

Supporting Information

**Accurate Predictions of C-SO₂R Bond Dissociation
Enthalpies with Density Functional Theory Methods**

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Complete reference of Ref. (30)

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Jr. Montgomery, J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Revision B.01, Gaussian, Inc., Wallingford CT, 2010.

Table 1: Total electronic energies (**E**) and thermal correction of enthalpy (**TCE**) for all optimized geometries calculated at different methods (hartree).

(a) The calculation results with different functionals (DFT/(LanL2DZ/6-31G*))

	B3LYP		BB1K		M05		M05-2X	
	E	TCE	E	TCE	E	TCE	E	TCE
1 (Me-SH)	-438.698348443	0.050950	-438.691166498	0.049622	-438.651461911	0.051704	-438.654199930	0.050597
2 (Et-SH)	-478.012894316	0.081011	-477.980002038	0.078247	-477.932130169	0.081990	-477.961862279	0.081345
3 (nPr-SH)	-517.326695121	0.110986	-517.268025235	0.106871	-517.211979045	0.112083	-517.269822355	0.112600
4 (iPr-SH)	-517.328818890	0.110457	-517.270676632	0.106216	-517.214373513	0.111744	-517.272343688	0.112106
5 (tBu-SH)	-556.643016413	0.139665	-556.559445633	0.134002	-556.494668891	0.141439	-556.582776733	0.140502
6 (cypen-SH)	-594.742320077	0.148598	-594.651560961	0.144915	-594.571306126	0.150583	-594.683419248	0.150845
7 (Ph-SH)	-630.434123019	0.106837	-630.371025519	0.104690	-630.240396046	0.107857	-630.379503400	0.108589
8 (Bn-SH)	-669.748056289	0.136939	-669.657680888	0.132538	-669.519229375	0.138197	-669.686544384	0.139589
9 (MeCO-SH)	-552.034945091	0.062381	-552.019854753	0.060861	-551.940860371	0.063218	-551.977951575	0.062286
10 (MeS-Me)	-478.013808509	0.082155	-477.981532953	0.079328	-477.933487323	0.082912	-477.963248448	0.083657
11 (MeS-Et)	-517.328220465	0.112340	-517.270349868	0.108020	-517.213910162	0.113029	-517.270867359	0.113947
12 (MeS-nPr)	-556.641951071	0.142347	-556.558220014	0.136833	-556.493763226	0.143566	-556.577619103	0.144709
13 (nPrS-	-635.270028742	0.202479	-635.134840061	0.193296	-635.053977752	0.204212	-635.191932136	0.204825

ⁿPr)								
14(MeS-^tBu)	-595.955880857	0.171055	-595.847707584	0.165026	-595.774037174	0.172241	-595.889980479	0.172595
15 (MeS-Ph)	-669.749374306	0.138350	-669.661662293	0.134645	-669.522089258	0.139155	-669.688790444	0.139842
16 (MeS-Bn)	-709.064559198	0.168263	-708.949740106	0.163323	-708.802824816	0.169365	-708.998050748	0.171043
17 (EtS-^tBu)	-635.269929933	0.201303	-635.136124245	0.193851	-635.054007158	0.203002	-635.197209058	0.203102
18 (EtS- COMe)	-630.668974178	0.123969	-630.602639504	0.119916	-630.505902255	0.123953	-630.597960245	0.125067
19 (MeSS- Me)	-876.207532741	0.085425	-876.200633282	0.081851	-876.128247251	0.086027	-876.132704745	0.086809
20 (MeSS- Et)	-915.522472604	0.115614	-915.499720741	0.111492	-915.409283696	0.116556	-915.440902966	0.117531
21 (MeSS- ⁱPr)	-954.838150254	0.145090	-954.790414115	0.139585	-954.691427414	0.146423	-954.751656573	0.147387
22 (MeSO₂- Me)	-628.400812804	0.092823	-628.370848925	0.090129	-628.283415530	0.094012	-628.333396666	0.094590
23 (MeSO₂- Et)	-667.716745296	0.123056	-667.661296783	0.119112	-667.565293187	0.124428	-667.642963605	0.124984

24 (MeSO₂- iPr)	-707.032189149	0.152761	-706.951732708	0.147424	-706.846909596	0.154456	-706.954180800	0.155163
25 (MeSO₂- ⁿBu)	-746.344483383	0.183114	-746.237411343	0.175441	-746.125154420	0.185146	-746.256976463	0.186218
26 (MeSO₂- Ph)	-820.135508051	0.149103	-820.048624442	0.144794	-819.869878688	0.150245	-820.058427622	0.151680
27 (MeSO₂- Bn)	-859.451312384	0.178879	-859.338517566	0.173328	-859.151727765	0.180347	-859.367103138	0.181984
Me•	-39.8382917656	0.033905	-39.7993848530	0.033654	-39.7956251843	0.034230	-39.8198821518	0.034437
•SH	-398.740027881	0.009402	-398.759497296	0.009621	-398.730310504	0.009698	-398.705508349	0.009554
Et•	-79.1578681142	0.064549	-79.0947942334	0.062830	-79.0820057398	0.065123	-79.1305257956	0.065521
nPr•	-118.471371530	0.094600	-118.382522247	0.091408	-118.361425406	0.095403	-118.436582794	0.095571
iPr•	-118.478152840	0.094688	-118.390557834	0.091548	-118.369148704	0.095405	-118.442560844	0.096215
nBu•	-157.785287244	0.124554	-157.670692795	0.120004	-157.641059144	0.124605	-157.743646095	0.125605
tBu•	-157.798308907	0.124587	-157.686007271	0.120177	-157.655874089	0.125746	-157.755412114	0.126550
Cypen•	-195.894857002	0.132605	-195.775051402	0.129678	-195.729217633	0.134040	-195.857287888	0.134620
Ph•	-231.561280845	0.092941	-231.469155922	0.091567	-231.372606315	0.093266	-231.529714200	0.094536
Bn•	-270.915143408	0.121567	-270.796889402	0.120032	-270.692116431	0.122172	-270.876008423	0.123507
MeCO•	-153.179838224	0.048316	-153.135546311	0.046953	-153.086198799	0.048670	-153.148118855	0.049107
MeS•	-438.059669071	0.038752	-438.055673888964	0.038373	-438.016347272	0.040859	-438.017677017	0.039141
nPrS•	-516.689192760	0.100331	-516.634328875	0.096929	-516.578143247	0.101373	-516.633461838	0.101933
EtS•	-477.375148104	0.070365	-477.345784126	0.068278	-477.298035441	0.071406	-477.325894282	0.071419

MeSS•	-836.277628436	0.044855	-836.313282136	0.043479	-836.234976173	0.045235	-836.210661405	0.045660
MeSO₂•	-588.460138869	0.050985	-588.466646812	0.049962	-588.373462950	0.051767	-588.395035945	0.052058
	M06		M06-2X		M06-L		MPW1K	
	E	TCE	E	TCE	E	TCE	E	TCE
1 (Me-SH)	-438.623457793	0.050757	-438.627397902	0.050328	-438.664288735	0.051192	-438.687295140	0.049819
2 (Et-SH)	-477.905908566	0.080554	-477.920853305	0.080774	-477.970946684	0.081203	-477.992076409	0.078631
3 (nPr-SH)	-517.185591755	0.110264	-517.213652492	0.111736	-517.277046706	0.111312	-517.296024440	0.107409
4 (iPr-SH)	-517.189641858	0.109809	-517.217199566	0.111368	-517.280296644	0.110699	-517.298635460	0.106776
5 (tBu-SH)	-556.474383195	0.139124	-556.513294568	0.139656	-556.588930672	0.140042	-556.603244790	0.134731
6 (cypen-SH)	-594.545758115	0.147858	-594.600859351	0.149868	-594.683724255	0.149047	-594.701035951	0.145700
7 (Ph-SH)	-630.212567901	0.106503	-630.288473046	0.107835	-630.377822957	0.106668	-630.399251310	0.105217
8 (Bn-SH)	-669.493371554	0.136294	-669.581377336	0.138581	-669.682451184	0.136879	-669.702105663	0.133164
9 (MeCO-SH)	-551.906833319	0.062395	-551.922730850	0.061969	-551.996094424	0.062764	-552.018603021	0.061152
10 (MeS-Me)	-477.905223482	0.081552	-477.921863742	0.082971	-477.971311701	0.082043	-477.993586892	0.079723
11 (MeS-Et)	-517.186933534	0.111461	-517.215474331	0.113012	-517.278440084	0.112310	-517.298196430	0.108588
12 (MeS-nPr)	-556.467291123	0.141376	-556.508048724	0.143599	-556.583962390	0.142441	-556.602126027	0.137533
13 (nPrS-	-635.029300428	0.201130	-635.094106421	0.204208	-635.196514190	0.202635	-635.210603594	0.194325

ⁿPr)								
14(MeS-^tBu)	-595.754625306	0.168922	-595.806239053	0.171364	-595.894915285	0.170309	-595.907000905	0.164874
15 (MeS-Ph)	-669.494433645	0.137753	-669.583367572	0.139633	-669.685660300	0.138199	-669.705507668	0.135400
16 (MeS-Bn)	-708.777842366	0.167180	-708.878423399	0.169578	-708.992440920	0.168139	-709.009855557	0.164114
17 (EtS-^tBu)	-635.035643621	0.200105	-635.099318468	0.203043	-635.201126218	0.201542	-635.211311216	0.194846
18 (EtS- COMe)	-630.472715963	0.123320	-630.513592563	0.125092	-630.615200495	0.124350	-630.632820764	0.120387
19 (MeSS- Me)	-876.070418301	0.084790	-876.080401691	0.086157	-876.146756319	0.085418	-876.194998289	0.082102
20 (MeSS- Et)	-915.352470380	0.114895	-915.374377494	0.116745	-915.455394901	0.115531	-915.500262419	0.111078
21 (MeSS- ⁱPr)	-954.637559831	0.144305	-954.671079503	0.146453	-954.763964636	0.145211	-954.806639144	0.139309
22 (MeSO₂- Me)	-628.241127582	0.092551	-628.254533646	0.093919	-628.361925602	0.092746	-628.379726191	0.090581
23 (MeSO₂- Et)	-667.524954097	0.122570	-667.550085301	0.124213	-667.670718647	0.123164	-667.685915268	0.119653

24 (MeSO₂- iPr)	-706.809405315	0.151693	-706.847146147	0.154129	-706.980394771	0.152867	-706.991892318	0.148172
25 (MeSO₂- nBu)	-746.086360859	0.182202	-746.135891502	0.184850	-746.282797527	0.183264	-746.293914581	0.176401
26 (MeSO₂- Ph)	-819.829648513	0.148450	-819.915457996	0.150509	-820.073678491	0.149112	-820.089522005	0.145480
27 (MeSO₂- Bn)	-859.112926939	0.178142	-859.210218349	0.180694	-859.382231792	0.178947	-859.395467965	0.174128
Me•	-39.7954260081	0.033400	-39.8042299171	0.034094	-39.8243893128	0.032497	-39.8224638632	0.033836
•SH	-398.700827054	0.009461	-398.693941321	0.009614	-398.712695757	0.009549	-398.737853015	0.009648
Et•	-79.0811744849	0.063149	-79.1005060515	0.065071	-79.1365541996	0.064581	-79.1328009889	0.063204
nPr•	-118.361147487	0.093935	-118.392651695	0.094919	-118.441927607	0.094721	-118.436412943	0.091942
iPr•	-118.368422240	0.094186	-118.398565891	0.095588	-118.449826803	0.094866	-118.443812605	0.092104
nBu•	-157.642100200	0.123740	-157.685630091	0.125661	-157.748180119	0.124733	-157.740496238	0.120723
tBu•	-157.656506847	0.123953	-157.697655052	0.125839	-157.763609445	0.124941	-157.754689347	0.120891
Cypen•	-195.728496335	0.132031	-195.785682657	0.133788	-195.856828883	0.133198	-195.849559252	0.130450
Ph•	-231.372444967	0.092535	-231.451696612	0.093871	-231.526995424	0.092870	-231.522186368	0.092145
Bn•	-270.690933038	0.120777	-270.779420791	0.122341	-270.869364660	0.121199	-270.865444033	0.120521
MeCO•	-153.079320742	0.048088	-153.103720484	0.048754	-153.157240268	0.048369	-153.157081718	0.047196
MeS•	-437.985815725	0.040173	-437.990899469	0.042055	-438.024107742	0.038276	-438.049257541	0.038608
nPrS•	-516.548976977	0.099814	-516.578646052	0.102843	-516.638888239	0.100298	-516.659441984	0.097409
EtS•	-477.267975514	0.070273	-477.284991710	0.072691	-477.331689298	0.070453	-477.355227037	0.068688

MeSS•	-836.173634715	0.044536	-836.171603676	0.045179	-836.225247322	0.044772	-836.277389475	0.043692
MeSO₂•	-588.329732220	0.050856	-588.331588099	0.051670	-588.427985025	0.051101	-588.454033964	0.050200
	MPW3LYP		MPWB1K		PBE		TPSS	
	E	TCE	E	TCE	E	TCE	E	TCE
1 (Me-SH)	-438.645990382	0.049147	-438.695005307	0.049667	-438.441836811	0.049877	-438.710017505	0.050620
2 (Et-SH)	-477.931651099	0.078644	-477.983048684	0.078307	-477.698939962	0.079259	-478.030661308	0.080412
3 (nPr-SH)	-517.216577877	0.107155	-517.270312540	0.106941	-516.955211108	0.108475	-517.350439902	0.109967
4 (iPr-SH)	-517.219049314	0.107507	-517.273219144	0.106291	-516.958129264	0.107958	-517.352820974	0.109438
5 (tBu-SH)	-556.504492839	0.136213	-556.561681529	0.134099	-556.215530455	0.136479	-556.673218427	0.138304
6 (cypen-SH)	-594.587976769	0.144082	-594.653663694	0.144062	-594.272237418	0.145109	-594.781810915	0.146915
7 (Ph-SH)	-630.303841316	0.104054	-630.373717053	0.104780	-629.939961928	0.104401	-630.483577835	0.105590
8 (Bn-SH)	-669.588650084	0.132633	-669.659473239	0.132630	-669.195111794	0.133743	-669.802665999	0.135316
9 (MeCO-SH)	-551.967538878	0.060402	-552.023758831	0.060900	-551.665443134	0.060042	-552.064375040	0.060787
10 (MeS-Me)	-477.933022516	0.078838	-477.984454611	0.079385	-477.700257241	0.080317	-478.032931778	0.081538
11 (MeS-Et)	-517.218582346	0.108412	-517.272617344	0.108055	-516.957337035	0.109685	-517.353390619	0.111268
12 (MeS-nPr)	-556.503412443	0.137996	-556.559589413	0.136923	-556.213430697	0.139102	-556.673191401	0.141067
13 (nPrS-	-635.073740078	0.196131	-635.134649969	0.193415	-634.726543268	0.197820	-635.313391893	0.200512

ⁿPr)								
14(MeS-^tBu)	-595.789171260	0.166143	-595.849323703	0.165192	-595.471715462	0.167053	-595.993788714	0.169336
15 (MeS-Ph)	-669.590794222	0.134026	-669.663569648	0.134708	-669.198512475	0.135139	-669.806591481	0.136777
16 (MeS-Bn)	-708.876883280	0.162502	-708.950926267	0.163367	-708.455321318	0.164331	-709.127097603	0.166363
17 (EtS-^tBu)	-635.074394930	0.194903	-635.136941608	0.194022	-634.728340797	0.196603	-635.314028193	0.199219
18 (EtS- COMe)	-630.543367211	0.119077	-630.604822071	0.119999	-630.185579743	0.121122	-630.712645853	0.122713
19 (MeSS- Me)	-876.119950869	0.082093	-876.221344098	0.081788	-875.712588471	0.083513	-876.235506761	0.084739
20 (MeSS- Et)	-915.406031912	0.110795	-915.509926050	0.111559	-914.970177278	0.113000	-915.556673033	0.114588
21 (MeSS- ⁱPr)	-954.693185024	0.139722	-954.800243222	0.138749	-954.229332102	0.141788	-954.878733959	0.143754
22 (MeSO₂- Me)	-628.311705388	0.089378	-628.374829885	0.090213	-627.956879938	0.090605	-628.444497572	0.091839
23 (MeSO₂- Et)	-667.598959703	0.118147	-667.664774327	0.119206	-667.215514765	0.120093	-667.766675682	0.121746

24 (MeSO₂- iPr)	-706.886013794	0.147341	-706.954882985	0.147535	-706.474330861	0.149122	-707.088575050	0.151065
25 (MeSO₂- ⁿBu)	-746.168966090	0.177200	-746.239259543	0.175554	-745.728120483	0.178782	-746.406374407	0.181135
26 (MeSO₂- Ph)	-819.968208517	0.144680	-820.051679504	0.144936	-819.452901969	0.145481	-820.216950134	0.147142
27 (MeSO₂- Bn)	-859.255764449	0.172068	-859.340879411	0.173296	-858.711423219	0.174558	-859.538493723	0.176590
Me•	-39.8012533588	0.033484	-39.7953010291	0.033692	-39.7683230727	0.033259	-39.8448220439	0.033626
•SH	-398.722318211	0.009392	-398.764706015	0.009638	-398.542908260	0.009274	-398.742957423	0.009363
Et•	-79.0924582572	0.062557	-79.0897313326	0.062884	-79.0308662498	0.063170	-79.1703590643	0.064030
nPr•	-118.377135600	0.091982	-118.376654327	0.091474	-118.286747129	0.092501	-118.489836057	0.093761
iPr•	-118.384413103	0.091144	-118.384695180	0.091612	-118.294241832	0.092539	-118.496514942	0.093915
nBu•	-157.662222214	0.120486	-157.664069379	0.120098	-157.543170907	0.121755	-157.809695630	0.123414
tBu•	-157.676331172	0.119599	-157.679542519	0.120286	-157.557624513	0.121669	-157.822605225	0.123526
Cypen•	-195.756748357	0.130067	-195.768856800	0.129755	-195.611821897	0.129471	-195.928865269	0.131133
Ph•	-231.447067045	0.091196	-231.463560988	0.091648	-231.254161228	0.090704	-231.606189106	0.091755
Bn•	-270.772951468	0.119568	-270.790770547	0.120140	-270.549576511	0.118898	-270.964146058	0.120121
MeCO•	-153.127480718	0.046598	-153.131235465	0.047001	-152.995275891	0.047160	-153.202820212	0.047769
MeS•	-438.014096394	0.039006	-438.059723211	0.038401	-437.806184187	0.037835	-438.070820813	0.039944
nPrS•	-516.585938909	0.097412	-516.636928683	0.096987	-516.321213145	0.098058	-516.712470373	0.099346
EtS•	-477.300804065	0.068022	-477.349010828	0.068322	-477.064464635	0.068723	-477.392434575	0.069784

MeSS•	-836.227518998	0.043172	-836.325466510	0.043511	-835.845629088	0.043856	-836.299325395	0.044479
MeSO₂•	-588.413259420	0.049290	-588.471252661	0.050024	-588.081603652	0.049789	-588.502513584	0.050367
TPSSLYP1W								
	E	TCE						
1 (Me-SH)	-438.738732965	0.050489						
2 (Et-SH)	-478.056480555	0.080234						
3 (nPr-SH)	-517.373470659	0.109781						
4 (iPr-SH)	-517.375703065	0.109282						
5 (tBu-SH)	-556.693163549	0.138161						
6 (cypen-SH)	-594.800538058	0.145667						
7 (Ph-SH)	-630.526442380	0.105297						
8 (Bn-SH)	-669.843744796	0.135001						
9 (MeCO-SH)	-552.115644006	0.060609						
10 (MeS-Me)	-478.058843339	0.081461						
11 (MeS-Et)	-517.376496049	0.111184						
12 (MeS-nPr)	-556.693432497	0.140941						
13 (nPrS-	-635.327964894	0.200340						

ⁿPr)		
14(MeS-^tBu)	-596.011127823	0.169283
15 (MeS-Ph)	-669.846662966	0.136541
16 (MeS-Bn)	-709.165068139	0.166107
17 (EtS-^tBu)	-635.328533186	0.198190
18 (EtS- COMe)	-630.757070750	0.120690
19 (MeSS- Me)	-876.298146811	0.084619
20 (MeSS- Et)	-915.616362037	0.114437
21 (MeSS- ⁱPr)	-954.935402455	0.143608
22 (MeSO₂- Me)	-628.500598928	0.091602
23 (MeSO₂- Et)	-667.820085224	0.121468

24 (MeSO₂- iPr)	-707.139295051	0.150784
25 (MeSO₂- ⁿBu)	-746.454252451	0.180828
26 (MeSO₂- Ph)	-820.288204454	0.146764
27 (MeSO₂- Bn)	-859.607376189	0.176139
Me•	-39.8413318798	0.033675
•SH	-398.779876010	0.009309
Et•	-79.1636859342	0.064003
nPr•	-118.480466309	0.093707
iPr•	-118.486822150	0.093857
nBu•	-157.797818405	0.123510
tBu•	-157.810048677	0.123462
Cypen•	-195.915068376	0.130910
Ph•	-231.616623796	0.091568
Bn•	-270.973725373	0.119994
MeCO•	-153.222899785	0.047693
MeS•	-438.104440051	0.039495
nPrS•	-516.740314363	0.099279
EtS•	-477.423138992	0.069741

MeSS•	-836.369159348	0.044403
MeSO₂•	-588.567865578	0.050088

(b) The calculation results with different basis sets (M05-2X/BS)

	6-31G(d)		6-31+G(d)		6-31+G(d,p)		6-311+G(d,p)	
	E	TCE	E	TCE	E	TCE	E	TCE
1 (Me-SH)	-438.654199930	0.050597	-438.656090471	0.050490	-438.663539886	0.050275	-438.701450744	0.050144
2 (Et-SH)	-477.961862279	0.081345	-477.965535928	0.082008	-477.975558464	0.081651	-478.020819366	0.081461
3 (nPr-SH)	-517.269822355	0.112600	-517.273381867	0.112332	-517.286006971	0.111861	-517.338430361	0.111719
4 (iPr-SH)	-517.272343688	0.112106	-517.276042192	0.111815	-517.288682521	0.111355	-517.341268043	0.111132
5 ('Bu-SH)	-556.582776733	0.140502	-556.587506825	0.140184	-556.602647213	0.139545	-556.662677960	0.139233
6 (cypen-SH)	-594.683419248	0.150845	-594.688264674	0.150488	-594.703394469	0.149902	-594.769497448	0.149657
7 (Ph-SH)	-630.379503400	0.108589	-630.387072660	0.108354	-630.398435035	0.108147	-630.470018274	0.108102
8 (Bn-SH)	-669.686544384	0.139589	-669.696387125	0.138993	-669.710430051	0.138637	-669.789479252	0.138435
9 (MeCO-SH)	-551.977951575	0.062286	-551.985895001	0.062200	-551.993317903	0.061953	-552.060964492	0.062725
10 (MeS-Me)	-477.963248448	0.083657	-477.965868080	0.083458	-477.974144960	0.082993	-478.018123970	0.082770
11 (MeS-Et)	-517.270867359	0.113947	-517.274283905	0.113664	-517.285146296	0.113072	-517.336595580	0.112741

12 (MeS-ⁿPr)	-556.577619103	0.144709	-556.582006259	0.144080	-556.595459769	0.143368	-556.654097582	0.143082
13 (ⁿPrS- ⁿPr)	-635.191932136	0.204825	-635.197434299	0.204259	-635.215946628	0.204214	-635.289023136	0.203777
14(MeS-^tBu)	-595.889980479	0.172595	-595.895133492	0.172221	-595.911157154	0.171283	-595.977482140	0.170520
15 (MeS-Ph)	-669.688790444	0.139842	-669.696922220	0.140500	-669.709181271	0.140070	-669.786967517	0.139671
16 (MeS-Bn)	-708.998050748	0.171043	-709.007059998	0.170714	-709.021962367	0.170131	-709.107347335	0.169737
17 (EtS-^tBu)	-635.197209058	0.203102	-635.203100954	0.203872	-635.221646118	0.202843	-635.295267563	0.202289
18 (EtS- COMe)	-630.597960245	0.125067	-630.606993072	0.124777	-630.617969509	0.124193	-630.698933494	0.123815
19 (MeSS- Me)	-876.132704745	0.086809	-876.136084056	0.086610	-876.144415340	0.086159	-876.217324974	0.085856
20 (MeSS- Et)	-915.440902966	0.117531	-915.445042390	0.117213	-915.455908072	0.116644	-915.536272492	0.116342
21 (MeSS- ⁱPr)	-954.751656573	0.147387	-954.756610360	0.146987	-954.770116029	0.146280	-954.858047950	0.145884
22 (MeSO₂- Me)	-628.333396666	0.094590	-628.344429939	0.094275	-628.353122021	0.093851	-628.436195300	0.093574

23 (MeSO₂- Et)	-667.642963605	0.124984	-667.654319425	0.124599	-667.665606858	0.124052	-667.756493309	0.123918
24 (MeSO₂- iPr)	-706.954180800	0.155163	-706.965781019	0.154718	-706.979667459	0.154007	-707.078091529	0.153546
25 (MeSO₂- ⁿBu)	-746.256976463	0.186218	-746.269509200	0.185642	-746.285903874	0.184815	-746.391146514	0.184421
26 (MeSO₂- Ph)	-820.058427622	0.151680	-820.073502763	0.151306	-820.086094036	0.150866	-820.202743022	0.150614
27 (MeSO₂- Bn)	-859.367103138	0.181984	-859.383573991	0.181542	-859.398777866	0.180984	-859.523386604	0.180536
Me•	-39.8198821518	0.034437	-39.8232485623	0.034469	-39.8283044636	0.034334	-39.8356093737	0.034212
•SH	-398.705508349	0.009554	-398.706806921	0.009550	-398.710343247	0.009575	-398.741482559	0.009568
Et•	-79.1305257956	0.065521	-79.1341699808	0.065379	-79.1415917356	0.065068	-79.1561310598	0.064915
nPr•	-118.436582794	0.095571	-118.440959247	0.095336	-118.450914642	0.094923	-118.472884472	0.094096
iPr•	-118.442560844	0.096215	-118.446527580	0.095874	-118.456364181	0.095410	-118.477996663	0.095142
nBu•	-157.743646095	0.125605	-157.748686641	0.125281	-157.761250074	0.124692	-157.789924961	0.124229
tBu•	-157.755412114	0.126550	-157.759702441	0.126181	-157.771926672	0.125497	-157.800574928	0.125146
Cypen•	-195.857287888	0.134620	-195.862198208	0.134232	-195.874573925	0.133651	-195.909741949	0.133466
Ph•	-231.529714200	0.094536	-231.537545559	0.094336	-231.545589089	0.094108	-231.586188863	0.094028
Bn•	-270.876008423	0.123507	-270.884878705	0.123296	-270.896150251	0.122971	-270.944027224	0.122868
MeCO•	-153.148118855	0.049107	-153.156194865	0.049030	-153.160468586	0.048804	-153.197890316	0.048704

MeS•	-438.017677017	0.039141	-438.019608528	0.038981	-438.023907989	0.038706	-438.060798613	0.038512
nPrS•	-516.633461838	0.101933	-516.636925168	0.101594	-516.646024122	0.100960	-516.697920468	0.100948
EtS•	-477.325894282	0.071419	-477.328734705	0.071294	-477.335535897	0.070858	-477.379759113	0.070681
MeSS•	-836.210661405	0.045660	-836.213137389	0.045560	-836.217356103	0.045334	-836.281795252	0.045075
MeSO₂•	-588.395035945	0.052058	-588.405957158	0.051864	-588.410350786	0.051655	-588.485389080	0.051510
6-311++								
6-311++G(d,p)								
G(2df,2p)								
	E	TCE	E	TCE				
1 (Me-SH)	-438.701797215	0.050162	-438.711391623	0.050143				
2 (Et-SH)	-478.021048748	0.081461	-478.032995995	0.081420				
3 (nPr-SH)	-517.338683752	0.111727	-517.353292357	0.110715				
4 (iPr-SH)	-517.341494212	0.111129	-517.355856893	0.111198				
5 (tBu-SH)	-556.662917099	0.139237	-556.679691821	0.139361				
6 (cypen-SH)	-594.769714757	0.149638	-594.788748370	0.149697				
7 (Ph-SH)	-630.470136280	0.108076	-630.495834367	0.108477				
8 (Bn-SH)	-669.789643505	0.138438	-669.816942504	0.138699				
9 (MeCO-SH)	-552.061090540	0.061648	-552.076846668	0.062731				
10 (MeS-Me)	-478.018435463	0.082789	-478.031639159	0.082757				

11 (MeS-Et)	-517.336835765	0.112719	-517.352415808	0.112761
12 (MeS-ⁿPr)	-556.654374464	0.143071	-556.672619996	0.143075
13 (ⁿPrS- ⁿPr)	-635.289415537	0.203771	-635.313056713	0.202850
14(MeS-^tBu)	-595.977782547	0.170531	-595.998288262	0.170711
15 (MeS-Ph)	-669.787169809	0.139688	-669.816519109	0.139999
16 (MeS-Bn)	-709.107605388	0.169732	-709.138502880	0.170054
17 (EtS-^tBu)	-635.295594732	0.202284	-635.318652692	0.202378
18 (EtS- COMe)	-630.699227220	0.123825	-630.721627117	0.123858
19 (MeSS- Me)	-876.217760912	0.085879	-876.241767473	0.085821
20 (MeSS- Et)	-915.536713971	0.116362	-915.562988747	0.116345
21 (MeSS- ⁱPr)	-954.858503311	0.145891	-954.887050649	0.145962
22 (MeSO₂-	-628.436466792	0.093560	-628.497995441	0.093691

Me)				
23 (MeSO₂-				
Et)	-667.756807747	0.123918	-667.820286253	0.124142
24 (MeSO₂-				
iPr)	-707.078447253	0.153543	-707.143687858	0.153863
25 (MeSO₂-				
nBu)	-746.391587789	0.184431	-746.460315130	0.184674
26 (MeSO₂-				
Ph)	-820.202912399	0.150571	-820.278835720	0.151152
27 (MeSO₂-				
Bn)	-859.523624028	0.180532	-859.602367053	0.181042
Me•	-39.8356400187	0.034211	-39.8387930338	0.034282
•SH	-398.741585539	0.009568	-398.745562133	0.009550
Et•	-79.1561906941	0.064912	-79.1623308881	0.065065
nPr•	-118.472963301	0.095002	-118.481953662	0.094315
iPr•	-118.478092674	0.095146	-118.487188546	0.095304
nBu•	-157.790043016	0.124225	-157.801768096	0.124453
tBu•	-157.800712928	0.125089	-157.812676499	0.125339
Cypen•	-195.909840650	0.133459	-195.923600246	0.133669
Ph•	-231.586241975	0.093994	-231.605119916	0.094284
Bn•	-270.944111973	0.122860	-270.966234181	0.123276

MeCO•	-153.197967932	0.048707	-153.207548753	0.048783
MeS•	-438.061014935	0.038507	-438.068789544	0.038483
nPrS•	-516.698146765	0.100967	-516.710470719	0.100364
EtS•	-477.379977818	0.070712	-477.390107537	0.070481
MeSS•	-836.282142176	0.045094	-836.304039292	0.044176
MeSO₂•	-588.485614252	0.051514	-588.538754846	0.051763

(c) The calculation results with different basis sets (M06-2X/*BS*)

	6-31G(d)		6-31+G(d)		6-31+G(d,p)		6-311+ G(d,p)	
	E	TCE	E	TCE	E	TCE	E	TCE
1 (Me-SH)	-438.627397902	0.050328	-438.629250561	0.050221	-438.635343443	0.049991	-438.675003639	0.049821
2 (Et-SH)	-477.920853305	0.080774	-477.923652776	0.080586	-477.932695006	0.081193	-477.979466810	0.079984
3 (nPr-SH)	-517.213652492	0.111736	-517.218471483	0.111717	-517.228608771	0.111264	-517.284254785	0.111090
4 (iPr-SH)	-517.217199566	0.111368	-517.220975490	0.111097	-517.231137914	0.110600	-517.286845308	0.110358
5 (tBu-SH)	-556.513294568	0.139656	-556.518118454	0.139327	-556.530222506	0.138673	-556.593959130	0.138275
6 (cypen-SH)	-594.600859351	0.149868	-594.605880779	0.149525	-594.617939748	0.148935	-594.688731133	0.148628
7 (Ph-SH)	-630.288473046	0.107835	-630.296328199	0.107581	-630.305598353	0.107373	-630.382599781	0.107145
8 (Bn-SH)	-669.581377336	0.138581	-669.591574331	0.138292	-669.602887209	0.137931	-669.688157314	0.137625
9 (MeCO-	-551.922730850	0.061969	-551.930252037	0.061866	-551.936308696	0.061586	-552.006926865	0.062331

SH)								
10 (MeS-Me)	-477.921863742	0.082971	-477.924510915	0.082769	-477.930986247	0.082330	-477.977792189	0.082194
11 (MeS-Et)	-517.215474331	0.113012	-517.218968460	0.112762	-517.227474630	0.112165	-517.282481932	0.111853
12 (MeS-ⁿPr)	-556.508048724	0.143599	-556.512665912	0.143042	-556.523200787	0.142330	-556.586165081	0.142026
13 (ⁿPrS- ⁿPr)	-635.094106421	0.204208	-635.099831835	0.203649	-635.114272638	0.202701	-635.193138593	0.202383
14(MeS-^tBu)	-595.806239053	0.171364	-595.811527659	0.170974	-595.824086506	0.170094	-595.895219625	0.169633
15 (MeS-Ph)	-669.583367572	0.139633	-669.591836533	0.139374	-669.601551166	0.138952	-669.685871257	0.138568
16 (MeS-Bn)	-708.878423399	0.169578	-708.887814414	0.169266	-708.899541154	0.168695	-708.992213091	0.168228
17 (EtS-^tBu)	-635.099318468	0.203043	-635.105388748	0.202543	-635.119897781	0.201544	-635.199025087	0.200992
18 (EtS- COMe)	-630.513592563	0.125092	-630.522330528	0.123813	-630.530878663	0.123217	-630.616637470	0.122799
19 (MeSS- Me)	-876.080401691	0.086157	-876.083690921	0.085976	-876.090190454	0.085537	-876.166680396	0.085191
20 (MeSS- Et)	-915.374377494	0.116745	-915.378472860	0.116440	-915.386934871	0.115879	-915.471610929	0.115517
21 (MeSS-	-954.671079503	0.146453	-954.676038662	0.146064	-954.686585996	0.145375	-954.779452727	0.144989

iPr)								
22 (MeSO₂- Me)	-628.254533646	0.093919	-628.264993337	0.093607	-628.271809319	0.093206	-628.358349510	0.093003
23 (MeSO₂- Et)	-667.550085301	0.124213	-667.560933680	0.123831	-667.569783480	0.123288	-667.664723325	0.122958
24 (MeSO₂- iPr)	-706.847146147	0.154129	-706.858333379	0.153690	-706.869196847	0.152981	-706.972657884	0.152557
25 (MeSO₂- ⁿBu)	-746.135891502	0.184850	-746.148056723	0.184322	-746.160861576	0.183534	-746.271951533	0.183248
26 (MeSO₂- Ph)	-819.915457996	0.150509	-819.930388079	0.150140	-819.940295258	0.149738	-820.064195323	0.149354
27 (MeSO₂- Bn)	-859.210218349	0.180694	-859.226528659	0.180208	-859.238475053	0.179667	-859.371124681	0.179203
Me•	-39.8042299171	0.034094	-39.8079783854	0.034127	-39.8119078464	0.034000	-39.8208781956	0.033827
•SH	-398.693941321	0.009614	-398.695179180	0.009608	-398.698262004	0.009622	-398.729951090	0.009621
Et•	-79.1005060515	0.065071	-79.1045685392	0.064895	-79.1103989633	0.064606	-79.1274031998	0.064365
nPr•	-118.392651695	0.094919	-118.397545421	0.094678	-118.405331264	0.094272	-118.430518257	0.094354
iPr•	-118.398565891	0.095588	-118.403000259	0.095201	-118.410749797	0.094748	-118.435598485	0.094497
nBu•	-157.685630091	0.125661	-157.691242231	0.125309	-157.701088510	0.124731	-157.733871719	0.124150
tBu•	-157.697655052	0.125839	-157.702517176	0.125491	-157.712141059	0.124745	-157.744724310	0.124411

Cypen•	-195.785682657	0.133788	-195.791193344	0.133419	-195.800902833	0.132842	-195.840849617	0.132561
Ph•	-231.451696612	0.093871	-231.460204636	0.093665	-231.466569566	0.093469	-231.512726063	0.093284
Bn•	-270.779420791	0.122341	-270.789037066	0.122132	-270.798003616	0.121868	-270.852192109	0.121620
MeCO•	-153.103720484	0.048754	-153.112044270	0.048678	-153.115384297	0.048456	-153.155483388	0.048323
MeS•	-437.990899469	0.042055	-437.992834470	0.041934	-437.996212001	0.041589	-438.034767750	0.041415
nPrS•	-516.578646052	0.102843	-516.581787880	0.102494	-516.589143510	0.102140	-516.643705840	0.101521
EtS•	-477.284991710	0.072691	-477.287915979	0.072674	-477.293244823	0.072393	-477.339888617	0.072104
MeSS•	-836.171603676	0.045179	-836.173981129	0.045084	-836.177263350	0.044874	-836.244312576	0.043671
MeSO₂•	-588.331588099	0.051670	-588.342003402	0.051475	-588.345420632	0.051270	-588.423182120	0.051120

6-311++

6-311++G(d,p)

G(2df,2p)

	E	TCE	E	TCE
1 (Me-SH)	-438.675318635	0.049835	-438.683938866	0.049687
2 (Et-SH)	-477.980612287	0.080899	-477.991026616	0.080683
3 (nPr-SH)	-517.284481573	0.111092	-517.295902135	0.109252
4 (iPr-SH)	-517.287050325	0.110351	-517.299313578	0.110240
5 (tBu-SH)	-556.594181442	0.138278	-556.608300887	0.138192
6 (cypen-SH)	-594.688918520	0.148603	-594.705097370	0.147488
7 (Ph-SH)	-630.382704278	0.107075	-630.405113049	0.107313
8 (Bn-SH)	-669.688304649	0.137658	-669.711688930	0.137636

9 (MeCO-SH)	-552.007062744	0.062321	-552.021295015	0.062227
10 (MeS-Me)	-477.978063543	0.082203	-477.989564963	0.082080
11 (MeS-Et)	-517.282688046	0.111823	-517.295967473	0.111640
12 (MeS-ⁿPr)	-556.586405535	0.142016	-556.601791371	0.141803
13 (ⁿPrS-ⁿPr)	-635.193488640	0.202373	-635.213162626	0.202168
14(MeS-^tBu)	-595.895492440	0.169631	-595.912601117	0.169533
15 (MeS-Ph)	-669.686046198	0.138581	-669.711387138	0.138652
16 (MeS-Bn)	-708.992440836	0.168216	-709.018652976	0.168152
17 (EtS-^tBu)	-635.199323695	0.200987	-635.218436796	0.200926
18 (EtS-COMe)	-630.616904575	0.122805	-630.636413489	0.122646
19 (MeSS-Me)	-876.167073245	0.085211	-876.189034389	0.085040
20 (MeSS-Et)	-915.472005810	0.115527	-915.495665683	0.115399

21 (MeSS- iPr)	-954.779867170	0.144992	-954.805217315	0.144871
22 (MeSO₂- Me)	-628.358627336	0.092986	-628.415648855	0.093074
23 (MeSO₂- Et)	-667.665052939	0.122950	-667.723432461	0.123193
24 (MeSO₂- iPr)	-706.973011419	0.152556	-707.032469559	0.152659
25 (MeSO₂- ⁿBu)	-746.272380341	0.183247	-746.334805398	0.183269
26 (MeSO₂- Ph)	-820.064357989	0.149310	-820.133351404	0.149659
27 (MeSO₂- Bn)	-859.371358554	0.179204	-859.442537755	0.179375
Me•	-39.8209116390	0.033826	-39.8232703096	0.033860
•SH	-398.730048102	0.009621	-398.733932681	0.009591
Et•	-79.1274692679	0.064361	-79.1323358801	0.064369
nPr•	-118.430593487	0.094345	-118.437706215	0.094358
iPr•	-118.435699291	0.094497	-118.443000387	0.094484

nBu•	-157.733971052	0.124142	-157.743226238	0.124070
tBu•	-157.744843314	0.124534	-157.754448475	0.124417
Cypen•	-195.840933361	0.132557	-195.852136480	0.132559
Ph•	-231.512778438	0.093264	-231.528535192	0.093375
Bn•	-270.852270261	0.121619	-270.870754150	0.121821
MeCO•	-153.155571915	0.048324	-153.164187390	0.048311
MeS•	-438.034970059	0.041433	-438.041855943	0.041322
nPrS•	-516.643940502	0.101568	-516.654729030	0.101145
EtS•	-477.340089689	0.072137	-477.348778304	0.071906
MeSS•	-836.244628338	0.043684	-836.265049169	0.043618
MeSO₂•	-588.423414517	0.051123	-588.473703290	0.051329

Table S2. Comparison between BDEs calculated by M05-2X/*BS* and the experimental results of selected C-S compounds.

Reactant	BDE ^{exp}	BDE ^{calc}					
		6-31G(d)	6-31+G(d)	6-31+G(d,p)	6-311+G(d,p)	6-311++G(d,p)	6-311++G(2df,2p)
1 (Me-SH)	74.7±1	76.7	75.0	74.4	74.0	74.2	75.8
2 (Et-SH)	73.6±0.5	75.0	73.7	73.2	72.9	73.0	74.2
3 (nPr-SH)	74.2±0.7	75.5	74.2	73.7	72.8	73.4	74.6
4 (iPr-SH)	73.4±0.9	74.0	73.0	72.5	72.4	72.4	73.3
5 (tBu-SH)	72.0±0.9	73.7	73.1	72.7	72.9	72.8	73.4
6 (cypen-SH)	71.0±1.2	71.5	70.6	70.2	70.1	70.1	71.0
7 (Ph-SH)	86.2±1.5	87.7	86.8	86.6	86.5	86.5	88.2
8 (Bn-SH)	61.7±1.5	61.8	61.8	61.4	61.5	61.5	62.3
9 (MeCO-SH)	73.6±1.5	75.7	74.8	74.6	73.5	74.2	74.9
10 (MeS-Me)	73.6±0.8	72.5	70.9	70.3	70.1	70.1	71.6
11 (MeS-Et)	72.4±1	71.1	69.8	69.2	69.3	69.2	70.3
12 (MeS-nPr)	73.3±1.5	71.1	70.1	69.6	69.0	69.6	70.0
13 (nPrS-nPr)	72.8±1.5	71.9	70.4	69.5	68.7	69.3	70.6
14(MeS-tBu)	70.4±1.5	69.0	68.3	67.9	68.6	68.5	67.0
15 (MeS-Ph)	85.4±1.5	84.9	83.2	83.1	83.4	83.3	85.0
16 (MeS-Bn)	60.5±1	60.2	59.1	58.6	59.1	59.1	59.7
17 (EtS-tBu)	71.1±1.5	69.5	67.9	67.6	68.1	68.0	68.6
18 (EtS-COMe)	76.2±2	74.9	73.8	73.7	73.3	73.3	74.9
19 (MeSS-Me)	57.4±1.5	59.9	58.4	57.9	58.6	58.6	57.5
20 (MeSS-Et)	56.2±2	58.6	57.4	56.9	57.7	57.8	56.2
21 (MeSS-iPr)	54.5±2	58.3	57.4	57.0	58.1	58.1	56.1
22 (MeSO₂-Me)	68	69.3	67.3	66.9	67.4	67.4	70.8
23 (MeSO₂-Et)	68.9±2	69.0	67.0	66.7	67.5	67.5	70.2

24 (MeSO₂-<i>i</i>Pr)	67.5±2	68.8	66.7	66.5	67.6	67.7	69.6
25 (MeSO₂-ⁿBu)	71.3±2	68.9	66.8	66.4	67.2	67.3	69.9
26 (MeSO₂-Ph)	82.3±2	80.7	78.4	78.5	79.1	79.1	81.5
27 (MeSO₂-Bn)	57.5±2	56.2	54.2	53.9	55.1	55.1	57.3
R	/	0.9794	0.9735	0.9740	0.9720	0.9728	0.9788
SD(kcal/mol)	/	1.7	1.9	1.8	1.9	1.9	1.7
RMSD(kcal/mol)	/	1.6	2.1	2.3	2.3	2.2	1.6

Table S3. Comparison between BDEs calculated by M06-2X/*BS* and the experimental results of selected C-S compounds.

Reactant	BDE ^{exp}	BDE ^{calc}					
		6-31G(d)	6-31+G(d)	6-31+G(d,p)	6-311+G(d,p)	6-311++G(d,p)	6-311++G(2df,2p)
1 (Me-SH)	74.7±1	76.9	75.1	74.6	73.9	74.0	75.6
2 (Et-SH)	73.6±0.5	75.5	73.9	73.5	72.9	72.9	74.1
3 (nPr-SH)	74.2±0.7	75.2	74.2	73.8	73.2	73.2	74.6
4 (iPr-SH)	73.4±0.9	74.4	73.1	72.7	72.2	72.2	72.9
5 (tBu-SH)	72.0±0.9	73.7	72.9	72.5	72.2	72.3	72.6
6 (cypen-SH)	71.0±1.2	72.0	70.9	70.5	70.0	70.0	71.3
7 (Ph-SH)	86.2±1.5	86.9	85.7	85.6	85.1	85.1	86.8
8 (Bn-SH)	61.7±1.5	63.6	63.3	62.9	62.5	62.5	63.2
9 (MeCO-SH)	73.6±1.5	76.2	75.0	74.8	73.5	73.5	74.6
10 (MeS-Me)	73.6±0.8	75.2	73.4	72.9	72.3	72.3	73.8
11 (MeS-Et)	72.4±1	74.2	72.6	72.1	71.7	71.7	72.7
12 (MeS-nPr)	73.3±1.5	74.0	72.7	72.3	71.9	71.9	72.9
13 (nPrS-nPr)	72.8±1.5	73.0	71.5	71.2	70.5	70.6	71.6
14 (MeS-tBu)	70.4±1.5	71.7	70.7	70.3	70.2	70.3	70.6
15 (MeS-Ph)	85.4±1.5	86.0	84.7	84.6	84.4	84.3	86.0
16 (MeS-Bn)	60.5±1	64.6	63.2	62.8	62.8	62.8	63.4
17 (EtS-tBu)	71.1±1.5	70.4	69.4	69.1	69.0	69.1	69.4
18 (EtS-COMe)	76.2±2	76.1	75.2	75.2	74.6	74.6	75.9
19 (MeSS-Me)	57.4±1.5	61.3	59.6	59.2	58.9	58.9	58.5
20 (MeSS-Et)	56.2±2	60.1	58.6	58.3	58.0	58.0	57.0
21 (MeSS-iPr)	54.5±2	59.8	58.5	58.2	58.2	58.2	56.7
22 (MeSO₂-Me)	68	69.4	67.1	66.9	66.7	66.7	69.5
23 (MeSO₂-Et)	68.9±2	69.4	67.1	66.9	66.9	67.0	69.0
24 (MeSO₂-iPr)	67.5±2	69.1	66.7	66.6	67.1	67.1	68.3
25 (MeSO₂-nBu)	71.3±2	69.8	67.3	67.0	67.1	67.2	69.0
26 (MeSO₂-Ph)	82.3±2	79.8	77.3	77.4	77.4	77.3	79.2

27 (MeSO₂-Bn)	57.5±2	58.1	55.8	55.5	56.0	56.0	57.6
R	/	0.9786	0.9722	0.9742	0.9758	0.9759	0.9878
SD(kcal/mol)	/	1.7	1.9	1.8	1.8	1.8	1.3
RMSD(kcal/mol)	/	2.1	1.9	1.9	1.9	1.9	1.3

Table S4. Comparison between BDEs calculated by DFT/*BS* (DFT=M05-2X/M06-2X) and the experimental results for the MeSO₂R compounds.

Reactant	BDE ^{exp}	BDE ^{calc} (M05-2X)					
					6-	6-	6-311++
		6-31G(d)	6-31+G(d)	6-31+G(d,p)	311+ G(d,p)	311++G(d,p)	G(2df,2p)
22 (MeSO₂-Me)	68	69.3	67.3	66.9	67.4	67.4	70.8
23 (MeSO₂-Et)	68.9±2	69.0	67.0	66.7	67.5	67.5	70.2
24 (MeSO₂-ⁱPr)	67.5±2	68.8	66.7	66.5	67.6	67.7	69.6
25 (MeSO₂-ⁿBu)	71.3±2	68.9	66.8	66.4	67.2	67.3	69.9
26 (MeSO₂-Ph)	82.3±2	80.7	78.4	78.5	79.1	79.1	81.5
27 (MeSO₂-Bn)	57.5±2	56.2	54.2	53.9	55.1	55.1	57.3
R	/	0.9805	0.9793	0.9800	0.9801	0.9802	0.9775
SD(kcal/mol)	/	1.6	1.6	1.6	1.6	1.6	1.7
RMSD(kcal/mol)	/	1.5	2.9	3.1	2.4	2.4	1.7

Reactant	BDE ^{exp}	BDE ^{calc} (M06-2X)					
					6-	6-	6-311++
		6-31G(d)	6-31+G(d)	6-31+G(d,p)	311+ G(d,p)	311++G(d,p)	G(2df,2p)
22 (MeSO₂-Me)	68	69.4	67.1	66.9	66.7	66.7	69.5
23 (MeSO₂-Et)	68.9±2	69.4	67.1	66.9	66.9	67.0	69.0
24 (MeSO₂-ⁱPr)	67.5±2	69.1	66.7	66.6	67.1	67.1	68.3
25 (MeSO₂-ⁿBu)	71.3±2	69.8	67.3	67.0	67.1	67.2	69.0
26 (MeSO₂-Ph)	82.3±2	79.8	77.3	77.4	77.4	77.3	79.2
27 (MeSO₂-Bn)	57.5±2	58.1	55.8	55.5	56.0	56.0	57.6

R	/	0.9861	0.9848	0.9844	0.9842	0.9844	0.9814
SD(kcal/mol)	/	1.7	1.7	1.7	1.8	1.8	1.8
RMSD(kcal/mol)	/	1.5	2.8	3.0	2.9	2.9	1.7

**Cartesian coordinates of all optimized geometries
calculated at M06-2X/6-31G* method**

1 (Me-SH)

S	-0.66319800	-0.08659400	0.00000300
H	-0.89420700	1.23668200	-0.00001500
C	1.15538200	0.01900300	0.00000400
H	1.52292800	-1.00823200	-0.00029800
H	1.52504600	0.52174700	-0.89438900
H	1.52511600	0.52129100	0.89463600

2 (Et-SH)

S	-1.10030600	-0.23315900	-0.00012000
H	-1.90856500	0.84012300	0.00207900
C	0.48784800	0.67636000	-0.00023800
H	0.54087500	1.31097300	-0.88779400
H	0.54070100	1.31135500	0.88705100
C	1.62584500	-0.33636100	0.00019100
H	1.57967900	-0.97623100	-0.88550000
H	2.59012900	0.17943500	-0.00031700
H	1.57992400	-0.97510600	0.88667800

3 (nPr-SH)

C	2.40306500	0.08189300	0.00010200
H	2.56875300	0.70478400	0.88531300
H	2.56881500	0.70563400	-0.88450100
H	3.15882000	-0.70838100	-0.00025500
C	0.99367300	-0.50548600	-0.00023200
H	0.85303600	-1.14334400	-0.88054800
H	0.85291100	-1.14396100	0.87962800
C	-0.06671400	0.59072400	0.00003100
H	0.04381700	1.22016400	-0.88782900
H	0.04401100	1.21999500	0.88799000
S	-1.72743900	-0.17659000	0.00012000
H	-2.43128700	0.96775500	-0.00111700

4 (iPr-SH)

S	-1.39128600	-0.00005300	-0.01676400
H	-1.24465600	0.00047100	1.32191100
C	0.40436800	-0.00001000	-0.39895600
H	0.41942500	-0.00004700	-1.49461000
C	1.08839100	1.26334500	0.11235500
H	1.05227800	1.30043000	1.20707100
H	2.14204700	1.27231500	-0.18870700

H	0.60471000	2.16253400	-0.27546200
C	1.08847600	-1.26329800	0.11241800
H	0.60481800	-2.16253300	-0.27531900
H	2.14211900	-1.27223400	-0.18869600
H	1.05241800	-1.30031400	1.20713800

5 (tBu-SH)

C	-0.34467000	-0.00505800	0.00000100
C	-0.83866000	-0.72176300	1.25581500
H	-0.48800200	-1.75891700	1.28225700
H	-0.48560400	-0.21670900	2.15890000
H	-1.93545600	-0.73635700	1.26870700
C	-0.83861900	-0.72241600	-1.25545500
H	-1.93541400	-0.73699600	-1.26838400
H	-0.48551700	-0.21784900	-2.15879400
H	-0.48798600	-1.75959500	-1.28133100
C	-0.81935500	1.44923600	-0.00038700
H	-0.46463100	1.98065800	0.88812500
H	-0.46466500	1.98016700	-0.88920400
H	-1.91471200	1.47477200	-0.00036700
S	1.50039500	0.07771300	0.00001400
H	1.70348700	-1.25257900	0.00002400

6 (cypen-SH)

S	-2.10293000	-0.07810000	-0.07595700
H	-2.45805300	1.11663700	0.42645300
C	-0.34457100	0.01794000	0.39871300
C	0.42869800	-1.19593600	-0.12382700
C	0.43557800	1.19037700	-0.19573800
H	-0.27822400	0.04395100	1.49266600
C	1.90653200	-0.77301600	0.01194900
H	0.17011800	-1.34885500	-1.17880600
H	0.18960900	-2.11608800	0.41544200
C	1.90380700	0.78167700	0.02164100
H	0.18089200	2.15076100	0.26278100
H	0.20364100	1.25598300	-1.26507500
H	2.32901400	-1.15934200	0.94394300
H	2.51116900	-1.17856100	-0.80309300
H	2.25850800	1.15399000	0.98762300
H	2.55994400	1.20486600	-0.74304700

7 (Ph-SH)

S	2.28232300	-0.08295700	-0.00491700
H	2.49427000	1.23962000	0.07016100

C	0.50660100	-0.00001200	0.00074700
C	-0.19842000	-1.20610300	0.00280900
C	-0.19293900	1.20774800	-0.00217600
C	-1.58862800	-1.19921500	0.00110600
H	0.34251200	-2.14816600	0.00764800
C	-1.58461100	1.20471700	-0.00118600
H	0.34564400	2.15123600	-0.00617800
C	-2.28883800	0.00452600	-0.00019800
H	-2.12632500	-2.14246400	0.00284600
H	-2.11837100	2.15029800	-0.00234900
H	-3.37388200	0.00681900	-0.00007200

8 (Bn-SH)

C	1.46927200	0.00036700	0.89968200
H	1.69735300	-0.88829600	1.49244800
H	1.69731500	0.88953200	1.49170600
C	0.02429300	0.00017600	0.47873000
C	-0.64889600	-1.20306700	0.26039700
C	-0.64911200	1.20323600	0.26006600
C	-1.97603500	-1.20475900	-0.15722900
H	-0.12520000	-2.14299900	0.41705200
C	-1.97625500	1.20457700	-0.15755100
H	-0.12558500	2.14330400	0.41646000
C	-2.64314300	-0.00017900	-0.36592700
H	-2.48929100	-2.14759100	-0.31959700
H	-2.48968000	2.14727300	-0.32016700
H	-3.67924800	-0.00031500	-0.69015700
S	2.51330000	-0.00022900	-0.61334000
H	3.70079100	0.00065200	0.01668200

9 (MeCO-SH)

C	-1.40303100	-0.93662400	-0.00000100
H	-1.23205700	-1.55689700	-0.88453300
H	-2.42550200	-0.55829400	-0.00054300
H	-1.23278200	-1.55618300	0.88517800
C	-0.45192900	0.23682300	-0.00001700
O	-0.78579500	1.38858200	-0.00000100
S	1.28511800	-0.26466100	-0.00000400
H	1.74457300	0.99610800	0.00007600

10 (MeS-Me)

S	0.00000000	0.00000000	0.66702800
C	0.00000000	1.37250400	-0.51685400
H	0.00000000	2.30074000	0.05756800

H	0.89332000	1.34789900	-1.14633300
H	-0.89332000	1.34789900	-1.14633300
C	0.00000000	-1.37250400	-0.51685400
H	0.89332000	-1.34789900	-1.14633300
H	0.00000000	-2.30074000	0.05756800
H	-0.89332000	-1.34789900	-1.14633300

11 (MeS-Et)

S	0.71854900	-0.68490100	-0.21715000
C	-0.94595200	-0.45430500	0.48421400
H	-0.84589600	-0.18646000	1.54178400
H	-1.40544800	-1.44626600	0.44485200
C	1.42617300	0.94610600	0.14104300
H	2.48302200	0.90402200	-0.12905100
H	0.94974000	1.73574100	-0.44396800
H	1.34642700	1.17743900	1.20691800
C	-1.80459600	0.56065000	-0.25961500
H	-1.90118500	0.28561000	-1.31314900
H	-2.80568300	0.60976200	0.18130100
H	-1.37151600	1.56385500	-0.20814100

12 (MeS-ⁿPr)

C	-2.42547600	0.67890100	-0.00003200
H	-3.40803300	0.20324900	-0.00008000
H	-2.33618600	1.30250800	-0.89337600
H	-2.33627000	1.30250400	0.89332200
S	-1.18039900	-0.63916800	0.00002300
C	0.31485600	0.39729100	0.00003900
H	0.30417200	1.04213900	0.88671200
H	0.30412100	1.04224500	-0.88655800
C	1.56635300	-0.47542400	-0.00005400
H	1.54991900	-1.12848100	-0.87997900
H	1.54994300	-1.12864300	0.87975000
C	2.83847300	0.36995100	0.00000800
H	2.88083200	1.01355800	0.88481100
H	3.73185700	-0.26044500	-0.00008100
H	2.88079100	1.01375000	-0.88465600

13 (ⁿPrS-ⁿPr)

C	3.90368400	0.59804000	0.00000000
H	3.88707500	1.24297100	0.88470900
H	3.88707600	1.24296600	-0.88471300
H	4.85150200	0.05262200	0.00000200
C	2.71573400	-0.36151900	0.00000200

H	2.76029400	-1.01383800	-0.87957600
H	2.76029400	-1.01383400	0.87958300
C	1.38687100	0.38853900	0.00000000
H	1.31520700	1.02941700	-0.88673300
H	1.31520500	1.02941700	0.88673300
S	0.00000000	-0.79001000	-0.00000100
C	-1.38687100	0.38853900	-0.00000200
H	-1.31520700	1.02941500	-0.88673600
H	-1.31520500	1.02941800	0.88673000
C	-2.71573400	-0.36151900	0.00000200
H	-2.76029300	-1.01383300	0.87958300
H	-2.76029500	-1.01383800	-0.87957600
C	-3.90368400	0.59804000	0.00000000
H	-3.88707700	1.24296600	-0.88471200
H	-4.85150200	0.05262200	0.00000300
H	-3.88707500	1.24297100	0.88471000

14(MeS-'Bu)

C	-0.66497100	0.08042300	-0.00033400
C	-0.73754200	1.02246000	-1.20134400
H	-1.72278700	1.50338500	-1.23409700
H	0.01326800	1.81637400	-1.13556500
H	-0.58620800	0.47704600	-2.13745500
C	-1.75370700	-0.98973100	-0.10869400
H	-1.65875700	-1.55414200	-1.04140000
H	-1.69993900	-1.69212300	0.72931300
H	-2.74008600	-0.51237900	-0.09258700
C	-0.83343200	0.86209200	1.30238100
H	-0.79572500	0.19320500	2.16661100
H	-0.05645400	1.62403600	1.42004000
H	-1.80180600	1.37760200	1.30251200
S	0.91786200	-0.86832200	0.00269000
C	2.16273000	0.45089300	0.00195800
H	2.04609000	1.12072300	0.85726600
H	3.13275700	-0.04367700	0.08452800
H	2.14539500	1.02628300	-0.92601300

15 (MeS-Ph)

C	-2.68807400	0.86693600	0.00022700
H	-3.75274200	0.62712600	0.00016000
H	-2.45676500	1.44809500	-0.89522100
H	-2.45683900	1.44774400	0.89590700
S	-1.82153200	-0.72104200	-0.00008400
C	-0.11602500	-0.23295900	-0.00013500

C	0.82900100	-1.26680900	-0.00001000
C	0.32322800	1.09163900	-0.00016400
C	2.18635500	-0.97666900	0.00012900
H	0.49237400	-2.30013600	-0.00002600
C	1.68895500	1.37285500	-0.00006400
H	-0.38398500	1.91343800	-0.00026000
C	2.62558900	0.34670400	0.00009700
H	2.90534500	-1.79044400	0.00024300
H	2.01591200	2.40849500	-0.00011400
H	3.68703700	0.57216700	0.00018800

16 (MeS-Bn)

C	-2.08811300	1.03827800	-1.10069700
H	-2.82051400	1.04758800	-1.91003900
H	-1.08234800	1.00432100	-1.52630600
H	-2.20598100	1.94868500	-0.50622100
S	-2.41585100	-0.43656800	-0.09957200
C	-1.11864000	-0.20854900	1.16793100
H	-1.34741700	0.68725800	1.75425300
C	0.27453100	-0.12605900	0.60137200
C	0.99031700	1.06984500	0.65536000
C	0.86392400	-1.23827300	-0.00713800
C	2.27618400	1.15470300	0.12375700
H	0.53714000	1.94205700	1.12117400
C	2.14683300	-1.15813100	-0.53511000
H	0.30228900	-2.16715300	-0.07063200
C	2.85788700	0.04012200	-0.47042100
H	2.82074800	2.09276300	0.17444000
H	2.59484200	-2.03144900	-0.99950000
H	3.85950400	0.10298200	-0.88447600
H	-1.22219500	-1.07358900	1.83014000

17 (EtS-'Bu)

C	3.10404000	-0.02800900	0.08278200
H	3.32882900	-0.75399500	-0.70400200
H	3.19946500	-0.53211400	1.04809200
H	3.85080300	0.76976800	0.03311300
C	1.70258900	0.54811600	-0.09335300
H	1.48042200	1.25439000	0.71279100
H	1.62989800	1.08080000	-1.04588800
S	0.49697600	-0.81788300	-0.06110200
C	-1.12145500	0.06653700	0.01411000
C	-1.23729400	1.09638600	-1.10919400
H	-2.24125500	1.53801400	-1.10197800

H	-0.51707300	1.91090200	-0.98285100
H	-1.06929000	0.63191900	-2.08548300
C	-2.17386700	-1.02934100	-0.17099300
H	-2.07916300	-1.79996300	0.60090900
H	-3.17592100	-0.59194800	-0.09583900
H	-2.07575900	-1.50618400	-1.15078600
C	-1.30702300	0.73787400	1.37562900
H	-2.28751900	1.22833300	1.41846200
H	-1.25045200	0.00230300	2.18272600
H	-0.54653500	1.50452700	1.55448500

18 (EtS-COMe)

C	2.84911500	-0.06794200	-0.02996500
H	2.98433400	-0.62534900	-0.96092700
H	3.03387300	-0.74840900	0.80602200
H	3.60220800	0.72424800	0.00507200
C	1.45602900	0.54223700	0.04904000
H	1.31365100	1.10967500	0.97149900
H	1.25706200	1.21582900	-0.78720300
S	0.20093700	-0.77802900	0.00286900
C	-1.26076500	0.24876900	-0.01559900
O	-1.20143100	1.45254400	-0.01881800
C	-2.56362200	-0.51991100	0.00018900
H	-2.42646100	-1.57791100	-0.23010700
H	-3.00524700	-0.42566700	0.99685100
H	-3.24750900	-0.06322800	-0.71855500

19 (MeSS-Me)

C	-1.81346100	0.80683800	0.38738100
H	-2.81295400	0.84167200	-0.05400900
H	-1.33321400	1.77809500	0.25498300
H	-1.89319400	0.56896400	1.44877500
S	-0.90508300	-0.50186600	-0.49343000
S	0.90511000	-0.50188700	0.49341000
C	1.81341500	0.80689400	-0.38735400
H	1.33296200	1.77806100	-0.25509600
H	2.81281800	0.84187000	0.05423600
H	1.89342300	0.56899100	-1.44872300

20 (MeSS-Et)

C	-2.13564500	1.04127400	0.36788200
H	-3.13433800	1.20384600	-0.04596700
H	-1.51576200	1.91389600	0.15444200
H	-2.20901800	0.88739400	1.44504100

S	-1.47375900	-0.44750600	-0.44574900
S	0.35232100	-0.66060900	0.48310100
C	1.42287400	0.43959300	-0.51427600
H	1.03319900	1.45989000	-0.45907000
H	1.38282200	0.10809200	-1.55434200
C	2.84192400	0.36849400	0.03714400
H	3.23042700	-0.65269900	-0.01094300
H	3.50274600	1.01253500	-0.54979900
H	2.87801500	0.70072300	1.07851400

21 (MeSS-iPr)

C	-2.38853700	-0.46260900	0.98284600
H	-3.33003800	0.03446200	1.23119000
H	-1.75004300	-0.48018600	1.86790200
H	-2.59218900	-1.48026600	0.64746000
S	-1.62643100	0.50697400	-0.35675900
S	0.05797400	-0.60400200	-0.77033300
C	1.28972200	0.03632900	0.44210900
H	0.84844200	-0.08083200	1.43797300
C	1.62969000	1.49769400	0.19015200
H	0.73578100	2.12550300	0.23426500
H	2.33717100	1.85333100	0.94768200
H	2.08872500	1.61536000	-0.79657700
C	2.51381600	-0.86728700	0.31826300
H	3.28318100	-0.54263700	1.02608100
H	2.26938600	-1.91219400	0.52750200
H	2.93675100	-0.80486000	-0.69022900

22 (MeSO₂-Me)

C	-1.40443200	0.91564900	-0.00001500
H	-1.38518600	1.52798000	-0.90257600
H	-1.38519700	1.52800100	0.90253100
H	-2.28969500	0.27660200	-0.00001300
S	0.00000000	-0.19179700	0.00000500
O	-0.00000300	-0.91149100	1.26899700
O	0.00000300	-0.91153300	-1.26897400
C	1.40443200	0.91564900	-0.00001100
H	1.38519300	1.52797800	-0.90257300
H	1.38519000	1.52800300	0.90253400
H	2.28969500	0.27660200	-0.00000100

23 (MeSO₂-Et)

C	-1.10099000	-0.55350100	-0.63877300
H	-1.16018900	-1.63925800	-0.51152400

H	-1.02912700	-0.34366800	-1.70987200
S	0.49953900	-0.15164300	0.07573000
O	0.38412200	-0.26291100	1.52773200
O	1.50621200	-0.91729100	-0.65396900
C	0.74229200	1.57820800	-0.31756800
H	0.72865500	1.70953600	-1.40051600
H	-0.02533800	2.17880400	0.17183500
H	1.72664300	1.83555500	0.07870500
C	-2.25718900	0.16153200	0.04429600
H	-2.22913000	1.24024700	-0.13466200
H	-3.20605600	-0.21532600	-0.34516900
H	-2.22542400	-0.01542000	1.12170100

24 (MeSO₂-ⁱPr)

C	1.03658100	0.12697700	-0.50984300
H	0.93565200	0.16424300	-1.60061200
S	-0.63829800	-0.20159000	0.09671000
O	-1.10381300	-1.43187400	-0.54166700
O	-0.62122100	-0.08388500	1.55478700
C	-1.63559300	1.14020500	-0.54753100
H	-1.32850400	2.08319300	-0.09506500
H	-1.54858200	1.16589700	-1.63496600
H	-2.66224700	0.90318900	-0.26128400
C	1.56843100	1.44079600	0.04949600
H	1.53842700	1.41912000	1.14257300
H	2.60647300	1.57458200	-0.26853800
H	0.99931400	2.30665000	-0.30078800
C	1.88992000	-1.07160800	-0.09958800
H	1.47493000	-2.00164200	-0.49317600
H	2.90400200	-0.94130900	-0.48685000
H	1.93753400	-1.14063400	0.99118100

25 (MeSO₂-ⁿBu)

C	-0.15211900	0.77706700	0.00000100
H	-0.12940800	1.40844800	0.89413600
S	1.35852300	-0.19473800	0.00000200
O	1.42868600	-0.91691600	1.26847500
O	1.42866800	-0.91694700	-1.26845400
C	2.65869200	1.03568500	-0.00002200
H	2.58226200	1.64336800	-0.90277600
H	2.58227600	1.64338800	0.90272000
H	3.59839200	0.47966600	-0.00002300
H	-0.12940700	1.40845100	-0.89413100
C	-1.36019100	-0.15568300	-0.00000200

H	-1.30652100	-0.80427600	0.88188100
H	-1.30652500	-0.80426400	-0.88189400
C	-2.67399300	0.62509300	0.00000700
H	-2.70754200	1.28062000	-0.87941600
H	-2.70754300	1.28059700	0.87944600
C	-3.88646800	-0.30208600	-0.00000600
H	-3.88277000	-0.94748400	0.88409900
H	-4.82116800	0.26519700	0.00000400
H	-3.88277200	-0.94745700	-0.88413000

26 (MeSO₂-Ph)

S	-1.46501700	0.00004100	-0.17204600
O	-1.88442300	1.27283400	-0.75112700
O	-1.88454800	-1.27256600	-0.75142800
C	-1.96403900	-0.00024800	1.54662800
H	-1.58076100	-0.90161600	2.02664800
H	-1.58007400	0.90047800	2.02731400
H	-3.05613800	0.00014300	1.54968700
C	0.31684200	-0.00010100	-0.08289500
C	0.99003900	-1.21735900	-0.04906500
C	0.98987500	1.21724700	-0.04896400
C	2.37905500	-1.21040300	0.03665600
H	0.42770000	-2.14409500	-0.11229500
C	2.37888900	1.21047200	0.03678000
H	0.42738900	2.14389700	-0.11221100
C	3.06829500	0.00007900	0.08271100
H	2.92419800	-2.14852500	0.05813000
H	2.92391700	2.14865700	0.05832800
H	4.15206900	0.00014800	0.14645700

27 (MeSO₂-Bn)

S	1.72976100	0.01644600	-0.25533900
O	1.55249300	-1.18335500	-1.06716300
O	1.60009300	1.34605900	-0.84363100
C	3.34245000	-0.08023400	0.51626800
H	3.46492600	0.75431000	1.20814600
H	3.44538200	-1.04100800	1.02236900
H	4.06860100	-0.00370300	-0.29557800
C	0.58944400	-0.08496800	1.14868400
H	0.81398100	-1.02169900	1.66681800
H	0.82347900	0.76364900	1.79798800
C	-0.82258300	-0.04253700	0.63976800
C	-1.44084100	1.18395600	0.39051200
C	-1.49963900	-1.22788000	0.35089600

C	-2.73509200	1.22288800	-0.11677300
H	-0.89884500	2.10534100	0.58467800
C	-2.79444100	-1.18781300	-0.15526800
H	-1.00593200	-2.18145700	0.51659100
C	-3.41488900	0.03738800	-0.38594200
H	-3.21167500	2.17983100	-0.30462900
H	-3.31714700	-2.11365100	-0.37373700
H	-4.42608700	0.06882500	-0.77973300

TS-S1PdCl

C	2.90637600	-1.25308500	-1.10998100
C	1.66145500	-0.63993600	-1.21561700
C	1.09647500	-0.05517000	-0.07625600
C	1.78992400	0.00186100	1.13525200
C	3.02992800	-0.62343800	1.23116100
C	3.58105600	-1.24800300	0.11188800
H	3.35175800	-1.72901200	-1.97756200
H	1.12591800	-0.63038700	-2.16275700
H	1.36458900	0.53729400	1.98224200
H	3.57307200	-0.60874800	2.17045900
H	4.55521900	-1.72056100	0.18817700
S	0.23946300	2.06698500	-0.43490700
O	0.26463400	2.65159400	0.89199200
O	-1.09114200	1.50005800	-0.85985900
Pd	-0.93461200	-0.39553100	0.03733200
Cl	-3.09347300	-1.23720900	0.25440700

TS-S2PdCl

C	-2.78109300	-0.73259100	1.17714800
C	-1.45154100	-0.33692700	1.24530000
C	-0.80018100	0.10743200	0.08565700
C	-1.49424300	0.23655300	-1.12346600
C	-2.81982300	-0.16950000	-1.20223600
C	-3.43415600	-0.64767000	-0.04894900
H	-3.32051900	-1.09543000	2.04484900
H	-0.91689300	-0.38620000	2.19154000
H	-0.99819900	0.66419600	-1.99279200
H	-3.38955600	-0.10598100	-2.12250200
S	0.29238800	2.15116600	0.40870700
O	0.33050300	2.70419300	-0.93042300
O	1.53509500	1.41910900	0.83798000
Pd	1.16504700	-0.46660200	-0.02752800
Cl	3.20662400	-1.56411300	-0.25909100
F	-4.71070600	-1.01909400	-0.11674900

TS-S3PdCl

C	-2.75951100	-0.67715200	1.17472400
C	-1.42413500	-0.29452100	1.24849500
C	-0.77431300	0.13854600	0.08768600
C	-1.47255900	0.26861600	-1.11793200
C	-2.80106000	-0.12924500	-1.17657200
C	-3.46007000	-0.60595200	-0.03437500
H	-3.26839200	-1.03003800	2.06735300
H	-0.88799300	-0.34508100	2.19413600
H	-0.97750900	0.68847900	-1.99177200
H	-3.34561700	-0.05328300	-2.11419200
S	0.34680300	2.15141200	0.40117900
O	0.39793400	2.70355900	-0.93873600
O	1.58004900	1.40501600	0.83678000
Pd	1.17837800	-0.47369600	-0.02896100
Cl	3.19731500	-1.62233600	-0.25803900
C	-4.90803600	-1.00833000	-0.11607300
H	-5.52870900	-0.16225800	-0.42823900
H	-5.04694300	-1.80488300	-0.85387900
H	-5.27915700	-1.36615200	0.84653600

TS-S4PdCl

C	2.06567000	-0.32938200	-0.85664200
C	0.69465000	-0.18957400	-1.01503300
C	-0.10770600	0.26707900	0.03959200
C	0.48369100	0.66548600	1.24579800
C	1.84890400	0.52631600	1.41354300
C	2.65232900	0.02645500	0.37151800
H	2.68394800	-0.69799000	-1.66185600
H	0.24077100	-0.45449700	-1.96826700
H	-0.12459300	1.09929000	2.03693700
H	2.31104300	0.82568300	2.35092900
S	-1.39365900	2.11819400	-0.61349100
O	-1.63924300	2.79643900	0.64471600
O	-2.47459200	1.16995600	-1.04978800
Pd	-1.96340900	-0.55466900	0.07227900
Cl	-3.84001600	-1.94187900	0.27255100
C	6.40669200	-0.42890500	0.37516900
H	7.11963200	-0.83520400	-0.34038600
H	6.68085100	0.60437400	0.61049000
H	6.44439300	-1.01297600	1.29963600
N	4.02008800	-0.06725200	0.61766500
H	4.31472300	0.21109900	1.54449500
C	5.02666400	-0.48049800	-0.24540100

O 4.82119500 -0.83830300 -1.38358400

TS-S5PdCl

C -2.13171900 1.16022300 -0.49999800
H -1.95410900 1.41049400 -1.54653500
H -1.42905600 1.70417100 0.15926300
H -3.13523700 1.45128800 -0.18430200
S -1.97288400 -0.65901300 -0.25404600
O -0.49884200 -0.79992500 -0.84358800
O -1.96033400 -0.80126900 1.22155800
Pd 0.58956000 0.46675900 0.18069900
Cl 2.55461900 -0.56732000 -0.15880000

TS-S1CuOAc

C 2.38131700 -2.30312600 -0.87270700
C 1.21962500 -1.54291300 -0.89339700
C 0.95780400 -0.55298900 0.07733800
C 1.94463100 -0.36383000 1.06396400
C 3.11209900 -1.12552500 1.10360000
C 3.33090100 -2.09568800 0.13121500
H 2.55106700 -3.06424000 -1.62891300
H 0.48077000 -1.73627500 -1.66922500
H 1.81229500 0.41371000 1.81800300
H 3.84999100 -0.95660600 1.88224700
H 4.24164200 -2.68730100 0.14784600
S 1.11815300 1.94929800 -0.68891000
O 2.20418500 2.66206700 -0.05823900
O -0.19263900 2.10310900 0.00281000
Cu -0.88149900 0.18878400 0.20749400
O -2.11591700 -1.29918300 -0.35014400
O -2.78696300 0.58235100 0.52827400
C -3.06732800 -0.56246400 0.04893300
C -4.48761800 -1.03748400 -0.04336000
H -5.17349800 -0.27961300 0.33205200
H -4.71704200 -1.27542000 -1.08494800
H -4.59011000 -1.96037700 0.53306300

TS-S2CuOAc

C 2.50958500 -1.68908900 -0.92428600
C 1.22296500 -1.17032000 -0.93456800
C 0.76278800 -0.26558900 0.04805100
C 1.69104900 0.09648700 1.04476200
C 2.98711700 -0.41169500 1.08928500
C 3.37080600 -1.29814300 0.09647600

H 2.86073300 -2.38997300 -1.67413900
H 0.54386300 -1.49679600 -1.71966100
H 1.40724900 0.81910000 1.81076600
H 3.69638100 -0.13006000 1.85971600
S 0.46586000 2.24337800 -0.67728900
O 1.39268400 3.12329800 -0.00461800
O -0.85947700 2.12788400 -0.00669000
Cu -1.18200300 0.11803200 0.18603000
O -2.13160500 -1.57198300 -0.36837700
O -3.11596500 0.15168100 0.53799200
C -3.19217800 -1.02493100 0.05417400
C -4.51412200 -1.73236100 0.00479900
H -4.86350100 -1.89753800 1.02746700
H -5.24645900 -1.09281600 -0.49279000
H -4.42030700 -2.68465400 -0.51489700
F 4.61479800 -1.79082400 0.11185100

TS-S3CuOAc

C 2.53444500 -1.61977700 -0.91296500
C 1.23130700 -1.15073400 -0.93471500
C 0.73476500 -0.26693400 0.04994400
C 1.65011700 0.11709200 1.04788600
C 2.96146400 -0.35628200 1.08345900
C 3.42327500 -1.22969900 0.10164700
H 2.88075400 -2.30487200 -1.68417600
H 0.56728400 -1.49456100 -1.72593900
H 1.34377600 0.82656300 1.81838100
H 3.63457800 -0.03625400 1.87495400
S 0.43354100 2.23457800 -0.66985000
O 1.33706000 3.14841600 -0.00956700
O -0.89425900 2.10890800 -0.00445500
Cu -1.21116000 0.09739800 0.17925000
O -2.15949400 -1.59944300 -0.36689600
O -3.14767500 0.12688800 0.53158000
C -3.22011200 -1.05226700 0.05385100
C -4.54089000 -1.76330700 0.00911300
H -5.27487300 -1.12853400 -0.49217800
H -4.44508900 -2.71844500 -0.50503400
H -4.88977900 -1.92328500 1.03277100
C 4.83722200 -1.74730900 0.11247300
H 4.85174500 -2.83862900 0.20299700
H 5.35588400 -1.49215500 -0.81749500
H 5.40808400 -1.33045700 0.94561200

TS-S4CuOAc

C	2.04475800	-0.89274600	-0.59147500	H	-0.21661100	2.53961700	0.60260100
C	0.66413800	-0.78609600	-0.66452200	H	-1.19689400	2.31937100	-0.83233700
C	-0.10330800	0.03134500	0.19347700	H	-1.85765500	1.96607500	0.76850500
C	0.63428900	0.75423300	1.15468100				
C	2.01504900	0.66545500	1.26122800				
C	2.73523800	-0.15655400	0.38728500				
H	2.59524800	-1.53264500	-1.26605500				
H	0.15495700	-1.38594100	-1.41687900				
H	0.11990900	1.43055100	1.83867900				
H	2.54374500	1.24187100	2.01746200				
S	-0.88401800	2.34462300	-0.83963000				
O	-0.26405900	3.51155500	-0.25413900				
O	-2.18345300	1.96940500	-0.21713100				
Cu	-2.07952400	-0.04273900	0.17306400				
O	-2.60676600	-1.94907600	-0.23815400				
O	-4.00216000	-0.39605400	0.39848600				
C	-3.78870800	-1.60416700	0.05253600				
C	-4.92481000	-2.58373600	0.00956800				
H	-5.29487200	-2.73770900	1.02684000				
H	-5.74347100	-2.16215700	-0.57752600				
H	-4.59704200	-3.53239500	-0.41290400				
N	4.12711000	-0.19364300	0.54180400				
C	5.06302000	-0.87967200	-0.20605000				
H	4.48805600	0.36235500	1.30584100				
O	4.78766000	-1.57871800	-1.15832600				
C	6.48465600	-0.68842400	0.28881500				
H	6.73175800	0.37223000	0.39340600				
H	6.61383000	-1.16802200	1.26420600				
H	7.16145800	-1.15061200	-0.42809400				

TS-S5CuOAc

S	-2.46126000	-0.33799200	-0.43513500
O	-3.49618600	-0.39871400	0.56624100
O	-1.27929100	-1.19258300	-0.18039000
Cu	0.20009400	0.23380000	0.09057000
O	2.03725900	0.95816400	-0.33804300
O	1.64195000	-1.06545200	0.37470000
C	2.47711600	-0.17940200	-0.00420400
C	3.94214600	-0.49998000	-0.04458500
H	4.27033200	-0.79020000	0.95655800
H	4.10142700	-1.35758700	-0.70273400
H	4.51315100	0.35811300	-0.39565400
C	-0.96362600	1.87620900	0.14189200