Supporting Information

The Lewis Acid Catalyzed [4+3] Cycloaddition of 2-(Trimethylsilyloxy)acrolein with Furan. Insights on the Nature of the Mechanism from a DFT Analysis.

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Page **Contents**

S2 **Table 1S**.- Total (in au.) and relative (in kcal/mol, in parenthesis) energies for the stationary points corresponding to the LA catalyzed [4+3] cycloaddition between 2-(trimethylsilyloxy)acrolein **1** and furan **2**, in vacuo and in dichloromethane.

S3 B3LYP/6-31G* computed total energies, unique imaginary frequency (for TSs) and cartesian coordinates for the optimized stationary points corresponding to the LA catalyzed [4+3] cycloaddition between 2-(trimethylsilyloxy)acrolein **1** and furan **2**.

Table 1S.- Total (in au.) and relative (in kcal/mol, in parenthesis) energies for the stationary points corresponding to the LA catalyzed [4+3] cycloaddition between 2-(trimethylsilyloxy)acrolein **1** and furan **2**, in vacuo and in dichloromethane.

	in vacuo		in dichloromethane	
1	-2299.135657		-2299.142753	
2	-230.020582		-230.0223841	
TS1	-2529.151321	(3.1)	-2529.163732	(0.9)
IN1	-2529.156507	(-0.2)	-2529.171626	(-4.1)
TS2	-2529.153998	(1.4)	-2529.168127	(-1.9)
IN2	-2529.159795	(-2.2)	-2529.175464	(-6.5)
TS3	-2529.145070	(7.0)	-2529.157249	(4.9)
3	-2529.159774	(-2.2)	-2529.167558	(-1.5)

B3LYP/6-31G* computed total energies, unique imaginary frequency (for TSs) and cartesian coordinates for the optimized stationary points corresponding to the LA catalyzed [4+3] cycloaddition between 2-(trimethylsilyloxy)acrolein **1** and furan **2**.

1
E(B3LYP/6-31G*) = -2299.13565729 au.

C	0.000000000000	0.000000000000	0.000000000000
C	0.000000000000	0.000000000000	1.357325750000
O	1.128367386811	0.000000000000	2.061026303699
Si	1.706420105178	0.043590877713	3.686618061101
C	-1.311475954536	-0.005469428222	1.980293832220
O	-1.469694866472	-0.007427953485	3.219233503485
H	-2.191731061209	-0.008188037589	1.328145893108
H	0.930529120767	0.002837696984	-0.556555097417
H	-0.930076573684	-0.003983685765	-0.556020804028
Al	-3.107792172573	-0.016127508622	4.225302198834
Cl	-2.945984281042	-1.820722782061	5.335057493767
Cl	-2.969542547213	1.794508106147	5.328745542097
Cl	-4.577373008638	-0.027820522679	2.666792702445
C	1.153754812777	1.628409243179	4.526954217831
H	1.673794470874	1.730628460531	5.488205549862
H	1.413473880666	2.506122584948	3.923182662829
H	0.079460879393	1.658811560358	4.730757640314
C	1.196524013059	-1.517940931362	4.594360159866
H	1.489042207332	-2.412748692579	4.032181404732
H	1.710753044889	-1.560566561228	5.563213641063
H	0.121831814231	-1.573735711765	4.790347764033
C	3.562673604055	0.061527707624	3.399482557182
H	3.890794195259	-0.830433856989	2.853987892210
H	3.869508639395	0.940739082091	2.821850312203
H	4.102617783938	0.085222097885	4.353947270969

2
E(B3LYP/6-31G*) = -230.020581726 au.

C	0.000000000000	0.000000000000	0.000000000000
C	0.000000000000	0.000000000000	1.360693170000
C	1.379535278667	0.000000000000	1.758733641507
C	2.104164428211	-0.000003742057	0.607056725462
O	1.277599219084	-0.000137043202	-0.478237132801
H	1.771344332812	-0.000097968764	2.766382086085
H	-0.868336097547	-0.000111776745	2.004791820328
H	-0.778369965141	-0.000056641794	-0.747718382349
H	3.161231008435	-0.000036589656	0.388952951026

TS1

E(B3LYP/6-31G*) = -2529.15132149 au.
1 imaginary frequency -341.5341 cm**-1

C	0.000000000000	0.000000000000	0.000000000000
C	0.000000000000	0.000000000000	1.391283760000
C	1.335692728816	0.000000000000	1.783779547751
C	2.100409616241	-0.112422896047	0.597766423018
O	1.252188010907	0.102195939985	-0.479128869236
C	2.362091354323	-2.099014504120	0.316210561437
C	0.193957520733	-2.808878473627	-0.516031857799
C	1.119840721649	-2.727236418466	0.539764547332
O	0.842363172118	-3.082125655356	1.805092324090
O	-0.969545785097	-3.342292132186	-0.389736413722
H	0.520022226603	-2.485258912390	-1.507495082550
H	2.707249479833	-2.011756373489	-0.708882041885
H	3.138966118825	-2.276964704883	1.053893034384
H	3.114425482851	0.228825322276	0.431636869104
H	1.729109223811	-0.033979196889	2.790159578541
H	-0.880529222127	-0.034138733118	2.016610424811
H	-0.807842271354	0.038664223897	-0.718299908392
Si	-0.309730605599	-4.078791680382	2.610815016697
C	0.524930024228	-4.309949037657	4.282194986275
C	-1.930523535289	-3.152964504321	2.830709613584
C	-0.497991753953	-5.731671031083	1.740307383682
Al	-2.360328447108	-3.238534479244	-1.601295110880
Cl	-1.406098265044	-3.109935579353	-3.523359361685
Cl	-3.542608184914	-4.979070238065	-1.271512237465
Cl	-3.320955854295	-1.382668371243	-1.052541967961
H	-0.115735458384	-4.891178738924	4.956804562171
H	0.728298007551	-3.348219018704	4.767329808472
H	1.476692148373	-4.844807710378	4.185718354717
H	-2.657301356987	-3.791952341047	3.348289767007
H	-2.372685426118	-2.856682710549	1.875420970261
H	-1.793952803884	-2.253995551624	3.444189552327
H	-0.984464601933	-6.446666558235	2.416205142211
H	0.478077779394	-6.152311979368	1.470049692919
H	-1.106356938719	-5.659324041243	0.834690225180

IN1

E(B3LYP/6-31G*) = -2529.15650696 au.

C	0.000000000000	0.000000000000	0.000000000000
C	0.000000000000	0.000000000000	1.417116140000
C	1.310607628774	0.000000000000	1.803470654247
C	2.115006584493	-0.144714998857	0.575860640515
O	1.221033030587	0.217639862322	-0.484641806369
C	2.410031657212	-1.728978485981	0.250801311507
C	0.252610995843	-2.629895293163	-0.630948477243

C	1.177510969544	-2.518763573921	0.401453443430
O	0.971616459838	-2.955698099478	1.649287636202
O	-0.866879782522	-3.285547778099	-0.507976142052
H	0.534796256067	-2.254400263572	-1.616991912323
H	2.805116192528	-1.732819847395	-0.766067648806
H	3.177639061082	-2.060111548781	0.952863768681
H	3.046172116185	0.412144278594	0.481599683201
H	1.707833359987	-0.036193217592	2.808798704637
H	-0.887286395313	-0.045308892767	2.033001800432
H	-0.833213465351	0.052485166257	-0.690490680517
Si	-0.105755071468	-4.063498321116	2.433815828678
C	0.791324800734	-4.314680376716	4.070247484369
C	-1.766592727777	-3.240153090748	2.736282870648
C	-0.208603330047	-5.681803281303	1.490915297212
Al	-2.314331019264	-3.133891945357	-1.609814382652
Cl	-3.480934599196	-4.894800601679	-1.314913039049
Cl	-3.275047169325	-1.318088472230	-0.902455951828
Cl	-1.518718479179	-2.864257432048	-3.591338714522
H	0.210826923628	-4.972827330417	4.728529000619
H	0.940606875049	-3.367140459498	4.600900387132
H	1.774486421239	-4.776525189832	3.924240559253
H	-2.439558287939	-3.938670827781	3.249678000082
H	-2.253732391598	-2.934848627665	1.806229381720
H	-1.661082159213	-2.358878638405	3.380855908666
H	-0.612942296565	-6.462121193349	2.148368380143
H	0.783416688562	-6.014200523317	1.162373991115
H	-0.855754807441	-5.605917296896	0.613549402707

TS2

E(B3LYP/6-31G*) = -2529.15399807 au.

1 imaginary frequency -171.0069 cm**-1

C	0.000000000000	0.000000000000	0.000000000000
C	0.000000000000	0.000000000000	1.460337270000
C	1.293760395667	0.000000000000	1.844121377527
C	2.106529332736	-0.091696606556	0.591049483864
O	1.232659627532	0.400666190996	-0.421880942294
C	2.325795806635	-1.632425715251	0.145709994957
C	-0.038025637710	-1.934093962132	-0.718550745830
C	1.007136770072	-2.310673542423	0.173447407863
O	0.790192777000	-3.027513731581	1.242472693685
O	-1.226077234467	-2.494216933117	-0.584459399435
H	0.257351779918	-1.581605055247	-1.709125786244
H	2.758922844884	-1.585181358452	-0.854955140802
H	3.015746378595	-2.125186408259	0.833320253648
H	3.059091721824	0.436154175433	0.552417929985
H	1.695739426780	-0.049765820840	2.847809874493
H	-0.892752342532	-0.049335267518	2.069059979351
H	-0.829466280757	0.334581339247	-0.614475574599

Si	-0.421620182687	-4.155495280854	1.856351267177
C	0.590602126516	-4.945409933401	3.231342013892
C	-1.859944242060	-3.203108762555	2.586928719175
C	-0.854394503088	-5.426773909460	0.552301730499
Al	-2.746856750558	-2.041570906872	-1.466230292793
Cl	-3.877210265414	-3.839478784912	-1.712321027040
Cl	-3.694171850519	-0.593505057907	-0.164267570918
Cl	-2.080869393981	-1.117009810140	-3.300118791662
H	-0.017882040292	-5.672277251061	3.783533412062
H	0.948622681498	-4.200326133960	3.950927875757
H	1.462824420059	-5.478316286916	2.835835297170
H	-2.562714721870	-3.912153081709	3.043545639423
H	-2.409224788778	-2.623299687914	1.841167126668
H	-1.521865469068	-2.526407862384	3.380656397333
H	-1.290235051344	-6.307408747536	1.041652457480
H	0.040865847915	-5.764690688066	0.016636415399
H	-1.573748945705	-5.048614050642	-0.177698565708

IN2

E(B3LYP/6-31G*) = -2529.15979497 au.

C	0.000000000000	0.000000000000	0.000000000000
C	0.000000000000	0.000000000000	1.512430540000
C	1.275731613738	0.000000000000	1.909924905959
C	2.135260712186	-0.015831213758	0.657609569694
O	1.278603146485	0.518026125924	-0.342045712451
C	2.434211957120	-1.490712817561	0.193915744125
C	-0.049355547232	-1.499109412713	-0.578904537855
C	1.120513447748	-2.195971175050	0.049329366146
O	1.020341401270	-3.331098247580	0.592900166496
O	-1.217968220216	-2.169456994254	-0.336650192128
H	0.173674973449	-1.373457785836	-1.655155128529
H	2.929632280114	-1.424422359075	-0.781934492332
H	3.073386104993	-2.047704141201	0.884984264671
H	3.061376062982	0.561574940822	0.695207099955
H	1.662775072845	-0.051323639880	2.920871748574
H	-0.899323165225	-0.048291982550	2.113144859680
H	-0.784530848676	0.580047941990	-0.485332408480
Si	-0.203105154203	-4.682753390130	0.734116569278
C	0.980798211072	-5.921768747191	1.508643192646
C	-1.525637908894	-4.194823169192	1.961123749166
C	-0.684151270981	-5.233400563369	-0.985782650706
Al	-2.797906682946	-1.720637863126	-1.087971330685
Cl	-4.059223698387	-3.458675836794	-0.944732471897
Cl	-3.608331445852	-0.054999976486	0.028048707730
Cl	-2.310037704964	-1.164363392896	-3.120435667995
H	0.461814171642	-6.870646194700	1.693765958946
H	1.370322056635	-5.566805796860	2.469624115846
H	1.834194075882	-6.136025443407	0.855252205211

H	-1.789369496075	-5.068674273741	2.569886179113
H	-2.424647015388	-3.827679157267	1.462548956835
H	-1.164392282458	-3.416081073511	2.641795069174
H	-0.853322416814	-6.317548282232	-0.974849173377
H	0.118532216463	-5.039906709879	-1.707193791936
H	-1.594903245493	-4.744067777427	-1.335534861189

TS3

E(B3LYP/6-31G*) = -2529.14506990 au.
1 imaginary frequency -134.1500 cm**-1

C	0.000000000000	0.000000000000	0.000000000000
C	0.000000000000	0.000000000000	1.515423110000
C	1.275176327585	0.000000000000	1.914782805908
C	2.147453799706	-0.002198507397	0.669079222771
O	1.283970385793	0.525339424586	-0.336649444576
C	2.491441899916	-1.464296443596	0.210103755584
C	0.018014052336	-1.472168217823	-0.577490580741
C	1.176810592595	-2.171965458145	0.062156265968
O	0.963822400484	-3.275833987783	0.577090460265
O	-1.137596843208	-2.249949514220	-0.343668315103
H	0.211275566991	-1.367921700315	-1.652943267418
H	3.001356142707	-1.395146129789	-0.757600140737
H	3.124473718128	-2.010038547295	0.915709736456
H	3.053636663233	0.605450321886	0.720834297190
H	1.656020119294	-0.051396166450	2.928291543237
H	-0.896164771918	-0.043913658503	2.122031637355
H	-0.777823060523	0.589565404660	-0.485507987360
Si	-0.965230103530	-3.985338886322	0.908676134165
C	-0.142821996710	-4.548297706230	2.533397677731
C	-2.686997403459	-3.544698354477	1.557339892370
C	-0.913696220431	-5.333929469298	-0.390072236314
Al	-2.659790922968	-1.761321090476	-1.350175502687
Cl	-3.768672447486	-3.504695448028	-1.906854326076
Cl	-3.724539178475	-0.370451706282	-0.105148186042
Cl	-1.860580980173	-0.793748707892	-3.106383627771
H	-0.817378498369	-5.250216475680	3.039194798432
H	0.016341845916	-3.709174931638	3.222412736266
H	0.821304943611	-5.040153544036	2.378043135290
H	-2.993850795739	-4.362113360363	2.222984274443
H	-3.461663021178	-3.430206829180	0.798118673953
H	-2.665799100956	-2.629556836580	2.159581618434
H	-1.464467350400	-6.203241747951	-0.008807136382
H	0.114084311605	-5.651098613633	-0.595066629570
H	-1.390015008775	-5.030878378566	-1.325567379186

3

E(B3LYP/6-31G*) = -2529.15977432 au.

C	0.000000000000	0.000000000000	0.000000000000
C	0.000000000000	0.000000000000	1.516698370000
C	1.271888916646	0.000000000000	1.920190409720
C	2.150693995518	0.007987140105	0.680196755380
O	1.280515048636	0.545857362881	-0.327317444187
C	2.507877698728	-1.426875465617	0.223612223209
C	0.055887765573	-1.431348772762	-0.626816192352
C	1.241059572947	-2.226474406405	-0.076920154712
O	1.182865652860	-3.430221724416	0.075815202236
O	-1.213569432068	-2.160557829281	-0.591090174950
H	0.278921216778	-1.269161262806	-1.685718731101
H	3.097881936719	-1.361256934985	-0.700259540894
H	3.095806853834	-1.987444565702	0.957715040032
H	3.038982387730	0.641105479181	0.746514031569
H	1.647041795853	-0.048344895549	2.936204218171
H	-0.894553412968	-0.029595084660	2.126748907772
H	-0.781857974411	0.599033507551	-0.469856106927
Si	-1.701628113590	-3.482895036568	0.583186467427
C	-0.818841691293	-3.367393989500	2.241407736133
C	-3.512190059124	-3.106439414737	0.922845047015
C	-1.462570836550	-5.139282088907	-0.252622621760
Al	-2.452489257628	-1.593903079939	-2.002637246163
Cl	-3.561896816442	-3.296607189129	-2.652265152141
Cl	-3.598582211530	-0.054023861329	-1.059092396243
Cl	-1.220889277490	-0.853248308759	-3.593463648305
H	-1.434514532878	-3.935605327143	2.951643976118
H	-0.740747984501	-2.348647448030	2.629498048669
H	0.178488418562	-3.809690015067	2.223782156307
H	-4.168549853095	-3.249726370130	0.061996208594
H	-3.663208304854	-2.090475849245	1.301661485622
H	-3.841087831866	-3.803196724563	1.706102046349
H	-1.921499900998	-5.917721534232	0.371317548450
H	-0.402436716058	-5.371713646849	-0.373614796535
H	-1.950213052365	-5.168766941032	-1.230691704460