Supporting Information

Mechanistic study of the gold-catalyzed C-S bond formation of α-thioallenes to form 2,5-dihydrothiophenes

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Contents

1) The xyz coordinates:

2a

C	0.42485	1.45871	-0.94485
Au	-0.35170	-1.23654	0.40486
C	-0.56540	0.75279	-0.44704
C	0.31429	2.85634	-1.53067
C	-1.80349	0.35184	-0.03365
H	-2.20424	0.68681	0.92175
H	-2.51972	-0.06728	-0.73921
S	-1.35911	3.62878	-1.45783
H	0.61666	2.80578	-2.58299
C	1.29646	3.80934	-0.82720
H	1.24189	4.80345	-1.29782
O	2.58805	3.25832	-0.95967
H	1.02098	3.91836	0.23534
C	3.58538	4.02236	-0.30731
H	4.53679	3.51242	-0.47426
H	3.39798	4.09076	0.77524
H	3.64571	5.04181	-0.71853
H	-1.90420	2.89179	-2.44784
Cl	0.65007	-3.18926	1.09513
H	1.43512	1.05640	-0.94683

2b

C	2.85100	0.48817	0.68224
C	2.95570	1.10304	-0.46705
C	1.72658	0.63218	1.68744
C	3.05858	1.71517	-1.61905
H	2.66048	1.27521	-2.53144
H	3.55776	2.67847	-1.71008
S	0.21376	1.50354	1.04403
H	2.06313	1.25089	2.52858
C	1.29607	-0.72711	2.26038
H	0.42470	-0.60421	2.92611
O	2.40265	-1.22926	2.97310
H	1.00423	-1.40123	1.43952
C	2.18651	-2.53764	3.47525
H	3.09821	-2.82945	4.00110
H	1.99103	-3.25316	2.66281
H	1.34053	-2.56272	4.17863
H	0.88310	2.31012	0.18620
H	3.63316	-0.19668	1.00944
Au	-0.84544	0.06675	-0.49687
Cl	-1.93608	-1.30956	-1.98245

2a-TS1

C	1.73602	0.65002	-0.03603
Au	-0.98781	-0.76848	-0.33481
C	0.40777	0.69801	-0.17163
C	2.53054	1.93354	0.15007
C	-0.26638	1.98750	-0.19022
H	-0.86955	2.24680	0.68190
H	-0.75447	2.29146	-1.11771
S	1.34055	3.34719	-0.06755
H	3.30767	2.05972	-0.61257
C	3.19614	2.05838	1.53304
H	3.68776	3.03984	1.64436
O	4.13327	1.01401	1.60045
H	2.43305	1.96517	2.32478
C	4.77293	0.91988	2.86194
H	5.47379	0.08506	2.79846
H	4.04790	0.72294	3.66553
H	5.32732	1.84020	3.10196
H	1.49026	3.49345	-1.40013
Cl	-2.53515	-2.50660	-0.52146
H	2.31315	-0.26748	0.00718

2a-TS2

C	1.41127	-0.88377	1.04667
Au	-0.54770	1.03473	-0.30963
C	0.10598	-0.53252	0.72567
C	1.65250	-2.34217	1.44357
C	-0.86652	-1.54636	1.27254
H	-1.26859	-2.21019	0.49954
H	-1.69793	-1.10329	1.82356
S	0.14576	-2.52353	2.50669
H	2.50319	-2.43549	2.12336
C	1.78486	-3.34930	0.30157
H	1.86243	-4.37408	0.70286
O	2.95148	-2.98437	-0.39457
H	0.90095	-3.30820	-0.35605
C	3.18471	-3.77981	-1.54518
H	4.10432	-3.41006	-2.00296
H	2.36035	-3.69047	-2.26821
H	3.31270	-4.84080	-1.28116
H	0.76620	-1.02680	2.56237
Cl	-1.31428	2.85174	-1.54035
H	2.26016	-0.28599	0.73094

2a-TS3

C	1.73363	0.00755	0.78451
Au	-1.25829	0.03172	0.04831
C	0.65241	-0.66432	0.21129
C	3.12293	-0.51473	0.55548
C	1.10559	-1.89851	-0.54658
H	0.94536	-1.72027	-1.61409
H	0.53517	-2.78665	-0.26693
S	2.90783	-2.18536	-0.19045
H	3.67044	-0.59404	1.49980
C	3.88593	0.46694	-0.35922
H	4.89503	0.06795	-0.54748

O	3.93341	1.70531	0.31315
H	3.37244	0.55359	-1.33020
C	4.61960	2.70878	-0.41803
H	4.59674	3.61578	0.18957
H	4.13059	2.90793	-1.38316
H	5.66604	2.42347	-0.60346
H	0.70085	-0.82178	1.42730
Cl	-3.39285	0.86535	-0.27868
H	1.59126	0.91447	1.36789

2a'-TS2

C	1.56400	-0.14977	1.15993
Au	-1.25023	-0.00592	0.03408
C	0.68510	-0.54419	0.21465
C	3.01005	-0.60439	1.06849
C	1.26973	-1.49713	-0.79632
H	1.06333	-1.21886	-1.83199
H	0.90541	-2.51696	-0.63796
S	3.13714	-1.49075	-0.55337
H	3.33220	-1.24982	1.89762
C	3.96142	0.59445	1.03784
H	3.87430	1.23750	1.91442
O	3.49766	1.45501	-0.10964
H	5.00264	0.33596	0.83461
C	4.52679	1.99287	-1.01031
H	3.99020	2.58156	-1.75375
H	5.07594	1.16575	-1.46383
H	5.16729	2.62772	-0.40076
H	2.87140	0.84237	-0.61649
Cl	-3.48375	0.67326	-0.20500
H	1.29170	0.48297	2.00210

3-TS1

C	-1.74666	-0.19802	0.41619
Au	1.36162	-0.12323	0.09772
C	-0.63545	0.20877	-0.19403
C	-3.10648	0.29917	-0.07146
C	-0.55055	1.10961	-1.28270
H	-0.38743	0.72969	-2.28982
H	-0.22207	2.13306	-1.11665
S	-2.89224	1.63235	-1.33269
H	-3.66229	0.74558	0.76023
C	-3.96728	-0.82715	-0.66752
H	-4.93475	-0.42887	-1.01466
O	-4.15235	-1.77459	0.35810
H	-3.45208	-1.27617	-1.53377
C	-4.88679	-2.90922	-0.06293
H	-4.97298	-3.57074	0.80188
H	-4.37207	-3.44394	-0.87575
H	-5.89545	-2.63247	-0.40724
H	-2.57606	2.59606	-0.42995
Cl	3.58038	-0.56804	0.63900
H	-1.76475	-0.91042	1.23425
O	-1.41981	3.02789	1.20885
H	-1.01389	2.18563	1.47388
H	-0.82617	3.71642	1.54467

3-TS2

C	1.51443	-0.91255	0.18184
Au	-0.84490	0.80090	-0.63026
C	0.18759	-0.69165	0.26484
C	2.18311	-1.70490	1.29369
C	-0.45441	-1.42566	1.43279
H	-0.83442	-2.41372	1.15352
H	-1.26003	-0.88523	1.93489
S	0.93695	-1.62020	2.67393
H	3.09374	-1.20943	1.64868
C	2.54216	-3.15833	0.94960
H	2.92957	-3.68595	1.83773
O	3.52049	-3.08990	-0.06162
H	1.64606	-3.69678	0.59909
C	3.90145	-4.36236	-0.55002
H	4.65897	-4.19445	-1.31889
H	3.04795	-4.89543	-0.99621
H	4.32997	-4.99023	0.24702
H	0.84141	0.11221	2.65350
Cl	-1.95857	2.66392	-1.50532
H	2.14503	-0.52077	-0.60985
O	0.54201	1.24660	2.42403
H	0.08556	1.23847	1.51640
H	1.35289	1.77899	2.30237

3-TS3

C	1.54308	-0.75532	0.53930
Au	-0.78687	0.80719	-0.58453
C	0.20652	-0.68081	0.38728
C	2.08791	-1.80931	1.48382
C	-0.55529	-1.71262	1.20316
H	-0.87205	-2.55399	0.57502
H	-1.45280	-1.32166	1.69115
S	0.62612	-2.27685	2.51817
H	2.85055	-1.38730	2.14783
C	2.70503	-3.01853	0.76895
H	3.01634	-3.77728	1.50569
O	3.81707	-2.54755	0.03446
H	1.95876	-3.48193	0.10285
C	4.46476	-3.56874	-0.69660
H	5.30556	-3.10637	-1.21972
H	3.79091	-4.02814	-1.43680
H	4.84682	-4.36225	-0.03444
H	0.15666	0.55800	2.52634
Cl	-1.89586	2.58958	-1.62233
H	2.24837	-0.13202	-0.00304
O	-0.38111	1.37567	2.34603
H	-0.63194	1.24404	1.20800
H	0.22369	2.14417	2.40472

3-TS4

C	1.73722	-0.03983	0.61114
Au	-1.25824	0.13217	-0.11988
C	0.66519	-0.57998	-0.07364
C	3.11801	-0.58040	0.36355
C	1.09489	-1.69392	-1.01095
H	0.95415	-1.35669	-2.04221
H	0.50212	-2.60143	-0.87399
S	2.88619	-2.07622	-0.68756
H	3.59655	-0.85861	1.30834
C	3.98621	0.49976	-0.31100
H	4.98126	0.07936	-0.52659
O	4.06853	1.58637	0.58508
H	3.53455	0.80086	-1.26994
C	4.85581	2.65546	0.08967
H	4.85419	3.43371	0.85594
H	4.43818	3.06570	-0.84215
H	5.89230	2.33664	-0.09900
H	0.62445	-0.93529	1.13393
Cl	-3.43318	0.93597	-0.19091
H	1.61412	0.76995	1.32640
O	-0.21355	-1.42270	2.68266
H	-0.59183	-2.31187	2.58057
H	-0.97278	-0.82699	2.54292

4-TS1

C	-2.15340	0.21052	0.58574
Au	0.57255	-1.05167	-0.19802
C	-1.12724	0.06949	-0.25186
C	-3.27204	1.19204	0.25859
C	-0.99549	0.83277	-1.45985
H	-1.17954	0.33722	-2.41362
H	-0.21954	1.59708	-1.51482
S	-2.81319	2.12206	-1.28125
H	-3.39346	1.93869	1.05134
C	-4.63452	0.51056	0.03891
H	-5.40091	1.25252	-0.24058
O	-4.95562	-0.11066	1.25896
H	-4.55812	-0.22763	-0.77792
C	-6.15992	-0.85476	1.20561
H	-6.30966	-1.28440	2.19834
H	-6.09816	-1.66709	0.46605
H	-7.01935	-0.21356	0.95607
H	-2.15442	3.13288	-0.67825
Cl	2.58419	-2.22892	0.00865
H	-2.27951	-0.35777	1.50081
H	2.98548	0.62263	0.36524
C	3.20634	1.67099	0.56141
Cl	2.55779	2.64759	-0.80985
H	4.27514	1.86362	0.61521
Cl	2.47734	2.12555	2.13066

5-TS1

C	-2.21245	0.18277	0.58012
Au	0.49551	-1.16509	-0.21666
C	-1.24206	-0.08363	-0.28686
C	-3.31542	1.16811	0.19885
C	-1.04968	0.45653	-1.57502
H	-1.31976	-0.11910	-2.45869
H	-0.31644	1.24436	-1.72765
S	-2.91302	2.02725	-1.38580
H	-3.39739	1.94564	0.96635
C	-4.69062	0.49374	0.06455
H	-5.45570	1.23464	-0.21971
O	-4.98556	-0.07578	1.31930
H	-4.65450	-0.27929	-0.72185
C	-6.21236	-0.78069	1.33103
H	-6.34341	-1.17473	2.34137
H	-6.20404	-1.61790	0.61623
H	-7.06024	-0.12092	1.08891
Cl	2.53295	-2.26966	0.11227
H	-2.29788	-0.27738	1.55866
H	3.19769	0.30203	0.53389
C	3.46376	1.33429	0.76187
Cl	3.29826	2.31127	-0.74134
H	4.49078	1.43262	1.10485
Cl	2.39117	1.92181	2.07896
O	-0.12305	3.20062	-0.04904
H	0.14212	2.62139	0.68454
H	-1.95046	2.83495	-0.86581
H	0.72379	3.46951	-0.43990

5-TS2

C	1.57418	-1.45824	-0.41508
Au	-1.13149	-0.18145	-0.71521
C	0.26869	-1.49890	-0.08679
C	2.57715	-2.11194	0.52014
C	-0.00398	-2.35367	1.13900
H	-0.24890	-3.39158	0.89103
H	-0.77855	-1.97518	1.80975
S	1.61087	-2.31222	2.09795
H	3.41485	-1.44097	0.74077
C	3.15554	-3.45497	0.05012
H	3.79539	-3.89903	0.83169
O	3.90099	-3.17521	-1.11123
H	2.33874	-4.16457	-0.16313
C	4.45130	-4.33456	-1.70776
H	5.00402	-4.00615	-2.59079
H	3.66569	-5.04102	-2.01675
H	5.14082	-4.85331	-1.02322
Cl	-2.57583	1.60509	-1.24130
H	1.96379	-0.93753	-1.28368
H	-0.81951	3.12051	-0.03551
C	-0.19827	3.82227	0.52416
Cl	-0.88444	4.04332	2.15363
H	-0.12597	4.79242	0.03871
Cl	1.49598	3.15892	0.58129
O	0.64656	0.40120	2.20427
H	0.03216	0.33427	1.41922
H	1.25213	-0.70577	2.25151
H	1.22756	1.16235	1.98050

5-TS3

C	2.19772	0.55966	-0.43572
Au	-0.24338	-1.12819	0.07736
C	1.49901	-0.15728	0.46701
C	3.35336	1.40223	0.06898
C	2.01588	-0.00458	1.88848
H	2.62325	-0.86974	2.18070
H	1.22974	0.10368	2.64131
S	3.03527	1.54738	1.88617
H	3.32565	2.40985	-0.36065
C	4.73180	0.80003	-0.23317
H	5.52476	1.41998	0.21676
O	4.87020	0.75345	-1.63930
H	4.80405	-0.20927	0.20434
C	6.09776	0.18878	-2.05165
H	6.10695	0.20099	-3.14448
H	6.20386	-0.85099	-1.70398
H	6.95734	0.76906	-1.67926
Cl	-2.36793	-2.03742	-0.42465
H	2.00592	0.53442	-1.50457
H	-3.34164	0.27738	-0.90727
C	-3.81856	1.25384	-1.01691
Cl	-4.72800	1.64303	0.45631
H	-4.48375	1.30294	-1.87551
Cl	-2.50162	2.48107	-1.35521
O	-0.62180	1.74734	1.06482
H	-0.58500	0.69720	0.80772
H	0.33421	2.01767	0.99712
H	-1.14487	2.16961	0.32445

5-TS4

C	-2.17086	0.68820	0.20838
Au	0.38352	-1.01998	-0.02564
C	-1.31264	-0.02711	-0.59851
C	-3.47342	1.18691	-0.35178
C	-1.86386	-0.20664	-2.00154
H	-2.06537	-1.26855	-2.16982
H	-1.15558	0.12318	-2.76594
S	-3.43364	0.78048	-2.14948
H	-3.55637	2.27061	-0.21458
C	-4.65274	0.52307	0.38346
H	-5.59742	0.85154	-0.07812

O	-4.57761	0.91856	1.73634
H	-4.59216	-0.57225	0.27974
C	-5.62346	0.38380	2.52819
H	-5.47312	0.75161	3.54565
H	-5.60214	-0.71654	2.53570
H	-6.60960	0.71408	2.16732
Cl	2.33192	-2.14394	0.61008
H	-1.93591	0.91127	1.24672
H	3.40749	0.17329	0.54326
C	3.81358	1.18480	0.49934
Cl	3.61692	1.80755	-1.17593
H	4.87209	1.22527	0.74406
Cl	2.94228	2.19620	1.71002
O	0.24035	2.49633	-0.44418
H	0.90828	2.29918	-1.12488
H	-0.83304	1.14195	-0.40416
H	0.76370	2.47838	0.37901

6-TS

C	-1.19400	0.79658	1.19052
Au	0.74188	-0.40672	0.09086
C	-0.07852	1.52227	1.48639
C	-2.14188	1.41879	0.19286
C	0.02482	2.86564	0.80646
H	1.01582	3.07901	0.40186
H	-0.21916	3.65981	1.52493
S	-1.20841	2.82943	-0.56277
H	-3.00605	1.80817	0.74885
C	-2.68889	0.46172	-0.86894
H	-3.19678	1.03107	-1.66683
O	-3.59210	-0.39594	-0.21092
H	-1.86089	-0.09995	-1.32724
C	-3.95083	-1.52686	-0.98756
H	-4.66158	-2.10484	-0.39238
H	-3.07303	-2.14985	-1.20400
H	-4.43364	-1.22798	-1.93188
Cl	-0.53354	-2.44301	0.58845
H	-1.51251	-0.08295	1.74073
C	2.48084	-1.03669	-1.03859
H	0.57228	1.28975	2.32661
H	2.11507	-1.45784	-1.97388
C	2.55354	0.33300	-0.85874
C	3.12434	1.51158	-1.00420
H	2.69967	2.42916	-0.61359
H	4.06569	1.60056	-1.54509
H	3.04144	-1.71678	-0.39904

2) The Gibbs free energies (hartree) and the imaginary frequencies of the transition structures are as follows (B3LYP level):

2a-TS1	-1303.891432	70.82i
2a-TS2	-1303.857531	1321.35i
2a-TS3	-1303.892904	940.39i
2a'-TS1	-1303.883191	119.65i
2a'-TS2	-1303.871388	237.13i
2a'-TS3	-1303.893804	885.81i
3-TS1	-1380.298298	222.4i
3-TS2	-1380.291201	478.19i
3-TS3	-1380.289195	72.00i
3-TS4	-1380.300908	745.80i
4-TS1	-2263.572964	181.02i
5-TS1	-2339.978548	224.91i
5-TS2	-2339.974891	758.95i
5-TS3	-2339.972545	61.90i
5-TS4	-2339.981426	688.42i
6-TS	-1420.548030	30.27i