

Supporting Information
Mechanistic Studies Inform Design of Improved Ti(salen) Catalysts for
Enantioselective [3+2] Cycloaddition
(Computational Part)

Sophia G. Robinson,^{a,†} Xiangyu Wu,^{b,†} Binyang Jiang,^b Matthew S. Sigman,^{a*} Song Lin,^{b*}

^aDepartment of Chemistry, University of Utah, 315 South 1400 East, Salt Lake City, UT 84112, United States

^bDepartment of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853, United States

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I. Full list of authors in the Gaussian09 reference

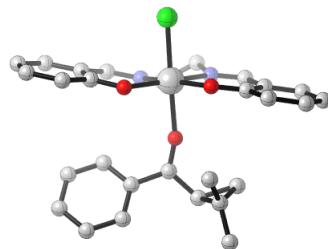
M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, 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, Inc., Wallingford CT, 2013.

II. Computational Methods for Catalytic Cycle

Conformers for each TS of the catalytic cycle were generated by performing a conformational search with MacroModel¹ version 11.7 and the OPLS_2005 force field using the mixed Monte Carlo Multiple Minimum (MCMM)/Low-Mode conformational search method and default RMSE atom coordinate cutoff (0.5 Å). The lowest energy conformer from the conformational search for each TS (TS1, TS2, TS3) was then used as the candidate structure for TS optimization with DFT using the ωB97XD functional,¹¹ LANL2DZ basis set¹² for Ti, and 6-31G(d) basis set for all other atoms as implemented in Gaussian09 (revision D.01).⁵ Intrinsic reaction coordinate calculations were performed using Gaussian09 (revision D.01)⁵ and confirmed that these TS structures connected to the correct pre- and post-TS structures. Once each TS (TS1, TS2, and TS3) was located, the remaining conformers were then used for TS optimization with DFT using the ωB97XD functional,¹¹ LANL2DZ basis set¹² for Ti, and 6-31G(d) basis set for all other atoms as implemented in Gaussian09 (revision D.01).⁵ Conformational searches of the pre- and post-TS structures were performed in Macromodel¹ version 11.7 using the OPLS_2005 force field. All conformers within 10 kJ/mol of the minimum were optimized with DFT using the ωB97XD functional,¹¹ LANL2DZ basis set¹² for Ti, and 6-31G(d) basis set for all other atoms as implemented in Gaussian09 (revision D.01).⁵ Single point energy calculations were performed on the optimized geometries with the IEFPCM(EtOAc)M06/def2-TZVP level of theory. These energy values were used to correct the Gibbs free energy derived from the geometry optimization calculations. The lowest energy conformer for each structure was utilized in constructing the catalytic cycle. TS structures were generated in CylView.¹³

III. Cartesian Coordinates of Catalytic Cycle Structures

Pre-TS1



ω B97XD/6-31G(d)-LANL2DZ Electronic Energy = -1937.037791

ω B97XD/6-31G(d)-LANL2DZ Free Energy = -1936.590939

IEFPCM(EtOAc)M06/def2-TZVP Electronic Energy = -2728.399015

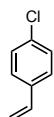
IEFPCM(EtOAc)M06/def2-TZVP// ω B97XD/6-31G(d)-LANL2DZ Corrected Free Energy = -2727.952162

Number of imaginary frequencies = 0

Ti	0.04977	-1.30424	-0.34586	H	0.31610	-3.96196	1.59512
O	-1.50597	-0.49129	-1.09791	H	1.18891	-3.27537	2.99691
C	-2.59883	-1.87010	1.17712	H	5.19760	-1.78022	1.56542
N	-1.31385	-1.81238	1.27522	H	6.78424	-0.68568	0.01216
C	-0.67865	-2.28119	2.49799	H	5.94282	0.22775	-2.14721
C	-2.79637	-0.65752	-1.00137	H	3.53448	0.07839	-2.71681
C	-3.65063	-0.09238	-1.97271	Cl	-0.32783	-3.40503	-1.34095
C	-5.01960	-0.22176	-1.86988	H	3.09635	-2.62944	2.08977
C	-5.60759	-0.91151	-0.79505	H	-3.16544	-2.30967	2.00680
C	-4.79038	-1.46512	0.16635	O	0.48341	0.64418	0.69714
C	-3.38625	-1.35380	0.08877	C	0.29760	1.85333	0.84303
H	-0.40657	-1.40402	3.09944	C	-1.06380	2.43871	0.76532
H	-1.34797	-2.91628	3.09285	C	-1.25216	3.75363	0.32486
H	-3.19071	0.44080	-2.79777	C	-2.17191	1.65260	1.08593
H	-5.65426	0.21757	-2.63475	C	-2.53846	4.26131	0.18428
H	-6.68576	-1.00995	-0.72676	H	-0.39478	4.36651	0.06239
H	-5.22556	-1.99899	1.00880	C	-3.45632	2.16127	0.95113
O	1.71402	-0.90953	-1.20248	H	-2.00954	0.63915	1.43107
C	2.98032	-0.89531	-0.89021	C	-3.63946	3.46525	0.49545
C	3.91181	-0.31165	-1.77755	H	-2.68361	5.27456	-0.17742
C	5.24968	-0.23452	-1.44958	H	-4.31158	1.53159	1.17675
C	5.72971	-0.74968	-0.23408	H	-4.64334	3.86203	0.37655
C	4.84124	-1.35473	0.62940	C	1.42859	2.78180	1.06703
C	3.46656	-1.43896	0.32949	C	2.85229	2.29914	0.95842
C	2.59799	-2.12295	1.25424	C	2.31880	3.16932	-0.13242
N	1.31695	-2.20531	1.16197	H	1.20766	3.59768	1.75007
C	0.58781	-3.03352	2.11010	H	2.99152	1.24302	0.74977

H	3.56788	2.72661	1.65518	C	2.75839	4.61883	-0.17306
C	2.01889	2.57868	-1.49395	H	3.68468	4.71470	-0.75133
H	1.22529	3.14720	-1.99440	H	1.99901	5.24682	-0.65496
H	2.91648	2.62859	-2.12032	H	2.94470	5.01769	0.82983
H	1.71046	1.53187	-1.44063				

p-chlorostyrene



ω B97XD/6-31G(d)-LANL2DZ Electronic Energy = -769.1182333

ω B97XD/6-31G(d)-LANL2DZ Free Energy = -769.025949

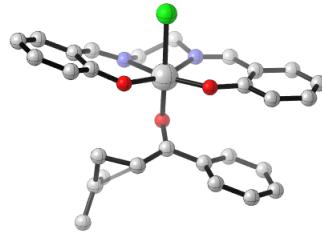
IEFPCM(EtOAc)M06/def2-TZVP Electronic Energy = -769.1027282

IEFPCM(EtOAc)M06/def2-TZVP// ω B97XD/6-31G(d)-LANL2DZ Corrected Free Energy = -769.0104439

Number of imaginary frequencies = 0

C	-3.81245	-0.54129	0.12585	C	0.78094	1.24835	0.02300
C	-2.88993	0.40293	-0.06276	H	-1.05718	2.34449	0.01356
C	-1.42657	0.22537	-0.04782	C	0.57012	-1.16006	-0.05282
H	-4.86998	-0.30054	0.09247	H	-1.41630	-1.93224	-0.13947
H	-3.22434	1.42531	-0.23472	C	1.35864	-0.01440	0.00089
H	-3.56083	-1.57913	0.32658	H	1.40605	2.13378	0.05977
C	-0.60444	1.35665	-0.00488	H	1.03600	-2.13899	-0.08079
C	-0.81149	-1.03269	-0.07981	Cl	3.09986	-0.16834	0.03251

TS1 (reductive opening of cyclopropane)



ω B97XD/6-31G(d)-LANL2DZ Electronic Energy = -1936.990256

ω B97XD/6-31G(d)-LANL2DZ Free Energy = -1936.547572

IEFPCM(EtOAc)M06/def2-TZVP Electronic Energy = -2728.361345

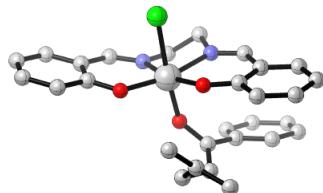
IEFPCM(EtOAc)M06/def2-TZVP// ω B97XD/6-31G(d)-LANL2DZ Corrected Free Energy = -2727.918661

Number of imaginary frequencies = 1 (-572.70)

Ti	0.37664	-1.04133	-0.13931	H	7.06261	-0.82785	0.41123
O	-0.98139	-1.67324	-1.25630	H	6.39242	-1.26245	-1.94643
C	-2.33703	-1.48564	1.28403	H	3.99350	-1.27758	-2.58366
N	-1.09609	-1.19746	1.44188	Cl	0.98802	-3.21822	0.59906
C	-0.57178	-1.02602	2.79122	H	3.11163	-0.03777	2.74497
C	-2.27872	-1.87317	-1.19177	H	-2.97899	-1.52216	2.17089
C	-2.99117	-2.16427	-2.36834	O	-0.12646	0.73414	-0.31499
C	-4.36149	-2.34876	-2.33278	C	-0.42645	1.94612	0.12337
C	-5.07218	-2.25804	-1.12823	C	-1.86304	2.21249	0.35499
C	-4.38155	-1.98291	0.03574	C	-2.30609	3.12338	1.32340
C	-2.98962	-1.78416	0.03071	C	-2.82015	1.51607	-0.39335
H	-1.35419	-0.71071	3.49201	C	-3.66512	3.33173	1.53197
H	-0.16408	-1.99083	3.11301	H	-1.58328	3.65486	1.93681
H	-2.43375	-2.23403	-3.29616	C	-4.17811	1.71811	-0.17880
H	-4.89114	-2.56838	-3.25549	H	-2.48716	0.81244	-1.14796
H	-6.14649	-2.40706	-1.10948	C	-4.60777	2.62789	0.78477
H	-4.91541	-1.90661	0.98019	H	-3.98971	4.03836	2.29054
O	2.03342	-0.84922	-0.98396	H	-4.89892	1.15757	-0.76710
C	3.29427	-0.86533	-0.60431	H	-5.66856	2.78735	0.95435
C	4.29889	-1.08939	-1.56013	C	0.55833	2.89543	0.29625
C	5.63192	-1.07872	-1.19281	C	2.00029	2.69827	-0.05047
C	6.01401	-0.83463	0.13369	C	1.73838	3.37385	-1.34760
C	5.03642	-0.60326	1.08033	H	0.26324	3.88065	0.64216
C	3.67120	-0.61733	0.73984	H	2.27821	1.65008	-0.15145
C	2.70124	-0.32925	1.77170	H	2.69535	3.22024	0.61320
N	1.42580	-0.37031	1.63171	C	1.43771	2.55833	-2.56230
C	0.55130	0.00208	2.73037	H	2.36822	2.31261	-3.09941
H	1.09058	0.05312	3.68452	H	0.95968	1.60982	-2.30110
H	0.13440	0.99258	2.50828	H	0.79012	3.09953	-3.26191
H	5.31460	-0.40957	2.11393	C	1.95017	4.84757	-1.48873

H	1.97042	5.35485	-0.51798	H	1.17342	5.31549	-2.10585
H	2.91503	5.05267	-1.98106				

Post-TS1 (Intermediate I)



ω B97XD/6-31G(d)-LANL2DZ Electronic Energy = -1936.998941

ω B97XD/6-31G(d)-LANL2DZ Free Energy = -1936.55596

IEFPCM(EtOAc)M06/def2-TZVP Electronic Energy = -2728.368605

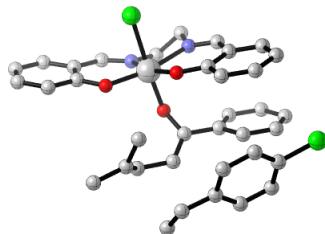
IEFPCM(EtOAc)M06/def2-TZVP// ω B97XD/6-31G(d)-LANL2DZ Corrected Free Energy = -2727.925624

Number of imaginary frequencies = 0

Ti	0.82090	-0.08694	0.48098	H	0.63770	-3.06695	2.16120
O	2.35800	0.77139	-0.11413	H	-0.68153	-3.76082	1.17210
C	3.13790	-1.99313	-0.22581	H	-4.25911	-1.17380	2.16276
N	1.87815	-1.90914	0.01035	H	-5.54378	0.93720	2.33155
C	1.05850	-3.11012	0.04867	H	-4.39153	3.10520	1.90915
C	3.63085	0.46166	-0.25577	H	-1.97685	3.14462	1.32517
C	4.58161	1.48645	-0.37794	Cl	1.78394	-0.33218	2.65511
C	5.91953	1.18130	-0.55051	H	-2.30112	-2.36086	1.82956
C	6.35535	-0.14924	-0.61543	H	3.57382	-2.98713	-0.37576
C	5.42690	-1.16473	-0.50301	O	0.02229	-0.24687	-1.18435
C	4.06042	-0.88609	-0.31780	C	-1.16349	0.13756	-1.70921
H	0.49347	-3.16424	-0.88629	C	-2.21263	-0.91399	-1.73465
H	1.66780	-4.01696	0.14628	C	-3.53509	-0.61741	-1.39378
H	4.23409	2.51258	-0.32554	C	-1.88346	-2.23313	-2.06341
H	6.64213	1.98774	-0.63614	C	-4.50350	-1.61671	-1.37591
H	7.40690	-0.37639	-0.75312	H	-3.79040	0.39603	-1.09680
H	5.74775	-2.20279	-0.55368	C	-2.84833	-3.23385	-2.04210
O	-0.48295	1.07510	1.07252	H	-0.86260	-2.45882	-2.35578
C	-1.75935	1.02086	1.40295	C	-4.16350	-2.92924	-1.69321
C	-2.49312	2.21088	1.51371	H	-5.52401	-1.37033	-1.09679
C	-3.83770	2.17348	1.83765	H	-2.57826	-4.25268	-2.30640
C	-4.48945	0.95602	2.07703	H	-4.91826	-3.70987	-1.67259
C	-3.76917	-0.21910	1.98810	C	-1.35768	1.37606	-2.18563
C	-2.40531	-0.21238	1.64830	C	-0.32088	2.46861	-2.15468
C	-1.71524	-1.47911	1.55001	C	-0.59489	3.53224	-1.12412
N	-0.49986	-1.64843	1.17562	H	-2.32409	1.59542	-2.63154
C	0.08771	-2.98079	1.21798	H	-0.27553	2.93056	-3.15846

H	0.66287	2.02361	-1.97390	C	-1.86244	4.31825	-1.24031
C	0.53185	4.04429	-0.28756	H	-1.99943	4.99782	-0.39124
H	0.16915	4.51869	0.63292	H	-1.87910	4.93752	-2.15494
H	1.21809	3.23832	-0.00462	H	-2.74356	3.66379	-1.29043
H	1.12958	4.80646	-0.82078				

Pre-TS2



ω B97XD/6-31G(d)-LANL2DZ Electronic Energy = -2706.130808

ω B97XD/6-31G(d)-LANL2DZ Free Energy = -2705.571854

IEFPCM(EtOAc)M06/def2-TZVP Electronic Energy = -3497.480886

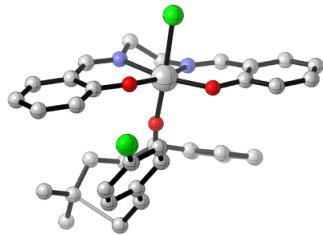
IEFPCM(EtOAc)M06/def2-TZVP// ω B97XD/6-31G(d)-LANL2DZ Corrected Free Energy = -3496.921932

Number of imaginary frequencies = 0

Ti	0.57189	0.19273	-1.00445	C	-0.94517	-2.87889	-0.56086
O	0.70008	2.04822	-0.84924	C	0.32464	-2.88420	-1.24865
C	3.20469	1.33898	-2.07071	N	1.05459	-1.86067	-1.51505
N	2.40439	0.33621	-2.11219	C	2.34928	-2.07218	-2.15663
C	2.71028	-0.81870	-2.94443	H	3.09299	-2.24095	-1.37106
C	1.70578	2.90056	-0.81256	H	2.32886	-2.94786	-2.81543
C	1.52315	4.15972	-0.21827	H	-1.14269	-5.01766	-0.71661
C	2.56575	5.06688	-0.16648	H	-3.30825	-5.10680	0.48095
C	3.81733	4.76225	-0.71797	H	-4.33142	-2.99792	1.31922
C	4.00189	3.53506	-1.32332	H	-3.18940	-0.82302	0.96676
C	2.96620	2.58449	-1.37643	Cl	-0.48656	0.28414	-3.14995
H	2.08344	-0.74637	-3.83892	H	0.69052	-3.87060	-1.55278
H	3.76626	-0.83532	-3.24152	H	4.14905	1.27357	-2.62241
H	0.55019	4.39416	0.20061	O	1.56756	-0.05924	0.53316
H	2.40638	6.03191	0.30563	C	1.59160	-1.00637	1.49926
H	4.62571	5.48413	-0.67797	C	2.66065	-2.02238	1.32540
H	4.96230	3.28899	-1.77060	C	2.40751	-3.38280	1.52090
O	-0.95050	-0.52120	-0.26555	C	3.94172	-1.62210	0.92645
C	-1.53627	-1.68802	-0.08236	C	3.41593	-4.32409	1.33161
C	-2.75636	-1.74794	0.60351	H	1.40507	-3.69848	1.79766
C	-3.37990	-2.96785	0.79658	C	4.95092	-2.56211	0.74525
C	-2.80814	-4.15705	0.32496	H	4.13218	-0.56585	0.75927
C	-1.60083	-4.10416	-0.34443	C	4.69048	-3.91730	0.94430

H	3.20436	-5.37901	1.48131	C	-4.33899	1.64328	1.29258
H	5.94463	-2.23776	0.44870	C	-3.19227	2.00123	0.57127
H	5.47652	-4.65220	0.79753	C	-3.10034	1.59614	-0.76516
C	0.75247	-0.99915	2.54639	C	-4.10432	0.84871	-1.36912
C	-0.29009	0.06016	2.82361	C	-5.22884	0.51019	-0.62705
C	0.27823	1.16942	3.66628	C	-5.35887	0.90735	0.70134
H	0.90771	-1.76056	3.30687	H	-4.43483	1.92254	2.33763
H	-0.66293	0.47112	1.88114	H	-2.21720	1.84468	-1.34642
H	-1.14475	-0.40477	3.33184	H	-3.99519	0.52004	-2.39658
C	0.32331	1.01313	5.15213	H	-6.24198	0.63060	1.26752
H	1.17396	0.38594	5.47476	C	-2.06632	2.74339	1.16532
H	0.44148	1.98115	5.65478	H	-1.16531	2.75108	0.55366
H	-0.58626	0.53581	5.53693	C	-2.04533	3.36376	2.34669
C	1.22978	2.11710	3.00905	H	-2.90681	3.40495	3.00838
H	1.32354	3.05462	3.57197	H	-1.14477	3.85760	2.69715
H	2.24315	1.68717	2.92631	Cl	-6.49216	-0.45438	-1.35898
H	0.91289	2.34894	1.98656				

TS2 (radical addition to styrene)



ω B97XD/6-31G(d)-LANL2DZ Electronic Energy = -2706.127505

ω B97XD/6-31G(d)-LANL2DZ Free Energy = -2705.565658

IEFPCM(EtOAc)M06/def2-TZVP Electronic Energy = -3497.48018

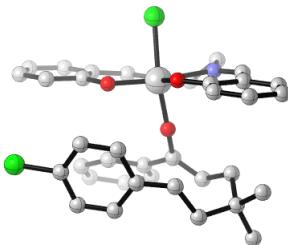
IEFPCM(EtOAc)M06/def2-TZVP// ω B97XD/6-31G(d)-LANL2DZ Corrected Free Energy = -3496.918333

Number of imaginary frequencies = 1 (-375.83)

Ti	-0.78190	0.51711	1.12998	H	-1.65843	-2.54749	3.61511
O	1.03514	0.78458	1.34812	H	-2.10272	-0.84688	3.94524
C	0.57966	-1.52717	2.99753	H	3.48520	1.37306	0.83540
N	-0.54454	-1.05288	2.60000	H	5.45413	0.07943	1.59661
C	-1.78823	-1.55339	3.17015	H	5.15610	-1.95889	3.00044
C	2.06490	0.08354	1.78215	H	2.87098	-2.67146	3.63421
C	3.36575	0.48642	1.44607	O	-1.57739	1.77344	0.01252
C	4.45692	-0.24560	1.87872	C	-2.80195	2.22069	-0.19958
C	4.29331	-1.39261	2.66664	C	-2.97843	3.39860	-0.94022
C	3.01716	-1.78769	3.01733	C	-4.24985	3.87338	-1.21190
C	1.88778	-1.06886	2.58566	C	-5.38528	3.18798	-0.76330

C	-5.22180	2.02277	-0.03894	C	2.29023	-3.31759	-1.23986
C	-3.94376	1.52059	0.26041	H	-0.59627	-3.83974	-1.42424
C	-3.85655	0.26961	0.98151	H	1.19154	-3.84038	0.50837
N	-2.77608	-0.29999	1.37153	H	1.35682	-2.10979	0.23500
C	-2.82667	-1.58346	2.05422	C	3.64075	-2.90793	-0.72877
H	-3.82708	-1.79374	2.45043	H	3.94300	-3.52410	0.13530
H	-2.56415	-2.36488	1.33146	H	4.41701	-3.02193	-1.49531
H	-6.09347	1.47385	0.30945	H	3.63450	-1.86617	-0.38912
H	-6.37821	3.56706	-0.97971	C	2.23581	-4.57276	-2.06161
H	-4.36403	4.79194	-1.78023	H	2.99660	-4.56501	-2.85082
H	-2.09240	3.92080	-1.28483	H	2.42787	-5.46183	-1.43708
Cl	-1.37699	1.81149	3.02597	H	1.25942	-4.71665	-2.53745
H	-4.81107	-0.22505	1.18870	C	2.00124	1.79083	-1.61671
H	0.57066	-2.34699	3.72410	C	2.54128	0.57334	-2.06330
O	-0.57316	-0.78603	-0.15350	C	3.94069	0.47069	-2.13846
C	-0.99625	-1.89607	-0.78170	C	4.76379	1.53477	-1.79733
C	-2.33494	-1.78671	-1.42117	C	4.19229	2.73128	-1.37119
C	-3.25442	-2.83894	-1.38362	C	2.81086	2.86642	-1.27520
C	-2.69932	-0.59315	-2.05277	H	0.92322	1.89376	-1.52446
C	-4.51485	-2.69646	-1.95765	H	4.39805	-0.45806	-2.46522
H	-2.98676	-3.76570	-0.88233	H	5.84263	1.44087	-1.86331
C	-3.95767	-0.44967	-2.62443	H	2.37504	3.79536	-0.92391
H	-1.99357	0.23100	-2.07121	C	1.63441	-0.50521	-2.44049
C	-4.87209	-1.50001	-2.57495	H	0.58417	-0.30444	-2.25145
H	-5.22374	-3.51842	-1.91355	C	1.96739	-1.71873	-2.95330
H	-4.22819	0.49088	-3.09515	H	2.97417	-1.94389	-3.29565
H	-5.85832	-1.38600	-3.01518	H	1.18170	-2.36759	-3.32476
C	-0.21846	-2.98971	-0.86191	Cl	5.22681	4.07335	-0.93402
C	1.15928	-3.05544	-0.27292				

Post-TS2 (Intermediate II)



ω B97XD/6-31G(d)-LANL2DZ Electronic Energy = -2706.187786

ω B97XD/6-31G(d)-LANL2DZ Free Energy = -2705.618804

IEFPCM(EtOAc)M06/def2-TZVP Electronic Energy = -3497.533297

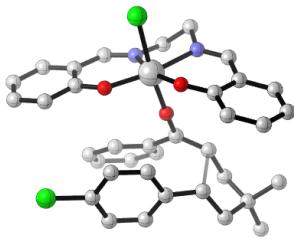
IEFPCM(EtOAc)M06/def2-TZVP// ω B97XD/6-31G(d)-LANL2DZ Corrected Free Energy = -3496.964315

Number of imaginary frequencies = 0

Ti	0.14218	-1.52988	-0.61882	H	5.52299	-2.04739	0.12251
O	-1.52037	-0.98951	-1.20979	H	6.72688	-0.68416	-1.55584
C	-2.19500	-2.43555	1.18951	H	5.43561	0.47076	-3.34442
N	-0.91863	-2.36270	1.07377	H	2.96690	0.25526	-3.44254
C	-0.06185	-2.84233	2.14770	Cl	-0.20115	-3.67257	-1.58496
C	-2.78773	-1.19253	-0.90359	H	3.60698	-3.03254	0.97454
C	-3.78475	-0.62867	-1.71175	H	-2.60933	-2.89836	2.09092
C	-5.12033	-0.78854	-1.38663	O	0.48048	-0.10956	0.49856
C	-5.50423	-1.51405	-0.25185	C	0.33087	0.48003	1.69547
C	-4.52762	-2.06800	0.55292	C	-1.07418	0.64373	2.15336
C	-3.16341	-1.92158	0.24953	C	-2.04508	1.05217	1.23456
H	0.25977	-1.97415	2.73700	C	-1.45215	0.38966	3.47441
H	-0.59065	-3.53947	2.80828	C	-3.36967	1.20201	1.62620
H	-3.48021	-0.05861	-2.58201	H	-1.75498	1.23857	0.20681
H	-5.87746	-0.33924	-2.02253	C	-2.78087	0.53442	3.86599
H	-6.55375	-1.63521	-0.00618	H	-0.70442	0.06079	4.19187
H	-4.80806	-2.61707	1.44861	C	-3.74265	0.93827	2.94248
O	1.52588	-1.07570	-1.78581	H	-4.11139	1.50573	0.89335
C	2.83782	-0.99452	-1.70797	H	-3.06504	0.32604	4.89374
C	3.53781	-0.23553	-2.66126	H	-4.77994	1.04410	3.24665
C	4.91664	-0.12612	-2.60010	C	1.39125	0.93069	2.38979
C	5.64714	-0.77604	-1.59777	C	2.79832	0.86889	1.88116
C	4.97073	-1.53446	-0.66158	C	3.45187	2.24948	1.60467
C	3.57065	-1.65480	-0.69069	H	1.19494	1.43820	3.33101
C	2.93099	-2.47140	0.32003	H	2.80258	0.29166	0.95349
N	1.66805	-2.59157	0.49936	H	3.44339	0.33155	2.59307
C	1.15653	-3.50328	1.51327	C	4.75139	2.01524	0.82279
H	0.85373	-4.42437	1.00491	H	4.56410	1.54459	-0.14848
H	1.91679	-3.73654	2.26864	H	5.27894	2.96077	0.64806

H	5.42360	1.35240	1.38120	H	0.02271	4.35953	0.47957
C	3.78532	2.95180	2.92822	H	-2.26911	4.59673	-0.36337
H	4.24138	3.93252	2.74718	C	1.90177	2.55403	-0.42243
H	2.88697	3.11100	3.53585	C	2.49478	3.16835	0.80322
H	4.49225	2.35702	3.51896	H	3.05472	4.08241	0.54034
C	0.09850	1.99802	-1.98333	H	1.69215	3.49139	1.47708
C	0.58887	2.77690	-0.90148	Cl	-3.69393	3.21501	-2.42198
C	-0.30356	3.72773	-0.33972	H	-1.55133	1.49843	-3.25777
C	-1.59762	3.87245	-0.81192	H	0.74556	1.24552	-2.42347
C	-2.04364	3.06586	-1.85835	H	2.50508	1.83701	-0.97454
C	-1.19487	2.12916	-2.45087				

Cis-TS3 (*cis* radical cyclization)



ω B97XD/6-31G(d)-LANL2DZ Electronic Energy = -2706.170748

ω B97XD/6-31G(d)-LANL2DZ Free Energy = -2705.602077

IEFPCM(EtOAc)M06/def2-TZVP Electronic Energy = -3497.51701

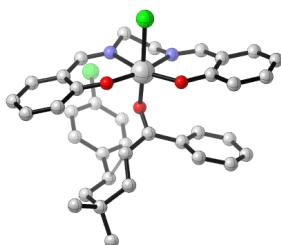
IEFPCM(EtOAc)M06/def2-TZVP// ω B97XD/6-31G(d)-LANL2DZ Corrected Free Energy = -3496.948339

Number of imaginary frequencies = 1 (-590.87)

Ti	0.50241	1.95810	-0.39237	O	-0.81462	2.19367	-1.71544
O	2.03967	1.10322	-0.99633	C	-2.12505	2.12966	-1.63232
C	2.68720	1.56379	1.77683	C	-2.86540	1.67377	-2.73908
N	1.48532	1.95393	1.54835	C	-4.24313	1.56770	-2.67331
C	0.65293	2.39231	2.66025	C	-4.94072	1.93596	-1.51493
C	3.22485	0.76186	-0.53621	C	-4.23025	2.41582	-0.43125
C	4.12847	0.10643	-1.38755	C	-2.82717	2.51220	-0.45932
C	5.36345	-0.30225	-0.91758	C	-2.14941	3.00406	0.72287
C	5.74482	-0.06625	0.41025	N	-0.88338	2.96314	0.91919
C	4.86252	0.57637	1.25622	C	-0.29851	3.47070	2.14783
C	3.59705	0.99732	0.80977	H	0.26548	4.37483	1.89820
H	0.07191	1.52695	3.00543	H	-1.06290	3.71074	2.89757
H	1.25543	2.76392	3.49762	H	-4.75640	2.71361	0.47306
H	3.82389	-0.08172	-2.41090	H	-6.02119	1.85191	-1.47132
H	6.04192	-0.81794	-1.59081	H	-4.78896	1.19806	-3.53658
H	6.71580	-0.38956	0.77006	H	-2.32031	1.40400	-3.63773
H	5.13417	0.75200	2.29454	Cl	1.46769	4.08896	-0.69227

H	-2.78999	3.43415	1.50087	H	-5.46155	-3.99641	1.41053
H	3.06824	1.62526	2.80195	H	-3.94099	-4.19994	2.29999
O	-0.34542	0.43669	0.20800	C	-5.13242	-1.34077	0.74772
C	-0.79711	-0.46730	1.05787	H	-5.53815	-0.85129	1.64164
C	0.24675	-1.21906	1.78587	H	-4.76396	-0.55827	0.07700
C	1.42650	-1.55808	1.11045	H	-5.96275	-1.84380	0.23803
C	0.12919	-1.54115	3.14342	C	-3.39216	-2.96322	-0.12934
C	2.46161	-2.20401	1.77217	H	-4.17756	-3.30731	-0.81941
H	1.52035	-1.31035	0.05883	H	-2.83598	-3.85657	0.17463
C	1.16764	-2.18974	3.80664	C	-2.48664	-1.98482	-0.81973
H	-0.76674	-1.25798	3.68910	H	-2.97882	-1.15944	-1.33078
C	2.33626	-2.52061	3.12439	C	-1.18480	-2.32022	-1.35420
H	3.37125	-2.44722	1.23068	C	-0.48529	-3.50121	-1.03485
H	1.06678	-2.42537	4.86229	C	-0.52467	-1.38754	-2.18117
H	3.14771	-3.02098	3.64506	C	0.78908	-3.74548	-1.52644
C	-2.15617	-0.72095	1.04927	H	-0.93356	-4.24597	-0.38601
H	-2.74336	0.06494	0.58414	C	0.75415	-1.61110	-2.66676
C	-2.90306	-1.68924	1.91864	H	-1.02189	-0.45370	-2.42363
H	-2.22350	-2.46962	2.28148	C	1.40437	-2.79782	-2.33855
H	-3.31644	-1.18561	2.80540	H	1.31003	-4.66175	-1.27052
C	-4.04904	-2.35963	1.13299	H	1.24545	-0.86462	-3.28091
C	-4.68865	-3.46517	1.97845	Cl	3.01706	-3.10345	-2.94787
H	-5.16095	-3.04912	2.87635				

Trans-TS3 (*trans* radical cyclization)



ω B97XD/6-31G(d)-LANL2DZ Electronic Energy = -2706.167085

ω B97XD/6-31G(d)-LANL2DZ Free Energy = -2705.598109

IEFPCM(EtOAc)M06/def2-TZVP Electronic Energy = -3497.511959

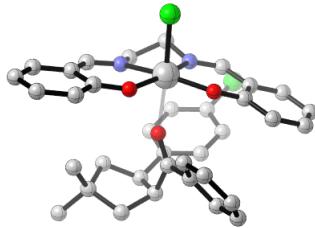
IEFPCM(EtOAc)M06/def2-TZVP// ω B97XD/6-31G(d)-LANL2DZ Corrected Free Energy = -3496.942983

Number of imaginary frequencies = 1 (-556.26)

Ti	0.36127	-1.71930	-0.49740	C	1.57749	0.66484	-1.98809
O	1.56076	-2.33730	0.76880	C	2.87292	-2.37074	0.91823
C	3.20219	-0.54929	-0.76611	C	3.43816	-3.24924	1.85360
N	1.97176	-0.42205	-1.10705	C	4.80910	-3.27826	2.04283

C	5.65641	-2.43069	1.31790	H	-0.74262	-1.03159	2.84143
C	5.10802	-1.55676	0.39878	C	-4.03859	-1.52059	3.50963
C	3.72012	-1.51492	0.17612	H	-5.65761	-0.81689	2.27582
H	1.15438	1.45824	-1.36202	H	-2.22121	-2.12371	4.49640
H	2.43451	1.07883	-2.53200	H	-4.68870	-2.00940	4.22939
H	2.77384	-3.89970	2.41190	C	-1.60344	1.60321	0.07525
H	5.23013	-3.96978	2.76702	H	-0.89879	1.78629	-0.73003
H	6.72893	-2.45925	1.47722	C	-2.85312	2.44006	0.04752
H	5.74852	-0.88497	-0.16762	H	-3.50986	2.13949	-0.78353
O	-1.28838	-2.56839	-0.43433	H	-3.42333	2.29217	0.97169
C	-2.50707	-2.32512	-0.87204	C	-2.50379	3.93282	-0.07709
C	-3.58455	-3.05441	-0.34655	C	-1.86098	4.23304	-1.43944
C	-4.87664	-2.78777	-0.75937	H	-2.54190	3.95736	-2.25419
C	-5.13972	-1.79475	-1.71271	H	-1.64511	5.30399	-1.53510
C	-4.08374	-1.08668	-2.25363	H	-0.92036	3.69497	-1.59094
C	-2.75868	-1.33358	-1.85151	C	-3.76727	4.78723	0.06374
C	-1.69573	-0.57784	-2.47909	H	-4.47222	4.58733	-0.75211
N	-0.44919	-0.63434	-2.17923	H	-4.27977	4.58035	1.01054
C	0.52453	0.12567	-2.95189	H	-3.52305	5.85602	0.04009
H	0.99525	-0.56776	-3.65702	C	-1.51970	4.23137	1.08849
H	0.04859	0.94159	-3.51023	H	-2.11480	4.41193	1.99190
H	-4.26900	-0.32404	-3.00700	H	-0.98183	5.16718	0.88604
H	-6.15726	-1.59286	-2.02985	C	-0.57335	3.08985	1.37396
H	-5.69890	-3.35236	-0.32964	H	-0.78214	2.53558	2.28491
H	-3.37082	-3.80290	0.40803	C	0.81251	3.06360	0.96982
Cl	1.19335	-3.19102	-2.15443	C	1.67284	2.07677	1.50123
H	-2.00472	0.08652	-3.29381	C	1.36248	3.95041	0.01958
H	3.93692	0.14164	-1.19155	C	2.99698	1.97456	1.11000
O	-0.28051	-0.27479	0.49666	H	1.27897	1.36563	2.22086
C	-1.44051	0.37082	0.67887	C	2.68563	3.84946	-0.39016
C	-2.35741	-0.25483	1.65151	H	0.74881	4.73919	-0.40331
C	-3.74992	-0.22000	1.49815	C	3.49503	2.85651	0.15249
C	-1.82098	-0.96432	2.73648	H	3.63747	1.20643	1.53160
C	-4.58160	-0.84297	2.42197	H	3.08889	4.54090	-1.12277
H	-4.18552	0.23941	0.61759	Cl	5.15731	2.70113	-0.38520
C	-2.65394	-1.58490	3.65848				

Cis-post-TS3



ω B97XD/6-31G(d)-LANL2DZ Electronic Energy = -2706.235202

ω B97XD/6-31G(d)-LANL2DZ Free Energy = -2705.662991

IEFPCM(EtOAc)M06/def2-TZVP Electronic Energy = -3497.562264

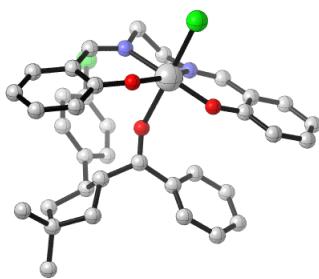
IEFPCM(EtOAc)M06/def2-TZVP// ω B97XD/6-31G(d)-LANL2DZ Corrected Free Energy = -3496.990053

Number of imaginary frequencies = 0

Ti	-0.70499	0.40312	-1.60861	H	5.71180	2.46445	-0.95350
O	-2.48150	0.84188	-1.00667	H	4.13147	4.33281	-0.48419
C	-2.66267	-2.00028	-1.38870	H	1.68417	3.99869	-0.74360
N	-1.42665	-1.63870	-1.43255	Cl	-1.19653	0.47436	-3.90102
C	-0.39800	-2.66807	-1.49144	H	3.05860	-1.17576	-2.17190
C	-3.65767	0.27110	-1.06664	H	-2.89237	-3.07165	-1.43592
C	-4.82300	1.04401	-0.88366	O	-0.30435	0.15221	0.63054
C	-6.07166	0.45590	-0.90760	C	-0.03830	0.77918	1.65048
C	-6.21869	-0.92660	-1.10344	C	0.02763	2.26543	1.66079
C	-5.08907	-1.69876	-1.27398	C	1.00109	2.94414	2.40220
C	-3.80135	-1.12730	-1.26337	C	-0.89769	2.99159	0.90268
H	-0.00449	-2.81576	-0.47992	C	1.06318	4.33212	2.36987
H	-0.79688	-3.62277	-1.85849	H	1.73944	2.39488	2.97887
H	-4.70261	2.11199	-0.73424	C	-0.84947	4.38001	0.89697
H	-6.95439	1.07508	-0.77300	H	-1.65505	2.46421	0.33001
H	-7.20443	-1.37891	-1.12121	C	0.13293	5.05088	1.62284
H	-5.18277	-2.77258	-1.42262	H	1.83702	4.85156	2.92627
O	0.56279	1.80705	-1.47219	H	-1.57252	4.93899	0.31159
C	1.85521	1.94659	-1.33271	H	0.17598	6.13593	1.60391
C	2.38463	3.19288	-0.93692	C	0.11709	0.05238	2.97172
C	3.74684	3.36480	-0.79427	H	0.84098	0.58948	3.59001
C	4.64195	2.31323	-1.05209	C	-1.25617	0.03159	3.68974
C	4.13833	1.08813	-1.43928	H	-1.07175	-0.01600	4.76879
C	2.75239	0.87385	-1.56463	H	-1.83825	0.94114	3.50666
C	2.28366	-0.44314	-1.92085	C	-1.99459	-1.25279	3.20938
N	1.05110	-0.81224	-1.95422	C	-2.57266	-2.00363	4.41461
C	0.73057	-2.16632	-2.38115	H	-3.26408	-1.36698	4.97922
H	0.38610	-2.11431	-3.42027	H	-3.12384	-2.89447	4.09200
H	1.60099	-2.83270	-2.31867	H	-1.77834	-2.32674	5.09924
H	4.81389	0.25944	-1.64403	C	-3.12085	-0.90021	2.23069

H	-3.91023	-0.32443	2.72831	C	2.67461	-0.89769	1.76202
H	-2.74498	-0.30750	1.39193	C	2.81809	-3.40748	0.58392
H	-3.57927	-1.80565	1.81620	H	0.94922	-3.79851	1.54327
C	-0.89732	-2.10031	2.50136	C	3.77592	-1.22585	0.98119
H	-1.04376	-2.07146	1.41810	H	2.64159	0.09470	2.20167
H	-0.93876	-3.14799	2.81907	C	3.83172	-2.47816	0.38448
C	0.45103	-1.44516	2.85459	H	2.87817	-4.38803	0.12359
H	0.70922	-1.76081	3.87736	H	4.56639	-0.50213	0.81977
C	1.62911	-1.79950	1.97174	Cl	5.18615	-2.88150	-0.64856
C	1.73208	-3.06286	1.38311				

Trans-post-TS3



ω B97XD/6-31G(d)-LANL2DZ Electronic Energy = -2706.229305

ω B97XD/6-31G(d)-LANL2DZ Free Energy = -2705.660075

IEFPCM(EtOAc)M06/def2-TZVP Electronic Energy = -3497.558723

IEFPCM(EtOAc)M06/def2-TZVP// ω B97XD/6-31G(d)-LANL2DZ Corrected Free Energy = -3496.989493

Number of imaginary frequencies = 0

Ti	1.30687	-1.12036	-1.45212	O	2.67372	0.19892	-1.31174
O	-0.06835	-0.70152	-2.72439	C	3.74407	0.42211	-0.60285
C	-1.35925	-2.64465	-1.03596	C	4.59953	1.49065	-0.94749
N	-0.10289	-2.60040	-0.77202	C	5.71407	1.77392	-0.18704
C	0.49438	-3.58616	0.11252	C	6.03192	1.00926	0.94919
C	-1.36900	-0.77311	-2.69937	C	5.21127	-0.04287	1.29614
C	-2.13579	0.11159	-3.49271	C	4.06326	-0.35811	0.54033
C	-3.51560	0.06704	-3.47556	C	3.20544	-1.41915	1.00166
C	-4.20103	-0.86977	-2.68372	N	2.10205	-1.80295	0.45507
C	-3.46793	-1.75425	-1.91753	C	1.30615	-2.81450	1.14622
C	-2.06166	-1.71679	-1.89167	H	1.93413	-3.49105	1.73910
H	-0.25982	-4.21457	0.60415	H	0.61348	-2.29843	1.82213
H	1.15882	-4.21383	-0.49102	H	5.44301	-0.64792	2.17080
H	-1.59872	0.82317	-4.11152	H	6.91523	1.23784	1.53642
H	-4.07971	0.76426	-4.08933	H	6.35767	2.60184	-0.47240
H	-5.28534	-0.90719	-2.68793	H	4.34157	2.07932	-1.82130
H	-3.98017	-2.49648	-1.30754	Cl	2.54018	-2.68988	-2.67929

H	3.52540	-1.91322	1.92733	H	-5.03852	4.82388	0.80987
H	-1.96511	-3.43492	-0.57829	H	-3.35474	5.16214	1.25165
O	-0.00825	0.25306	-0.24420	C	-4.56649	2.79728	-0.98142
C	-0.26181	1.42793	-0.00613	H	-4.53005	3.43049	-1.87587
C	0.82814	2.33328	0.44843	H	-4.31063	1.77543	-1.28478
C	1.68597	1.85427	1.44380	H	-5.60058	2.78803	-0.61701
C	1.05523	3.59073	-0.11604	C	-3.65164	2.39070	1.35028
C	2.74613	2.63319	1.88797	H	-4.44663	1.64484	1.24735
H	1.52255	0.85877	1.84566	H	-3.85997	2.94339	2.27193
C	2.13402	4.35698	0.31335	C	-2.27048	1.70033	1.44189
H	0.42345	3.95220	-0.92042	H	-1.62189	2.30892	2.08650
C	2.97232	3.88410	1.31964	C	-2.25616	0.28397	1.96064
H	3.42231	2.24668	2.64352	C	-1.38243	-0.08987	2.98158
H	2.32404	5.32200	-0.14592	C	-3.06729	-0.69981	1.38981
H	3.81594	4.48287	1.64887	C	-1.30494	-1.40826	3.42355
C	-1.71402	1.83354	-0.00847	H	-0.74063	0.65944	3.43869
H	-2.22214	1.10455	-0.64905	C	-3.00611	-2.01958	1.81714
C	-2.14910	3.24890	-0.37752	H	-3.74255	-0.44342	0.57778
H	-1.54882	3.98177	0.17421	C	-2.11538	-2.36623	2.82761
H	-2.04772	3.46148	-1.44737	H	-0.62014	-1.68916	4.21665
C	-3.61913	3.32778	0.10415	H	-3.64044	-2.77662	1.36795
C	-4.00146	4.76680	0.45933	Cl	-1.99960	-4.03543	3.33750
H	-3.90654	5.42400	-0.41319				

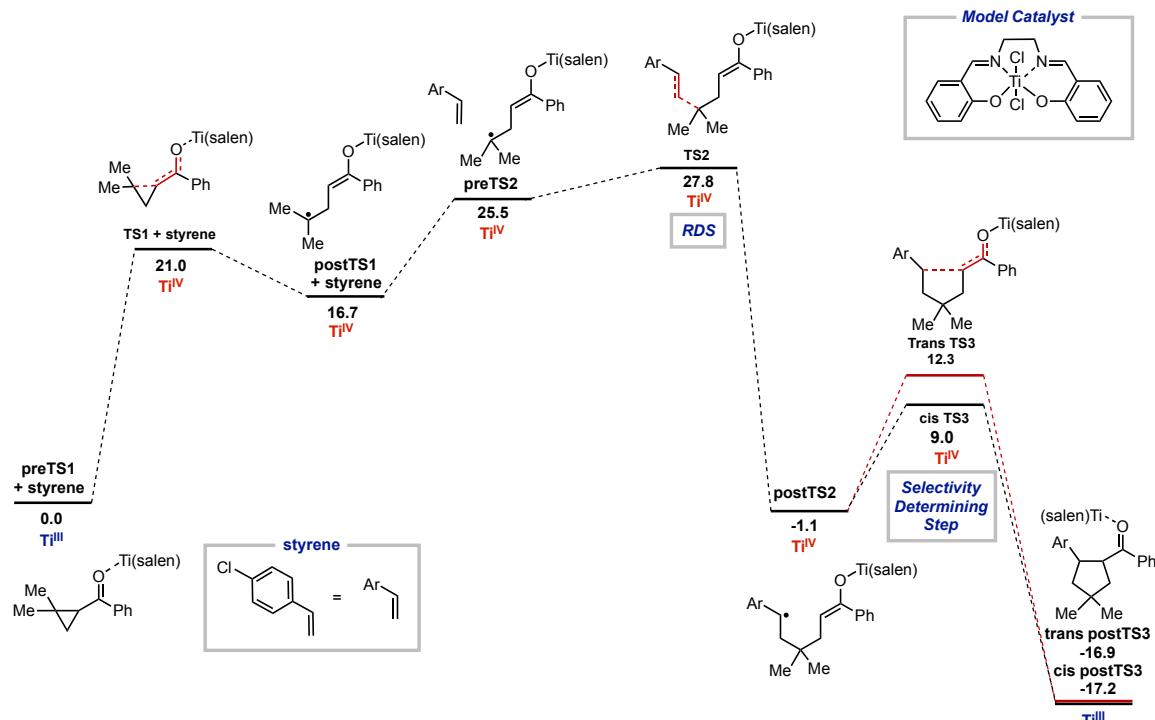


Figure SC1. Catalytic cycle for Ti(salen)-catalyzed [3+2] cycloaddition with *p*-chlorostyrene.

IV. Computational Methods for Transition State Analysis

Conformers in each of the TS categories (*cis*-Re, *cis*-Si, *trans*-Re, *trans*-Si) with the **(R,R)-4a** catalyst were generated by performing a conformational search with Macromodel¹ version 11.7 and the OPLS_2005 force field using the mixed Monte Carlo Multiple Minimum (MCMM)/Low-Mode conformational search method and default RMSE atom coordinate cutoff (0.5 Å). These were then used as candidate structures for TS optimization with DFT. Conformers within 20 kJ/mol of the minimum were taken forward for TS optimization with DFT using the M06 functional,⁶ SDD basis set¹⁴ for Ti, and 6-31G(d) basis set for all other atoms as implemented in Gaussian09 (revision D.01).⁵ Conformers 20-100 kJ/mol of the minimum were clustered into 10 clusters based on atomic RMSD using default cut-offs in Macromodel¹ version 11.7. Unique conformers not represented in the conformers within 20 kJ/mol of the minimum were manually selected from these 10 clusters. These conformers were then used for TS optimization with DFT using the M06 functional,⁶ SDD basis set¹⁴ for Ti, and 6-31G(d) basis set for all other atoms as implemented in Gaussian09 (revision D.01).⁵ Single point energy calculations were performed on the resulting structures using various levels of theory as outlined in Table SC8. These values were used to correct the Gibbs free energy derived from the TS calculations. It was ultimately determined that the IEFPCM(EtOAc)M06/6-31+G(d,p) level of theory provided values in closest agreement with experiment. TS structures were generated in CylView.¹³

Table SC1. Benchmark of level of theory for single point energy calculations used to correct Gibbs free energies from TS calculations

Level of Theory w/ IEFPCM(EtOAc) for calculating electronic energies used to correct free energies	Diastereoselectivity	Enantioselectivity
	Corrected Free Energy $\Delta\Delta G^\ddagger$ (kcal/mol)	Corrected Free Energy $\Delta\Delta G^\ddagger$ (kcal/mol)
M06/def2TZVP	+0.6	+1.2
M06/6-31+G(d,p)	+0.8	+1.5
M06/6-311+G(d,p)	+0.7	+1.1
M06/6-31+G(d,p)-Lanl2dz	+0.7	+1.6
M06/6-31+G(d,p)-SDD	+0.6	+1.5
M06/6-311+G(d,p)-SDD	+0.6	+1.2
M06/def2TZVP-SDD	+0.4	+1.2
M06-D3/6-31+G(d,p)	+1.5	+1.2
M06-D3/def2-TZVP	+1.3	+0.8
wB97XD/6-31+G(d,p)	+0.9	+1.0
wB97XD/def2-TZVP	+0.8	+1.0
Experimental Values	+1.8	+2.3

The corrected Gibbs free energies for each of the three TS3 scenarios to consider for calculating $\Delta\Delta G^\ddagger$ values are presented in Figure SC2. These corrected free energies were utilized for calculating the relative $\Delta\Delta G^\ddagger$ values for enantioselectivity and diastereoselectivity (converted to kcal/mol).

These major TS structures were modified to calculate TS with *p*-fluorostyrene and styrene substrates with the IEFPCM(EtOAc)-M06-6-31+G(d,p)//M06/SDD-6-31G(d) level of theory as implemented in Gaussian09 (version D.01).⁵ These calculations were performed to assess the robustness of the computational method and the results are presented below (Figure SC3).

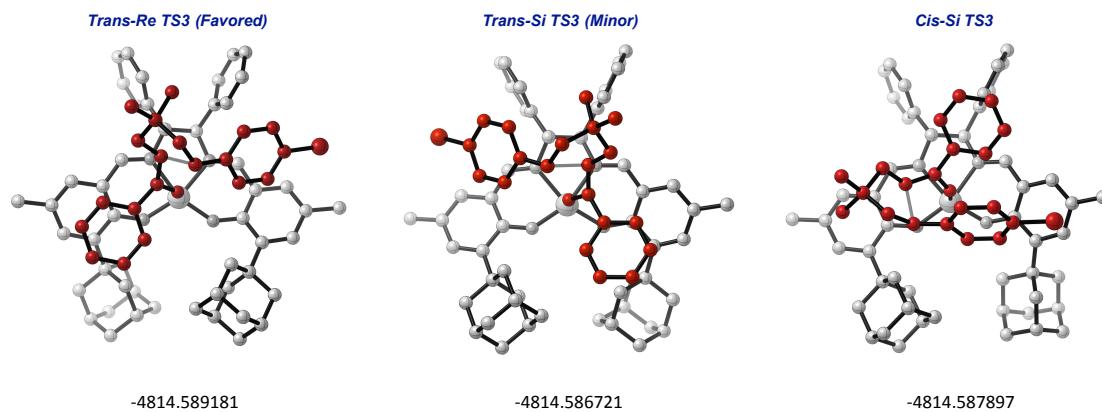


Figure SC2. Corrected Gibbs Free Energies for each major TS3 (in Hartrees).

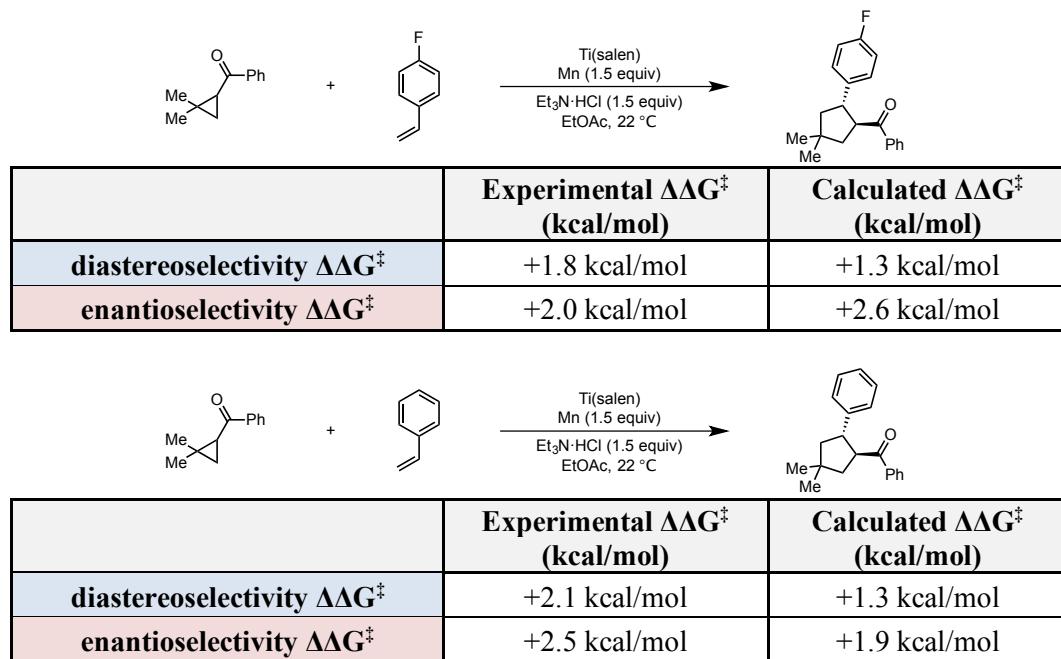
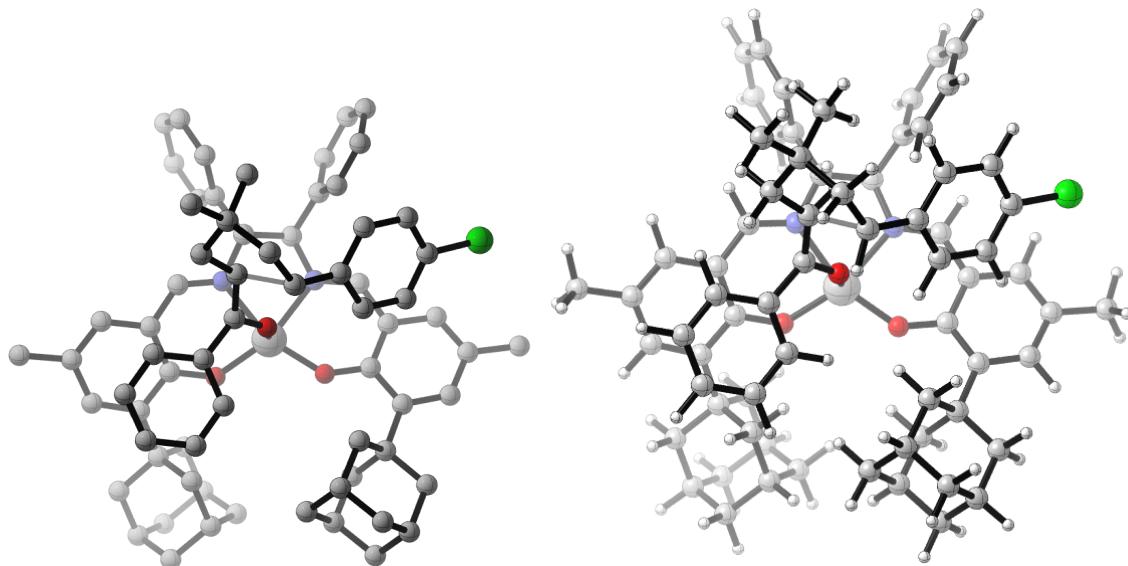


Figure SC3. TS calculations with *p*-fluorostyrene (top) and styrene (bottom).

V. Cartesian Coordinates of Transition State Structures

Major (*Trans-Re*) TS3 with *p*-chlorostyrene 2b



M06/6-31G(d)-SDD Electronic Energy = -4024.435259

M06/6-31G(d)-SDD Free Energy = -4023.238511

IEFPCM(EtOAc)M06/6-31+G(d,p) Electronic Energy = -4815.785929

IEFPCM(EtOAc)M06/6-31+G(d,p)//M06/6-31G(d)-SDD Corrected Free Energy = -4814.589181

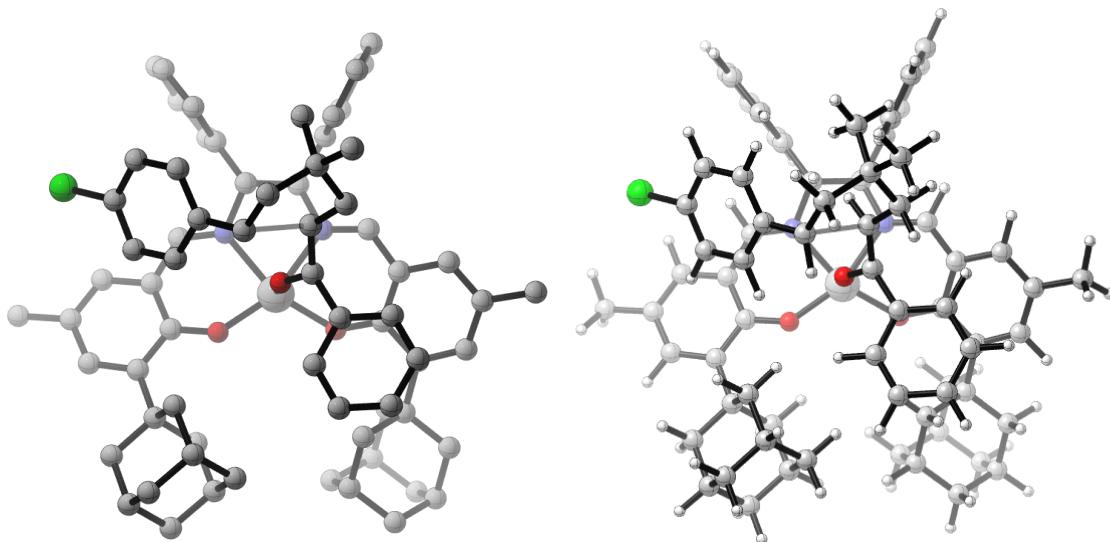
Number of imaginary frequencies = 1 (-590.93)

Ti	0.21016	-0.22771	-1.00544	C	2.75502	-5.08861	0.42518
O	0.47476	1.62467	-0.98505	C	1.44546	-4.74375	0.17564
C	-2.13099	1.43024	-2.09996	C	1.10361	-3.44241	-0.23425
N	-1.76421	0.25107	-1.72552	C	-0.27816	-3.19397	-0.53668
C	-2.61548	-0.88750	-2.09767	N	-0.79861	-2.11079	-1.01301
C	-0.16119	2.73814	-1.28464	C	-2.25534	-2.07196	-1.19253
C	0.37616	4.01177	-0.94789	H	-2.68872	-1.86059	-0.20079
C	-0.33355	5.13080	-1.37275	H	0.65063	-5.48336	0.29628
C	-1.54866	5.08255	-2.07559	C	3.14452	-6.44895	0.91963
C	-2.08642	3.83853	-2.32477	H	4.77429	-4.42520	0.30503
C	-1.42350	2.66611	-1.92392	Cl	0.65819	-0.52609	-3.31374
H	-2.33977	-1.15756	-3.13155	H	-0.94115	-4.05798	-0.38033
H	0.06026	6.12092	-1.14741	H	-3.11118	1.53884	-2.58616
C	-2.24253	6.34664	-2.48384	O	-0.42708	-0.20986	0.78648
H	-3.05700	3.75066	-2.81677	C	-0.49187	-1.02131	1.83120
O	1.75017	-1.19966	-0.59129	C	0.78862	-1.31309	2.50374
C	2.10619	-2.44896	-0.36871	C	1.73228	-0.28463	2.63176
C	3.47419	-2.82175	-0.25595	C	1.11859	-2.58598	2.98614
C	3.73823	-4.11819	0.16907	C	2.95536	-0.51278	3.24635

H	1.48902	0.70360	2.23875	H	3.37685	-1.00022	-2.27922
C	2.34951	-2.81717	3.59082	H	4.34764	-2.38923	-2.77946
H	0.42094	-3.41106	2.84442	C	7.11022	-0.36196	-0.23000
C	3.27056	-1.78274	3.72581	H	7.33648	-0.62763	0.81587
H	3.67251	0.30344	3.34119	H	7.90877	0.31784	-0.56955
H	2.59732	-3.81948	3.93880	C	6.81649	-1.22312	-2.55458
H	4.23529	-1.96578	4.19674	H	6.82632	-2.11773	-3.19823
C	-1.74521	-1.36159	2.31946	H	7.61590	-0.55591	-2.91619
C	-2.05996	-2.33326	3.41369	C	5.97547	-2.55253	-0.60804
H	-2.20447	-3.35568	3.01645	H	5.97778	-3.47138	-1.21819
H	-1.21820	-2.38811	4.12268	H	6.19293	-2.85115	0.43197
C	-3.31889	-1.90476	4.17491	C	7.08244	-1.61753	-1.10058
C	-4.55627	-2.00018	3.28219	H	8.04804	-2.14230	-1.02762
H	-4.68790	-3.03043	2.91746	C	4.09111	3.58669	0.10656
H	-5.46169	-1.73337	3.84755	C	4.42337	5.05398	0.37662
H	-4.51354	-1.33985	2.40552	C	3.23801	5.71500	1.07970
C	-3.53289	-2.80219	5.38841	C	1.99552	5.60825	0.19222
H	-3.73351	-3.84022	5.08534	C	1.63321	4.13908	-0.09750
H	-2.64818	-2.80658	6.04125	C	2.85199	3.48699	-0.78581
H	-4.39002	-2.45991	5.98668	H	4.93947	3.10560	-0.40507
C	-3.05597	-0.45051	4.63459	H	4.64137	5.57278	-0.57098
H	-2.42638	-0.49738	5.53682	H	5.32796	5.13229	1.00162
H	-4.00643	0.01089	4.95140	H	3.45559	6.77963	1.25768
C	-2.34456	0.38266	3.60646	H	1.15048	6.11087	0.69189
C	-2.99367	1.32536	2.73556	H	2.17958	6.14330	-0.75468
C	-2.21216	2.18797	1.93279	H	3.03314	3.99306	-1.74915
C	-4.39643	1.43285	2.61581	H	2.63631	2.43235	-1.01457
C	-2.78397	3.10210	1.06431	C	2.97991	5.01304	2.41481
H	-1.12478	2.11588	1.98607	H	2.14892	5.50342	2.94735
C	-4.98100	2.34607	1.75160	H	3.86909	5.09081	3.06114
C	-4.17344	3.16791	0.97118	C	3.81569	2.87196	1.43343
H	-2.15686	3.75931	0.46125	H	3.58247	1.80976	1.24543
Cl	-4.92805	4.28921	-0.14312	H	4.71478	2.89618	2.07303
H	-2.52119	6.95303	-1.61058	C	1.39388	3.45813	1.27080
H	-1.60255	6.97339	-3.12020	H	1.11158	2.40619	1.11422
H	-3.16137	6.13306	-3.04317	H	0.53983	3.95283	1.76793
H	3.57131	-6.40137	1.93202	C	2.64217	3.54491	2.15123
H	2.28111	-7.12448	0.95717	H	2.44634	3.02920	3.10601
H	3.90395	-6.91373	0.27607	C	-4.07394	-5.64712	-2.73961
C	5.45815	-0.52650	-2.64520	C	-3.00336	-5.06240	-3.41332
C	5.46514	0.72630	-1.76604	C	-2.40113	-3.91749	-2.90636
C	5.75170	0.33491	-0.31313	C	-2.86432	-3.34732	-1.71690
C	4.65219	-0.60661	0.18443	C	-3.93055	-3.94155	-1.04464
C	4.59146	-1.87827	-0.68470	C	-4.53651	-5.08648	-1.55427
C	4.36053	-1.47546	-2.16135	H	-4.54482	-6.54356	-3.13987
H	5.25002	-0.24492	-3.68848	H	-2.63542	-5.50105	-4.33946
H	4.48811	1.23421	-1.83569	H	-1.55542	-3.46322	-3.42701
H	6.22699	1.43941	-2.12366	H	-4.29651	-3.48967	-0.11998
H	5.76375	1.23601	0.32105	H	-5.37154	-5.54090	-1.02364
H	4.83847	-0.89510	1.23342	C	-6.86670	-0.28365	-1.81503
H	3.67815	-0.09549	0.16389	C	-6.03730	0.07515	-0.75482

C	-4.66241	-0.09545	-0.85453	H	-4.49891	-1.39907	-3.98468
C	-4.09948	-0.62630	-2.01980	H	-6.95378	-1.08764	-3.81208
C	-4.93461	-0.97613	-3.07840	H	-6.06420	2.43332	1.68182
C	-6.31302	-0.80849	-2.97733	H	-5.04300	0.80347	3.22607
H	-7.94417	-0.14907	-1.73533	H	-1.30086	0.61713	3.82700
H	-6.45730	0.49539	0.15856	H	-2.55755	-1.13525	1.62660
H	-4.01925	0.20685	-0.02292				

Minor (*Trans-Si*) TS3 with *p*-chlorostyrene 2b



M06/6-31G(d)-SDD Electronic Energy = -4024.434167

M06/6-31G(d)-SDD Free Energy = -4023.235727

IEFPCM(EtOAc)M06/6-31+G(d,p) Electronic Energy = -4815.78516

IEFPCM(EtOAc)M06/6-31+G(d,p)//M06/6-31G(d)-SDD Corrected Free Energy = -4814.586721

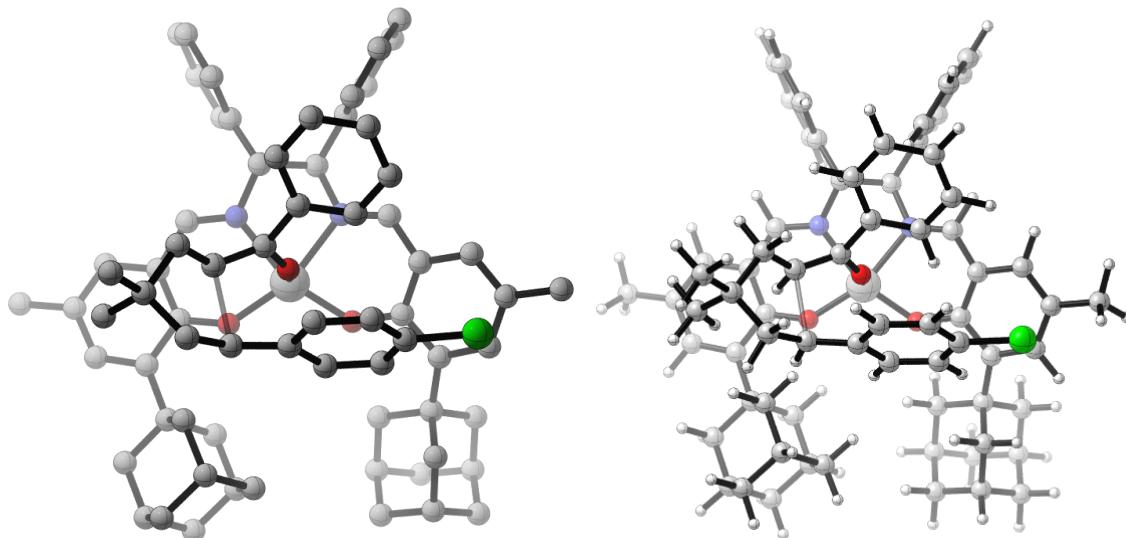
Number of imaginary frequencies = 1 (-541.49)

Ti	-0.08402	-0.00076	-1.05384	C	-2.35942	-6.63301	0.06910
O	-1.55062	-1.17770	-1.11201	H	0.01419	-5.36637	-0.47880
C	0.68168	-2.94708	-1.20033	O	-0.49332	1.78284	-0.63890
N	1.09373	-1.75241	-1.45966	C	0.01639	2.98230	-0.82625
C	2.44769	-1.51485	-1.97534	C	-0.68569	4.15293	-0.42983
C	-1.75844	-2.46280	-0.92955	C	-0.08130	5.37731	-0.69989
C	-3.07898	-2.99031	-0.85611	C	1.18198	5.52574	-1.29419
C	-3.20385	-4.33245	-0.52324	C	1.88183	4.37484	-1.58684
C	-2.12026	-5.20695	-0.32632	C	1.32707	3.10645	-1.35159
C	-0.85540	-4.70784	-0.54412	C	2.21507	1.98367	-1.46042
C	-0.65330	-3.35025	-0.85352	N	1.92777	0.74120	-1.27237
H	2.30222	-1.24032	-3.03345	C	2.99072	-0.27033	-1.25265
H	-4.20054	-4.75964	-0.41807	H	3.11820	-0.53905	-0.18806

H	2.89905	4.43724	-1.97748	C	-3.10495	3.13496	2.41632
C	1.75323	6.88650	-1.55641	C	-3.60766	4.52738	2.79898
H	-0.60076	6.29280	-0.42106	C	-3.83942	5.34310	1.52560
Cl	-0.24938	0.34923	-3.38230	C	-2.53419	5.44918	0.73459
H	3.25764	2.25289	-1.67520	C	-2.00309	4.06083	0.32866
H	1.39465	-3.77705	-1.29928	C	-1.79459	3.26002	1.63646
O	0.24716	-0.42372	0.73977	H	-2.92540	2.53999	3.32729
C	0.23466	-1.40055	1.63562	H	-2.87096	5.03162	3.44531
C	-1.08075	-1.73473	2.21237	H	-4.54398	4.45185	3.37556
C	-1.97887	-0.69890	2.51121	H	-4.17595	6.35720	1.79181
C	-1.46607	-3.05359	2.48479	H	-2.70768	6.06248	-0.16573
C	-3.20699	-0.97383	3.09805	H	-1.77982	5.97348	1.34490
H	-1.69798	0.33064	2.28197	H	-1.03301	3.77454	2.24966
C	-2.70852	-3.32818	3.04476	H	-1.39905	2.26129	1.39856
H	-0.80583	-3.87393	2.20469	C	-4.89874	4.65541	0.66410
C	-3.57790	-2.29014	3.36584	H	-5.09985	5.25223	-0.24021
H	-3.88943	-0.15578	3.33083	H	-5.84816	4.57953	1.21872
H	-2.99989	-4.36238	3.22535	C	-4.14955	2.43804	1.53937
H	-4.54726	-2.50471	3.81318	H	-3.79793	1.42966	1.26129
C	1.45084	-1.84544	2.12507	H	-5.09076	2.30885	2.10124
C	1.68546	-2.98789	3.06053	C	-3.09695	3.37768	-0.52026
H	0.80019	-3.13500	3.70022	H	-2.76072	2.37912	-0.83696
H	1.83347	-3.93671	2.50906	H	-3.25846	3.96702	-1.43842
C	2.90152	-2.72035	3.95610	C	-4.40042	3.26401	0.27381
C	3.01057	-3.79297	5.03318	H	-5.15621	2.76312	-0.35150
H	3.18884	-4.78373	4.59027	C	-5.34244	-0.68946	-2.98850
H	3.84348	-3.57943	5.71885	C	-6.62649	-1.51776	-2.93373
H	2.08991	-3.85135	5.63114	C	-6.80704	-2.07265	-1.51974
C	4.19256	-2.72950	3.13855	C	-5.60053	-2.93717	-1.14575
H	4.33650	-3.71036	2.65905	C	-4.28996	-2.12868	-1.19050
H	4.20647	-1.96381	2.35076	C	-4.14468	-1.57080	-2.62687
H	5.06357	-2.54834	3.78581	H	-5.19798	-0.29006	-4.00387
C	2.65617	-1.33603	4.60749	H	-6.57513	-2.34281	-3.66274
H	3.60854	-0.94577	5.00440	H	-7.49605	-0.89882	-3.20916
H	2.00712	-1.49401	5.48291	H	-7.71573	-2.69367	-1.47694
C	1.97836	-0.34543	3.70085	H	-5.75160	-3.34871	-0.13274
C	2.63827	0.72648	3.00757	H	-5.53545	-3.79270	-1.83919
C	4.04019	0.80803	2.85615	H	-4.07097	-2.41799	-3.32988
C	1.86660	1.75019	2.40881	H	-3.21446	-0.99323	-2.72001
C	4.63260	1.84221	2.14741	C	-6.92435	-0.91265	-0.53123
H	4.68146	0.05791	3.31788	H	-7.08926	-1.29750	0.48863
C	2.44709	2.79362	1.70720	H	-7.79456	-0.28533	-0.78468
C	3.83499	2.82688	1.57168	C	-5.43627	0.46933	-1.99110
H	5.71530	1.89718	2.04156	H	-4.51187	1.07085	-2.03294
Cl	4.60772	4.12336	0.67948	H	-6.27157	1.13679	-2.26188
H	-1.43434	-7.22131	0.02908	C	-4.44355	-0.95679	-0.19921
H	-2.75280	-6.70770	1.09367	H	-3.52375	-0.35187	-0.18584
H	-3.09318	-7.11924	-0.58821	H	-4.56966	-1.36709	0.81700
H	1.37068	7.31527	-2.49379	C	-5.64127	-0.08373	-0.57783
H	2.84711	6.84864	-1.63594	H	-5.72077	0.74685	0.14113
H	1.50050	7.59096	-0.75330	C	6.79841	1.07272	-2.73505

C	6.63872	0.75745	-1.39051	C	3.42050	-2.66488	-1.90278
C	5.40742	0.30661	-0.92534	C	3.86080	-3.17036	-0.67522
C	4.32395	0.17509	-1.79135	C	4.80366	-4.18892	-0.62501
C	4.49168	0.49585	-3.14204	H	6.06269	-5.51642	-1.76452
C	5.72260	0.93869	-3.61047	H	5.28032	-4.64343	-3.95632
H	7.75932	1.42793	-3.10361	H	3.60323	-2.82135	-4.03779
H	7.47334	0.86240	-0.69901	H	3.45221	-2.76856	0.25330
H	5.27642	0.05187	0.12771	H	5.14146	-4.56620	0.33966
H	3.64318	0.42671	-3.82621	H	1.82619	3.57113	1.26137
H	5.84160	1.18868	-4.66345	H	0.77950	1.71096	2.49483
C	5.32042	-4.72102	-1.80374	H	0.92857	-0.14822	3.93106
C	4.88299	-4.23271	-3.02969	H	2.30332	-1.52620	1.52170
C	3.93836	-3.21152	-3.07592				

Cis-Si TS3 with p-chlorostyrene 2b



M06/6-31G(d)-SDD Electronic Energy = -4024.430179

M06/6-31G(d)-SDD Free Energy = -4023.236533

IEFPCM(EtOAc)M06/6-31+G(d,p) Electronic Energy = -4815.781543

IEFPCM(EtOAc)M06/6-31+G(d,p)//M06/6-31G(d)-SDD Corrected Free Energy = -4814.587897

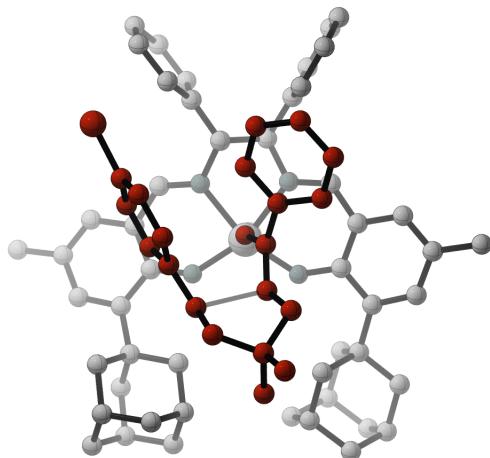
Number of imaginary frequencies = 1 (-525.94)

Ti	0.33453	0.23357	-1.08799	C	-0.85349	5.47543	-1.02490
O	-0.46872	1.89433	-0.74930	C	0.44622	5.89270	-1.35808
C	2.22661	2.63774	-1.28083	C	1.42473	4.92586	-1.43588
N	2.17082	1.35107	-1.21331	C	1.12715	3.56657	-1.23189
C	3.40248	0.55131	-1.19528	H	3.58458	0.30319	-0.13416
C	-0.20016	3.16860	-0.93389	H	-1.61240	6.25282	-0.93937
C	-1.21531	4.15453	-0.79278	C	0.73618	7.34345	-1.60121

H	2.45410	5.20850	-1.66717	C	-1.67716	-2.27519	2.47418
O	-0.88239	-1.18248	-1.14631	H	-1.98259	-0.28163	1.75055
C	-0.86942	-2.48787	-1.00214	C	-0.40865	-2.48214	4.52819
C	-2.06245	-3.25890	-0.98729	C	-1.09876	-3.05904	3.46806
C	-1.93853	-4.58593	-0.57846	H	-2.20186	-2.75066	1.64689
C	-0.72674	-5.23081	-0.29572	Cl	-1.20995	-4.80483	3.35984
C	0.43014	-4.50856	-0.50708	H	0.43904	7.96517	-0.74522
C	0.38165	-3.15374	-0.87012	H	1.80486	7.51338	-1.78057
C	1.63074	-2.51578	-1.19988	H	0.19036	7.72306	-2.47628
N	1.82041	-1.27091	-1.47157	H	-1.29381	-7.30415	-0.51312
C	3.12057	-0.77341	-1.93260	H	0.31560	-7.05372	0.18905
H	2.96443	-0.52432	-2.99562	H	-1.13485	-6.76621	1.16262
H	1.40616	-4.98550	-0.38790	C	-5.28306	-3.40045	-3.11108
C	-0.70733	-6.65922	0.15551	C	-6.27441	-3.51357	-1.94950
H	-2.84673	-5.18542	-0.48861	C	-5.88625	-2.52852	-0.84376
Cl	0.21843	0.59957	-3.42425	C	-4.48213	-2.85776	-0.32450
H	2.48959	-3.19916	-1.24663	C	-3.44122	-2.78456	-1.46176
H	3.21232	3.11068	-1.38793	C	-3.88269	-3.73800	-2.60259
O	0.79376	-0.06095	0.70575	H	-5.55831	-4.11339	-3.90396
C	1.52161	0.26672	1.75623	H	-6.27871	-4.54413	-1.55731
C	2.41283	-0.79868	2.24913	H	-7.29704	-3.29948	-2.30001
C	2.00529	-2.13621	2.12064	H	-6.60284	-2.60527	-0.01130
C	3.68755	-0.53884	2.77394	H	-4.19806	-2.14470	0.47042
C	2.82721	-3.17546	2.52948	H	-4.48324	-3.86009	0.13456
H	1.01301	-2.34057	1.72070	H	-3.87148	-4.78234	-2.25673
C	4.51553	-1.58355	3.17644	H	-3.14720	-3.66971	-3.42117
H	4.04691	0.48844	2.83712	C	-5.90067	-1.10819	-1.41118
C	4.08779	-2.90385	3.06288	H	-5.65710	-0.38463	-0.61804
H	2.47525	-4.20341	2.44010	H	-6.90955	-0.85670	-1.77807
H	5.50476	-1.36320	3.57564	C	-5.28810	-1.97680	-3.66565
H	4.73537	-3.71862	3.38368	H	-4.58484	-1.89763	-4.50996
C	1.26916	1.48621	2.36954	H	-6.28760	-1.71817	-4.05180
C	1.95826	2.06468	3.56344	C	-3.48436	-1.35243	-2.03208
H	2.34809	1.25387	4.20136	H	-2.74627	-1.24003	-2.84136
H	2.82441	2.68907	3.27680	H	-3.19986	-0.62734	-1.25460
C	0.98528	2.90733	4.39910	C	-4.88557	-1.01105	-2.55214
C	1.66059	3.37187	5.68347	H	-4.86395	0.01731	-2.94765
H	2.50296	4.04516	5.46814	C	-3.93628	2.66728	1.51603
H	0.95454	3.91806	6.32571	C	-4.82901	3.90257	1.64504
H	2.04932	2.51961	6.25970	C	-4.93950	4.58488	0.27972
C	0.51417	4.13753	3.62362	C	-3.54630	4.99125	-0.20797
H	1.36931	4.77266	3.34821	C	-2.62150	3.76771	-0.35354
H	-0.01857	3.88867	2.69561	C	-2.55006	3.08954	1.03272
H	-0.16466	4.74374	4.24079	H	-3.83973	2.16827	2.49500
C	-0.19474	1.97185	4.73034	H	-4.40590	4.60082	2.38562
H	-1.03566	2.57630	5.11496	H	-5.82959	3.61575	2.00682
H	0.11055	1.31772	5.56083	H	-5.56201	5.48901	0.36662
C	-0.63970	1.15695	3.55660	H	-3.63689	5.51063	-1.17697
C	-0.84228	-0.26815	3.59251	H	-3.10877	5.70899	0.50652
C	-1.54926	-0.89704	2.54346	H	-2.09941	3.79683	1.75256
C	-0.27966	-1.10309	4.58036	H	-1.88813	2.21317	0.97314

C	-5.56900	3.61848	-0.72380	H	4.54281	-1.87146	-3.94420
H	-5.68648	4.11061	-1.70290	H	4.28604	-1.78823	0.34799
H	-6.57684	3.32546	-0.38742	H	6.20847	-3.31949	0.49370
C	-4.54610	1.69890	0.50176	C	6.94440	2.36586	-2.83172
H	-3.91154	0.79931	0.41233	C	5.80966	2.21088	-3.62499
H	-5.53594	1.36097	0.85185	C	4.66022	1.63970	-3.09382
C	-3.28809	2.80112	-1.36047	C	4.63105	1.21833	-1.76003
H	-2.65886	1.91158	-1.51698	C	5.76815	1.38426	-0.97238
H	-3.37012	3.30640	-2.33723	C	6.92200	1.95305	-1.50441
C	-4.67519	2.38529	-0.86181	H	7.84627	2.80973	-3.25019
H	-5.12178	1.68461	-1.58476	H	5.82078	2.53606	-4.66395
C	6.46522	-3.47010	-1.64300	H	3.76725	1.53405	-3.71340
C	5.99530	-3.06325	-2.88675	H	5.75080	1.04796	0.06583
C	4.90947	-2.19695	-2.96984	H	7.80566	2.07057	-0.87949
C	4.28411	-1.72520	-1.81665	H	0.04244	-3.11359	5.29091
C	4.76519	-2.13715	-0.56909	H	0.29258	-0.66947	5.39959
C	5.84700	-3.00506	-0.48465	H	-1.24722	1.67917	2.81602
H	7.31373	-4.14906	-1.57494	H	0.72442	2.18352	1.72853
H	6.47371	-3.42049	-3.79715				

Cis-Re TS3 with p-chlorostyrene 2b



M06/6-31G(d)-SDD Electronic Energy = -4024.425542

M06/6-31G(d)-SDD Free Energy = -4023.229916

IEFPCM(EtOAc)M06/6-31+G(d,p) Electronic Energy = -4815.778015

IEFPCM(EtOAc)M06/6-31+G(d,p)//M06/6-31G(d)-SDD Corrected Free Energy = -4814.582389

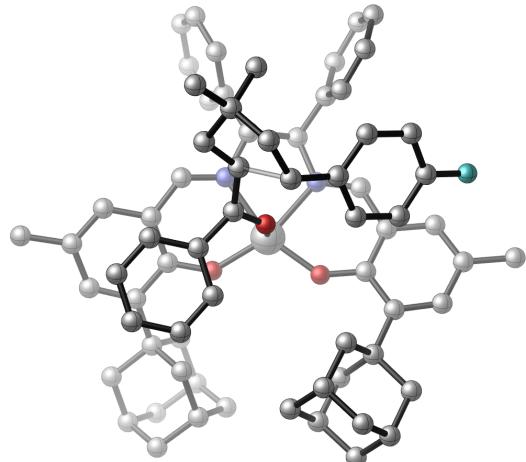
Number of imaginary frequencies = 1 (-559.88)

Ti	0.28226	-0.22961	-1.27396	N	1.82763	-1.72120	-1.46268
O	-0.92981	-1.67577	-1.19708	C	3.16470	-1.22463	-1.82408
C	1.63379	-2.96674	-1.20519	C	-0.87168	-2.96859	-0.95639

C	-2.05431	-3.75069	-0.80464	H	-3.42859	-2.25066	5.33415
C	-1.89034	-5.08678	-0.45545	C	-1.79839	0.67003	4.36916
C	-0.65139	-5.72635	-0.29650	H	-1.07926	0.53242	5.19086
C	0.47665	-4.98005	-0.55106	H	-2.52917	1.42098	4.72246
C	0.39092	-3.61659	-0.88280	C	-1.09741	1.13865	3.13258
H	3.12461	-1.02683	-2.90832	C	0.20940	1.75289	3.12598
H	-2.77538	-5.70302	-0.30622	C	0.68478	2.33711	1.93058
C	-0.58562	-7.17130	0.09738	C	1.09486	1.73188	4.22332
H	1.46417	-5.44287	-0.49232	C	1.96687	2.85148	1.82287
O	-0.52848	1.46056	-1.17772	H	0.03748	2.33953	1.05220
C	-0.26884	2.71044	-1.49264	C	2.37746	2.25349	4.13391
C	-1.24650	3.73503	-1.39375	C	2.81091	2.79903	2.93065
C	-0.86487	5.00842	-1.81270	H	2.31450	3.28975	0.88655
C	0.41094	5.35901	-2.27005	Cl	4.45324	3.40640	2.79957
C	1.37459	4.37221	-2.25014	H	-0.96929	-7.33247	1.11487
C	1.06000	3.06010	-1.86542	H	-1.18703	-7.80171	-0.57204
C	2.16217	2.14845	-1.71155	H	0.44474	-7.54649	0.07092
N	2.10151	0.90065	-1.39750	H	0.31643	7.50279	-2.01883
C	3.31199	0.12302	-1.09894	H	1.78620	6.92410	-2.82437
H	3.24039	-0.09922	-0.02208	H	0.25030	6.96884	-3.70088
H	2.40387	4.60553	-2.53092	C	-4.42879	2.13044	0.26954
C	0.70690	6.75663	-2.72382	C	-4.43767	3.00055	1.52601
H	-1.60325	5.81067	-1.76205	C	-4.07969	4.43619	1.14177
Cl	0.22382	-0.20775	-3.63180	C	-2.69036	4.45915	0.50219
H	3.15212	2.61047	-1.82941	C	-2.64216	3.58841	-0.77857
H	2.49778	-3.64351	-1.23880	C	-3.04051	2.15469	-0.37605
O	0.57215	-0.35620	0.55529	H	-4.66223	1.08967	0.54411
C	0.32783	-0.98624	1.69547	H	-3.71403	2.61419	2.26444
C	1.51364	-1.51965	2.38817	H	-5.43046	2.96561	2.00416
C	1.54138	-2.81322	2.92373	H	-4.07303	5.07399	2.03936
C	2.67425	-0.73553	2.46946	H	-2.41623	5.49812	0.26070
C	2.69703	-3.30427	3.52462	H	-1.92961	4.09627	1.21471
H	0.65655	-3.44502	2.83914	H	-2.30395	1.73314	0.32542
C	3.81907	-1.21713	3.08974	H	-3.02486	1.49934	-1.26151
H	2.65055	0.27846	2.06992	C	-5.10579	4.96835	0.13721
C	3.83722	-2.50959	3.61443	H	-4.86148	6.00806	-0.13649
H	2.70749	-4.31790	3.92279	H	-6.10891	4.98412	0.59304
H	4.69965	-0.57714	3.16103	C	-5.47270	2.65031	-0.71843
H	4.73645	-2.89496	4.09314	H	-5.50076	2.00850	-1.61324
C	-0.95381	-0.88160	2.21981	H	-6.47733	2.61772	-0.26573
C	-1.48130	-1.56524	3.44015	C	-3.72356	4.09913	-1.75861
H	-1.93930	-2.53949	3.18939	H	-3.71322	3.46917	-2.66338
H	-0.65577	-1.77201	4.14255	H	-3.49452	5.12429	-2.08747
C	-2.51476	-0.67378	4.14531	C	-5.11155	4.08266	-1.11164
C	-3.77001	-0.48844	3.29029	H	-5.84710	4.46805	-1.83473
H	-4.25987	-1.45680	3.10237	C	-4.91244	-2.00417	-2.76182
H	-4.49550	0.15623	3.80879	C	-5.96882	-3.10371	-2.64882
H	-3.56615	-0.03021	2.31142	C	-5.92701	-3.69218	-1.23783
C	-2.92159	-1.28577	5.47952	C	-4.53496	-4.25688	-0.95458
H	-2.04555	-1.45921	6.12138	C	-3.44277	-3.17324	-1.06300
H	-3.61228	-0.62532	6.02374	C	-3.52361	-2.59103	-2.49360

H	-4.92746	-1.57538	-3.77535	C	5.14200	1.00722	-2.62032
H	-5.77798	-3.89217	-3.39476	C	6.32573	1.71338	-2.80047
H	-6.97121	-2.69615	-2.85902	H	7.91457	2.81460	-1.84870
H	-6.66413	-4.50576	-1.15075	H	6.96690	2.53056	0.43800
H	-4.53102	-4.69534	0.05760	H	4.86665	1.26056	0.75476
H	-4.31932	-5.07285	-1.66434	H	4.61516	0.60135	-3.48566
H	-3.30752	-3.39471	-3.21750	H	6.73171	1.84236	-3.80248
H	-2.75471	-1.81983	-2.63582	C	6.49029	-3.82534	-0.98244
C	-6.23886	-2.60121	-0.21479	C	5.71507	-3.32485	0.06137
H	-6.23753	-3.02288	0.80446	C	4.63596	-2.49352	-0.20764
H	-7.24494	-2.18701	-0.39047	C	4.31607	-2.14960	-1.52522
C	-5.21505	-0.90615	-1.73763	C	5.09113	-2.66284	-2.56343
H	-4.46765	-0.09979	-1.82353	C	6.17500	-3.49471	-2.29573
H	-6.20160	-0.45702	-1.94133	H	7.33853	-4.47437	-0.77085
C	-3.79257	-2.06331	-0.05022	H	5.94742	-3.57962	1.09486
H	-3.04473	-1.25645	-0.11152	H	4.02956	-2.11693	0.61807
H	-3.73982	-2.48105	0.97061	H	4.84496	-2.40224	-3.59386
C	-5.18815	-1.49703	-0.32509	H	6.77390	-3.88410	-3.11730
H	-5.41040	-0.71356	0.41733	H	3.04969	2.22346	4.98917
C	6.98926	2.25947	-1.70382	H	0.78393	1.28934	5.16826
C	6.46458	2.09780	-0.42576	H	-1.74902	1.48647	2.32712
C	5.28485	1.38356	-0.24762	H	-1.69707	-0.59798	1.47055
C	4.61546	0.82960	-1.33867				

Major (*Trans*-Re) TS3 with *p*-fluorostyrene 2c



M06/6-31G(d)-SDD Electronic Energy = -3663.82935

M06/6-31G(d)-SDD Free Energy = -3662.62889

IEFPCM(EtOAc)M06/6-31+G(d,p) Electronic Energy = -4455.430505

IEFPCM(EtOAc)M06/6-31+G(d,p)//M06/6-31G(d)-SDD Corrected Free Energy = -4454.230045

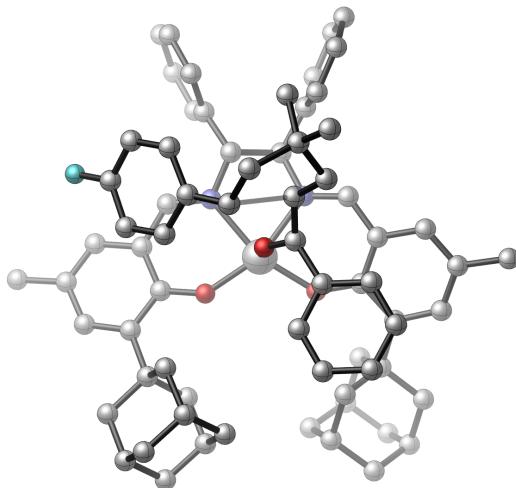
Number of imaginary frequencies = 1 (-533.11)

Ti	0.12790	-0.21100	-0.98452	N	-1.06604	-1.97964	-0.91801
O	0.58645	1.60376	-1.05207	C	-2.50595	-1.82374	-1.15124
C	-2.04233	1.64047	-2.11514	H	-2.96418	-1.58915	-0.17495
N	-1.78426	0.43834	-1.72413	H	0.01072	-5.43375	0.53398
C	-2.74229	-0.61824	-2.07363	C	2.39374	-6.65518	1.13676
C	0.05664	2.76899	-1.35676	H	4.22534	-4.83829	0.44620
C	0.72472	3.98775	-1.05653	Cl	0.52987	-0.68459	-3.27822
C	0.11173	5.16484	-1.47736	H	-1.42402	-3.86531	-0.19309
C	-1.13121	5.22562	-2.12770	H	-3.00967	1.82736	-2.60290
C	-1.79075	4.03547	-2.34616	O	-0.53602	-0.02079	0.79486
C	-1.22527	2.80967	-1.95991	C	-0.73024	-0.79186	1.85193
H	-2.49511	-0.92948	-3.10296	C	0.48738	-1.24084	2.55340
H	0.60680	6.11503	-1.28240	C	1.57211	-0.35725	2.65608
C	-1.74276	6.54542	-2.48968	C	0.62894	-2.53417	3.07036
H	-2.78641	4.03719	-2.79414	C	2.75149	-0.74880	3.27325
O	1.55526	-1.32571	-0.50409	H	1.47825	0.64570	2.23592
C	1.77822	-2.59853	-0.24303	C	1.81706	-2.93126	3.67399
C	3.09888	-3.11232	-0.13012	H	-0.18252	-3.25230	2.95443
C	3.22721	-4.42163	0.31842	C	2.88179	-2.04102	3.77862
C	2.14845	-5.27188	0.61394	H	3.58091	-0.04440	3.34515
C	0.87968	-4.78966	0.38075	H	1.91676	-3.95036	4.04613
C	0.67593	-3.47145	-0.06356	H	3.81365	-2.35447	4.24698
C	-0.66929	-3.08657	-0.38082	C	-2.03136	-0.97214	2.29205

C	-2.52316	-1.89523	3.36008	H	5.52843	-4.04096	-1.05430
H	-2.74685	-2.89937	2.95035	H	5.78900	-3.40173	0.58155
H	-1.74494	-2.03795	4.12797	C	6.81579	-2.31007	-0.97502
C	-3.78321	-1.33343	4.02982	H	7.72146	-2.92909	-0.87700
C	-4.94774	-1.27551	3.04010	C	4.38399	3.20685	0.01571
H	-5.15658	-2.27533	2.62975	C	4.87128	4.63947	0.23025
H	-5.86244	-0.92770	3.54317	C	3.76319	5.44888	0.90288
H	-4.76449	-0.59940	2.19453	C	2.51476	5.43985	0.01857
C	-4.19485	-2.21126	5.20483	C	1.99789	4.00730	-0.21967
H	-4.48934	-3.21531	4.86649	C	3.14101	3.20513	-0.87760
H	-3.37299	-2.32503	5.92627	H	5.17588	2.62007	-0.47489
H	-5.05210	-1.77511	5.73812	H	5.14122	5.09514	-0.73624
C	-3.40738	0.08318	4.53154	H	5.77987	4.64664	0.85422
H	-2.89268	-0.03195	5.49841	H	4.09224	6.49062	1.04053
H	-4.32966	0.64967	4.74412	H	1.72986	6.04466	0.50295
C	-2.49536	0.82619	3.59927	H	2.74659	5.92039	-0.94712
C	-2.90112	1.85855	2.68497	H	3.37468	3.65047	-1.85929
C	-1.90491	2.58695	1.99377	H	2.81811	2.17098	-1.06360
C	-4.24695	2.17416	2.39842	C	3.43213	4.82958	2.26265
C	-2.22318	3.56810	1.07271	H	2.65743	5.42450	2.77312
H	-0.85643	2.35215	2.18386	H	4.32446	4.83790	2.90930
C	-4.57748	3.15822	1.47461	C	4.03593	2.57546	1.36830
C	-3.56197	3.83524	0.81513	H	3.69097	1.53691	1.22263
H	-1.45089	4.12706	0.54516	H	4.93381	2.53097	2.00851
H	-2.21431	7.01947	-1.61679	C	1.69159	3.40387	1.17286
H	-0.99348	7.24842	-2.87648	H	1.30559	2.37938	1.05242
H	-2.52066	6.42950	-3.25410	H	0.89425	4.00039	1.65109
H	2.78389	-6.63391	2.16479	C	2.94142	3.39605	2.05447
H	1.47212	-7.25004	1.14735	H	2.69190	2.94399	3.02873
H	3.13212	-7.19459	0.52815	C	-4.50935	-5.23187	-2.84025
C	5.32346	-1.10658	-2.56808	C	-3.33798	-4.75055	-3.42215
C	5.45186	0.16525	-1.72537	C	-2.67823	-3.66183	-2.86569
C	5.68614	-0.20935	-0.25852	C	-3.18372	-3.04710	-1.71629
C	4.49179	-1.01687	0.25636	C	-4.35237	-3.53594	-1.13657
C	4.30747	-2.30091	-0.57829	C	-5.01632	-4.62368	-1.69721
C	4.12859	-1.91961	-2.06757	H	-5.02583	-6.08336	-3.28048
H	5.15343	-0.83647	-3.62122	H	-2.93719	-5.22553	-4.31618
H	4.53126	0.76555	-1.81983	H	-1.75631	-3.28365	-3.31310
H	6.28523	0.78658	-2.09456	H	-4.75435	-3.04167	-0.24947
H	5.78744	0.70427	0.34854	H	-5.93189	-4.99513	-1.23981
H	4.64153	-1.29327	1.31502	C	-6.92277	0.34201	-1.74990
H	3.57485	-0.40832	0.21540	C	-6.04817	0.66213	-0.71349
H	3.20271	-1.34523	-2.20919	C	-4.69251	0.38555	-0.83507
H	4.02278	-2.84448	-2.65951	C	-4.19524	-0.21864	-1.99475
C	6.96525	-1.03820	-0.14089	C	-5.07443	-0.52870	-3.02932
H	7.15365	-1.29591	0.91441	C	-6.43348	-0.25032	-2.90891
H	7.83230	-0.45397	-0.49002	H	-7.98560	0.55815	-1.65398
C	6.60222	-1.93536	-2.44267	H	-6.42112	1.13001	0.19754
H	6.52506	-2.84577	-3.05916	H	-4.00571	0.65908	-0.02827
H	7.46897	-1.36545	-2.81561	H	-4.69047	-1.01253	-3.92852
C	5.61418	-3.11034	-0.46859	H	-7.11061	-0.49993	-3.72400

H	-5.61316	3.41386	1.25850	H	-2.77412	-0.63315	1.56819
H	-5.04998	1.64889	2.91595	F	-3.87968	4.77583	-0.08684
H	-1.45108	0.88668	3.91316				

Minor (*Trans*-Si) TS3 with *p*-fluorostyrene 2c



M06/6-31G(d)-SDD Electronic Energy = -3663.829644

M06/6-31G(d)-SDD Free Energy = -3662.624012

IEFPCM(EtOAc)M06/6-31+G(d,p) Electronic Energy = -4455.431603

IEFPCM(EtOAc)M06/6-31+G(d,p)//M06/6-31G(d)-SDD Corrected Free Energy = -4454.225971

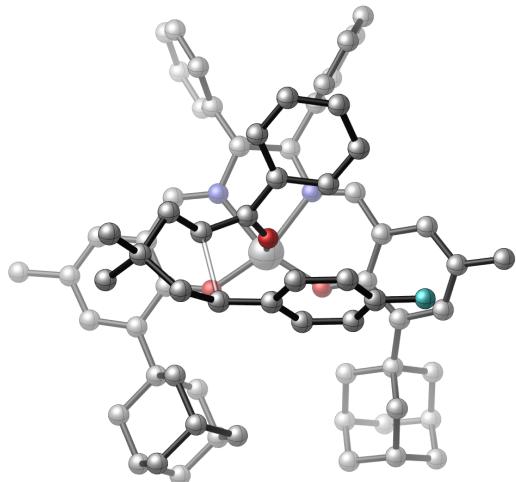
Number of imaginary frequencies = 1 (-520.22)

Ti	-0.01227	0.06605	-0.92181	C	-0.81209	5.38715	-0.65943
O	-1.31863	-1.28723	-0.93916	C	0.41415	5.71426	-1.26312
C	1.11682	-2.75614	-1.11507	C	1.29173	4.68279	-1.51740
N	1.37117	-1.51256	-1.34875	C	0.94359	3.34787	-1.24811
C	2.66670	-1.09418	-1.88677	C	1.98160	2.36046	-1.35750
C	-1.36577	-2.59863	-0.85925	N	1.87091	1.08691	-1.18297
C	-2.60752	-3.29427	-0.88138	C	3.05931	0.23083	-1.19834
C	-2.56801	-4.66150	-0.64090	H	3.28462	0.00064	-0.14058
C	-1.38753	-5.39956	-0.44213	H	2.28692	4.89606	-1.91136
C	-0.19167	-4.72951	-0.57728	C	0.74711	7.14067	-1.58197
C	-0.15823	-3.34079	-0.80103	H	-1.47148	6.21712	-0.40774
H	2.46691	-0.85284	-2.94431	Cl	-0.26442	0.37610	-3.25812
H	-3.50329	-5.21937	-0.61738	H	2.97690	2.77255	-1.57357
C	-1.45335	-6.86727	-0.14518	H	1.93048	-3.48463	-1.23266
H	0.75313	-5.27527	-0.51980	O	0.44855	-0.30471	0.86301
O	-0.65973	1.77937	-0.51664	C	0.55768	-1.28285	1.74910
C	-0.33582	3.03666	-0.72456	C	-0.71086	-1.80316	2.28765
C	-1.21458	4.09244	-0.35432	C	-1.77194	-0.90913	2.49064

C	-0.90611	-3.15583	2.59290	H	-2.59363	5.74111	1.40203
C	-2.98136	-1.34920	3.00872	H	-1.52097	3.70638	2.33228
H	-1.62562	0.14231	2.23805	H	-1.61556	2.14680	1.49545
C	-2.12561	-3.59820	3.09254	C	-5.45970	3.93443	0.72750
H	-0.11399	-3.87517	2.38692	H	-5.75296	4.48693	-0.17981
C	-3.16417	-2.69769	3.31029	H	-6.38599	3.70921	1.28099
H	-3.79291	-0.63647	3.16133	C	-4.36766	1.86770	1.61316
H	-2.26838	-4.65772	3.30216	H	-3.85414	0.92872	1.34185
H	-4.11779	-3.04653	3.70384	H	-5.27641	1.58774	2.17386
C	1.81654	-1.57516	2.23799	C	-3.47274	2.95360	-0.44620
C	2.20613	-2.63313	3.21993	H	-2.97955	2.01935	-0.75634
H	1.36715	-2.83513	3.90603	H	-3.72242	3.50512	-1.36844
H	2.43894	-3.59332	2.72091	C	-4.74445	2.63887	0.34473
C	3.42490	-2.18505	4.03740	H	-5.40994	2.02459	-0.28059
C	3.70101	-3.18293	5.15648	C	-5.01113	-1.19886	-3.06444
H	3.96487	-4.17080	4.75153	C	-6.16821	-2.19477	-3.15089
H	4.53650	-2.84790	5.78844	C	-6.37169	-2.84675	-1.78239
H	2.82058	-3.30753	5.80286	C	-5.08793	-3.56038	-1.35258
C	4.67215	-2.10398	3.15637	C	-3.90130	-2.58198	-1.25497
H	4.89847	-3.09031	2.72267	C	-3.73295	-1.92834	-2.64825
H	4.57221	-1.39015	2.32683	H	-4.84881	-0.72764	-4.04574
H	5.54526	-1.79621	3.75050	H	-5.94996	-2.96385	-3.90972
C	3.07515	-0.79865	4.63879	H	-7.09283	-1.68390	-3.46610
H	4.00733	-0.26454	4.88706	H	-7.18590	-3.58630	-1.83980
H	2.56274	-0.97249	5.59825	H	-5.25619	-4.04466	-0.37527
C	2.17172	0.04376	3.78266	H	-4.85592	-4.35941	-2.07675
C	2.57821	1.19002	3.02067	H	-3.49150	-2.71646	-3.38171
C	3.91526	1.43220	2.63496	H	-2.88826	-1.22600	-2.64358
C	1.60054	2.11429	2.58302	C	-6.72042	-1.77132	-0.75352
C	4.25428	2.52394	1.84685	H	-6.90362	-2.23209	0.23107
H	4.70407	0.75668	2.96661	H	-7.64787	-1.25210	-1.04566
C	1.93060	3.21947	1.81971	C	-5.33863	-0.12179	-2.02615
C	3.25628	3.40025	1.44557	H	-4.50702	0.60107	-1.96832
H	5.28269	2.71632	1.54654	H	-6.23746	0.44100	-2.33007
H	-0.45894	-7.32930	-0.17935	C	-4.28600	-1.49825	-0.22729
H	-1.87116	-7.05796	0.85405	H	-3.46338	-0.77502	-0.11756
H	-2.09320	-7.39855	-0.86301	H	-4.42624	-1.96984	0.76115
H	0.17060	7.50645	-2.44355	C	-5.56387	-0.77568	-0.65947
H	1.81016	7.25833	-1.82478	H	-5.80572	-0.00535	0.09026
H	0.52043	7.80719	-0.73892	C	6.64886	1.65415	-3.08929
C	-3.45403	2.72868	2.49058	C	6.67102	1.25596	-1.75724
C	-4.17393	4.02454	2.86476	C	5.49817	0.83121	-1.14035
C	-4.52693	4.78787	1.58617	C	4.29702	0.79667	-1.84553
C	-3.25269	5.09758	0.79477	C	4.28214	1.20274	-3.18398
C	-2.50564	3.80833	0.40151	C	5.45143	1.63013	-3.80081
C	-2.17754	3.06456	1.71798	H	7.56499	1.98600	-3.57516
H	-3.18650	2.17229	3.40430	H	7.60402	1.27132	-1.19632
H	-3.52960	4.64207	3.51148	H	5.51073	0.50221	-0.09948
H	-5.08975	3.80429	3.43703	H	3.34341	1.18735	-3.74272
H	-5.02200	5.73663	1.84554	H	5.42935	1.94399	-4.84309
H	-3.51986	5.66840	-0.11055	C	6.07535	-3.72056	-1.71102

C	5.63113	-3.22284	-2.93092	H	3.71272	-2.36015	0.31694
C	4.50188	-2.41214	-2.98304	H	5.72093	-3.79934	0.41274
C	3.80638	-2.08066	-1.82081	H	1.18179	3.94066	1.49699
C	4.25609	-2.59428	-0.60033	H	0.55855	1.94728	2.86197
C	5.38038	-3.40880	-0.54549	H	1.12159	0.05422	4.08568
H	6.96047	-4.35296	-1.66766	H	2.62297	-1.15136	1.63706
H	6.16660	-3.46351	-3.84770	F	3.58077	4.44746	0.67268
H	4.16428	-2.00929	-3.93857				

cis-Si TS3 with *p*-fluorostyrene 2c



M06/6-31G(d)-SDD Electronic Energy = -3663.825452

M06/6-31G(d)-SDD Free Energy = -3662.62604

IEFPCM(EtOAc)M06/6-31+G(d,p) Electronic Energy = -4455.431603

IEFPCM(EtOAc)M06/6-31+G(d,p)//M06/6-31G(d)-SDD Corrected Free Energy = -4454.225971

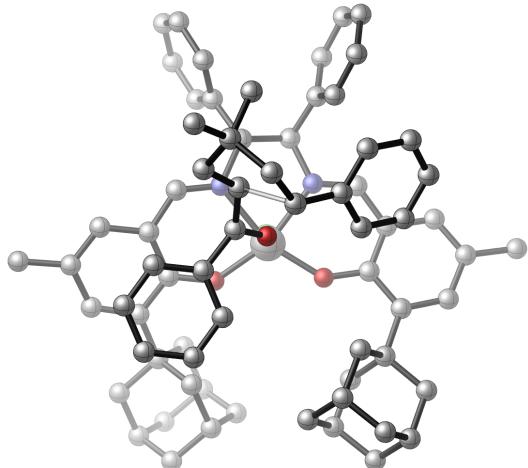
Number of imaginary frequencies = 1 (-498.12)

Ti	0.29827	0.08854	-1.07900	H	2.45567	5.04176	-1.74814
O	-0.49845	1.76174	-0.81021	O	-0.92576	-1.32282	-1.06029
C	2.20531	2.47329	-1.34686	C	-0.90643	-2.59638	-0.74245
N	2.13925	1.18771	-1.26312	C	-2.09612	-3.36259	-0.63057
C	3.36807	0.38312	-1.23531	C	-1.97456	-4.61083	-0.02155
C	-0.22081	3.02942	-1.02304	C	-0.76446	-5.18787	0.38682
C	-1.23565	4.02090	-0.92571	C	0.39415	-4.51251	0.05568
C	-0.86210	5.33648	-1.16826	C	0.34695	-3.23276	-0.51743
C	0.44770	5.74150	-1.47713	C	1.59351	-2.64820	-0.94896
C	1.42162	4.76783	-1.52734	N	1.77758	-1.44387	-1.36571
C	1.11328	3.41285	-1.30968	C	3.06643	-0.98309	-1.88850
H	3.57785	0.19144	-0.16817	H	2.88670	-0.79701	-2.96060
H	-1.61956	6.11821	-1.11232	H	1.36962	-4.96583	0.24924
C	0.75138	7.18779	-1.73027	C	-0.74448	-6.48867	1.12999

H	-2.88159	-5.19493	0.14802	C	-4.53242	-2.92859	-0.06943
Cl	0.17524	0.33837	-3.42929	C	-3.46744	-2.96373	-1.18573
H	2.44861	-3.33831	-0.93612	C	-3.86771	-4.04711	-2.22043
H	3.19465	2.93671	-1.46449	H	-5.50847	-4.59342	-3.50536
O	0.77490	-0.12731	0.72762	H	-6.27574	-4.77240	-1.14050
C	1.52648	0.30870	1.72160	H	-7.29423	-3.63636	-2.04105
C	2.44679	-0.68986	2.29366	H	-6.66276	-2.67744	0.17134
C	2.07630	-2.04494	2.27995	H	-4.27333	-2.13059	0.64973
C	3.72040	-0.35534	2.77973	H	-4.53228	-3.87452	0.49610
C	2.93193	-3.02293	2.76437	H	-3.84315	-5.04439	-1.75541
H	1.09419	-2.31416	1.89216	H	-3.11574	-4.05820	-3.02672
C	4.58076	-1.33950	3.25817	C	-5.95160	-1.33537	-1.37373
H	4.05538	0.68120	2.74836	H	-5.73816	-0.52304	-0.66239
C	4.18890	-2.67574	3.26027	H	-6.95523	-1.14511	-1.78872
H	2.61073	-4.06460	2.76011	C	-5.27491	-2.43954	-3.50228
H	5.56760	-1.05926	3.62430	H	-4.55437	-2.44383	-4.33557
H	4.86212	-3.44300	3.64005	H	-6.26991	-2.24447	-3.93452
C	1.27761	1.58155	2.21389	C	-3.51719	-1.60502	-1.91470
C	1.99694	2.30039	3.30900	H	-2.76513	-1.57455	-2.71794
H	2.46282	1.57470	3.99591	H	-3.25367	-0.79191	-1.22088
H	2.81215	2.93548	2.91558	C	-4.91195	-1.34730	-2.49602
C	1.02635	3.17134	4.11754	H	-4.89895	-0.36961	-3.00391
C	1.74555	3.79861	5.30520	C	-4.00860	2.61095	1.36510
H	2.52607	4.49754	4.97091	C	-4.91345	3.84228	1.41877
H	1.04459	4.36267	5.93762	C	-4.99208	4.46813	0.02418
H	2.22445	3.03319	5.93312	C	-3.58797	4.86641	-0.44041
C	0.43805	4.28921	3.25734	C	-2.65272	3.64490	-0.51351
H	1.23591	4.92803	2.84999	C	-2.61358	3.02309	0.90048
H	-0.14616	3.91527	2.40668	H	-3.93451	2.15336	2.36587
H	-0.22604	4.92699	3.85877	H	-4.51605	4.57310	2.14200
C	-0.07221	2.20968	4.60844	H	-5.92159	3.56217	1.76464
H	-0.90295	2.79885	5.03780	H	-5.62282	5.37019	0.05827
H	0.34247	1.61902	5.43907	H	-3.65209	5.34954	-1.43012
C	-0.57445	1.31550	3.51955	H	-3.17640	5.61263	0.26015
C	-0.79560	-0.10187	3.66286	H	-2.18714	3.76301	1.60152
C	-1.52788	-0.79290	2.67062	H	-1.94444	2.14986	0.89424
C	-0.23928	-0.87231	4.70525	C	-5.58970	3.45594	-0.95395
C	-1.70227	-2.16723	2.71764	H	-5.68695	3.90633	-1.95502
H	-1.94837	-0.23330	1.83069	H	-6.60325	3.16889	-0.62974
C	-0.41505	-2.24693	4.76858	C	-4.58145	1.59681	0.37499
C	-1.14137	-2.87710	3.76968	H	-3.93273	0.70374	0.33892
H	-2.24278	-2.70402	1.93943	H	-5.57586	1.25993	0.71301
H	0.45430	7.81862	-0.88090	C	-3.28806	2.63650	-1.49952
H	1.82251	7.34756	-1.90424	H	-2.64979	1.74751	-1.60980
H	0.21381	7.56497	-2.61143	H	-3.35133	3.10486	-2.49589
H	-0.96419	-6.32865	2.19509	C	-4.68278	2.22651	-1.01821
H	-1.49385	-7.19194	0.74367	H	-5.10358	1.49133	-1.72263
H	0.23756	-6.97388	1.06475	C	6.44018	-3.63361	-1.51611
C	-5.26142	-3.79244	-2.79116	C	5.94634	-3.29445	-2.77087
C	-6.27738	-3.79242	-1.64603	C	4.84790	-2.44715	-2.87992
C	-5.92916	-2.68235	-0.64974	C	4.23353	-1.92630	-1.74203

C	4.73904	-2.27036	-0.48356	C	6.88801	1.73341	-1.70151
C	5.83305	-3.12006	-0.37258	H	7.76859	2.51370	-3.50475
H	7.29887	-4.29730	-1.42820	H	5.70147	2.20695	-4.84865
H	6.41645	-3.68930	-3.66998	H	3.66622	1.26108	-3.80248
H	4.46408	-2.17422	-3.86372	H	5.75317	0.90214	-0.06498
H	4.27097	-1.87903	0.42180	H	7.79049	1.86629	-1.10729
H	6.21216	-3.37962	0.61511	H	0.01604	-2.83938	5.57257
C	6.87548	2.09467	-3.04397	H	0.35271	-0.39038	5.48201
C	5.71674	1.92151	-3.79811	H	-1.20410	1.79442	2.76767
C	4.57744	1.38333	-3.21325	H	0.69194	2.19833	1.52787
C	4.58361	1.01475	-1.86389	F	-1.30384	-4.20834	3.82096
C	5.74465	1.19827	-1.11555				

Major (*Trans*-Re) TS3 with styrene



M06/6-31G(d)-SDD Electronic Energy = -3564.863617

M06/6-31G(d)-SDD Free Energy = -3563.658198

IEFPCM(EtOAc)M06/6-31+G(d,p) Electronic Energy = -4356.212846

IEFPCM(EtOAc)M06/6-31+G(d,p)//M06/6-31G(d)-SDD Corrected Free Energy = -4355.007426

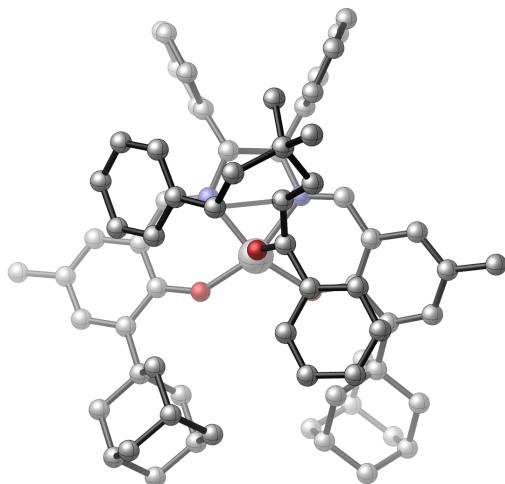
Number of imaginary frequencies = 1 (-543.97)

Ti	0.06383	-0.14957	-1.00626	N	-1.27149	-1.81704	-1.00514
O	0.66353	1.62657	-1.01819	C	-2.69624	-1.51723	-1.18894
C	-1.91167	1.88542	-2.17900	H	-3.09004	-1.24380	-0.19558
N	-1.77624	0.67260	-1.75958	H	-0.47902	-5.39627	0.30611
C	-2.84101	-0.28372	-2.09148	C	1.79056	-6.82208	0.89944
C	0.25817	2.82592	-1.37251	H	3.76959	-5.12403	0.32052
C	1.02383	3.98540	-1.06178	Cl	0.49279	-0.55825	-3.30234
C	0.55125	5.20159	-1.54155	H	-1.77454	-3.69658	-0.35158
C	-0.64145	5.36042	-2.26908	H	-2.85180	2.15420	-2.68220
C	-1.40804	4.23599	-2.48213	O	-0.59896	0.03231	0.76650
C	-0.98671	2.97220	-2.03326	C	-0.85212	-0.72950	1.81879
H	-2.66157	-0.60633	-3.13159	C	0.32873	-1.27778	2.51435
H	1.12363	6.10558	-1.33798	C	1.45974	-0.46332	2.66704
C	-1.05671	6.71542	-2.75819	C	0.38578	-2.59594	2.98215
H	-2.36893	4.31743	-2.99487	C	2.60339	-0.94515	3.28838
O	1.38956	-1.38467	-0.54816	H	1.42775	0.55849	2.28545
C	1.51595	-2.67928	-0.33213	C	1.53970	-3.08518	3.58478
C	2.79129	-3.29819	-0.21393	H	-0.46765	-3.25703	2.83220
C	2.80880	-4.62899	0.18784	C	2.65048	-2.26198	3.74303
C	1.66261	-5.40377	0.43121	H	3.47046	-0.29313	3.40075
C	0.44020	-4.81715	0.19236	H	1.57466	-4.12240	3.91636
C	0.34707	-3.47211	-0.20592	H	3.55482	-2.64649	4.21247
C	-0.96259	-2.97222	-0.51420	C	-2.15625	-0.78835	2.28617

C	-2.69741	-1.67389	3.36422	H	5.18380	-4.37675	-1.08594
H	-3.03419	-2.64643	2.95747	H	5.43049	-3.79968	0.57546
H	-1.90801	-1.89795	4.10022	C	6.58556	-2.74467	-0.91548
C	-3.86886	-0.99905	4.08685	H	7.44085	-3.42968	-0.80475
C	-5.06302	-0.82377	3.14717	C	4.56015	2.91693	0.15338
H	-5.39359	-1.79919	2.75803	C	5.14924	4.30792	0.38711
H	-5.91350	-0.37991	3.68599	C	4.08471	5.20252	1.02140
H	-4.85015	-0.17575	2.28602	C	2.87586	5.29045	0.08727
C	-4.31378	-1.84211	5.27560	C	2.25646	3.90295	-0.16832
H	-4.71031	-2.81384	4.94689	C	3.35377	3.00888	-0.78517
H	-3.47852	-2.03367	5.96450	H	5.32228	2.26911	-0.30644
H	-5.10749	-1.33392	5.84242	H	5.48888	4.73961	-0.56838
C	-3.33316	0.36863	4.57710	H	6.03201	4.24393	1.04386
H	-2.77873	0.19275	5.51237	H	4.49051	6.21489	1.17324
H	-4.18337	1.01827	4.84429	H	2.12147	5.95960	0.53419
C	-2.40871	1.03189	3.59769	H	3.18780	5.74399	-0.86894
C	-2.78274	2.09485	2.70370	H	3.65712	3.42838	-1.75925
C	-1.77795	2.73569	1.94462	H	2.95152	2.00330	-0.97947
C	-4.11317	2.52554	2.51071	C	3.65482	4.61294	2.36570
C	-2.08243	3.73865	1.04085	H	2.91030	5.26792	2.84676
H	-0.74420	2.41062	2.06929	H	4.51969	4.55357	3.04614
C	-4.41294	3.53794	1.60820	C	4.11347	2.31722	1.49026
C	-3.40611	4.14384	0.85778	H	3.69461	1.30901	1.32685
H	-1.28106	4.21387	0.47348	H	4.98047	2.20264	2.16319
H	-1.10316	7.44648	-1.93918	C	1.84907	3.33026	1.20961
H	-0.34876	7.11207	-3.49934	H	1.38484	2.34106	1.07536
H	-2.04530	6.68283	-3.23208	H	1.08477	3.99100	1.65613
H	2.23884	-6.87730	1.90198	C	3.06136	3.22205	2.13780
H	0.81284	-7.31703	0.94810	H	2.74068	2.79192	3.10112
H	2.43113	-7.41538	0.23246	C	-5.12661	-4.67102	-2.81114
C	5.23538	-1.40126	-2.52447	C	-3.93937	-4.30911	-3.44482
C	5.42364	-0.16270	-1.64370	C	-3.14040	-3.30640	-2.90941
C	5.58186	-0.58850	-0.18056	C	-3.52155	-2.65744	-1.73135
C	4.31865	-1.32281	0.27429	C	-4.70617	-3.02957	-1.09908
C	4.07065	-2.56786	-0.60196	C	-5.50937	-4.03076	-1.63781
C	3.97043	-2.14009	-2.08498	H	-5.75293	-5.45483	-3.23406
H	5.12250	-1.09390	-3.57502	H	-3.63528	-4.81109	-4.36189
H	4.55146	0.50391	-1.75292	H	-2.20662	-3.02421	-3.40028
H	6.31052	0.40701	-1.96917	H	-5.00902	-2.50833	-0.18837
H	5.72487	0.30129	0.45293	H	-6.43600	-4.30934	-1.13870
H	4.41427	-1.64035	1.32700	C	-6.90235	1.06347	-1.64548
H	3.45166	-0.64700	0.22823	C	-5.97294	1.30096	-0.63498
H	3.09044	-1.50085	-2.24043	C	-4.65143	0.90165	-0.79157
H	3.82111	-3.04105	-2.70372	C	-4.24507	0.25633	-1.96457
C	6.79540	-1.50704	-0.04271	C	-5.17825	0.03076	-2.97441
H	6.92775	-1.80300	1.01097	C	-6.50244	0.43013	-2.81682
H	7.71295	-0.97752	-0.34714	H	-7.93770	1.37639	-1.51969
C	6.44894	-2.31993	-2.37845	H	-6.27045	1.80509	0.28425
H	6.33068	-3.20740	-3.02132	H	-3.92647	1.10860	0.00227
H	7.36461	-1.80234	-2.70844	H	-4.86612	-0.48517	-3.88365
C	5.31345	-3.47026	-0.47129	H	-7.22265	0.24437	-3.61189

H	-5.44702	3.86313	1.49092	H	-2.88514	-0.38079	1.58361
H	-4.91662	2.06893	3.08952	H	-3.64260	4.93309	0.14544
H	-1.34925	1.01582	3.86318				

Minor (*Trans-Si*) TS3 with styrene



M06/6-31G(d)-SDD Electronic Energy = -3564.863889

M06/6-31G(d)-SDD Free Energy = -3563.654687

IEFPCM(EtOAc)M06/6-31+G(d,p) Electronic Energy = -4356.213541

IEFPCM(EtOAc)M06/6-31+G(d,p)//M06/6-31G(d)-SDD Corrected Free Energy = -4355.004339

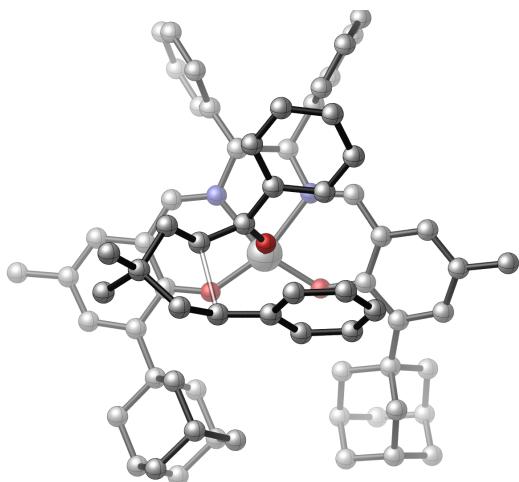
Number of imaginary frequencies = 1 (-528.80)

Ti	0.05977	0.18294	-0.96188	C	0.22260	5.85409	-1.02140
O	-1.17242	-1.22889	-1.12719	C	1.15283	4.87662	-1.29920
C	1.34744	-2.55775	-1.22744	C	0.86075	3.51578	-1.10299
N	1.54064	-1.29685	-1.41969	C	1.94968	2.58722	-1.23066
C	2.82703	-0.78885	-1.90167	N	1.90028	1.30500	-1.10837
C	-1.14398	-2.53599	-0.98961	C	3.13294	0.51178	-1.12990
C	-2.34528	-3.30020	-0.95926	H	3.33531	0.24268	-0.07589
C	-2.22585	-4.64557	-0.63936	H	2.14384	5.15252	-1.66687
C	-1.00321	-5.30977	-0.43623	C	0.49336	7.30801	-1.26597
C	0.15081	-4.58644	-0.63818	H	-1.70601	6.22733	-0.20107
C	0.10370	-3.20881	-0.91892	Cl	-0.13372	0.62720	-3.28057
H	2.63965	-0.49811	-2.94888	H	2.92643	3.05590	-1.40876
H	-3.13011	-5.24715	-0.55634	H	2.19814	-3.24130	-1.35304
C	-0.98162	-6.75465	-0.03918	O	0.43426	-0.28271	0.80769
H	1.12613	-5.07448	-0.56781	C	0.59172	-1.28717	1.66042
O	-0.68182	1.83938	-0.48764	C	-0.64828	-1.89316	2.17739
C	-0.41394	3.11898	-0.62932	C	-1.75408	-1.06705	2.42804
C	-1.35140	4.11637	-0.23675	C	-0.76736	-3.26566	2.43371
C	-1.00193	5.44100	-0.46954	C	-2.92726	-1.59338	2.95128

H	-1.67454	0.00034	2.21436	H	-1.72418	2.06161	1.50650
C	-1.95276	-3.79390	2.93142	C	-5.61237	3.74012	0.71672
H	0.05987	-3.93206	2.19242	H	-5.90346	4.32322	-0.17214
C	-3.03356	-2.96016	3.20208	H	-6.54346	3.45493	1.23318
H	-3.77279	-0.93451	3.15239	C	-4.46355	1.67989	1.53972
H	-2.03331	-4.86714	3.10193	H	-3.90793	0.77533	1.23911
H	-3.95980	-3.37309	3.59892	H	-5.37546	1.34099	2.06112
C	1.86097	-1.52248	2.15538	C	-3.55814	2.89381	-0.44415
C	2.29861	-2.61924	3.07364	H	-3.01998	1.99613	-0.78286
H	1.46083	-2.91495	3.72583	H	-3.80517	3.47761	-1.34698
H	2.59379	-3.52707	2.51227	C	-4.83646	2.49197	0.29575
C	3.47224	-2.15988	3.94791	H	-5.45969	1.87943	-0.37429
C	3.77788	-3.20883	5.01133	C	-4.90024	-1.41406	-3.16513
H	4.11606	-4.15111	4.55599	C	-5.99211	-2.48377	-3.20910
H	4.57163	-2.86284	5.68959	C	-6.13948	-3.11022	-1.82175
H	2.88913	-3.42880	5.62006	C	-4.80923	-3.73296	-1.39039
C	4.73354	-1.95544	3.10889	C	-3.68558	-2.67968	-1.33660
H	5.02833	-2.89942	2.62486	C	-3.57411	-2.05223	-2.74718
H	4.61319	-1.19834	2.32173	H	-4.77982	-0.96080	-4.16084
H	5.57229	-1.63531	3.74447	H	-5.73231	-3.25789	-3.94955
C	3.03135	-0.83540	4.62294	H	-6.95086	-2.04212	-3.52677
H	3.92551	-0.26701	4.92813	H	-6.90818	-3.89853	-1.84958
H	2.50609	-1.09586	5.55555	H	-4.93506	-4.19755	-0.39711
C	2.10199	0.00549	3.79305	H	-4.53474	-4.53735	-2.09369
C	2.46026	1.21732	3.11161	H	-3.29034	-2.84126	-3.46442
C	3.79064	1.56858	2.79371	H	-2.77451	-1.29883	-2.76568
C	1.43944	2.10297	2.69541	C	-6.54146	-2.03037	-0.81735
C	4.07677	2.74059	2.10531	H	-6.68461	-2.47426	0.18155
H	4.61052	0.92294	3.11105	H	-7.50292	-1.57845	-1.11142
C	1.72950	3.27621	2.02204	C	-5.28138	-0.33155	-2.15058
C	3.05297	3.60407	1.71663	H	-4.49665	0.44382	-2.12331
H	5.11353	2.99315	1.88158	H	-6.21773	0.16462	-2.45665
H	0.02993	-7.17436	-0.10420	C	-4.12460	-1.59641	-0.33096
H	-1.32799	-6.89084	0.99639	H	-3.34527	-0.82360	-0.24561
H	-1.63818	-7.36353	-0.67555	H	-4.22740	-2.05305	0.66869
H	-0.09432	7.69044	-2.11255	C	-5.44864	-0.96267	-0.76524
H	1.55116	7.48577	-1.49583	H	-5.73172	-0.18994	-0.03343
H	0.23220	7.92151	-0.39296	C	6.68512	2.26799	-2.80730
C	-3.60617	2.53212	2.47952	C	6.67669	1.83362	-1.48657
C	-4.38516	3.78149	2.89159	C	5.51610	1.29506	-0.93876
C	-4.73694	4.58750	1.63945	C	4.35763	1.17909	-1.70395
C	-3.45641	4.98278	0.89958	C	4.37283	1.62332	-3.03065
C	-2.64838	3.74280	0.46878	C	5.52891	2.16605	-3.57748
C	-2.32424	2.94849	1.75660	H	7.59261	2.68825	-3.23793
H	-3.34040	1.94461	3.37392	H	7.57719	1.90980	-0.87935
H	-3.78062	4.39401	3.58007	H	5.50547	0.94878	0.09619
H	-5.30469	3.50086	3.43047	H	3.46544	1.55305	-3.63480
H	-5.27668	5.50304	1.92773	H	5.52881	2.50869	-4.61090
H	-3.72363	5.58299	0.01345	C	6.30353	-3.32983	-1.80385
H	-2.83881	5.62301	1.55202	C	5.84761	-2.80602	-3.00828
H	-1.70586	3.58238	2.41723	C	4.70473	-2.01284	-3.03488

C	4.00538	-1.72904	-1.86274	H	5.95917	-3.46934	0.31909
C	4.46898	-2.26597	-0.65773	H	0.91878	3.94269	1.72432
C	5.60813	-3.06088	-0.62782	H	0.40277	1.84817	2.92451
H	7.19885	-3.94883	-1.78022	H	1.04749	-0.05623	4.07431
H	6.38410	-3.01217	-3.93287	H	2.64724	-1.01992	1.58919
H	4.35640	-1.59017	-3.97795	H	3.28262	4.53029	1.19079
H	3.92326	-2.06718	0.26630				

cis-Re TS3 with styrene



M06/6-31G(d)-SDD Electronic Energy = -3564.858761

M06/6-31G(d)-SDD Free Energy = -3563.655059

IEFPCM(EtOAc)M06/6-31+G(d,p) Electronic Energy = -4356.209063

IEFPCM(EtOAc)M06/6-31+G(d,p)//M06/6-31G(d)-SDD Corrected Free Energy = -4355.005361

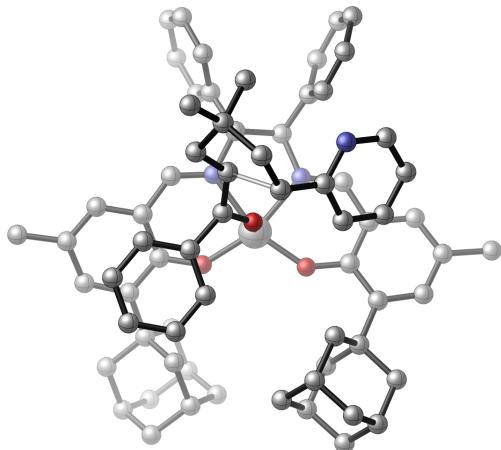
Number of imaginary frequencies = 1 (-517.18)

Ti	0.26475	-0.08089	-1.00250	O	-0.87822	-1.53788	-0.79174
O	-0.62244	1.56760	-0.91170	C	-0.80185	-2.78752	-0.40551
C	2.04381	2.34725	-1.54534	C	-1.96008	-3.59318	-0.24994
N	2.03987	1.07251	-1.34777	C	-1.78251	-4.81515	0.39512
C	3.30852	0.33601	-1.25757	C	-0.54356	-5.33334	0.79960
C	-0.40342	2.82276	-1.23711	C	0.58365	-4.61515	0.45139
C	-1.45694	3.77931	-1.20760	C	0.47911	-3.35781	-0.16269
C	-1.13944	5.08362	-1.56624	C	1.69159	-2.74449	-0.64694
C	0.14845	5.51402	-1.92701	N	1.81020	-1.57075	-1.16448
C	1.16077	4.57960	-1.90762	C	3.06700	-1.10388	-1.75619
C	0.91054	3.23647	-1.57408	H	2.86344	-1.04070	-2.83841
H	3.54428	0.27257	-0.18052	H	1.57805	-5.02200	0.65045
H	-1.92697	5.83682	-1.56557	C	-0.46228	-6.64393	1.52343
C	0.39006	6.94508	-2.30342	H	-2.66287	-5.43310	0.58493
H	2.18082	4.87534	-2.16259	Cl	0.08326	-0.11360	-3.36568

H	2.58073	-3.38813	-0.59193	C	-3.71167	-4.40779	-1.80084
H	3.00990	2.84189	-1.71665	H	-5.33617	-5.06902	-3.05217
O	0.79282	-0.06127	0.79962	H	-6.08943	-5.17434	-0.67904
C	1.52474	0.51828	1.73079	H	-7.15031	-4.11419	-1.62242
C	2.52271	-0.35528	2.37317	H	-6.54721	-3.04055	0.54476
C	2.23731	-1.72117	2.53137	H	-4.17888	-2.38242	0.98388
C	3.78759	0.11101	2.76260	H	-4.37220	-4.14165	0.91172
C	3.17100	-2.58072	3.09090	H	-3.64787	-5.38314	-1.29459
H	1.25938	-2.08916	2.22172	H	-2.96299	-4.42492	-2.61013
C	4.72637	-0.75566	3.31547	C	-5.89116	-1.74061	-1.05979
H	4.05048	1.15590	2.59674	H	-5.70262	-0.89118	-0.38559
C	4.41981	-2.10232	3.49042	H	-6.90268	-1.60358	-1.47668
H	2.91999	-3.63300	3.22424	C	-5.18076	-2.91010	-3.14272
H	5.70514	-0.37582	3.60557	H	-4.46284	-2.92422	-3.97813
H	5.15259	-2.77922	3.92755	H	-6.18338	-2.76982	-3.57871
C	1.20133	1.81340	2.10812	C	-3.45092	-1.94225	-1.59932
C	1.88936	2.66817	3.12349	H	-2.70037	-1.90981	-2.40397
H	2.39867	2.03550	3.86959	H	-3.22415	-1.09160	-0.93846
H	2.66779	3.30417	2.66288	C	-4.85582	-1.76338	-2.18599
C	0.87888	3.56306	3.85326	H	-4.88008	-0.80848	-2.73557
C	1.56559	4.31987	4.98364	C	-4.13432	2.51250	1.27512
H	2.32065	5.01844	4.59462	C	-5.07662	3.71540	1.23163
H	0.83845	4.90636	5.56394	C	-5.20644	4.19895	-0.21457
H	2.06952	3.62958	5.67571	C	-3.82665	4.59104	-0.75098
C	0.25219	4.57949	2.89830	C	-2.85297	3.39697	-0.72991
H	1.02574	5.22740	2.45934	C	-2.76437	2.91645	0.73484
H	-0.29413	4.11822	2.06411	H	-4.02244	2.15919	2.31379
H	-0.45662	5.22515	3.43715	H	-4.68683	4.52484	1.87027
C	-0.18022	2.60459	4.42997	H	-6.06714	3.44009	1.62871
H	-1.04194	3.19546	4.79040	H	-5.86467	5.08103	-0.25187
H	0.24781	2.12030	5.32051	H	-3.92805	4.97482	-1.78031
C	-0.63443	1.57861	3.44047	H	-3.42373	5.41351	-0.13633
C	-0.76447	0.17141	3.72513	H	-2.34247	3.73047	1.35149
C	-1.51165	-0.64835	2.85100	H	-2.07215	2.06458	0.79362
C	-0.10463	-0.46141	4.79881	C	-5.79282	3.07750	-1.07291
C	-1.59324	-2.01965	3.04163	H	-5.92684	3.42330	-2.11057
H	-2.02201	-0.19124	1.99774	H	-6.78865	2.79325	-0.69565
C	-0.19555	-1.83213	4.99181	C	-4.69712	1.38787	0.40511
C	-0.93438	-2.62257	4.11349	H	-4.02197	0.51429	0.44410
H	-2.17271	-2.62718	2.34664	H	-5.67366	1.05779	0.79758
H	0.07173	7.63268	-1.50751	C	-3.47890	2.27971	-1.59594
H	1.45253	7.13350	-2.50029	H	-2.81509	1.40484	-1.63821
H	-0.16789	7.22506	-3.20794	H	-3.58213	2.64800	-2.63029
H	-1.05023	-7.42353	1.02022	C	-4.84794	1.87579	-1.03979
H	0.57314	-6.99987	1.59117	H	-5.26250	1.06456	-1.65880
H	-0.84981	-6.56501	2.54934	C	6.58338	-3.52228	-1.17899
C	-5.11580	-4.22949	-2.37435	C	6.04440	-3.35632	-2.45003
C	-6.12746	-4.21727	-1.22548	C	4.90026	-2.58372	-2.62479
C	-5.81681	-3.05390	-0.27913	C	4.28341	-1.96796	-1.53687
C	-4.40976	-3.22261	0.30428	C	4.83240	-2.14036	-0.26181
C	-3.34760	-3.26738	-0.81431	C	5.97313	-2.91369	-0.08489

H	7.47928	-4.12518	-1.03968	H	7.55057	2.44501	-3.82734
H	6.51660	-3.82726	-3.31066	H	5.48475	1.88508	-5.08950
H	4.48104	-2.44559	-3.62229	H	3.52060	0.94718	-3.90864
H	4.36083	-1.67330	0.60470	H	5.67882	1.09472	-0.19778
H	6.38807	-3.03749	0.91477	H	7.64362	2.05579	-1.37585
C	6.68964	2.02816	-3.30721	H	0.32908	-2.29188	5.82878
C	5.53151	1.71359	-4.01535	H	0.50624	0.12831	5.48178
C	4.43210	1.18054	-3.35414	H	-1.30269	1.93851	2.65737
C	4.47863	0.95769	-1.97437	H	0.57488	2.33168	1.38009
C	5.63894	1.27960	-1.27305	H	-0.99860	-3.70023	4.25890
C	6.74194	1.81132	-1.93499				

Major (*Trans*-Re) TS3 with 2-vinylpyridine 2l with (R,R)-4a catalyst



M06/6-31G(d)-SDD Electronic Energy = -3580.907982

M06/6-31G(d)-SDD Free Energy = -3579.713

IEFPCM(EtOAc)M06/6-31+G(d,p) Electronic Energy = -4372.256125

IEFPCM(EtOAc)M06/6-31+G(d,p)//M06/6-31G(d)-SDD Corrected Free Energy = -4371.06114

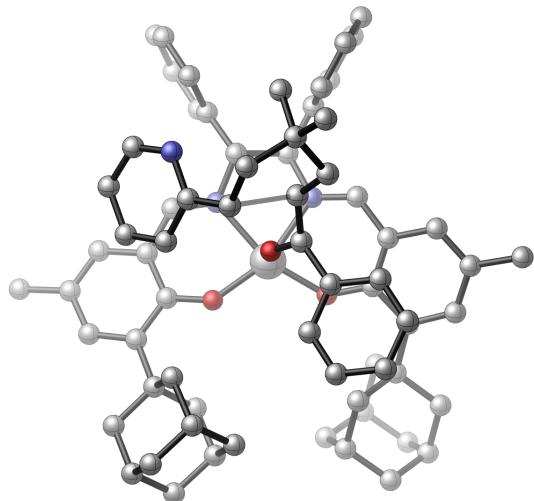
Number of imaginary frequencies = 1 (-501.3988)

Ti	0.04703	-0.15176	-0.98691	C	-2.71877	-1.50796	-1.17276
O	0.65154	1.62238	-0.99898	H	-3.11251	-1.23072	-0.18038
C	-1.93071	1.89688	-2.14211	H	-0.52498	-5.39168	0.33509
N	-1.79200	0.67937	-1.73952	C	1.73629	-6.82922	0.93615
C	-2.85536	-0.27662	-2.07879	H	3.72441	-5.14935	0.33763
C	0.25212	2.82376	-1.35244	Cl	0.47219	-0.55585	-3.28252
C	1.03564	3.97634	-1.05983	H	-1.80679	-3.69248	-0.33922
C	0.56788	5.19597	-1.53559	H	-2.87411	2.17109	-2.63638
C	-0.63494	5.36439	-2.24439	O	-0.61462	0.04367	0.78266
C	-1.41489	4.24641	-2.44331	C	-0.86818	-0.70217	1.84623
C	-0.99981	2.97977	-1.99691	C	0.31211	-1.25627	2.53755
H	-2.66435	-0.60033	-3.11635	C	1.45973	-0.46086	2.66196
H	1.15320	6.09450	-1.34518	C	0.35052	-2.56853	3.02310
C	-1.04399	6.72182	-2.73208	C	2.60425	-0.95713	3.26998
H	-2.38176	4.33550	-2.94360	H	1.44168	0.55707	2.26877
O	1.36663	-1.39368	-0.52981	C	1.50520	-3.07285	3.61148
C	1.48761	-2.68978	-0.31465	H	-0.52013	-3.21253	2.89945
C	2.75869	-3.31870	-0.20163	C	2.63428	-2.26942	3.73884
C	2.76689	-4.64781	0.20694	H	3.48544	-0.32064	3.35979
C	1.61678	-5.41333	0.45877	H	1.52544	-4.10509	3.95929
C	0.39821	-4.81969	0.21825	H	3.53948	-2.66552	4.19693
C	0.31441	-3.47568	-0.18485	C	-2.16898	-0.74788	2.31729
C	-0.99197	-2.97072	-0.49718	C	-2.71412	-1.57889	3.43485
N	-1.29540	-1.81316	-0.98510	H	-3.05496	-2.56754	3.07355

H	-1.92583	-1.77210	4.18133	C	5.19452	4.25409	0.29577
C	-3.88773	-0.86559	4.11669	C	4.15559	5.16378	0.95067
C	-5.07260	-0.72047	3.16106	C	2.92707	5.26335	0.04407
H	-5.36741	-1.70130	2.75564	C	2.28639	3.88254	-0.19302
H	-5.93906	-0.30440	3.69453	C	3.35837	2.97246	-0.83090
H	-4.86642	-0.03909	2.32679	H	5.32875	2.21214	-0.39456
C	-4.34334	-1.65738	5.33625	H	5.51724	4.67842	-0.66882
H	-4.75117	-2.63629	5.04388	H	6.09144	4.18250	0.93219
H	-3.51239	-1.83224	6.03521	H	4.57688	6.17160	1.08974
H	-5.13242	-1.11808	5.88001	H	2.19021	5.94233	0.50548
C	-3.36284	0.52673	4.54986	H	3.22247	5.71044	-0.92032
H	-2.87534	0.41495	5.53130	H	3.64467	3.38487	-1.81307
H	-4.21624	1.20917	4.67968	H	2.93836	1.97140	-1.01267
C	-2.37219	1.11692	3.59310	C	3.74898	4.58413	2.30670
C	-2.69531	2.15191	2.65200	H	3.02265	5.24939	2.80136
C	-1.97563	3.80563	1.04486	H	4.62781	4.51732	2.96816
C	-4.27522	3.39458	1.53464	C	4.16189	2.27976	1.43028
C	-3.31917	4.10125	0.80953	H	3.72750	1.27572	1.28262
H	-1.18572	4.33584	0.51084	H	5.04263	2.15862	2.08387
H	-1.07049	7.45627	-1.91526	C	1.90467	3.31732	1.19528
H	-0.34325	7.10856	-3.48513	H	1.42827	2.33228	1.07191
H	-2.03983	6.69786	-3.19103	H	1.15817	3.98731	1.65829
H	2.17787	-6.87966	1.94188	C	3.13527	3.19926	2.09716
H	0.75639	-7.32006	0.98191	H	2.83050	2.77569	3.06858
H	2.37884	-7.42892	0.27692	C	-5.16037	-4.65549	-2.78931
C	5.20594	-1.44097	-2.52617	C	-3.97525	-4.29463	-3.42746
C	5.42562	-0.21383	-1.63727	C	-3.17292	-3.29345	-2.89425
C	5.59255	-0.65369	-0.17928	C	-3.54859	-2.64539	-1.71393
C	4.32223	-1.37145	0.28286	C	-4.73116	-3.01627	-1.07698
C	4.04465	-2.60474	-0.59989	C	-5.53762	-4.01587	-1.61382
C	3.93415	-2.16283	-2.07786	H	-5.78940	-5.43811	-3.21038
H	5.08555	-1.12238	-3.57251	H	-3.67534	-4.79636	-4.34605
H	4.56524	0.47021	-1.73032	H	-2.24038	-3.01296	-3.38855
H	6.31913	0.34223	-1.96826	H	-5.02904	-2.49695	-0.16355
H	5.75708	0.22831	0.46014	H	-6.46239	-4.29392	-1.11107
H	4.42244	-1.69710	1.33271	C	-6.93242	1.02380	-1.66353
H	3.46613	-0.68161	0.24854	C	-6.02411	1.23308	-0.62761
H	3.06311	-1.50785	-2.21707	C	-4.69512	0.85733	-0.77880
H	3.76204	-3.05569	-2.70237	C	-4.26189	0.25889	-1.96670
C	6.79231	-1.59306	-0.06292	C	-5.17406	0.06247	-3.00130
H	6.93161	-1.90112	0.98638	C	-6.50479	0.44326	-2.85229
H	7.71490	-1.07553	-0.37258	H	-7.97452	1.31506	-1.54209
C	6.40611	-2.37999	-2.40233	H	-6.35057	1.68310	0.30937
H	6.26587	-3.26017	-3.05071	H	-3.98600	1.03480	0.03589
H	7.32599	-1.87454	-2.73934	H	-4.84064	-0.41862	-3.92194
C	5.27459	-3.52789	-0.49125	H	-7.20963	0.27933	-3.66568
H	5.12199	-4.42763	-1.11048	H	-5.33638	3.61452	1.38543
H	5.40011	-3.86635	0.55153	H	-1.32081	1.07650	3.88677
C	6.55281	-2.81887	-0.94464	H	-2.90096	-0.34507	1.61486
H	7.39811	-3.51842	-0.84941	H	-3.61529	4.86667	0.09503
C	4.58453	2.86911	0.08075	N	-3.99943	2.43934	2.41780

C	-1.66032	2.83013	1.97041	H	-0.62218	2.57654	2.18500
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Minor (*Trans*-Si) TS3 with 2-vinylpyridine **2l with (*R,R*)-**4a** catalyst**



M06/6-31G(d)-SDD Electronic Energy = -3580.909163

M06/6-31G(d)-SDD Free Energy = -3579.71186

IEFPCM(EtOAc)M06/6-31+G(d,p) Electronic Energy = -4372.257127

IEFPCM(EtOAc)M06/6-31+G(d,p)//M06/6-31G(d)-SDD Corrected Free Energy = -4371.059824

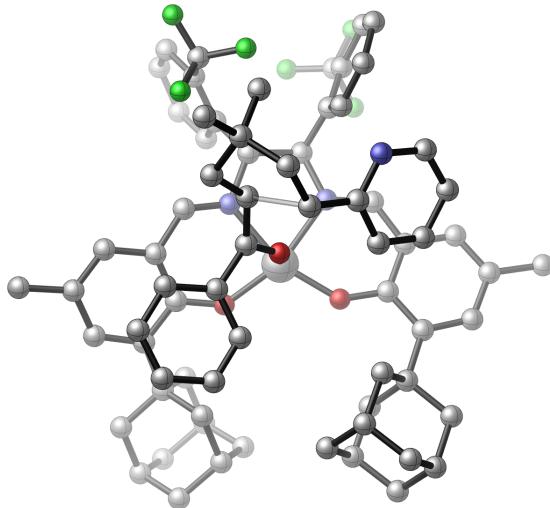
Number of imaginary frequencies = 1 (-486.6907)

Ti	0.02645	0.12118	-0.93558	C	0.16833	5.78140	-1.26215
O	-1.19876	-1.29768	-0.96376	C	1.09428	4.79344	-1.51668
C	1.31398	-2.62913	-1.10688	C	0.81080	3.44202	-1.25305
N	1.49568	-1.37644	-1.35919	C	1.90242	2.51149	-1.36122
C	2.77486	-0.88701	-1.88828	N	1.86126	1.23700	-1.17689
C	-1.17385	-2.60814	-0.84494	C	3.09426	0.43984	-1.17455
C	-2.37470	-3.37208	-0.83060	H	3.29924	0.21256	-0.11300
C	-2.25513	-4.72631	-0.54715	H	2.07552	5.05417	-1.91988
C	-1.03339	-5.39015	-0.33889	C	0.43598	7.22514	-1.56453
C	0.12141	-4.65968	-0.51177	H	-1.74663	6.18832	-0.42335
C	0.07419	-3.27947	-0.77863	Cl	-0.22200	0.44091	-3.26729
H	2.56112	-0.63662	-2.94118	H	2.87285	2.97822	-1.57649
H	-3.15807	-5.33276	-0.49111	H	2.16927	-3.31064	-1.20867
C	-1.01244	-6.84454	0.02223	O	0.49173	-0.20709	0.84907
H	1.09654	-5.14762	-0.44225	C	0.69827	-1.17098	1.73714
O	-0.71885	1.79329	-0.53526	C	-0.51076	-1.79030	2.30334
C	-0.45327	3.06589	-0.73620	C	-1.65525	-1.00103	2.49008
C	-1.38593	4.07857	-0.37047	C	-0.56475	-3.14576	2.65407
C	-1.04487	5.39214	-0.66861	C	-2.80741	-1.54577	3.04007

H	-1.62122	0.05162	2.20255	H	-6.54660	3.46214	1.23056
C	-1.72766	-3.69339	3.18231	C	-4.44884	1.70981	1.56812
H	0.29328	-3.78726	2.45708	H	-3.89261	0.79717	1.29299
C	-2.84975	-2.89529	3.38494	H	-5.34664	1.38630	2.12254
H	-3.68526	-0.91599	3.18849	C	-3.59327	2.84265	-0.48219
H	-1.75947	-4.75416	3.42874	H	-3.05945	1.93283	-0.79462
H	-3.75911	-3.32405	3.80343	H	-3.86089	3.38768	-1.40318
C	1.98731	-1.35181	2.19756	C	-4.85394	2.46779	0.30024
C	2.50058	-2.35624	3.17669	H	-5.48795	1.82532	-0.33025
H	1.70319	-2.63691	3.88458	C	-4.92070	-1.47390	-3.03324
H	2.81802	-3.29069	2.67512	C	-6.01907	-2.53695	-3.07648
C	3.68719	-1.78210	3.96411	C	-6.16931	-3.16218	-1.68885
C	4.09294	-2.75298	5.06653	C	-4.84213	-3.79308	-1.26015
H	4.48321	-3.69172	4.64640	C	-3.71299	-2.74585	-1.20469
H	4.87969	-2.31961	5.70086	C	-3.59803	-2.11881	-2.61513
H	3.23890	-3.00211	5.71313	H	-4.79785	-1.02132	-4.02891
C	4.89389	-1.54363	3.05632	H	-5.76475	-3.31294	-3.81686
H	5.15558	-2.46215	2.50705	H	-6.97515	-2.08930	-3.39370
H	4.73036	-0.72644	2.34138	H	-6.94244	-3.94612	-1.71616
H	5.76755	-1.25679	3.65899	H	-4.96845	-4.26218	-0.26923
C	3.20857	-0.44242	4.58061	H	-4.57419	-4.59525	-1.96836
H	4.08340	0.19817	4.77010	H	-3.31756	-2.90921	-3.33206
H	2.74774	-0.66198	5.55688	H	-2.79438	-1.36955	-2.63366
C	2.20052	0.29170	3.74695	C	-6.56444	-2.08044	-0.68376
C	2.49794	1.44935	2.95525	H	-6.70895	-2.52395	0.31511
C	4.04298	2.77558	1.88572	H	-7.52376	-1.62334	-0.97669
C	1.75156	3.44877	1.82372	C	-5.29501	-0.38954	-2.01863
C	3.08240	3.69995	1.48110	H	-4.50529	0.38073	-1.99149
H	5.09214	2.93743	1.62159	H	-6.22835	0.11267	-2.32428
H	0.00297	-7.25660	-0.02837	C	-4.14463	-1.65915	-0.19913
H	-1.38375	-7.00886	1.04449	H	-3.36152	-0.88965	-0.11927
H	-1.64919	-7.44013	-0.64604	H	-4.24764	-2.11239	0.80263
H	-0.27682	7.62171	-2.30092	C	-5.46570	-1.01881	-0.63257
H	1.44389	7.36761	-1.97298	H	-5.74306	-0.24333	0.09900
H	0.34805	7.85211	-0.66631	C	6.62667	2.22011	-2.86449
C	-3.57917	2.60520	2.45462	C	6.60518	1.84030	-1.52696
C	-4.35801	3.86645	2.82892	C	5.45392	1.27983	-0.98124
C	-4.73771	4.61847	1.55120	C	4.31792	1.09021	-1.76638
C	-3.47424	4.98730	0.76854	C	4.34708	1.47476	-3.11079
C	-2.66848	3.73320	0.37502	C	5.49449	2.03804	-3.65557
C	-2.31441	3.00074	1.69137	H	7.52648	2.65869	-3.29294
H	-3.29214	2.05592	3.36652	H	7.48751	1.97818	-0.90421
H	-3.74440	4.50957	3.48050	H	5.43290	0.97534	0.06734
H	-5.26595	3.60425	3.39591	H	3.45539	1.34611	-3.72856
H	-5.27541	5.54340	1.81176	H	5.50600	2.33589	-4.70271
H	-3.76273	5.54839	-0.13632	C	6.10609	-3.61870	-1.82847
H	-2.84717	5.65712	1.38111	C	5.56177	-3.19652	-3.03596
H	-1.69412	3.67227	2.31167	C	4.48208	-2.31855	-3.04351
H	-1.70739	2.11064	1.47285	C	3.93495	-1.84909	-1.85015
C	-5.62774	3.72920	0.68349	C	4.49121	-2.27858	-0.64092
H	-5.93942	4.27236	-0.22338	C	5.56792	-3.15644	-0.63009

H	6.95120	-4.30495	-1.81898	H	1.15946	0.21673	4.07097
H	5.97696	-3.55150	-3.97767	H	2.74167	-0.85392	1.58669
H	4.05872	-1.98301	-3.99104	H	3.36658	4.58486	0.91432
H	4.07166	-1.93190	0.30487	C	1.45462	2.31331	2.55024
H	5.99094	-3.48201	0.31943	H	0.42783	2.07666	2.83112
H	0.95789	4.13171	1.51794	N	3.78472	1.68048	2.59540

Major (*Trans*-Re) TS3 with 2-vinylpyridine 2l with (R,R)-4e catalyst



M06/6-31G(d)-SDD Electronic Energy = -4254.786737

M06/6-31G(d)-SDD Free Energy = -4253.58456

IEFPCM(EtOAc)M06/6-31+G(d,p) Electronic Energy = -5046.1648

IEFPCM(EtOAc)M06/6-31+G(d,p)//M06/6-31G(d)-SDD Corrected Free Energy = -5044.962584

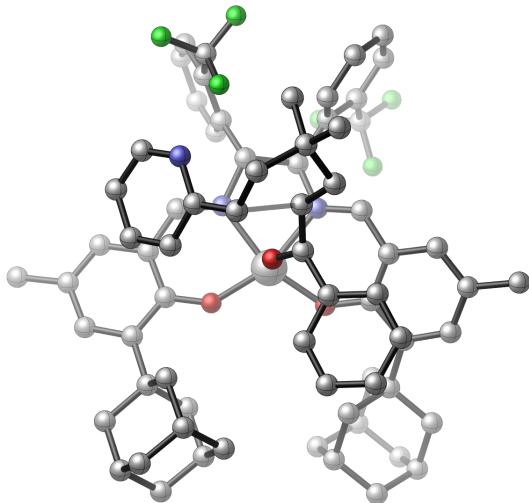
Number of imaginary frequencies = 1 (-501.9075)

Ti	0.40429	-0.00049	-0.81650	O	1.57254	-1.44524	-0.60905
O	1.27117	1.66221	-0.86439	C	1.52114	-2.72449	-0.29895
C	-1.38150	2.37326	-1.58414	C	2.68205	-3.54513	-0.32227
N	-1.38262	1.12664	-1.24566	C	2.55056	-4.83150	0.18568
C	-2.62162	0.37163	-1.49819	C	1.34727	-5.38243	0.65980
C	1.01027	2.92763	-1.10830	C	0.21124	-4.61229	0.55111
C	1.99581	3.93700	-0.91475	C	0.27466	-3.29555	0.06077
C	1.65021	5.23586	-1.26862	C	-0.96533	-2.60280	-0.13167
C	0.39097	5.61735	-1.76431	N	-1.14639	-1.43434	-0.66366
C	-0.56989	4.63642	-1.87065	C	-2.54567	-0.99986	-0.78676
C	-0.28714	3.29918	-1.53936	H	-2.93013	-0.86859	0.23298
H	-2.64827	0.18789	-2.57917	H	-0.75924	-5.01753	0.84650
H	2.38981	6.02687	-1.15093	C	1.32156	-6.76924	1.22778
C	0.12283	7.04420	-2.13812	H	3.42794	-5.47623	0.21500
H	-1.57754	4.89122	-2.20600	Cl	0.43026	-0.32552	-3.16818

H	-1.85654	-3.18083	0.15168	H	6.41231	-0.53795	-2.81781
H	-2.32547	2.81062	-1.94055	H	6.24310	-0.50132	-0.32919
O	0.06685	0.16185	1.04250	H	4.78692	-2.16283	0.83861
C	-0.14141	-0.61386	2.09685	H	3.83078	-1.04696	-0.14614
C	1.05236	-1.27709	2.65012	H	2.92178	-1.87506	-2.46320
C	2.28367	-0.60754	2.59216	H	3.30228	-3.52726	-2.96745
C	1.01734	-2.56249	3.20689	C	6.89217	-2.47612	-0.91110
C	3.43581	-1.19109	3.09967	H	7.15248	-2.77026	0.11904
H	2.32254	0.38242	2.13674	H	7.81932	-2.11912	-1.38847
C	2.17473	-3.15103	3.70329	C	6.02383	-3.25822	-3.11605
H	0.08397	-3.12418	3.20637	H	5.65124	-4.12214	-3.69020
C	3.38654	-2.46774	3.65553	H	6.94427	-2.91218	-3.61422
H	4.38152	-0.65007	3.05312	C	5.05420	-4.16240	-0.99211
H	2.13062	-4.15943	4.11324	H	4.66759	-5.04602	-1.52744
H	4.29234	-2.93039	4.04449	H	5.29650	-4.48354	0.03541
C	-1.39451	-0.58027	2.68781	C	6.33338	-3.67510	-1.67737
C	-1.91810	-1.39760	3.82523	H	7.06982	-4.49391	-1.67659
H	-2.37942	-2.33513	3.46238	C	5.45749	2.24764	-0.39375
H	-1.09368	-1.69033	4.49617	C	6.30806	3.50910	-0.24674
C	-2.95381	-0.60005	4.63098	C	5.54277	4.53592	0.58760
C	-4.18585	-0.27348	3.78799	C	4.21933	4.86892	-0.10505
H	-4.63306	-1.18794	3.37280	C	3.33749	3.61609	-0.26738
H	-4.94485	0.22262	4.40985	C	4.13789	2.58471	-1.09235
H	-3.96518	0.40859	2.95742	H	6.00125	1.50473	-0.99768
C	-3.39622	-1.40373	5.84745	H	6.54195	3.92525	-1.24005
H	-3.93796	-2.31254	5.54727	H	7.26899	3.26877	0.23645
H	-2.53492	-1.70885	6.45974	H	6.13624	5.45889	0.67892
H	-4.06783	-0.81010	6.48433	H	3.68235	5.62875	0.48765
C	-2.24856	0.70510	5.08005	H	4.42691	5.31394	-1.09301
H	-1.72569	0.50280	6.02862	H	4.33039	2.99907	-2.09628
H	-3.00503	1.47911	5.27657	H	3.54311	1.66945	-1.23171
C	-1.24737	1.20779	4.08736	C	5.26663	3.96179	1.97895
C	-1.44639	2.36592	3.26311	H	4.74439	4.70668	2.60113
C	-0.54517	4.00701	1.73516	H	6.21636	3.72622	2.48567
C	-2.83099	3.99607	2.42064	C	5.15969	1.66737	0.99280
C	-1.81623	4.57971	1.66756	H	4.54863	0.75431	0.89357
H	0.28804	4.42694	1.16984	H	6.09920	1.37560	1.49286
H	0.39871	7.73417	-1.32896	C	3.09183	3.05450	1.15211
H	0.69991	7.34467	-3.02392	H	2.44315	2.16838	1.08580
H	-0.93753	7.20546	-2.36755	H	2.54980	3.81198	1.74635
H	1.90141	-6.83174	2.15998	C	4.41234	2.70082	1.83881
H	0.29756	-7.09053	1.45419	H	4.19865	2.28001	2.83555
H	1.75553	-7.50171	0.53337	C	-4.80022	-3.85627	-3.11051
C	4.97403	-2.14618	-3.10124	C	-3.60505	-3.32205	-3.58027
C	5.51249	-0.94120	-2.32355	C	-2.89773	-2.41747	-2.80227
C	5.84532	-1.36242	-0.88893	C	-3.36367	-2.03027	-1.54323
C	4.57217	-1.85830	-0.20011	C	-4.54370	-2.60927	-1.05704
C	3.97763	-3.06084	-0.95967	C	-5.25983	-3.50812	-1.84862
C	3.69813	-2.65167	-2.42540	H	-5.36905	-4.55621	-3.71917
H	4.73484	-1.84346	-4.13185	H	-3.22424	-3.60404	-4.55997
H	4.75659	-0.13703	-2.31723	H	-1.96056	-1.99377	-3.17113

H	-6.17737	-3.94379	-1.46268	H	-2.15559	-0.10859	2.06274
C	-6.18327	2.29855	0.01575	H	-2.01258	5.46043	1.05991
C	-5.05676	2.13468	0.81307	N	-2.68257	2.91785	3.18545
C	-3.91315	1.55614	0.27994	C	-0.35614	2.89949	2.53798
C	-3.87034	1.10697	-1.04185	H	0.62092	2.42128	2.61396
C	-4.99488	1.32599	-1.85134	C	-4.99034	0.97081	-3.31140
C	-6.14233	1.91230	-1.31654	C	-5.03088	-2.33213	0.33664
H	-7.09010	2.74025	0.42398	F	-4.90908	-0.34961	-3.51712
H	-5.05860	2.43880	1.85885	F	-6.09262	1.39474	-3.93560
H	-3.02384	1.45689	0.90813	F	-3.94463	1.52876	-3.94684
H	-7.00565	2.06996	-1.95693	F	-4.09044	-2.65954	1.25264
H	-3.83458	4.42993	2.39517	F	-5.32415	-1.04283	0.54472
H	-0.20071	0.97081	4.29123	F	-6.12128	-3.03720	0.64312

Minor (*Trans*-Si) TS3 with 2-vinylpyridine 2l with (R,R)-4e catalyst



M06/6-31G(d)-SDD Electronic Energy = -4254.778754

M06/6-31G(d)-SDD Free Energy = - -4253.57408

IEFPCM(EtOAc)M06/6-31+G(d,p) Electronic Energy = -5046.1593

IEFPCM(EtOAc)M06/6-31+G(d,p)//M06/6-31G(d)-SDD Corrected Free Energy = -5044.95462

Number of imaginary frequencies = 1 (-476.8066)

Ti	-0.34392	0.08932	-0.74283	C	-2.62759	-3.45333	-0.28988
O	-1.51039	-1.38225	-0.70949	C	-2.50216	-4.71212	0.28282
C	1.03417	-2.56657	-0.26195	C	-1.29820	-5.24665	0.77416
N	1.20441	-1.37583	-0.73241	C	-0.15582	-4.49844	0.60003
C	2.49864	-0.95168	-1.26915	C	-0.21322	-3.20445	0.05131
C	-1.46157	-2.63624	-0.31347	H	2.34465	-0.93229	-2.35445

H	-3.38348	-5.34852	0.35119	C	3.06141	3.36267	2.17097
C	-1.27790	-6.59411	1.42965	C	0.74803	3.84575	1.81065
H	0.81674	-4.90389	0.88962	C	2.08792	4.14166	1.54916
O	-1.18965	1.76643	-0.69010	H	4.11963	3.55306	1.97489
C	-0.93408	3.02079	-0.98685	H	-0.25288	-6.96199	1.56178
C	-1.93794	4.02459	-0.87515	H	-1.74649	-6.56314	2.42445
C	-1.59279	5.31416	-1.26013	H	-1.82880	-7.34113	0.84237
C	-0.31562	5.69356	-1.70928	H	-0.53714	7.33693	-3.09262
C	0.66349	4.72505	-1.71954	H	1.02572	7.28812	-2.26521
C	0.38040	3.39604	-1.35683	H	-0.42571	7.83003	-1.40155
C	1.49660	2.49809	-1.25529	C	-4.47512	2.83082	1.78710
N	1.47854	1.23812	-0.97964	C	-5.34895	4.08376	1.85109
C	2.75022	0.51111	-0.84497	C	-5.56043	4.62140	0.43416
H	2.98678	0.53032	0.22327	C	-4.20651	4.95214	-0.19874
H	1.68581	4.98390	-2.00538	C	-3.30453	3.70608	-0.28335
C	-0.04811	7.10548	-2.13577	C	-3.12401	3.18317	1.16165
H	-2.34639	6.09881	-1.20417	H	-4.30862	2.43522	2.80260
Cl	-0.30927	0.03638	-3.11258	H	-4.86725	4.85022	2.47984
H	2.46952	2.97877	-1.42609	H	-6.32078	3.84973	2.31513
H	1.91295	-3.21529	-0.14721	H	-6.16745	5.53932	0.47280
O	-0.11725	0.05143	1.11127	H	-4.36946	5.36703	-1.20794
C	0.02933	-0.74716	2.16273	H	-3.70790	5.73475	0.39764
C	-1.21520	-1.32333	2.69935	H	-2.62413	3.96562	1.76073
C	-2.39948	-0.57701	2.59727	H	-2.46256	2.30391	1.16000
C	-1.27432	-2.58793	3.30168	C	-6.27082	3.56593	-0.41308
C	-3.59493	-1.06767	3.10308	H	-6.45608	3.95528	-1.42734
H	-2.36409	0.39941	2.11186	H	-7.25349	3.32616	0.02459
C	-2.47646	-3.08347	3.79227	C	-5.16777	1.76862	0.92926
H	-0.38182	-3.21038	3.33705	H	-4.54392	0.85964	0.88316
C	-3.64017	-2.32565	3.70030	H	-6.12843	1.47815	1.38858
H	-4.50269	-0.46852	3.02005	C	-4.05095	2.64727	-1.12329
H	-2.50577	-4.07605	4.24027	H	-3.43901	1.73718	-1.21467
H	-4.58046	-2.71525	4.08727	H	-4.19706	3.03790	-2.14441
C	1.26964	-0.78349	2.76873	C	-5.40057	2.31140	-0.48450
C	1.72962	-1.64525	3.89886	H	-5.90491	1.54806	-1.09675
H	0.87733	-1.90156	4.54908	C	-4.93639	-2.16821	-3.11342
H	2.14243	-2.60438	3.52843	C	-5.98292	-3.28274	-3.08117
C	2.79171	-0.92860	4.74311	C	-6.28450	-3.64404	-1.62596
C	3.11818	-1.76475	5.97466	C	-5.00130	-4.10067	-0.92682
H	3.60040	-2.71262	5.69291	C	-3.92700	-2.99585	-0.94190
H	3.80726	-1.22652	6.64130	C	-3.65640	-2.64526	-2.42476
H	2.21176	-2.00391	6.54976	H	-4.70268	-1.90451	-4.15604
C	4.08114	-0.70553	3.95308	H	-5.61035	-4.16719	-3.62318
H	4.43211	-1.64983	3.50517	H	-6.90673	-2.95858	-3.58779
H	3.97268	0.05382	3.16994	H	-7.01843	-4.46441	-1.58970
H	4.87334	-0.34298	4.62377	H	-5.24011	-4.37903	0.11403
C	2.18137	0.43522	5.16460	H	-4.61285	-5.00480	-1.42533
H	2.99632	1.15116	5.34949	H	-3.26333	-3.54206	-2.93317
H	1.65087	0.29034	6.11912	H	-2.88165	-1.87020	-2.49767
C	1.20896	1.00589	4.17584	C	-6.84362	-2.41830	-0.90416
C	1.50351	2.08748	3.28189	H	-7.09888	-2.67367	0.13755

H	-7.77357	-2.08271	-1.39147	C	3.66649	-1.85699	-0.93372
C	-5.47473	-0.93582	-2.38032	C	4.20792	-1.83582	0.35320
H	-4.72157	-0.12955	-2.41063	C	5.27601	-2.65079	0.70760
H	-6.37811	-0.55545	-2.88612	H	6.65749	-4.16421	0.03787
C	-4.52318	-1.76783	-0.22576	H	5.67618	-4.28390	-2.23109
H	-3.78507	-0.95198	-0.20435	H	3.78692	-1.16670	1.10229
H	-4.73642	-2.03191	0.82470	H	5.68446	-2.59090	1.71551
C	-5.79988	-1.30162	-0.92884	H	-0.05161	4.41598	1.33554
H	-6.19876	-0.42118	-0.40115	H	0.14895	0.87720	4.40940
C	5.85195	2.01700	-3.47548	H	2.05396	-0.30540	2.17638
C	6.12270	1.91366	-2.12352	H	2.36741	4.95484	0.88141
C	5.15411	1.45836	-1.21926	C	0.45180	2.80625	2.66923
C	3.88580	1.07987	-1.68273	H	-0.58049	2.53463	2.89265
C	3.63025	1.20613	-3.05734	N	2.79992	2.36750	3.01290
C	4.58909	1.66502	-3.94392	C	5.65660	1.40826	0.20017
H	6.61804	2.37487	-4.16015	C	3.62661	-2.91046	-3.24211
H	7.10305	2.19436	-1.74288	F	4.19929	-3.90811	-3.92102
H	2.63822	0.94596	-3.43127	F	3.79194	-1.79834	-3.97172
H	4.35004	1.74352	-5.00260	F	2.31096	-3.16370	-3.20459
C	5.81702	-3.52533	-0.22516	F	6.62850	0.49515	0.32644
C	5.27165	-3.58849	-1.50102	F	6.19252	2.58946	0.54846
C	4.20161	-2.77045	-1.85763	F	4.73298	1.12802	1.12388

VI. Distortion/Interaction Analysis of Transition States

Distortion/interaction analysis of TS3 was performed for three reaction scenarios: (1) p-chlorostyrene substrate **2b** with catalyst **(R,R)-4a**, (2) 2-vinylpyridine substrate **2l** with catalyst **(R,R)-4a**, and (3) 2-vinylpyridine substrate **2l** with the new optimal catalyst **(R,R)-4e**. Single point energy calculations were performed for each necessary structure (optimized pre-TS3, TS3, and the separated, distorted reactants from TS3) using the M06/6-31+G(d,p)-SDD level of theory as implemented in Gaussian09 (version D.01).⁵ To generate the separated, distorted reactants, each optimized TS3 structure was visualized in GaussView and the substrate was manually removed in Gaussview. The distortion and interaction energies were then computed using the electronic energies.

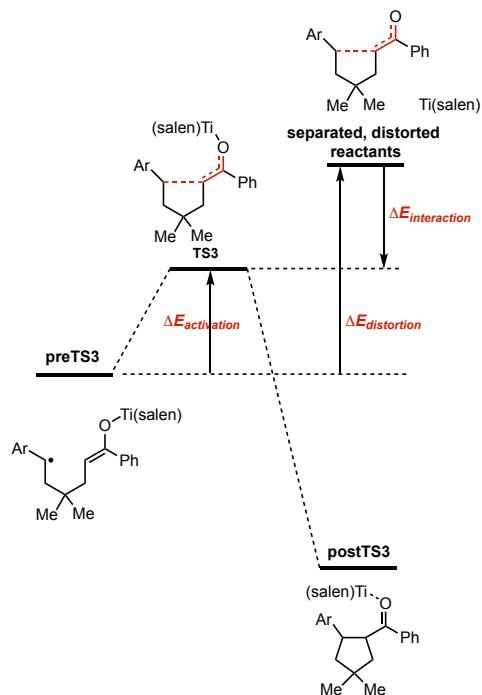


Figure SC4. Distortion/Interaction Analysis

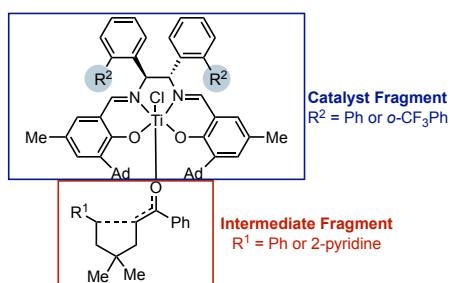


Figure SC5. Fragments used for separated, distorted reactants.

i. Reaction of *p*-chlorostyrene **2b** with catalyst (*R,R*)-**4a**

The relative $\Delta E_{\text{Interaction}}$ and $\Delta E_{\text{distortion}}$ energies from the distortion/interaction analysis for *p*-chlorostyrene **2b** with catalyst (*R,R*)-**4a** are presented in **Table SC2**. As Table SC2 shows, the minor TS3 has higher distortion energy, but more stabilizing interaction energy relative to the major TS3. Overall, the distortion energy outweighs the stabilizing interaction energy such that the major TS3 is energetically favored. Comparing *cis*-Si TS3 relative to the major TS3 reveals that *cis*-Si TS3 has higher distortion energy and essentially equal interaction energy. This suggests that both diastereoselectivity and enantioselectivity are distortion controlled. However, in comparing minor and major TS3 it is apparent that disparate interactions are established in the diastereomeric TS3s.

The geometry of the *trans*-Re TS catalyst structure is extremely similar to the lowest energy ground state optimized structure of the catalyst (coordinates in “Cartesian Coordinates of Ti(salen) structures”). Catalyst distortion was quantified by comparing the energies of the different separated, distorted catalyst structures from the TS3s relative to the major TS3. The same analysis was also performed for the relative energies of the separated, distorted intermediates. This revealed that catalyst distortion, and not intermediate distortion, was the primary factor for the difference in relative distortion energies (Table SC2).

Table SC2. Results of distortion/interaction analysis for *p*-chlorostyrene **2b** with catalyst (*R,R*)-**4a**.

Catalyst Structure	$\Delta E_{\text{Interaction}}$ relative to major TS3 (kcal/mol)	$\Delta E_{\text{distortion}}$ relative to major TS3 (kcal/mol)	Catalyst $\Delta E_{\text{distortion}}$ relative to major TS3 (kcal/mol)	Intermediate $\Delta E_{\text{distortion}}$ relative to major TS3 (kcal/mol)
Minor TS3	-2.5	+3.2	+3.1	+0.1
<i>cis</i> -Si TS3	-0.2	+3.1	+5.8	-2.7

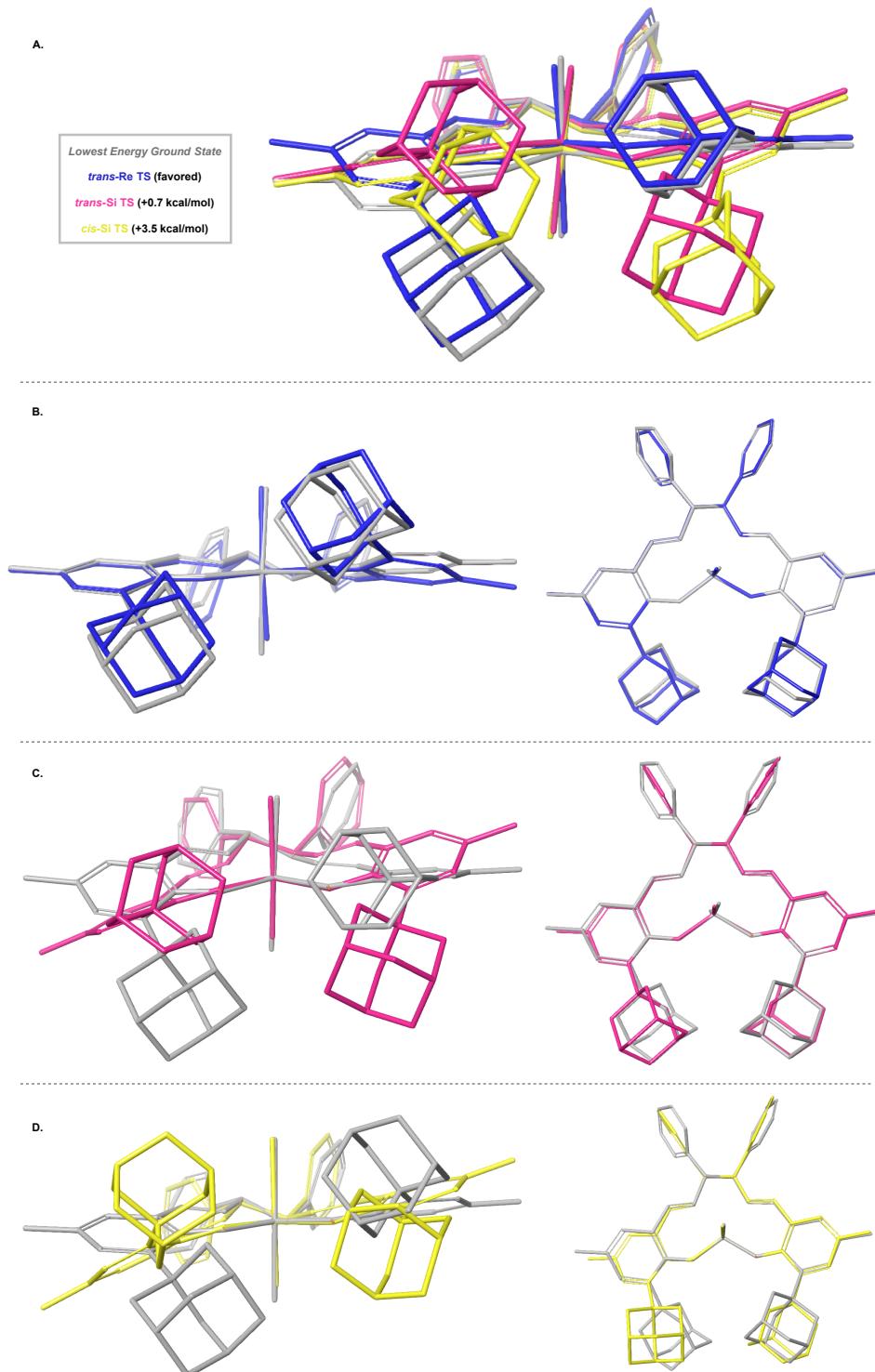


Figure SC6. **A.** Overlay of the different TS3 catalyst geometries for reaction of p-chlorostyrene **2b** with catalyst **(R,R)-4a** and the lowest-energy ground state catalyst geometry for **(R,R)-4a** (gray) to demonstrate catalyst distortion. *Trans*-Re TS3 = major TS3 (blue). *Trans*-Si TS3 = minor TS3 (pink). **B.** Overlay of major TS3 with ground state catalyst. **C.** Overlay of minor TS3 with ground state catalyst. **D.** Overlay of *cis*-Si TS3 with ground state catalyst.

ii. Reaction of 2-vinylpyridine **2l** with catalyst (*R,R*)-**4a**

The relative $\Delta E_{\text{Interaction}}$ and $\Delta E_{\text{distortion}}$ energies from the distortion/interaction analysis for 2-vinylpyridine **2l** with catalyst (*R,R*)-**4a** are presented in **Table SC3**. The minor TS3 has higher distortion energy, but more stabilizing interaction energy relative to the major TS3, such that these two energies are not able to outweigh one diastereomeric TS over the other. This suggests that distinct interactions are established between this catalyst and 2-vinylpyridine relative to the p-chlorostyrene substrate that performed well. As such, low enantioselectivities result with this substrate and catalyst combination. For this substrate, there is a factor of both catalyst and intermediate distortion accounting for the total relative distortion energy difference, but the catalyst distortion is still more significant.

Table SC3. Results of distortion/interaction analysis for 2-vinylpyridine **2l** with catalyst (*R,R*)-**4a**.

Catalyst Structure	$\Delta E_{\text{Interaction}}$ relative to major TS3 (kcal/mol)	$\Delta E_{\text{distortion}}$ relative to major TS3 (kcal/mol)	Catalyst $\Delta E_{\text{distortion}}$ relative to major TS3 (kcal/mol)	Substrate $\Delta E_{\text{distortion}}$ relative to major TS3 (kcal/mol)
Minor TS3	-4.3	+3.7	+2.7	+1.0

iii. Reaction of 2-vinylpyridine **2l** with catalyst (*R,R*)-**4a**

The relative $\Delta E_{\text{Interaction}}$ and $\Delta E_{\text{distortion}}$ energies from the distortion/interaction analysis for 2-vinylpyridine **2l** with catalyst (*R,R*)-**4e** are presented in **Table SC4**. Again, the minor TS3 has higher distortion energy and more stabilizing interaction energy relative to the major TS3. However, with this catalyst the distortion energy greatly outweighs the stabilizing interaction energy of the minor TS and the reaction proceeds in high enantioselectivity. Relative to the results for this substrate with the original catalyst (*R,R*)-**4a**, it is evident that a significant increase in catalyst distortion has occurred (+2 kcal/mol) whereas a modest increase in intermediate distortion resulted (+0.2 kcal/mol). Thus, the primary factor for the overall increase in the relative distortion energy relative to the major TS3 is catalyst distortion. Comparing the interaction energies with the (*R,R*)-**4e** catalyst to those with the (*R,R*)-**4a** catalyst, there is also a reduction in the relative interaction energy difference between minor and major TS3, suggesting that the stabilizing interactions established in the minor TS3 with the original (*R,R*)-**4a** catalyst are disrupted with the (*R,R*)-**4e** catalyst.

Table SC4. Results of distortion/interaction analysis for 2-vinylpyridine **2l** with catalyst (*R,R*)-**4e**.

Catalyst Structure	$\Delta E_{\text{Interaction}}$ relative to major TS3 (kcal/mol)	$\Delta E_{\text{distortion}}$ relative to major TS3 (kcal/mol)	Catalyst $\Delta E_{\text{distortion}}$ relative to major TS3 (kcal/mol)	Substrate $\Delta E_{\text{distortion}}$ relative to major TS3 (kcal/mol)
Minor TS3	-1.6	+6.0	+4.7	+1.3

VII. Natural Energy Decomposition of Transition States

Natural Energy Decomposition Analysis (NEDA) calculations were performed with M06/6-31+G(d,p)-SDD level of theory as implemented in Gaussian09 (version D.01).⁵ NEDA of TS3 was performed for three reaction scenarios: (1) p-chlorostyrene substrate **2b** with catalyst (**R,R**)-**4a**, (2) 2-vinylpyridine substrate **2l** with catalyst (**R,R**)-**4a**, and (3) 2-vinylpyridine substrate **2l** with the new optimal catalyst (**R,R**)-**4e**. The results are presented in Tables SC5, SC6, and SC7. Overall, NEDA calculations agreed with distortion/interaction analysis results for the minor TS having a more stabilizing interaction energy than the major TS. NEDA revealed that while more stabilizing attractive interactions were established in the minor TS, the minor TS also featured more destabilizing steric interactions relative to the major TS.

Table SC5. NEDA results for *p*-chlorostyrene **2b** with catalyst (**R,R**)-**4a**

	MAJOR	MINOR	CIS
Electrical (ES+POL+SE)	-148.695	-154.914	-149.012
Charge Transfer (CT)	-231.871	-250.249	-230.234
Core (XC+DEF-SE)	324.376	346.812	322.204
Total Interaction (E)	-56.19	-58.351	-57.043

Table SC6. NEDA results for 2-vinylpyridine **2l** with catalyst (**R,R**)-**4a**

	MAJOR	MINOR
Electrical (ES+POL+SE)	-149.885	-155.333
Charge Transfer (CT)	-231.688	-246.875
Core (XC+DEF-SE)	325.56	342.161
Total Interaction (E)	-56.012	-60.047

Table SC7. NEDA results for 2-vinylpyridine **2l** with catalyst (**R,R**)-**4e**

	MAJOR	MINOR
Electrical (ES+POL+SE)	-157.454	-161.025
Charge Transfer (CT)	-235.835	-249.779
Core (XC+DEF-SE)	336.136	352.155
Total Interaction (E)	-57.152	-58.648

VIII. Analysis of Noncovalent Interactions in Transition States

Isosurfaces were generated using NCI plot^{15,16} with default settings, which were visualized in VMD.¹⁷ On inspecting these isosurfaces, a $\pi\text{-}\pi$ interaction between salen core and the benzoyl arene is clearly present in the minor and major TS3 (Figure SC7).

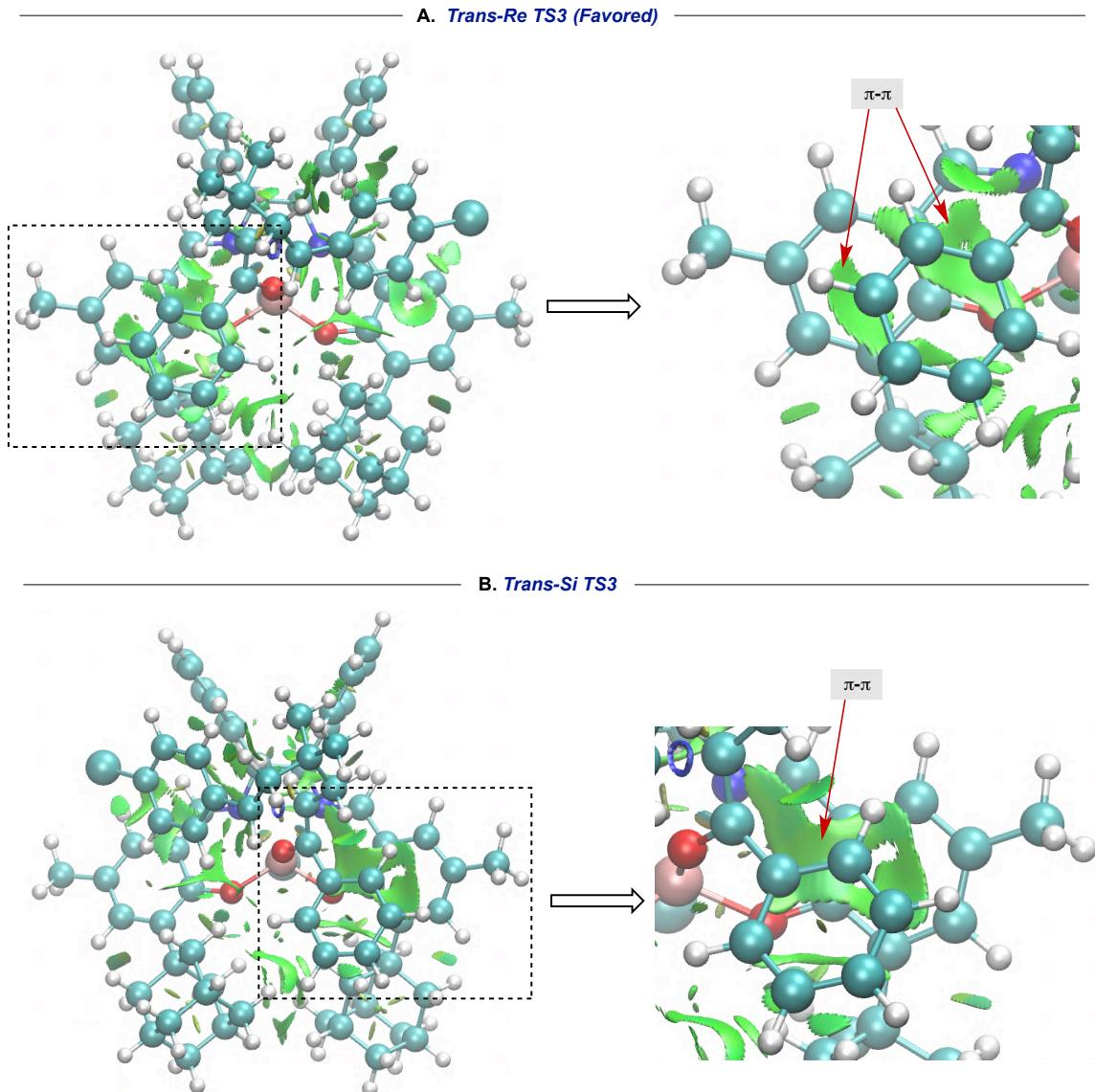


Figure SC7. Comparing similar $\pi\text{-}\pi$ stacking with benzoyl arene in **A.** *trans-Re* and **B.** *trans-Si* TSs.

The more striking and important difference is in the attractive NCIs between the catalyst and the *p*-chlorostyrene. In the major TS3, a CH- π interaction is established between a styrene CH and the salen core arene (Figure SC8A). In the minor TS3 the styrene does not establish this CH- π interaction, instead additional π - π interaction exists between the styrene and salen core (Figure SC8B).

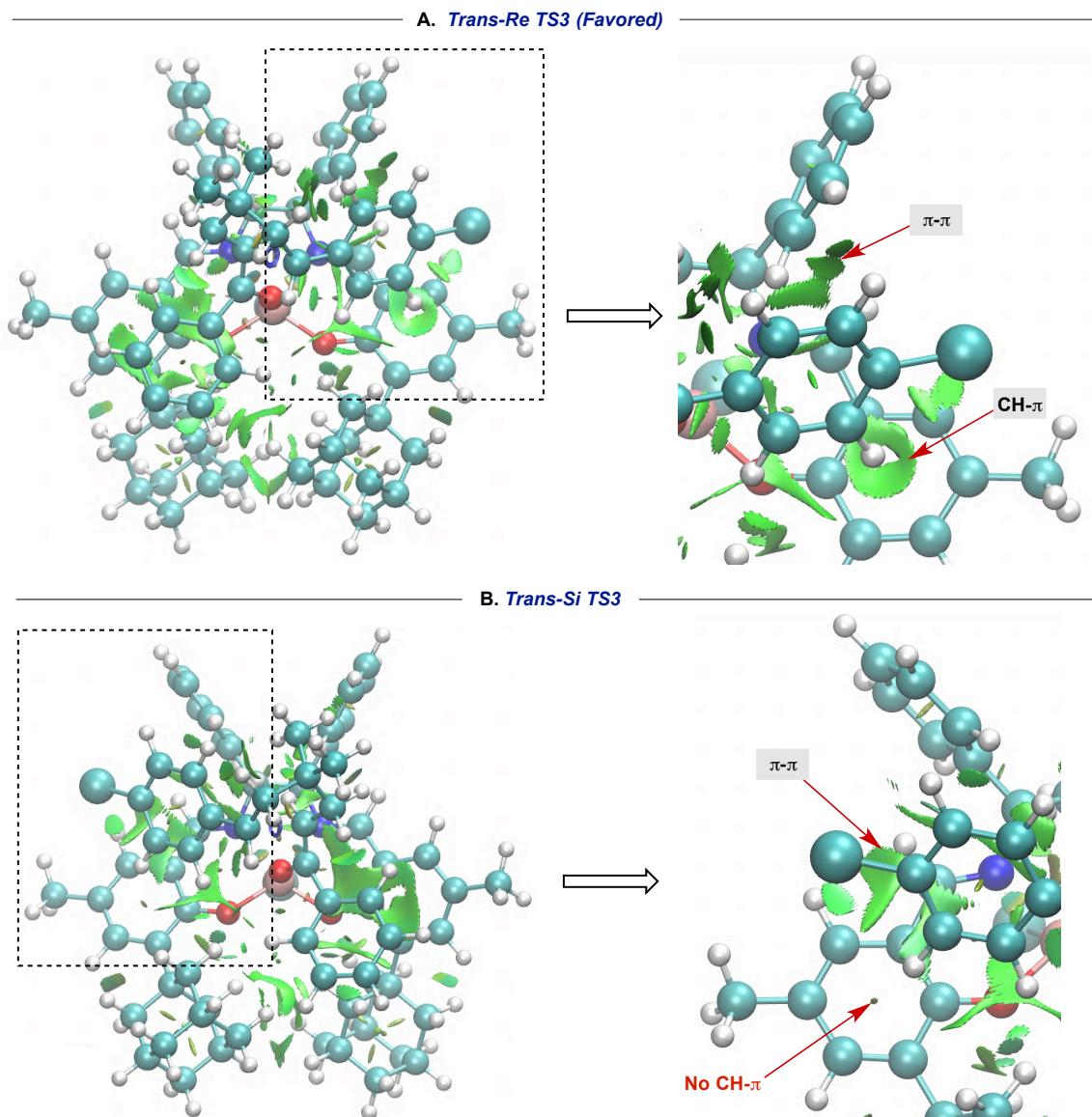


Figure SC8. Comparing NCIs with *p*-chlorostyrene in **A.** *trans*-Re and **B.** *trans*-Si TSs. Most notable difference is that the CH- π interaction in *trans*-Re TS is nonexistent in the *trans*-Si TS.

The *cis*-Si TS has a significantly different positioning of the intermediate than the major TS3. In the *cis*-Si TS, the adamantyl groups and chiral backbone substituents still play a similar role in positioning the substrate as in the major TS3. However, the substrate is orientated toward the chiral backbone rather than the salen core as a result of the more compact arrangement. Essentially, the *cis* arrangement allows for positioning of the styrene arene away from the catalyst bulk to minimize repulsive interactions. Specifically, the benzoyl arene is positioned near the chiral backbone in the *cis*-Si TS and forms a CH- π interaction with the diamine backbone phenyl substituent (Figure SC9). In this interaction, the C-H of the backbone phenyl substituent interacts with the benzoyl arene. The styrene engages in no other significant attractive interactions with the catalyst. The only other substantial attractive NCI is internal stacking interactions between the two arenes of the intermediate. Ultimately, the total interaction energy in the *cis*-Si TS3 is comparable to that of the major TS3.

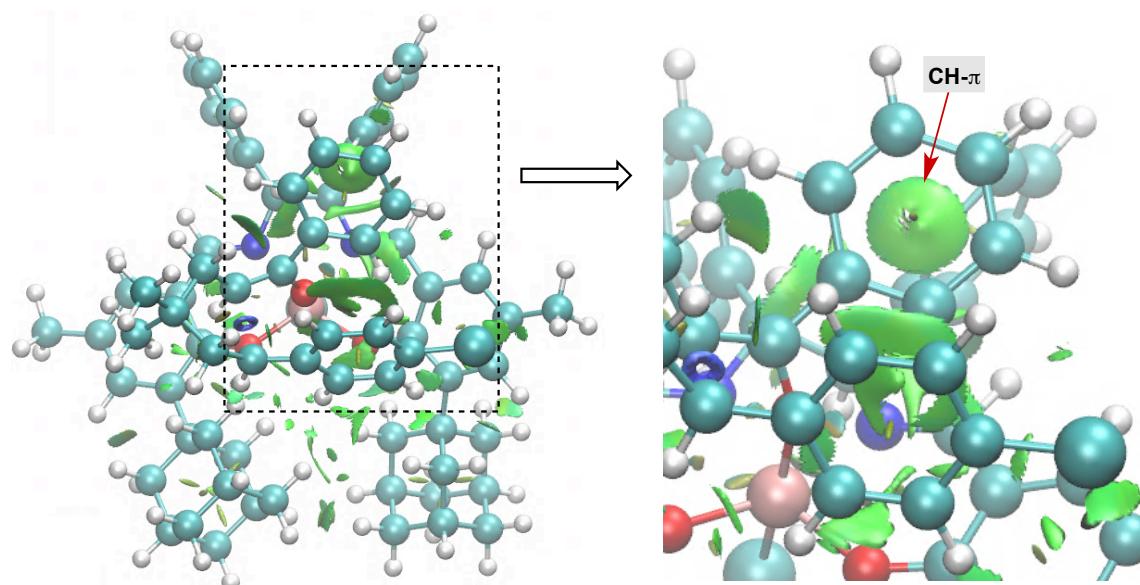


Figure SC9. NCI plot for *cis*-Si TS.

IX. Computational Methods for Catalyst-Substrate Matrix Parameterization

Conformational searches for intermediate II structures coordinated with a TiCl₃ catalyst surrogate were performed with MacroModel¹ version 11.7 using the OPLS_2005 force field with the forming bond constrained. All conformers within 10 kJ/mol of the minimum were optimized with the B3LYP^{3,4} functional and the 6-31G(d,p) basis set as implemented in Gaussian09 (revision D.01).⁵ Single point energy calculations were performed on these geometries with the M06 functional⁶ and the triple- ξ valence quality def2-TZVP basis set of Weigend and Ahlrichs.⁷ The lowest energy conformer was re-optimized in the gas phase at the M06/def2-TZVP level of theory. All of the optimized geometries were verified by frequency computations as minima (zero imaginary frequencies).

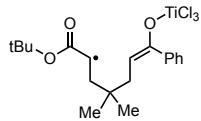
Conformational searches for Ti(salen) catalyst structures were performed in MacroModel¹ version 11.7 using the OPLS_2005 force field. All conformers within 10 kJ/mol of the minimum were optimized using the ω B97XD functional¹¹ and LANL2DZ¹² basis set for Ti and 6-31G(d) basis set for all other atoms as implemented in Gaussian09 (revision D.01).⁵ The lowest energy conformer was identified based on the energies for these optimized geometries. All of the optimized geometries were verified by frequency computations as minima (zero imaginary frequencies).

Conformational searches for ethylene diamine backbone arene structures were performed in MacroModel¹ version 11.7 with the OPLS3 force field.² All conformers within 10 kJ/mol of the minimum were optimized with the ω B97XD functional¹¹ and 6-31G(d) basis set as implemented in Gaussian09 (revision D.01).⁵ All of the optimized geometries were verified by frequency computations as minima (zero imaginary frequencies). Parameters such as quadrupole moment, molecular surface area, and polarizability were acquired from these optimized geometries to capture isolated parameters for the backbone substituents.

Parameters were acquired from the lowest energy ground state structures of catalysts, backbone arenes, and intermediates coordinated with TiCl₃ for MLR model development.

X. Cartesian Coordinates of Intermediate II Structures Bound with TiCl_3

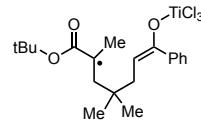
t-butylacrylate (2e) intermediate II bound with TiCl_3



C	2.49099	-2.09854	0.91151
C	1.04455	-1.81788	0.96967
C	0.47175	-0.59323	1.43736
C	1.10299	-1.03235	-1.54113
C	0.31519	0.06817	-1.58985
C	0.70959	1.47240	-1.75443
C	1.40793	4.16691	-2.04104
O	-1.00309	-0.12548	-1.45221
H	2.72696	-3.00142	1.49219
C	3.01688	-2.33006	-0.52632
C	2.52845	-3.66602	-1.06845
H	2.83864	-3.79473	-2.10935
H	2.95964	-4.48725	-0.48979
H	1.44364	-3.77898	-1.03000
C	4.53704	-2.35630	-0.47746
H	4.93994	-1.39685	-0.14117
H	4.89189	-3.12985	0.20898
H	4.95467	-2.57111	-1.46496
C	2.57888	-1.15849	-1.42266
H	3.00900	-0.23813	-1.00954
H	3.04681	-1.30576	-2.40761
C	1.95973	1.84099	-2.25770
C	-0.19860	2.48733	-1.44651
C	2.30704	3.17186	-2.38837
H	2.65731	1.08309	-2.58695
C	0.14887	3.81697	-1.58414
H	3.28227	3.43363	-2.78193
H	-0.57243	4.58559	-1.33249
H	1.68119	5.21020	-2.14652
H	3.04897	-1.27378	1.36208
O	-0.68711	-0.23473	1.18036
O	1.28612	0.13614	2.17341
C	0.89696	1.38691	2.83959
C	-0.24769	1.13134	3.79631
H	-0.41131	2.03105	4.39344
H	-1.17513	0.89456	3.27719
H	0.00032	0.31436	4.47753
C	0.57178	2.44312	1.80899
H	0.47243	3.40927	2.30941
H	1.37772	2.52314	1.07389

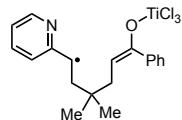
H	-0.36224	2.23100	1.29092
C	2.15384	1.75234	3.59899
H	1.99493	2.68150	4.14893
H	2.41664	0.96837	4.31154
H	2.99077	1.89545	2.91279
Ti	-2.27198	-0.57585	-0.24104
Cl	-3.88564	-0.90445	-1.73527
Cl	-2.34514	-2.65331	0.59301
Cl	-3.26635	1.10838	0.83482
H	0.54397	-1.96181	-1.59599
H	-1.18896	2.23035	-1.09101
H	0.32250	-2.56401	0.65906

t-butylmethacrylate (2f) intermediate II bound with TiCl_3



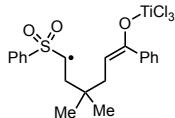
C	-3.74028	1.04228	-0.44736
C	-2.53609	1.78559	-0.00984
C	-1.86724	1.34034	1.20673
C	-1.11142	-0.67762	-1.20480
C	-0.10444	-1.29607	-0.57305
C	-0.11543	-2.50680	0.25884
C	-0.09594	-4.79906	1.85968
O	1.13236	-0.73596	-0.69431
H	-4.50451	1.76200	-0.77108
C	-3.55818	0.03175	-1.60443
C	-3.17172	0.72792	-2.90121
H	-3.04829	-0.00403	-3.70533
H	-3.95632	1.42684	-3.20544
H	-2.24293	1.29577	-2.82615
C	-4.90745	-0.64662	-1.81063
H	-5.20636	-1.20756	-0.92079
H	-5.68573	0.09211	-2.01965
H	-4.87084	-1.34194	-2.65380
C	-2.54874	-1.06520	-1.23344
H	-2.84120	-1.49578	-0.26802
H	-2.68030	-1.86580	-1.97748
C	-1.06596	-3.51127	0.08222
C	0.86261	-2.68988	1.23737
C	-1.05680	-4.64239	0.87682
H	-1.80312	-3.42923	-0.70437
C	0.86755	-3.81978	2.03137
H	-1.80290	-5.41214	0.71767

H	1.63297	-3.93663	2.78954	C	2.77821	-2.55200	-0.35296
H	-0.09085	-5.68593	2.48226	C	2.25151	-1.47205	-1.31668
H	-4.14359	0.49034	0.40657	H	2.85821	-0.57145	-1.17887
O	-2.22198	0.38576	1.86383	H	2.44756	-1.82803	-2.33963
O	-0.81888	2.12687	1.50074	C	1.91400	-3.80468	-0.36737
C	0.01664	1.88506	2.66514	H	1.77210	-4.16885	-1.38986
C	0.62290	0.49802	2.60417	H	2.40041	-4.60075	0.20311
H	1.44671	0.42720	3.31928	H	0.92564	-3.64772	0.07128
H	-0.10575	-0.28020	2.82421	C	4.18195	-2.92624	-0.80884
H	1.03267	0.31982	1.60603	H	4.82314	-2.04268	-0.87423
C	-0.78197	2.10474	3.93357	H	4.64499	-3.62615	-0.10808
H	-0.11542	2.02568	4.79587	H	4.15986	-3.40230	-1.79338
H	-1.22288	3.10428	3.93666	H	0.14383	-2.00990	-1.04113
H	-1.57444	1.36548	4.04080	C	1.84510	1.58974	-2.23061
C	1.10017	2.93449	2.53039	C	0.15613	2.46339	-0.77293
H	1.79249	2.86847	3.37212	C	2.36998	2.85935	-2.38048
H	1.66339	2.78954	1.60539	H	2.27799	0.76502	-2.78259
H	0.66474	3.93564	2.51515	C	0.67916	3.73255	-0.92915
C	-2.08431	3.01219	-0.70740	H	3.22704	3.01152	-3.02582
H	-2.04652	3.86437	-0.02143	H	0.21554	4.56849	-0.41777
H	-1.06347	2.90419	-1.09164	H	2.20386	4.93067	-1.84776
H	-2.74273	3.26573	-1.53876	H	3.64967	-1.19324	1.07412
H	-0.81064	0.18957	-1.78867	N	2.41467	0.82073	1.62292
Ti	2.49795	0.28006	-1.06948	C	1.06489	2.59557	2.49199
Cl	3.93722	0.23007	0.59015	H	0.96843	3.65631	2.68786
Cl	3.43112	-0.43590	-2.91711	Ti	-2.66599	-0.42720	-0.21379
Cl	1.72990	2.31443	-1.37308	Cl	-2.25264	-2.17112	1.06167
H	1.62537	-1.93467	1.38351	Cl	-4.08485	-0.98099	-1.78954
				Cl	-3.44395	1.25227	0.97443
				H	-0.87088	2.04653	3.26172
				H	-0.53043	-0.36591	2.77115
				H	-0.70289	2.31060	-0.12988



C	2.88922	-1.97898	1.07587
C	1.64329	-1.43174	1.65021
C	1.43837	-0.06457	1.93871
C	0.80656	-1.16065	-1.18573
C	0.18993	0.02679	-1.20303
C	0.74301	1.36949	-1.40578
C	1.79331	3.93519	-1.72589
O	-1.14823	0.02342	-0.94055
H	0.83662	-2.11246	1.91033
H	3.25975	-2.79136	1.71753
C	0.23357	0.36724	2.53315
C	2.21762	2.09263	1.89528
C	0.05246	1.70230	2.80929
H	3.01942	2.77507	1.61714

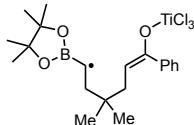
**Phenyl vinyl sulfone (2g) intermediate II
bound with TiCl_3**



C	1.50560	-2.29700	0.82335
C	0.93993	-0.89358	0.71525
S	1.11109	-0.17283	-0.90836
C	-0.53440	-0.99189	1.24688
C	-1.62484	-0.60869	0.28022
C	-2.45112	-1.47953	-0.52088
C	-4.10731	-3.05974	-2.12896
O	-1.85854	0.65650	0.21743
H	2.59733	-2.31395	0.88801
H	1.49334	-0.19550	1.35172
O	0.49444	1.14143	-0.86646
O	0.68550	-1.10364	-1.90741
C	2.84413	0.09199	-1.05833
C	3.41016	1.22203	-0.48667
C	3.60796	-0.84276	-1.73940
C	4.77499	1.41120	-0.60122
H	2.78439	1.94421	0.02800
C	4.97181	-0.63978	-1.84630
C	5.55102	0.48274	-1.27700
H	5.23324	2.29149	-0.16717
H	5.58308	-1.35592	-2.38181
H	6.61966	0.63918	-1.36635
C	0.83037	-2.86896	2.07321
H	1.21192	-2.88216	-0.05640
C	0.90693	-4.38232	2.10569
H	0.35865	-4.78060	2.96367
H	0.47713	-4.81860	1.19907
H	1.94340	-4.72159	2.18727
C	1.46495	-2.29976	3.33637
H	1.38636	-1.21053	3.39638
H	0.97300	-2.70817	4.22299
H	2.52514	-2.56200	3.39117
C	-0.61119	-2.36989	1.92120
H	-1.18640	-3.07372	1.32009
H	-1.11663	-2.30329	2.88796
H	-0.60857	-0.21830	2.01987
C	-2.03597	-2.74552	-0.95770
C	-3.71042	-1.01870	-0.93364
C	-2.85508	-3.51977	-1.75235
H	-1.04149	-3.10533	-0.72400
C	-4.52690	-1.80315	-1.71853
H	-2.50715	-4.48742	-2.09434
H	-5.50059	-1.43191	-2.01582

H	-4.74897	-3.67382	-2.74955
Ti	-1.06963	2.32633	0.31547
Cl	0.62729	2.52678	1.79771
Cl	-2.65373	3.29914	1.55263
Cl	-1.17869	3.61042	-1.48791
H	-4.03731	-0.03693	-0.61372
H	3.12731	-1.70283	-2.19059

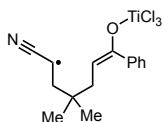
**Vinyl pinaolborane (2h) intermediate II
bound with TiCl_3**



C	3.21351	-1.63426	-1.14159
C	2.24691	-0.68199	-1.73513
B	2.02422	0.73861	-1.22648
C	0.35358	-2.26037	-0.17744
C	-0.31945	-1.39194	0.58530
C	0.00374	-0.89272	1.93327
C	0.54956	0.08519	4.48595
O	-1.48485	-0.89670	0.09720
H	3.62315	-1.21951	-0.21166
H	1.72559	-0.99686	-2.63672
C	1.03557	2.74030	-0.87718
C	2.39876	2.68040	-0.12541
O	1.12296	1.61631	-1.76953
O	2.70806	1.27571	-0.16090
C	0.80361	3.99165	-1.68923
H	-0.16978	3.92654	-2.17996
H	0.79983	4.87520	-1.04493
H	1.56121	4.12332	-2.46111
C	-0.15487	2.49194	0.02913
H	-0.34213	3.33123	0.70196
H	-1.03946	2.36153	-0.59700
H	-0.02163	1.58828	0.63089
C	3.51789	3.39303	-0.86190
H	3.40105	4.47788	-0.81912
H	4.46777	3.13232	-0.39172
H	3.56330	3.08807	-1.90951
C	2.35297	3.14086	1.31172
H	3.34974	3.06212	1.75162
H	2.04127	4.18733	1.36920
H	1.67062	2.53939	1.91302
C	2.69548	-3.05732	-0.86303
C	3.84514	-3.87119	-0.28503
H	3.52386	-4.88788	-0.04168
H	4.66840	-3.94304	-1.00096
H	4.23331	-3.41283	0.62921

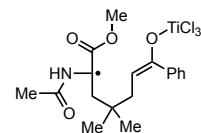
C	2.23089	-3.72884	-2.14755	H	0.64834	-1.45270	-1.29683
H	1.38149	-3.22603	-2.61315	H	3.10417	-0.58153	1.53850
H	3.04178	-3.74817	-2.88133	C	1.44439	-1.90268	1.54234
H	1.93500	-4.76346	-1.95141	H	-0.33020	2.06353	1.31428
C	1.56602	-3.03797	0.18225	H	0.43954	4.33825	1.86445
H	1.25909	-4.08433	0.32982	H	2.15590	5.44175	0.46841
H	1.97055	-2.70546	1.14187	H	3.07759	4.26739	-1.50204
H	-0.10858	-2.48165	-1.13644	H	2.29032	2.00482	-2.06831
C	-1.00673	-0.79441	2.88791	H	3.27469	-3.95044	-0.13064
C	1.28804	-0.47431	2.27038	H	1.78452	-3.29321	-0.80780
C	-0.73495	-0.31453	4.15463	H	3.25741	-3.31159	-1.77595
H	-2.01501	-1.10305	2.63249	H	5.27438	-2.49748	0.24084
C	1.55672	0.00761	3.53968	H	5.14432	-1.73309	-1.34678
H	-1.53086	-0.25010	4.88709	H	5.14704	-0.73725	0.11477
H	0.76193	0.46674	5.47775	H	3.49695	-2.27384	1.82952
H	4.07612	-1.74495	-1.81989	H	1.04574	-2.89736	1.36987
Ti	-2.94978	-0.18916	-0.52898	N	-0.13609	-0.20553	2.59209
Cl	-3.63296	1.39155	0.83375	C	0.58963	-0.98482	2.12704
Cl	-4.46175	-1.77647	-0.62246				
Cl	-2.55872	0.60271	-2.53458				
H	2.07152	-0.47729	1.52175				
H	2.55948	0.34145	3.78127				

Acrylonitrile (2i) intermediate II bound with TiCl_3



C	3.28115	-1.79029	-0.24536
C	2.69524	-0.65573	-1.10715
C	1.21558	-0.55306	-1.06895
C	2.86367	-1.60453	1.22865
C	0.48692	0.51201	-0.71373
O	-0.84920	0.34809	-0.57717
C	0.95431	1.86945	-0.39448
C	0.41847	2.54896	0.69791
C	0.85591	3.82320	1.00684
C	1.81922	4.44057	0.22581
C	2.34063	3.78065	-0.87407
C	1.90877	2.50457	-1.18504
Ti	-2.42420	-0.32997	-0.22060
Cl	-3.66993	-0.11861	-2.01109
Cl	-2.14692	-2.47416	0.18166
Cl	-3.36888	0.72086	1.44440
C	2.86735	-3.15817	-0.76614
C	4.79857	-1.68238	-0.31100
H	3.03712	-0.82191	-2.13864
H	3.14923	0.28401	-0.77827

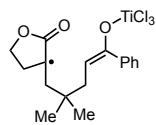
Methyl-2-acetamidoacrylate (2j) intermediate II bound with TiCl_3



C	2.90408	-2.01321	0.51221
C	1.71030	-1.47520	1.19501
C	1.76627	-0.14916	1.80737
C	1.00176	-0.42926	-1.57748
C	0.41736	0.73408	-1.25125
C	1.05719	2.01271	-0.91156
C	2.24650	4.42725	-0.18325
O	-0.92854	0.77278	-1.17746
O	0.74219	0.08706	2.63447
C	2.84535	-2.12194	-1.03421
C	2.44576	-0.77172	-1.66126
C	4.25835	-2.45219	-1.49864
C	1.92214	-3.25232	-1.46621
C	0.47047	2.83291	0.04985
C	2.22955	2.44061	-1.52808
C	1.06394	4.02547	0.41537
C	2.82086	3.63572	-1.16298
O	2.67555	0.62195	1.61827
Ti	-2.39969	0.09419	-0.43508
Cl	-2.94683	0.82386	1.62267
Cl	-3.91803	1.29903	-1.51915
Cl	-3.02509	-1.89373	-1.29273
N	0.64946	-2.34128	1.47515
C	-0.65838	-2.08218	1.24291

C	-1.65400	-3.08307	1.70738	C	0.83915	4.89367	0.90455
O	-0.98306	-1.05817	0.65637	O	-0.95354	0.52127	-0.56498
C	0.77664	1.33383	3.31522	C	3.55790	-0.79885	-0.81031
H	3.12135	-3.02159	0.89751	C	2.69904	0.39741	-1.24966
H	3.75157	-1.37510	0.77335	C	5.01204	-0.34507	-0.79730
H	0.30298	-1.22073	-1.83532	C	3.42720	-1.95544	-1.79018
H	2.71038	5.36443	0.10098	C	1.25727	3.27548	-0.81349
H	3.06358	0.00975	-1.20905	C	-0.08204	2.68551	1.08985
H	2.73931	-0.82135	-2.72092	C	1.42184	4.55055	-0.30313
H	4.27808	-2.63212	-2.57660	C	0.08685	3.95895	1.59777
H	4.94577	-1.63045	-1.28006	Ti	-2.48532	-0.30156	-0.44206
H	4.63693	-3.35026	-1.00228	Cl	-3.35020	0.01059	1.54137
H	1.86425	-3.30244	-2.55748	Cl	-3.83498	0.51040	-1.96479
H	2.30991	-4.21244	-1.11182	Cl	-2.13459	-2.43597	-0.87484
H	0.90184	-3.14700	-1.09114	C	1.38616	-3.15830	0.50108
H	-0.45959	2.52318	0.51539	C	0.25395	-3.39059	1.49836
H	2.66485	1.84885	-2.32417	O	-0.10921	-2.10754	1.99496
H	0.59677	4.64850	1.16972	C	0.89208	-1.21167	1.77328
H	3.73064	3.95690	-1.65651	O	0.87941	-0.11139	2.25400
H	0.88250	-3.27851	1.77624	H	3.96721	-1.95348	0.93952
H	-2.22085	-3.43559	0.84396	H	3.31220	-0.34820	1.28240
H	-1.20670	-3.92432	2.23468	H	0.85259	-0.77389	-1.60271
H	-2.36289	-2.57608	2.36564	H	0.96700	5.89281	1.30471
H	-0.14764	1.39284	3.88422	H	2.95537	1.25518	-0.61865
H	1.63873	1.38089	3.98347	H	3.01089	0.66069	-2.27121
H	0.84028	2.16075	2.60686	H	5.30869	0.03227	-1.77963
				H	5.17019	0.45337	-0.06731

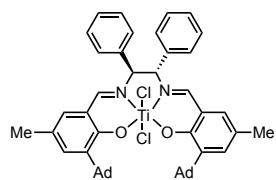
**3-methyldihydrofuranone (2k)
intermediate II bound with TiCl₃**



C	3.20134	-1.22414	0.63277	H	5.67849	-1.17355	-0.54210
C	1.87594	-1.81708	0.89077	H	3.83330	-1.67011	-2.76457
C	1.23355	0.16329	-1.20148	H	3.98900	-2.82639	-1.43911
C	0.32056	0.97552	-0.66084	H	2.39431	-2.26849	-1.94864
C	0.51196	2.32812	-0.11792	H	1.68637	3.01813	-1.77554
				H	-0.65043	1.94635	1.64139
				H	1.99771	5.28210	-0.85778
				H	-0.36877	4.22277	2.54481
				H	0.99667	-3.16227	-0.52635
				H	2.16272	-3.92800	0.54282
				H	0.57974	-4.00832	2.34113
				H	-0.63203	-3.84485	1.05601

XI. Cartesian coordinates of Ti(salen) Structures

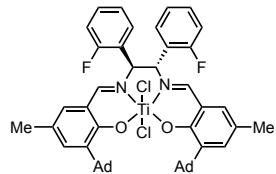
Phenyl backbone, (S,S)-4a



Ti	-0.50833	0.01142	0.00476	H	3.23568	-5.34191	-0.93201
O	0.49833	1.51833	-0.28880	H	3.97580	-4.87825	0.60848
C	-2.12643	2.47335	-0.80709	H	3.71595	-2.50996	1.48083
N	-2.20759	1.24781	-0.43154	H	2.81854	-1.31234	0.54547
C	-3.50917	0.57048	-0.51554	C	4.66191	-3.65550	-2.55618
C	0.32934	2.82919	-0.46190	H	4.18426	-4.46990	-3.11729
C	1.39729	3.74743	-0.29563	H	5.57991	-3.38492	-3.09477
C	1.13919	5.07469	-0.62775	C	4.40587	-1.31114	-1.70203
C	-0.10143	5.55963	-1.06589	H	3.73563	-0.44433	-1.64933
C	-1.14535	4.66189	-1.12803	H	5.31314	-0.98985	-2.23170
C	-0.94941	3.30690	-0.81695	C	2.42910	-2.84853	-1.73712
H	-3.56297	0.13724	-1.52081	H	1.73288	-2.00497	-1.72158
H	1.93966	5.80015	-0.53807	H	1.92733	-3.66570	-2.27277
C	-0.27154	7.01401	-1.42260	C	3.71719	-2.44858	-2.47138
H	-2.14082	4.99790	-1.41103	H	3.45816	-2.10656	-3.48033
O	0.51352	-1.48525	0.30252	C	5.04788	4.11244	1.05610
C	0.36113	-2.78649	0.54467	C	4.78799	3.56768	2.46774
C	1.43313	-3.70330	0.39582	C	3.84391	2.36142	2.37394
C	1.20246	-5.00891	0.82043	C	2.51278	2.78617	1.73590
C	-0.01940	-5.47836	1.32432	C	2.74259	3.33200	0.30127
C	-1.07574	-4.59327	1.34862	C	3.71629	4.52986	0.41593
C	-0.90504	-3.25771	0.95024	H	5.70173	4.99166	1.11274
C	-2.09454	-2.44461	0.89206	H	4.34192	4.34923	3.09734
N	-2.19290	-1.24058	0.45463	H	5.73554	3.27390	2.93874
C	-3.51083	-0.59107	0.49562	H	3.64544	1.96411	3.37635
H	-3.60890	-0.15944	1.49841	H	1.82255	1.93743	1.71307
H	-2.06077	-4.92439	1.67117	H	2.03513	3.56737	2.34228
C	-0.15881	-6.90589	1.78719	H	3.26488	5.32229	1.02765
H	2.00848	-5.73063	0.75231	H	3.91214	4.95287	-0.57905
Cl	-0.81412	-0.61531	-2.23431	C	4.49226	1.27151	1.50826
H	-3.00841	-2.94585	1.21904	H	3.82199	0.40640	1.45227
H	-3.04542	2.97501	-1.11790	H	5.42930	0.92857	1.96802
Cl	-0.81167	0.63734	2.24435	C	5.70929	3.02833	0.19629
H	0.29474	7.26806	-2.32634	H	6.66760	2.72632	0.63936
H	-1.32206	7.25621	-1.60934	H	5.92412	3.42111	-0.80663
H	0.08641	7.66617	-0.61828	C	3.43948	2.24419	-0.55052
H	0.22924	-7.60742	1.04052	H	3.61887	2.63414	-1.56174
H	0.39726	-7.07549	2.71667	H	2.78196	1.37603	-0.64949
H	-1.20601	-7.16083	1.97593	C	4.76627	1.82261	0.09926
C	4.76448	-1.78925	-0.28569	H	5.23174	1.04901	-0.52070
C	5.70790	-2.99531	-0.37394	C	-6.88826	-3.12149	-0.37272

C	-5.80000	-3.08256	-1.24384	C	-0.71231	-3.23631	-0.98601
C	-4.70268	-2.28040	-0.95386	C	-1.89733	-2.41636	-0.93216
C	-4.67991	-1.51112	0.21452	N	-1.99014	-1.21498	-0.48681
C	-5.76884	-1.55714	1.08206	C	-3.29996	-0.55162	-0.52272
C	-6.87121	-2.35764	0.78963	H	-3.39570	-0.10833	-1.51815
H	-7.74616	-3.74664	-0.60182	H	-1.86660	-4.89073	-1.73759
H	-5.80706	-3.67732	-2.15242	C	0.02305	-6.88389	-1.83518
H	-3.85107	-2.25665	-1.63094	H	2.17744	-5.73403	-0.73926
H	-7.71500	-2.38225	1.47258	Cl	-0.61258	-0.57415	2.20955
C	-6.97580	3.01503	0.24011	Cl	-0.58469	0.64103	-2.27600
C	-6.88753	2.27697	-0.93561	H	-2.81244	-2.91065	-1.26677
C	-5.75636	1.50427	-1.19105	H	-2.82832	3.03400	1.01669
C	-4.70956	1.46069	-0.27310	C	-6.85349	2.95125	-0.02090
C	-4.80352	2.20589	0.90750	C	-6.67233	2.22090	1.14762
C	-5.92959	2.97972	1.16133	C	-5.50381	1.48892	1.30207
H	-7.85709	3.61706	0.44040	C	-4.50741	1.45548	0.33264
H	-7.69799	2.29988	-1.65773	C	-4.71496	2.19829	-0.83433
H	-3.98409	2.18710	1.62317	C	-5.87364	2.94349	-1.01279
H	-5.99212	3.55485	2.08027	H	-7.41666	2.20461	1.93580
H	-5.69218	0.91996	-2.10521	H	-6.01600	3.51007	-1.92697
H	-5.76053	-0.95226	1.98511	C	-6.70997	-3.06155	0.30826

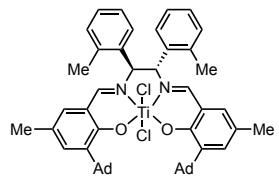
***o*-fluorophenyl backbone (*S,S*)-4b**



Ti	-0.29758	0.03101	-0.03322	C	3.81702	-2.46171	2.54259
O	0.71320	1.53612	0.24955	C	2.54941	-2.85443	1.77038
C	-1.91186	2.52061	0.71752	C	2.90458	-3.32984	0.33606
N	-1.99444	1.28271	0.38791	C	3.67278	-2.20508	-0.39624
C	-3.28179	0.58927	0.50987	H	5.46103	-1.02501	-0.14890
C	0.54880	2.85341	0.37474	H	3.87816	-0.46126	1.71082
C	1.62608	3.75859	0.19609	H	5.43172	-1.01704	2.34575
C	1.37024	5.09918	0.47070	H	3.52941	-2.11266	3.54130
C	0.12518	5.60734	0.86796	H	2.02494	-3.66538	2.29368
C	-0.92408	4.71759	0.95120	H	1.86079	-2.00555	1.72967
C	-0.73198	3.35066	0.69470	H	3.02295	-1.33261	-0.50592
H	-3.28807	0.14100	1.50702	H	3.93862	-2.54224	-1.40754
H	2.17725	5.81566	0.36739	C	4.74741	-3.67694	2.66170
C	-0.04246	7.07597	1.16198	H	4.24514	-4.48386	3.21207
H	-1.92077	5.06935	1.20976	H	5.65134	-3.41237	3.22651
O	0.71209	-1.47729	-0.31279	C	5.86635	-3.03695	0.51053
C	0.55081	-2.77682	-0.55776	H	6.17018	-3.38129	-0.48729
C	1.61030	-3.70433	-0.38722	H	6.78184	-2.76146	1.05092
C	1.37865	-5.00569	-0.82335	C	3.86245	-4.53726	0.47502
C	0.16399	-5.46164	-1.35690	H	4.14975	-4.90749	-0.51895
C	-0.88535	-4.56851	-1.39500	H	3.35575	-5.35950	0.99811

C	5.13038	-4.15777	1.25454	N	2.01274	1.29333	0.36396
H	5.77589	-5.04184	1.32781	C	3.32372	0.63352	0.46011
C	4.13595	2.25772	-2.35058	C	-0.54246	2.84965	0.42514
C	5.09583	3.45001	-2.45883	C	-1.62610	3.75327	0.28219
C	5.31881	4.04244	-1.06022	C	-1.37575	5.08599	0.59730
C	3.97249	4.49557	-0.47667	C	-0.13049	5.58854	1.00120
C	2.98350	3.31146	-0.34819	C	0.92459	4.70295	1.04817
C	2.79060	2.71723	-1.76866	C	0.73760	3.34360	0.75093
H	3.96343	1.82590	-3.34351	H	3.38765	0.25533	1.48388
H	4.67861	4.21275	-3.12988	H	-2.18712	5.80103	0.52255
H	6.05364	3.12892	-2.88960	C	0.03116	7.04804	1.34063
H	5.98329	4.91279	-1.12803	H	1.92177	5.05227	1.30803
H	4.14216	4.95315	0.50779	O	-0.69292	-1.46271	-0.33689
H	3.54863	5.26872	-1.13130	C	-0.53861	-2.75230	-0.63157
H	2.33931	3.48033	-2.41674	C	-1.59686	-3.68460	-0.48275
H	2.09173	1.87591	-1.73701	C	-1.37092	-4.96938	-0.96851
C	5.94288	2.98399	-0.14186	C	-0.16232	-5.40616	-1.53120
H	6.13162	3.41129	0.85214	C	0.88796	-4.51340	-1.54621
H	6.91073	2.65669	-0.54455	C	0.71972	-3.19709	-1.08720
C	4.74596	1.19429	-1.42671	C	1.90710	-2.38556	-0.99186
H	4.06434	0.33941	-1.36038	N	2.00510	-1.20166	-0.50138
H	5.69200	0.82465	-1.84585	C	3.34177	-0.58587	-0.48439
C	3.64417	2.25016	0.56414	H	3.52106	-0.21666	-1.49832
H	2.97553	1.39245	0.67807	H	1.86652	-4.82426	-1.90641
H	3.79918	2.67758	1.56422	C	-0.02712	-6.81037	-2.06176
C	4.98439	1.79175	-0.03035	H	-2.16913	-5.70010	-0.90146
H	5.42149	1.03489	0.63016	Cl	0.65468	-0.57309	2.19629
H	0.30112	7.69138	0.32305	H	2.82485	-2.87703	-1.32434
H	-1.09035	7.32490	1.35435	H	2.83975	3.03283	1.02961
H	0.53812	7.37117	2.04379	Cl	0.60463	0.66591	-2.28783
H	-1.02416	-7.13501	-2.02907	H	-0.53515	7.30911	2.24231
H	0.58064	-7.04412	-2.76543	H	1.08047	7.29899	1.52235
H	0.40852	-7.59405	-1.09546	H	-0.33235	7.68839	0.52928
H	-7.76470	3.52520	-0.15701	H	-0.41139	-7.54565	-1.34635
H	-3.94767	2.19141	-1.60469	H	-0.58896	-6.93557	-2.99483
H	-3.69512	-2.20117	1.61389	H	1.01868	-7.05690	-2.26872
H	-7.57762	-3.67816	0.52122	C	-4.92392	-1.83653	0.36319
F	-5.53462	-0.79145	-2.24044	C	-5.84697	-3.05796	0.45589
F	-5.33935	0.78103	2.43176	C	-5.10403	-4.19539	1.16710
				C	-3.83843	-4.54853	0.37208
				C	-2.88560	-3.33425	0.26181
				C	-3.66039	-2.19198	-0.43542
				H	-5.45235	-1.02691	-0.14963
				H	-6.15219	-3.37629	-0.55010
				H	-6.76203	-2.80076	1.00599
				H	-5.74602	-5.08360	1.21913
				H	-3.32605	-5.38301	0.86957
				H	-4.12983	-4.89175	-0.63029
Ti	0.32176	0.04125	-0.04687	H	-3.92807	-2.50047	-1.45536
O	-0.69829	1.53634	0.25849	H	-3.01352	-1.31445	-0.52170
C	1.92191	2.52036	0.73235	C	-4.71719	-3.75136	2.58518

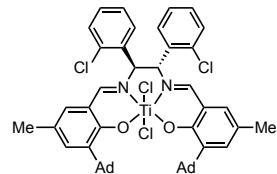
o-tolyl backbone (*S,S*)-4c



Ti	0.32176	0.04125	-0.04687
O	-0.69829	1.53634	0.25849
C	1.92191	2.52036	0.73235

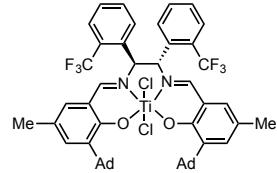
H	-4.20992	-4.57106	3.11160	C	5.55168	3.03809	-1.45417
H	-5.61977	-3.50540	3.16050	H	7.53651	3.70108	-0.93739
C	-4.52146	-1.38486	1.77631	H	7.59870	2.43920	1.17940
H	-3.86547	-0.50714	1.71908	C	5.73001	0.84228	2.26961
H	-5.41368	-1.08793	2.34457	H	3.58970	2.19670	-1.69212
C	-2.52566	-2.89741	1.70735	H	5.50966	3.59078	-2.38757
H	-1.83998	-2.04545	1.68775	H	6.64235	1.11688	2.80627
H	-1.99738	-3.72110	2.20637	H	4.88162	1.05828	2.92888
C	-3.79173	-2.52989	2.49525	H	5.75135	-0.24038	2.10583
H	-3.50115	-2.20731	3.50200	H	6.87178	-1.29081	-2.45884
C	-5.32501	4.05657	-0.94834	H	5.14860	-1.03610	-2.74621
C	-5.10689	3.50046	-2.36257	H	6.06984	0.14844	-1.81586
C	-4.14358	2.30831	-2.28943				
C	-2.79662	2.75696	-1.70276				
C	-2.98428	3.31484	-0.26683				
C	-3.97743	4.49859	-0.35986				
H	-5.99261	4.92618	-0.99094				
H	-4.69448	4.28118	-3.01563				
H	-6.06592	3.18818	-2.79710				
H	-3.97492	1.90246	-3.29392				
H	-2.09510	1.91720	-1.69484				
H	-2.35089	3.53750	-2.33369	Ti	-0.12222	0.03997	-0.05811
H	-3.55832	5.29011	-0.99530	O	0.89587	1.54013	0.22062
H	-4.14423	4.92982	0.63691	C	-1.72506	2.53966	0.66593
C	-4.74641	1.21987	-1.39031	N	-1.81489	1.30331	0.32960
H	-4.06257	0.36523	-1.34957	C	-3.11354	0.62977	0.45511
H	-5.69384	0.85904	-1.81393	C	0.74003	2.85785	0.35021
C	-5.94114	2.97320	-0.05415	C	1.82522	3.75617	0.18651
H	-6.91020	2.65339	-0.45987	C	1.57534	5.09722	0.46402
H	-6.12588	3.37445	0.95142	C	0.32960	5.61212	0.85078
C	-3.63645	2.22766	0.62083	C	-0.72641	4.72925	0.91963
H	-3.78683	2.62776	1.63282	C	-0.54046	3.36209	0.65904
H	-2.96411	1.36938	0.70781	H	-3.14817	0.24419	1.47677
C	-4.97889	1.78107	0.02208	H	2.38817	5.80867	0.37213
H	-5.41073	1.00680	0.66556	C	0.16889	7.08063	1.14909
C	6.40480	-3.24326	0.97686	H	-1.72322	5.08641	1.16997
C	5.19343	-3.11204	1.65105	O	0.88661	-1.47182	-0.31997
C	4.22035	-2.26409	1.14113	C	0.72816	-2.76710	-0.58617
C	4.43593	-1.54380	-0.04047	C	1.78342	-3.69852	-0.41292
C	5.64941	-1.67758	-0.73098	C	1.55718	-4.99230	-0.87355
C	6.62020	-2.53453	-0.19848	C	0.35035	-5.43758	-1.43381
H	7.17861	-3.90099	1.36164	C	-0.69848	-4.54365	-1.47040
H	5.00889	-3.65991	2.56985	C	-0.53004	-3.21862	-1.03649
H	3.27212	-2.15144	1.66346	C	-1.71606	-2.40290	-0.96473
C	5.94740	-0.92346	-2.00450	N	-1.81182	-1.20943	-0.49666
H	7.56602	-2.64443	-0.72279	C	-3.13688	-0.57386	-0.50717
C	6.68259	3.09766	-0.64377	H	-3.29244	-0.19978	-1.52249
C	6.71498	2.38551	0.54883	H	-1.67551	-4.85970	-1.83023
C	5.63610	1.59757	0.96566	C	0.21569	-6.85045	-1.94086
C	4.50556	1.53139	0.13701	H	2.35388	-5.72283	-0.78764
C	4.47531	2.25382	-1.06188	Cl	-0.46203	-0.53819	2.19106

***o*-chlorophenyl backbone (*S,S*)-4d**



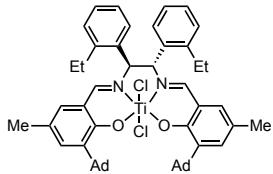
Cl	-0.40187	0.62637	-2.30733	H	4.91399	4.19167	-3.10782
H	-2.63169	-2.89659	-1.29951	H	6.28115	3.10140	-2.85223
H	-2.64025	3.05915	0.95860	H	6.20138	4.88708	-1.09299
C	-6.52600	3.13148	-0.43510	H	4.34385	4.93740	0.52372
C	-6.46588	2.47743	0.78782	H	3.76821	5.25558	-1.12124
C	-5.36231	1.68244	1.09221	H	2.56442	3.47173	-2.41918
C	-4.31116	1.51916	0.18750	H	2.30129	1.86900	-1.74043
C	-4.39604	2.19398	-1.03697	C	6.14055	2.95963	-0.10528
C	-5.48511	2.99370	-1.35067	H	6.32088	3.38712	0.89021
H	-7.26543	2.57795	1.51338	H	7.11098	2.62689	-0.49718
H	-5.52452	3.50232	-2.30822	C	4.94875	1.17467	-1.40116
C	-6.29923	-3.21850	0.79633	H	4.26241	0.32319	-1.34158
C	-6.42981	-2.56172	-0.41972	H	5.89745	0.80017	-1.80985
C	-5.41038	-1.71996	-0.86175	C	3.83064	2.23751	0.57678
C	-4.25703	-1.51383	-0.10360	H	3.15627	1.38320	0.68389
C	-4.14871	-2.19387	1.11648	H	3.97685	2.66484	1.57820
C	-5.15199	-3.03867	1.56587	C	5.17502	1.77220	-0.00281
H	-7.31439	-2.69559	-1.03240	H	5.60126	1.01397	0.66323
H	-5.04130	-3.55006	2.51634	H	0.51812	7.69691	0.31312
C	5.10624	-1.83814	0.42344	H	-0.87820	7.33446	1.33926
C	4.68848	-1.35344	1.82107	H	0.74844	7.36983	2.03351
C	3.95005	-2.48118	2.55831	H	-0.83070	-7.10329	-2.13690
C	2.69236	-2.86520	1.76561	H	0.77109	-6.98803	-2.87604
C	3.06688	-3.33509	0.33431	H	0.60756	-7.57344	-1.21716
C	3.85102	-2.21041	-0.38078	Cl	-5.34013	0.90077	2.65813
H	5.64151	-1.04126	-0.10204	H	-7.38680	3.74951	-0.67039
H	4.03375	-0.47703	1.73602	H	-3.57987	2.08814	-1.74827
H	5.57444	-1.04364	2.39214	H	-3.24867	-2.05411	1.71134
H	3.64885	-2.13498	3.55400	Cl	-5.62454	-0.93855	-2.41471
H	2.15755	-3.67677	2.27741	H	-7.09376	-3.87405	1.13867
H	2.00811	-2.01315	1.71975				
H	3.20667	-1.33429	-0.49490				
H	4.12966	-2.54352	-1.38996				
C	4.87254	-3.70149	2.68606				
H	4.35823	-4.50807	3.22573				
H	5.76939	-3.44380	3.26518				
C	6.02647	-3.05811	0.55457				
H	6.34354	-3.39972	-0.44005				
H	6.93526	-2.78950	1.10962				
C	4.01637	-4.54799	0.48175	Ti	-0.19623	0.02957	-0.04334
H	4.31816	-4.91408	-0.50944	O	-1.21807	1.53893	0.16544
H	3.49714	-5.37061	0.99188	C	1.39529	2.53772	0.62357
C	5.27393	-4.17844	1.28273	N	1.49209	1.30155	0.28181
H	5.91381	-5.06606	1.36184	C	2.83073	0.69323	0.36240
C	4.35380	2.24004	-2.33255	C	-1.06693	2.85474	0.30850
C	5.32048	3.42756	-2.43176	C	-2.15015	3.75385	0.13839
C	5.53176	4.02022	-1.03144	C	-1.90306	5.09268	0.42841
C	4.18173	4.48046	-0.46231	C	-0.66164	5.60445	0.83407
C	3.18554	3.30142	-0.34359	C	0.39386	4.72152	0.90704
C	3.00460	2.70689	-1.76552	C	0.21007	3.35620	0.63405
H	4.18973	1.80803	-3.32683	H	3.00750	0.49900	1.42035

***o*-trifluorotolyl backbone (*S,S*)-4e**



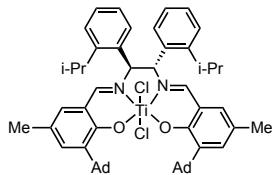
H	-2.71445	5.80520	0.33159	H	-4.03587	-2.08127	3.57854
C	-0.50475	7.07039	1.14656	C	-5.84449	4.02026	-1.11451
H	1.38832	5.07663	1.16908	C	-5.62475	3.41750	-2.50911
O	-1.21103	-1.48615	-0.25278	C	-4.66161	2.22846	-2.39461
C	-1.06318	-2.78376	-0.51054	C	-3.31554	2.69711	-1.82116
C	-2.12871	-3.70444	-0.34502	C	-3.50555	3.30016	-0.40399
C	-1.90683	-5.00276	-0.79454	C	-4.49802	4.48072	-0.53711
C	-0.69600	-5.46176	-1.33574	H	-6.51144	4.88831	-1.18671
C	0.36079	-4.57731	-1.36404	H	-5.21157	4.17586	-3.18760
C	0.19670	-3.24804	-0.94087	H	-6.58321	3.09077	-2.93412
C	1.38661	-2.44266	-0.85171	H	-4.49116	1.78941	-3.38472
N	1.48753	-1.24325	-0.39565	H	-2.61404	1.85821	-1.78682
C	2.84182	-0.66364	-0.38300	H	-2.87054	3.45793	-2.47633
H	3.10291	-0.47673	-1.42486	H	-4.07639	5.25199	-1.19556
H	1.34008	-4.90331	-1.70832	H	-4.66807	4.94238	0.44530
C	-0.56681	-6.87984	-1.82939	C	-5.26593	1.17025	-1.46049
H	-2.71027	-5.72663	-0.71510	H	-4.58228	0.31716	-1.39014
Cl	0.11084	-0.42005	2.23929	H	-6.21250	0.79548	-1.87379
H	2.30229	-2.94694	-1.16778	C	-6.46256	2.96732	-0.18577
H	2.31056	3.06180	0.90599	H	-7.43084	2.63411	-0.58252
Cl	0.10255	0.50208	-2.32148	H	-6.64914	3.40186	0.80548
H	-1.08251	7.34862	2.03569	C	-4.15946	2.24302	0.51789
H	0.54205	7.32553	1.33647	H	-4.31093	2.67638	1.51591
H	-0.85845	7.69403	0.31803	H	-3.48803	1.38741	0.63421
H	-0.95644	-7.59478	-1.09646	C	-5.50094	1.77809	-0.06804
H	-1.12727	-7.02561	-2.76023	H	-5.93445	1.02661	0.60069
H	0.47805	-7.13673	-2.02796	C	5.57940	-3.31633	1.66535
C	-5.44908	-1.81286	0.42544	C	4.40910	-2.87134	2.27215
C	-6.37899	-3.02521	0.55913	C	3.54923	-2.02838	1.58274
C	-5.64356	-4.14157	1.31038	C	3.83669	-1.60988	0.28049
C	-4.37821	-4.52819	0.53010	C	5.00157	-2.08698	-0.33348
C	-3.41863	-3.32345	0.38150	C	5.86820	-2.93050	0.36362
C	-4.18528	-2.20189	-0.35713	H	6.26158	-3.97016	2.19904
H	-5.97237	-1.01971	-0.11724	H	4.16548	-3.17568	3.28510
H	-6.68538	-3.37676	-0.43535	H	2.63033	-1.68826	2.05538
H	-7.29297	-2.74396	1.09906	C	5.33240	-1.73823	-1.76243
H	-6.29023	-5.02404	1.39136	H	6.76776	-3.28981	-0.12137
H	-3.87055	-5.34880	1.05500	C	5.79365	3.26399	-1.46232
H	-4.67001	-4.90278	-0.46085	C	5.96604	2.87243	-0.14190
H	-4.45197	-2.54488	-1.36620	C	5.02158	2.05657	0.48279
H	-3.53418	-1.33072	-0.47225	C	3.89794	1.61014	-0.22318
C	-5.25754	-3.65057	2.71312	C	3.72780	2.03369	-1.54453
H	-4.75542	-4.45386	3.26889	C	4.66321	2.85230	-2.16156
H	-6.16015	-3.38046	3.27737	H	6.53455	3.89816	-1.93840
C	-5.04706	-1.31396	1.82273	H	6.83322	3.20683	0.41474
H	-4.38554	-0.44276	1.73620	C	5.22124	1.70917	1.93659
H	-5.93847	-0.99203	2.37826	H	2.83953	1.71985	-2.08905
C	-3.05993	-2.83911	1.81213	H	4.50942	3.16369	-3.18983
H	-2.36987	-1.99170	1.76555	F	4.16321	2.10066	2.68142
H	-2.53761	-3.64836	2.34034	F	5.36709	0.38852	2.13304
C	-4.32568	-2.43765	2.58307	F	6.30307	2.30535	2.45727

F	4.33141	-2.09757	-2.59898	H	-7.38236	3.80639	-0.40962
F	6.43818	-2.35917	-2.19586	H	-7.19988	2.62519	1.74832
F	5.52676	-0.42067	-1.93735	C	-5.26734	0.99087	2.64404
				H	-3.66773	2.06227	-1.65258
<i>o</i>-ethylphenyl backbone (<i>S,S</i>)-4f				H	-5.59874	3.52556	-2.12935
				C	-6.53035	-3.16028	0.21864
				C	-5.53629	-3.00283	1.18038
				C	-4.45881	-2.16885	0.91334
				C	-4.35643	-1.48281	-0.30247
				C	-5.34686	-1.64954	-1.28253
				C	-6.42610	-2.49261	-0.99527
				H	-7.38201	-3.80607	0.41107
Ti	-0.16805	0.00013	-0.00043	H	-5.59775	-3.52511	2.13009
O	0.84538	1.51212	0.23430	H	-3.66704	-2.06169	1.65258
C	-1.77098	2.48755	0.75954	C	-5.26851	-0.99015	-2.64331
N	-1.85824	1.25344	0.41548	H	-7.20053	-2.62476	-1.74690
C	-3.16036	0.57433	0.51140	C	4.10630	-2.25082	2.53224
C	0.68085	2.82830	0.37268	C	5.04660	-3.45093	2.70699
C	1.74484	3.74051	0.15575	C	5.34924	-4.05484	1.32836
C	1.49744	5.07583	0.46264	C	4.03894	-4.49929	0.66114
C	0.26853	5.57236	0.92038	C	3.07124	-3.30709	0.46689
C	-0.77633	4.67885	1.02359	C	2.79700	-2.70501	1.87071
C	-0.59001	3.31684	0.73975	H	3.87553	-1.81207	3.51009
H	-3.18137	0.12329	1.50535	H	4.58107	-4.20482	3.35588
H	2.29687	5.79703	0.33445	H	5.97990	-3.13656	3.19293
C	0.10939	7.03379	1.25252	H	6.00003	-4.93066	1.44209
H	-1.76521	5.02410	1.31842	H	4.26879	-4.96039	-0.30931
O	0.84511	-1.51211	-0.23515	H	3.56567	-5.26750	1.28722
C	0.68031	-2.82828	-0.37339	H	2.30200	-3.46284	2.49268
C	1.74404	-3.74073	-0.15623	H	2.10663	-1.86014	1.79373
C	1.49641	-5.07600	-0.46316	C	6.03933	-3.00678	0.44626
C	0.26746	-5.57226	-0.92109	H	6.98268	-2.68589	0.90784
C	-0.77721	-4.67854	-1.02440	H	6.28713	-3.44057	-0.53180
C	-0.59063	-3.31656	-0.74055	C	4.78117	-1.19676	1.64223
C	-1.77143	-2.48704	-0.76024	H	4.11183	-0.33643	1.52642
N	-1.85845	-1.25292	-0.41612	H	5.70214	-0.83157	2.11693
C	-3.16056	-0.57373	-0.51160	C	3.79608	-2.25548	-0.40616
H	-3.18194	-0.12270	-1.50555	H	3.14067	-1.39417	-0.56196
H	-1.76614	-5.02358	-1.31929	H	4.00722	-2.68720	-1.39409
C	0.10810	-7.03363	-1.25337	C	5.10147	-1.80622	0.26797
H	2.29568	-5.79734	-0.33479	H	5.58945	-1.05910	-0.36658
Cl	-0.47996	-0.55035	2.26268	C	4.10778	2.24992	-2.53182
Cl	-0.48006	0.55085	-2.26342	C	5.04834	3.44986	-2.70636
H	-2.68659	-3.00092	-1.06152	C	5.35059	4.05385	-1.32769
H	-2.68601	3.00159	1.06094	C	4.04014	4.49857	-0.66096
C	-6.53054	3.16070	-0.21752	C	3.07215	3.30655	-0.46693
C	-6.42575	2.49308	0.99638	C	2.79832	2.70439	-1.87079
C	-5.34631	1.65012	1.28323	H	3.87729	1.81112	-3.50971
C	-4.35629	1.48341	0.30276	H	4.58316	4.20376	-3.35549
C	-4.45921	2.16942	-0.91303	H	5.98176	3.13529	-3.19194
C	-5.53685	3.00333	-1.17965	H	6.00156	4.92955	-1.44126



H	4.26974	4.95969	0.30954	C	-0.71395	-4.50302	-1.63905
H	3.56719	5.26682	-1.28723	C	-0.53397	-3.19319	-1.16548
H	2.30366	3.46224	-2.49301	H	-3.19890	-0.05811	-1.51229
H	2.10778	1.85963	-1.79398	H	2.35538	-5.70236	-1.07967
C	6.04020	3.00576	-0.44524	C	0.17926	-6.80318	-2.17875
H	6.28771	3.43961	0.53287	H	-1.69873	-4.80442	-1.99072
H	6.98366	2.68467	-0.90646	O	0.89187	1.48137	0.38848
C	4.78218	1.19584	-1.64149	C	0.73166	2.76107	0.71832
H	4.11267	0.33562	-1.52583	C	1.79751	3.69088	0.62277
H	5.70326	0.83046	-2.11582	C	1.55601	4.97098	1.11368
C	3.79652	2.25490	0.40647	C	0.33176	5.40138	1.64652
H	3.14093	1.39370	0.56213	C	-0.71382	4.50303	1.63905
H	4.00738	2.68668	1.39443	C	-0.53388	3.19320	1.16545
C	5.10208	1.80537	-0.26717	C	-1.71585	2.37312	1.06670
H	5.58972	1.05825	0.36762	N	-1.81153	1.20885	0.53131
H	-0.93807	7.28497	1.44461	C	-3.12925	0.55164	0.53780
H	0.68526	7.30048	2.14659	H	-3.19884	0.05816	1.51232
H	0.46356	7.66968	0.43369	H	-1.69860	4.80444	1.99074
H	-0.93951	-7.28480	-1.44466	C	0.17936	6.80321	2.17864
H	0.46293	-7.66966	-0.43494	H	2.35551	5.70235	1.07963
H	0.68325	-7.30015	-2.14796	Cl	-0.35141	0.72664	-2.22088
H	-6.25157	1.06105	3.12005	Cl	-0.35115	-0.72667	2.22080
H	-5.06353	-0.08017	2.53691	H	-2.63135	2.83627	1.44278
C	-4.22328	1.63467	3.56711	H	-2.63144	-2.83619	-1.44276
H	-4.24477	1.16724	4.55639	C	-6.69388	-2.96514	-0.22678
H	-3.20530	1.52451	3.17713	C	-5.69116	-3.11404	0.72335
H	-4.42405	2.70457	3.68992	C	-4.50204	-2.37831	0.67414
C	-4.22475	-1.63367	-3.56690	C	-4.33498	-1.46694	-0.38822
H	-6.25292	-1.06040	-3.11893	C	-5.34663	-1.33022	-1.34357
H	-5.06481	0.08091	-2.53614	C	-6.52269	-2.06411	-1.27130
H	-4.24673	-1.16613	-4.55611	H	-7.60493	-3.55140	-0.15017
H	-3.20662	-1.52337	-3.17733	H	-5.83527	-3.82488	1.53279
H	-4.42538	-2.70359	-3.68973	C	-3.45747	-2.61414	1.75847
				H	-5.21267	-0.61798	-2.15315
				H	-7.29409	-1.93308	-2.02374
				C	-6.69389	2.96517	0.22691
				C	-6.52265	2.06414	1.27143
				C	-5.34658	1.33028	1.34367
				C	-4.33495	1.46701	0.38830
				C	-4.50206	2.37838	-0.67407
				C	-5.69119	3.11409	-0.72324
				H	-7.60494	3.55143	0.15032

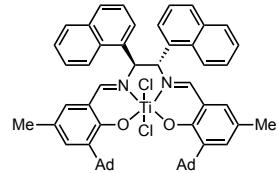
o-*i*-propyl-phenyl backbone (*S,S*)-4g



Ti	-0.11765	-0.00000	-0.00003	H	-7.29404	1.93310	2.02389
O	0.89184	-1.48131	-0.38874	H	-5.21259	0.61803	2.15323
C	-1.71591	-2.37307	-1.06671	C	-3.45753	2.61421	-1.75844
N	-1.81156	-1.20881	-0.53129	H	-5.83535	3.82492	-1.53269
C	-3.12927	-0.55157	-0.53776	C	4.14613	2.57272	-2.25340
C	0.73158	-2.76107	-0.71839	C	5.08275	3.78844	-2.26696
C	1.79741	-3.69088	-0.62280	C	5.39328	4.19918	-0.82048
C	1.55589	-4.97099	-1.11371	C	4.08694	4.54736	-0.09315
C	0.33164	-5.40137	-1.64656	C	3.12010	3.33992	-0.06037

C	2.83909	2.93281	-1.53165	H	-2.59384	-1.97273	1.58130
H	3.91148	2.27208	-3.28135	C	-3.99151	-2.25900	3.15228
H	4.61046	4.62296	-2.80242	C	-2.93116	-4.05626	1.73389
H	6.01375	3.54766	-2.79729	H	-2.12375	-4.16778	2.46504
H	6.04412	5.08251	-0.81809	H	-3.71794	-4.77839	1.98215
H	4.32158	4.86947	0.93082	H	-2.52903	-4.32236	0.75104
H	3.61020	5.39492	-0.60373	C	-2.93127	4.05635	-1.73397
H	2.34337	3.76873	-2.04367	H	-2.59388	1.97283	-1.58129
H	2.14953	2.08472	-1.56671	C	-3.99162	2.25900	-3.15222
C	6.08700	3.04158	-0.09150	H	-2.12390	4.16786	-2.46516
H	6.33757	3.33777	0.93608	H	-3.71808	4.77843	-1.98225
H	7.02915	2.78786	-0.59519	H	-2.52911	4.32254	-0.75116
C	4.82704	1.40849	-1.51808	H	-3.19081	2.35382	-3.89268
H	4.16319	0.53561	-1.51892	H	-4.36150	1.22844	-3.18995
H	5.74825	1.11715	-2.04105	H	-4.81449	2.91800	-3.45283
C	3.84664	2.17768	0.65835	H	-3.19075	-2.35411	3.89276
H	3.19192	1.30221	0.69399	H	-4.36114	-1.22836	3.19014
H	4.05971	2.46629	1.69670	H	-4.81455	-2.91784	3.45277
C	5.15083	1.82628	-0.07450				
H	5.64071	0.99997	0.45174				
C	4.14601	-2.57267	2.25339				
C	5.08256	-3.78844	2.26705				
C	5.39310	-4.19930	0.82060				
C	4.08677	-4.54744	0.09324				
C	3.12000	-3.33995	0.06036				
C	2.83898	-2.93275	1.53162				
H	3.91134	-2.27197	3.28132				
H	4.61022	-4.62290	2.80256	Ti	0.04631	0.00028	-0.00129
H	6.01356	-3.54768	2.79737	O	1.05472	1.46492	-0.44946
H	6.04388	-5.08268	0.81829	C	-1.55985	2.34619	-1.12487
H	4.32144	-4.86961	-0.93071	N	-1.64626	1.18329	-0.58568
H	3.60995	-5.39495	0.60384	C	-2.95120	0.50528	-0.58280
H	2.34322	-3.76863	2.04366	C	0.88970	2.74293	-0.78994
H	2.14943	-2.08465	1.56663	C	1.95581	3.67428	-0.71692
C	6.08691	-3.04179	0.09159	C	1.70974	4.94640	-1.22702
H	6.33749	-3.33804	-0.93598	C	0.48068	5.36924	-1.75363
H	7.02907	-2.78810	0.59528	C	-0.56596	4.47279	-1.71833
C	4.82702	-1.40851	1.51803	C	-0.38109	3.17005	-1.22892
H	4.16323	-0.53557	1.51878	H	-2.98322	-0.06506	-1.51596
H	5.74823	-1.11720	2.04101	H	2.50961	5.67790	-1.21367
C	3.84663	-2.17777	-0.65837	C	0.32423	6.76208	-2.30792
H	3.19196	-1.30226	-0.69404	H	-1.55458	4.77002	-2.06183
H	4.05970	-2.46643	-1.69671	O	1.05592	-1.46382	0.44616
C	5.15083	-1.82643	0.07450	C	0.89202	-2.74099	0.79016
H	5.64079	-1.00020	-0.45177	C	1.95890	-3.67170	0.71796
H	0.73713	-6.93392	-3.11334	C	1.71537	-4.94154	1.23434
H	0.55749	-7.54295	-1.46470	C	0.48824	-5.36282	1.76703
H	-0.86980	-7.03812	-2.38236	C	-0.55892	-4.46726	1.73245
H	0.73725	6.93403	3.11320	C	-0.37710	-3.16705	1.23465
H	0.55753	7.54295	1.46453	C	-1.55660	-2.34444	1.12977
H	-0.86971	7.03812	2.38227	N	-1.64478	-1.18379	0.58588

1-naphthyl backbone (*S,S*)-4h



C	-2.95068	-0.50753	0.58235	H	4.47672	4.85348	-1.05628
H	-2.98418	0.06274	1.51549	H	4.22217	2.43385	-1.77392
H	-1.54538	-4.76281	2.08348	H	3.35904	1.28804	-0.74668
C	0.33288	-6.75916	2.31291	C	5.24740	3.83947	2.16083
H	2.51618	-5.67214	1.22376	H	4.77298	4.68315	2.67977
Cl	-0.21582	0.84413	2.17757	H	6.18007	3.61278	2.69442
H	-2.47296	-2.79674	1.51633	C	4.99878	1.44433	1.46060
H	-2.47710	2.79922	-1.50839	H	4.33775	0.56973	1.48080
Cl	-0.21675	-0.84290	-2.18011	H	5.92202	1.16647	1.98741
H	0.87870	6.87850	-3.24646	C	3.00578	2.96051	1.44660
H	-0.72592	6.99200	-2.51150	H	2.31980	2.11024	1.49868
H	0.70373	7.51393	-1.60726	H	2.50662	3.80375	1.94276
H	0.48032	-7.51120	1.52903	C	4.31523	2.62046	2.17347
H	-0.66322	-6.91120	2.73905	H	4.08347	2.34009	3.20781
H	1.06833	-6.95938	3.10013	C	-6.59894	-2.82990	0.48432
C	5.31976	-1.83001	-0.01154	C	-4.17464	-1.40014	0.53710
C	6.25233	-3.04827	-0.00167	C	-5.14061	-1.20590	1.49601
C	5.55623	-4.21910	-0.70717	C	-6.36024	-1.91845	1.47565
C	4.24810	-4.54791	0.02562	H	-7.53541	-3.38091	0.45294
C	3.28484	-3.33716	0.03225	H	-7.10223	-1.73164	2.24551
C	4.01374	-2.16231	0.72728	C	-6.60288	2.82245	-0.48743
H	5.81161	-0.99342	0.49643	C	-4.17657	1.39598	-0.53829
H	6.50037	-3.32347	1.03237	C	-5.14132	1.20080	-1.49824
H	7.19606	-2.80788	-0.50896	C	-6.36195	1.91166	-1.47882
H	6.20454	-5.10404	-0.68538	H	-7.54011	3.37222	-0.45683
H	3.76936	-5.40432	-0.46789	H	-4.97220	0.46293	-2.27827
H	4.48066	-4.84915	1.05641	H	-7.10292	1.72411	-2.24949
H	4.22491	-2.42936	1.77178	H	-4.97333	-0.46746	2.27590
H	3.36074	-1.28495	0.74382	C	-5.62876	-3.07520	-0.52324
C	5.24823	-3.83829	-2.16239	C	-4.39485	-2.36059	-0.50665
H	4.77386	-4.68259	-2.68036	C	-3.44272	-2.64571	-1.52594
H	6.18049	-3.61166	-2.69673	C	-3.71165	-3.56808	-2.50577
C	4.99906	-1.44260	-1.46411	C	-4.93886	-4.26633	-2.52342
H	4.33764	-0.56829	-1.48459	C	-5.87257	-4.02463	-1.54986
H	5.92181	-1.16481	-1.99182	H	-2.47971	-2.14713	-1.54121
C	3.00675	-2.95977	-1.44742	H	-2.96562	-3.76249	-3.27019
H	2.32026	-2.10997	-1.49998	H	-5.13655	-4.99547	-3.30334
H	2.50781	-3.80380	-1.94249	H	-6.81947	-4.55865	-1.54806
C	4.31554	-2.61969	-2.17547	C	-5.63403	3.06874	0.52117
H	4.08295	-2.34032	-3.20989	C	-4.39918	2.35574	0.50562
C	5.31829	1.83314	0.00814	C	-3.44841	2.64197	1.52590
C	6.25043	3.05172	-0.00126	C	-3.71946	3.56390	2.50556
C	5.55433	4.22163	0.70572	C	-4.94760	4.26053	2.52216
C	4.24546	4.55067	-0.02566	C	-5.88007	4.01769	1.54772
C	3.28268	3.33953	-0.03290	H	-2.48475	2.14470	1.54206
C	4.01165	2.16568	-0.72958	H	-2.97436	3.75928	3.27064
H	5.81007	0.99715	-0.50092	H	-5.14697	4.98934	3.30195
H	6.49773	3.32792	-1.03520	H	-6.82767	4.55046	1.54508
H	7.19455	2.81123	0.50525				
H	6.20226	5.10686	0.68429				
H	3.76701	5.40617	0.46966				

XII. Cartesian Coordinates of Ethylene Diamine Backbone Arene Structures

Phenyl for (S,S)-4a



C	-1.21694	-0.67736	0.00000
C	-0.02179	-1.39247	-0.00002
C	1.19516	-0.71532	0.00001
C	1.21694	0.67735	-0.00000
C	0.02179	1.39247	-0.00001
C	-1.19516	0.71532	0.00001
H	-2.16586	-1.20501	-0.00000
H	-0.03961	-2.47816	0.00001
H	2.12708	-1.27232	0.00002
H	2.16586	1.20500	0.00002
H	0.03960	2.47815	-0.00002
H	-2.12708	1.27233	0.00002

H	0.73413	2.14320	-0.01707
H	-1.73443	2.14656	0.00220
C	2.41881	-0.00001	0.00951
H	2.79625	0.00063	1.03932
H	2.82581	-0.88598	-0.48764
H	2.82580	0.88538	-0.48872

o-chlorophenyl for (S,S)-4d



C	2.26628	-0.00000	0.00001
C	1.56822	1.20426	-0.00002
C	0.17632	1.21253	0.00000
C	-0.50407	0.00001	-0.00002
C	0.17632	-1.21253	-0.00002
C	1.56821	-1.20426	0.00002
H	3.35125	0.00000	0.00001
H	2.10557	2.14705	0.00002
H	-0.37541	2.14558	0.00002
H	-0.37541	-2.14557	-0.00004
H	2.10556	-2.14706	0.00003
Cl	-2.25407	-0.00000	0.00001

o-fluorophenyl for (S,S)-4b



C	1.83013	0.00001	0.00000
C	1.13152	1.20496	-0.00003
C	-0.26046	1.21399	0.00001
C	-0.93024	0.00001	-0.00001
C	-0.26044	-1.21400	-0.00002
C	1.13153	-1.20495	0.00002
H	2.91499	0.00002	0.00000
H	1.67014	2.14714	0.00003
H	-0.82559	2.13893	0.00003
H	-0.82556	-2.13894	-0.00005
H	1.67016	-2.14714	0.00004
F	-2.27293	-0.00001	0.00001

o-trifluorotolyl for (S,S)-4e



C	2.82844	-0.00044	0.01429
C	2.13347	1.20582	0.00183
C	0.74306	1.20901	-0.02190
C	0.05036	0.00070	-0.03422
C	0.74218	-1.20825	-0.02196
C	2.13249	-1.20625	0.00185
H	3.91418	-0.00088	0.03169
H	2.67387	2.14722	0.00772
H	0.19753	2.14648	-0.03745
H	0.19583	-2.14529	-0.03760

o-tolyl for (S,S)-4c



C	-1.89920	0.00001	0.00827
C	-1.19761	-1.20215	0.00209
C	0.19413	-1.19916	-0.00899
C	0.91033	-0.00002	-0.01188
C	0.19415	1.19915	-0.00899
C	-1.19759	1.20217	0.00209
H	-2.98524	0.00002	0.01424
H	-1.73448	-2.14654	0.00220
H	0.73408	-2.14322	-0.01707

H	2.67217	-2.14805	0.00776
C	-1.45373	0.00029	-0.00170
F	-1.96840	1.08923	-0.59773
F	-1.92079	-0.01218	1.26045
F	-1.96762	-1.07758	-0.61841

o-ethylphenyl for (S,S)-4f



C	-2.31353	-0.00003	0.23904
C	-1.62748	1.20277	0.09565
C	-0.26512	1.19956	-0.18895
C	0.43498	0.00003	-0.33581
C	-0.26508	-1.19953	-0.18899
C	-1.62745	-1.20281	0.09560
H	-3.37745	-0.00005	0.45718
H	-2.15399	2.14690	0.20272
H	0.26407	2.14323	-0.30262
H	0.26415	-2.14317	-0.30271
H	-2.15391	-2.14696	0.20263
C	1.92368	0.00007	-0.59336
H	2.19476	0.87952	-1.18958
H	2.19478	-0.87918	-1.18985
C	2.73355	-0.00006	0.70925
H	3.80942	-0.00016	0.50509
H	2.49852	0.88411	1.31134
H	2.49835	-0.88423	1.31127

1-naphthyl for (S,S)-4h



C	2.42614	-0.70778	0.00001
C	1.24245	-1.39850	-0.00001
C	-0.00001	-0.71150	-0.00000
C	0.00001	0.71151	-0.00001
C	1.24247	1.39850	-0.00000
C	2.42614	0.70776	0.00001
H	-1.23889	-2.48528	-0.00002
H	3.37018	-1.24341	0.00001
H	1.23887	-2.48528	-0.00001
C	-1.24246	-1.39850	0.00000
C	-1.24245	1.39850	-0.00001
H	1.23891	2.48529	0.00001
H	3.37019	1.24340	0.00002
C	-2.42614	0.70777	0.00000
C	-2.42615	-0.70776	0.00001
H	-1.23887	2.48528	-0.00002
H	-3.37019	1.24341	0.00003
H	-3.37019	-1.24340	0.000

o-*i*-propylphenyl for (S,S)-4g



C	2.64156	0.22054	-0.00013
C	2.12824	-1.07197	0.00086
C	0.75055	-1.27645	0.00098
C	-0.13838	-0.20076	0.00018
C	0.39215	1.09336	-0.00102
C	1.76636	1.30437	-0.00119
H	3.71516	0.38433	-0.00015
H	2.80080	-1.92513	0.00175
H	0.35779	-2.29080	0.00167
H	-0.27773	1.95006	-0.00185
H	2.15673	2.31824	-0.00198
C	-1.63938	-0.43315	0.00066
C	-2.29701	0.13078	-1.26572
H	-3.37005	-0.09106	-1.27580
H	-2.18058	1.21933	-1.31976
H	-1.84758	-0.29890	-2.16656
H	-1.80125	-1.51895	0.00221
C	-2.29678	0.13469	1.26544
H	-3.36985	-0.08688	1.27652
H	-1.84712	-0.29211	2.16753
H	-2.18016	1.22337	1.31605

XIII. Catalyst-Substrate Matrix Parameter Tables

Parameters were collected from the optimized ground state structures of intermediate II bound with TiCl₃ for computational efficiency. Parameterization of the intermediate, rather than the olefin substrate, was performed to more effectively capture structural effects relevant to the TS of interest. To capture catalyst structural features, parameters were acquired from optimized Ti(salen) structures as well as optimized structures of the backbone arene structure. Representative parameters considered for modeling this system are presented in the tables that follow.

Table SC8. Arene parameters

Backbone substituent / Catalyst	Polarizability	Quadrupole Moment	Molecular Surface Area
Ph / (<i>S,S</i>)-4a	54.08	-38.9	105.7
<i>o</i> -F-phenyl / (<i>S,S</i>)-4b	54.55	-42.3	111.2
<i>o</i> -Cl-phenyl / (<i>S,S</i>)-4d	65.05	-50.5	120.3
<i>o</i> -tolyl / (<i>S,S</i>)-4c	66.21	-45.0	123.6
<i>o</i> -trifluorotolyl / (<i>S,S</i>)-4e	65.76	-58.2	136.8
<i>o</i> -Et-phenyl / (<i>S,S</i>)-4f	77.25	-51.2	140.5
1-naphthyl / (<i>S,S</i>)-4h	97.07	-62.5	148.9
<i>o</i> - <i>i</i> -Pr-phenyl / (<i>S,S</i>)-4h	87.94	-57.5	154.3

Table SC9. Sterimol parameters for Ti(salen) measured for both diamine substituents

Backbone substituent / Catalyst	L _{Aryl} (1)	L _{Aryl} (2)	B1 _{Aryl} (1)	B1 _{Aryl} (2)	B5 _{Aryl} (1)	B5 _{Aryl} (2)
Ph / (<i>S,S</i>)-4a	6.88	6.88	1.7	1.7	3.25	3.25
<i>o</i> -F-phenyl / (<i>S,S</i>)-4b	6.89	6.89	1.7	1.69	3.83	3.83
<i>o</i> -Cl-phenyl / (<i>S,S</i>)-4d	6.9	6.89	1.71	1.71	4.50	4.50
<i>o</i> -tolyl / (<i>S,S</i>)-4c	6.88	6.88	1.74	1.75	4.42	4.43
<i>o</i> -trifluorotolyl / (<i>S,S</i>)-4e	6.9	6.9	1.95	1.95	4.97	4.98
<i>o</i> -Et-phenyl / (<i>S,S</i>)-4f	6.88	6.88	1.74	1.74	5.27	5.27
1-naphthyl / (<i>S,S</i>)-4h	7.06	7.06	1.7	1.7	5.70	5.70
<i>o</i> - <i>i</i> -Pr-phenyl / (<i>S,S</i>)-4h	6.88	6.88	2.12	2.12	5.61	5.61

Table SC10. Parameters from intermediate II bound with TiCl₃

Intermediate II (Listed based on olefin substrate)		NBO _{C2}	Spin density C2	NBO _O (enolate)	NBO _{Ti}	Ti-O Bond distance
<i>Training set</i>	2e	-0.306	0.587	-0.554	0.490	1.81
	2f	0.089	0.833	-0.537	0.508	1.76
	2g	-0.353	-0.028	-0.535	0.476	1.75
	2l	-0.058	0.727	-0.525	0.494	1.75
<i>Prediction set</i>	2h	-0.55	0.777	-0.569	0.414	1.86
	2i	-0.157	0.760	-0.535	0.500	1.75
	2j	0.209	0.777	-0.540	0.427	1.78
	2k	0.08	0.764	-0.530	0.510	1.74

XIV. Model Development for Catalyst-Substrate Matrix

Measured ΔΔG[‡] values were calculated using the formula $\Delta\Delta G^{\ddagger} = -RT\ln(er)$ where R is the gas constant, T is temperature (295.15 K), and er is the enantiomeric ratio. The descriptors in the dataset were normalized using the equation: $P_{\text{normalized}} = (P - \mu)/\sigma$ where μ is the mean and σ is the standard deviation of the parameter dataset being normalized. Normalized values are employed to enable the interpretation of the parameter coefficients. Linear regression models were developed using a previously reported in-house script,⁹ which employs forward stepwise linear regression implemented in MATLAB[®] (version R2017b)¹⁰ to obtain the predicted ΔΔG[‡]. A good linear correlation (R^2 approaching 1.0 and intercept near 0.0) between the predicted ΔΔG[‡] and the measured ΔΔG[‡] indicates that the obtained model adequately approximates the system under study. This process generates a variety of models, which are filtered based on the number of parameters in the model, avoidance of cross-terms in the model, and the recorded statistics.

The process for developing models is iterative and involves analysis of the model based on various criteria throughout the development process. In developing MLR models for this catalyst-substrate matrix dataset, the initial optimal model identified consisted of two catalyst parameters, namely polarizability and B5 Sterimol value, and the NBO charge at C2 of the intermediate was the only intermediate descriptor (Figure 8, plot I). While this model was highly capable of out-of-sample predictions, demonstrated by successful prediction of results for five different olefin substrates, the interpretation of this intermediate parameter was vexing. Our workflow in MATLAB generates a variety of models that we assess on the basis of the descriptors' relevance, number of descriptors, fit of the model, etc. In this instance, no appropriate alternative model resulted from the forward stepwise linear regression script. Thus, we generated a correlation matrix to look for correlations between the NBO_{C2} parameter with other intermediate descriptors that were more digestible for mechanistic inference. From this we discovered that the NBO_{C2} parameter was correlated with the spin density at C2 and the Ti-O bond distance in the intermediate structure (Figure SC). Another parameter found to correlate with NBO_{C2} was the C-C bond forming distance; however the best models resulted from combining Ti-O bond distance and spin density at C2. We then generated the model with the same catalyst parameters but with Ti-O bond distance and C2 spin density in place of the original NBO_{C2} intermediate descriptor (Figure 8, plot II).

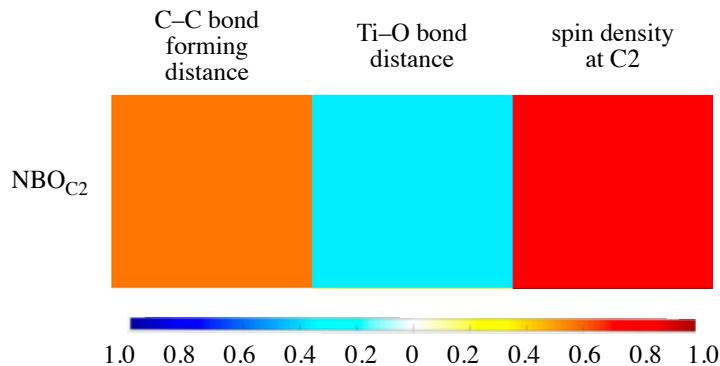


Figure SC10. Correlation matrix for Intermediate Parameters

Models were validated by cross-validation techniques such as leave-one-out and K-fold. Leave-one-out (LOO) cross validation is an iterative process in which a single data point is excluded and the remaining data points are used to predict the excluded point.⁸ This is done for every data point and the plotted predicted values are fit with a linear regression to give the R² value, which is referred to as Q² (see Figures SC and SC for LOO plots for Figure 8 Plot I and II). K-fold cross validation is another method for testing model robustness. In this process, the dataset is randomly divided into k subsets ($k = 4$ for this model) of similar sizes. Each set is then predicted by the other $k-1$ subsets and these predictions are plotted and fit with linear regression.

As an additional validation effort, the model was assessed by excluding each substrate subset in model developing and predicting those points. The model was determined to be robust at predicting each substrate subset when excluded, with relatively minor adjustment of the parameter coefficients in the model observed and comparable statistics. A final test of model robustness was the successful external prediction of the vinyl pinacolborane subset (Table SC7).

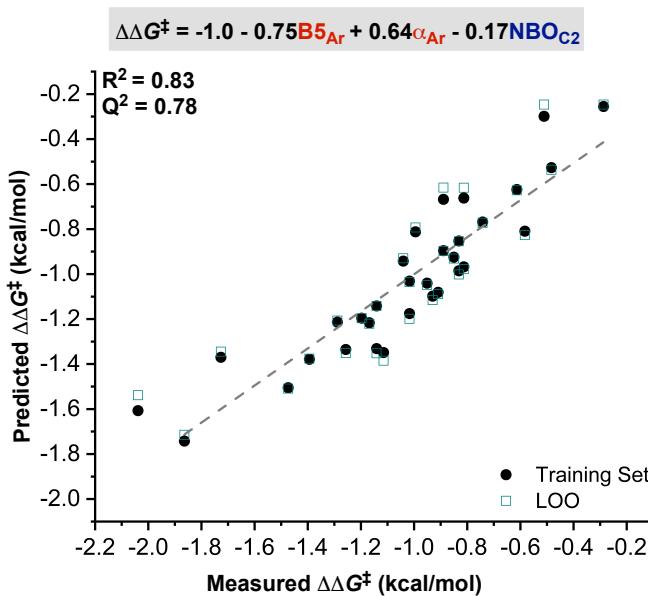


Figure SC11. Catalyst-substrate matrix MLR model with LOO (Q²) predictions from 3-parameter model (Figure 8, plot 1).

Table SC11. Measured and predicted values for catalyst-substrate matrix model training set with 3-parameter model (**Figure 8, plot I**).

substrate	Catalyst backbone	Measured $\Delta\Delta G^\ddagger$ (kcal/mol)	Predicted $\Delta\Delta G^\ddagger$ (kcal/mol)	LOO $\Delta\Delta G^\ddagger$ (kcal/mol)
<i>t</i> -Bu-acrylate 2e 	Ph	-0.51	-0.30	-0.25
	<i>o</i> -F-phenyl	-0.99	-0.81	-0.79
	<i>o</i> -Cl-phenyl	-0.81	-0.97	-0.98
	<i>o</i> -tolyl	-0.83	-0.85	-0.85
	<i>o</i> -trifluorotolyl	-1.39	-1.38	-1.38
	<i>o</i> -Et-phenyl	-1.14	-1.14	-1.14
	1-naphthyl	-0.89	-0.67	-0.62
	<i>o</i> - <i>i</i> -Pr-phenyl	-0.83	-0.99	-1.00
<i>t</i> -Bu-methacrylate 2f 	Ph	-0.81	-0.66	-0.62
	<i>o</i> -F-phenyl	-1.02	-1.18	-1.20
	<i>o</i> -Cl-phenyl	-1.14	-1.33	-1.35
	<i>o</i> -tolyl	-1.17	-1.22	-1.22
	<i>o</i> -trifluorotolyl	-1.86	-1.74	-1.71
	<i>o</i> -Et-phenyl	-1.47	-1.51	-1.51
	1-naphthyl	-1.02	-1.03	-1.04
	<i>o</i> - <i>i</i> -Pr-phenyl	-1.11	-1.35	-1.38
<i>p</i> henyl vinyl sulfone 2g 	Ph	-0.29	-0.26	-0.25
	<i>o</i> -F-phenyl	-0.74	-0.77	-0.77
	<i>o</i> -Cl-phenyl	-0.85	-0.92	-0.93
	<i>o</i> -tolyl	-0.58	-0.81	-0.83
	<i>o</i> -trifluorotolyl	-1.26	-1.34	-1.35
	<i>o</i> -Et-phenyl	-0.93	-1.10	-1.12
	1-naphthyl	-0.61	-0.62	-0.63
	<i>o</i> - <i>i</i> -Pr-phenyl	-1.04	-0.94	-0.93
vinyl-2-pyridine 2l 	Ph	-0.48	-0.53	-0.54
	<i>o</i> -F-phenyl	-0.95	-1.04	-1.05
	<i>o</i> -Cl-phenyl	-1.20	-1.20	-1.20
	<i>o</i> -tolyl	-0.91	-1.08	-1.09
	<i>o</i> -trifluorotolyl	-2.04	-1.61	-1.54
	<i>o</i> -Et-phenyl	-1.73	-1.37	-1.34
	1-naphthyl	-0.89	-0.90	-0.90
	<i>o</i> - <i>i</i> -Pr-phenyl	-1.29	-1.21	-1.21

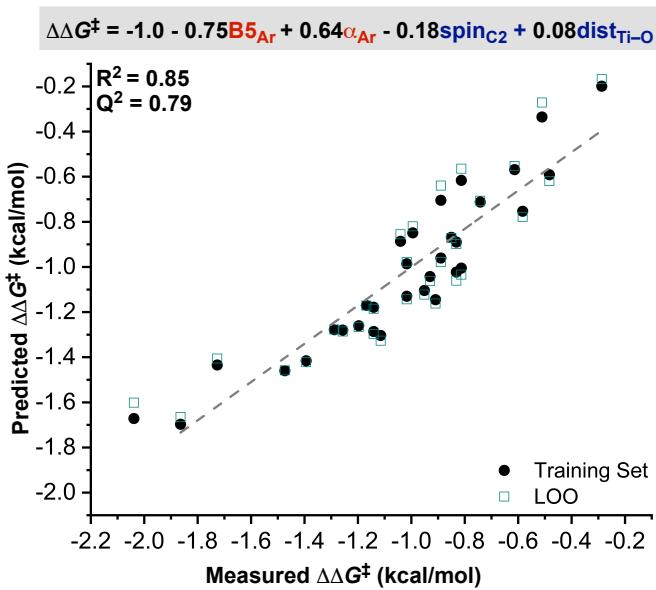


Figure SC12. Catalyst-substrate matrix MLR model with LOO (Q^2) predictions from 4-parameter model (**Figure 8, plot 1I**).

Table SC12. Measured and predicted values for catalyst-substrate matrix model training set with 4-parameter model (Figure 8, plot II).

substrate	Catalyst backbone	Measured $\Delta\Delta G^\ddagger$ (kcal/mol)	Predicted $\Delta\Delta G^\ddagger$ (kcal/mol)	LOO $\Delta\Delta G^\ddagger$ (kcal/mol)
<i>t</i> -Bu-acrylate 2e 	Ph	-0.51	-0.34	-0.27
	<i>o</i> -F-phenyl	-0.99	-0.85	-0.82
	<i>o</i> -Cl-phenyl	-0.81	-1.00	-1.03
	<i>o</i> -tolyl	-0.83	-0.89	-0.90
	<i>o</i> -trifluorotolyl	-1.39	-1.42	-1.42
	<i>o</i> -Et-phenyl	-1.14	-1.18	-1.18
	1-naphthyl	-0.89	-0.70	-0.64
	<i>o</i> - <i>i</i> -Pr-phenyl	-0.83	-1.02	-1.06
<i>t</i> -Bu-methacrylate 2f 	Ph	-0.81	-0.62	-0.57
	<i>o</i> -F-phenyl	-1.02	-1.13	-1.14
	<i>o</i> -Cl-phenyl	-1.14	-1.29	-1.30
	<i>o</i> -tolyl	-1.17	-1.17	-1.17
	<i>o</i> -trifluorotolyl	-1.86	-1.70	-1.66
	<i>o</i> -Et-phenyl	-1.47	-1.46	-1.46
	1-naphthyl	-1.02	-0.99	-0.98
	<i>o</i> - <i>i</i> -Pr-phenyl	-1.11	-1.30	-1.33
<i>p</i> henyl vinyl sulfone 2g 	Ph	-0.29	-0.20	-0.17
	<i>o</i> -F-phenyl	-0.74	-0.71	-0.71
	<i>o</i> -Cl-phenyl	-0.85	-0.87	-0.87
	<i>o</i> -tolyl	-0.58	-0.75	-0.78
	<i>o</i> -trifluorotolyl	-1.26	-1.28	-1.29
	<i>o</i> -Et-phenyl	-0.93	-1.04	-1.06
	1-naphthyl	-0.61	-0.57	-0.55
	<i>o</i> - <i>i</i> -Pr-phenyl	-1.04	-0.89	-0.86
<i>v</i> inyl-2-pyridine 2l 	Ph	-0.48	-0.59	-0.62
	<i>o</i> -F-phenyl	-0.95	-1.10	-1.12
	<i>o</i> -Cl-phenyl	-1.20	-1.26	-1.27
	<i>o</i> -tolyl	-0.91	-1.15	-1.16
	<i>o</i> -trifluorotolyl	-2.04	-1.67	-1.60
	<i>o</i> -Et-phenyl	-1.73	-1.43	-1.41
	1-naphthyl	-0.89	-0.96	-0.98
	<i>o</i> - <i>i</i> -Pr-phenyl	-1.29	-1.28	-1.28

Comparing the two models overall requires consideration of statistics, parameter interpretability, and predictive power. The two intermediate parameters are more interpretable for mechanistic analysis than just a single intermediate $\text{NBO}_{\text{C}2}$ parameter. The 4-parameter model also has a slightly higher R^2 and Q^2 value than the 3-parameter model. However, given our detailed TS analysis providing significant mechanistic insight, we regard the predictive power the most important detail for assessing these two similar models. In regard to out-of-sample prediction, the 3-parameter model (predicted $R^2 = 0.70$) is more accurate than the 4-parameter model (predicted $R^2 = 0.50$) (see Table SC for a summary of values predicted by the two models). The ability to accurately predict the performance of novel substrates with different catalysts is challenging, and perhaps more useful than the mechanistic information the model affords in light of the TS analysis.

Table SC13. Measured and predicted values for catalyst-substrate matrix model external predictions of vinyl pinacolborane using 3-parameter model (Figure , plot I) or 4-parameter model for predictions (**Figure 8, plot II**).

substrate	Catalyst backbone	Measured $\Delta\Delta G^\ddagger$ (kcal/mol)	3-parameter model PLOT I Predicted $\Delta\Delta G^\ddagger$ (kcal/mol)	4-parameter model PLOT II Predicted $\Delta\Delta G^\ddagger$ (kcal/mol)
(2h) 	Ph	-0.24	-0.07	-0.29
	<i>o</i> -F-phenyl	-0.76	-0.59	-0.81
	<i>o</i> -Cl-phenyl	-0.63	-0.74	-0.96
	<i>o</i> -tolyl	-0.40	-0.63	-0.85
	<i>o</i> -Et-phenyl	-0.64	-0.92	-1.14
	<i>o</i> -trifluorotolyl	-1.36	-1.15	-1.38
	1-naphthyl	-0.50	-0.44	-0.66
	<i>o</i> - <i>i</i> -Pr-phenyl	-1.17	-0.76	-0.98
(2i) 	<i>o</i> -trifluorotolyl	-0.66	-1.52	-1.67
(2j) 	<i>o</i> -trifluorotolyl	-2.15	-1.85	-1.60
(2k) 	<i>o</i> -trifluorotolyl	-1.79	-1.73	-1.70

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