Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Electrophilic Trifluoromethylthiolation of Thiols with Trifluoromethanesulfenamide

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Computational details

Final optimized geometries and energies of species, appearing in Scheme

Geometries optimized at MPW1K/6-311**+ level of theory in dichloromethane, using Poisson-Boltzmann model.

Enthalpies are calculated from solution optimized geometries and energies, corrected by vibrational contribution computed in vacuum: H(sol) = E_{tot}(sol) – E_{tot}(vac) + H(vac)

$PhNH_2$
final geometry:

	angstroms		
atom	x	y	z
C1	-1.4197109564	-0.7636274957	-1.8836995515
C2	-1.0204717347	-1.9595860016	-1.2860717972
C3	-1.8044062715	-2.5569581249	-0.3140725627
C4	-3.0023301175	-1.9839136112	0.0843447465
C5	-3.4075858294	-0.8008207393	-0.5146399158
C6	-2.6318875689	-0.1962192916	-1.4883508559
H7	-0.0888200416	-2.4206662491	-1.5854491752
H8	-1.4706951350	-3.4797701360	0.1393659765
H9	-3.6078792080	-2.4495853448	0.8473417081
H10	-4.3395879429	-0.3389155421	-0.2203263814
H11	-2.9650720406	0.7244191340	-1.9481647937
N17	-0.6580782571	-0.1817661996	-2.8911103472
H18	-0.7747774658	0.8142302554	-2.9862042610
H19	0.3193719674	-0.4247417208	-2.8738590247

E_{tot}(vac) -287.59610888789 hartrees
Total enthalpy, Htot (Utot + pV): -287.469312 hartrees
E_{tot}(sol) -287.60846329315 hartrees

$MeSO_3H$
final geometry:

	angstroms		
atom	x	y	z
S1	-0.7906516857	0.3480676509	-0.0859850385
O2	-2.1801786363	-0.1145666175	-0.2428671330
O5	-0.6965316685	1.5941206758	0.6936674236
C5	0.0416600009	-0.8959381679	0.8639148957
H6	1.0741135717	-0.5906145023	1.0032822582
H7	-0.4586361587	-0.9890363337	1.8229764349
H8	-0.0059163723	-1.8338650887	0.3193018737
O8	-0.0782866507	0.4324231797	-1.3724023970

E_{tot}(vac) -663.80175100915 hartrees
Total enthalpy, Htot (Utot + pV): -663.744055 hartrees
E_{tot}(sol) -663.90882875403 hartrees

$PhNH_3^+$*$MeSO_3^-$-Ion Pair

final geometry:

angstroms

atom	x	y	z
C1	-1.4393358364	-0.7755623178	-1.8529372708
C2	-1.0073780464	-1.9546028048	-1.2747661723
C3	-1.7926147563	-2.5554474660	-0.3024841987
C4	-2.9947681786	-1.9820677051	0.0786276189
C5	-3.4117466648	-0.7983863449	-0.5085881242
C6	-2.6341613668	-0.1874316139	-1.4803914269
H7	-0.0765075134	-2.4114341872	-1.5813186841
H8	-1.4657916960	-3.4791299212	0.1525084211
H9	-3.6077587354	-2.4589491355	0.8302792243
H10	-4.3503610301	-0.3502064264	-0.2165424868
H11	-2.9673760936	0.7303316668	-1.9444891503
N17	-0.6681578025	-0.1881368497	-2.9442684213
H18	-0.7156690757	0.8306890442	-2.9581596146
H19	0.3200019827	-0.4386302076	-2.9086334103
H15	-1.0644598431	-0.5502969464	-3.8438727279
O16	-1.8599339941	-1.5281828253	-4.9875238051
S17	-3.2615919915	-1.8097346313	-5.3985246113
O18	-3.3111914754	-2.4429675004	-6.7206901293
O20	-4.1089376450	-0.6178216279	-5.2873945746
C20	-3.8917056648	-3.0038319975	-4.2515551350
H21	-3.8539181461	-2.5870072971	-3.2511243769
H22	-4.9182628233	-3.2225240614	-4.5303216479
H23	-3.2846129725	-3.9015851803	-4.3175576736

E_{tot}(vac) -951.90311284220 hartrees

Total enthalpy, Htot (Utot + pV): -951.702411 hartrees

E_{tot}(sol) -951.97792337242 hartrees

MeSH

final geometry:

angstroms

atom	x	y	z
S20	2.0419665628	0.2567851955	1.1980632207
C21	1.9680242525	1.1343775418	2.8115083462
H22	2.4226242235	0.5345060787	3.5986021445
H23	2.5403079460	2.0557901051	2.6913352537
H24	0.9399474146	1.3861371299	3.0679797982
H25	1.3098343490	-0.8312440138	1.5185789533

E_{tot}(vac) -438.73132234960 hartrees

Total enthalpy, Htot (Utot + pV): -438.679556hartrees

E_{tot}(sol) -438.74790202778hartrees

$PhNHSCF_3$

final geometry:

		angstroms	
atom	x	y	z
C1	-2.1457879778	0.8863314613	-0.5644325925
C2	-3.4929848844	1.0120806131	-0.2410895631
C3	-4.3897918820	0.0249583395	-0.6080935239
C4	-3.9598892066	-1.1015051753	-1.2923513992
C5	-2.6166624189	-1.2263041847	-1.6062364832
C6	-1.7113803961	-0.2415329957	-1.2500697223
H7	-3.8323251431	1.8837773025	0.3017470079
H8	-5.4324868779	0.1352577289	-0.3480794163
H9	-4.6617854219	-1.8713643878	-1.5761264244
H10	-2.2641905499	-2.0954216313	-2.1433222400
H11	-0.6706944272	-0.3506386178	-1.5100772528
S12	0.3444590552	1.6957501110	0.0853296063
C13	1.0543167963	2.2836698166	-1.4703730652
F14	2.3699153152	2.1483282852	-1.3769920022
F15	0.6444765800	1.5975600778	-2.5271126770
F16	0.7873364138	3.5577456666	-1.7167813304
N17	-1.2749919402	1.9261921861	-0.2153210567
H19	-1.6851634543	2.7174043921	0.2535910104

E_{tot}(vac) -1022.81627067316 hartrees

Total enthalpy, Htot (Utot + pV): -1022.678048 hartrees

E_{tot}(sol) -1022.82491302671 hartrees

$PhNH_2SCF_3^+$*$MeSO_3^-$-Ion Pair

final geometry:

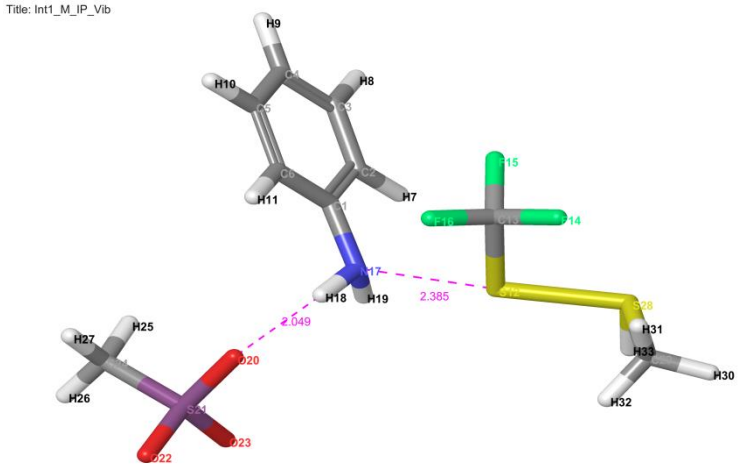
	angstroms		
atom	x	y	z
C1	-1.1515179130	1.3811921695	-0.7346724079
C2	-1.7745584229	1.0134570073	0.4418903421
C3	-2.7150862677	-0.0017715269	0.4054072555
C4	-3.0265375267	-0.6246373257	-0.7928647666
C5	-2.3997608652	-0.2310378385	-1.9626935483
C6	-1.4500407338	0.7775443868	-1.9403634461
H7	-1.5210866796	1.4870846390	1.3778078445
H8	-3.1989744653	-0.3115663828	1.3199088236
H9	-3.7576963268	-1.4196143080	-0.8137899225
H10	-2.6429406634	-0.7102495790	-2.8993052482
H11	-0.9621078313	1.0903586607	-2.8514419754
S12	1.0074645263	2.5068268308	0.6037599591
C13	1.6520448054	0.7970482748	0.5281103055
F14	2.8403324342	0.8333703738	1.0967989033
F15	0.9124482818	-0.0641017288	1.1987144226
F16	1.7651394383	0.3583914193	-0.7036628990
N17	-0.1328485071	2.4417603333	-0.7538769808
H18	0.4488476472	2.3957946415	-1.6509749769
H19	-0.5752840008	3.3716317342	-0.7554713937
O20	1.5216442545	2.4190066279	-2.7773718754
S21	1.6033713410	2.0209846132	-4.2137842541
O22	2.5241977881	2.8899561292	-4.9455129072
O24	0.2678702566	1.9204181403	-4.8105325512
C24	2.3037548016	0.3955845867	-4.2401186853
H25	1.6504971706	-0.2839947535	-3.7021988259
H26	2.3847189484	0.0932590906	-5.2802453543
H27	3.2860708359	0.4305062558	-3.7789305920

E_{tot}(vac) -1687.10713467076 hartrees

Total enthalpy, Htot (Utot + pV): -1686.896548 hartrees

E_{tot}(sol) -1687.16153625804 hartrees

Int



final geometry:

	angstroms		
atom	x	y	z
C1	-0.5101430000	0.5569230000	-0.9327650000
C2	-1.7848590000	0.7352830000	-0.4106230000
C3	-2.6546430000	-0.3379800000	-0.3281710000
C4	-2.2730280000	-1.5925750000	-0.7778660000
C5	-1.0080580000	-1.7645090000	-1.3155910000
C6	-0.1272630000	-0.6999400000	-1.3910630000
H7	-2.0879660000	1.7077310000	-0.0488980000
H8	-3.6415960000	-0.1929050000	0.0870460000
H9	-2.9582800000	-2.4256520000	-0.7158250000
H10	-0.7041540000	-2.7335850000	-1.6857730000
H11	0.8546860000	-0.8417190000	-1.8194830000
S12	1.0920130000	2.6746730000	1.0728750000
C13	1.3933760000	0.9816800000	1.7353700000
F14	2.1755590000	1.0231070000	2.8121230000
F15	0.2745180000	0.3829430000	2.0815790000
F16	2.0035300000	0.2408510000	0.8461220000
N17	0.4110660000	1.6255100000	-0.9583630000
H18	1.1918850000	1.5161850000	-1.5997760000
H19	-0.0512910000	2.5009220000	-1.1652640000
O20	2.3202210000	1.5991510000	-3.3081760000
S21	2.1298380000	2.3813840000	-4.5455590000
O22	3.3642760000	2.4736890000	-5.3401810000
O23	1.5265020000	3.6970480000	-4.2818910000
C24	0.9645070000	1.4813480000	-5.5274400000
H25	0.0459540000	1.3780160000	-4.9594160000
H26	0.7834620000	2.0388610000	-6.4410010000
H27	1.3868330000	0.5066600000	-5.7516730000
S28	1.5136200000	3.6678660000	3.0429020000
C29	3.2963630000	3.9757330000	3.1214630000
H30	3.4786420000	4.6477310000	3.9553330000
H31	3.7646600000	3.0196190000	3.3244320000
H32	3.6571870000	4.3850090000	2.1860700000
H33	1.0873130000	4.8658280000	2.5811870000

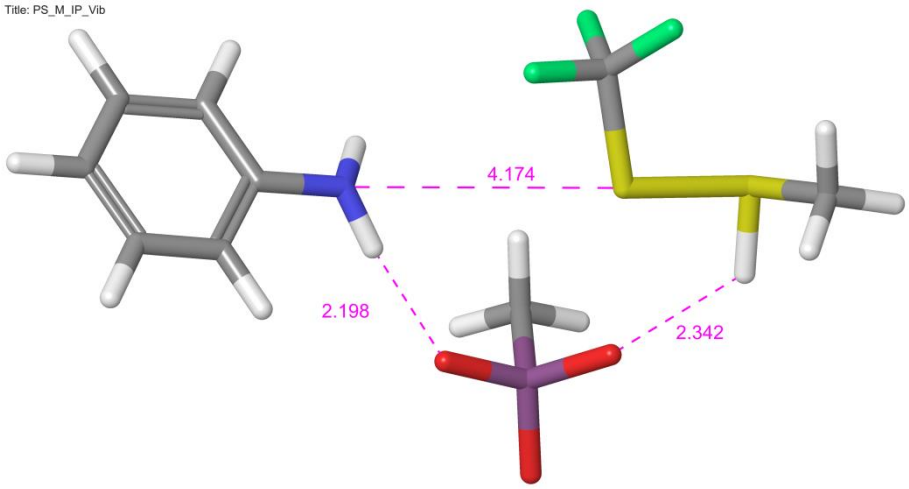
E_{tot}(vac) -2125.80158074047 hartrees
Total enthalpy, Htot (Utot + pV): -2125.537581 hartrees
E_{tot}(sol) -2125.887264

Charge on MeSH moiety (NBO): +0.561
N-S-S bond angle: 174.2°

Summary of Natural Population Analysis:

	Natural	Natural Population			
Atom	No	Charge	Core	Valence	Rydberg	Total
C	1	0.12465	1.99911	3.85401	0.02223	5.87535
C	2	-0.23265	1.99917	4.21679	0.01669	6.23265
C	3	-0.19281	1.99930	4.17585	0.01767	6.19281
C	4	-0.20991	1.99928	4.19297	0.01765	6.20991
C	5	-0.18852	1.99930	4.17169	0.01754	6.18852
C	6	-0.21433	1.99918	4.19790	0.01725	6.21433
H	7	0.21092	0.00000	0.78751	0.00157	0.78908
H	8	0.21495	0.00000	0.78360	0.00145	0.78505
H	9	0.21662	0.00000	0.78219	0.00119	0.78338
H	10	0.21943	0.00000	0.77919	0.00138	0.78057
H	11	0.24088	0.00000	0.75760	0.00152	0.75912
S	12	0.17389	9.99938	5.79220	0.03452	15.82611
C	13	0.93638	1.99985	2.98478	0.07900	5.06362
F	14	-0.35773	1.99991	7.35060	0.00723	9.35773
F	15	-0.32881	1.99990	7.32076	0.00816	9.32881
F	16	-0.31747	1.99990	7.30918	0.00839	9.31747
N	17	-0.76474	1.99941	5.74097	0.02436	7.76474
H	18	0.47827	0.00000	0.51948	0.00225	0.52173
H	19	0.40307	0.00000	0.59472	0.00221	0.59693
O	20	-1.09246	1.99978	7.07940	0.01328	9.09246
S	21	2.34845	9.99920	3.42417	0.22819	13.65155
O	22	-1.01397	1.99981	7.00186	0.01229	9.01397
O	23	-1.04056	1.99981	7.02815	0.01259	9.04056
C	24	-0.83740	1.99938	4.81876	0.01926	6.83740
H	25	0.21042	0.00000	0.78841	0.00117	0.78958
H	26	0.22962	0.00000	0.76950	0.00088	0.77038
H	27	0.22272	0.00000	0.77629	0.00099	0.77728
S	28	0.34518	9.99921	5.61227	0.04335	15.65482
C	29	-0.71158	1.99937	4.69837	0.01383	6.71158
H	30	0.24529	0.00000	0.75374	0.00097	0.75471
H	31	0.25718	0.00000	0.74186	0.00096	0.74282
H	32	0.25178	0.00000	0.74721	0.00101	0.74822
H	33	0.17324	0.00000	0.82106	0.00570	0.82676
* Total *		0.00000	61.99024	111.37305	0.63671	174.00000

TS



final geometry:

	angstroms		
atom	x	y	z
C1	-1.3694468786	-1.0817687195	-1.2478466763
C2	-2.7280310260	-1.1149787456	-0.9172996853
C3	-3.4624667057	-2.2794907861	-1.0583150125
C4	-2.8720792190	-3.4433508437	-1.5271774074
C5	-1.5230344660	-3.4189838740	-1.8472993464
C6	-0.7790488590	-2.2606954142	-1.7121455415
H7	-3.2105310498	-0.2198441605	-0.5491740074
H8	-4.5129097201	-2.2751591854	-0.8015361510
H9	-3.4514125730	-4.3470760961	-1.6447489883
H10	-1.0418502138	-4.3125706719	-2.2200247754
H11	0.2713456090	-2.2633927168	-1.9668682181
S12	2.1762095097	2.6850934622	0.5801098302
C13	0.9321575535	2.7150870117	1.9133837804
F14	1.4083273096	3.0092320602	3.1068135149
F15	-0.0764163959	3.5276162443	1.6781009404
F16	0.5003548800	1.4718893266	1.8996088672
N17	-0.6262859038	0.0661390278	-1.0848609952
H18	0.2303255078	0.1896095287	-1.6051861212
H19	-1.1660683808	0.9111297727	-1.0446179661
O20	1.7835010825	1.0913750301	-2.8747219812
S21	2.5211111132	2.3538362456	-3.0357879162
O22	3.3304483325	2.3845327850	-4.2609771082
O23	3.3262681850	2.7206757917	-1.8468074954
C24	1.2852746762	3.6160292083	-3.1954044205
H25	0.6838399021	3.6211263740	-2.2918194395
H26	1.7785182096	4.5741028746	-3.3254445040
H27	0.6674828655	3.3845220579	-4.0573161931
S28	3.1297467529	4.5189999983	0.8712932255
C29	4.4386601894	4.1752147220	2.0637828353
H30	5.0402817752	5.0804534845	2.1132786152
H31	3.9480584050	4.0084298202	3.0177402286
H32	5.0166276734	3.3119568069	1.7563388190
H33	3.8142920528	4.4313238393	-0.3007311538

E_{tot}(vac) -2125.80752098714 hartrees
Total enthalpy, Htot (Utot + pV): -2125.544819 hartrees
E_{tot}(sol) -2125.87846166324 hartrees

Charge on MeSH moiety (NBO): +0.775

Summary of Natural Population Analysis:

		Natural Population			
	Natural	---	---	---	---
Atom No	Charge	Core	Valence	Rydberg	Total
C 1	0.18020	1.99917	3.80094	0.01970	5.81980
C 2	-0.27630	1.99919	4.26019	0.01692	6.27630
C 3	-0.18720	1.99930	4.17008	0.01783	6.18720
C 4	-0.26925	1.99927	4.25104	0.01893	6.26925
C 5	-0.18341	1.99930	4.16642	0.01770	6.18341
C 6	-0.26340	1.99918	4.24705	0.01717	6.26340
H 7	0.19870	0.00000	0.79940	0.00189	0.80130
H 8	0.20375	0.00000	0.79473	0.00152	0.79625
H 9	0.20689	0.00000	0.79174	0.00137	0.79311
H 10	0.20625	0.00000	0.79226	0.00149	0.79375
H 11	0.21682	0.00000	0.78153	0.00165	0.78318
S 12	0.25963	9.99935	5.69812	0.04290	15.74037
C 13	0.90455	1.99985	3.01619	0.07941	5.09545
F 14	-0.34582	1.99990	7.33912	0.00680	9.34582
F 15	-0.33307	1.99990	7.32614	0.00703	9.33307
F 16	-0.31363	1.99990	7.30482	0.00891	9.31363
N 17	-0.82862	1.99948	5.80867	0.02047	7.82862
H 18	0.42719	0.00000	0.57077	0.00204	0.57281
H 19	0.36426	0.00000	0.63353	0.00221	0.63574
O 20	-1.03036	1.99980	7.01754	0.01302	9.03036
S 21	2.35296	9.99917	3.42158	0.22628	13.64704
O 22	-0.99221	1.99981	6.98002	0.01238	8.99221
O 23	-1.10134	1.99978	7.08613	0.01542	9.10134
C 24	-0.83898	1.99938	4.82013	0.01948	6.83898
H 25	0.20591	0.00000	0.79285	0.00124	0.79409
H 26	0.21909	0.00000	0.77987	0.00103	0.78091
H 27	0.24252	0.00000	0.75666	0.00082	0.75748
S 28	0.45282	9.99909	5.49638	0.05171	15.54718
C 29	-0.71600	1.99939	4.70121	0.01540	6.71600
H 30	0.25159	0.00000	0.74739	0.00102	0.74841
H 31	0.25900	0.00000	0.73996	0.00104	0.74100
H 32	0.26436	0.00000	0.73467	0.00097	0.73564
H 33	0.26310	0.00000	0.73075	0.00615	0.73690
* Total *	0.00000	61.99021	111.35788	0.65191	174.00000

MeSSCF3

final geometry:

		angstroms	
atom	x	y	z
S20	2.5730558424	-0.2614434485	1.4716059681
C21	1.4987956731	1.0046988424	2.1770462552
H22	1.2541926086	0.7727773290	3.2077946154
H23	2.0818044695	1.9230184325	2.1445820566
H24	0.5997954205	1.1264342037	1.5849546678
S6	1.4969041174	-1.9880156080	1.7096059292
C7	0.5945510807	-2.0623561752	0.1473300808
F8	-0.1730324762	-3.1413037434	0.1853788705
F9	-0.1835322748	-1.0100268079	-0.0533070814
F10	1.3850292390	-2.1629032301	-0.9085451424

E_{tot}(vac) -1173.97478928869 hartrees

Total enthalpy, Htot (Utot + pV): -1173.909419 hartrees

E_{tot}(sol) -1173.97804457676 hartrees