Aromatic Interactions as Control Elements in Stereoselective Organic Reactions

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SUPPORTING INFORMATION

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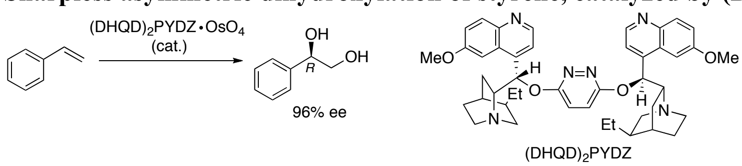
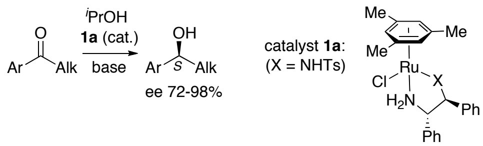
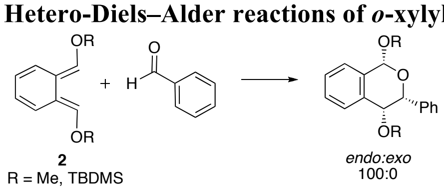
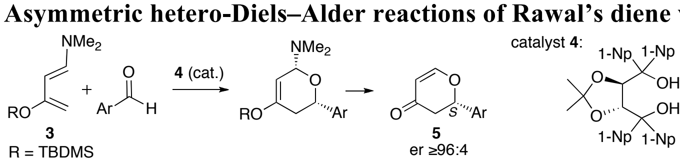
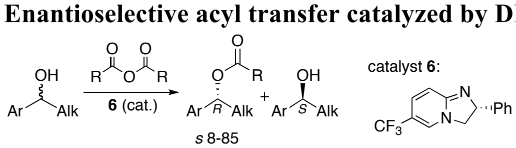
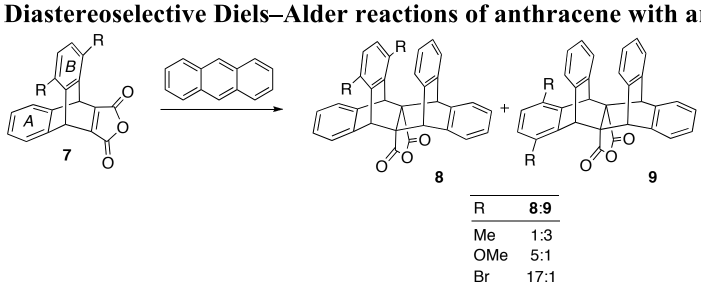
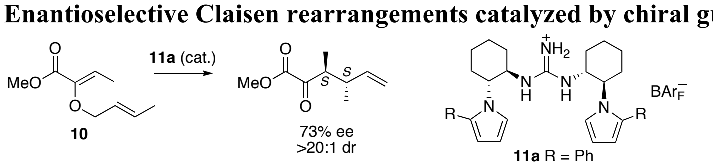
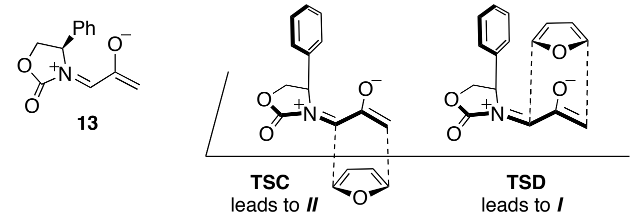
Table S1. Comparison of Stereoselectivities for Reactions in Schemes 1–7, as Predicted by B3LYP, B3LYP-D3, and M06-2X[a]

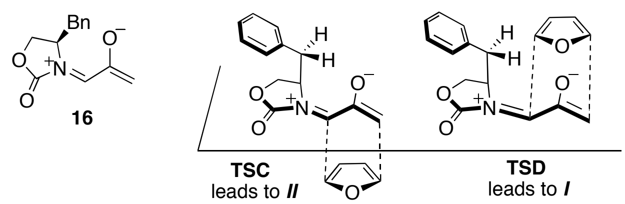
Reaction	ΔΔ$E^{‡}$		
	B3LYP	B3LYP-D3	M06-2X
Sharpless asymmetric dihydroxylation of styrene, catalyzed by (DHQD)$_2$PYDZ (Scheme 1)[21,22]			
	0.9	6.2	3.9
Ruthenium-catalyzed asymmetric transfer hydrogenation of ketones (Scheme 2)[23–26]			
	2.5	2.6	3.3
Hetero-Diels–Alder reactions of *o*-xylylenes with benzaldehyde (Scheme 3)[27,28]			
	R = TMS 0.6	0.1	0.7
Asymmetric hetero-Diels–Alder reactions of Rawal's diene with aldehydes, catalyzed by a TADDOL derivative (Scheme 4)[29,30]			
	1.5	4.5	3.0
Enantioselective acyl transfer catalyzed by DHIPs (Scheme 5)[32,33]			
	2.7	6.8	4.2
Diastereoselective Diels–Alder reactions of anthracene with aryl-substituted maleic anhydride derivatives (Scheme 6)[34]			
	R = Me –1.0 R = OMe 1.3 R = Br 3.3	–0.3 2.5 5.5	0.0 2.5 3.9
Enantioselective Claisen rearrangements catalyzed by chiral guanidinium salts (Scheme 7)[36]			
	3.0	2.1	2.8

[a] Transition state coordinates were obtained where possible from the publications cited. Where the coordinates had been optimized with a level of theory other than B3LYP/6-31G(d), the geometries were re-optimized at the B3LYP/6-31G(d) level (using the LANL2DZ effective core potential and basis set for Ru and Os). The one exception to this was the catalytic asymmetric hetero-Diels–Alder reaction of Rawal's diene, where transition state geometries were taken directly from the literature and not re-optimized. Subsequent B3LYP-D3 single-point calculations employed the same mixed basis set (LANL2DZ on Ru and Os, 6-31G(d) on other atoms), while M06-2X single-point calculations employed LANL2DZ on Ru and Os and 6-311+G(d,p) on other atoms. B3LYP-D3 calculations employed zero-damping. Predicted stereoselectivities (ΔΔ$E^{‡}$) are given in kcal/mol.



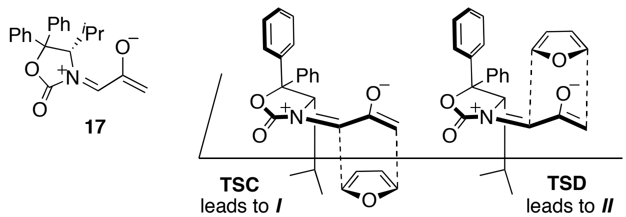
Exptal dr: 18:82

	ΔE‡rel	
	TSC	TSD
B3LYP	0	−0.3
B3LYP-D3	0	−2.0
M06-2X	0	−2.0



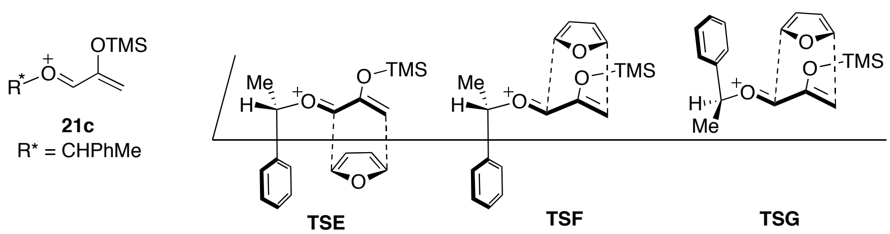
Exptal dr: 77:23

	ΔE‡rel	
	TSC	TSD
B3LYP	0	0
B3LYP-D3	0	−0.5
M06-2X	0	−0.1



Exptal dr: 6:94

	ΔE‡rel	
	TSC	TSD
B3LYP	0	2.1
B3LYP-D3	0	3.4
M06-2X	0	3.0



	ΔE‡rel		
	TSE	TSF	TSG
B3LYP	0	1.3	1.5
B3LYP-D3	0	2.8	1.3
M06-2X	0	2.9	1.3

Figure S1. Comparison of stereoselectivities for oxyallyl/furan cycloadditions, predicted by B3LYP, B3LYP-D3, and M06-2X. Transition state geometries were optimized at the B3LYP/6-31G(d) level. B3LYP and B3LYP-D3 single-point calculations employed the 6-31G(d) basis set, while M06-2X single-point calculations employed the 6-311+G(d,p) basis set. Predicted stereoselectivities ($\Delta E^{\ddagger}_{rel}$) are given in kcal/mol.

Geometries and energies of transition states from Table S1

The coordinates of transition states re-optimized with B3LYP are listed below. Below each structure is listed the B3LYP single-point energy (E), B3LYP-D3 dispersion energy (E_{disp}), and M06-2X single-point energy (E_{M06-2X}); the basis sets used for these calculations are described in the footnote to Table S1. Energies are given in Hartree. Calculations employed the Gaussian 09 software, the citation for which is given on page S20.

Sharpless asymmetric dihydroxylation of styrene, catalyzed by $(DHQD)_2PYDZ$

TS – Favored isomer

C	-0.428174	3.675455	1.167034
C	-0.128928	2.858177	0.079910
C	0.165277	3.422999	-1.177381
C	0.163751	4.824809	-1.300217
C	-0.138455	5.638929	-0.212035
C	-0.437243	5.066761	1.026400
C	0.482052	2.608619	-2.350691
C	0.236890	1.246813	-2.452690
O	1.860295	0.233742	-1.732124
Os	3.382557	1.129825	-1.592067
O	3.845892	1.538443	0.031462
O	2.691264	2.646308	-2.164312
O	4.531618	0.746762	-2.831753
N	4.327128	-1.098716	-0.707730
C	3.879386	-1.535149	0.664336
C	4.441646	-2.956188	0.966904
C	5.555274	-3.283777	-0.042842
C	4.959315	-3.429163	-1.462344
C	4.092879	-2.161430	-1.730222
C	6.545787	-2.106892	-0.059378
C	5.802677	-0.861821	-0.616255
C	2.366208	-1.401003	0.959696
C	2.080658	-1.632412	2.443178
C	2.254453	-0.599860	3.420980
C	1.988150	-0.950739	4.787873
N	1.584577	-2.188178	5.188346
C	1.427469	-3.103233	4.254235
C	1.662138	-2.873494	2.881697
C	2.144829	0.040364	5.796491
C	2.536023	1.312702	5.481294
C	2.792529	1.668317	4.127713
C	2.659476	0.731954	3.115692
O	3.161228	2.963603	3.956864
C	3.414931	3.431242	2.633425
C	4.181999	-4.736854	-1.685943
C	3.747891	-4.948029	-3.142082
O	1.666045	-2.382036	0.159930
C	0.346665	-2.203073	-0.088384
C	-0.288540	-3.217172	-0.845493
C	-1.622737	-3.057781	-1.105731
C	-2.239600	-1.889530	-0.597520
N	-1.593191	-0.971503	0.096175
N	-0.281851	-1.135022	0.363986
O	-3.564017	-1.747894	-0.852243
C	-4.234825	-0.560988	-0.365208
C	-4.010069	0.609259	-1.308708
C	-4.162352	1.953497	-0.843907
C	-3.981480	3.002545	-1.801948
N	-3.678877	2.779907	-3.111702
C	-3.547088	1.526683	-3.497294
C	-3.703086	0.414048	-2.639509
C	-4.123626	4.352726	-1.374831

C	-4.428555	4.654639	-0.074676
C	-4.605650	3.614054	0.877990
C	-4.479893	2.289872	0.502494
O	-4.898529	4.043466	2.136638
C	-5.065036	3.068884	3.156377
C	-5.741891	-0.867820	-0.193037
C	-6.401601	-1.662461	-1.360639
C	-7.412399	-2.652570	-0.741939
C	-6.671817	-3.723188	0.097978
C	-5.747636	-2.947983	1.095530
N	-6.038562	-1.498781	1.114793
C	-7.480073	-1.319632	1.379424
C	-8.348193	-1.872697	0.204564
C	-5.918323	-4.768000	-0.740733
C	-5.348956	-5.923473	0.092223
H	0.278707	-4.074636	-1.191827
H	-2.201699	-3.778469	-1.673475
H	-3.822773	-0.329410	0.618332
H	-5.904970	2.396975	2.936297
H	-3.306861	1.364292	-4.547875
H	-3.577005	-0.589283	-3.032400
H	-3.979238	5.129550	-2.118694
H	-4.536303	5.680278	0.263820
H	-5.275914	3.625730	4.070934
H	-4.154089	2.472049	3.292552
H	-4.617720	1.502686	1.232273
H	-6.211599	0.120120	-0.135496
H	-5.652132	-2.200971	-1.947253
H	-8.837162	-1.055431	-0.340724
H	-7.672047	-0.253212	1.546238
H	-7.707616	-1.837955	2.317735
H	-9.144343	-2.527297	0.579753
H	-4.696658	-3.077738	0.825496
H	-5.865172	-3.321469	2.119042
H	-7.437448	-4.265986	0.673385
H	-6.601037	-5.176571	-1.499506
H	-5.102315	-4.280503	-1.290950
H	-4.624755	-5.570407	0.836141
H	-6.145442	-6.450868	0.631787
H	-4.837917	-6.656130	-0.543070
H	2.013943	-0.414444	0.663482
H	2.861273	1.015532	2.090589
H	2.523435	3.343497	2.002420
H	3.686034	4.482924	2.741234
H	4.237175	2.881013	2.164498
H	2.656553	2.079519	6.240234
H	1.938606	-0.255049	6.820319
H	1.098818	-4.087953	4.585911
H	1.500897	-3.679005	2.174196
H	4.344396	-0.811269	1.339392
H	5.955328	0.018685	0.013675
H	6.138586	-0.610601	-1.624329
H	6.921507	-1.917951	0.953754
H	7.415437	-2.341224	-0.684488
H	6.064710	-4.210484	0.247799
H	4.829926	-2.989617	1.990288
H	3.646955	-3.704728	0.906935
H	4.323870	-1.718119	-2.701835
H	5.803644	-3.433970	-2.168248
H	-7.993725	-3.136983	-1.536270
H	-6.913175	-0.978210	-2.047521
H	3.028885	-2.396192	-1.712715
H	4.812792	-5.581102	-1.374025

H	3.295972	-4.757021	-1.036909
H	3.215800	-5.898731	-3.261441
H	3.079714	-4.150102	-3.487488
H	4.614524	-4.966035	-3.814209
H	0.303953	0.770830	-3.424181
H	-0.359509	0.732208	-1.710854
H	0.723291	3.154343	-3.256167
H	0.398725	5.271386	-2.263210
H	-0.139440	6.719339	-0.329137
H	-0.673438	5.699196	1.877917
H	-0.653818	3.223322	2.128919
H	-0.120136	1.780269	0.212462

1 imaginary frequency
E = -3038.935882
E_{disp} = -0.203501
E_{M06-2X} = -3038.317307

TS – Disfavored isomer

Os	3.283303	1.478476	0.365469
O	2.590926	2.866368	1.200556
O	1.830509	1.164837	-0.596638
O	4.569698	2.198798	-0.543651
O	3.565165	0.362514	1.667320
N	4.213639	-0.570512	-0.891309
C	5.672860	-0.596711	-0.560430
H	5.762623	-0.621751	0.529322
H	6.087320	0.352637	-0.905306
C	6.381891	-1.807162	-1.226758
H	7.316408	-1.484665	-1.700662
H	6.646485	-2.565993	-0.480187
C	3.672050	-1.928792	-0.520195
H	4.095500	-2.124606	0.468858
C	4.208543	-2.990434	-1.523425
H	4.488904	-3.900519	-0.983143
H	3.427558	-3.271906	-2.235310
C	5.421429	-2.406648	-2.269809
H	5.922613	-3.191989	-2.848334
C	4.962081	-1.265412	-3.206166
C	4.075608	-0.307647	-2.356047
H	3.019930	-0.421172	-2.602603
H	4.350248	0.737731	-2.516464
H	5.865361	-0.722406	-3.523034
C	4.254897	-1.743065	-4.485445
H	3.316425	-2.250929	-4.223841
H	4.886040	-2.495327	-4.978990
C	3.958271	-0.610342	-5.476488
H	3.473702	-0.994100	-6.381434
H	4.880849	-0.102540	-5.783250
H	3.294413	0.146762	-5.042160
C	2.145153	-2.013923	-0.292087
H	1.823368	-1.213441	0.372407
O	1.483620	-1.827441	-1.564439
C	0.188551	-1.426679	-1.557561
N	-0.443844	-1.251349	-0.413120
N	-1.724996	-0.838880	-0.416852
C	-2.342564	-0.631291	-1.564914
C	-1.722982	-0.809426	-2.824498
C	-0.415532	-1.218196	-2.820161
H	-2.278405	-0.624622	-3.737951
H	0.151138	-1.381723	-3.730750
C	1.768022	-3.365818	0.310989
C	1.310356	-4.386139	-0.498981

C	0.998946	-5.647475	0.052929
N	1.119625	-5.939826	1.331579
C	1.560411	-4.951434	2.158587
C	1.679508	-5.261914	3.542008
C	2.102853	-4.322945	4.442839
C	2.430946	-3.009525	4.005927
C	2.338492	-2.668404	2.667466
C	1.901415	-3.630563	1.711994
H	1.178691	-4.224424	-1.562981
H	0.639125	-6.444388	-0.597603
H	1.417579	-6.269034	3.850444
H	2.193454	-4.545130	5.501568
O	2.822460	-2.173160	5.002678
C	3.145759	-0.826771	4.669317
H	3.413327	-0.345599	5.611676
H	3.989566	-0.776068	3.972801
H	2.289512	-0.309795	4.220297
H	2.590835	-1.665512	2.347752
O	-3.639489	-0.231941	-1.575991
C	-4.309627	-0.066275	-0.302887
H	-3.977705	-0.874907	0.350247
C	-3.960424	1.276405	0.319193
C	-3.577477	2.349528	-0.458727
C	-3.294788	3.595655	0.145871
N	-3.375390	3.821005	1.441943
C	-3.756661	2.780197	2.235015
C	-4.065759	1.474857	1.732190
C	-4.454762	0.454066	2.645072
C	-4.528089	0.720829	3.999432
C	-4.224062	2.018048	4.496823
C	-3.848482	3.014508	3.635880
H	-3.610270	4.011749	3.992049
H	-4.295418	2.183849	5.567212
O	-4.881128	-0.181869	4.954848
C	-5.165477	-1.513425	4.549074
H	-6.025709	-1.549592	3.867780
H	-5.403517	-2.059840	5.463156
H	-4.298856	-1.976482	4.060406
H	-4.687422	-0.535299	2.273469
H	-3.482768	2.240598	-1.533943
H	-2.988668	4.436842	-0.475189
C	-5.834400	-0.215538	-0.511585
H	-6.268171	0.183473	0.412393
C	-6.426281	0.573936	-1.717371
H	-6.831683	1.535897	-1.383210
H	-5.656953	0.794841	-2.463189
C	-6.047912	-2.235244	-1.876954
N	-6.263526	-1.634092	-0.543693
C	-7.710488	-1.666381	-0.251664
H	-7.861069	-1.374280	0.794192
H	-8.040183	-2.707233	-0.345228
C	-8.506794	-0.734232	-1.219332
H	-8.893036	0.145187	-0.688356
H	-9.372881	-1.257600	-1.642663
C	-7.543607	-0.292320	-2.340656
H	-4.989474	-2.129740	-2.125625
H	-6.254710	-3.308123	-1.792526
C	-6.939708	-1.569272	-2.976829
H	-7.780632	-2.241424	-3.207703
H	-8.084093	0.285238	-3.100714
C	-6.190758	-1.321756	-4.295905
H	-5.305431	-0.699739	-4.107064
H	-6.836737	-0.742154	-4.970659

C	-5.760082	-2.613120	-5.003410
H	-6.627112	-3.243148	-5.237466
H	-5.078413	-3.207746	-4.383594
H	-5.244209	-2.396036	-5.945910
C	0.204539	2.360604	-0.263405
C	0.592894	3.479173	0.457982
H	0.074140	2.414913	-1.337471
C	0.994060	4.755192	-0.137240
H	-0.317103	1.553836	0.235752
H	0.361023	3.502958	1.517197
C	0.928691	5.924944	0.641217
C	1.280654	7.161545	0.105900
C	1.717759	7.252622	-1.217112
C	1.802321	6.096812	-1.999104
C	1.444983	4.861467	-1.467139
H	0.588434	5.856243	1.671285
H	1.216126	8.054306	0.721988
H	1.997209	8.215811	-1.635333
H	2.154202	6.159168	-3.025436
H	1.531506	3.968918	-2.080425

1 imaginary frequency
E = -3038.934524
E_{disp} = -0.194968
E_{M06-2X} = -3038.311094

Ruthenium-catalyzed asymmetric transfer hydrogenation of ketones

TS – Favored isomer

C	-3.190179	-1.645830	-0.513206
C	-2.837953	-1.270879	-1.831667
C	-1.711468	-1.885352	-2.440390
C	-1.006657	-2.938635	-1.774374
C	-1.450081	-3.375265	-0.487170
C	-2.534247	-2.736552	0.145697
Ru	-0.978232	-1.173448	-0.478175
O	0.655026	-1.439198	0.629267
C	1.554983	-0.354195	0.654051
C	1.593979	0.238470	-0.776640
N	0.156360	0.443286	-1.127204
O	-0.914078	2.196770	0.273507
C	-1.604188	1.409902	1.114839
H	0.081964	0.656533	-2.123272
H	1.985061	-0.555280	-1.428816
C	2.459695	1.471114	-0.963234
C	2.916327	-0.818638	1.144673
H	1.194628	0.445943	1.324019
H	-0.133739	-3.388850	-2.233013
H	-1.358860	-1.533658	-3.404975
H	-3.334639	-0.433564	-2.307749
H	-3.952154	-1.083677	0.015973
H	-2.807332	-2.999748	1.160814
H	-0.873172	-4.120123	0.050463
H	-1.446904	0.267378	0.830505
H	-0.333553	1.391727	-0.508597
H	-1.227602	1.408016	2.157927
C	-3.116142	1.585163	1.112229
C	3.404955	-2.081604	0.787938
C	4.664429	-2.502628	1.214619
C	5.454106	-1.665784	2.006520
C	4.972845	-0.407503	2.371285
C	3.711030	0.010046	1.944844
H	2.776885	-2.735894	0.191506

H	5.028910	-3.488026	0.933835
H	6.434400	-1.994840	2.341985
H	5.576793	0.248859	2.992762
H	3.340228	0.990793	2.232727
C	2.126037	2.710918	-0.393580
C	2.966104	3.811731	-0.566731
C	4.147883	3.696373	-1.301912
C	4.486833	2.468203	-1.870609
C	3.646300	1.367356	-1.702209
H	1.199213	2.815427	0.164305
H	2.692365	4.766416	-0.124458
H	4.797842	4.557831	-1.432888
H	5.403409	2.365193	-2.445951
H	3.919463	0.410485	-2.141936
C	-3.912885	0.960148	2.080760
C	-5.301309	1.103106	2.060554
C	-5.909972	1.880697	1.070613
C	-5.119721	2.516090	0.110149
C	-3.731085	2.369212	0.131484
H	-3.439984	0.362643	2.859261
H	-5.907947	0.617163	2.821051
H	-6.990532	1.998063	1.056349
H	-5.586299	3.134881	-0.652914
H	-3.096047	2.870433	-0.592174

1 imaginary frequency
E = -1344.193980
E_{disp} = -0.070320
E_{M06-2X} = -1343.873127

TS – Disfavored isomer

C	-4.111729	-0.795331	-0.456974
C	-3.637303	-1.813876	-1.312936
C	-2.837302	-2.854584	-0.762664
C	-2.607233	-2.926523	0.646086
C	-3.192713	-1.945991	1.508996
C	-3.930682	-0.879969	0.965635
Ru	-1.885857	-0.986931	-0.070838
O	-0.404842	-0.657441	1.216199
C	0.824168	-0.273814	0.637388
C	0.997664	-1.116673	-0.651102
N	-0.282651	-0.915630	-1.390386
O	-0.630980	1.416890	-2.182150
C	-1.517257	1.825563	-1.261077
H	-0.329933	-1.578604	-2.166242
H	1.034079	-2.166693	-0.327570
C	2.240090	-0.838996	-1.477969
C	1.952794	-0.473365	1.633828
H	0.804561	0.785912	0.332973
H	-1.977306	-3.707258	1.056901
H	-2.373767	-3.585097	-1.418233
H	-3.769506	-1.731498	-2.385759
H	-4.610188	0.070136	-0.880291
H	-4.286988	-0.080661	1.605091
H	-2.960330	-1.959600	2.568280
H	-1.723233	0.958352	-0.470803
H	-0.383905	0.219238	-1.872672
C	-1.124796	3.021264	-0.404700
H	-2.543207	1.982154	-1.656604
C	1.953857	-1.579097	2.493250
C	3.003634	-1.782006	3.388958
C	4.068491	-0.879365	3.438900
C	4.072368	0.228798	2.590321

C	3.019252	0.430380	1.696677
H	1.111900	-2.263943	2.465912
H	2.988896	-2.642775	4.053479
H	4.885735	-1.035249	4.138650
H	4.892803	0.941113	2.626762
H	3.023461	1.297681	1.041085
C	2.381829	0.326640	-2.247658
C	3.550870	0.551470	-2.976158
C	4.594992	-0.375052	-2.947398
C	4.462858	-1.536110	-2.184659
C	3.292918	-1.764428	-1.459859
H	1.568975	1.045636	-2.289117
H	3.643258	1.456256	-3.571824
H	5.502864	-0.195365	-3.517599
H	5.267650	-2.266266	-2.155098
H	3.198224	-2.668567	-0.862543
C	-2.011999	3.530187	0.552571
C	-1.666327	4.634587	1.329208
C	-0.424488	5.251483	1.152297
C	0.460940	4.755770	0.194368
C	0.112838	3.646475	-0.579473
H	-2.982619	3.054966	0.690613
H	-2.363374	5.016109	2.071364
H	-0.152609	6.113704	1.755786
H	1.425039	5.236291	0.045844
H	0.785980	3.258180	-1.336321

1 imaginary frequency
E = -1344.190018
E_{disp} = -0.070139
E_{M06-2X} = -1343.867832

Hetero-Diels–Alder reactions of *o*-xylylenes with benzaldehyde

TS – Favored isomer

C	1.788243	-0.702931	0.734156
C	0.958977	0.057512	1.568833
C	-0.477879	-0.007146	1.418434
C	-1.078619	-0.753774	0.381066
O	1.060930	0.009669	-1.237682
C	-0.188680	0.235753	-1.347522
O	3.101262	-0.499359	0.705947
H	1.439999	-1.622738	0.281802
O	-2.448775	-0.736315	0.270115
H	-0.598290	-1.663036	0.027244
C	1.525059	0.982693	2.500524
C	-1.267319	0.856810	2.239876
H	-0.799605	-0.461283	-1.946931
C	-0.735893	1.616919	-1.286127
C	-2.041947	1.885742	-1.721629
C	-2.551684	3.182675	-1.678971
C	-1.759401	4.230336	-1.203398
C	-0.454852	3.971628	-0.773005
C	0.054988	2.675990	-0.816154
H	-2.654787	1.072592	-2.102775
H	-3.564691	3.378298	-2.022138
H	-2.154054	5.242831	-1.173820
H	0.167336	4.785106	-0.407699
H	1.069525	2.462890	-0.495518
C	-0.686889	1.696914	3.155520
H	-2.344127	0.824374	2.121636
H	-1.315034	2.323484	3.783935
C	0.727671	1.765256	3.292599

H	2.605896	1.022988	2.584006
H	1.169016	2.438878	4.021773
Si	4.179777	-0.953256	-0.556941
C	5.769873	-1.380611	0.350401
C	3.464559	-2.429800	-1.475243
C	4.387808	0.535627	-1.677491
H	6.569302	-1.628404	-0.358808
H	6.116027	-0.536762	0.958227
H	5.635571	-2.240388	1.016615
H	4.140028	-2.738861	-2.282411
H	3.315460	-3.297478	-0.821416
H	2.503725	-2.156371	-1.923837
H	4.810804	1.388171	-1.133736
H	5.053530	0.310651	-2.520271
H	3.409990	0.830883	-2.070954
Si	-3.439033	-2.057620	-0.097668
C	-5.173600	-1.340589	-0.157570
C	-2.946998	-2.791713	-1.765705
C	-3.274797	-3.361275	1.255821
H	-5.914317	-2.115770	-0.388557
H	-5.447860	-0.891108	0.803435
H	-5.253008	-0.561486	-0.923958
H	-3.589610	-3.645370	-2.015734
H	-3.045683	-2.054600	-2.570847
H	-1.911448	-3.152521	-1.771764
H	-3.901470	-4.235622	1.040345
H	-2.240941	-3.713441	1.353573
H	-3.580756	-2.961698	2.229550

1 imaginary frequency
E = -1623.040962
E_{disp} = -0.062762
E_{M06-2X} = -1622.840321

TS – Disfavored isomer

C	2.013169	0.684766	0.426014
C	1.422015	1.819337	-0.150707
C	-0.015455	1.908271	-0.267199
C	-0.864915	0.837503	0.102214
O	1.148126	-0.874666	-0.853612
C	-0.037716	-0.676609	-1.277305
O	3.324900	0.494489	0.346696
H	1.484910	0.082768	1.155629
O	-2.217629	0.986273	-0.076625
H	-0.579042	0.162665	0.904829
C	2.237807	2.838450	-0.729947
C	-0.551010	3.055919	-0.932580
C	-1.094293	-1.709811	-1.091812
H	-0.191706	-0.032010	-2.158306
C	0.265157	4.038275	-1.434075
H	-1.628191	3.131162	-1.026557
H	-0.174312	4.909624	-1.913631
C	1.680030	3.932289	-1.338736
H	3.314500	2.734444	-0.650080
H	2.311405	4.716220	-1.747209
Si	4.183089	-0.979359	0.569073
C	5.830478	-0.423652	1.282951
C	3.233785	-2.070159	1.772327
C	4.376033	-1.783427	-1.113060
H	6.505637	-1.277793	1.417275
H	6.328418	0.290830	0.617513
H	5.703654	0.059250	2.258548
H	3.775004	-3.009622	1.939192

H	3.097574	-1.591240	2.749238
H	2.248135	-2.320453	1.366335
H	4.901413	-2.743880	-1.038843
H	3.386563	-1.953199	-1.548728
H	4.943798	-1.141110	-1.795920
Si	-3.415741	0.863205	1.115899
C	-5.023240	0.708286	0.156597
C	-3.116284	-0.640075	2.212739
C	-3.392551	2.435848	2.159651
H	-5.887321	0.692560	0.831997
H	-5.154156	1.549484	-0.533727
H	-5.035148	-0.215631	-0.431408
H	-3.947055	-0.756808	2.920434
H	-3.042775	-1.560075	1.623177
H	-2.198891	-0.546063	2.806157
H	-4.138375	2.389414	2.963237
H	-2.412491	2.589860	2.626940
H	-3.611214	3.321529	1.551882
C	-2.298411	-1.623128	-1.807340
C	-3.277860	-2.607240	-1.672621
C	-3.069429	-3.692822	-0.817744
C	-1.870013	-3.789594	-0.104703
C	-0.889547	-2.809222	-0.243847
H	-2.460090	-0.779770	-2.473597
H	-4.201762	-2.531616	-2.240961
H	-3.829721	-4.462928	-0.716444
H	-1.696060	-4.639150	0.551390
H	0.054750	-2.890294	0.285466

1 imaginary frequency
E = -1623.040004
E_{disp} = -0.063573
E_{M06-2X} = -1622.839260

Asymmetric hetero-Diels–Alder reactions of Rawal's diene with aldehydes, catalyzed by a TADDOL derivative

TS – Favored isomer

Coordinates were taken from ref. 30 and not re-optimized.
E = -3352.159785
E_{disp} = -0.226120
E_{M06-2X} = -3351.713667

TS – Disfavored isomer

Coordinates were taken from ref. 30 and not re-optimized.
E = -3352.157364
E_{disp} = -0.221290
E_{M06-2X} = -3351.708901

Enantioselective acyl transfer catalyzed by DHIPs

TS – Favored isomer

B3LYP coordinates and energy are available from ref. 32.
E_{disp} = -0.085677
E_{M06-2X} = -1716.785364

TS – Disfavored isomer

B3LYP coordinates and energy are available from ref. 32.
E_{disp} = -0.079190
E_{M06-2X} = -1716.778748

Diastereoselective Diels–Alder reactions of anthracene with aryl-substituted maleic anhydride derivatives – R = Me

TS – Favored isomer

C	2.034852	-3.582940	0.696625
C	2.034852	-3.582940	-0.696625
C	-4.256369	-2.590830	-0.696223
C	-4.256369	-2.590830	0.696223
C	1.191167	-2.738996	-1.429722
C	1.191167	-2.738996	1.429722
C	-3.151710	-2.094117	-1.406128
C	-3.151710	-2.094117	1.406128
C	-2.058568	-1.607164	-0.704207
C	-2.058568	-1.607164	0.704207
C	0.345220	-1.892167	-0.702711
C	0.345220	-1.892167	0.702711
H	2.698333	-4.260381	1.229583
H	2.698333	-4.260381	-1.229583
H	-5.117865	-2.969416	-1.239474
H	-5.117865	-2.969416	1.239474
C	1.189579	-2.775709	-2.940400
H	0.219510	-3.094731	-3.342383
H	1.408869	-1.791972	-3.374171
H	1.943890	-3.475932	-3.312548
C	1.189579	-2.775709	2.940400
H	0.219510	-3.094731	3.342383
H	1.408869	-1.791972	3.374171
H	1.943890	-3.475932	3.312548
H	-3.156778	-2.084620	-2.493217
H	-3.156778	-2.084620	2.493217
C	-0.760457	-1.025170	-1.303597
C	-0.760457	-1.025170	1.303597
C	-0.710350	0.386667	-0.705535
C	-0.710350	0.386667	0.705535
C	-1.705081	1.399098	-1.139914
C	-1.705081	1.399098	1.139914
O	-2.179453	2.056602	0.000000
O	-2.113141	1.667169	-2.238637
O	-2.113141	1.667169	2.238637
H	-0.775095	-1.019211	-2.393815
H	-0.775095	-1.019211	2.393815
C	4.125079	-0.490862	0.705167
C	4.125079	-0.490862	-0.705167
C	2.143266	0.901165	0.711764
C	2.143266	0.901165	-0.711764
C	3.134622	0.173712	-1.404365
C	3.134622	0.173712	1.404365
C	1.117560	1.667735	-1.360512
C	1.117560	1.667735	1.360512
C	-0.234179	5.116017	-0.705211
C	-0.234179	5.116017	0.705211
C	0.685189	2.876056	-0.712171
C	0.685189	2.876056	0.712171
C	0.197930	4.005625	-1.406360
C	0.197930	4.005625	1.406360
H	4.907877	-1.018238	1.242974
H	4.907877	-1.018238	-1.242974
H	3.133663	0.175911	-2.491620
H	3.133663	0.175911	2.491620
H	1.043066	1.619780	-2.444974
H	1.043066	1.619780	2.444974
H	-0.586333	5.991756	-1.242846

H	-0.586333	5.991756	1.242846
H	0.177299	3.994590	2.492458
H	0.177299	3.994590	-2.492458

1 imaginary frequency

E = -1535.719926

E_{disp} = -0.090892

E_{M06-2X} = -1535.513816

TS – Disfavored isomer

C	-3.909679	1.861523	0.697435
C	-3.909679	1.861523	-0.697435
C	1.993255	4.307365	-0.695711
C	1.993255	4.307365	0.695711
C	-2.732993	1.584219	-1.402915
C	-2.732993	1.584219	1.402915
C	1.316599	3.321299	-1.433536
C	1.316599	3.321299	1.433536
C	0.629619	2.348790	-0.703823
C	0.629619	2.348790	0.703823
C	-1.562495	1.313415	-0.702779
C	-1.562495	1.313415	0.702779
H	-4.823786	2.086342	1.240549
H	-4.823786	2.086342	-1.240549
H	2.541515	5.080569	-1.228900
H	2.541515	5.080569	1.228900
C	1.361649	3.311844	-2.944186
H	1.972889	4.137901	-3.320061
H	1.792569	2.376952	-3.322660
H	0.361702	3.414248	-3.384845
C	1.361649	3.311844	2.944186
H	1.972889	4.137901	3.320061
H	1.792569	2.376952	3.322660
H	0.361702	3.414248	3.384845
H	-2.729315	1.598887	-2.490434
H	-2.729315	1.598887	2.490434
C	-0.172225	1.165690	-1.303764
C	-0.172225	1.165690	1.303764
C	0.538256	-0.055021	-0.705508
C	0.538256	-0.055021	0.705508
C	1.920757	-0.372526	-1.138442
C	1.920757	-0.372526	1.138442
O	2.672138	-0.681452	0.000000
O	2.413594	-0.365624	-2.236132
O	2.413594	-0.365624	2.236132
H	-0.173759	1.163376	-2.394134
H	-0.173759	1.163376	2.394134
C	-4.017777	-1.888277	0.705329
C	-4.017777	-1.888277	-0.705329
C	-1.600023	-2.017302	0.711894
C	-1.600023	-2.017302	-0.711894
C	-2.826142	-1.924543	-1.404736
C	-2.826142	-1.924543	1.404736
C	-0.324094	-2.120380	-1.360861
C	-0.324094	-2.120380	1.360861
C	2.660354	-4.313469	-0.705304
C	2.660354	-4.313469	0.705304
C	0.687956	-2.908575	-0.712269
C	0.687956	-2.908575	0.712269
C	1.702726	-3.604423	-1.406295
C	1.702726	-3.604423	1.406295
H	-4.961284	-1.855171	1.242854
H	-4.961284	-1.855171	-1.242854

H	-2.823443	-1.918351	-2.491852
H	-2.823443	-1.918351	2.491852
H	-0.286837	-2.038649	-2.445194
H	-0.286837	-2.038649	2.445194
H	3.424796	-4.867064	-1.243033
H	3.424796	-4.867064	1.243033
H	1.713188	-3.586005	2.492493
H	1.713188	-3.586005	-2.492493

1 imaginary frequency
E = -1535.721576
E_{disp} = -0.089695
E_{M06-2X} = -1535.513799

Diastereoselective Diels–Alder reactions of anthracene with aryl-substituted maleic anhydride derivatives – R = OMe

TS – Favored isomer

C	1.133359	-3.704773	0.700763
C	1.133359	-3.704773	-0.700763
C	-4.786001	-1.391916	-0.696250
C	-4.786001	-1.391916	0.696250
C	0.508897	-2.678339	-1.411761
C	0.508897	-2.678339	1.411761
C	-3.601649	-1.138781	-1.406487
C	-3.601649	-1.138781	1.406487
C	-2.431148	-0.891186	-0.704513
C	-2.431148	-0.891186	0.704513
C	-0.143059	-1.664549	-0.697042
C	-0.143059	-1.664549	0.697042
H	1.629527	-4.517087	1.219366
H	1.629527	-4.517087	-1.219366
H	-5.707784	-1.581948	-1.239415
H	-5.707784	-1.581948	1.239415
O	0.466802	-2.582417	-2.779509
O	0.466802	-2.582417	2.779509
C	1.059855	-3.622038	-3.537436
H	0.900166	-3.359890	-4.585201
H	2.138610	-3.699135	-3.344223
H	0.589065	-4.592792	-3.331126
C	1.059855	-3.622038	3.537436
H	0.900166	-3.359890	4.585201
H	2.138610	-3.699135	3.344223
H	0.589065	-4.592792	3.331126
H	-3.602594	-1.131704	-2.493461
H	-3.602594	-1.131704	2.493461
C	-1.040310	-0.594699	-1.307618
C	-1.040310	-0.594699	1.307618
C	-0.694055	0.773535	-0.705396
C	-0.694055	0.773535	0.705396
C	-1.439131	1.980801	-1.140435
C	-1.439131	1.980801	1.140435
O	-1.757136	2.726235	0.000000
O	-1.776088	2.335152	-2.238828
O	-1.776088	2.335152	2.238828
H	-1.041105	-0.602692	-2.396716
H	-1.041105	-0.602692	2.396716
C	3.822723	-1.159551	0.705464
C	3.822723	-1.159551	-0.705464
C	2.202508	0.638551	0.711830
C	2.202508	0.638551	-0.711830
C	3.003019	-0.294241	-1.405784
C	3.003019	-0.294241	1.405784

C	1.376439	1.615784	-1.360998
C	1.376439	1.615784	1.360998
C	0.831382	5.278796	-0.705343
C	0.831382	5.278796	0.705343
C	1.224993	2.889577	-0.712325
C	1.224993	2.889577	0.712325
C	1.002776	4.099764	-1.406389
C	1.002776	4.099764	1.406389
H	4.469816	-1.847933	1.242183
H	4.469816	-1.847933	-1.242183
H	2.990535	-0.300422	-2.492536
H	2.990535	-0.300422	2.492536
H	1.289738	1.582217	-2.444883
H	1.289738	1.582217	2.444883
H	0.684266	6.211235	-1.242922
H	0.684266	6.211235	1.242922
H	0.979020	4.092909	2.492437
H	0.979020	4.092909	-2.492437

1 imaginary frequency
E = -1686.129616
E_{disp} = -0.093207
E_{M06-2X} = -1685.925391

TS – Disfavored isomer

C	-4.257600	0.719629	0.697330
C	-4.257600	0.719629	-0.697330
C	0.958679	4.382690	-0.699235
C	0.958679	4.382690	0.699235
C	-3.048863	0.698598	-1.403317
C	-3.048863	0.698598	1.403317
C	0.507497	3.266577	-1.416482
C	0.507497	3.266577	1.416482
C	0.067934	2.150691	-0.698427
C	0.067934	2.150691	0.698427
C	-1.847847	0.681249	-0.703434
C	-1.847847	0.681249	0.703434
H	-5.198647	0.746104	1.240491
H	-5.198647	0.746104	-1.240491
H	1.317419	5.264366	-1.218101
H	1.317419	5.264366	1.218101
O	0.457874	3.178131	-2.781155
O	0.457874	3.178131	2.781155
C	0.990138	4.251035	-3.539125
H	0.432360	5.182419	-3.370485
H	2.050635	4.418649	-3.309358
H	0.890471	3.957079	-4.585636
C	0.990138	4.251035	3.539125
H	0.432360	5.182419	3.370485
H	2.050635	4.418649	3.309358
H	0.890471	3.957079	4.585636
H	-3.047388	0.716440	-2.490617
H	-3.047388	0.716440	2.490617
C	-0.457038	0.831239	-1.307500
C	-0.457038	0.831239	1.307500
C	0.488891	-0.217510	-0.705938
C	0.488891	-0.217510	0.705938
C	1.907555	-0.261693	-1.140936
C	1.907555	-0.261693	1.140936
O	2.704899	-0.403197	0.000000
O	2.390592	-0.181154	-2.238931
O	2.390592	-0.181154	2.238931
H	-0.448316	0.848996	-2.396770

```
H   -0.448316    0.848996    2.396770
C   -3.601145   -2.962379    0.705303
C   -3.601145   -2.962379   -0.705303
C   -1.210846   -2.576317    0.711803
C   -1.210846   -2.576317   -0.711803
C   -2.428900   -2.744130   -1.404562
C   -2.428900   -2.744130    1.404562
C    0.059220   -2.411506   -1.360269
C    0.059220   -2.411506    1.360269
C    3.425358   -3.957558   -0.705191
C    3.425358   -3.957558    0.705191
C    1.209381   -2.981591   -0.712240
C    1.209381   -2.981591    0.712240
C    2.343820   -3.457415   -1.406345
C    2.343820   -3.457415    1.406345
H   -4.530215   -3.129719    1.243023
H   -4.530215   -3.129719   -1.243023
H   -2.427418   -2.736177   -2.491667
H   -2.427418   -2.736177    2.491667
H    0.078800   -2.322463   -2.444474
H    0.078800   -2.322463    2.444474
H    4.286562   -4.343996   -1.242877
H    4.286562   -4.343996    1.242877
H    2.351001   -3.434377    2.492413
H    2.351001   -3.434377   -2.492413
1 imaginary frequency
```

E = -1686.127509

E_{disp} = -0.091310

E_{M06-2X} = -1685.921358

Diastereoselective Diels–Alder reactions of anthracene with aryl-substituted maleic anhydride derivatives – R = Br

TS – Favored isomer

```
C    1.002588   -3.467126    0.695421
C    1.002588   -3.467126   -0.695421
C   -4.879237   -0.976832   -0.696480
C   -4.879237   -0.976832    0.696480
C    0.391188   -2.418787   -1.386098
C    0.391188   -2.418787    1.386098
C   -3.688545   -0.762057   -1.407610
C   -3.688545   -0.762057    1.407610
C   -2.512021   -0.548343   -0.704033
C   -2.512021   -0.548343    0.704033
C   -0.253177   -1.393632   -0.705349
C   -0.253177   -1.393632    0.705349
H    1.484185   -4.269631    1.242844
H    1.484185   -4.269631   -1.242844
H   -5.806446   -1.138544   -1.239143
H   -5.806446   -1.138544    1.239143
Br   0.487447   -2.410453   -3.296312
Br   0.487447   -2.410453    3.296312
H   -3.688990   -0.757433   -2.494356
H   -3.688990   -0.757433    2.494356
C   -1.114480   -0.290613   -1.306291
C   -1.114480   -0.290613    1.306291
C   -0.714731    1.061632   -0.705139
C   -0.714731    1.061632    0.705139
C   -1.419022    2.292895   -1.140585
C   -1.419022    2.292895    1.140585
O   -1.707712    3.049474    0.000000
O   -1.745698    2.655183   -2.239005
```

O	-1.745698	2.655183	2.239005
H	-1.114728	-0.297747	-2.395595
H	-1.114728	-0.297747	2.395595
C	3.716673	-1.057568	0.705511
C	3.716673	-1.057568	-0.705511
C	2.173575	0.805637	0.712056
C	2.173575	0.805637	-0.712056
C	2.930851	-0.161967	-1.407390
C	2.930851	-0.161967	1.407390
C	1.387258	1.816152	-1.361089
C	1.387258	1.816152	1.361089
C	0.981227	5.496621	-0.705315
C	0.981227	5.496621	0.705315
C	1.284414	3.094753	-0.712249
C	1.284414	3.094753	0.712249
C	1.108057	4.312076	-1.406706
C	1.108057	4.312076	1.406706
H	4.332053	-1.773820	1.242793
H	4.332053	-1.773820	-1.242793
H	2.906211	-0.180557	-2.493461
H	2.906211	-0.180557	2.493461
H	1.300238	1.786612	-2.445118
H	1.300238	1.786612	2.445118
H	0.870079	6.434010	-1.242758
H	0.870079	6.434010	1.242758
H	1.085454	4.306575	2.492746
H	1.085454	4.306575	-2.492746

1 imaginary frequency
E = -6599.299151
E_{disp} = -0.093439
$E_{M06\text{-}2X}$ = -6604.047904

TS – Disfavored isomer

C	4.295975	-0.336155	0.697546
C	4.295975	-0.336155	-0.697546
C	-0.861447	-4.069663	-0.694298
C	-0.861447	-4.069663	0.694298
C	3.088165	-0.324643	-1.404388
C	3.088165	-0.324643	1.404388
C	-0.431412	-2.933161	-1.392117
C	-0.431412	-2.933161	1.392117
C	-0.008341	-1.804897	-0.706822
C	-0.008341	-1.804897	0.706822
C	1.887794	-0.313476	-0.702724
C	1.887794	-0.313476	0.702724
H	5.237209	-0.357103	1.240198
H	5.237209	-0.357103	-1.240198
H	-1.196624	-4.944179	-1.240705
H	-1.196624	-4.944179	1.240705
H	3.086824	-0.345285	-2.491390
H	3.086824	-0.345285	2.491390
Br	-0.446172	-2.977574	-3.302641
Br	-0.446172	-2.977574	3.302641
C	0.498401	-0.473757	-1.305592
C	0.498401	-0.473757	1.305592
C	-0.464083	0.558708	-0.705573
C	-0.464083	0.558708	0.705573
C	-1.883955	0.575350	-1.141059
C	-1.883955	0.575350	1.141059
O	-2.682760	0.705162	0.000000
O	-2.362088	0.480675	-2.239282
O	-2.362088	0.480675	2.239282

H	0.491782	-0.490192	-2.395102
H	0.491782	-0.490192	2.395102
C	3.591697	3.343875	0.705346
C	3.591697	3.343875	-0.705346
C	1.205848	2.933348	0.711796
C	1.205848	2.933348	-0.711796
C	2.421918	3.113651	-1.404954
C	2.421918	3.113651	1.404954
C	-0.062183	2.754646	-1.360643
C	-0.062183	2.754646	1.360643
C	-3.452095	4.245584	-0.705230
C	-3.452095	4.245584	0.705230
C	-1.220962	3.306208	-0.712270
C	-1.220962	3.306208	0.712270
C	-2.362813	3.763230	-1.406824
C	-2.362813	3.763230	1.406824
H	4.518813	3.521896	1.242872
H	4.518813	3.521896	-1.242872
H	2.420552	3.106738	-2.492020
H	2.420552	3.106738	2.492020
H	-0.080621	2.665423	-2.444878
H	-0.080621	2.665423	2.444878
H	-4.319470	4.618012	-1.242659
H	-4.319470	4.618012	1.242659
H	-2.369743	3.740623	2.492847
H	-2.369743	3.740623	-2.492847

1 imaginary frequency
E = -6599.293837
E_{disp} = -0.089938
E_{M06-2X} = -6604.041700

Enantioselective Claisen rearrangements catalyzed by chiral guanidinium salts

TS – Favored isomer

B3LYP coordinates and energy are available from ref. 36.
E_{disp} = -0.146417
E_{M06-2X} = -2131.883994

TS – Disfavored isomer

B3LYP coordinates and energy are available from ref. 36.
E_{disp} = -0.147797
E_{M06-2X} = -2131.879479

Citation for Gaussian 09

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