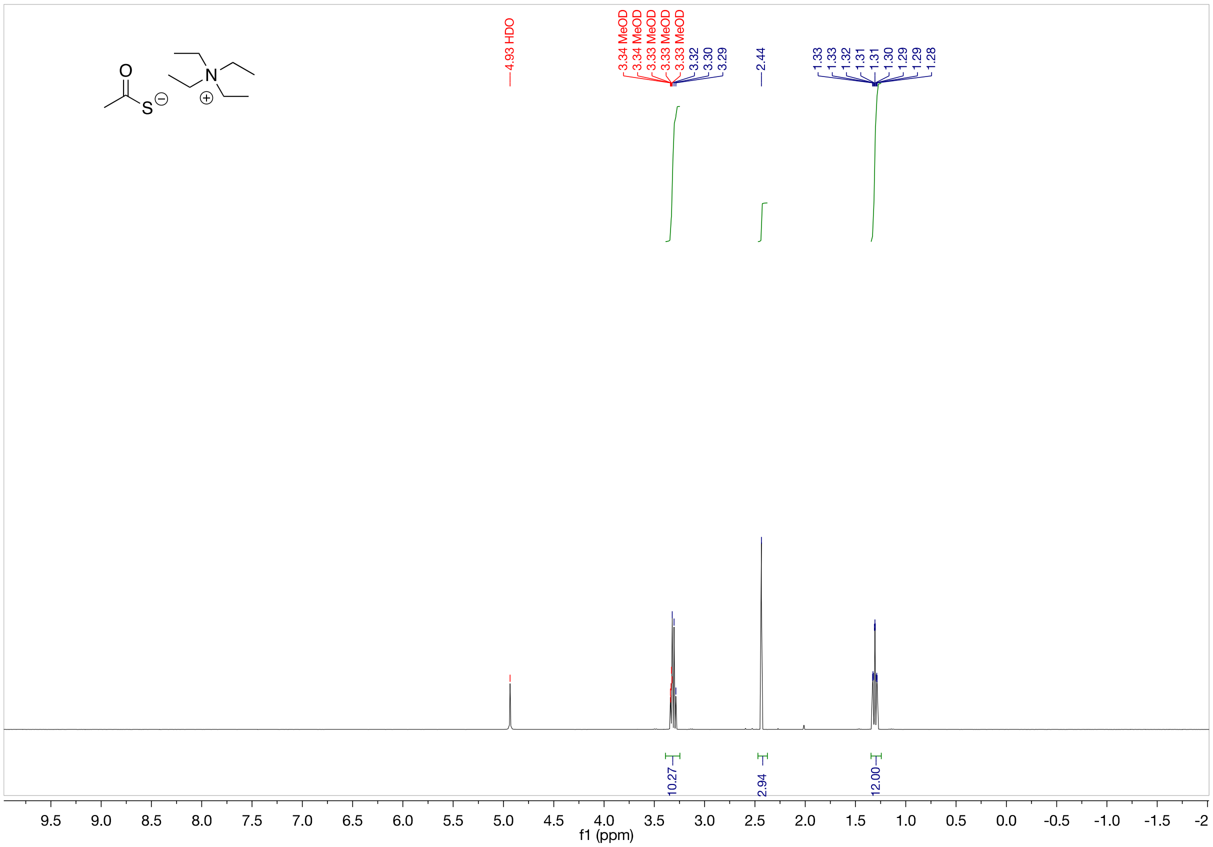


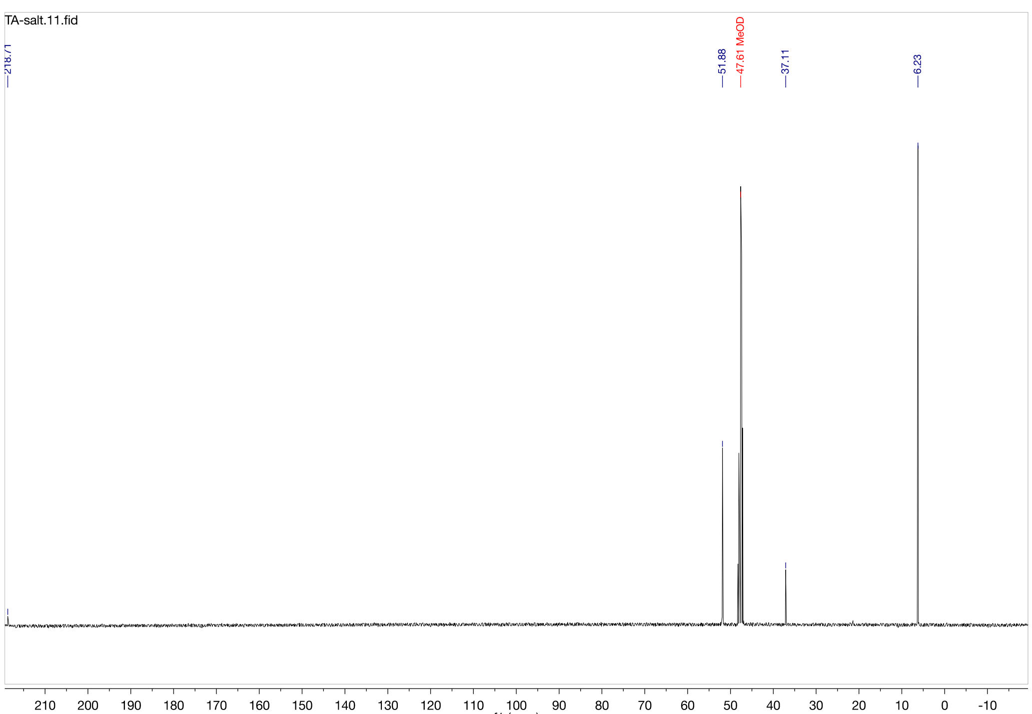
Tetraethylammonium/thiophenolate [Am1⁺TP⁻]



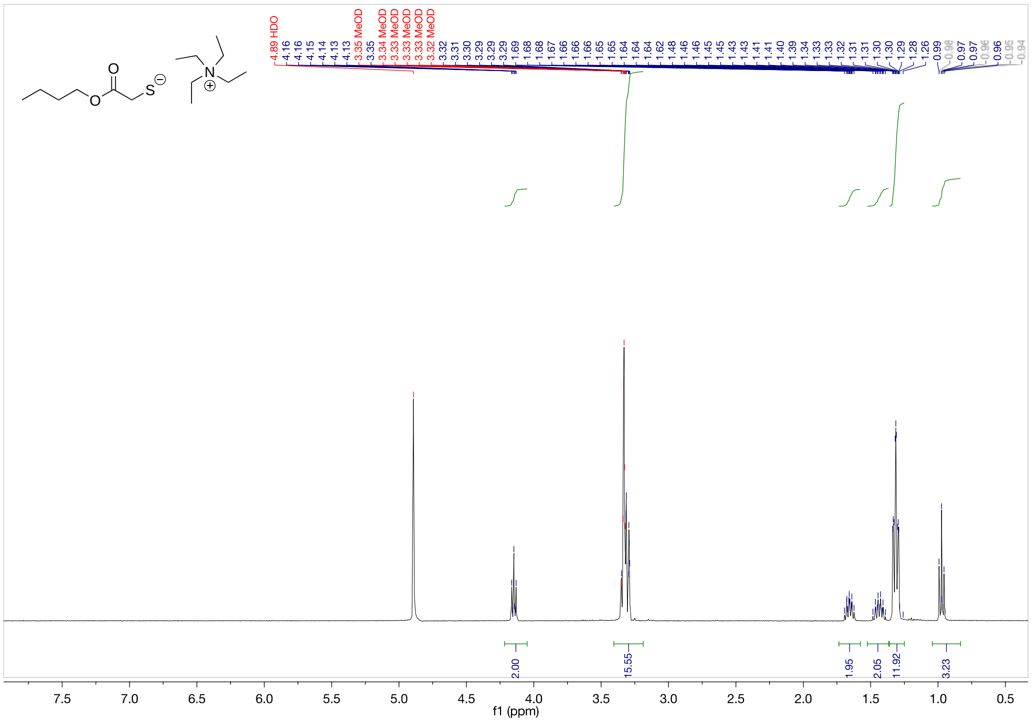


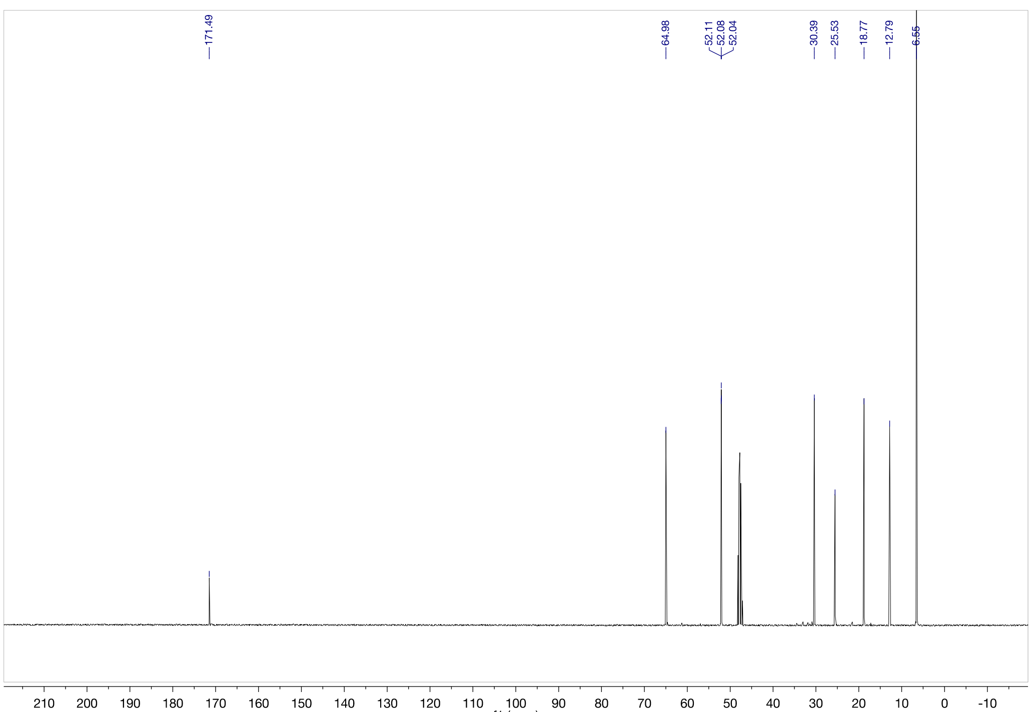
Tetraethylammonium/thioacetate [Am1⁺TA⁻]





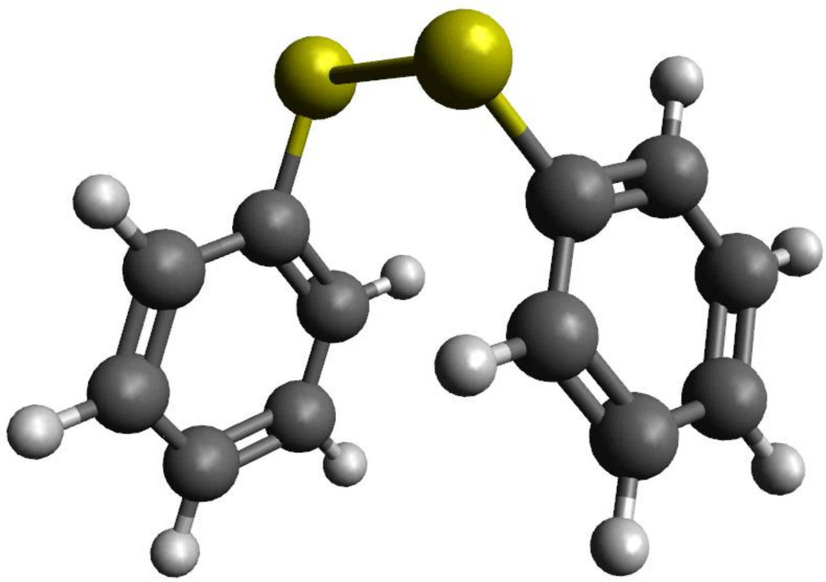
Tetraethylammonium/butyl 3-mercaptoacetate thiolate [Am1$^+$ MA$^-$]





11: Coordinates of Molecular Structures

All coordinates are reported as XYZ Cartesian coordinates. The total electronic energies from LC-*w*PBE/aug-cc-PVTZ//LC-*w*PBE/6-31+G**/CPCM-ethyl acetate were corrected with the thermochemical analysis (zero-point energy and thermal correction) at 298.15K and 1.0 atm from LC-*w*PBE/6-31+G**/ CPCM-ethyl acetate to give the reported Gibbs free energies in Hartrees.



TPTP (-1259.222946)

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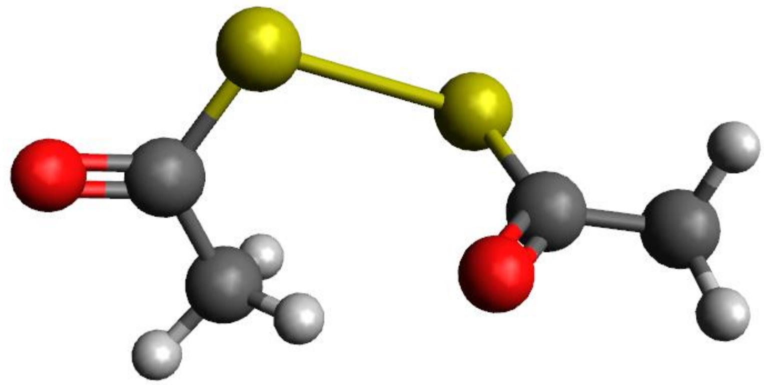
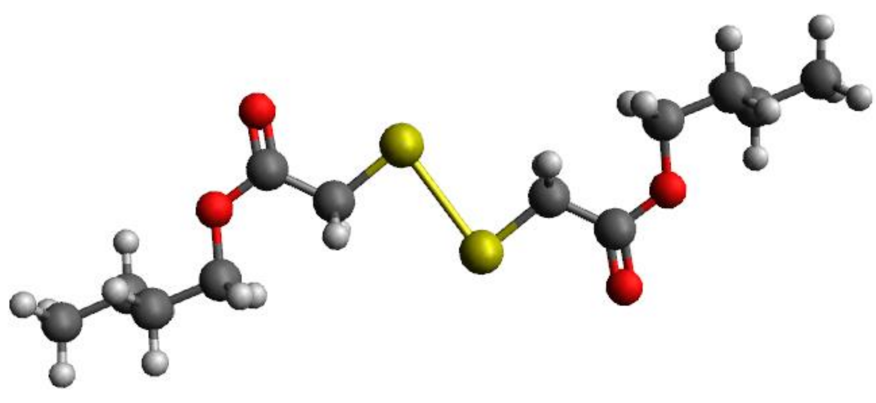
C	-2.92068800	-1.97098800	0.22304900
C	-3.20195000	-0.82424800	0.96014100
C	-2.62552800	0.39069200	0.61631700
C	-1.74857100	0.49306800	-0.47293300
C	-1.46961300	-0.67234100	-1.19979600
H	-1.81945500	-2.77435700	-1.44179900
H	-3.37387300	-2.92106400	0.49121400
H	-3.87800500	-0.87609100	1.80956900
H	-2.84937400	1.28263100	1.19450000
H	-0.78467200	-0.61371300	-2.04079000
S	-1.02516100	2.02483400	-0.91802800
S	1.02521300	2.02481900	0.91799500
C	1.74857800	0.49302500	0.47292300
C	1.46958600	-0.67236500	1.19980100
C	2.62553300	0.39060800	-0.61632500
C	2.05128700	-1.88656600	0.85944600
H	0.78464600	-0.61370500	2.04079500
C	3.20191900	-0.82435400	-0.96013200
H	2.84940600	1.28253300	-1.19452100
C	2.92062300	-1.97107500	-0.22302400
H	1.81936500	-2.77438800	1.44183400
H	3.87797300	-0.87622800	-1.80956000
H	3.37378000	-2.92116800	-0.49117600



TATA (-1102.636847)

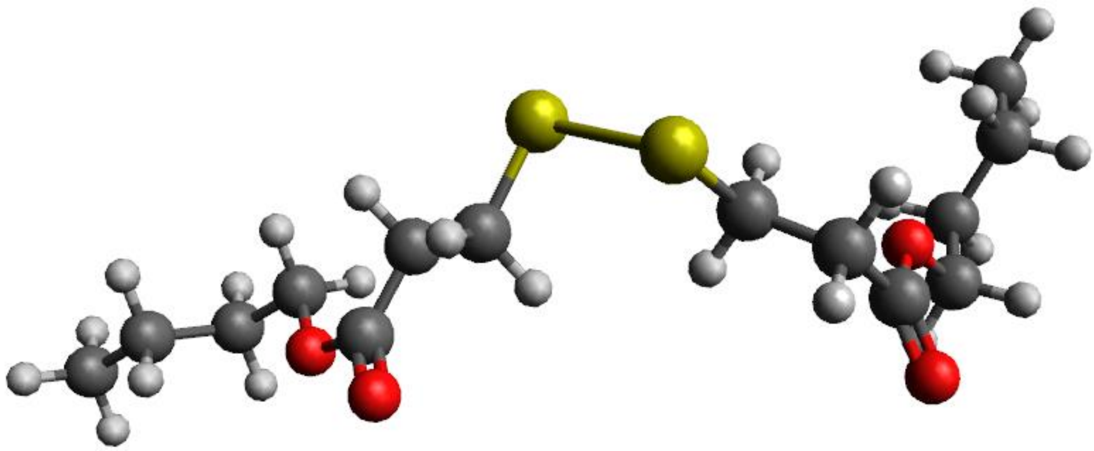
C	-1.47323200	1.32074700	0.88357400
H	-1.16410700	0.84679800	1.81745500
H	-2.13162800	2.16503800	1.09259600
H	-0.56612900	1.65220800	0.37399800
C	-2.20028200	0.32393100	0.02279500
O	-3.37180000	0.49639000	-0.29463200
S	-1.33407500	-1.09363200	-0.52267900
S	1.15440200	-0.96102400	0.60739000
C	1.96786100	0.28626900	-0.30330600
C	3.47700500	0.28804300	-0.17962000
O	1.40483800	1.11140300	-1.01019100
H	3.78769300	0.17623800	0.86036300
H	3.87605300	1.21483800	-0.59451100
H	3.88075700	-0.55986700	-0.73865400



MAMA (-1567.242355)

C	-8.40863200	0.72021200	0.92923400

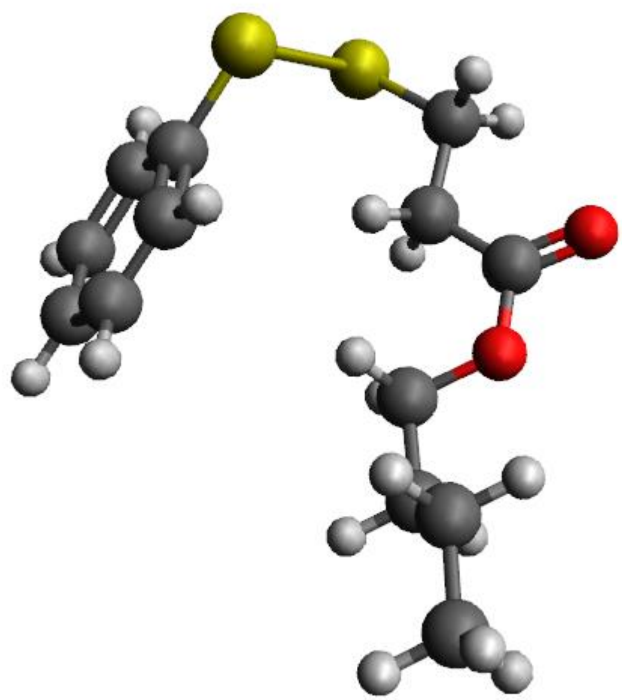
H	-8.61182200	1.78229500	0.76016300
H	-8.85557100	0.44335900	1.88763600
H	-8.92313800	0.15502600	0.14602900
C	-6.91243900	0.43766400	0.91350200
H	-6.42388300	0.99042900	1.72485500
H	-6.73454000	-0.62443000	1.10971900
C	-6.26374700	0.81959300	-0.41135200
H	-6.41531000	1.88804200	-0.60347400
H	-6.74377300	0.28002400	-1.23571800
C	-4.77401500	0.55897900	-0.45891400
H	-4.34873500	0.92544800	-1.39769200
H	-4.27074100	1.05599800	0.37614200
O	-4.57641000	-0.85966800	-0.37072700
C	-3.35136600	-1.41410600	-0.29697400
O	-3.28750800	-2.62244700	-0.25491300
C	-2.17298800	-0.47344000	-0.26073200
H	-2.25257100	0.20702800	-1.11342100
H	-2.27691300	0.14851100	0.63452800
S	-0.56484900	-1.27973700	-0.26286500
S	0.53793900	1.22467600	-0.12988200
C	2.15177500	0.43127200	-0.17376500
C	3.32061600	1.38345500	-0.21899700
H	2.21835600	-0.23050100	-1.04248000
H	2.28045900	-0.20826300	0.70544300
O	4.55015900	0.84190200	-0.31030600
O	3.24499800	2.59095800	-0.17260900
C	4.76240700	-0.57483700	-0.39345100
C	6.25616300	-0.81630800	-0.39112300
H	4.31216800	-0.95569700	-1.31462600
H	4.29240300	-1.07002300	0.46192800
C	6.94262900	-0.40693900	0.90624100
H	6.41516400	-1.88545400	-0.57313300
H	6.70211100	-0.28271600	-1.23819500
C	8.44226300	-0.66943200	0.87681900
H	6.48833400	-0.95410900	1.74097200
H	6.75683600	0.65545500	1.09312100
H	8.65450700	-1.73127200	0.71763700
H	8.91657600	-0.37132600	1.81548900
H	8.92290000	-0.10998500	0.06837700



MPMP (-1645.806433)

C	8.84341800	1.63368700	0.48164200
H	9.05362000	2.49691000	-0.15752400
H	9.68806300	0.94462500	0.40031400
H	8.80156200	1.98876400	1.51589700
C	7.53799600	0.95907600	0.08238600
H	7.61474800	0.58595600	-0.94593000
H	7.36391100	0.08520400	0.71814600
C	6.34406300	1.90047400	0.18370500
H	6.50013300	2.76783700	-0.46807100
H	6.25376800	2.28655400	1.20538100
C	5.03037300	1.26585900	-0.21688300
H	4.22447000	2.00494700	-0.20080900
H	5.10054800	0.83924100	-1.22225700
O	4.74009100	0.22578400	0.72901900
C	3.65842900	-0.56223100	0.60759100
O	3.47704400	-1.40603100	1.45944200
C	2.75055600	-0.34720700	-0.57561200
H	2.42341000	0.69769100	-0.58498300
H	3.33420600	-0.48747700	-1.49182100
C	1.54494100	-1.27338900	-0.57933000
H	0.96470700	-1.12267400	0.33434700
H	1.88081400	-2.31238100	-0.57733600
S	0.50473400	-0.95869400	-2.02839900
S	-1.44278100	-2.66899200	-1.18519900
C	-2.25930500	-1.37215900	-0.22153400
C	-3.47059900	-1.92585600	0.52737900
H	-1.54913400	-0.94790000	0.49503300
H	-2.57508000	-0.56480300	-0.88462200
C	-4.16674900	-0.90009900	1.38046400
H	-3.17938800	-2.74896900	1.18173000
H	-4.19890700	-2.31325300	-0.19279500
O	-4.50140900	0.19418900	0.69129800
O	-4.41910800	-1.03156100	2.56276500
C	-5.17232600	1.23538400	1.41875600
C	-5.44000200	2.37761500	0.46491700

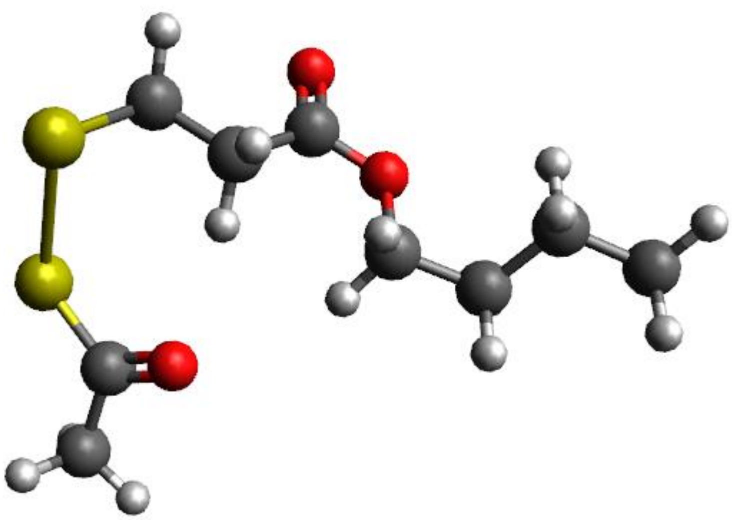
H	-4.53430000	1.54598800	2.25018000
H	-6.10037100	0.82992900	1.83358400
C	-6.40876500	2.02961100	-0.65905800
H	-5.84358100	3.20862400	1.05509200
H	-4.48781200	2.72371100	0.04678700
C	-6.66961800	3.20907200	-1.58617700
H	-7.35478900	1.68571000	-0.22377800
H	-6.00808400	1.18930200	-1.23503400
H	-7.09692100	4.05481700	-1.03835300
H	-7.36708400	2.94151200	-2.38423400
H	-5.74235500	3.55184400	-2.05535300



MPTP (-1452.512084)

C	5.61272800	0.24409100	-0.71518000
H	5.84000800	1.08962500	-0.05842500
H	5.94508400	0.50572800	-1.72314100
H	6.21055800	-0.60823300	-0.37792500
C	4.12661100	-0.08685000	-0.69029200
H	3.55110100	0.77060700	-1.05912800
H	3.92097300	-0.91648700	-1.37415000
C	3.63663000	-0.45236900	0.70552100
H	3.81704800	0.38325300	1.39156400
H	4.20401400	-1.30621600	1.09316900
C	2.16005700	-0.77555200	0.76784900
H	1.84532500	-0.94794300	1.80111400
H	1.56902800	0.04487000	0.34981900
O	1.94008800	-1.97157400	0.00305600
C	0.70473000	-2.45243000	-0.21392900
O	0.60341800	-3.48442000	-0.84486300

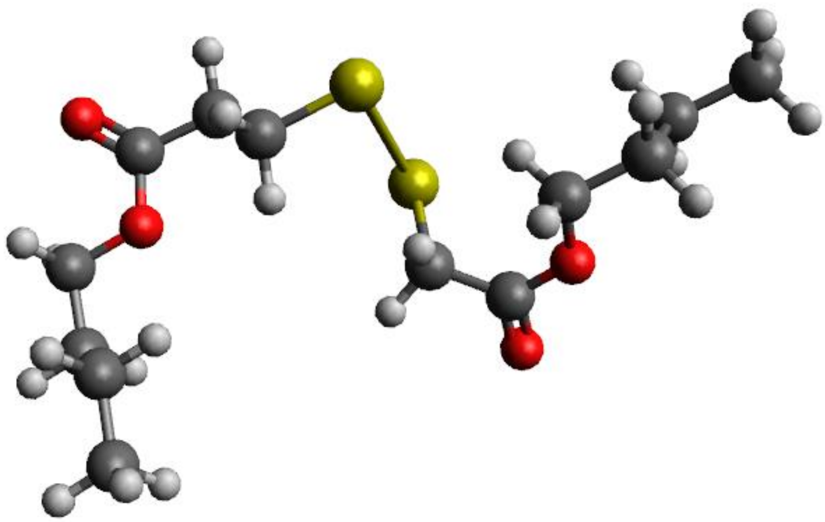
C	-0.46445100	-1.68078400	0.33529700
H	-0.33237700	-1.55572800	1.41503100
H	-0.45465100	-0.67194900	-0.08977700
C	-1.80530900	-2.33064500	0.04353500
H	-1.83728300	-3.33645200	0.47270800
H	-1.93663200	-2.44041200	-1.03510000
S	-3.18336100	-1.38273700	0.72577900
S	-2.98433000	0.60652800	-1.15273400
C	-1.92132400	1.76061400	-0.36439700
C	-0.64158900	2.02775600	-0.87198300
C	-2.31856900	2.45033000	0.78957400
C	0.19904800	2.94805700	-0.25861700
H	-0.31138100	1.50384300	-1.76521100
C	-1.47430700	3.36271600	1.40808500
H	-3.30556400	2.25867700	1.20031400
C	-0.20972500	3.62071700	0.88807400
H	1.18317200	3.13789800	-0.67960400
H	-1.80943900	3.87987300	2.30343900
H	0.44836300	4.33773100	1.37034600



MPTA (-1374.221462)

C	5.91965800	1.09509600	-0.27267000
H	5.93866200	2.01676600	-0.86262500
H	6.77525500	0.48638600	-0.57676900
H	6.06257000	1.37009000	0.77687200
C	4.60857600	0.34541300	-0.46714700
H	4.50182300	0.05565400	-1.51944800
H	4.62520500	-0.58398100	0.11101700
C	3.39856400	1.17407300	-0.05330400
H	3.36257800	2.09670700	-0.64399200
H	3.48953100	1.47632500	0.99627200
C	2.07594800	0.46543200	-0.24484300
H	1.23906200	1.12988500	-0.01468000
H	1.97284300	0.11508000	-1.27684700
O	2.05057600	-0.66227700	0.64686100
C	1.00064900	-1.49782000	0.68861700

O	1.03672800	-2.41282200	1.48679700
C	-0.13832200	-1.24865900	-0.25962600
H	-0.46960600	-0.20718500	-0.18183600
H	0.23476100	-1.36563000	-1.28339700
C	-1.32297600	-2.16852800	-0.02740200
H	-1.65502400	-2.09975400	1.01048300
H	-1.04312500	-3.21136400	-0.20446400
S	-2.70474000	-1.77988900	-1.11863800
S	-3.44900100	0.43812600	0.40666000
C	-2.51664800	1.85245100	0.01334300
C	-3.14218800	3.17986500	0.39221700
O	-1.42142100	1.83692000	-0.54536900
H	-3.49597300	3.16234600	1.42447000
H	-4.00842200	3.36393700	-0.24816600
H	-2.41583600	3.98315400	0.25753100



MPMA (-1606.53198)

C	4.63915400	3.38986600	1.15348300
H	5.66081900	3.75610700	1.01193200
H	4.28761700	3.74805700	2.12459200
H	4.01227800	3.84852100	0.38271300
C	4.58381800	1.87045400	1.06987400
H	5.19529000	1.43411500	1.86890000
H	3.55816700	1.52849900	1.24182000
C	5.07099200	1.34379600	-0.27487500
H	6.10370500	1.66909500	-0.44636600
H	4.46944300	1.77019000	-1.08581500
C	5.04841400	-0.16413300	-0.38459200
H	5.47246800	-0.50585500	-1.33256000
H	5.60705100	-0.63619000	0.42924000
O	3.68018700	-0.59539000	-0.31352100
C	3.46084900	-1.91234000	-0.35881400
O	4.36358300	-2.72271100	-0.44953400
C	1.99769000	-2.25618900	-0.31032000

H	1.56270600	-2.00136000	-1.28274500
H	1.91915900	-3.33693800	-0.18271300
C	1.21657100	-1.52315700	0.77511700
H	1.30476400	-0.44411100	0.62954800
H	1.64047100	-1.75108200	1.75899500
S	-0.52992600	-1.98369800	0.80894000
S	-1.09889200	-0.46621100	-1.38682000
C	-1.08120600	1.11454000	-0.49248100
C	-2.33112900	1.90369700	-0.77631800
H	-0.24259200	1.73019400	-0.81853200
H	-0.97124000	0.91500700	0.57682400
O	-3.46266300	1.60020700	-0.12913900
O	-2.36739600	2.80423000	-1.59406000
C	-3.48556700	0.61095800	0.91589400
C	-4.93225000	0.27021100	1.19673800
H	-3.00714400	1.03523700	1.80416000
H	-2.92599000	-0.27195500	0.59481200
C	-5.63131500	-0.42824500	0.03665800
H	-4.94944000	-0.37631700	2.08186100
H	-5.47176400	1.18614500	1.46531600
C	-7.08347000	-0.76301600	0.34952000
H	-5.08452800	-1.34554700	-0.21078100
H	-5.58187300	0.21046000	-0.85111200
H	-7.15770500	-1.42366000	1.21907500
H	-7.56665500	-1.26516700	-0.49281200
H	-7.65678400	0.14262900	0.57101400

TP radical (-629.5168192)

C	1.53449300	1.19972000	0.00000500
C	2.23519700	0.00000000	0.00000600
C	1.53449300	-1.19972000	0.00000300
C	0.14607700	-1.20740900	0.00000200
C	-0.55304400	0.00000000	-0.00000100
C	0.14607700	1.20740900	-0.00000100
H	2.07011000	2.14437800	0.00000700
H	3.32062300	0.00000000	0.00000900
H	2.07011000	-2.14437800	0.00000400
H	-0.39020100	-2.15170400	0.00000200
H	-0.39020100	2.15170400	-0.00000400
S	-2.30904800	0.00000000	-0.00000600

TP Anion (-629.683827)

C	1.54053200	1.19616300	0.00000400
C	2.25147500	0.00000000	0.00000600
C	1.54053200	-1.19616300	0.00000500
C	0.15169900	-1.19536200	0.00000100
C	-0.58754000	0.00000000	-0.00000100
C	0.15169900	1.19536200	0.00000000
H	2.07305100	2.14442500	0.00000500
H	3.33775000	0.00000000	0.00000900
H	2.07305100	-2.14442500	0.00000600
H	-0.38691800	-2.13937700	0.00000000
H	-0.38691800	2.13937700	-0.00000100
S	-2.34372700	0.00000000	-0.00000600

TA radical (-551.2218676)

C	1.32222500	-0.97839800	-0.00361300

H	1.26354200	-1.47972000	0.96578000
H	2.34322000	-0.63619400	-0.17287500
H	1.03238500	-1.69517300	-0.77420300
C	0.40526900	0.20564100	0.00197900
O	0.76779800	1.36066700	0.06487400
S	-1.32401200	-0.13017800	-0.06235000

TA Anion (-551.3970583)

C	1.31840000	-0.96726700	0.00419100
H	1.18126500	-1.54936200	0.91812900
H	2.34968100	-0.61409200	-0.05647600
H	1.10577200	-1.63076300	-0.83689700
C	0.35952200	0.21022600	-0.00866000
O	0.82743300	1.35048300	-0.07850700
S	-1.33164500	-0.15258100	0.07781300

MA radical (-783.5313271)

C	4.49327000	0.21095800	0.44323500
H	4.98779200	-0.75087800	0.27620400
H	4.94259900	0.66792000	1.32854200
H	4.71776900	0.85340300	-0.41356000
C	2.99075900	0.03408200	0.61513700
H	2.79098200	-0.58799400	1.49585300
H	2.52416700	1.00551300	0.80719600
C	2.34024500	-0.60512300	-0.60564100
H	2.78637200	-1.58871100	-0.79159400
H	2.53138700	0.00106100	-1.49809700
C	0.84844700	-0.80924700	-0.46470200
H	0.44820300	-1.34050600	-1.33271400
H	0.62445800	-1.37863100	0.44237600
O	0.23611100	0.49115400	-0.38444000
C	-1.07063900	0.66310600	-0.16159900
O	-1.51509200	1.78559700	-0.13569100
C	-1.90125900	-0.58895600	0.06273700
H	-1.74823400	-1.29766500	-0.75771800
H	-1.54179200	-1.10575800	0.95928300
S	-3.65129700	-0.33080500	0.23877200

MA Anion (-783.689256)

C	4.49038600	0.21161700	0.44329500
H	4.98740300	-0.74898900	0.27516400
H	4.94018700	0.66968300	1.32812100
H	4.71252900	0.85458800	-0.41395100
C	2.98825400	0.03075200	0.61550500
H	2.79002800	-0.59040100	1.49731900
H	2.51811800	1.00055000	0.80661000
C	2.33624100	-0.61100900	-0.60301700
H	2.78319400	-1.59512500	-0.78642700
H	2.52984100	-0.00565200	-1.49598100
C	0.84214700	-0.80945200	-0.46160400
H	0.44344700	-1.34893000	-1.32596100
H	0.61711900	-1.38158600	0.44403200
O	0.23548500	0.48546200	-0.38549000
C	-1.08907300	0.65891300	-0.16017200
O	-1.49035800	1.80060500	-0.14453800
C	-1.91548400	-0.58654900	0.06150500
H	-1.70106500	-1.25800000	-0.77653600
H	-1.48603800	-1.07771700	0.94262200

S	-3.69811300	-0.37024000	0.26308400

MP radical (-822.8142455)

C	-4.96526000	-0.26228100	-0.43901600
H	-5.31903000	-1.27164900	-0.20742900
H	-5.47206700	0.06829300	-1.34919400
H	-5.28144000	0.39581700	0.37600000
C	-3.45222900	-0.23510800	-0.60783500
H	-3.16310100	-0.87824700	-1.44765400
H	-3.12776900	0.77816100	-0.86520400
C	-2.72151600	-0.69476400	0.64793300
H	-3.02455200	-1.71746300	0.89972500
H	-3.00102000	-0.06507300	1.50000300
C	-1.21506200	-0.69352100	0.51341700
H	-0.74705300	-1.10284500	1.41304900
H	-0.90561600	-1.28570500	-0.35334900
O	-0.79206200	0.67012000	0.33936700
C	0.48852900	0.99417800	0.13308200
O	0.77610200	2.16623100	0.01380600
C	1.50639000	-0.11676000	0.05526600
H	1.45252300	-0.71935700	0.96652800
H	1.24107100	-0.78321200	-0.77098500
C	2.91323900	0.42373500	-0.13766900
H	3.19210700	1.09557600	0.68012000
H	2.97946800	1.03080400	-1.04596500
S	4.16968200	-0.84033300	-0.24666200

MP Anion (-822.9682607)

C	-4.96304600	-0.27957600	-0.43712100
H	-5.30662000	-1.29339200	-0.20898700
H	-5.47429100	0.04949700	-1.34557900
H	-5.28516400	0.37197700	0.38099700
C	-3.45031900	-0.23686200	-0.60624000
H	-3.15503800	-0.87335200	-1.44898600
H	-3.13525500	0.78033500	-0.85955400
C	-2.71310100	-0.69416300	0.64651500
H	-3.00619100	-1.72098000	0.89413900
H	-2.99931500	-0.07031400	1.50096000
C	-1.20620200	-0.67495100	0.51040100
H	-0.73334400	-1.08691300	1.40640400
H	-0.89065900	-1.26249700	-0.35735600
O	-0.79895200	0.69073400	0.34310800
C	0.48777600	1.02625500	0.13358000
O	0.74519200	2.20718300	0.02284500
C	1.50748300	-0.07791100	0.04659500
H	1.44183500	-0.69483800	0.94884200
H	1.23534700	-0.73871800	-0.78369400
C	2.93581300	0.41070600	-0.13716700
H	3.19039500	1.07425100	0.69452200
H	2.98592200	1.01962200	-1.04430300
S	4.11906900	-0.96949200	-0.23258800