Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.
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Friedel–Crafts alkylation mechanism using aminoindanol derived thiourea catalyst

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ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

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Summary of electronic and free energies

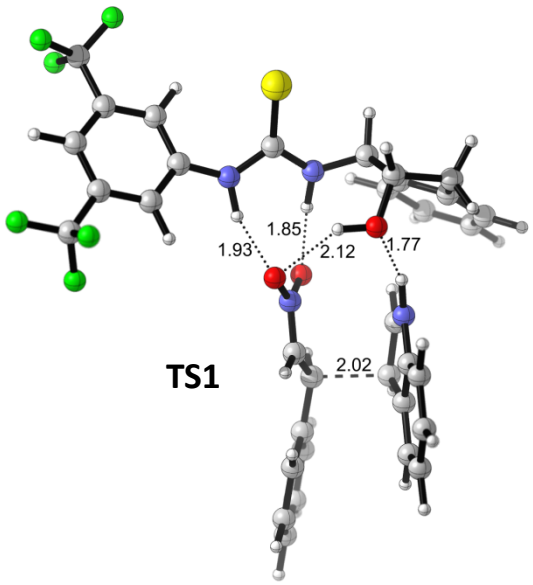
Absolute (in hartrees) and relative (in kcal/mol) electronic energies (E_0) and free energies (G) calculated at −24 ºC. Also the imaginary frequency of each TS given as a negative number. Electronic energies include ZPE correction. PCM(CH_2Cl_2)/M06-2X/6-311G(d,p) level of theory.

TS1. Electronic and free energies, and imaginary frequency for each TS

	TS freq.	E_0	ΔE_0	G	ΔG
TS1	-390.2	-2753.518619	0.0	-2753.578049	0.0
TS2	-398.0	-2753.515185	2.2	-2753.574681	2.1
TS3	-417.9	-2753.512457	3.9	-2753.570773	4.6
TS4	-421.4	-2753.509802	5.5	-2753.569896	5.1
TS5	-402.2	-2753.510635	5.0	-2753.572061	3.8
TS6	-421.1	-2753.505648	8.1	-2753.565149	8.1
TS7	-400.3	-2678.287562	0.0	-2678.347660	0.0
TS8	-410.8	-2678.287086	0.3	-2678.347004	0.4
TS9	-404.2	-2753.504834	0.0	-2753.566230	0.0
TS10	-406.8	-2753.503730	0.7	-2753.564174	1.3
TS11	-385.1	-2601.128833	0.0	-2601.187719	0.0
TS12	-393.3	-2601.126102	1.7	-2601.184654	1.9
TS13	-386.4	-2792.802070	1.0	-2792.865400	0.0
TS14	-368.1	-2792.803698	0.0	-2792.864567	0.5

Cartesian Coordinates

PCM(CH_2Cl_2)/M06-2X/6-311G(d,p) level of theory.



Bond	Distances (Å) X^1-H---X^2	Angle (°) X^1---H---X^2
N-H---O^1NO^2	1.93	154
N-H---O^2NO^1	1.85	172
O-H---O^1NO^2	2.12	143
H-O---H-N	1.77	161

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C	4.526970	-0.031845	-0.768472
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O	0.225326	-0.565973	0.627398
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C	2.132324	4.252935	0.312827
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H	1.262559	5.283268	1.993191
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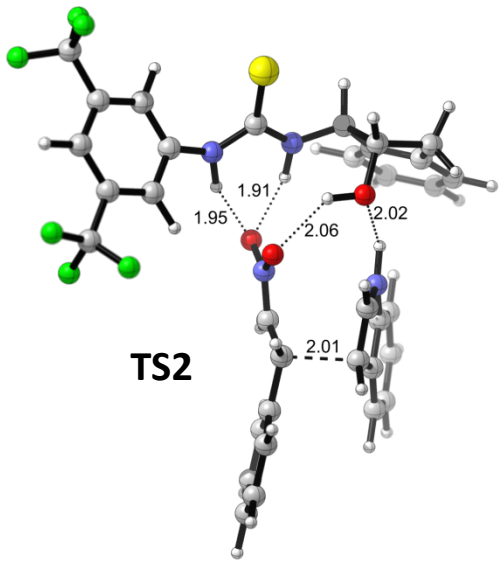

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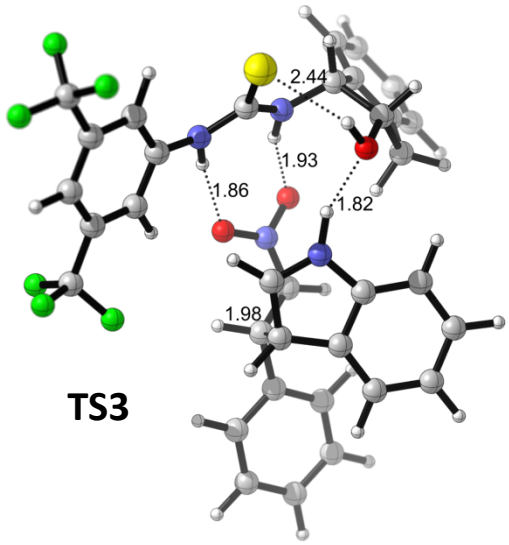

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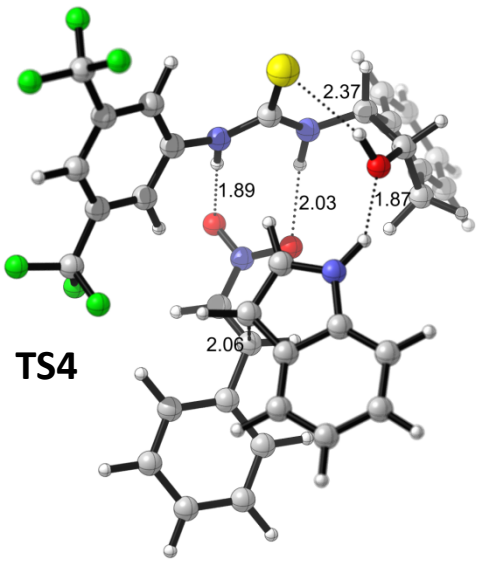

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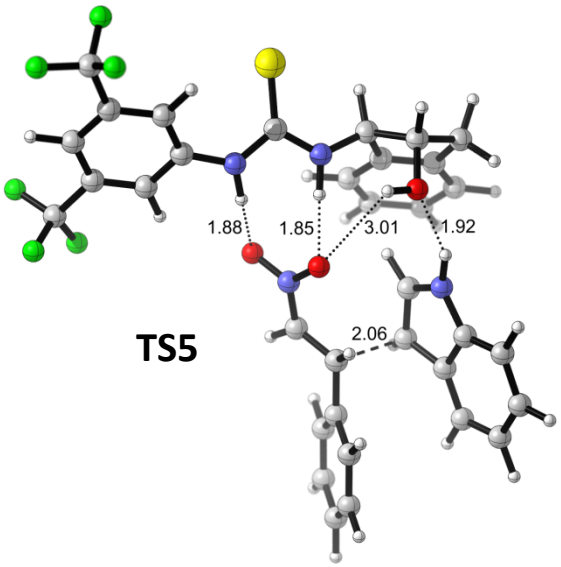

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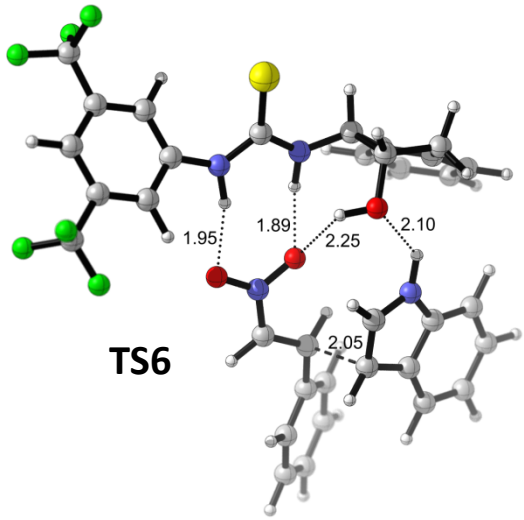
H	-0.161233	-1.364243	-0.179717
H	3.135633	-2.234052	-1.298656
N	3.722427	-1.509557	-0.882051
C	3.373991	-0.886121	0.237606
C	4.243791	0.203656	0.486232
H	2.508439	-1.198159	0.798240
O	-0.256245	0.984344	1.005160
N	0.815170	0.931503	0.347368
O	0.945294	0.069742	-0.563856
C	1.830835	1.777346	0.622855
C	3.006119	1.725793	-0.158134
H	1.658562	2.447747	1.448296
H	2.882035	1.297770	-1.148898
O	1.420525	-3.096718	-1.425726
H	0.738384	-2.612712	-1.905803
C	-0.084519	-3.350639	0.478656
C	0.793465	-4.061464	-0.583855
H	-0.834021	-4.047987	0.859230
C	0.925212	-2.997634	1.548206
C	1.905959	-4.724638	0.237256
H	0.218498	-4.765706	-1.188640
C	2.068610	-3.781260	1.408863
C	0.833992	-2.008504	2.516920
H	1.580876	-5.711795	0.578626
H	2.814201	-4.853379	-0.354180
C	3.148682	-3.591271	2.260882
H	-0.047709	-1.379148	2.582864
C	1.921317	-1.815110	3.369727
H	4.051538	-4.182331	2.154352
C	3.065683	-2.601823	3.242260
H	1.879823	-1.042973	4.128634
H	3.906430	-2.433058	3.904661

C	-3.616504	0.020782	-0.164179
C	-3.684241	1.297640	0.407721
C	-4.739811	-0.503269	-0.798326
C	-4.866141	2.014443	0.362055
H	-2.804318	1.712660	0.886704
C	-5.918999	0.235809	-0.817456
H	-4.695728	-1.471852	-1.274910
C	-6.006398	1.491843	-0.241145
C	-4.933142	3.395756	0.944846
C	-7.116621	-0.381909	-1.479017
H	-6.931901	2.052313	-0.261037
F	-6.035467	3.566339	1.688716
F	-3.879779	3.672737	1.721740
F	-4.971543	4.334541	-0.014379
F	-8.140471	0.473777	-1.581134
F	-7.560898	-1.449589	-0.799103
F	-6.831091	-0.811023	-2.717840
H	4.392891	0.611664	1.474779
C	4.883684	-0.936305	-1.408173
C	5.275402	0.097998	-0.539799
C	5.592574	-1.266066	-2.556783
C	6.433071	0.824064	-0.821504
C	6.741018	-0.530634	-2.817570
H	5.265731	-2.063203	-3.212651
C	7.158585	0.496857	-1.959759
H	6.754545	1.626479	-0.167258
H	7.326960	-0.758927	-3.699423
H	8.063536	1.044771	-2.192117
C	3.955922	2.857812	-0.077453
C	4.560225	3.319100	-1.248621
C	4.271628	3.467756	1.141149
C	5.450564	4.387105	-1.207483
H	4.330988	2.837250	-2.192792
C	5.169925	4.524326	1.182544
H	3.826021	3.104737	2.061558

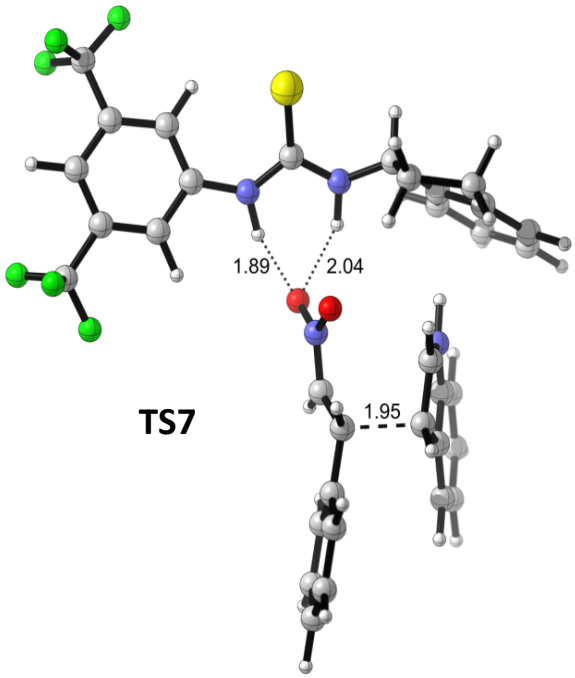
C	5.758961	4.988585	0.007081
H	5.907721	4.741825	-2.123214
H	5.412494	4.987790	2.131030
H	6.457565	5.815771	0.042081



N	-0.654478	-2.093696	0.266754
C	-1.968814	-1.864330	0.063575
S	-3.046665	-3.070828	-0.419890
N	-2.310249	-0.558231	0.264610
H	-1.558647	0.137737	0.233139
H	-0.072451	-1.287326	0.491528
H	3.003925	-1.686930	-1.525475
N	3.508855	-0.803657	-1.490923
C	2.925316	0.341955	-1.818829
C	3.760985	1.434185	-1.471771
H	1.941623	0.353250	-2.257891
C	5.020725	0.819371	-1.062571
H	3.669214	2.405332	-1.935016
O	-0.618529	1.823891	-0.012156
N	0.582849	1.467488	0.018408
O	0.875604	0.240291	-0.092262
C	1.572307	2.371812	0.159366
C	2.903215	1.923183	0.319944

H	1.258364	3.402585	0.170166
H	3.001113	0.914915	0.714764
O	0.988463	-2.041883	-1.999037
H	0.430015	-1.340906	-1.636109
C	0.041931	-3.295045	-0.135638
C	0.448736	-3.307921	-1.631909
H	-0.604504	-4.154135	0.063596
C	1.377949	-3.469240	0.550712
C	1.607680	-4.306915	-1.671553
H	-0.388371	-3.568652	-2.282212
C	2.274125	-4.077476	-0.331449
C	1.756381	-3.128884	1.839152
H	1.224009	-5.329061	-1.744300
H	2.261220	-4.128098	-2.527304
C	3.565975	-4.370420	0.078571
H	1.055527	-2.651130	2.515262
C	3.061595	-3.411419	2.246504
H	4.266931	-4.846148	-0.599416
C	3.954590	-4.030894	1.376855
H	3.381683	-3.146724	3.247028
H	4.964514	-4.243830	1.707824
C	-3.594559	0.004654	0.183001
C	-3.726232	1.235400	-0.466747
C	-4.706511	-0.581773	0.779598
C	-4.966089	1.849252	-0.527951
H	-2.852789	1.701242	-0.906613
C	-5.942848	0.047741	0.687160
H	-4.606144	-1.513552	1.318360
C	-6.093949	1.260963	0.035290
C	-5.131033	3.160689	-1.238539
C	-7.128642	-0.634971	1.303963
H	-7.060950	1.744453	-0.022293
F	-5.747525	4.067312	-0.464769
F	-3.962420	3.689336	-1.616909
F	-5.883140	3.030952	-2.342964

F	-8.192668	0.172487	1.388305
F	-6.860189	-1.072337	2.543164
F	-7.505325	-1.709180	0.593353
C	4.802999	-0.567714	-1.013224
C	5.769895	-1.466150	-0.577891
C	6.993328	-0.932877	-0.195179
H	5.576360	-2.530109	-0.544991
C	7.235258	0.447140	-0.244707
H	7.777676	-1.598143	0.144244
C	6.255316	1.334373	-0.669293
H	8.204120	0.825573	0.057357
H	6.442030	2.402049	-0.694015
C	3.897008	2.893174	0.834291
C	4.790227	2.481804	1.825101
C	3.968484	4.201807	0.347408
C	5.728342	3.370789	2.339207
H	4.749776	1.460845	2.189127
C	4.915742	5.083352	0.849866
H	3.292568	4.526334	-0.437018
C	5.794731	4.670441	1.850082
H	6.411938	3.043242	3.112965
H	4.970337	6.093474	0.462707
H	6.530817	5.361770	2.242508



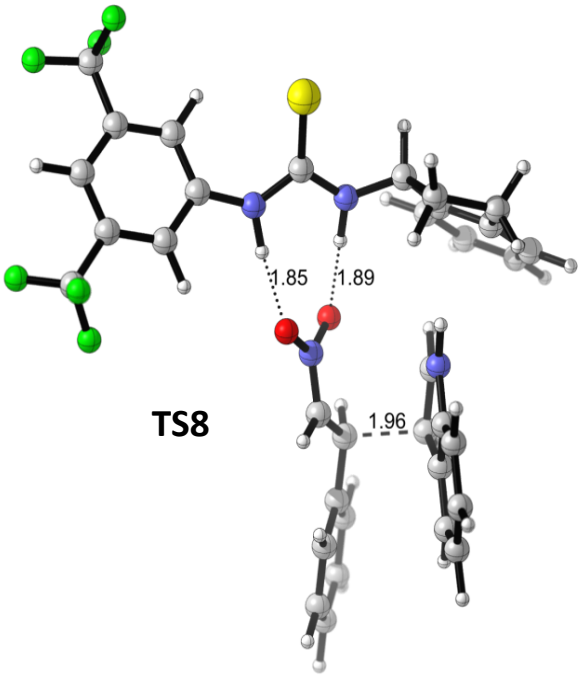
TS7

Bond	Distances (Å) X^1-H---X^2	Angle (º) X^1---H---X^2
N-H---O^1NO^2	1.89	162
N-H---O^1NO^2	2.04	155

N	-0.709973	-2.432990	-0.049926
C	-1.976896	-2.050185	-0.280161
S	-3.088286	-3.007663	-1.121827
N	-2.233084	-0.807935	0.228673
H	-1.399253	-0.290109	0.525305
H	-0.092665	-1.720247	0.337410
H	2.941414	-2.088099	0.307190
N	3.498265	-1.279936	0.042446
C	3.500107	-0.735274	-1.161141
H	2.910204	-1.147090	-1.964736
C	-0.057497	-3.558856	-0.686336
C	0.361567	-3.316272	-2.155822
H	-0.725769	-4.422197	-0.617930
C	1.259763	-3.870863	-0.011290
C	1.626909	-4.174581	-2.350971
H	-0.438385	-3.554390	-2.854602
C	2.219172	-4.226216	-0.961831
C	1.564733	-3.848639	1.345233
H	1.364605	-5.187235	-2.673690
H	2.315862	-3.764678	-3.091557
C	3.504519	-4.572738	-0.559726
H	0.814575	-3.564363	2.075277
C	2.857856	-4.191511	1.745754
H	4.257764	-4.843342	-1.291209
C	3.818720	-4.550235	0.799640
H	3.115903	-4.179854	2.798180
H	4.819860	-4.807248	1.124454
C	-3.420203	-0.069205	0.218939
C	-3.304855	1.318564	0.119883
C	-4.686375	-0.639983	0.378649
C	-4.438705	2.117164	0.165972
H	-2.324417	1.768073	0.010517
C	-5.803496	0.180839	0.403923
H	-4.790793	-1.707755	0.491430
C	-5.703308	1.562798	0.296654

C	-4.305942	3.603817	0.010527
C	-7.172697	-0.414622	0.563238
H	-6.585331	2.190807	0.329305
F	-4.487457	3.986507	-1.263578
F	-5.214094	4.263608	0.742469
F	-3.096751	4.045291	0.379043
F	-7.822559	0.117220	1.610716
F	-7.139682	-1.738302	0.748132
F	-7.938173	-0.183984	-0.514783
C	4.285320	0.458470	-1.136846
H	4.714693	0.862138	-2.043085
C	2.884170	1.780121	-0.831195
C	2.065567	1.403042	0.272041
H	2.397849	1.639189	-1.791482
N	1.090659	0.498901	0.074687
H	2.172481	1.741507	1.287986
O	0.360102	0.135131	1.052267
O	0.905938	-0.009722	-1.056959
H	0.604228	-2.254181	-2.254193
C	3.666579	3.043849	-0.746580
C	4.043816	3.676132	-1.935142
C	4.037444	3.618550	0.471826
C	4.768964	4.859880	-1.910318
H	3.757637	3.237189	-2.885684
C	4.761124	4.805794	0.496873
H	3.772106	3.142514	1.407760
C	5.129390	5.428039	-0.691369
H	5.048151	5.341132	-2.839679
H	5.039213	5.243050	1.448171
H	5.693765	6.352463	-0.668618
C	4.989496	0.411893	0.149160
C	4.404154	-0.621726	0.890332
C	5.970081	1.203036	0.740663
C	4.739055	-0.902286	2.206575
C	6.331869	0.928830	2.055571

H	6.441841	2.007588	0.189159
C	5.719812	-0.102166	2.779653
H	4.260686	-1.705121	2.753191
H	7.102923	1.522521	2.530909
H	6.021218	-0.285037	3.803579

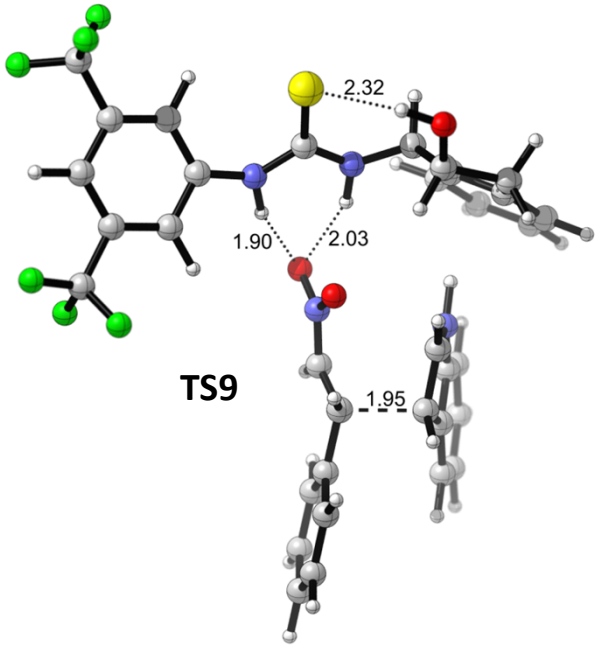


TS8

N	-0.740040	2.312570	-0.125921
C	-2.018175	1.977456	0.102295
S	-3.176614	3.075036	0.661888
N	-2.243742	0.649397	-0.143023
H	-1.399191	0.067882	-0.092730
H	-0.105809	1.584575	-0.468841
H	2.524014	1.771908	1.328925
N	3.212087	1.148104	0.924957
C	3.504627	1.114036	-0.364994
C	4.426428	0.052720	-0.607514
H	3.019078	1.772798	-1.068631
H	5.065740	0.061429	-1.479154
O	0.106602	-0.808962	0.518452
N	1.071713	-0.681450	-0.284522
O	1.046994	0.248345	-1.141825

C	2.125343	-1.513502	-0.220620
C	3.188925	-1.362173	-1.155088
H	2.074640	-2.241428	0.570341
H	2.885565	-0.873920	-2.075803
C	-0.125378	3.567803	0.254472
C	0.359160	3.606307	1.725794
H	-0.846083	4.368171	0.067650
C	1.143112	3.808558	-0.533674
C	1.652568	4.448358	1.712568
H	-0.402515	3.996463	2.399054
C	2.151911	4.299348	0.292920
C	1.352249	3.631203	-1.896965
H	1.431372	5.500819	1.913093
H	2.381804	4.127985	2.460429
C	3.399385	4.612909	-0.238128
H	0.561077	3.243747	-2.529703
C	2.598742	3.954044	-2.429197
H	4.192083	4.988045	0.399653
C	3.615423	4.438283	-1.603520
H	2.783273	3.822715	-3.488696
H	4.582666	4.677230	-2.029543
C	-3.437797	-0.070661	-0.070374
C	-3.350831	-1.401903	0.350921
C	-4.674601	0.437594	-0.466590
C	-4.487486	-2.192908	0.393154
H	-2.384753	-1.807157	0.634190
C	-5.800383	-0.374526	-0.398759
H	-4.754604	1.450289	-0.834195
C	-5.732216	-1.690791	0.031948
C	-4.373092	-3.601760	0.896417
C	-7.113572	0.223520	-0.812259
H	-6.616029	-2.312914	0.068751
F	-5.349218	-4.385620	0.420108
F	-3.205278	-4.163186	0.555430
F	-4.450280	-3.658940	2.236013

F	-8.100616	-0.679770	-0.838462
F	-7.046162	0.773218	-2.034596
F	-7.495619	1.201805	0.023328
H	0.568054	2.576533	2.036116
C	4.121421	-2.503782	-1.363502
C	4.821241	-2.587402	-2.571038
C	4.330513	-3.486381	-0.391760
C	5.707271	-3.629917	-2.806683
H	4.664293	-1.829649	-3.332089
C	5.214179	-4.533111	-0.629542
H	3.814799	-3.436930	0.559253
C	5.905726	-4.606794	-1.834121
H	6.238861	-3.683351	-3.748936
H	5.364088	-5.290061	0.130866
H	6.595301	-5.422186	-2.016157
C	4.866813	-0.371696	0.724787
C	4.025296	0.258150	1.649723
C	5.821461	-1.278247	1.176466
C	4.078878	0.017443	3.014573
C	5.901148	-1.523242	2.543020
H	6.486566	-1.774493	0.479909
C	5.038038	-0.891067	3.446238
H	3.411806	0.513894	3.707795
H	6.644339	-2.215703	2.918767
H	5.123088	-1.107448	4.503827

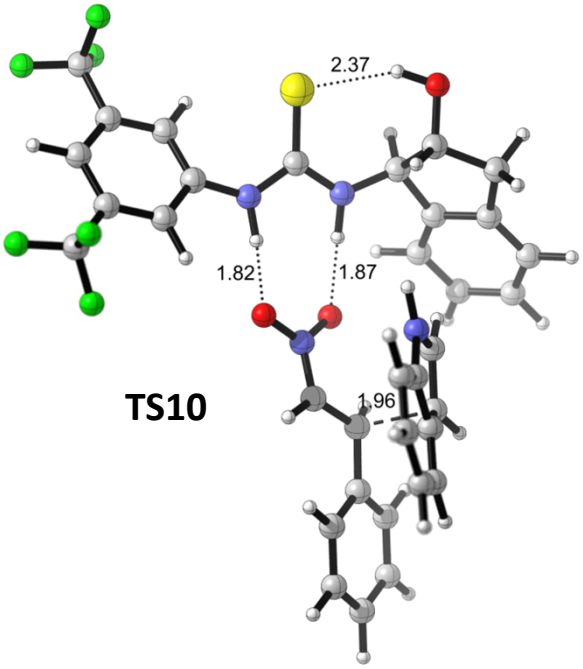


Bond	Distances (Å) X^1-H---X^2	Angle (º) X^1---H---X^2
N-H---O^1NO^2	1.90	161
N-H---O^1NO^2	2.03	155
O-H---S	2.32	154

N	0.698361	-2.475084	-0.246563
C	1.946463	-2.035661	-0.040873
S	3.110209	-2.903531	0.839022
N	2.173504	-0.820017	-0.612399
H	1.334761	-0.351025	-0.969777
H	0.055087	-1.800330	-0.660281
C	0.096162	-3.661874	0.334591
C	-0.191832	-3.582208	1.864032
H	0.742741	-4.525223	0.141535
C	-1.279133	-3.866873	-0.259391
C	-1.521283	-4.326703	2.068546
C	-2.195368	-4.240020	0.725518
C	-1.669746	-3.718634	-1.585768
H	-1.291869	-5.368421	2.314236
H	-2.119703	-3.913807	2.881933
C	-3.522403	-4.485581	0.387306
H	-0.955161	-3.415424	-2.343283
C	-3.001241	-3.964047	-1.922398
H	-4.241374	-4.769825	1.147198
C	-3.918881	-4.346796	-0.942406
H	-3.324190	-3.857909	-2.951137
H	-4.951181	-4.529162	-1.216925
C	3.306513	-0.003946	-0.455998

C	3.107104	1.334172	-0.128708
C	4.602200	-0.475675	-0.673956
C	4.196513	2.190345	-0.016846
H	2.101142	1.696374	0.054233
C	5.673540	0.392629	-0.534042
H	4.761854	-1.505307	-0.958925
C	5.490229	1.732291	-0.206892
C	3.939765	3.635928	0.293771
C	7.071775	-0.126361	-0.704622
H	6.335458	2.401273	-0.111394
F	5.051060	4.278756	0.669313
F	3.447722	4.290030	-0.770298
F	3.040563	3.779145	1.278167
F	7.881850	0.796189	-1.243062
F	7.118130	-1.207753	-1.491682
F	7.615478	-0.476034	0.471632
O	0.790575	-4.177741	2.673320
H	1.644860	-3.814880	2.394874
H	-0.312330	-2.514957	2.102473
H	-3.002610	-2.004551	-0.209110
N	-3.459149	-1.154758	0.110815
C	-3.191092	-0.547479	1.253930
H	-2.468779	-0.946394	1.947377
C	-3.915468	0.683361	1.312911
H	-4.126516	1.161982	2.259105
C	-4.502364	-0.501998	-0.570494
C	-4.881578	0.594583	0.212636
C	-5.124673	-0.832170	-1.765678
C	-5.939120	1.398645	-0.199791
C	-6.180611	-0.018529	-2.161022
H	-4.807168	-1.682189	-2.355951
C	-6.587881	1.074335	-1.386411
H	-6.250138	2.251584	0.391814
H	-6.702783	-0.241209	-3.083173
H	-7.423782	1.677323	-1.719043

C	-2.582652	1.921545	0.614124
C	-1.982630	1.401938	-0.570091
H	-1.932268	1.861502	1.481120
N	-1.013024	0.481865	-0.441366
H	-2.254562	1.641059	-1.583701
O	-0.466511	-0.021573	-1.476338
O	-0.648205	0.091545	0.694977
C	-3.344316	3.197316	0.535022
C	-3.500515	3.954691	1.699427
C	-3.915044	3.659662	-0.653723
C	-4.204673	5.151265	1.678527
H	-3.060302	3.601841	2.626678
C	-4.615488	4.860493	-0.676266
H	-3.827316	3.083190	-1.566533
C	-4.764149	5.607310	0.487724
H	-4.312296	5.729003	2.588417
H	-5.048979	5.210072	-1.605538
H	-5.312611	6.541297	0.467592



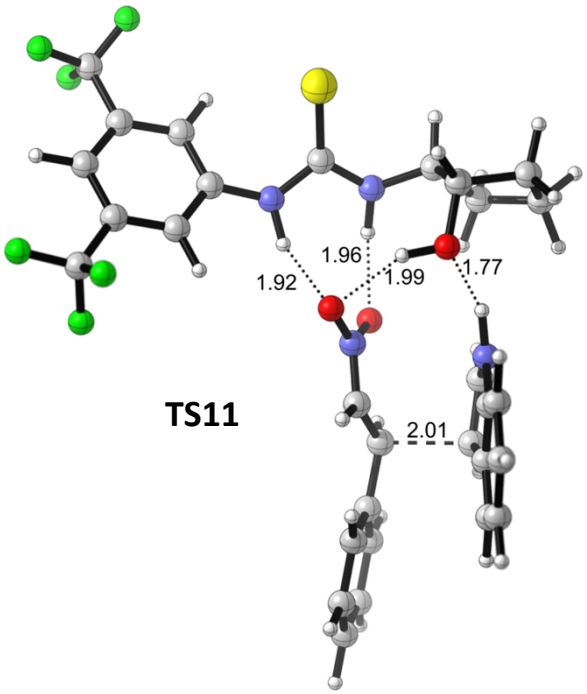
TS10

N	-0.716110	2.280398	-0.290486

C	-1.977508	1.866439	-0.112744
S	-3.207231	2.889179	0.458959
N	-2.150010	0.547980	-0.411447
H	-1.290162	-0.009561	-0.506032
H	-0.033405	1.602651	-0.643684
C	-0.242074	3.640034	-0.077106
C	-0.121891	4.062865	1.421719
H	-0.924210	4.336271	-0.577536
C	1.164973	3.772188	-0.610588
C	1.251591	4.744649	1.573360
C	2.005559	4.371283	0.324928
C	1.641432	3.376870	-1.856032
H	1.091115	5.825746	1.614050
H	1.770997	4.450701	2.487034
C	3.349141	4.577145	0.024419
H	0.983226	2.897849	-2.572621
C	2.985436	3.584960	-2.156758
H	4.011822	5.037374	0.748826
C	3.832717	4.181103	-1.220490
H	3.375316	3.280373	-3.120593
H	4.877210	4.335384	-1.464429
C	-3.307520	-0.234213	-0.299228
C	-3.141810	-1.557823	0.118458
C	-4.578179	0.215004	-0.658655
C	-4.238889	-2.402226	0.194381
H	-2.149399	-1.918458	0.366143
C	-5.661710	-0.647824	-0.554588
H	-4.716480	1.219344	-1.030443
C	-5.515610	-1.959534	-0.126696
C	-4.043961	-3.803577	0.694030
C	-7.024119	-0.118581	-0.895918
H	-6.367008	-2.624158	-0.065267
F	-4.993347	-4.633850	0.243412
F	-2.859589	-4.308549	0.324638
F	-4.085010	-3.861421	2.035589

F	-7.898129	-1.099162	-1.154721
F	-6.993564	0.683790	-1.969391
F	-7.537652	0.607003	0.109971
O	-1.120770	4.968063	1.827519
H	-1.968026	4.545119	1.624677
H	-0.162587	3.144692	2.022875
O	0.060788	-1.211455	-0.284007
N	1.158907	-0.793194	-0.742149
O	1.219333	0.359054	-1.261239
C	2.263857	-1.554269	-0.665992
H	2.126110	-2.500847	-0.172135
C	3.494405	-1.040585	-1.167184
H	3.362570	-0.271053	-1.921355
C	4.601731	-1.986331	-1.476566
C	4.691993	-3.257364	-0.903521
C	5.591803	-1.578196	-2.375756
C	5.747690	-4.101516	-1.232121
H	3.945257	-3.597870	-0.196922
C	6.647009	-2.418977	-2.700994
H	5.527160	-0.592453	-2.825554
C	6.726952	-3.685663	-2.127819
H	5.804357	-5.086572	-0.784951
H	7.402846	-2.088816	-3.403176
H	7.547714	-4.345682	-2.381270
H	1.742284	1.018783	1.815203
N	2.605710	0.608670	1.481241
C	3.262118	1.019986	0.408849
C	4.345016	0.128022	0.152029
H	2.920528	1.858528	-0.177596
H	5.200895	0.446064	-0.426837
C	3.280394	-0.455851	2.105118
C	4.428507	-0.717214	1.347244
C	2.954912	-1.148031	3.261699
C	5.305854	-1.714783	1.763615
C	3.843404	-2.138511	3.661524

H	2.056433	-0.926052	3.823623
C	5.004195	-2.413238	2.928102
H	6.202486	-1.936768	1.197553
H	3.635560	-2.703292	4.561745
H	5.679925	-3.184158	3.277257



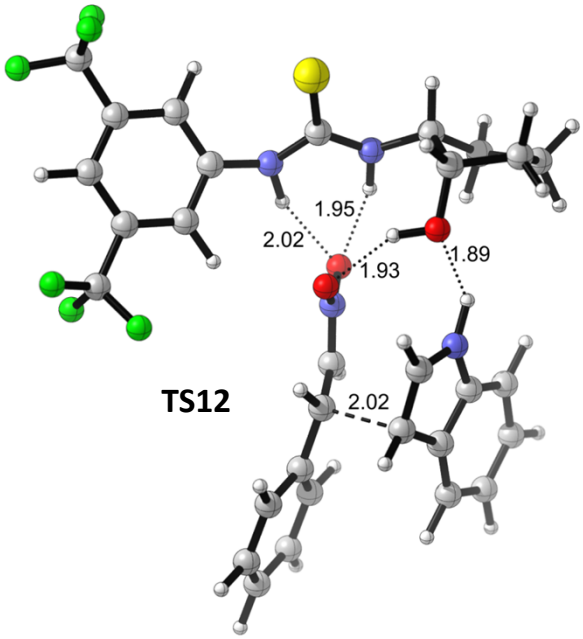
TS11

Bond	Distances (Å) X^1-H---X^2	Angle (º) X^1---H---X^2
N-H---O^1NO^2	1.92	152
N-H--- O^2NO^1	1.96	169
O-H--- O^1NO^2	1.99	152
H-O---H-N	1.77	154

N	0.796291	-2.235225	-0.529258
C	2.093865	-1.923216	-0.246754
O	2.918546	-2.735440	0.135335
N	2.353961	-0.572822	-0.444618
H	1.530071	0.024435	-0.381432
H	0.161938	-1.505059	-0.854358
H	-2.426969	-1.716744	1.108122
N	-3.241477	-1.172410	0.785469
C	-3.633495	-1.075139	-0.472860
C	-4.555675	0.004744	-0.597711
H	-3.193252	-1.692818	-1.242110
H	-5.229557	0.094927	-1.437428
O	-0.173670	0.553933	0.491427

N	-1.140435	0.575606	-0.331184
O	-1.145723	-0.237381	-1.294552
C	-2.152640	1.445419	-0.169185
H	-2.074347	2.070129	0.704259
O	-0.813116	-2.069131	1.721860
H	-0.233245	-1.355719	1.406454
C	0.198792	-3.447042	-0.029075
C	-0.248847	-3.351106	1.456813
H	0.920511	-4.263606	-0.127581
C	-1.095571	-3.787205	-0.732183
C	-1.396039	-4.362086	1.561939
H	0.574456	-3.543356	2.147692
C	-2.012790	-4.308526	0.180326
C	-1.420646	-3.636272	-2.072659
H	-1.000368	-5.361864	1.764743
H	-2.086477	-4.102008	2.366515
C	-3.280989	-4.686339	-0.241731
H	-0.702565	-3.218499	-2.770017
C	-2.692045	-4.022074	-2.497920
H	-4.004049	-5.081388	0.463374
C	-3.614302	-4.539728	-1.588474
H	-2.968278	-3.911247	-3.539715
H	-4.601605	-4.826184	-1.930889
C	3.578011	0.057008	-0.252007
C	3.569193	1.443094	-0.053348
C	4.805122	-0.614589	-0.283571
C	4.759149	2.132270	0.110431
H	2.623742	1.973363	-0.025479
C	5.979511	0.104691	-0.107911
H	4.831463	-1.683808	-0.426601
C	5.984549	1.478474	0.089812
C	4.720319	3.606434	0.387671
C	7.290908	-0.620439	-0.201137
H	6.911137	2.020829	0.224140
F	5.798866	4.235806	-0.097617

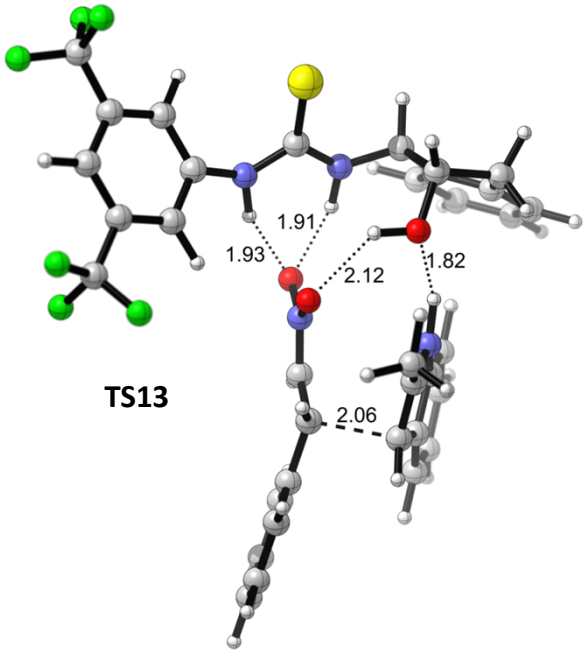
F	3.640624	4.193611	-0.145471
F	4.686534	3.860416	1.706205
F	8.235786	-0.048793	0.558740
F	7.762898	-0.627997	-1.459287
F	7.191569	-1.899742	0.180350
C	-3.232916	1.428781	-1.093695
H	-2.977548	0.988885	-2.051827
C	-4.125591	2.610612	-1.198012
C	-4.281285	3.532498	-0.158779
C	-4.842351	2.799966	-2.384121
C	-5.131095	4.622619	-0.310104
H	-3.748357	3.402342	0.775090
C	-5.692669	3.886313	-2.533684
H	-4.726014	2.087104	-3.194269
C	-5.839303	4.801465	-1.493859
H	-5.241468	5.332467	0.500702
H	-6.236492	4.022078	-3.460542
H	-6.501627	5.651163	-1.607516
C	-3.980399	-0.302656	1.599758
C	-4.887831	0.377427	0.776822
C	-3.907355	-0.109639	2.972115
C	-5.781870	1.281733	1.344755
C	-4.806529	0.796648	3.521023
H	-3.185105	-0.641479	3.578560
C	-5.735839	1.474922	2.721292
H	-6.494424	1.818680	0.730096
H	-4.792893	0.976601	4.588827
H	-6.429921	2.164793	3.185625



N	-0.877606	3.021144	-0.739206
C	-2.010890	2.380070	-0.411999
S	-3.197994	3.035450	0.594110
N	-2.090415	1.138602	-0.987337
H	-1.205087	0.803353	-1.367031
H	-0.174382	2.467338	-1.228173
H	2.792362	2.462512	0.741352
N	3.360748	1.615532	0.825625
C	3.063710	0.674202	1.706562
H	2.245050	0.804574	2.397254
O	1.052513	2.951595	1.281826
H	0.575388	2.142791	1.025111
C	-0.408190	4.256228	-0.142537
C	0.159956	4.062844	1.274832
H	-1.234037	4.969028	-0.098161
C	0.783036	4.826281	-0.926005
C	0.968590	5.331759	1.486275
H	-0.624313	3.913342	2.019539
C	1.586445	5.656220	0.103143
H	0.292075	6.129482	1.800594
H	1.712839	5.196036	2.271573
C	-2.988426	0.118704	-0.620490

C	-2.460005	-1.103709	-0.210693
C	-4.368804	0.284376	-0.702377
C	-3.312609	-2.150582	0.110752
H	-1.385006	-1.213285	-0.117153
C	-5.201521	-0.771025	-0.353629
H	-4.779565	1.224517	-1.043374
C	-4.691141	-1.997351	0.052346
C	-2.731369	-3.479414	0.494487
C	-6.686686	-0.556491	-0.379618
H	-5.351073	-2.813346	0.316482
F	-3.523901	-4.146821	1.343020
F	-2.556752	-4.271327	-0.575691
F	-1.532365	-3.354370	1.080261
F	-7.360543	-1.707016	-0.506949
F	-7.060413	0.240106	-1.390105
F	-7.120605	0.025484	0.749413
C	3.882222	-0.464997	1.482754
H	4.043566	-1.217541	2.240644
C	2.581630	-1.488835	0.331397
C	2.188192	-0.704362	-0.783062
H	1.819768	-1.580940	1.098356
N	1.166925	0.161718	-0.665918
H	2.645520	-0.724291	-1.757540
O	0.792291	0.828314	-1.675156
O	0.563030	0.307428	0.435451
C	3.355949	-2.735103	0.105047
C	3.291704	-3.741251	1.074834
C	4.136975	-2.942174	-1.035505
C	3.986572	-4.930936	0.909258
H	2.684706	-3.586642	1.961116
C	4.831978	-4.135134	-1.200944
H	4.214272	-2.176267	-1.797266
C	4.759780	-5.130189	-0.231472
H	3.919895	-5.703626	1.665429
H	5.430394	-4.286691	-2.091096

H	5.300371	-6.059326	-0.365447
C	4.477606	1.241960	0.066169
C	4.885806	-0.022393	0.517055
C	5.133506	1.935508	-0.941809
C	6.008829	-0.620961	-0.050123
C	6.248365	1.320564	-1.496829
H	4.793338	2.907910	-1.275460
C	6.684547	0.064934	-1.052864
H	6.347563	-1.593446	0.286212
H	6.794842	1.825872	-2.283587
H	7.566444	-0.376664	-1.500192
H	1.524389	6.723745	-0.108269
H	2.642826	5.385808	0.071058
H	0.460070	5.407421	-1.789329
H	1.392110	3.996494	-1.296785



TS13

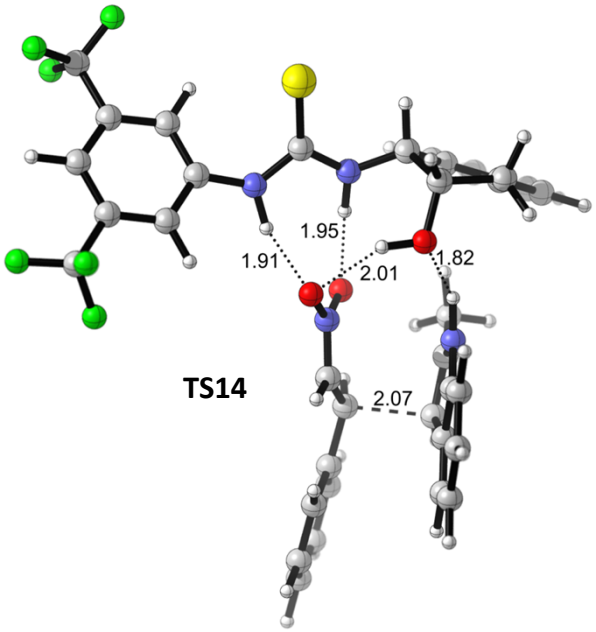
Bond	Distances (Å) X^1-H---X^2	Angle (º) X^1---H---X^2
N-H---O^1NO^2	1.93	156
N-H---O^1NO^2	1.91	155
O-H---O^2NO^1	2.12	136
H-O---H-N	1.82	151

N	0.583388	-2.615391	-0.356100
C	1.849209	-2.207183	-0.133256
S	2.949883	-3.076954	0.803066
N	2.120452	-1.012386	-0.734378
H	1.295256	-0.515399	-1.075400

H	-0.039946	-1.947482	-0.813774
H	-2.504642	-1.403054	1.327134
N	-3.132233	-0.600547	1.197083
C	-3.055731	0.492469	1.950834
O	-0.927324	-2.108455	1.884521
H	-0.287929	-1.475649	1.518387
C	-0.043233	-3.739142	0.301126
C	-0.457376	-3.445872	1.769904
H	0.647374	-4.587188	0.288591
C	-1.358360	-4.113280	-0.344825
C	-1.660846	-4.364107	2.008173
H	0.365167	-3.611666	2.465872
C	-2.281042	-4.483305	0.634100
C	-1.684916	-4.151933	-1.692838
H	-1.322983	-5.343343	2.359877
H	-2.332189	-3.948368	2.761404
C	-3.549918	-4.914165	0.270189
H	-0.963520	-3.855069	-2.446436
C	-2.959616	-4.585913	-2.058036
H	-4.274021	-5.201943	1.024167
C	-3.881373	-4.967732	-1.084377
H	-3.235696	-4.624363	-3.104942
H	-4.869212	-5.298843	-1.382424
C	3.253273	-0.208538	-0.510488
C	3.052124	1.107040	-0.100248
C	4.546017	-0.676924	-0.735792
C	4.144580	1.946226	0.078931
H	2.043228	1.454074	0.098224
C	5.621996	0.174673	-0.528402
H	4.700709	-1.690685	-1.077611
C	5.439596	1.491579	-0.123413
C	3.907000	3.377605	0.461502
C	7.013954	-0.357552	-0.709137
H	6.287104	2.147083	0.027801
F	4.964709	3.916220	1.080228

F	3.655552	4.141000	-0.614275
F	2.853616	3.508568	1.279125
F	7.887418	0.612083	-1.011079
F	7.077875	-1.272368	-1.685304
F	7.464276	-0.951417	0.406909
C	-3.874637	1.504297	1.370899
H	-4.197600	2.371993	1.927306
C	-2.336787	2.365596	0.295335
C	-1.904143	1.464075	-0.701702
H	-1.652405	2.482082	1.129214
N	-0.941031	0.553981	-0.453326
H	-2.309490	1.402732	-1.697398
O	-0.588626	-0.217191	-1.396970
O	-0.373596	0.466154	0.665973
C	-2.201737	0.591857	3.162055
H	-1.597020	-0.304022	3.284473
H	-1.541848	1.458264	3.087270
H	-2.836560	0.729700	4.040246
C	-3.022775	3.618717	-0.102979
C	-2.992901	4.704865	0.779148
C	-3.694310	3.755079	-1.321922
C	-3.616384	5.900760	0.452560
H	-2.471601	4.605742	1.725865
C	-4.322012	4.952846	-1.645973
H	-3.734586	2.931428	-2.023355
C	-4.285839	6.026628	-0.762397
H	-3.578617	6.734611	1.142792
H	-4.837439	5.047016	-2.594034
H	-4.773270	6.958959	-1.020305
C	-4.629115	0.846535	0.314808
C	-4.070209	-0.434036	0.174306
C	-5.613087	1.259820	-0.582560
C	-4.431731	-1.318812	-0.831564
C	-5.999921	0.380642	-1.588263
H	-6.064670	2.240950	-0.497413

C	-5.412216	-0.886128	-1.715533
H	-3.964810	-2.292788	-0.921724
H	-6.769775	0.678727	-2.289425
H	-5.731021	-1.542795	-2.515999



TS14

N	-0.767677	2.365657	-0.054737
C	-2.028727	1.971369	0.204440
S	-3.197523	2.967141	0.902406
N	-2.224767	0.659293	-0.138857
H	-1.370749	0.099334	-0.084686
H	-0.138809	1.695782	-0.505832
H	2.825904	1.641134	0.941177
N	3.543111	0.963511	0.655724
C	3.962200	0.768141	-0.590936
C	4.673576	-0.464705	-0.642449
H	5.328148	-0.718116	-1.463831
O	0.260381	-0.472198	0.735993
N	1.139102	-0.528741	-0.181157
O	1.133398	0.342701	-1.085429
C	2.046189	-1.524812	-0.165250
C	3.028964	-1.608122	-1.178085

H	1.959861	-2.185350	0.680857
H	2.797409	-1.042129	-2.074619
O	1.256817	2.020314	1.781417
H	0.623906	1.301103	1.614593
C	-0.142778	3.551443	0.480995
C	0.612251	3.287377	1.814930
H	-0.918059	4.302772	0.647520
C	0.942219	4.100967	-0.414994
C	1.722763	4.342780	1.826000
H	-0.055231	3.343648	2.677318
C	2.015008	4.547646	0.355695
C	0.945708	4.224713	-1.796888
H	1.355454	5.272856	2.269988
H	2.582717	4.006928	2.408420
C	3.123181	5.118961	-0.256281
H	0.104928	3.872049	-2.384491
C	2.054363	4.807889	-2.410081
H	3.965979	5.461524	0.333938
C	3.133932	5.247460	-1.645476
H	2.080008	4.914613	-3.487974
H	3.992375	5.691094	-2.136032
C	-3.412073	-0.079283	-0.068178
C	-3.335481	-1.389464	0.401265
C	-4.636258	0.420061	-0.517341
C	-4.475071	-2.182972	0.431215
H	-2.382076	-1.781681	0.739440
C	-5.761385	-0.387613	-0.460137
H	-4.702509	1.424666	-0.909117
C	-5.703128	-1.693708	0.012976
C	-4.372533	-3.572884	0.987682
C	-7.064148	0.131991	-0.995699
H	-6.590575	-2.312163	0.045830
F	-5.359979	-4.363955	0.550129
F	-3.212828	-4.157595	0.656894
F	-4.435796	-3.576834	2.328629

F	-8.112761	-0.367415	-0.327778
F	-7.235060	-0.203710	-2.285492
F	-7.143231	1.465916	-0.928844
C	3.672921	1.712567	-1.697653
H	3.417729	1.164830	-2.605961
H	2.848625	2.373844	-1.437612
H	4.564162	2.312803	-1.901462
C	3.721410	-2.893037	-1.433460
C	4.317138	-3.090074	-2.684821
C	3.801873	-3.910714	-0.478264
C	4.977254	-4.274331	-2.977830
H	4.255461	-2.304181	-3.430821
C	4.464082	-5.097578	-0.773131
H	3.353932	-3.784589	0.499556
C	5.053717	-5.282221	-2.019334
H	5.428700	-4.413595	-3.952695
H	4.519014	-5.879822	-0.025740
H	5.568087	-6.208478	-2.245003
C	4.849795	-0.880500	0.740800
C	4.051299	-0.020903	1.511441
C	5.501283	-1.946248	1.359517
C	3.856367	-0.185924	2.875740
C	5.330113	-2.117174	2.728877
H	6.125211	-2.621786	0.786530
C	4.513235	-1.255129	3.473266
H	3.218279	0.485155	3.437090
H	5.835602	-2.932282	3.232428
H	4.395077	-1.422262	4.536875

CALCULATIONS OF THE GLOBAL REACTIVITY INDICES

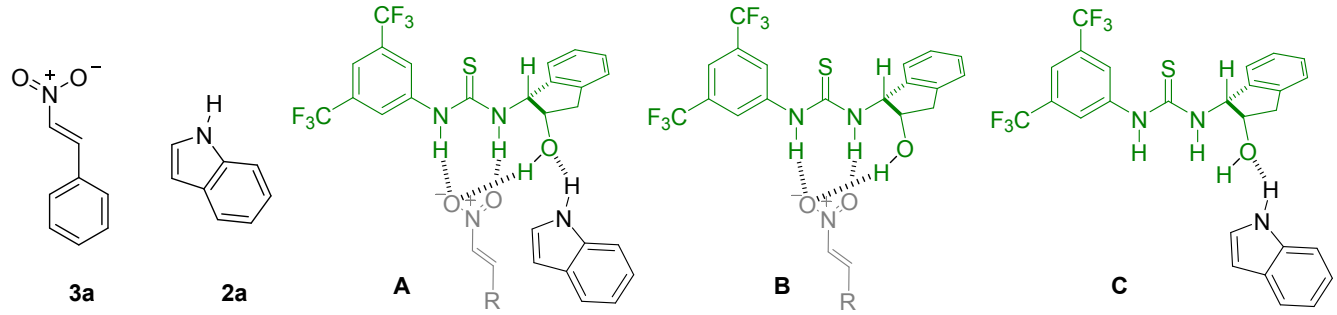


Figure S1. Model Structure

Table S2. Calculated (PCM(DCM)/M06-2X/6-311G(d,p)) global electrophilicity (ω) and total charge transfer (ΔN_{max}) at the ground state[1]

	Global indices			
	HOMO	**LUMO**	**ω (eV)**	**ΔN_{max}**
Nitrostyrene **3a**	-0.30644	-0.06780	**2.00**	0.784
Indole **2a**	-0.26130	0.01387	**0.76**	0.450
Active complex **A**	-0.25862	-0.08550	**2.33**	0.994
model **B**	-0.27830	-0.09048	**2.46**	0.982
model **C**	-0.25632	-0.02585	**1.18**	0.612

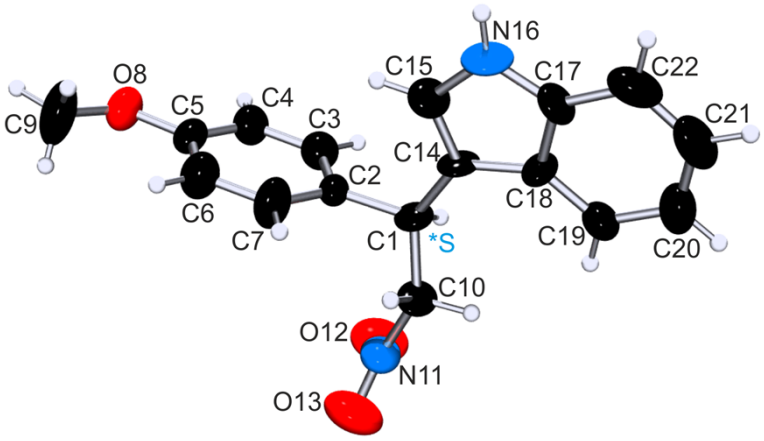
The calculated global electrophilicity (ω) for each species is in agreement with the experimental results observed, that is with the reactivity found in our reaction. Based on these results, the nitrostyrene is the electrophile (ω = 2.00 eV) and the indole is the nucleophile (ω = 0.76 eV), with a gap of 1.24 eV between them. Upon activation with the thiourea[2] both reagents increase their electrophilicity (ω = 2.46 eV and ω = 1.18 eV for **3a** and **2a**, respectively) even though a gap of 1.28 eV between the activated reagents is found, thus indicating a slightly higher reactivity than in the absence of thiourea. It should be pointed out that a higher value in the electrophilicity of the indole activated by the catalyst could be understood as an increasing in the acidity of the H atom of the NH, resulting in a higher nucleophilicity of this species. These concomitant interactions with the catalyst and the subsequent increasing in the

[1] P. K. Chattaraj, U. Sarkar and D. R. Roy, *Chem. Rev.*, 2006, **106**, 2065.

[2] With the purpose of comparing electrophilicities in activated reagents we have defined separated models **B** and **C** in which both of them are coordinated to the catalyst. Although it is not possible any sort of comparison in the active complex since an only ω value (2.33 eV) is obtained, the difference between such a value and that of nitrostyrene (Δω = 0.13) as well as that of indole (Δω =1.21 eV) clearly indicated an electrophilic contribution to complex **A** for the former and a nucleophilic contribution for the latter.

nucleophilicity or electrophilicity of both species would be in agreement with a more favourable Friedel-Crafts reaction as indicated by the observed higher gap between the activated reagents.

X-RAY CRYSTALLOGRAPHY



Crystal data of (*S*)-**4ab**: $[C_{17}H_{16}N_2O_3]$, orthorhombic, *P212121*, a = 9.3671(6) Å, b = 9.5385(7) Å, c = 17.0984(12) Å, Z = 4, M_r = 296.32 g mol^{-1}, V = 1527.71(18) Å^3, D_{calcd} = 1.288 g cm^{-3}, λ(Cu Kα) = 1.54178 Å, T = 297 K, μ = 0.732 mm^{-1}, 1016 reflections collected, 843 unique, $R1(F_o)$ = 0.0492 [$I > 2\sigma(I)$], $wR2$ (F_o^2) = 0.1197 (all data), GOF = 1.002. **CCDC-976490**.

The level A alert appeared in the checkcif of this structure because the crystals were of poor quality and the data collection was recorded at room temperature, due to the sensibility of the crystals (cracking). Unquestionably, the chirality determination is not affected by this alert, which is the most important information derived from this measure.