

## **Computational Evaluation of Sulfonyl Radical as a Universal Leaving Group for RAFT Polymerisation**

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### **SUPPORTING INFORMATION**

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*Dedicated to the memory of our mentor and colleague, Athel Beckwith.*

Table S1 – Calculated<sup>a</sup> thermodynamic parameters of the addition-fragmentation reactions in studied RAFT systems in the gas phase (entropy, enthalpy and Gibbs free energy) and toluene solution (Gibbs free energy and logarithm of a corresponding equilibrium constant) at 60 °C.

Polymer unit	$\Delta S$ , J mol <sup>-1</sup> K <sup>-1</sup>	$\Delta H$ , kJ mol <sup>-1</sup>	$\Delta G$ , kJ mol <sup>-1</sup>	$\Delta G_{solv}$ , kJ mol <sup>-1</sup>	lg $K_{eq}$
R = cyanoisopropyl					
ET: addition	-162.051	-105.013	-51.026	-60.775	9.529
ET: fragmentation	177.681	47.127	-12.067	-5.414	0.849
STY: addition	-195.373	-62.038	3.050	2.254	-0.353
STY: fragmentation	211.383	48.564	-21.859	-21.816	3.420
VA: addition	-212.126	-103.653	-32.983	-34.951	5.480
VA: fragmentation	214.300	50.814	-20.580	-18.529	2.905
MMA: addition	-191.048	-73.043	-9.395	-14.751	2.313
MMA: fragmentation	177.881	50.914	-8.347	-2.531	0.397
R = methylsulfonyl					
ET: addition	-197.589	-122.336	-56.509	-69.941	10.966
ET: fragmentation	199.933	31.272	-35.335	-23.787	3.729
STY: addition	-200.161	-89.498	-22.814	-27.250	4.272
STY: fragmentation	202.885	42.845	-24.746	-19.850	3.112
VA: addition	-198.222	-124.140	-58.102	-59.819	9.379
VA: fragmentation	187.111	38.123	-24.213	-21.199	3.324
MMA: addition	-200.470	-84.956	-18.169	-26.329	4.128
MMA: fragmentation	174.017	29.649	-28.325	-18.492	2.899
R = phenylsulfonyl					
ET: addition	-188.157	-127.401	-64.717	-74.006	11.603
ET: fragmentation	183.907	35.319	-25.950	-17.372	2.724
STY: addition	-216.185	-116.435	-44.414	-48.054	7.534
STY: fragmentation	212.315	56.675	-14.058	-8.785	1.377
VA: addition	-210.426	-134.768	-64.664	-69.351	10.873
VA: fragmentation	192.721	45.430	-18.775	-11.619	1.822
MMA: addition	-221.155	-115.702	-42.024	-44.368	6.956
MMA: fragmentation	188.108	52.574	-10.094	-4.905	0.769

<sup>a</sup> Gas-phase free energies are calculated using G3(MP2)-RAD method or an ONIOM approximation to it in conjunction with M06-2X/6-31G(d) geometries and frequencies; free energies of solvation are calculated using COSMO-RS/BP/TZVP method in conjunction with CPCM-UAKS/M06-2X/6-31G(d) solution-phase geometries.

## APPENDIX 1

Table S3 – Contributions to the gas and solution-phase free energies of all the species in this study.

Species	$E_{gas}^0$ , Hartrees		$E_{gas}^{ONIOM, b}$ Hartrees	$ZPVE$ , Hartrees	$T_c^T$ , $T_{c_{gas}}^T, ^c$ Hartrees	$S_{gas}^T$ , J mol <sup>-1</sup> K <sup>-1</sup>	$G_{gas}^T$ , Hartrees	$\Delta G_{solv}^T$ , kcal mol <sup>-1</sup>
	R(O)MP2 <sup>a</sup>	G3(MP2)- RAD						
•Et	-78.94875	-79.04834	-79.04834	0.05775	0.00573	262.1605	-79.01813	-0.76
S=C(SMe)S( <i>i</i> PrCN)	-1481.30148	-1481.69887	-1481.69887	0.13640	0.01669	501.5530	-1481.60942	-6.08
EtS–C•(SMe)S( <i>i</i> PrCN)	-1560.29432	-1560.79229	-1560.79229	0.20012	0.02153	601.6628	-1560.64699	-6.98
EtS–C(SMe)=S	-1350.00536	-1350.31197	-1350.31197	0.11070	0.01290	435.0163	-1350.24358	-2.80
• <i>i</i> PrCN	-210.26659	-210.45908	-210.45908	0.08584	0.00893	344.3271	-210.40800	-4.78
•CH(Me)Ph	-309.50445	-309.80216	-309.80216	0.13850	0.01046	376.9884	-309.70104	-5.69
S(CH(Me)Ph)– C•(SMe)S( <i>i</i> PrCN)	-1790.83785	-1791.52877	-1791.52877	0.27920	0.02695	683.1689	-1791.30930	-9.77
S(CH(Me)Ph)–C(SMe)=S	-1580.54757	-1581.04770	-1581.04770	0.18915	0.01874	550.2243	-1580.90962	-7.17
•CH(Me)OC(O)Me	-306.44756	-306.68566	-306.68566	0.10108	0.01034	380.2421	-306.62248	-4.55
S(CH(Me)OC(O)Me)– C•(SMe)S( <i>i</i> PrCN)	-1787.79162	-1788.42798	-1788.42798	0.24218	0.02630	669.6692	-1788.24447	-8.91
S(CH(Me)OC(O)Me)– C(SMe)=S	-1577.50173	-1577.94598	-1577.94598	0.15196	0.01820	539.6422	-1577.84430	-5.83
•CMe <sub>2</sub> C(O)OMe	-345.67555	-345.95746	-345.95746	0.12954	0.01204	413.8489	-345.86839	-5.19
S(CMe <sub>2</sub> C(O)OMe)– C•(SMe)S( <i>i</i> PrCN)	-1827.00977	-1827.68746	-1827.68746	0.26961	0.02836	724.3535	-1827.48140	-10.36
S(CMe <sub>2</sub> C(O)OMe)–C(SMe)=S	-1616.71911	-1617.20546	-1617.20546	0.17980	0.01988	557.9074	-1617.07657	-6.38
S=C(SMe)S–SO <sub>2</sub> Me	-1858.72805	-1859.09120	-1859.09120	0.09320	0.01518	477.8429	-1859.04345	-5.43
•SO <sub>2</sub> Me	-587.71230	-587.86495	-587.86495	0.04424	0.00672	307.3314	-587.85299	-3.84
EtS–C•(SMe)S–SO <sub>2</sub> Me	-1937.72541	-1938.18922	-1938.18922	0.15653	0.01841	542.4144	-1938.08311	-7.21
S(CH(Me)Ph)–C•(SMe)S– SO <sub>2</sub> Me	-2168.27525	-2168.93181	-2168.93181	0.23637	0.02533	654.6707	-2168.75319	-9.99
S(CH(Me)OC(O)Me)– C•(SMe)S–SO <sub>2</sub> Me	-2165.22666	-2165.82815	-2165.82815	0.19881	0.02500	659.8631	-2165.68807	-8.20
S(CMe <sub>2</sub> C(O)OMe)–C•(SMe)S–	-2204.44002	-2205.08442	-2205.08442	0.22652	0.02684	691.2216	-2204.91877	-10.38

SO <sub>2</sub> Me									
S=C(SMe)S–SO <sub>2</sub> Ph	-2050.04566	-2050.55911	-2050.55911	0.14445	0.01940	567.8010	-2050.46731	-8.73	
•SO <sub>2</sub> Ph	-779.02911	-779.33337	-779.33337	0.09596	0.01059	390.6958	-779.27639	-6.86	
•Et (as core)	-78.94875	-79.04834	-0.09959						
•CH(Me)Ph (as full)	-309.50445		-309.60404	0.13850	0.01046	376.9884	-309.50292	-5.69	
•CH(Me)OC(O)Me (as full)	-306.44756		-306.54714	0.10108	0.01034	380.2421	-306.48397	-4.55	
•CMe <sub>2</sub> C(O)OMe (as full)	-345.67555		-345.77513	0.12954	0.01204	413.8489	-345.68607	-5.19	
EtS–C•(SMe)S–SO <sub>2</sub> Ph	-2129.04732	-2129.66123	-2129.66123	0.20874	0.02385	641.8050	-2129.51009	-9.52	
EtS–C•(SMe)S–SO <sub>2</sub> Ph (as core)	-2129.04732	-2129.66123	-0.61391						
S(CH(Me)Ph)–C•(SMe)S– SO <sub>2</sub> Ph (full)	-2359.59778		-2360.21169	0.28749	0.02952	728.6049	-2359.98715	-13.10	
S(CH(Me)OC(O)Me)– C•(SMe)S–SO <sub>2</sub> Ph (full)	-2356.54765		-2357.16156	0.25000	0.02925	737.6171	-2356.97591	-12.21	
EtS–C•(SMe)S–SO <sub>2</sub> Ph (as core)	-2129.04927	-2129.66263	-0.61336						
S(CMe <sub>2</sub> C(O)OMe)–C•(SMe)S– SO <sub>2</sub> Ph (full)	-2395.76834		-2396.38171	0.27803	0.03078	760.4954	-2396.16939	-12.29	
EtS–C(SMe)=S (as core)	-1350.00536	-1350.31197	-0.30661						
S(CH(Me)Ph)–C(SMe)=S (as full)	-1580.54757		-1580.85418	0.18915	0.01874	550.2243	-1580.71611	-7.17	
S(CH(Me)OC(O)Me)– C(SMe)=S (as full)	-1577.50173		-1577.80834	0.15196	0.01820	539.6422	-1577.70666	-5.83	
S(CMe <sub>2</sub> C(O)OMe)–C(SMe)=S (as full)	-1616.71911		-1617.02572	0.17980	0.01988	557.9074	-1616.89684	-6.38	

<sup>a</sup> Found with a GTMP2Large basis set; <sup>b</sup> Value used in the determination of  $G_{gas}^T$ , equal to either G3(MP2)-RAD  $E_{gas}^0$  or an ONIOM approximation to it (ONIOM correction is given for the core layers); <sup>c</sup> Superscript *T* refers to 333.15 K.

## APPENDIX 2

NOTE: All species had zero imaginary frequencies, as determined from frequency calculations at the M06-2X/6-31G(d) level.

### •Et

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1\1\GINC-V1366\FOpt\UM062X\Gen\C2H5(2)\GXG501\08-Mar-2012\0\#\M062X/gen
6D SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=268435456\
\et_r.freq\0,2\C,-0.0155313658,-0.0269006471,-0.0418772312\C,-0.1107457618,-0.1918181927,1.4347100148\H,1.0259518463,0.0059298634,-0.3767320381\H,-0.4952413364,-0.8577842004,-0.5830910008\H,-0.5078429104,0.8914646772,-0.3767314376\H,-1.0060115654,0.1074498189,1.9653651606\H,0.5960623772,-0.817505912,1.9653645334\Version=EM64L-G09RevB.01\State=2-A\HF=-79.1005112\S2=0.754971\S2-1=0.\S2A=0.750019\RMSD=9.452e-09\RMSF=1.019e-05\Dipole=-0.0285893,-0.0495181,-0.0787065\Quadrupole=0.2491976,-0.2780957,0.0288981,-0.4566475,-0.1385675,-0.2400062\PG=CS [SG(C2H1),X(H4)]\@\
```

### S=C(SMe)S(iPrCN)

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1\1\GINC-V1263\FOpt\RM062X\Gen\C6H9N1S3\GXG501\09-Mar-2012\0\#\M062X/gen
6D SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=268435456\
\mesn.freq\0,1\C,0.1189325001,0.0269510063,0.1588030294\S,0.2302562321,-0.0523651048,1.7851444919\S,1.4771642832,-0.019525782,-0.9608533614\S,-1.352375141,0.1558426584,-0.812832682\C,2.8840150833,-0.0805020966,0.1697046052\H,3.7709272491,-0.0915949526,-0.4666281426\H,2.8927501436,0.7980278148,0.8161172437\H,2.8433483858,-0.9845371343,0.7781000595\C,-2.7796962045,0.0586071392,0.354870153\C,-2.7031835357,-1.1649558117,1.1679113632\C,-2.9088891923,1.3112979862,1.2271043002\C,-3.9994264789,-0.0692471455,-0.5775301587\H,-3.8034760963,1.220537356,1.8512409939\H,-2.0413366606,1.4410094343,1.8729204617\H,-3.0156223668,2.1846747428,0.5785164976\H,-4.9050727874,-0.1209900205,0.0324937297\H,-4.0631247583,0.8094929914,-1.2256352877\H,-3.9372592678,-0.9687280545,-1.1937167059\N,-2.7308371542,-2.1424932064,1.7841655226\Version=EM64L-G09RevB.01\State=1-A\HF=-1483.1146167\RMSD=5.144e-09\RMSF=6.492e-06\Dipole=0.1080986,1.1673282,-0.7579498\Quadrupole=11.5716762,-6.1228333,-5.4488429,-4.7555632,2.236419,4.0298677\PG=C01 [X(C6H9N1S3)]\@\
```

### EtS-C•(SMe)S(iPrCN)

```
1\1\GINC-V1296\FOpt\UM062X\Gen\C8H14N1S3(2)\GXG501\20-Mar-2012\0\#\M062X/gen
6D SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) maxdisk=268435456\
\cniert_r.freq\0,2\C,0.3792073411,-0.6212730289,0.287614471\S,0.0818167641,0.7435143759,1.3320803446\S,1.9684674694,-0.6971873597,-0.4234097352\S,-0.950559384,-1.6238372372,-0.240603796\C,-1.2001252651,0.1180831702,2.4582853693\H,-1.2789436248,0.8511265728,3.2635143332\H,-2.1626563965,0.0191401277,1.9571588695\H,-0.892984642,-0.8464350691,2.8670100651\C,1.7096504331,-0.1917754658,-2.2059947937\C,3.1152199507,0.1010191715,-2.7473572383\C,1.1373324556,-1.3280211248,-2.9443073186\C,0.7963277579,1.0283896923,-2.3122305717\H,3.0567081848,0.3447357787,-3.8119970931\H,3.5396344334,0.9524213413,-2.2090912667\H,3.7742247668,-0.7625503308,-2.6249563027\H,0.7074516261,1.3304902528,-3.3606286894\H,-0.2020839916,0.8098778033,-1.926678485\H,1.2270693757,1.8527921685,-1.7369612673\N,0.7113682272,-2.2281816529,-3.533420712\C,-0.1712165918,-3.2754055035,-0.3159743503\C,0.3124399425,-3.759550108,1.0419606532\H,
```

-0.9600068528,-3.9164960923,-0.7197075192\H,0.6351317974,-3.2446448982  
, -1.0521529601\H,0.7542474805,-4.7564881868,0.9497143219\H,1.075710758  
1,-3.0850035867,1.4411197987\H,-0.5129529375,-3.8095424569,1.757680539  
6\\Version=EM64L-G09RevB.01\State=2-A\HF=-1562.2641143\S2=0.755324\S2-  
1=0.\S2A=0.750025\RMSD=7.110e-09\RMSF=3.579e-06\Dipole=0.0570861,0.500  
2506,0.7526082\Quadrupole=0.9647979,0.9102793,-1.8750772,0.7634293,-6.  
5804062,-6.698334\PG=C01 [X(C8H14N1S3)]\ \@

**EtS-C (SMe)=S**

1\1\GINC-V1462\FOpt\RM062X\Gen\C4H8S3\GXG501\09-Mar-2012\0\#\M062X/gen  
6D SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk  
=268435456\\meset.freq\\0,1\C,0.0233427871,0.,0.0782696482\S,0.0257943  
44,0.,1.718286142\S,1.4561734702,0.,-0.9425115249\S,-1.4050890405,0.,-  
0.9439971813\C,2.7866680661,0.,0.2786862133\H,3.7143437363,0.,-0.29688  
10009\H,2.7299665748,0.891142591,0.9048015467\H,2.7299665748,-0.891142  
591,0.9048015467\C,-2.7603752949,0.,0.268066762\H,-2.652395212,0.88332  
72968,0.9014509004\C,-4.0844733907,0.,-0.4879252559\H,-2.652395212,-0.  
8833272968,0.9014509004\H,-4.9098428629,0.,0.2287497948\H,-4.183275418  
5,0.8866879428,-1.1198091263\H,-4.1832754185,-0.8866879428,-1.11980912  
63\\Version=EM64L-G09RevB.01\State=1-A'\HF=-1351.6172283\RMSD=3.174e-0  
9\RMSF=2.202e-05\Dipole=-0.1339958,0.,-0.0906867\Quadrupole=8.8672378,  
-2.9902797,-5.8769581,0.,-0.0720587,0.\PG=CS [SG(C4H2S3),X(H6)]\ \@

**iPrCN**

1\1\GINC-V1463\FOpt\UM062X\Gen\C4H6N1(2)\GXG501\08-Mar-2012\0\#\M062X/  
gen 6D SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxd  
isk=268435456\\cn\_r.freq\\0,2\C,-0.0399285471,0.,-0.0230528596\C,-0.03  
287466,0.,1.4727191575\C,1.2589748804,0.,-0.7648301648\C,-1.2514897485  
,0.,-0.722547957\H,-1.0422687699,0.,1.8861750971\H,0.5006192859,-0.881  
0075452,1.8523098056\H,0.5006192859,0.8810075452,1.8523098056\H,1.1123  
410542,0.,-1.8457190602\H,1.8544570274,0.8810075452,-0.4926062442\H,1.  
8544570274,-0.8810075452,-0.4926062442\N,-2.2631873376,0.,-1.306651758  
6\\Version=EM64L-G09RevB.01\State=2-B1\HF=-210.6290295\S2=0.765239\S2-  
1=0.\S2A=0.750121\RMSD=4.565e-09\RMSF=4.595e-05\Dipole=1.4243776,0.,0.  
8223647\Quadrupole=-2.4419629,1.2853245,1.1566384,0.,-3.1164794,0.\PG=  
C02V [C2(C1C1N1),SGV(C2H2),X(H4)]\ \@

**CH (Me) Ph**

1\1\GINC-V1375\FOpt\UM062X\Gen\C8H9(2)\GXG501\08-Mar-2012\0\#\M062X/ge  
n 6D SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdis  
k=268435456\\bz\_r.freq\\0,2\C,-0.0053117039,0.,0.0566569259\C,-0.01231  
54208,0.,1.4752123775\C,1.206283907,0.,2.1996423197\C,1.2184443984,0.,  
3.5829713822\C,0.0184179965,0.,4.2999044909\C,-1.1943695696,0.,3.60826  
56957\C,-1.2164224628,0.,2.2226435535\H,2.1420199559,0.,1.6462075767\H  
,2.1663204764,0.,4.1128735201\H,0.0293170973,0.,5.3850061391\H,-2.1303  
704286,0.,4.1591413369\H,-2.1685207037,0.,1.7002674688\H,0.9584553183,  
0.,-0.4429168754\C,-1.2439766674,0.,-0.7770262807\H,-1.0043538557,0.,-  
1.8419784342\H,-1.8686921686,-0.8806283975,-0.5745420983\H,-1.86869216  
86,0.8806283975,-0.5745420983\\Version=EM64L-G09RevB.01\State=2-A'\HF=  
-310.0769896\S2=0.77386\S2-1=0.\S2A=0.750348\RMSD=9.306e-09\RMSF=7.279  
e-05\Dipole=-0.0560633,0.,-0.1871243\Quadrupole=1.8245896,-4.435602,2.  
6110125,0.,0.15362,0.\PG=CS [SG(C8H7),X(H2)]\ \@

**S (CH (Me) Ph) -C• (SMe) S (iPrCN)**

1\1\GINC-V1414\FOpt\UM062X\Gen\C14H18N1S3(2)\GXG501\04-Apr-2012\0\#\M0  
62X/gen 6D SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) maxdisk=26843  
5456\\cnibz\_r.freq\\0,2\C,0.2886380824,-1.3053813684,0.3673077841\S,0.  
5385208932,-0.8324007245,2.0327902519\S,1.6400073765,-1.2824086065,-0.

7555320595\S,-0.9915027392,-2.4641808324,0.0717389373\C,1.5545457014,0.666060144,1.9241361281\H,1.8386485485,0.9062687799,2.9506191094\H,2.4509175132,0.4768866485,1.3318212437\H,0.9900185628,1.4905949206,1.4883149778\C,1.1674274081,-0.033412008,-2.0571123204\C,-0.0969713081,-0.431016885,-2.8185228144\C,0.9845984953,1.2703228281,-1.4053264358\C,2.3829751857,0.0327649602,-2.9920224858\H,-0.3118427642,0.3175338504,-3.5887739407\H,0.064500062,-1.4029615667,-3.2926067135\H,-0.9592412252,-0.5005777065,-2.1549652351\H,2.1916470185,0.7565318309,-3.7891405164\H,3.2853167481,0.3314178268,-2.4531776492\H,2.5443233529,-0.9506695989,-3.4424265596\N,0.8515759711,2.300880891,-0.8959670091\C,-2.605526948,-1.6193991332,0.4717390387\C,-2.8457149394,-1.3567490649,1.9554005016\C,-2.8244971833,-0.422458794,-0.4174180945\H,-3.2894823059,-2.4143558523,0.1506191779\H,-3.8935283477,-1.0723392656,2.0984666826\H,-2.6384008277,-2.2537661524,2.5444921052\H,-2.2183752551,-0.5489338546,2.333954104\C,-2.2154762977,0.8068309968,-0.1480626462\C,-2.3775567829,1.8818796282,-1.0190167823\C,-3.1553737217,1.7439715858,-2.1659478601\C,-3.7718993509,0.5250451199,-2.4393912196\C,-3.6040119305,-0.5490631711,-1.5710015926\H,-1.5911130344,0.9231658924,0.7342992484\H,-1.8744780823,2.8195760989,-0.8071903982\H,-3.279088368,2.5827455847,-2.8438845675\H,-4.3817260936,0.4086938228,-3.3301792032\H,-4.0738398824,-1.504100381,-1.794033187\\Version=EM64L-G09RevB.01\State=2-A\HF=-1793.2204324\S2=0.755216\S2-1=0.\S2A=0.750023\RMSD=5.524e-09\RMSF=1.002e-06\Dipole=-0.2907843,-0.0023309,-0.5920337\Quadrupole=2.8211444,-8.6738995,5.8527551,2.499646,-0.2274451,0.9415194\PG=C01 [X(C14H18N1S3)]\@

**S (CH (Me) Ph) -C (SMe) =S**

1\1\GINC-V1462\FOpt\RM062X\Gen\C10H12S3\GXG501\09-Mar-2012\0\#\M062X/gen 6D SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=268435456\mesbz.freq\0,1\C,0.0220852749,0.0324426196,0.1091740847\S,0.0302804978,-0.4933524229,1.6636027149\S,1.4556645696,0.2746083573,-0.8813351347\S,-1.3926740776,0.4155233903,-0.8635084226\C,2.7735942342,-0.305834532,0.2090228459\H,3.6968838579,-0.200854062,-0.3640858244\H,2.8178148051,0.3031329434,1.1124857123\H,2.6131535421,-1.3502856232,0.4792020487\C,-2.7834738301,0.3346291469,0.3399705821\H,-2.5939395049,-0.5543270614,0.948158982\C,-2.8215042326,1.5734237,1.2309836016\C,-4.0451919352,0.1375595368,-0.4706246449\H,-3.6547474557,1.4845126223,1.9351704551\H,-1.8934570105,1.6679029684,1.7990162105\H,-2.9654847331,2.4805909724,0.6385565243\C,-4.5342380663,1.1511510623,-1.3000928213\C,-5.6998604183,0.9615010073,-2.0353596043\C,-6.3939459445,-0.2429388447,-1.9472210763\C,-5.9124825362,-1.2583105018,-1.1257429245\C,-4.74214468,-1.0692647416,-0.3962251793\H,-3.9967022907,2.0930912817,-1.3770146029\H,-6.0667688952,1.7558362787,-2.6779000796\H,-7.3053163593,-0.3895778232,-2.5183401611\H,-6.4466508037,-2.2005791224,-1.0532188268\H,-4.3642987763,-1.8649009824,0.2405540667\\Version=EM64L-G09RevB.01\State=1-A\HF=-1582.5723412\RMSD=8.597e-09\RMSF=7.978e-06\Dipole=-0.1933724,0.0648835,-0.1195786\Quadrupole=8.9693169,-2.0912028,-6.878114,0.1314696,2.0528038,-0.5044435\PG=C01 [X(C10H12S3)]\@

**•CH (Me) OC (O) Me**

1\1\GINC-V1296\FOpt\UM062X\Gen\C4H7O2(2)\GXG501\11-Mar-2012\0\#\M062X/gen 6D SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=268435456\va\_r.freq\0,2\C,1.3408228116,0.2428976518,-0.2837367367\C,2.2033767906,1.4165166521,-0.0089047303\O,-0.0000818543,0.4757061973,-0.0715499668\H,1.835038027,2.3024748861,-0.536724244\H,2.2374483046,1.6660609931,1.0625071884\H,3.2252973883,1.2162584896,-0.3386671158\H,1.6588618715,-0.7854707954,-0.1749791448\C,-0.8404252206,-0.5933664197,-0.0690103069\O,-0.467687005,-1.7270265758,-0.2145791036\C,-2.26108

20421,-0.1437797938,0.1367189161\H,-2.5556770593,0.528392818,-0.673358  
0674\H,-2.9135470275,-1.0150204612,0.1562068066\H,-2.3438835116,0.4117  
7282,1.0741757733\Version=EM64L-G09RevB.01\State=2-A\HF=-306.9003254\  
S2=0.754193\S2-1=0.\S2A=0.750014\RMSD=5.723e-09\RMSF=5.711e-06\Dipole=  
-0.118897,0.7511524,0.2124782\Quadrupole=4.3711598,-3.9796897,-0.39147  
01,0.0401307,-0.0435593,-0.4512885\PG=C01 [X(C4H7O2)]\@

**S (CH (Me) OC (O) Me) -C• (SMe) S (iPrCN)**

1\1\GINC-V1258\FOpt\UM062X\Gen\C10H16N1O2S3(2)\GXG501\06-Apr-2012\0\#\#  
M062X/gen 6D SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) maxdisk=268  
435456\cniva\_r.freq\0,2\C,0.9515809582,-1.5678802873,0.3774371084\S,  
1.1117644318,-1.0989136092,2.0476529812\S,2.271253275,-1.3141653628,-0  
.7469001986\S,-0.2969787149,-2.7486109441,0.024450712\C,1.761292553,0.  
5925449718,1.9516543835\H,2.0172861912,0.8844264879,2.9721736366\H,2.6  
565933208,0.6244886445,1.3291435411\H,0.9861805181,1.2529769254,1.5565  
154581\C,1.5282812592,-0.2516149347,-2.0822873906\C,2.6424052393,-0.07  
58487048,-3.1222846753\C,0.382803299,-0.9344590245,-2.7033293667\C,1.0  
611512658,1.0931394097,-1.5192659221\H,2.279388804,0.5454999721,-3.945  
6159643\H,3.4967748864,0.4231358569,-2.6561462805\H,2.9663718144,-1.03  
89048054,-3.5235208355\H,0.6558498457,1.7107600654,-2.3276827837\H,0.2  
852021217,0.9566586024,-0.7606456135\H,1.9158930485,1.6105549575,-1.07  
36412812\N,-0.5427706661,-1.4219880735,-3.1973207665\C,-1.7924895491,-  
1.6886963299,-0.1061789836\C,-2.8981853539,-2.518861552,-0.7258002101\  
O,-2.2236724456,-1.2481024581,1.1794194443\H,-1.5404617636,-0.82339684  
97,-0.7192976397\H,-3.8134352202,-1.9228259615,-0.7659686505\H,-2.6133  
493424,-2.804995561,-1.7406553571\H,-3.0907439552,-3.415507469,-0.1300  
834093\C,-1.9063440927,0.0041900302,1.5608328723\O,-1.3377137709,0.807  
6524778,0.8599269311\C,-2.3519920105,0.2526748702,2.9748297495\H,-3.39  
35189197,-0.0491091474,3.1033920658\H,-1.7395895037,-0.3610366656,3.64  
19598109\H,-2.2243834554,1.3069146394,3.2157890844\Version=EM64L-G09R  
evB.01\State=2-A\HF=-1790.0611209\S2=0.75529\S2-1=0.\S2A=0.750024\RMSD  
=6.292e-09\RMSF=3.268e-06\Dipole=0.2502158,1.2521873,0.6813567\Quadrup  
ole=4.0645111,-3.8341924,-0.2303187,4.1558133,-6.4500644,-0.1714844\PG  
=C01 [X(C10H16N1O2S3)]\@

**S (CH (Me) OC (O) Me) -C (SMe) =S**

1\1\GINC-V1281\FOpt\RM062X\Gen\C6H10O2S3\GXG501\09-Mar-2012\0\#\#M062X/  
gen 6D SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxd  
isk=268435456\mesva.freq\0,1\C,-1.3199521331,0.1205502784,-0.0542165  
441\S,-0.7873261865,-1.2786143878,-0.7175227354\S,-2.9666081925,0.4397  
168917,0.4667183439\S,-0.3478524401,1.5618502768,0.2551129771\C,-3.795  
7620262,-1.1130840845,0.0639010284\H,-4.8356668798,-0.9789774921,0.367  
6506792\H,-3.7364361824,-1.3101812496,-1.0070231734\H,-3.3441749845,-1  
.939370698,0.6141669072\C,1.295631471,1.04352047,-0.3211382519\H,1.183  
974632,0.5610416466,-1.2942008913\C,2.2052484509,2.2565178918,-0.39247  
12092\O,1.7972018044,0.0946943016,0.6127920836\H,3.1846419537,1.922508  
1104,-0.7438870849\H,1.8121625946,2.996558799,-1.0934855255\H,2.317426  
569,2.715240623,0.5933040228\C,2.6173814064,-0.8520471228,0.0914085013  
\O,3.038043712,-0.812047023,-1.0350383872\C,2.8961365561,-1.9235941651  
,1.1076706435\H,1.9760993435,-2.490482597,1.2770085848\H,3.6757902086,  
-2.5842154114,0.7321587827\H,3.1934493226,-1.475988058,2.0582972485\Ver  
sion=EM64L-G09RevB.01\State=1-A\HF=-1579.4094373\RMSD=4.570e-09\RMSF  
=5.166e-06\Dipole=-0.4285729,0.0337853,0.588027\Quadrupole=4.5034155,0  
.1376188,-4.6410343,4.2841759,4.0215019,-3.7986693\PG=C01 [X(C6H10O2S3  
)\@

**•CMe<sub>2</sub>C (O) OMe**

1\1\GINC-V1487\FOpt\UM062X\Gen\C5H9O2(2)\GXG501\09-Mar-2012\0\#\M062X/  
gen 6D SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxd  
isk=268435456\mma\_r.freq\0,2\C,-0.0423590535,0.,-0.001229266\C,0.021  
2581826,0.,1.4864347721\C,1.2249916455,0.,-0.785332514\C,-1.3535324559  
,0.,-0.6300866566\H,-0.9796212528,0.,1.9188656252\H,0.5692262223,-0.87  
93668655,1.8502842726\H,0.5692262223,0.8793668655,1.8502842726\H,1.043  
883395,0.,-1.8594953824\H,1.8324138759,0.8785190208,-0.5292479488\H,1.  
8324138759,-0.8785190208,-0.5292479488\O,-1.2955184901,0.,-1.984045905  
2\O,-2.411023516,0.,-0.0246146533\C,-2.5650886075,0.,-2.6261043503\H,-  
2.3579116817,0.,-3.6955060409\H,-3.137733939,-0.8872598439,-2.34556247  
1\H,-3.137733939,0.8872598439,-2.345562471\Version=EM64L-G09RevB.01\St  
ate=2-A\HF=-346.2058847\S2=0.758556\S2-1=0.\S2A=0.750048\RMSD=3.504e  
-09\RMSE=2.022e-05\Dipole=0.6944497,0.,-0.3452284\Quadrupole=-0.509043  
8,-0.6108624,1.1199062,0.,4.3771194,0.\PG=CS [SG(C5H3O2),X(H6)]\@

**S (CMe<sub>2</sub>C (O) OMe) -C• (SMe) S (iPrCN)**

1\1\GINC-V1364\FOpt\UM062X\Gen\C11H18N1O2S3(2)\GXG501\06-Apr-2012\0\#\M062X/  
gen 6D SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) maxdisk=268  
435456\cnimma\_r.freq\0,2\C,0.5577753027,-0.7247397387,0.0823504749\S  
,0.0161022364,0.210474067,1.4373140737\S,2.1391355928,-0.5573744223,-0  
.6395829064\S,-0.6272553437,-1.8904816583,-0.4889968585\C,1.3767762356  
,1.348204852,1.8019027389\H,1.0541858903,1.9128864396,2.6790204724\H,2  
.2875469634,0.795317267,2.0338056803\H,1.5431484909,2.0317962975,0.968  
5674427\C,1.8509753816,0.5007866907,-2.1567561356\C,0.8542516752,-0.13  
89240014,-3.1240015609\C,1.3578078421,1.8111672957,-1.7159694103\C,3.2  
3676033,0.6482412913,-2.7963533555\H,0.8105656868,0.4505978642,-4.0458  
565859\H,1.178190774,-1.1574634186,-3.3564866639\H,-0.1463714364,-0.18  
69239423,-2.6923647177\H,3.1673765009,1.2808984949,-3.6856000688\H,3.9  
511299601,1.0952384516,-2.1008931913\H,3.6006744835,-0.3390227145,-3.0  
962258382\N,0.9663573939,2.8378095913,-1.3526401545\C,0.0135411795,-3.  
5078979207,0.1724309826\C,-0.9153988125,-4.5719781572,-0.4186941795\C,  
1.4433837553,-3.6987210873,-0.3215946428\C,-0.0063193338,-3.5161689292  
,1.6940277295\H,-0.5949075612,-5.5636458067,-0.083004874\H,-1.93870504  
13,-4.4073147536,-0.0688841112\H,-0.9009486791,-4.5507407309,-1.509935  
0384\H,0.3650225505,-4.4773181304,2.0640987284\H,0.6376996144,-2.73235  
75444,2.0979786064\H,-1.0273127298,-3.3617173192,2.051986754\O,1.51192  
49785,-3.8602582977,-1.6509814885\O,2.4110508763,-3.7072940704,0.39882  
61336\C,2.836804564,-3.9755731131,-2.1659653329\H,2.7262189358,-4.1043  
118461,-3.2418446516\H,3.4038355314,-3.0692661715,-1.9374637128\H,3.34  
54991839,-4.8351736569,-1.7243172177\Version=EM64L-G09RevB.01\State=2  
-A\HF=-1829.3475814\S2=0.755108\S2-1=0.\S2A=0.750024\RMSD=6.863e-09\RM  
SF=1.472e-06\Dipole=0.6082207,-0.8909877,-0.7032797\Quadrupole=-0.8543  
48,-6.0938819,6.9482299,5.8113943,-5.1464077,4.0498348\PG=C01 [X(C11H1  
8N1O2S3)]\@

**S (CMe<sub>2</sub>C (O) OMe) -C (SMe) =S**

1\1\GINC-V1263\FOpt\RM062X\Gen\C7H12O2S3\GXG501\09-Mar-2012\0\#\M062X/  
gen 6D SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxd  
isk=268435456\mesmma.freq\0,1\C,0.0386029549,0.068410181,0.122231608  
\S,0.1268697867,0.4069837362,1.723309603\S,1.4233068679,-0.1791191297,  
-0.9368497216\S,-1.4191655378,-0.0849759603,-0.8439790578\C,2.80714060  
38,0.1697021697,0.1699131702\H,3.7061903687,0.0578649773,-0.4391954348  
\H,2.7379178174,1.1864959996,0.5586601739\H,2.8210789344,-0.5389015425  
,0.998611505\C,-2.8173575035,-0.0911422971,0.3481296152\C,-4.065632726  
2,0.0351101323,-0.545735323\C,-2.8639551828,-1.3865075763,1.1525295786  
\C,-2.8300272144,1.1207427806,1.2827241414\H,-3.7179638091,-1.35033191  
71,1.8334538994\H,-2.9738509403,-2.236813331,0.474956317\H,-1.95967486

14,-1.51428255,1.7502012741\H,-4.9528984865,0.0201859328,0.0943616824\  
H,-4.0536589012,0.9678614161,-1.1151472674\H,-4.1261095373,-0.80819541  
54,-1.2398467166\O,-2.3959016796,2.236383711,0.6879575619\O,-3.2955343  
102,1.0840343161,2.3929156338\C,-2.3846546974,3.387793376,1.5306264892  
\H,-1.99816335,4.1996356274,0.917040509\H,-3.3931273442,3.6126857323,1  
.8838704894\H,-1.7341658166,3.2086849904,2.3902809091\\Version=EM64L-G  
09RevB.01\State=1-A\HF=-1618.6980346\RMSD=6.934e-09\RMSF=4.615e-06\Dip  
ole=0.2359843,0.2598875,-0.5456446\Quadrupole=6.8200637,1.9352817,-8.7  
553454,0.3677547,2.8226611,0.9964329\PG=C01 [X(C7H12O2S3)]\@

**S=C (SMe) S-SO<sub>2</sub>Me**

1\1\GINC-V1383\FOpt\RM062X\Gen\C3H6O2S4\GXG501\09-Mar-2012\0\#\M062X/g  
en 6D SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdi  
sk=268435456\messome.freq\0,1\C,0.0162414605,0.2733172295,0.24041554  
76\S,0.1524311814,0.4465510652,1.8553579935\S,1.2920340967,-0.18541655  
51,-0.8612533644\S,-1.4482682359,0.5658751283,-0.736581601\C,2.7394433  
842,-0.163205062,0.2187473479\H,3.5951648819,-0.3778533194,-0.42390746  
74\H,2.8515431295,0.8180212158,0.6832736109\H,2.644924955,-0.926990610  
3,0.9913649754\S,-3.0611227635,-0.0782158945,0.5215391238\O,-4.1648504  
422,-0.1051912582,-0.4210513334\O,-2.6616111604,-1.2482199421,1.275553  
5459\C,-3.3206636291,1.2791623928,1.6487918404\H,-4.1697385017,0.98611  
57414,2.2712139354\H,-2.4183722619,1.4081523699,2.2466653218\H,-3.5562  
871573,2.1671474986,1.0623544031\\Version=EM64L-G09RevB.01\State=1-A\H  
F=-1860.794586\RMSD=5.622e-09\RMSF=1.050e-05\Dipole=1.147077,1.0744688  
,0.4491834\Quadrupole=5.4009048,-2.5175749,-2.8833298,-5.9882631,-5.98  
02798,2.1776697\PG=C01 [X(C3H6O2S4)]\@

**•SO<sub>2</sub>Me**

1\1\GINC-V1485\FOpt\UM062X\Gen\C1H3O2S1(2)\GXG501\09-Mar-2012\0\#\M062  
X/gen 6D SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman ma  
xdisk=268435456\some\_r.freq\0,2\S,0.0115508658,-0.1195455826,0.01420  
60364\O,-0.0729413052,-0.1000073893,1.4841553995\O,1.2405982216,0.2621  
146436,-0.7013492563\C,-1.2850638521,1.009320167,-0.5779961053\H,-1.30  
89719909,0.956553504,-1.665544148\H,-2.2303737536,0.7025105703,-0.1327  
327667\H,-1.0017664678,2.0087906408,-0.2421200864\\Version=EM64L-G09Re  
vB.01\State=2-A\HF=-588.3315983\S2=0.756832\S2-1=0.\S2A=0.750028\RMSD=  
8.051e-09\RMSF=1.206e-05\Dipole=-1.2702575,0.3270663,-0.7092307\Quadru  
pole=0.0745467,2.10438,-2.1789267,-0.8378048,1.9666831,0.4138504\PG=C0  
1 [X(C1H3O2S1)]\@

**EtS-C• (SMe) S-SO<sub>2</sub>Me**

1\1\GINC-V1258\Freq\UM062X\Gen\C5H11O2S4(2)\GXG501\21-Mar-2012\0\#\M06  
2X/gen 6D SCF=Tight INT(grid=ultrafine) OPT=(calcall) IOP(2/17=4) maxd  
isk=268435456\someiet\_r.freq\0,2\C,0.3317191097,-1.105910788,0.59196  
40664\S,-0.2219762916,-0.6880881703,2.2080788752\S,1.971471064,-0.9879  
904915,0.1108843836\S,-0.9753625332,-1.5164971907,-0.4730622773\C,1.07  
25549178,-1.4335755296,3.2399607477\H,0.7933959435,-1.2319689082,4.275  
9021263\H,1.1149666522,-2.5111318962,3.0742669233\H,2.0451658078,-0.98  
53111596,3.0303780678\S,2.1435169429,1.1444060894,-0.425673697\O,3.399  
6572307,1.2825663931,-1.1526565965\O,0.870199775,1.5698011803,-1.00046  
44419\C,2.3093802973,1.9643462058,1.1571848323\H,2.3756224323,3.034606  
0335,0.947583813\H,1.4223191522,1.7380709908,1.7516315644\H,3.22102624  
84,1.6052951677,1.6352047558\C,-0.292718146,-1.2720553652,-2.146652956  
4\C,-1.4017637349,-1.5455176064,-3.1566629176\H,0.0697192121,-0.243813  
9975,-2.2116591802\H,0.5462864858,-1.9579713064,-2.2827044879\H,-1.008  
5738184,-1.4148792209,-4.168069737\H,-1.7814036508,-2.5673448778,-3.06  
8706598\H,-2.2368541079,-0.8528031862,-3.0244792516\\Version=EM64L-G09

RevB.01\State=2-A\HF=-1939.950338\S2=0.759336\S2-1=0.\S2A=0.75005\RMSD=6.091e-09\RMSF=9.205e-07\Dipole=-0.0210953,-0.390611,1.1291236\Polar=137.363948,28.1319438,125.2660696,10.695158,0.9012633,159.5889164\PG=C01 [X(C5H11O2S4)]\ \@

**S (CH (Me) Ph) -C• (SMe) S-SO<sub>2</sub>Me**

1\1\GINC-V1351\FOpt\UM062X\Gen\C11H15O2S4 (2) \GXG501\05-Apr-2012\0\ \#M062X/gen 6D SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) maxdisk=268435456\ \someibz\_r.freq\ \0,2\C,0.406567805,-0.4899251871,-0.4754807584\S,0.1227198606,1.2056256095,-0.1906301448\S,1.9846674203,-1.1889482895,-0.4896892025\S,-0.9411887139,-1.4257976681,-1.0822850359\C,1.6273906719,1.767918634,0.6483071527\H,1.438538897,2.8094179685,0.9160953585\H,1.8023398947,1.1721353043,1.5453292543\H,2.4837991448,1.7112629704,-0.0242130446\S,2.1964171451,-1.900173397,1.5570200606\O,3.5903986541,-2.3072684709,1.6754758832\O,1.6216921752,-0.9032599039,2.4580311782\C,1.1613230203,-3.3537430087,1.6096958647\H,1.1601872325,-3.6995562056,2.6459626647\H,0.151076894,-3.0758767827,1.3017138644\H,1.5975511118,-4.0960090146,0.9412935538\C,-2.3384024231,-1.0658429704,0.0988160461\C,-3.6198272307,-1.4354198813,-0.6447754228\C,-2.1263566223,-1.7913783836,1.4032298299\H,-2.323439904,0.0116258395,0.2798032907\H,-4.4761550169,-1.3382591693,0.0285757004\H,-3.7656675787,-0.7757708435,-1.5029222423\H,-3.594172828,-2.4650311006,-1.0144698711\C,-2.5453281835,-3.1147595154,1.5866189887\C,-2.2972287808,-3.7750329648,2.7857088754\C,-1.6188292101,-3.1258267337,3.8170865614\C,-1.1886797467,-1.8143718486,3.6396140974\C,-1.4458272373,-1.1512273061,2.4415798335\H,-3.0652511839,-3.6366687423,0.7885213722\H,-2.6341220376,-4.7990390264,2.9154070279\H,-1.4249489563,-3.643114741,4.7518344025\H,-0.6388727084,-1.3042252188,4.4237574139\H,-1.0949406169,-0.1317420356,2.3041134399\ \Version=EM64L-G09 RevB.01\State=2-A\HF=-2170.9130621\S2=0.758014\S2-1=0.\S2A=0.750045\RM SD=5.123e-09\RMSF=5.567e-06\Dipole=-1.4514213,-0.1643354,0.1651484\Qua drupole=-7.2028394,9.4675579,-2.2647184,4.5706608,-0.8350667,-2.0602754\PG=C01 [X(C11H15O2S4)]\ \@

**S (CH (Me) OC (O) Me) -C• (SMe) S-SO<sub>2</sub>Me**

1\1\GINC-V1474\FOpt\UM062X\Gen\C7H13O4S4 (2) \GXG501\11-Apr-2012\0\ \#M062X/gen 6D SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) maxdisk=268435456\ \someiva\_r.freq\ \0,2\C,0.1393913239,-1.2699427792,-0.1850455684\S,-0.2491707006,0.1267974975,0.7528539852\S,1.7082226992,-1.6462157605,-0.7674392307\S,-1.2307675252,-2.3386577135,-0.4712781826\C,1.352485448,0.9134727105,1.0565337857\H,1.1496944047,1.738621234,1.7419058981\H,2.0446174416,0.2099564558,1.5217437154\H,1.7795953977,1.3063814476,0.1319620792\S,2.0139338201,-0.1034509901,-2.3165654364\O,0.7872829929,0.6901645369,-2.3686239388\O,3.2933192449,0.5320457711,-2.0233457368\C,2.1889668376,-0.9972565039,-3.8565181271\H,2.4677377939,-0.2476578257,-4.6013432921\H,2.9872530537,-1.7303306478,-3.7355647257\H,1.2326242538,-1.4502898355,-4.1189653977\C,-1.4289340258,-2.1158898021,-2.2676486702\C,-2.436314559,-3.1131236101,-2.808795099\O,-1.8721897398,-0.7819816761,-2.4970520666\H,-0.4489307342,-2.2525347434,-2.7318388171\H,-2.5271026322,-2.9651618066,-3.8878931692\H,-2.1072087839,-4.137123531,-2.6176965568\H,-3.4129633933,-2.955551525,-2.3436775105\C,-1.5001606551,-0.2252019444,-3.6700465185\O,-0.8973419786,-0.8298400828,-4.5256920976\C,-1.9387641811,1.2074836042,-3.7444323215\H,-2.9949946517,1.2933735047,-3.4808051131\H,-1.3531580555,1.7762229174,-3.0178832764\H,-1.7601760483,1.5880844975,-4.7488486109\ \Version=EM64L-G09 RevB.01\State=2-A\HF=-2167.7494532\S2=0.758189\S2-1=0.\S2A=0.750043\RMSD=5.536e-09\RMSF=4.110e-06\Dipole=-0.2665848,-0.2544568,-0.2338373\Quadrupole=-2.5755607,0.8255078,1.7500529,-2.8863414,1.2026508,3.9643547\PG=C01 [X(C7H13O4S4)]\ \@

)]\ \@

**S (CMe<sub>2</sub>C (O) OMe) -C• (SMe) S-SO<sub>2</sub>Me**

1\1\GINC-V1249\FOpt\UM062X\Gen\C8H15O4S4(2)\GXG501\03-Apr-2012\0\#\M062X/gen 6D SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) maxdisk=268435456\someimma\_r.freq\0,2\C,0.561985158,-1.5925279478,0.2662703452\S,0.3634581869,-0.879228308,1.8443452558\S,2.0287228755,-1.4488074108,-0.6296412457\S,-0.6515696127,-2.695153826,-0.3293521279\C,1.329391197,0.6512475208,1.7085719466\H,1.1465050797,1.1994111797,2.6348855029\H,2.3933786336,0.4295097977,1.6201683402\H,0.9870239755,1.232487643,0.8508210519\S,1.4860332676,0.1052764278,-2.0554289211\O,0.4565325725,0.9433987949,-1.4441949653\O,2.7386260376,0.6666738373,-2.5430787128\C,0.7109945118,-0.7953514153,-3.3915599273\H,0.3776526408,-0.0498118991,-4.1171886134\H,1.4524521007,-1.4634417398,-3.8297442011\H,-0.1325444284,-1.3535715115,-2.9821420643\C,-2.2710735198,-1.8870693345,0.0537419981\C,-3.3133733455,-2.8209020902,-0.5832337204\C,-2.5243498476,-1.9327588686,1.5638248557\C,-2.3448729124,-0.4871710455,-0.5453706887\H,-4.3147675215,-2.4247497898,-0.3863156865\H,-3.1686185969,-2.8688040005,-1.6662990457\H,-3.2455755375,-3.8272739977,-0.1624381668\H,-3.3315797632,-0.0578093644,-0.3522186406\H,-1.5869483516,0.1782096512,-0.1274116374\H,-2.1895769153,-0.5421762281,-1.6268146677\O,-3.1214406445,-0.8174480664,2.0015990232\O,-2.2863771757,-2.88267617,2.265544898\C,-3.3896370409,-0.8028079272,3.4042738101\H,-3.8600019542,0.1580212012,3.6056100106\H,-4.0546231156,-1.625955393,3.6732891231\H,-2.4555009241,-0.9035453269,3.9616991676\Version=EM64L-G09RevB.01\State=2-A\HF=-2207.0338847\S2=0.757659\S2-1=0.\S2A=0.750043\RMSD=9.052e-09\RMSF=7.042e-06\Dipole=-1.3933425,0.1102602,-0.0969122\Quadrupole=-0.4394622,-8.4749948,8.914457,-3.374877,2.6326146,10.8473145\PG=C01 [X(C8H15O4S4)]\ \@

**S=C (SMe) S-SO<sub>2</sub>Ph**

1\1\GINC-V1296\FOpt\RM062X\Gen\C8H8O2S4\GXG501\09-Mar-2012\0\#\M062X/gen 6D SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=268435456\messoph.freq\0,1\C,0.0067112374,0.1374352821,0.1484634423\S,0.3240520347,0.3891737112,1.7251850937\S,1.1873294122,-0.1910538898,-1.1065105573\S,-1.5881050985,0.181379626,-0.637091026\C,2.7416964409,0.0525564899,-0.2195071765\H,3.5308877374,-0.0857367056,-0.9608254281\H,2.7871991948,1.0592287333,0.1989585002\H,2.839504672,-0.6826204818,0.5798529495\S,-3.0142216637,-0.2709123416,0.9013730159\O,-4.2053325772,-0.4207356319,0.0822580328\O,-2.5122716317,-1.3333792852,1.7484526766\C,-3.1960211826,1.2051217996,1.8694721943\C,-2.710366032,1.2241185439,3.1715512549\C,-2.9082257081,2.3738288674,3.9307395042\C,-3.5723611764,3.4683652762,3.3818544549\C,-4.0556261319,3.4247435534,2.0741176717\C,-3.8745065443,2.2815504597,1.3049276425\H,-2.1955001554,0.3554425126,3.5664046178\H,-2.5418609713,2.4134754338,4.9510772168\H,-3.7193054298,4.3628968998,3.978929823\H,-4.580108682,4.2777800842,1.6568954889\H,-4.2580654946,2.2140910627,0.2916925443\Version=EM64L-G09RevB.01\State=1-A\HF=-2052.4538076\RMSD=4.118e-09\RMSF=6.635e-06\Dipole=0.9781579,1.676883,0.491648\Quadrupole=3.1345447,-3.1486803,0.0141356,-8.7965209,-5.8569039,3.2193561\PG=C01 [X(C8H8O2S4)]\ \@

**•SO<sub>2</sub>Ph**

1\1\GINC-V1472\FOpt\UM062X\Gen\C6H5O2S1(2)\GXG501\10-Mar-2012\0\#\M062X/gen 6D SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=268435456\soph\_r.freq\0,2\S,-0.0266622661,-0.0341604112,0.070378365\O,0.3555459149,0.1088554695,1.4859400426\O,0.9536886371,-0.350038441,-0.9829822622\C,-0.8502238186,1.4888222584,-0.412476571\C,-0.8996608441,1.8197847287,-1.7621176524\C,-1.5760214363,2.9785769777,-2.1308

046895\C,-2.1926821532,3.7674588148,-1.1610893103\C,-2.136874885,3.408  
9926298,0.1847344425\C,-1.4649284591,2.2538090569,0.5726075347\H,-0.40  
20328452,1.1919184983,-2.4936160445\H,-1.6184159621,3.2670525576,-3.17  
59488936\H,-2.7200291748,4.6689118953,-1.4564712701\H,-2.614264678,4.0  
308573296,0.9348752689\H,-1.3963282575,1.9558435036,1.6134853148\\Vers  
ion=EM64L-G09RevB.01\State=2-A\HF=-779.9936693\S2=0.756634\S2-1=0.\S2A  
=0.750027\RMSD=7.138e-09\RMSF=5.320e-05\Dipole=-1.350207,1.1846872,-0.  
5479222\Quadrupole=-2.8720272,1.6577695,1.2142577,0.382022,-1.1306955,  
0.0655469\PG=C01 [X(C6H5O2S1)]\@

**EtS-C•(SMe)S-SO<sub>2</sub>Ph**

1\1\GINC-V1407\FOpt\UM062X\Gen\C10H13O2S4(2)\GXG501\14-Apr-2012\0\#\M0  
62X/gen 6D SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) maxdisk=26843  
5456\sophiet\_r.freq\0,2\C,-0.4366487269,-0.2982081146,-0.5837035727\  
S,-1.382310053,1.1509656611,-0.3764211824\S,1.2712269538,-0.3230244213  
, -0.7667629909\S,-1.3772635418,-1.7601961888,-0.3739331559\C,-0.165137  
0969,2.4010173155,0.1118360871\H,-0.7426702332,3.2914365255,0.36808269  
94\H,0.3948684037,2.0625204606,0.9851875718\H,0.5194491415,2.635417916  
6,-0.7056918777\S,1.6213106807,0.0289757015,-2.9025730394\O,3.05844798  
4,-0.1625397201,-3.0571223273\O,0.646147774,-0.7290176523,-3.680586558  
6\C,1.2578310397,1.7560805751,-3.1238477649\C,-0.0362980494,2.13468651  
4,-3.4647056092\C,-0.3297624306,3.4934990137,-3.5435802897\C,0.6627607  
173,4.4383662336,-3.2893740792\C,1.9581184357,4.0371144768,-2.96146320  
89\C,2.2652852686,2.6832900278,-2.8711232086\H,-0.788877825,1.37765522  
47,-3.6596182399\H,-1.333143364,3.8127550132,-3.8054502653\H,0.4273013  
832,5.4961512546,-3.3521592748\H,2.7282095881,4.7787970701,-2.77650938  
08\H,3.2630302468,2.3389137947,-2.6179405682\C,-0.9729592303,-2.728328  
5175,-1.8715452302\C,-1.8426887752,-2.3430700671,-3.0585547663\H,0.089  
0081528,-2.5863692439,-2.0873324788\H,-1.1233686642,-3.7714092386,-1.5  
792699825\H,-1.5246113344,-2.897069907,-3.9471915689\H,-2.8950493603,-  
2.5635425975,-2.8609646504\H,-1.7376135164,-1.2781087779,-3.2765144204  
\\Version=EM64L-G09RevB.01\State=2-A\HF=-2131.6132441\S2=0.758493\S2-1  
=0.\S2A=0.750046\RMSD=7.127e-09\RMSF=8.384e-06\Dipole=-0.5659848,1.887  
5724,0.2240882\Quadrupole=-6.3747717,11.9032999,-5.5285283,4.4677725,4  
.9069775,-0.3071186\PG=C01 [X(C10H13O2S4)]\@

**EtS-C•(SMe)S-SO<sub>2</sub>Ph (core)**

1\1\GINC-X99\FOpt\UM062X\Gen\C10H13O2S4(2)\GXG501\28-May-2012\0\#\M062  
X/gen 6D SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) maxdisk=1342177  
280\sophimma\_r\_core.freq\0,2\C,0.9650182949,-0.7763838332,0.49961871  
51\S,1.7555748248,0.1735045878,1.7333419735\S,1.5429713011,-0.94501274  
3,-1.0877359235\S,-0.4388439627,-1.6096882065,1.1393817699\C,3.4593972  
554,0.2953309604,1.1297470533\H,3.5011563269,0.8632673811,0.1998655393  
\H,4.0073617373,0.8278730301,1.9096323752\H,3.8765018867,-0.7035872495  
,0.9917476782\S,2.7450288593,-2.8504502328,-0.9755092576\O,3.538898336  
3,-2.8896482373,-2.2008047536\O,3.3507303607,-2.9129853865,0.354422225  
4\C,1.506894401,-4.1263843016,-1.0673878893\C,0.9799172874,-4.64126995  
43,0.1122115731\C,-0.0560671962,-5.5677154797,0.0255933868\C,-0.543293  
9952,-5.9571156826,-1.2206711692\C,0.0042145774,-5.433234027,-2.391983  
6476\C,1.0382953391,-4.5054208848,-2.3225084756\H,1.3774360493,-4.3163  
11841,1.0679112667\H,-0.4804226879,-5.9859672049,0.9325555765\H,-1.352  
4967322,-6.6781964058,-1.2811437644\H,-0.3728846068,-5.7496388486,-3.3  
590016731\H,1.4877344174,-4.0841643851,-3.2163688265\C,-1.4333239461,-  
1.9547871414,-0.3471819756\C,-2.0395722579,-0.7071946762,-0.9735186306  
\H,-0.8134216184,-2.5097755593,-1.0577657021\H,-2.2071001428,-2.637293  
2807,0.0171597733\H,-2.6383759622,-0.9816254678,-1.84734517\H,-2.68193  
71602,-0.1856039494,-0.2598216324\H,-1.2578209865,-0.0169019803,-1.301

2594154\\Version=EM64L-G09RevB.01\State=2-A\HF=-2131.6148917\S2=0.7626  
1\S2-1=0.\S2A=0.750065\RMSD=9.847e-09\RMSF=8.860e-06\Dipole=-1.7070516  
, -0.5426613, -0.1958617\Quadrupole=-1.6640308, 4.6539325, -2.9899017, 9.44  
93643, 6.2500412, 1.6189539\PG=C01 [X(C10H13O2S4)]\@