Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Information

DFT Study of Trialkylborohydride-Catalysed Hydrosilylation of Alkenes – the Mechanism and Its Implications

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Cartesian coordinates, Mulliken and APT charges of all atoms, and absolute energies at all stationary points

All coordinates are given in ångströms.

All energies are given in hartrees.

Styrene + phenylsilane, Markovnikov mode

S

Electronic energy: -454.727438

Electronic energy + zero-point energy: -454.469600

Electronic energy + thermal energy correction: -454.448794

Electronic energy + thermal enthalpy correction: -454.447612

Electronic energy + thermal free energy correction: -454.525329

Table S01. Cartesian coordinates, Mulliken and APT charges of all atoms at **S** in the reaction of styrene with phenylsilane (Markovnikov mode).

Symbol	X	Y	Z	Mulliken	APT
C	-3.779070	-0.539130	0.088559	-0.274053	-0.035519
C	-3.128640	0.693370	0.074239	0.256598	-0.078645
C	-3.041980	-1.713300	-0.051691	0.015569	-0.072276
C	-1.738450	0.777590	-0.081391	0.671882	0.063431
C	-1.004780	-0.411330	-0.224591	-1.048043	-0.103224
C	-1.655790	-1.639980	-0.207831	-0.169335	-0.026664
H	-4.858100	-0.581200	0.211609	0.135160	0.018444
H	-3.541870	-2.677940	-0.036951	0.140951	0.023276
H	-1.068080	-2.547600	-0.311891	0.170941	0.036487
H	0.076110	-0.380810	-0.349061	-0.068035	0.144698
H	-3.704370	1.610060	0.186979	0.128765	0.024771
C	-1.090020	2.103020	-0.082431	-0.202878	0.065997
C	0.220000	2.336230	-0.217561	-0.149507	-0.176922
H	-1.770080	2.946440	0.046769	0.101007	-0.010619
H	0.957560	1.545700	-0.351321	0.099196	0.140046
H	0.594130	3.355950	-0.196621	0.154966	0.020045
C	3.798500	-1.624480	-0.568011	-0.851289	-0.139150
B	2.863070	-0.331250	-0.162401	0.496460	0.725739

C	3.792730	1.027200	-0.054421	-0.836767	-0.147311
C	2.116270	-0.613410	1.282489	-0.897735	-0.159595
H	2.011140	-0.169280	-1.062891	-0.184584	-0.456282
H	1.454080	0.205640	1.612989	0.203771	-0.093447
H	2.869080	-0.739420	2.079449	0.125328	-0.102253
H	1.505580	-1.531910	1.284789	0.168399	-0.087547
H	3.226010	1.927800	0.236169	0.170534	-0.088335
H	4.304740	1.265600	-1.000421	0.130619	-0.097253
H	4.580770	0.901490	0.708449	0.131752	-0.098784
H	4.575540	-1.810200	0.194209	0.124634	-0.101162
H	4.323170	-1.482640	-1.526281	0.115987	-0.099750
H	3.216630	-2.556100	-0.658121	0.139706	-0.088196

TS1

Electronic energy: -454.700826

Electronic energy + zero-point energy: -454.446921

Electronic energy + thermal energy correction: -454.427491

Electronic energy + thermal enthalpy correction: -454.426310

Electronic energy + thermal free energy correction: -454.500030

Table S02. Cartesian coordinates, Mulliken and APT charges of all atoms at **TS1** in the reaction of styrene with phenylsilane (Markovnikov mode).

Symbol	X	Y	Z	Mulliken	APT
C	-3.836028	-0.300143	0.447149	-0.290771	0.200546
C	-2.749528	-1.159252	0.362529	0.013418	-0.407050
C	-3.713589	1.047528	0.090699	-0.003765	-0.381405
C	-1.478728	-0.721061	-0.089091	0.007262	0.826438
C	-1.369779	0.655479	-0.413801	-0.700878	-0.263578
C	-2.464709	1.508358	-0.334721	-0.293342	0.193759
H	-4.793428	-0.683153	0.795009	0.118790	-0.003172
H	-4.563039	1.720857	0.157649	0.126408	0.013058
H	-2.335039	2.557698	-0.591191	0.144886	0.014128
H	-0.401119	1.056239	-0.699831	-0.006996	0.042478
H	-2.867347	-2.205572	0.638359	0.111435	0.008162
C	-0.369718	-1.629131	-0.190331	0.719516	-1.277510
C	0.850832	-1.288550	-0.764431	-0.749325	1.417320
H	-0.461127	-2.581611	0.326749	0.129283	-0.019362

H	0.877862	-0.521430	-1.540021	0.214600	-0.056486
H	1.584483	-2.077170	-0.917721	0.173368	-0.038891
C	3.266122	0.155291	1.772009	-0.735345	-0.327757
B	2.874902	0.250431	0.198469	0.961615	1.406704
C	3.933252	-0.476679	-0.798091	-0.888591	-0.266207
C	2.437451	1.733960	-0.301041	-0.899247	-0.303077
H	1.748792	-0.490680	0.094619	-0.437873	-1.104247
H	2.017891	1.734910	-1.319801	0.147944	-0.057976
H	3.314791	2.401981	-0.330071	0.115317	-0.092316
H	1.697091	2.206900	0.359009	0.165278	-0.050778
H	3.574712	-0.525409	-1.838171	0.133186	-0.046415
H	4.179202	-1.503609	-0.488491	0.144251	-0.066457
H	4.883182	0.082091	-0.823191	0.125966	-0.122862
H	4.184661	0.733341	1.972639	0.137647	-0.132499
H	3.465262	-0.875379	2.098709	0.155863	-0.061582
H	2.485191	0.563050	2.428139	0.160103	-0.042966

I1

Electronic energy: -454.710828

Electronic energy + zero-point energy: -454.454449

Electronic energy + thermal energy correction: -454.432180

Electronic energy + thermal enthalpy correction: -454.430998

Electronic energy + thermal free energy correction: -454.512741

Table S03. Cartesian coordinates, Mulliken and APT charges of all atoms at **I1** in the reaction of styrene with phenylsilane (Markovnikov mode).

Symbol	X	Y	Z	Mulliken	APT
C	3.341920	-0.333953	-0.937640	-0.148479	0.375908
C	2.226100	-1.095712	-0.664840	0.059833	-0.415358
C	3.578071	0.900157	-0.295740	-0.292088	-0.735671
C	1.221120	-0.692081	0.292480	-0.182014	0.788465
C	1.490661	0.576359	0.931290	-0.362754	-0.517683
C	2.622582	1.323868	0.636400	-0.164380	0.473369
H	4.059740	-0.701093	-1.671770	0.106138	-0.018578
H	4.458312	1.495036	-0.518510	0.104046	0.005569
H	2.765592	2.274238	1.151950	0.109065	-0.014572
H	0.781371	0.958959	1.661920	0.122264	0.010870

H	2.081059	-2.042702	-1.183870	0.113910	-0.015724
C	0.090750	-1.454020	0.565350	-0.211581	-0.981922
C	-0.909830	-1.047050	1.599650	-0.771787	0.453852
H	-0.030461	-2.414970	0.071050	0.075412	-0.018766
H	-0.466530	-0.883840	2.599970	0.144757	-0.143260
H	-1.695381	-1.803889	1.715800	0.140378	-0.053553
C	-3.219440	-1.021788	-0.993000	-0.818407	-0.331939
B	-2.890439	0.454542	-0.540860	0.920316	0.891533
C	-3.802438	1.185982	0.528090	-0.825698	-0.315281
C	-1.666398	1.170891	-1.213470	-0.802103	-0.338750
H	-1.429909	-0.089999	1.370760	0.133732	-0.191249
H	-1.569908	2.239581	-0.998010	0.137632	-0.026887
H	-1.632219	1.015891	-2.299100	0.142079	-0.005690
H	-0.763869	0.662500	-0.827210	0.210604	0.089736
H	-3.304978	2.016242	1.039440	0.170446	-0.006159
H	-4.220799	0.501123	1.274120	0.168892	-0.006492
H	-4.659458	1.612063	-0.019470	0.157185	-0.013486
H	-3.348260	-1.085458	-2.081370	0.148938	-0.003598
H	-4.086960	-1.480057	-0.505940	0.138880	-0.043487
H	-2.323731	-1.622249	-0.766920	0.274781	0.108802

I2

Electronic energy: -454.772817

Electronic energy + zero-point energy: -454.513658

Electronic energy + thermal energy correction: -454.493209

Electronic energy + thermal enthalpy correction: -454.492027

Electronic energy + thermal free energy correction: -454.569791

Table S04. Cartesian coordinates, Mulliken and APT charges of all atoms at **I2** in the reaction of styrene with phenylsilane (Markovnikov mode).

Symbol	X	Y	Z	Mulliken	APT
C	2.706540	1.131190	-0.502080	-0.242638	0.058156
C	1.385300	0.920020	-0.885630	0.525437	-0.149807
C	3.357190	0.216300	0.328120	-0.051631	-0.187616
C	0.655550	-0.204820	-0.458850	-0.749226	0.318115
C	1.331670	-1.110860	0.377710	-0.305010	-0.167752
C	2.654650	-0.906010	0.765760	-0.225500	0.059943

H	3.233540	2.015760	-0.853370	0.127672	0.005626
H	4.389180	0.377020	0.628480	0.126734	0.013490
H	3.139280	-1.629000	1.418450	0.129110	0.006171
H	0.800730	-1.986420	0.742090	0.124766	0.034671
H	0.886570	1.644370	-1.526250	0.150543	0.025385
C	-0.776720	-0.387590	-0.842640	-0.192834	-0.389968
C	-1.143550	-1.862230	-1.054100	-0.526023	0.121324
H	-0.927720	0.140130	-1.798540	0.040982	-0.096164
H	-0.388210	-2.410760	-1.637690	0.149350	-0.090750
H	-2.099810	-1.936600	-1.581210	0.140281	-0.039910
C	-3.374330	0.065860	-0.215910	-0.870477	-0.161143
B	-1.824340	0.374160	0.259490	0.795261	0.773735
C	-1.585040	-0.190210	1.787610	-0.797555	-0.171509
C	-1.571100	2.000390	0.228930	-0.830100	-0.163754
H	-1.271940	-2.387800	-0.099300	0.164946	-0.026888
H	-0.567730	2.292280	0.575600	0.185391	-0.070491
H	-2.292700	2.514780	0.884180	0.115817	-0.097881
H	-1.701640	2.429420	-0.779750	0.150262	-0.087220
H	-0.591380	0.065340	2.187250	0.190707	-0.071615
H	-1.695290	-1.284030	1.879810	0.147637	-0.079837
H	-2.325360	0.251120	2.474290	0.123981	-0.091676
H	-4.084320	0.661670	0.380040	0.121438	-0.103705
H	-3.670790	-0.987850	-0.091770	0.135657	-0.082567
H	-3.551690	0.327550	-1.273320	0.145022	-0.086361

I2 (with phenylsilane)

Electronic energy: -977.580109

Electronic energy + zero-point energy: -977.202453

Electronic energy + thermal energy correction: -977.171782

Electronic energy + thermal enthalpy correction: -977.170600

Electronic energy + thermal free energy correction: -977.270411

Table S05. Cartesian coordinates, Mulliken and APT charges of all atoms at **I2** (with phenylsilane) in the reaction of styrene with phenylsilane (Markovnikov mode).

Symbol	X	Y	Z	Mulliken	APT
H	-1.262289	3.130841	2.173400	0.141352	0.009572
H	-1.348680	0.673491	1.955960	0.137878	0.038401

C	-1.515720	2.684361	1.214400	-0.134285	0.056854
C	-1.561790	1.299361	1.092050	0.692119	-0.165089
H	-2.872350	-1.473949	2.514810	0.137119	-0.081528
H	-1.228650	-1.233959	0.507450	0.022570	-0.088184
C	-1.792539	3.501491	0.115610	-0.063168	-0.177021
C	-1.879560	0.669151	-0.125600	-1.564295	0.299081
C	-1.942720	-0.819419	-0.225520	-0.429742	-0.447661
H	-1.756019	4.583681	0.206750	0.127851	0.014902
H	-3.784230	-0.014079	2.090640	0.171201	-0.068769
H	-2.576800	-3.538979	0.566180	0.149946	-0.088870
C	-3.686970	-1.089419	1.876770	-0.852495	-0.178227
H	-0.719110	-0.819779	-2.071470	0.160240	-0.085020
C	-1.578450	-1.340669	-1.621020	-0.494649	0.103195
B	-3.456550	-1.423149	0.281930	1.043220	0.810668
H	3.441680	1.803261	-0.035460	0.162869	0.035342
H	-1.336640	-2.406979	-1.570780	0.140141	-0.028523
H	-4.614620	-1.564279	2.234350	0.117930	-0.097122
H	0.977600	0.534981	-0.762660	-0.083417	-0.275945
C	-2.120720	2.900341	-1.098480	-0.220251	0.060564
C	-2.161600	1.511221	-1.215310	0.118797	-0.162970
C	-3.440520	-3.058919	0.074800	-0.852992	-0.165341
H	5.896730	2.027111	-0.064530	0.151059	0.022401
C	4.058510	0.907191	-0.006410	0.046096	-0.055372
H	-4.344190	-3.508579	0.516280	0.121573	-0.107446
H	-3.422760	-3.370239	-0.981680	0.133940	-0.081187
C	5.446240	1.039171	-0.024200	-0.079296	-0.046082
H	-2.422100	-1.241589	-2.315620	0.142745	-0.025702
H	1.104530	-0.356999	1.492530	0.030655	-0.318674
Si	1.557860	-0.520369	0.092610	i 0.524857	i 1.389391
H	-2.348999	3.516831	-1.965180	0.133594	0.006579
H	-2.426110	1.066331	-2.170970	0.159636	0.037005
C	-4.670030	-0.751579	-0.602120	-0.762935	-0.184903
C	3.444590	-0.353469	0.041520	-0.891191	-0.356167
H	-4.754250	0.336071	-0.453640	0.162594	-0.068055
C	6.254930	-0.096730	0.003660	-0.125405	-0.040176
H	-4.576310	-0.920289	-1.687850	0.130299	-0.075717
H	7.336640	0.002580	-0.013110	0.150958	0.028633
H	1.230590	-1.879569	-0.394100	-0.051963	-0.302473
H	-5.637700	-1.187629	-0.306340	0.122750	-0.096601
C	4.277790	-1.481199	0.064640	0.132575	-0.051878
C	5.667240	-1.359689	0.047430	-0.160309	-0.047255
H	3.834560	-2.474659	0.091620	0.149423	0.034374
H	6.290050	-2.249850	0.063900	0.150407	0.020998

TS2

Electronic energy: -977.538415

Electronic energy + zero-point energy: -977.161597

Electronic energy + thermal energy correction: -977.128133

Electronic energy + thermal enthalpy correction: -977.126951

Electronic energy + thermal free energy correction: -977.234168

Table S06. Cartesian coordinates, Mulliken and APT charges of all atoms at **TS2** in the reaction of styrene with phenylsilane (Markovnikov mode).

Symbol	X	Y	Z	Mulliken	APT
H	-1.873370	3.122431	2.178830	0.136863	-0.000219
H	-1.330441	0.739611	1.978850	0.091099	0.020787
C	-1.856710	2.662771	1.192260	0.001782	0.229543
C	-1.553980	1.314191	1.082860	0.309971	-0.326159
H	-2.721901	-1.882639	2.512270	0.148223	-0.017613
H	-1.159571	-1.339879	0.607870	0.267604	0.093153
C	-2.135560	3.437901	0.059030	-0.179507	-0.421796
C	-1.525271	0.645621	-0.174190	-0.941535	0.683563
C	-1.186411	-0.735099	-0.294960	-0.678527	-1.489470
H	-2.375950	4.492961	0.148830	0.121720	0.012033
H	-3.399171	-0.254469	2.246310	0.219120	0.018351
H	-2.521202	-3.578789	0.398070	0.162661	-0.006971
C	-3.508131	-1.315109	1.999940	-0.824380	-0.328505
H	-0.468241	-0.980639	-2.328200	0.176083	-0.073604
C	-1.204001	-1.422169	-1.633380	-0.580136	0.274012
B	-3.589171	-1.586199	0.435130	0.999519	1.249965
H	3.218180	1.844470	0.184480	0.160860	0.028422
H	-0.943451	-2.479889	-1.525570	0.134950	-0.018106
H	-4.467801	-1.643218	2.432210	0.145112	-0.038636
H	1.036369	0.424140	-1.232320	-0.058426	-0.353400
C	-2.084520	2.813931	-1.189090	-0.254567	0.236260
C	-1.783270	1.461361	-1.310600	0.015856	-0.362683
C	-3.391162	-3.088859	-0.055080	-0.809634	-0.323353
H	5.666900	2.094109	0.335980	0.134127	0.003026
C	3.846189	0.954029	0.152690	-0.040885	-0.076324
H	-4.277002	-3.654368	0.277600	0.146191	-0.060698
H	-3.329152	-3.204119	-1.142070	0.146309	-0.007972
C	5.229849	1.103009	0.237810	0.182074	-0.021359

H	-2.178241	-1.376239	-2.148800	0.137912	-0.093816
H	0.947499	0.031170	1.276840	0.029973	-0.376547
Si	1.302019	-0.477800	-0.077750	i 0.382561	i 1.905165
H	-2.288560	3.390911	-2.089360	0.128027	-0.003449
H	-1.762971	1.010691	-2.299340	0.131968	0.032391
C	-4.424991	-0.580068	-0.459720	-0.770443	-0.338617
C	3.238619	-0.306190	0.024800	-1.158803	-0.429283
H	-4.359351	0.458852	-0.118330	0.201944	0.006627
C	6.056409	-0.021661	0.196590	-0.118865	-0.087135
H	-4.141391	-0.604978	-1.518760	0.172580	0.003526
H	7.135879	0.088249	0.262360	0.137886	0.014330
H	1.249319	-1.952720	-0.317840	-0.124107	-0.448118
H	-5.483621	-0.884488	-0.409560	0.136556	-0.042033
C	4.094259	-1.415351	-0.016280	0.274045	-0.070772
C	5.482879	-1.285261	0.068690	-0.178579	-0.021263
H	3.663039	-2.410621	-0.120260	0.152448	0.028531
H	6.116609	-2.168631	0.034490	0.132370	-0.001783

I3

Electronic energy: -977.543370

Electronic energy + zero-point energy: -977.168375

Electronic energy + thermal energy correction: -977.136400

Electronic energy + thermal enthalpy correction: -977.135218

Electronic energy + thermal free energy correction: -977.240588

Table S07. Cartesian coordinates, Mulliken and APT charges of all atoms at **I3** in the reaction of styrene with phenylsilane (Markovnikov mode).

Symbol	X	Y	Z	Mulliken	APT
H	-2.210721	2.977550	2.221390	0.142633	0.008540
H	-1.284490	0.712060	1.944490	0.121915	0.027006
C	-2.090110	2.566500	1.221420	0.008642	0.126787
C	-1.572830	1.286530	1.067200	0.639057	-0.224501
H	-2.892910	-2.297010	2.443580	0.157288	-0.010516
H	-1.049800	-1.274460	0.518100	0.236523	-0.028759
C	-2.452421	3.328920	0.106150	-0.040655	-0.268712
C	-1.406170	0.694120	-0.206780	-1.052927	0.463230
C	-0.813820	-0.634910	-0.343460	-1.098661	-0.977044

H	-2.862141	4.327750	0.225660	0.134471	0.013117
H	-3.234140	-0.549500	2.293810	0.222894	0.023623
H	-2.465240	-3.348150	-0.137530	0.210141	0.029183
C	-3.571650	-1.552280	2.014690	-0.784690	-0.310888
H	-0.431890	-0.839170	-2.467050	0.181098	-0.026090
C	-1.011570	-1.337340	-1.675000	-0.438089	0.148746
B	-3.792910	-1.695390	0.456630	0.987371	0.920099
H	3.302670	1.878110	0.232000	0.151128	0.012869
H	-0.639480	-2.366440	-1.618330	0.122601	-0.025128
H	-4.554300	-1.693350	2.493450	0.155905	-0.007001
H	1.263180	0.482690	-1.341590	-0.103912	-0.401105
C	-2.265661	2.780180	-1.162340	-0.211545	0.133092
C	-1.750680	1.494550	-1.317580	-0.143179	-0.240120
C	-3.532140	-3.103430	-0.217740	-0.845852	-0.294057
H	5.752910	2.103131	0.427560	0.125082	-0.008428
C	3.923800	0.981370	0.192450	-0.083838	-0.076957
H	-4.062770	-3.889570	0.338050	0.139509	-0.016158
H	-3.814270	-3.168200	-1.273320	0.143382	-0.024403
C	5.307340	1.117771	0.303530	0.194724	-0.006674
H	-2.058070	-1.376760	-2.017830	0.152279	-0.088091
H	1.087140	0.234090	1.221570	-0.066326	-0.413672
Si	1.316550	-0.409950	-0.123320	i 0.628948	i 1.951765
H	-2.530481	3.357530	-2.045570	0.128193	0.003357
H	-1.629500	1.091020	-2.318900	0.126873	0.034554
C	-4.476300	-0.526660	-0.349760	-0.791074	-0.308725
C	3.300420	-0.267390	0.030630	-1.112654	-0.470890
H	-4.357490	0.463550	0.101710	0.213044	0.003689
C	6.125560	-0.013939	0.255390	-0.159355	-0.115320
H	-4.134880	-0.475900	-1.389600	0.187932	0.021484
H	7.205210	0.083651	0.341440	0.130266	0.007182
H	1.397190	-1.917900	-0.278320	-0.208026	-0.496207
H	-5.554320	-0.758040	-0.388210	0.137898	-0.012466
C	4.149850	-1.380640	-0.014550	0.239474	-0.081388
C	5.539460	-1.268659	0.095820	-0.153666	-0.000950
H	3.707620	-2.370080	-0.141090	0.151344	0.020616
H	6.165380	-2.158499	0.057370	0.123833	-0.014688

I4

Electronic energy: -977.582517

Electronic energy + zero-point energy: -977.203069

Electronic energy + thermal energy correction: -977.172771

Electronic energy + thermal enthalpy correction: -977.171589

Electronic energy + thermal free energy correction: -977.269717

Table S08. Cartesian coordinates, Mulliken and APT charges of all atoms at **I4** in the reaction of styrene with phenylsilane (Markovnikov mode).

Symbol	X	Y	Z	Mulliken	APT
H	0.490661	3.808551	-1.868929	0.160812	0.024856
H	-1.063279	2.119371	-0.938979	0.215092	0.079598
C	0.798371	3.204481	-1.019679	-0.352529	0.025099
C	-0.077549	2.256501	-0.498509	-0.232538	-0.135345
H	-5.107518	0.448630	1.586511	0.133325	-0.085814
H	-1.685238	0.742911	0.958331	0.075796	0.024907
C	2.064611	3.380952	-0.457329	-0.192172	-0.114122
C	0.288001	1.456861	0.597241	0.299004	0.140749
C	-0.656118	0.388951	1.080461	-1.472637	-0.405288
H	2.750040	4.118502	-0.865089	0.146949	0.023785
H	-6.204218	0.026779	0.265281	0.136390	-0.109520
H	-3.422699	1.740960	-0.246169	0.134133	-0.091124
C	-5.301558	-0.305830	0.806911	-0.806714	-0.152139
H	0.480252	-0.630779	2.661591	0.164495	-0.016507
C	-0.446198	-0.056389	2.530691	-0.806960	0.076332
B	-4.029948	-0.501360	-0.219229	0.878565	0.760684
H	1.709032	0.119372	-1.669829	0.174081	0.037367
H	-1.280138	-0.693799	2.838411	0.159610	-0.003523
H	-5.571508	-1.238891	1.326171	0.136617	-0.094211
H	-1.084667	-2.357099	0.540451	-0.095724	-0.350346
C	2.436431	2.601182	0.635481	-0.193753	0.003931
C	1.557531	1.651072	1.155741	0.613902	-0.138168
C	-3.675399	0.932720	-0.954509	-0.845986	-0.175646
H	4.121322	-0.330277	-1.863059	0.161381	0.020924
C	2.140812	-0.711318	-1.112799	0.106378	-0.036052
H	-4.546389	1.291420	-1.528719	0.110668	-0.100485
H	-2.843819	0.858180	-1.675709	0.126978	-0.083999
C	3.508002	-0.957568	-1.221659	0.055120	-0.046559
H	-0.401978	0.804991	3.208961	0.175267	-0.041708
H	-1.087648	-0.830039	-1.420379	0.054166	-0.311267
Si	-0.542228	-1.127489	-0.080269	i 1.090480	i 1.579794
H	3.419581	2.723872	1.082231	0.151153	0.021862
H	1.874321	1.037602	1.994451	0.177258	0.045927
C	-4.363048	-1.647850	-1.349889	-0.854599	-0.148818
C	1.316432	-1.494568	-0.287149	-1.171714	-0.406282

H	-5.236018	-1.362920	-1.962419	0.131297	-0.104679
C	4.089682	-2.001357	-0.501179	-0.277189	-0.039125
H	-3.529638	-1.812640	-2.052419	0.157955	-0.083653
H	5.155872	-2.195097	-0.583709	0.142617	0.021729
H	-3.052618	-0.887750	0.455951	-0.448175	-0.492583
H	-4.599057	-2.625810	-0.901099	0.147434	-0.090099
C	1.925433	-2.538608	0.424521	0.161909	-0.034051
C	3.294813	-2.793408	0.325101	0.076274	-0.040868
H	1.315223	-3.169848	1.068501	0.144336	0.029041
H	3.739563	-3.609488	0.888891	0.151247	0.015398

P

Electronic energy: -977.583782

Electronic energy + zero-point energy: -977.203682

Electronic energy + thermal energy correction: -977.172502

Electronic energy + thermal enthalpy correction: -977.171320

Electronic energy + thermal free energy correction: -977.272194

Table S09. Cartesian coordinates, Mulliken and APT charges of all atoms at **P** in the reaction of styrene with phenylsilane (Markovnikov mode).

Symbol	X	Y	Z	Mulliken	APT
H	-4.323701	1.491717	-0.565669	0.148727	0.032597
H	-1.963770	1.157409	0.088041	-0.151364	0.130027
C	-3.971840	0.490308	-0.333209	0.062400	0.012500
C	-2.644140	0.308128	0.035801	-0.390594	-0.135119
H	-0.744071	3.511829	2.239611	0.129586	-0.088550
H	-0.410930	-0.241261	1.306081	0.268100	0.020365
C	-4.843150	-0.599763	-0.404449	0.137970	-0.110637
C	-2.154319	-0.971032	0.348501	0.172415	0.188383
C	-0.698259	-1.119581	0.715371	-0.820410	-0.430609
H	-5.880730	-0.456073	-0.692889	0.142459	0.019318
H	-1.165872	4.691869	0.992621	0.135721	-0.111962
H	2.272019	3.348461	-0.383329	0.152599	-0.090761
C	-1.047802	3.611819	1.185531	-0.811379	-0.145621
H	-0.471498	-3.295921	0.876611	0.167053	-0.017844
C	-0.347199	-2.394021	1.488441	-0.907765	0.066530
B	0.046549	2.953110	0.144701	1.256368	0.724428

H	2.129340	1.182411	0.112451	0.010345	0.138727
H	0.697581	-2.363750	1.813941	0.162954	-0.010578
H	-2.057141	3.174679	1.106091	0.187107	-0.093378
H	0.151981	-2.286890	-1.599709	-0.232648	-0.361525
C	-4.367729	-1.872293	-0.101089	-0.224876	-0.002034
C	-3.034069	-2.056472	0.271821	0.254798	-0.136448
C	1.512708	3.682910	0.343531	-0.941789	-0.154604
H	4.522730	1.296502	0.696521	0.164937	0.028995
C	2.752490	0.295711	0.009521	-0.298966	-0.070950
H	1.421278	4.773730	0.207441	0.118610	-0.107755
H	1.938439	3.527180	1.348701	0.142424	-0.079880
C	4.105080	0.357531	0.343431	-0.109390	-0.059076
H	-0.978899	-2.504511	2.378591	0.174854	-0.042292
H	-0.088770	0.125509	-1.729989	0.240285	-0.309342
Si	0.346781	-0.994550	-0.871299	0.764947	1.520911
H	-5.034108	-2.729723	-0.150939	0.133899	0.011834
H	-2.683128	-3.056942	0.509381	0.109449	0.039001
C	-0.457051	3.122709	-1.413549	-0.907720	-0.148060
C	2.182241	-0.901409	-0.455299	-0.662263	-0.397699
H	-0.571642	4.189659	-1.671319	0.128852	-0.100548
C	4.912011	-0.773908	0.223931	-0.057169	-0.027932
H	0.257389	2.700240	-2.138629	0.127707	-0.085868
H	5.965961	-0.724108	0.485161	0.141150	0.019022
H	0.160899	1.736200	0.405121	-0.636105	-0.468119
H	-1.431121	2.648189	-1.621879	0.174152	-0.092811
C	3.009341	-2.028779	-0.570559	0.084847	-0.043732
C	4.362101	-1.970958	-0.233659	-0.018538	-0.065821
H	2.592302	-2.967149	-0.932499	0.128291	0.024934
H	4.985302	-2.856508	-0.329239	0.147968	0.011980

Styrene + phenylsilane, anti-Markovnikov mode

S

Electronic energy: -454.727438

Electronic energy + zero-point energy: -454.469600

Electronic energy + thermal energy correction: -454.448794

Electronic energy + thermal enthalpy correction: -454.447612

Electronic energy + thermal free energy correction: -454.525329

Table S10. Cartesian coordinates, Mulliken and APT charges of all atoms at **S** in the reaction of styrene with phenylsilane (anti-Markovnikov mode).

Symbol	X	Y	Z	Mulliken	APT
H	4.580770	0.901490	0.708449	0.131752	-0.098784
H	4.304740	1.265600	-1.000421	0.130619	-0.097253
H	3.226010	1.927800	0.236169	0.170534	-0.088335
C	3.792730	1.027200	-0.054421	-0.836767	-0.147311
H	-3.541870	-2.677940	-0.036951	0.140951	0.023276
C	-3.041980	-1.713300	-0.051691	0.015569	-0.072276
C	-1.655790	-1.639980	-0.207831	-0.169335	-0.026664
C	-3.779070	-0.539130	0.088559	-0.274053	-0.035519
H	-1.068080	-2.547600	-0.311891	0.170941	0.036487
H	-4.858100	-0.581200	0.211609	0.135160	0.018444
C	-1.004780	-0.411330	-0.224591	-1.048043	-0.103224
C	-3.128640	0.693370	0.074239	0.256598	-0.078645
C	-1.738450	0.777590	-0.081391	0.671882	0.063431
H	0.076110	-0.380810	-0.349061	-0.068035	0.144698
H	-3.704370	1.610060	0.186979	0.128765	0.024771
C	-1.090020	2.103020	-0.082431	-0.202878	0.065997
B	2.863070	-0.331250	-0.162401	0.496460	0.725739
H	4.323170	-1.482640	-1.526281	0.115987	-0.099750
H	2.869080	-0.739420	2.079449	0.125328	-0.102253
C	0.220000	2.336230	-0.217561	-0.149507	-0.176922
H	3.216630	-2.556100	-0.658121	0.139706	-0.088196
C	3.798500	-1.624480	-0.568011	-0.851289	-0.139150
H	-1.770080	2.946440	0.046769	0.101007	-0.010619
H	0.957560	1.545700	-0.351321	0.099196	0.140046
C	2.116270	-0.613410	1.282489	-0.897735	-0.159595
H	1.454080	0.205640	1.612989	0.203771	-0.093447
H	0.594130	3.355950	-0.196621	0.154966	0.020045
H	2.011140	-0.169280	-1.062891	-0.184584	-0.456282
H	4.575540	-1.810200	0.194209	0.124634	-0.101162
H	1.505580	-1.531910	1.284789	0.168399	-0.087547

TS1

Electronic energy: -454.669812

Electronic energy + zero-point energy: -454.414126

Electronic energy + thermal energy correction: -454.391923

Electronic energy + thermal enthalpy correction: -454.390742

Electronic energy + thermal free energy correction: -454.472540

Table S11. Cartesian coordinates, Mulliken and APT charges of all atoms at **TS1** in the reaction of styrene with phenylsilane (anti-Markovnikov mode).

Symbol	X	Y	Z	Mulliken	APT
H	-4.148197	0.499690	1.047319	0.147275	-0.007536
H	-2.682804	1.464525	1.159979	0.186282	0.028204
H	-3.531291	1.331709	-0.396981	0.153412	-0.008457
C	-3.231886	0.781313	0.501028	-0.811327	-0.324702
H	2.963650	-2.664451	0.034257	0.135486	0.015377
C	2.407287	-1.730633	-0.013646	0.005686	-0.090339
C	1.554528	-1.473048	-1.083161	-0.175935	-0.060507
C	2.550252	-0.770092	0.995910	-0.194384	-0.029192
H	1.445674	-2.204145	-1.882334	0.136730	0.014236
H	3.220964	-0.960534	1.831740	0.133997	0.005658
C	0.829295	-0.275869	-1.126512	0.070321	-0.060933
C	1.843437	0.427587	0.930449	0.120883	-0.042032
C	0.947494	0.682254	-0.117953	-0.831688	0.088122
H	0.149620	-0.079253	-1.954343	0.133409	0.032477
H	1.971544	1.203296	1.681885	0.136352	0.060815
C	0.146529	1.961335	-0.145009	0.313941	0.306896
B	-2.413539	-0.541769	0.223195	0.969828	0.932289
H	-1.960207	-0.920161	2.407383	0.133624	-0.027385
H	-3.459518	-1.754275	-1.254795	0.143769	-0.021832
C	1.041741	3.165662	-0.381248	-1.471868	-0.632877
H	-0.588871	-1.026431	1.296280	0.261000	0.048759
C	-1.660159	-1.258859	1.408636	-0.767053	-0.289044
H	-0.340096	2.064188	0.841053	0.229818	-0.087036
H	1.511780	3.112044	-1.377778	0.078567	-0.119170
C	-2.485620	-1.237474	-1.196196	-0.849796	-0.320977
H	-2.467692	-0.517653	-2.022709	0.196695	0.013483
H	0.467792	4.102920	-0.301721	0.076100	-0.134393
H	-0.701714	1.767371	-0.856836	-0.009883	-0.271830
H	-1.733979	-2.353270	1.358479	0.153121	-0.015478
H	-1.706353	-1.989781	-1.360641	0.195639	-0.002595

I1

Electronic energy: -454.671925

Electronic energy + zero-point energy: -454.415817

Electronic energy + thermal energy correction: -454.392928

Electronic energy + thermal enthalpy correction: -454.391746

Electronic energy + thermal free energy correction: -454.474145

Table S12. Cartesian coordinates, Mulliken and APT charges of all atoms at **I1** in the reaction of styrene with phenylsilane (anti-Markovnikov mode).

Symbol	X	Y	Z	Mulliken	APT
H	-2.417405	-2.680937	-1.079210	0.139611	-0.009251
H	-1.022468	-1.850126	-1.799164	0.151827	-0.000376
H	-0.930052	-2.500859	-0.150165	0.243323	0.034820
C	-1.583151	-1.990502	-0.868310	-0.792880	-0.320402
H	0.043194	3.530964	0.238744	0.137429	0.016933
C	0.366768	2.492512	0.209891	-0.167656	-0.110468
C	-0.013345	1.608544	1.212772	-0.040618	-0.075331
C	1.169608	2.028911	-0.842000	-0.035945	-0.003051
H	-0.631567	1.953282	2.039992	0.142978	0.016871
H	1.470961	2.713377	-1.633045	0.144832	0.005904
C	0.401901	0.269542	1.162330	-0.034764	-0.098666
C	1.599927	0.705994	-0.869482	0.241704	-0.056843
C	1.217245	-0.203246	0.130508	-1.129476	0.070034
H	0.111268	-0.419447	1.955297	0.155761	0.045049
H	2.282996	0.342165	-1.633466	0.169792	0.075351
C	1.750782	-1.619525	0.105544	0.444546	0.277026
B	-2.187957	-0.657654	-0.277422	0.760280	0.894436
H	-2.708244	0.354432	-2.185862	0.127656	-0.008609
H	-3.931158	-0.867140	1.016880	0.150006	-0.007106
C	3.271039	-1.631001	0.152766	-1.409983	-0.596601
H	-1.273954	0.976446	-1.387089	0.241234	0.056182
C	-2.297240	0.615411	-1.199991	-0.802196	-0.298209
H	1.422822	-2.079283	-0.842566	0.214014	-0.075866
H	3.633379	-1.271839	1.130947	0.071346	-0.125792
C	-2.854540	-0.673452	1.160275	-0.749738	-0.308473
H	-2.470124	-1.455973	1.824233	0.191573	-0.001034
H	3.655638	-2.648640	-0.020873	0.072828	-0.137372
H	1.182827	-2.171616	0.898306	-0.001003	-0.241838
H	-2.871663	1.449650	-0.780778	0.162546	-0.026540
H	-2.780619	0.294685	1.669112	0.200974	0.009224

I2

Electronic energy: -454.765578

Electronic energy + zero-point energy: -454.506689

Electronic energy + thermal energy correction: -454.488604

Electronic energy + thermal enthalpy correction: -454.487422

Electronic energy + thermal free energy correction: -454.557628

Table S13. Cartesian coordinates, Mulliken and APT charges of all atoms at **I2** in the reaction of styrene with phenylsilane (anti-Markovnikov mode).

Symbol	X	Y	Z	Mulliken	APT
H	-4.155254	-1.075426	1.412738	0.132978	-0.096177
H	-2.544586	-1.796321	1.384520	0.134651	-0.085130
H	-2.826003	-0.294545	2.281923	0.134593	-0.092511
C	-3.080657	-0.831864	1.351020	-0.856405	-0.165328
H	5.163409	0.578542	-0.000088	0.129741	0.021744
C	4.100486	0.349411	-0.000048	-0.162376	-0.116030
C	3.155730	1.372612	0.000023	-0.325087	0.018243
C	3.662758	-0.976849	-0.000072	-0.062289	-0.017368
H	3.480795	2.410893	0.000043	0.147034	0.015007
H	4.386239	-1.789532	-0.000124	0.129903	0.014600
C	1.790366	1.077746	0.000066	-1.258153	-0.141746
C	2.299883	-1.261163	-0.000048	0.548564	-0.106330
C	1.333005	-0.243714	0.000027	0.509608	0.085477
H	1.061088	1.882396	0.000118	0.089187	0.074445
H	1.964785	-2.297836	-0.000072	0.134615	0.026564
C	-0.144975	-0.597042	0.000097	-0.163802	0.119193
B	-2.747829	0.060449	0.000014	1.151171	0.760186
H	-4.155251	-1.076395	-1.411854	0.132973	-0.097160
H	-4.764860	1.172020	-0.000588	0.110857	-0.101697
C	-1.160275	0.543639	-0.000112	-1.050548	-0.165994
H	-2.544772	-1.797681	-1.382822	0.134645	-0.087262
C	-3.080598	-0.833052	-1.350235	-0.856431	-0.160858
H	-0.328788	-1.240811	0.873758	0.172730	-0.045310
H	-0.975865	1.183764	0.882900	0.101970	-0.093317
C	-3.688486	1.415836	-0.000716	-0.835232	-0.150826
H	-3.507428	2.050356	0.884849	0.132877	-0.088866
H	-0.975875	1.183426	-0.883373	0.101985	-0.092998
H	-0.328815	-1.241078	-0.873356	0.172736	-0.046098

H	-2.825707	-0.296644	-2.281603	0.134594	-0.094447
H	-3.507393	2.049268	-0.887053	0.132909	-0.090007

I2 (with phenylsilane)

Electronic energy: -977.577232

Electronic energy + zero-point energy: -977.200561

Electronic energy + thermal energy correction: -977.170691

Electronic energy + thermal enthalpy correction: -977.169509

Electronic energy + thermal free energy correction: -977.267710

Table S14. Cartesian coordinates, Mulliken and APT charges of all atoms at **I2** (with phenylsilane) in the reaction of styrene with phenylsilane (anti-Markovnikov mode).

Symbol	X	Y	Z	Mulliken	APT
H	2.392440	2.920639	0.109849	0.144331	0.029604
C	1.361489	2.586339	0.187279	-0.272099	-0.140453
C	0.449190	2.855320	-0.833091	-0.103474	0.019164
C	0.936589	1.874459	1.310499	0.042325	-0.019628
H	0.765780	3.409060	-1.713751	0.158570	0.019180
H	1.641349	1.650749	2.107719	0.164703	0.027820
C	-0.868501	2.411090	-0.730791	-0.002208	-0.117009
C	-0.384511	1.440630	1.406789	-0.086694	-0.129426
C	-1.311711	1.691150	0.386159	-0.311987	0.147815
H	-1.572631	2.605880	-1.537071	0.155152	0.033373
H	-0.707151	0.870620	2.275839	0.152989	0.039072
C	-2.702491	1.118190	0.441089	-0.265112	0.065260
C	-2.786901	-0.318570	-0.110711	-1.231866	-0.196394
H	-3.382521	1.762250	-0.131201	0.177567	-0.045594
H	-2.371831	-0.315940	-1.135391	0.148093	-0.081428
H	-2.109531	-0.954080	0.490129	0.174450	-0.088345
H	-3.058661	1.120740	1.479099	0.169550	-0.043202
H	-4.904481	0.027831	-2.108321	0.135829	-0.086372
H	-5.495981	0.932571	-0.704651	0.127899	-0.083096
B	-4.309451	-0.974899	-0.117911	1.270475	0.800986
H	-3.781402	-2.525120	-1.738251	0.134592	-0.086557
C	-5.307301	-0.084449	-1.087161	-0.891942	-0.168848
H	-5.082871	-0.025429	1.853679	0.126706	-0.087445
H	-4.253761	-1.569709	2.110269	0.133991	-0.090015

C	-4.190812	-2.507500	-0.714171	-0.873104	-0.163487
C	-4.916891	-1.024339	1.416809	-0.903810	-0.170576
H	-3.534282	-3.145160	-0.098491	0.140167	-0.090111
H	-6.295171	-0.562689	-1.188911	0.127319	-0.106077
H	-5.171562	-3.009349	-0.756401	0.128400	-0.113387
H	-5.891571	-1.538449	1.443289	0.129768	-0.099453
H	0.414919	-0.170750	-1.063971	-0.104218	-0.246841
H	5.327039	1.026269	-1.339381	0.167726	0.024613
H	2.883829	0.673439	-1.493741	0.150416	0.042840
C	4.864479	0.203139	-0.801521	-0.103386	-0.037815
C	3.487459	-0.002611	-0.892141	0.332099	-0.060198
C	5.645519	-0.643321	-0.016561	-0.208226	-0.035351
Si	0.992019	-1.319111	-0.339251	0.539786	1.343135
C	2.860989	-1.052591	-0.206301	-0.868652	-0.360918
H	6.717549	-0.483862	0.059019	0.144814	0.026852
H	0.754508	-2.575560	-1.094521	-0.064511	-0.330638
C	5.042949	-1.693601	0.675969	-0.160937	-0.054021
C	3.666389	-1.891081	0.578979	-0.079162	-0.030387
H	5.645329	-2.354591	1.293079	0.154075	0.021380
H	3.210588	-2.711721	1.130319	0.153380	0.030673
H	0.443469	-1.489110	1.024029	-0.053784	-0.308696

TS2

Electronic energy: -977.518861

Electronic energy + zero-point energy: -977.140612

Electronic energy + thermal energy correction: -977.109131

Electronic energy + thermal enthalpy correction: -977.107949

Electronic energy + thermal free energy correction: -977.209696

Table S15. Cartesian coordinates, Mulliken and APT charges of all atoms at **TS2** in the reaction of styrene with phenylsilane (anti-Markovnikov mode).

Symbol	X	Y	Z	Mulliken	APT
H	-0.281115	4.993132	-1.061691	0.139408	0.023277
C	-0.616952	4.059809	-0.619552	-0.248224	-0.091543
C	-1.579681	3.280664	-1.263873	-0.269371	0.003902
C	-0.089622	3.626124	0.595406	0.002051	-0.005521
H	-1.997761	3.608304	-2.211705	0.156590	0.019201

H	0.662864	4.220928	1.105916	0.165376	0.023198
C	-2.001423	2.078809	-0.699344	-0.263116	-0.106012
C	-0.519068	2.422575	1.156405	0.411061	-0.114822
C	-1.474850	1.627330	0.517188	-0.070872	0.101906
H	-2.743105	1.469623	-1.211211	0.114282	0.051149
H	-0.091041	2.081387	2.095723	0.170620	0.040417
C	-1.912617	0.295765	1.088507	-0.515121	0.215768
C	-1.472368	-0.880594	0.228869	-1.344786	-1.227541
H	-3.001338	0.336650	1.249847	0.166366	-0.092825
H	-1.667169	-0.843194	-0.839201	0.341881	0.122245
H	-1.450647	-1.856203	0.702256	0.193086	0.124511
H	-1.460983	0.183077	2.083469	0.053619	-0.044345
H	-3.876250	-0.657108	-1.869398	0.129225	-0.034846
H	-4.466946	-0.021897	-0.318149	0.147449	-0.030460
B	-3.319292	-1.990409	-0.106147	1.119339	1.241318
H	-2.381398	-2.917306	-1.966007	0.134993	-0.034565
C	-4.262993	-0.941874	-0.881725	-0.791754	-0.295593
H	-3.959093	-1.501744	2.031116	0.147740	-0.024532
H	-3.137766	-3.068122	1.897133	0.144743	-0.042063
C	-2.801635	-3.225927	-1.000055	-0.777850	-0.272085
C	-3.810945	-2.372408	1.379363	-0.760972	-0.287126
H	-2.048088	-3.844737	-0.496122	0.142561	-0.030240
H	-5.239867	-1.421979	-1.051215	0.141750	-0.083631
H	-3.656319	-3.883990	-1.221394	0.136152	-0.063715
H	-4.789230	-2.872873	1.304721	0.147096	-0.080027
H	0.589875	0.311914	-0.916486	-0.070869	-0.421631
H	5.322274	1.438196	0.244230	0.139238	-0.005534
H	2.853978	1.332958	0.298388	0.117134	0.007660
C	4.817273	0.485155	0.102533	0.018548	-0.010547
C	3.424095	0.415249	0.134690	-0.080090	-0.060690
C	5.566736	-0.673870	-0.117064	-0.215880	-0.110748
Si	0.745073	-0.826279	0.045783	0.371164	2.040962
C	2.727689	-0.792080	-0.045532	-1.057576	-0.485001
H	6.652252	-0.628649	-0.144666	0.128550	0.007406
H	0.665783	-2.246666	-0.450809	-0.213549	-0.426792
C	4.906301	-1.887654	-0.304338	-0.092038	-0.008511
C	3.508532	-1.934052	-0.268386	0.371182	-0.075453
H	5.479970	-2.795071	-0.480094	0.129202	-0.009794
H	3.009359	-2.891915	-0.423052	0.139282	0.014990
H	0.726361	-0.502897	1.519625	0.052384	-0.461713

I3

Electronic energy: -977.528515

Electronic energy + zero-point energy: -977.153349

Electronic energy + thermal energy correction: -977.122793

Electronic energy + thermal enthalpy correction: -977.121612

Electronic energy + thermal free energy correction: -977.222742

Table S16. Cartesian coordinates, Mulliken and APT charges of all atoms at **I3** in the reaction of styrene with phenylsilane (anti-Markovnikov mode).

Symbol	X	Y	Z	Mulliken	APT
H	3.516801	-4.263119	-1.595350	0.137694	0.019803
C	3.109681	-3.471939	-0.971800	-0.029415	-0.097733
C	3.923990	-2.426499	-0.539910	-0.248835	-0.008827
C	1.765341	-3.489939	-0.597230	-0.362081	-0.001961
H	4.973040	-2.398949	-0.823800	0.152388	0.017168
H	1.119271	-4.297310	-0.931340	0.144108	0.022641
C	3.393200	-1.412809	0.257640	-0.103756	-0.094863
C	1.241520	-2.473650	0.198440	0.151250	-0.081629
C	2.046520	-1.414999	0.638270	-0.110953	0.104793
H	4.031650	-0.597589	0.593160	0.102876	0.028147
H	0.191150	-2.481020	0.477000	0.184819	0.059967
C	1.471580	-0.293069	1.465030	-0.224469	0.085150
C	0.673710	0.719670	0.630110	-1.188322	-0.437429
H	2.298070	0.182761	2.013510	0.127632	-0.098046
H	1.187210	0.934410	-0.321220	0.382475	-0.064303
H	0.614330	1.668370	1.188200	0.309947	-0.083737
H	0.793820	-0.719190	2.221660	0.162579	-0.037376
H	2.671100	2.264161	-2.374850	0.155268	-0.011298
H	3.538510	1.118001	-1.326420	0.213231	0.011524
B	2.786310	2.903431	-0.209070	0.992320	0.954577
H	1.897489	4.708311	-1.135060	0.147329	-0.018852
C	3.329820	2.178781	-1.504880	-0.801120	-0.311109
H	4.172560	1.816051	1.220030	0.184257	-0.016733
H	2.828280	2.677031	2.011370	0.170546	0.014766
C	1.645049	3.986061	-0.345800	-0.810343	-0.291010
C	3.530610	2.701591	1.170690	-0.853040	-0.311797
H	0.722009	3.489940	-0.673380	0.223946	0.029385
H	4.293300	2.644081	-1.768560	0.150103	-0.014311
H	1.421549	4.535141	0.574730	0.133964	-0.024338
H	4.170389	3.584311	1.331140	0.140059	-0.012118
H	-1.353940	1.676000	-0.444110	-0.193075	-0.498318
H	-5.902920	1.362409	-1.761500	0.121405	-0.015515

H	-3.454850	1.634410	-1.475450	0.128655	0.018756
C	-5.367280	0.748749	-1.038780	-0.095187	-0.004215
C	-3.987710	0.893890	-0.875280	0.178850	-0.082450
C	-6.065080	-0.183061	-0.268130	-0.166284	-0.116673
Si	-1.246770	0.273870	0.184910	0.107305	1.869312
C	-3.254080	0.125690	0.039340	-0.943582	-0.503204
H	-7.139950	-0.301041	-0.385710	0.124402	0.002780
H	-1.359510	-0.408710	1.569830	-0.106642	-0.496877
C	-5.366200	-0.955781	0.660790	-0.074917	-0.000763
C	-3.986360	-0.791730	0.804950	0.001122	-0.086905
H	-5.900780	-1.680321	1.273270	0.128596	-0.015066
H	-3.452230	-1.393160	1.543740	0.115960	0.018557
H	-0.978990	-0.752040	-0.884960	0.038937	-0.419870

I4

Electronic energy: -977.578120

Electronic energy + zero-point energy: -977.198115

Electronic energy + thermal energy correction: -977.167259

Electronic energy + thermal enthalpy correction: -977.166078

Electronic energy + thermal free energy correction: -977.265502

Table S17. Cartesian coordinates, Mulliken and APT charges of all atoms at **I4** in the reaction of styrene with phenylsilane (anti-Markovnikov mode).

Symbol	X	Y	Z	Mulliken	APT
H	2.934770	3.417649	-1.618779	0.143679	0.025520
C	2.392370	2.847559	-0.869679	-0.172937	-0.076153
C	0.998800	2.826619	-0.873859	-0.146391	0.001640
C	3.084060	2.115629	0.095731	-0.207308	-0.010085
H	0.445930	3.380569	-1.627459	0.174782	0.032418
H	4.170720	2.103169	0.096871	0.158900	0.023585
C	0.300160	2.081799	0.076561	-0.598487	-0.104264
C	2.383120	1.371009	1.040081	0.493236	-0.097004
C	0.984540	1.340959	1.046661	-0.028111	0.045647
H	-0.786470	2.060219	0.039871	0.148851	0.075372
H	2.927690	0.766659	1.762931	0.153630	0.034617
C	0.246050	0.502799	2.068731	-0.456613	0.136533
C	-1.065270	-0.114311	1.563641	-0.685289	-0.329817

H	0.034760	1.130789	2.947051	0.188265	-0.087910
H	-1.821170	0.657239	1.391961	0.203686	0.012617
H	-1.493290	-0.757781	2.342361	0.156144	-0.030647
H	0.930080	-0.281881	2.413961	0.160319	-0.038967
H	-2.739740	1.457099	-1.292909	0.160370	-0.073538
H	-3.280340	1.947200	0.327591	0.130594	-0.081144
B	-4.031900	-0.165590	-0.269419	0.863788	0.858731
H	-3.725440	-0.922480	-2.416489	0.149103	-0.070976
C	-3.572960	1.383380	-0.574639	-0.943744	-0.201765
H	-4.848820	0.236730	1.842921	0.142185	-0.078580
H	-5.502910	-1.245420	1.129961	0.138790	-0.084308
C	-4.511570	-0.914040	-1.644759	-0.852062	-0.179719
C	-5.184450	-0.217850	0.897111	-0.783351	-0.186008
H	-4.804841	-1.961220	-1.473409	0.147913	-0.081273
H	-4.412340	1.942740	-1.019999	0.116695	-0.084909
H	-5.384590	-0.408530	-2.091189	0.131885	-0.102233
H	-6.089180	0.332330	0.587301	0.133807	-0.114800
H	-1.286490	-0.477241	-1.314049	0.027612	-0.326893
H	3.520439	-3.149591	1.234661	0.147440	0.009595
H	1.095269	-2.773791	1.483001	0.131293	0.020348
C	2.991249	-2.537501	0.507941	-0.121808	-0.030504
C	1.619779	-2.318251	0.642141	-0.153107	-0.049555
C	3.683459	-1.972381	-0.564109	-0.201762	-0.067068
Si	-0.979900	-1.158611	-0.035909	0.919524	1.799596
C	0.901929	-1.526871	-0.268119	-1.250304	-0.420336
H	4.752089	-2.138281	-0.674179	0.148711	0.017542
H	-3.045420	-0.813300	0.175101	-0.457568	-0.635225
C	2.992280	-1.195551	-1.492789	-0.075727	-0.026075
C	1.622650	-0.978941	-1.338689	0.440193	-0.078315
H	3.522580	-0.743741	-2.327579	0.155750	0.016071
H	1.102290	-0.346751	-2.057069	0.145505	0.033947
H	-1.534621	-2.528231	0.115711	-0.078081	-0.395705

P

Electronic energy: -977.579634

Electronic energy + zero-point energy: -977.200561

Electronic energy + thermal energy correction: -977.171513

Electronic energy + thermal enthalpy correction: -977.170331

Electronic energy + thermal free energy correction: -977.265496

Table S18. Cartesian coordinates, Mulliken and APT charges of all atoms at **P** in the reaction of styrene with phenylsilane (anti-Markovnikov mode).

Symbol	X	Y	Z	Mulliken	APT
H	2.461658	3.762461	-1.631319	0.144995	0.026653
C	2.023328	3.115861	-0.876259	-0.145240	-0.070070
C	0.645288	2.912300	-0.837599	-0.071375	-0.004148
C	2.835759	2.473881	0.058961	-0.234497	-0.023806
H	-0.002202	3.397440	-1.562679	0.183023	0.037693
H	3.913539	2.610341	0.030861	0.155029	0.024764
C	0.081519	2.072990	0.124011	-0.717832	-0.112701
C	2.269499	1.633431	1.013531	0.568645	-0.093078
C	0.887899	1.415820	1.058871	-0.087576	0.032872
H	-0.993791	1.915130	0.122541	0.170644	0.098476
H	2.911769	1.101121	1.712491	0.163436	0.033768
C	0.299239	0.464050	2.080531	-0.368728	0.138971
C	-0.952991	-0.290030	1.609891	-0.754854	-0.323479
H	0.060939	1.031060	2.992211	0.195797	-0.082179
H	-1.803781	0.383819	1.470671	0.191755	0.024519
H	-1.271020	-0.990880	2.391071	0.146842	-0.026787
H	1.083229	-0.251030	2.360271	0.149916	-0.041573
H	-2.743281	1.295659	-1.138649	0.160187	-0.088223
H	-3.351251	1.753419	0.469531	0.114440	-0.089540
B	-4.133161	-0.321711	-0.231769	0.817641	0.768263
H	-3.609260	-1.039701	-2.359139	0.149680	-0.082991
C	-3.614351	1.227289	-0.465129	-0.948788	-0.179107
H	-5.246161	0.119008	1.739811	0.131425	-0.085550
H	-5.831540	-1.346862	0.939301	0.123999	-0.091386
C	-4.477410	-1.018191	-1.680249	-0.825940	-0.154148
C	-5.450311	-0.330292	0.754351	-0.815665	-0.156927
H	-4.826890	-2.057561	-1.576859	0.147757	-0.091037
H	-4.411531	1.827529	-0.935569	0.116279	-0.097814
H	-5.274881	-0.467722	-2.209029	0.136448	-0.104959
H	-6.283101	0.244338	0.312631	0.135864	-0.109316
H	-1.213131	-0.578030	-1.225649	0.163512	-0.307347
H	3.745090	-3.318289	1.023071	0.150062	0.013354
H	1.310930	-3.028550	1.303551	0.146471	0.022489
C	3.206080	-2.624779	0.382351	-0.067872	-0.038537
C	1.829720	-2.455449	0.535181	-0.122488	-0.037720
C	3.889860	-1.904969	-0.597979	-0.257452	-0.048112
Si	-0.770890	-1.283130	-0.005389	0.631465	1.611573
C	1.101320	-1.567090	-0.270969	-1.223417	-0.395730
H	4.961960	-2.033309	-0.722249	0.147546	0.020551
H	-3.236530	-0.993221	0.324381	-0.406711	-0.519149

C	3.188210	-1.021299	-1.416509	-0.033189	-0.034900
C	1.813150	-0.857939	-1.249369	0.524250	-0.065578
H	3.712869	-0.449529	-2.177569	0.159258	0.019660
H	1.283979	-0.143910	-1.879029	0.151177	0.041935
H	-1.344190	-2.643850	0.117961	-0.095920	-0.359648

1,1-diphenylethene + phenylsilane

S

Electronic energy: -685.699507

Electronic energy + zero-point energy: -685.361116

Electronic energy + thermal energy correction: -685.335140

Electronic energy + thermal enthalpy correction: -685.333958

Electronic energy + thermal free energy correction: -685.422928

Table S19. Cartesian coordinates, Mulliken and APT charges of all atoms at **S** in the reaction of 1,1-diphenylethene with phenylsilane.

Symbol	X	Y	Z	Mulliken	APT
H	-2.157741	-1.653410	1.414900	0.206151	-0.102262
H	-3.633870	-2.565861	1.729990	0.129412	-0.108310
H	-2.585670	-3.023791	0.383040	0.163076	-0.080359
C	-3.006541	-2.156741	0.919380	-0.873593	-0.144990
H	-1.254774	4.580830	-0.109020	0.147957	0.021003
C	-0.845863	3.575090	-0.153220	-0.227103	-0.049565
C	-1.648803	2.475930	0.150280	-0.059890	-0.041117
C	0.486177	3.375311	-0.515160	-0.294864	-0.046950
H	-2.690873	2.606419	0.427780	0.143686	0.050641
H	1.119526	4.223861	-0.759920	0.143372	0.017609
C	-1.126772	1.186180	0.100850	-0.267417	-0.094297
C	1.008327	2.084871	-0.572700	-0.392086	-0.083390
C	0.208338	0.972961	-0.270550	0.686941	0.038761
H	-1.772662	0.344020	0.333980	0.026689	0.136541
H	2.044167	1.935882	-0.866970	0.136123	0.038938
C	0.742879	-0.413669	-0.378140	-0.711496	0.159839
B	-3.901561	-1.169721	-0.055760	0.404414	0.716784

H	-5.804370	-2.443722	0.043410	0.126583	-0.106423
H	-5.051772	0.819298	0.213330	0.132219	-0.088734
C	-0.058961	-1.444709	-0.687770	-0.019169	-0.250420
H	-4.787310	-2.867802	-1.340530	0.135738	-0.089874
C	-5.139141	-2.020992	-0.729840	-0.828929	-0.140819
H	-1.120891	-1.313280	-0.889870	0.228967	0.142171
C	-4.505772	0.087068	0.830090	-0.836647	-0.148717
H	-5.219261	-0.281742	1.587330	0.127657	-0.099894
H	0.330860	-2.459099	-0.704740	0.121101	0.031937
H	-5.771011	-1.398182	-1.382890	0.125010	-0.097021
H	-3.738502	0.649029	1.390180	0.184604	-0.095278
H	-3.188511	-0.722671	-0.977310	-0.135611	-0.458065
C	2.191259	-0.640718	-0.108730	0.181482	0.088507
C	2.947739	-1.501278	-0.914360	0.070913	-0.090259
H	2.473879	-1.963378	-1.775740	0.186952	0.050549
C	4.289199	-1.754287	-0.632950	-0.184881	-0.020762
H	4.857260	-2.423397	-1.273260	0.146314	0.023666
C	4.904169	-1.143437	0.458280	-0.133156	-0.082486
H	5.950049	-1.337816	0.677520	0.140811	0.028666
C	4.165299	-0.275567	1.263120	-0.237185	-0.004843
H	4.633438	0.204383	2.117890	0.152854	0.025680
C	2.825848	-0.024278	0.979600	-0.223017	-0.100775
H	2.251558	0.648632	1.610570	0.176018	0.054317

TS1

Electronic energy: -685.678028

Electronic energy + zero-point energy: -685.341727

Electronic energy + thermal energy correction: -685.315603

Electronic energy + thermal enthalpy correction: -685.314421

Electronic energy + thermal free energy correction: -685.402514

Table S20. Cartesian coordinates, Mulliken and APT charges of all atoms at **TS1** in the reaction of 1,1-diphenylethene with phenylsilane.

Symbol	X	Y	Z	Mulliken	APT
H	0.646233	1.256334	1.699100	0.224296	-0.050025
H	-0.004096	2.721150	2.449250	0.094417	-0.073648
H	-1.020100	1.743094	1.377380	0.195527	-0.051661

C	-0.000412	2.129410	1.518350	-0.873485	-0.252993
H	4.355457	-3.023975	0.534530	0.132500	0.014845
C	3.461823	-2.470220	0.261050	-0.151269	-0.225009
C	3.513036	-1.090820	0.060930	-0.462842	0.086970
C	2.236657	-3.126207	0.114000	-0.233292	0.105505
H	4.451123	-0.557435	0.193560	0.143383	0.015748
H	2.175253	-4.201448	0.265040	0.134803	0.003463
C	2.366842	-0.378317	-0.283130	-0.421869	-0.216763
C	1.091973	-2.418494	-0.234000	-0.024240	-0.243125
C	1.125785	-1.025454	-0.452800	0.153181	0.539533
H	2.410616	0.703284	-0.385160	0.122652	0.064704
H	0.149956	-2.946669	-0.357410	0.158436	0.038714
C	-0.057749	-0.265960	-0.874250	0.359781	-1.049189
B	0.506193	3.027073	0.262360	0.664544	1.146838
H	-0.726698	4.908536	0.550590	0.134326	-0.132233
H	2.401057	4.094164	-0.481180	0.152679	-0.074469
C	0.126545	0.894931	-1.603240	-0.398435	1.107364
H	-1.563071	3.708291	-0.437900	0.163696	-0.059522
C	-0.574274	4.144287	-0.230400	-0.804166	-0.235458
H	1.039224	1.026166	-2.179140	0.180591	-0.064568
C	2.015329	3.624791	0.436250	-0.807401	-0.249305
H	2.023585	4.406941	1.215000	0.130710	-0.135925
H	-0.735648	1.442216	-1.973260	0.168335	-0.022915
H	-0.254367	4.681599	-1.136220	0.144289	-0.082496
H	2.748074	2.866756	0.751110	0.168369	-0.060141
H	0.562548	2.143133	-0.719970	-0.228694	-0.966321
C	-1.396667	-0.635148	-0.383500	0.104109	0.477713
C	-2.554378	-0.395404	-1.149180	0.072361	-0.204208
H	-2.446671	0.032006	-2.142300	0.133796	0.035910
C	-3.824386	-0.709691	-0.675090	-0.319308	0.081976
H	-4.692458	-0.505586	-1.297260	0.135189	0.008708
C	-3.988063	-1.295422	0.580670	-0.222199	-0.221520
H	-4.978192	-1.546498	0.949920	0.135049	0.019328
C	-2.854112	-1.547486	1.354610	-0.251822	0.096955
H	-2.959209	-1.985217	2.344290	0.152605	0.013226
C	-1.586854	-1.220519	0.884750	-0.315637	-0.231527
H	-0.720153	-1.387864	1.518080	0.155032	0.045520

I1

Electronic energy: -685.697821

Electronic energy + zero-point energy: -685.358454

Electronic energy + thermal energy correction: -685.330628

Electronic energy + thermal enthalpy correction: -685.329446

Electronic energy + thermal free energy correction: -685.422739

Table S21. Cartesian coordinates, Mulliken and APT charges of all atoms at **I1** in the reaction of 1,1-diphenylethene with phenylsilane.

Symbol	X	Y	Z	Mulliken	APT
H	-0.629051	0.973140	-1.029390	0.361724	0.144168
H	-1.914341	0.740329	-2.206870	0.158042	-0.003335
H	-0.741591	2.093500	-2.377710	0.128123	-0.003302
C	-1.351391	1.513450	-1.674820	-0.897437	-0.387025
H	-3.171838	-3.933281	-0.468030	0.116621	0.004156
C	-2.443259	-3.174871	-0.198150	-0.197444	-0.622955
C	-2.818009	-2.012441	0.478050	-0.218102	0.357364
C	-1.080219	-3.334280	-0.490870	-0.064112	0.378048
H	-3.861639	-1.856912	0.749450	0.122226	-0.012970
H	-0.737108	-4.246980	-0.976180	0.114459	-0.006283
C	-1.889880	-1.037131	0.822660	-0.294807	-0.633241
C	-0.145459	-2.367330	-0.164060	-0.370375	-0.399889
C	-0.500200	-1.138910	0.485650	0.184413	1.125366
H	-2.246200	-0.166761	1.363180	0.114580	0.028465
H	0.899311	-2.569299	-0.372590	0.124662	0.026671
C	0.420480	-0.110649	0.846220	-0.125330	-1.607538
B	-2.199251	2.392529	-0.698680	0.900484	0.912031
H	-1.897793	4.522949	-1.086980	0.166023	-0.013756
H	-3.722371	2.078689	0.907280	0.185362	0.004892
C	-0.092911	0.965020	1.768170	-0.739163	0.348471
H	-0.555692	3.828300	-0.190190	0.190948	0.006112
C	-1.647872	3.819240	-0.277230	-0.816215	-0.298498
H	-0.441251	0.587720	2.744880	0.166824	-0.134710
C	-3.622931	1.937319	-0.176500	-0.884937	-0.318888
H	-4.380042	2.595058	-0.633270	0.139300	-0.022330
H	0.659079	1.735751	1.952690	0.113039	-0.008660
H	-2.082542	4.219809	0.645030	0.150760	-0.018761
H	-3.873451	0.901178	-0.420410	0.208035	0.009494
H	-0.963861	1.495580	1.334940	0.075245	-0.167458
C	1.781110	-0.027919	0.379400	0.359702	1.144452
C	2.806549	0.612492	1.137950	-0.408503	-0.570779
H	2.569099	0.989552	2.128650	0.107293	0.018745
C	4.112799	0.733962	0.681830	-0.013150	0.306630

H	4.849079	1.220193	1.319900	0.121413	-0.014338
C	4.498330	0.229232	-0.563200	-0.295225	-0.564765
H	5.520930	0.320573	-0.916740	0.117347	0.007223
C	3.513840	-0.390598	-1.341500	-0.016160	0.358180
H	3.766130	-0.766578	-2.331700	0.123085	-0.001719
C	2.206580	-0.513399	-0.893970	-0.396119	-0.396361
H	1.466060	-0.944279	-1.560290	0.187367	0.027093

I2

Electronic energy: -685.737470

Electronic energy + zero-point energy: -685.394720

Electronic energy + thermal energy correction: -685.368075

Electronic energy + thermal enthalpy correction: -685.366894

Electronic energy + thermal free energy correction: -685.455402

Table S22. Cartesian coordinates, Mulliken and APT charges of all atoms at **I2** in the reaction of 1,1-diphenylethene with phenylsilane.

Symbol	X	Y	Z	Mulliken	APT
H	-0.831391	1.256695	2.385842	0.172482	-0.064852
H	0.919995	1.434504	2.293903	0.144586	-0.072554
H	-0.112168	2.861277	2.392129	0.103856	-0.098086
C	-0.028894	1.861201	1.934782	-0.721200	-0.177427
H	4.662275	-2.239990	0.297796	0.130849	0.014408
C	3.735408	-1.690400	0.150149	-0.082771	-0.113938
C	3.624702	-0.363868	0.559269	-0.090150	0.002460
C	2.633914	-2.302228	-0.449963	-0.005704	-0.006482
H	4.469880	0.130959	1.033321	0.136479	0.008375
H	2.695516	-3.338063	-0.777961	0.136220	0.006695
C	2.434107	0.342102	0.374120	0.236477	-0.109009
C	1.451385	-1.589916	-0.630137	-0.242207	-0.121175
C	1.314329	-0.250039	-0.223314	0.521614	0.136750
H	2.369020	1.369864	0.706879	0.152385	0.078486
H	0.598860	-2.084159	-1.092967	0.162144	0.040394
C	0.020542	0.513588	-0.534469	-1.751183	-0.340741
B	-0.215464	2.008401	0.300313	0.656121	0.721576
H	-1.869969	3.545628	0.473436	0.100633	-0.089753
H	0.429520	3.506266	-1.328481	0.135441	-0.080781

C	0.095223	0.818720	-2.046233	-0.287959	0.044383
H	-2.520303	1.903936	0.563805	0.169890	-0.073878
C	-1.765290	2.528304	0.061004	-0.672876	-0.164505
H	0.046005	-0.095552	-2.659442	0.161881	-0.071923
C	0.763757	3.192927	-0.325835	-0.683889	-0.171060
H	0.692009	4.089655	0.311547	0.114975	-0.105415
H	-0.711090	1.489871	-2.362640	0.142996	-0.025569
H	-2.065739	2.595858	-0.998876	0.144057	-0.070985
H	1.836801	2.966924	-0.423643	0.132264	-0.075300
H	1.041012	1.322169	-2.270826	0.152265	-0.019268
C	-1.164252	-0.370090	-0.212780	-0.112711	0.250269
C	-2.277649	-0.490928	-1.057777	-0.036735	-0.149245
H	-2.290739	0.040011	-2.004884	0.106419	0.045714
C	-3.387930	-1.261281	-0.706964	-0.300128	0.037642
H	-4.233550	-1.321557	-1.389353	0.136110	0.004824
C	-3.420610	-1.945961	0.504601	-0.235586	-0.162959
H	-4.283875	-2.547090	0.779920	0.127896	0.012390
C	-2.320892	-1.844645	1.360174	-0.060043	0.049702
H	-2.322344	-2.370403	2.312890	0.144123	0.011173
C	-1.219612	-1.072999	1.005485	-0.205877	-0.145017
H	-0.371839	-1.005725	1.683356	0.166856	0.044680

I2 (with phenylsilane)

Electronic energy: -1208.547226

Electronic energy + zero-point energy: -1208.087219

Electronic energy + thermal energy correction: -1208.049719

Electronic energy + thermal enthalpy correction: -1208.048537

Electronic energy + thermal free energy correction: -1208.161663

Table S23. Cartesian coordinates, Mulliken and APT charges of all atoms at **I2** (with phenylsilane) in the reaction of 1,1-diphenylethene with phenylsilane.

Symbol	X	Y	Z	Mulliken	APT
H	0.931309	4.363540	1.548259	0.139453	0.012454
C	0.337229	3.547770	1.144739	0.026134	-0.101774
C	-1.039301	3.683880	0.984139	-0.187132	0.001288
C	0.940600	2.342940	0.781599	0.403646	-0.022112
H	-1.528801	4.614040	1.262909	0.131572	0.002991

H	2.013710	2.205961	0.896879	0.130852	0.015046
C	-1.807240	2.634940	0.473039	0.292534	-0.112243
C	0.164350	1.306750	0.271219	-0.900223	-0.097152
C	-1.227980	1.414220	0.105119	0.859013	0.127653
H	-2.876030	2.762769	0.364539	0.147360	0.076695
H	0.644970	0.368740	0.000789	0.008636	0.019849
C	-2.007460	0.262860	-0.543211	-1.711946	-0.347849
C	-1.635610	0.321710	-2.041151	-0.100727	0.057303
H	-1.813540	1.332030	-2.420741	0.148361	-0.017360
H	-2.251120	-0.360290	-2.637181	0.135840	-0.026688
H	-3.842660	1.405919	1.687619	0.147081	-0.070540
H	-4.023280	-0.344911	1.763329	0.169633	-0.059213
B	-3.731810	0.331769	-0.414471	0.641742	0.740539
H	-3.892800	2.499439	-1.370651	0.138353	-0.074577
C	-4.240880	0.537699	1.142949	-0.679736	-0.183591
H	-4.174249	-1.942371	-0.252101	0.155271	-0.070401
H	-4.058100	-1.407521	-1.933881	0.139125	-0.065575
C	-4.342060	1.497129	-1.425301	-0.623552	-0.177117
C	-4.380830	-1.097811	-0.926041	-0.613677	-0.172682
H	-4.270210	1.190529	-2.480751	0.140218	-0.076989
H	-5.337230	0.645379	1.144679	0.103960	-0.103192
H	-5.416180	1.623839	-1.218031	0.102620	-0.108148
H	-5.476110	-0.991781	-0.975511	0.098882	-0.091805
H	-0.575990	0.075510	-2.216361	0.121486	-0.079104
C	-1.574750	-1.048200	0.074189	-0.592082	0.236682
C	-1.368439	-2.212240	-0.682841	-0.241629	-0.157999
H	-1.467219	-2.170150	-1.763061	0.108447	0.050284
C	-1.054259	-3.434270	-0.086001	-0.131470	0.006072
H	-0.908869	-4.312620	-0.711151	0.150474	0.013785
C	-0.932269	-3.535470	1.297939	-0.364430	-0.163955
H	-0.688389	-4.485400	1.765659	0.138148	0.017010
C	-1.127669	-2.389640	2.071949	-0.019540	0.040859
H	-1.036029	-2.442110	3.154149	0.167550	0.013196
C	-1.438840	-1.174710	1.469579	-0.081702	-0.137906
H	-1.589560	-0.292940	2.087229	0.176071	0.043865
Si	2.209381	-1.930689	-0.473131	0.787461	1.344358
C	3.638660	-0.698619	-0.388701	-0.875671	-0.360930
C	4.824440	-0.994259	0.300109	-0.091803	-0.034205
H	4.943291	-1.966559	0.774759	0.149982	0.029746
C	5.860740	-0.066759	0.391299	-0.081828	-0.049928
H	6.768870	-0.318208	0.932169	0.153854	0.021289
C	5.729460	1.184381	-0.211441	-0.283938	-0.027266
H	6.533430	1.911422	-0.139461	0.152953	0.030040
C	4.561140	1.498151	-0.903221	-0.222693	-0.054707
H	4.446900	2.472271	-1.370241	0.169522	0.034620

C	3.529520	0.563131	-0.991701	0.287540	-0.055846
H	2.621260	0.828531	-1.529671	0.178707	0.046289
H	1.396251	-1.854910	0.758209	-0.142251	-0.262293
H	2.785901	-3.295819	-0.597201	-0.106743	-0.327335
H	1.416881	-1.605020	-1.678571	0.050288	-0.291434

I3

Electronic energy: -1208.517909

Electronic energy + zero-point energy: -1208.060061

Electronic energy + thermal energy correction: -1208.021020

Electronic energy + thermal enthalpy correction: -1208.019838

Electronic energy + thermal free energy correction: -1208.138550

Table S24. Cartesian coordinates, Mulliken and APT charges of all atoms at **I3** in the reaction of 1,1-diphenylethene with phenylsilane.

Symbol	X	Y	Z	Mulliken	APT
H	2.118811	-3.974630	2.033739	0.137851	0.014697
C	1.829070	-3.085180	1.482669	-0.277254	-0.396514
C	2.004220	-3.002990	0.104069	-0.189876	0.170918
C	1.258650	-1.984520	2.135989	0.059190	0.239621
H	2.448311	-3.836010	-0.437301	0.137629	0.003174
H	1.088690	-2.021410	3.209889	0.155975	0.010339
C	1.634130	-1.859580	-0.604131	-0.289940	-0.432221
C	0.894510	-0.842860	1.439159	-0.302241	-0.304767
C	1.065220	-0.721930	0.028779	-0.616891	0.758313
H	1.795160	-1.846070	-1.677841	0.122557	0.050009
H	0.425730	-0.029650	1.982799	0.136875	0.044687
C	0.565390	0.406560	-0.737131	-1.449701	-1.495258
C	0.580090	0.235600	-2.243311	0.067428	0.214288
H	0.071730	-0.693390	-2.540101	0.148249	-0.052820
H	1.598040	0.195010	-2.666971	0.176302	-0.102663
H	3.724590	-1.117389	1.566339	0.273753	0.059966
H	4.487160	0.478001	1.480519	0.163623	-0.015453
B	4.560010	-0.766549	-0.404101	0.992846	0.880940
H	5.112640	-2.956089	-0.304011	0.186487	-0.005445
C	4.584550	-0.563939	1.158209	-0.802943	-0.303184
H	3.212320	0.882851	-1.020841	0.318244	0.051280

H	4.088800	0.184881	-2.407601	0.129527	-0.024120
C	5.097230	-2.124749	-1.016591	-0.833977	-0.296323
C	4.161340	0.434291	-1.343611	-0.858276	-0.294356
H	4.546050	-2.430809	-1.912691	0.194123	0.001831
H	5.475650	-1.007019	1.621709	0.122310	-0.024257
H	6.136270	-1.945559	-1.337841	0.138753	-0.016814
H	4.914290	1.228971	-1.229361	0.128993	-0.008426
H	0.059100	1.051570	-2.748691	0.079751	-0.010333
C	0.672640	1.775040	-0.226231	0.835869	0.809250
C	0.031460	2.863980	-0.874161	-0.056960	-0.372545
H	-0.558620	2.681400	-1.765681	0.102659	0.038769
C	0.110830	4.167660	-0.396931	0.075672	0.178833
H	-0.412591	4.956940	-0.932501	0.143336	-0.002332
C	0.842990	4.473690	0.750979	-0.279345	-0.357823
H	0.904649	5.492340	1.122179	0.124534	0.008559
C	1.505770	3.428950	1.397819	-0.352018	0.204603
H	2.112190	3.633670	2.277809	0.148908	0.002107
C	1.426710	2.124370	0.924249	-0.193677	-0.304479
H	1.998130	1.354840	1.433069	0.107486	0.040254
Si	-1.920230	-0.065070	-0.376431	0.483020	1.742418
C	-3.807070	-0.455570	-0.138251	-1.083366	-0.402528
C	-4.651780	0.432000	0.546789	0.010737	-0.073540
H	-4.229490	1.340110	0.976959	0.156859	0.028181
C	-6.016160	0.185519	0.698919	0.090804	-0.021378
H	-6.641790	0.893569	1.237519	0.134512	0.003332
C	-6.578570	-0.974351	0.163769	-0.137230	-0.085290
H	-7.640570	-1.173731	0.281709	0.135052	0.013867
C	-5.763500	-1.876961	-0.517321	-0.067042	-0.018993
H	-6.189440	-2.787401	-0.932641	0.137696	0.001348
C	-4.399190	-1.614020	-0.660211	0.139253	-0.076043
H	-3.775270	-2.334580	-1.188131	0.144102	0.030431
H	-1.610400	0.471600	0.974969	-0.084383	-0.338528
H	-2.014730	0.947020	-1.465831	0.115734	-0.405916
H	-1.453440	-1.421380	-0.781681	-0.081584	-0.359666

I4

Electronic energy: -1208.542695

Electronic energy + zero-point energy: -1208.081136

Electronic energy + thermal energy correction: -1208.044511

Electronic energy + thermal enthalpy correction: -1208.043329

Electronic energy + thermal free energy correction: -1208.153365

Table S25. Cartesian coordinates, Mulliken and APT charges of all atoms at **I4** in the reaction of 1,1-diphenylethene with phenylsilane.

Symbol	X	Y	Z	Mulliken	APT
H	1.430879	-3.559900	2.831466	0.164770	0.024815
C	0.873445	-2.755226	2.359223	-0.005394	-0.092490
C	0.896069	-1.471675	2.893852	-0.344393	0.004397
C	0.140020	-2.992346	1.194014	-0.114020	0.003389
H	1.476238	-1.261902	3.789097	0.144363	0.023551
H	0.128511	-3.983431	0.747600	0.163770	0.025482
C	0.195381	-0.432177	2.276512	0.154202	-0.118006
C	-0.554395	-1.956597	0.582695	-0.227142	-0.122390
C	-0.543190	-0.651919	1.109178	-0.218208	0.098093
H	0.264098	0.565823	2.696000	0.165597	0.072574
H	-1.096385	-2.146791	-0.342094	0.165085	0.050590
C	-1.197906	0.482718	0.339275	-1.411300	-0.345356
C	-1.335855	1.766016	1.182573	-0.274126	-0.017570
H	-0.370970	2.144495	1.518233	0.117858	0.044441
H	-1.976164	1.572961	2.055441	0.165094	-0.048022
H	2.720807	2.627407	-1.773974	0.140074	-0.050227
H	3.781007	1.840032	-0.600633	0.171008	-0.063545
B	1.870306	2.729394	0.355919	1.671634	0.909554
H	0.502754	4.162288	-0.822523	0.142118	-0.046384
C	3.085860	2.681543	-0.735263	-0.715468	-0.200481
H	1.595756	2.631082	2.650018	0.123325	-0.073356
H	3.099629	3.395576	2.140147	0.138626	-0.105617
C	0.985958	4.094542	0.165036	-0.803251	-0.207405
C	2.403163	2.574379	1.900300	-0.701173	-0.200761
H	0.197239	4.236165	0.920121	0.125346	-0.073436
H	3.686738	3.603869	-0.662922	0.124642	-0.105292
H	1.650538	4.971244	0.244917	0.122335	-0.098097
H	2.951270	1.637436	2.092563	0.178164	-0.068273
H	-1.803524	2.557675	0.588289	0.139239	-0.000401
C	-2.617375	0.145321	-0.118814	0.706958	0.153239
C	-3.205288	0.862153	-1.171522	-0.139105	-0.110067
H	-2.608610	1.592973	-1.713695	0.134431	0.053526
C	-4.532748	0.661514	-1.538242	-0.210136	0.000283
H	-4.953414	1.231160	-2.363118	0.151046	0.017737
C	-5.318070	-0.268595	-0.856493	-0.141140	-0.103748
H	-6.353268	-0.432594	-1.144329	0.135061	0.018962
C	-4.756807	-0.979692	0.200959	-0.030188	0.000329

H	-5.355478	-1.701293	0.751829	0.145394	0.014095
C	-3.426166	-0.770203	0.566073	-0.076094	-0.140808
H	-3.009438	-1.328890	1.399644	0.167261	0.054270
Si	0.006948	0.723052	-1.210707	1.298937	1.801015
C	1.532917	-0.415371	-1.307055	-0.270880	-0.421432
C	1.640683	-1.267116	-2.416366	0.159900	-0.048244
H	0.889613	-1.213348	-3.202309	0.134961	0.034478
C	2.676607	-2.195982	-2.531531	-0.083334	-0.050315
H	2.738208	-2.835888	-3.409133	0.147590	0.005429
C	3.619627	-2.311284	-1.512342	-0.265110	-0.021455
H	4.421488	-3.042549	-1.586812	0.143636	0.012646
C	3.524240	-1.482421	-0.394095	-0.360450	-0.057835
H	4.251093	-1.565917	0.410530	0.174824	0.017306
C	2.501127	-0.541062	-0.300757	-0.365359	-0.058929
H	2.448358	0.107132	0.568833	0.089809	0.086210
H	-0.813334	-0.027833	-2.243955	0.034942	-0.450786
H	0.028027	2.079895	-1.817760	-0.141135	-0.360181
H	1.105750	1.714322	0.125575	-2.044594	-0.665500

P

Electronic energy: -1208.543563

Electronic energy + zero-point energy: -1208.082561

Electronic energy + thermal energy correction: -1208.045259

Electronic energy + thermal enthalpy correction: -1208.044077

Electronic energy + thermal free energy correction: -1208.157366

Table S26. Cartesian coordinates, Mulliken and APT charges of all atoms at **P** in the reaction of 1,1-diphenylethene with phenylsilane.

Symbol	X	Y	Z	Mulliken	APT
H	1.527615	-1.929281	3.828714	0.164674	0.024257
C	0.957375	-1.384782	3.080576	0.049299	-0.076677
C	1.151651	-0.019285	2.902586	-0.359735	-0.005559
C	0.038882	-2.053928	2.268344	-0.153184	-0.023481
H	1.885853	0.514233	3.500034	0.127148	0.036827
H	-0.110216	-3.125430	2.375007	0.162234	0.022170
C	0.434639	0.680479	1.928273	0.184405	-0.092591
C	-0.663603	-1.356275	1.294128	-0.327857	-0.095699

C	-0.483359	0.024900	1.103627	-0.179104	0.049644
H	0.646499	1.734116	1.781770	0.120618	0.083879
H	-1.349955	-1.896492	0.643731	0.153698	0.041015
C	-1.173261	0.725490	-0.061171	-1.767040	-0.291532
C	-1.073841	2.267951	0.027450	-0.204840	-0.028670
H	-0.039286	2.613566	-0.026032	0.144942	0.068355
H	-1.528694	2.617767	0.964347	0.185511	-0.034333
H	3.068901	2.365010	-2.559867	0.124288	-0.077353
H	3.991373	1.128622	-1.695793	0.163023	-0.082673
B	2.700118	2.434235	-0.287940	1.417923	0.754615
H	1.562384	4.256029	-1.136403	0.125541	-0.072312
C	3.617209	2.163862	-1.624639	-0.775882	-0.160760
H	2.995385	2.338346	2.007979	0.171045	-0.088211
H	4.479856	2.685688	1.119203	0.114966	-0.106485
C	2.168460	3.991647	-0.253160	-0.845225	-0.163588
C	3.548690	2.093650	1.084653	-0.847262	-0.158111
H	1.554701	4.225536	0.634921	0.126632	-0.080580
H	4.506870	2.818101	-1.635024	0.129722	-0.116104
H	3.017327	4.697131	-0.233361	0.132662	-0.103896
H	3.853201	1.035601	1.175005	0.214050	-0.088124
H	-1.624478	2.725888	-0.800946	0.131010	-0.010139
C	-2.671697	0.410139	-0.132810	0.586015	0.149961
C	-3.397274	0.659345	-1.307713	-0.115649	-0.117272
H	-2.872855	0.998122	-2.197797	0.103614	0.046849
C	-4.778123	0.491320	-1.365768	-0.142076	-0.001291
H	-5.303193	0.689508	-2.296763	0.150487	0.018914
C	-5.483307	0.071918	-0.238383	-0.090582	-0.100155
H	-6.560537	-0.065235	-0.280460	0.139878	0.021609
C	-4.785330	-0.158999	0.944166	-0.045256	0.009079
H	-5.317412	-0.471259	1.839450	0.149715	0.016938
C	-3.401935	0.013171	0.995777	-0.103195	-0.142712
H	-2.881130	-0.162108	1.932201	0.171983	0.063159
Si	-0.199646	0.140277	-1.658785	1.970956	1.536842
C	1.048212	-1.237533	-1.333853	-0.509156	-0.400113
C	0.754001	-2.516262	-1.832863	0.158678	-0.044301
H	-0.140440	-2.665990	-2.435211	0.123466	0.029215
C	1.577247	-3.610847	-1.563115	0.032375	-0.062260
H	1.324758	-4.591614	-1.959659	0.152074	0.012568
C	2.717666	-3.442205	-0.780550	-0.124872	-0.007313
H	3.360265	-4.291876	-0.561179	0.149651	0.016368
C	3.029710	-2.177256	-0.281500	-0.455384	-0.063014
H	3.916561	-2.032802	0.330500	0.160322	0.031988
C	2.206898	-1.086413	-0.553978	-0.320080	-0.063438
H	2.458469	-0.108094	-0.154243	-0.173818	0.139562
H	-1.186652	-0.533438	-2.556956	-0.128819	-0.375035

H	0.320718	1.313438	-2.394141	-0.215996	-0.338503
H	1.705101	1.681349	-0.346788	-1.307591	-0.501529

Propene + phenylsilane

S

Electronic energy: -263.047136

Electronic energy + zero-point energy: -262.844572

Electronic energy + thermal energy correction: -262.826913

Electronic energy + thermal enthalpy correction: -262.825732

Electronic energy + thermal free energy correction: -262.896716

Table S27. Cartesian coordinates, Mulliken and APT charges of all atoms at **S** in the reaction of propene with phenylsilane.

Symbol	X	Y	Z	Mulliken	APT
C	3.298136	0.257545	-0.012130	-0.864354	-0.135437
C	1.075300	-0.437193	-1.353807	-0.874617	-0.136488
H	1.543746	-0.048585	-2.274190	0.131596	-0.103030
H	1.299892	-1.519836	-1.322292	0.126085	-0.095257
H	-0.013577	-0.348992	-1.507106	0.191347	-0.098945
C	1.086968	-0.384174	1.374976	-0.872173	-0.137457
B	1.650024	0.329962	-0.006162	0.722466	0.723711
H	-0.000452	-0.288690	1.534273	0.189257	-0.098136
H	1.563893	0.038674	2.275725	0.132082	-0.101927
H	1.310176	-1.467450	1.382673	0.126409	-0.092680
H	1.295900	1.526890	-0.028175	-0.339803	-0.439837
H	3.749136	0.760391	0.860102	0.121712	-0.097416
H	3.653362	-0.789533	0.009940	0.124211	-0.097068
H	3.740298	0.720155	-0.910763	0.121777	-0.098028
C	-2.521125	-1.111145	0.021508	-0.624183	0.034165
C	-2.895219	0.344041	-0.009560	0.064740	0.055603
H	-2.940705	-1.604927	0.907700	0.153482	-0.026817
H	-1.435053	-1.234000	0.038954	0.192127	0.019552
H	-2.914473	-1.636036	-0.858840	0.153946	-0.025967
C	-2.017345	1.348776	-0.021061	-0.331489	-0.166780

H	-3.964551	0.569482	-0.023592	0.131188	-0.020120
H	-0.939445	1.183445	-0.009172	0.073795	0.126235
H	-2.358561	2.382107	-0.043993	0.150400	0.012125

TS1

Electronic energy: -262.956710

Electronic energy + zero-point energy: -262.755010

Electronic energy + thermal energy correction: -262.738661

Electronic energy + thermal enthalpy correction: -262.737479

Electronic energy + thermal free energy correction: -262.801994

Table S28. Cartesian coordinates, Mulliken and APT charges of all atoms at **TS1** in the reaction of propene with phenylsilane.

Symbol	X	Y	Z	Mulliken	APT
C	-1.496008	1.510825	-0.083087	-0.818035	-0.230366
C	-0.943564	-0.585968	1.534119	-0.889072	-0.198971
H	-0.361489	-0.006810	2.268744	0.163908	-0.037771
H	-1.993159	-0.549425	1.868228	0.120182	-0.062393
H	-0.621740	-1.635031	1.613397	0.133361	-0.061730
C	-1.406063	-0.950961	-1.133885	-0.860879	-0.184544
B	-0.830061	0.024039	0.030864	1.109489	0.752494
H	-0.948456	-1.950374	-1.159781	0.120354	-0.052860
H	-1.300857	-0.514102	-2.138774	0.128254	-0.057903
H	-2.485354	-1.105340	-0.969493	0.128684	-0.079895
H	0.494284	0.890485	0.184526	0.359590	0.505658
H	-1.313833	1.979675	-1.062434	0.132641	-0.050207
H	-2.587003	1.409988	0.033715	0.139243	-0.066228
H	-1.145106	2.222264	0.676811	0.140132	-0.025280
C	1.632958	-1.250180	-0.003402	-0.567999	0.085090
C	1.095275	0.098717	-0.442206	-0.202152	-0.204792
H	0.989854	-2.101105	-0.260502	0.103547	-0.052369
H	1.775200	-1.250832	1.083241	0.189494	-0.019157
H	2.622879	-1.389392	-0.461996	0.152276	-0.064013
C	1.951359	1.322492	0.050194	-1.131164	-0.689707
H	0.920589	0.189819	-1.516208	0.161308	-0.051587
H	2.567694	1.036077	0.907261	0.112203	-0.062020

TS1 – anti-Markovnikov

Electronic energy: -262.952696

Electronic energy + zero-point energy: -262.750979

Electronic energy + thermal energy correction: -262.735051

Electronic energy + thermal enthalpy correction: -262.733870

Electronic energy + thermal free energy correction: -262.797299

Table S29. Cartesian coordinates, Mulliken and APT charges of all atoms at hypothetical **anti-Markovnikov TS1** in the reaction of propene with phenylsilane.

Symbol	X	Y	Z	Mulliken	APT
C	-1.470778	-1.332463	-0.848078	-0.791980	-0.195117
C	-1.859859	1.337901	-0.513024	-0.804526	-0.174809
H	-1.648892	1.546624	-1.572674	0.153639	-0.052659
H	-2.952478	1.224702	-0.420219	0.127570	-0.077825
H	-1.582408	2.234564	0.061658	0.123767	-0.057534
C	-1.366878	-0.219877	1.627658	-0.811819	-0.228942
B	-1.128680	-0.005802	0.026309	0.746919	0.780663
H	-1.045650	0.651351	2.218940	0.128006	-0.058451
H	-0.856655	-1.098680	2.046481	0.149031	-0.023173
H	-2.445689	-0.352628	1.807049	0.139093	-0.063461
H	0.373835	-0.375393	0.393649	0.598303	0.546187
H	-0.876314	-2.206834	-0.542122	0.168465	-0.040877
H	-2.530674	-1.608665	-0.725848	0.122232	-0.065595
H	-1.300036	-1.182086	-1.925650	0.144389	-0.062367
C	3.203986	0.204448	0.095576	-0.843114	0.358422
C	1.873722	-0.513793	0.056058	-0.488691	-0.686582
H	4.029051	-0.485385	0.325495	0.135896	-0.094265
H	3.224188	0.980303	0.875331	0.114041	-0.071481
H	3.472625	0.726574	-0.858317	0.079749	-0.260737
C	0.713551	0.425744	-0.389025	-0.518558	-0.213634
H	1.891341	-1.371942	-0.626401	0.063964	-0.080082
H	0.802401	1.395046	0.108355	0.204294	-0.020885
H	0.526298	0.539691	-1.472264	0.059331	-0.156796

I2

Electronic energy: -263.090078

Electronic energy + zero-point energy: -262.886085

Electronic energy + thermal energy correction: -262.871276

Electronic energy + thermal enthalpy correction: -262.870094

Electronic energy + thermal free energy correction: -262.930940

Table S30. Cartesian coordinates, Mulliken and APT charges of all atoms at **I2** in the reaction of propene with phenylsilane.

Symbol	X	Y	Z	Mulliken	APT
C	-0.335820	-1.522820	1.340878	-0.912724	-0.149584
C	1.769013	-0.513605	0.000000	-0.865607	-0.158022
H	2.158737	0.016844	0.886098	0.134324	-0.091150
H	2.249641	-1.507430	0.000000	0.129053	-0.088643
H	2.158737	0.016844	-0.886098	0.134324	-0.091150
C	-0.335820	-1.522820	-1.340878	-0.912724	-0.149584
B	0.121862	-0.668044	0.000000	1.160520	0.713691
H	0.040349	-1.093986	-2.285457	0.131426	-0.086747
H	-1.434381	-1.593481	-1.439520	0.136763	-0.095849
H	0.042935	-2.558762	-1.299867	0.119720	-0.096183
H	0.739023	1.882836	1.306386	0.159920	-0.044145
H	-1.434381	-1.593481	1.439520	0.136763	-0.095849
H	0.042935	-2.558762	1.299867	0.119720	-0.096183
H	0.040349	-1.093986	2.285457	0.131426	-0.086747
C	-0.335820	1.657280	-1.244958	-0.615511	0.124089
C	-0.637134	0.815222	0.000000	-0.312730	-0.120839
H	-0.608766	1.126605	-2.165344	0.154695	-0.046348
H	0.739023	1.882836	-1.306386	0.159920	-0.044145
H	-0.869668	2.623986	-1.244490	0.107018	-0.120061
C	-0.335820	1.657280	1.244958	-0.615511	0.124089
H	-1.726998	0.616343	0.000000	0.057497	-0.134231
H	-0.869668	2.623986	1.244490	0.107018	-0.120061
H	-0.608766	1.126605	2.165344	0.154695	-0.046348

I2 (with phenylsilane)

Electronic energy: -785.897130

Electronic energy + zero-point energy: -785.573065

Electronic energy + thermal energy correction: -785.546285

Electronic energy + thermal enthalpy correction: -785.545103

Electronic energy + thermal free energy correction: -785.635932

Table S31. Cartesian coordinates, Mulliken and APT charges of all atoms at **I2** in the reaction of propene with phenylsilane.

Symbol	X	Y	Z	Mulliken	APT
C	2.125480	-0.198731	-1.747611	-0.292616	0.206313
C	2.479469	-0.469011	-0.282571	-1.251964	-1.080600
C	2.574709	-1.981911	-0.065091	-0.307563	0.204986
H	1.642720	-0.098001	0.343059	0.567639	0.161900
H	1.234589	-0.757991	-2.083561	0.139746	-0.072967
H	4.366291	2.592618	0.457759	0.126404	-0.066221
H	2.616351	2.346589	0.369859	0.162430	-0.037551
B	3.815640	0.375878	0.252629	0.929083	1.079489
H	5.144920	-0.013233	-1.610111	0.134942	-0.045625
C	3.582621	1.988488	-0.028011	-0.821900	-0.257070
H	4.793950	0.779397	2.286249	0.123976	-0.072926
H	4.236449	-0.888932	2.156139	0.146308	-0.041500
C	5.192200	-0.120793	-0.513621	-0.848894	-0.264633
C	3.986050	0.148458	1.880749	-0.821951	-0.249038
H	6.056160	0.478117	-0.181601	0.117024	-0.084079
H	3.603741	2.254398	-1.097521	0.154766	-0.035457
H	5.446769	-1.173153	-0.306061	0.150963	-0.026720
H	3.069650	0.414088	2.436119	0.154545	-0.032274
H	2.762238	-2.225741	0.986879	0.179868	-0.021932
H	3.408088	-2.396222	-0.649561	0.114742	-0.093958
H	1.662038	-2.516841	-0.379411	0.134849	-0.058399
H	1.939520	0.866209	-1.927981	0.166943	-0.012910
H	2.957699	-0.498892	-2.399221	0.150047	-0.077875

TS2

Electronic energy: -785.844510

Electronic energy + zero-point energy: -785.521614

Electronic energy + thermal energy correction: -785.494344

Electronic energy + thermal enthalpy correction: -785.493162

Electronic energy + thermal free energy correction: -785.585536

Table S32. Cartesian coordinates, Mulliken and APT charges of all atoms at **TS2** in the reaction of propene with phenylsilane.

Symbol	X	Y	Z	Mulliken	APT
C	1.941951	-0.812230	-1.738661	-0.612078	0.101653
C	1.751751	-0.607600	-0.257421	-0.706421	-0.133719
C	1.946781	-1.821090	0.611189	-0.590774	0.109075
H	1.757991	0.391170	0.170929	0.300563	-0.179189
H	1.129781	-1.439670	-2.147311	0.150543	-0.111264
H	4.083620	2.676550	-0.157081	0.122278	-0.095288
H	2.355340	2.582130	0.189519	0.147830	-0.091428
B	3.472961	0.574610	0.257409	1.053536	0.740618
H	4.696051	-0.038400	-1.573491	0.128052	-0.080670
C	3.182220	2.064250	-0.316061	-0.849102	-0.149556
H	4.329731	1.178560	2.217869	0.124153	-0.101981
H	3.770421	-0.494820	2.259629	0.136126	-0.087761
C	4.686381	-0.178680	-0.485341	-0.806659	-0.170606
C	3.531051	0.503590	1.871949	-0.825870	-0.153459
H	5.624461	0.253151	-0.101101	0.127374	-0.098418
H	2.975110	2.084320	-1.393831	0.137208	-0.090603
H	4.734191	-1.256710	-0.282351	0.129682	-0.083950
H	2.603891	0.836730	2.358489	0.144474	-0.095331
H	1.668771	-1.621010	1.652349	0.147259	-0.038507
H	2.978171	-2.209500	0.610939	0.157322	-0.053634
H	1.296111	-2.635670	0.252759	0.109501	-0.106760
H	1.923701	0.136590	-2.285731	0.151784	-0.032490
H	2.886041	-1.320290	-1.984581	0.141370	-0.041759
H	-4.884020	2.401768	-0.230861	0.150268	0.022200
C	-4.440330	1.416398	-0.102681	-0.220805	-0.046829
H	-2.434400	2.127209	-0.386641	0.151783	0.034248
H	-6.337219	0.430228	0.203279	0.151389	0.028676
C	-3.055989	1.253399	-0.185791	0.078026	-0.054228
C	-5.258229	0.312188	0.139739	-0.105595	-0.041255
C	-2.437199	0.003679	-0.030551	-0.762093	-0.365056
C	-4.674869	-0.946112	0.292879	-0.176580	-0.045991
H	-0.557999	-1.643441	-0.563581	-0.031675	-0.298111
Si	-0.471399	-0.215231	-0.090201	0.295794	1.441634
C	-3.288469	-1.086061	0.204759	0.174114	-0.054273
H	-0.259909	0.944289	-1.025611	-0.006419	-0.297491
H	-5.302439	-1.816062	0.476709	0.147468	0.021335
H	-2.851359	-2.079531	0.315509	0.157041	0.033642
H	-0.261549	0.042209	1.375869	-0.020868	-0.333477

I3

Electronic energy: -785.857314

Electronic energy + zero-point energy: -785.537177

Electronic energy + thermal energy correction: -785.511015

Electronic energy + thermal enthalpy correction: -785.509834

Electronic energy + thermal free energy correction: -785.600220

Table S33. Cartesian coordinates, Mulliken and APT charges of all atoms at **I3** in the reaction of propene with phenylsilane.

Symbol	X	Y	Z	Mulliken	APT
C	1.792320	-1.509581	-1.630440	-0.386223	0.110180
C	1.449670	-0.960141	-0.253430	-1.206348	-0.418211
C	1.857190	-1.927231	0.846690	-0.403104	0.113480
H	1.950580	0.013629	-0.109350	0.405210	-0.191251
H	1.189610	-2.408821	-1.831520	0.163800	-0.042788
H	4.068739	2.969999	-0.660390	0.151230	-0.015041
H	2.452559	2.754729	0.038770	0.183820	-0.006582
B	3.857240	0.995449	0.257670	0.846000	1.018406
H	4.807550	0.092099	-1.590190	0.164304	-0.018627
C	3.254359	2.244469	-0.503640	-0.763472	-0.319853
H	4.247130	1.710979	2.295380	0.145711	-0.009962
H	4.069130	-0.055491	2.251380	0.155535	-0.017060
C	4.833800	0.009519	-0.498930	-0.821678	-0.313100
C	3.694270	0.881709	1.827150	-0.809311	-0.312259
H	5.862160	0.220149	-0.166120	0.141164	-0.009132
H	2.883170	1.975359	-1.498540	0.185576	0.012849
H	4.632150	-1.032031	-0.222150	0.217885	0.025055
H	2.646620	1.004119	2.125420	0.201494	0.015417
H	1.661050	-1.507391	1.841760	0.164495	-0.030690
H	2.920540	-2.221961	0.809920	0.121446	-0.115471
H	1.265660	-2.851551	0.762210	0.145788	-0.040260
H	1.559760	-0.780831	-2.418070	0.154894	-0.033010
H	2.850710	-1.799521	-1.740790	0.118173	-0.106620
H	-4.652801	2.557708	-0.605220	0.124217	-0.016156
C	-4.314470	1.564088	-0.314930	-0.028826	0.002621
H	-2.258780	1.961738	-0.801760	0.119423	0.004517
H	-6.289930	0.883398	0.239360	0.131172	0.005856
C	-2.964560	1.221008	-0.419540	-0.049220	-0.080658

C	-5.236040	0.627398	0.157130	-0.153115	-0.124659
C	-2.477370	-0.044152	-0.060240	-0.926451	-0.496190
C	-4.786880	-0.645242	0.513870	-0.012670	0.002671
H	-0.858230	-1.967822	-0.267860	-0.206892	-0.462854
Si	-0.505140	-0.479712	-0.121560	0.657496	1.865981
C	-3.431160	-0.963292	0.399890	0.025123	-0.077028
H	-0.335990	0.527628	-1.262410	-0.183434	-0.449959
H	-5.496530	-1.387402	0.876850	0.121122	-0.017736
H	-3.098150	-1.966752	0.673840	0.126901	0.010607
H	-0.317690	0.055448	1.291540	-0.021235	-0.462485

I4

Electronic energy: -785.904885

Electronic energy + zero-point energy: -785.579883

Electronic energy + thermal energy correction: -785.554188

Electronic energy + thermal enthalpy correction: -785.553007

Electronic energy + thermal free energy correction: -785.640100

Table S34. Cartesian coordinates, Mulliken and APT charges of all atoms at **I4** in the reaction of propene with phenylsilane.

Symbol	X	Y	Z	Mulliken	APT
C	-1.262739	3.416361	0.080149	-0.660517	0.105385
C	-1.081640	1.905951	0.269429	-0.521561	-0.262446
C	-0.561830	1.583390	1.673349	-0.320207	0.059601
H	-2.049610	1.406071	0.149059	0.140267	-0.013832
H	-0.309169	3.947130	0.196459	0.167175	-0.038962
H	-4.213632	-1.439368	-1.200571	0.140270	-0.100474
H	-2.814811	-1.094318	-2.226321	0.115892	-0.080351
B	-2.268642	-1.378459	-0.005041	1.704976	0.788474
H	-3.216141	-0.023878	1.616559	0.149287	-0.082717
C	-3.251141	-0.900908	-1.233501	-0.827206	-0.163607
H	-2.784193	-3.605938	-0.106031	0.133138	-0.107790
H	-1.207743	-3.325089	0.640419	0.139271	-0.081948
C	-2.969001	-1.086818	1.455279	-0.787374	-0.164532
C	-1.883043	-2.971759	-0.156711	-0.876684	-0.167563
H	-3.916432	-1.643588	1.555569	0.137418	-0.111334
H	-3.498341	0.173992	-1.202511	0.134384	-0.085918

H	-2.332452	-1.393849	2.300779	0.125247	-0.085871
H	-1.394463	-3.202699	-1.118031	0.138909	-0.080527
H	-0.507481	0.501020	1.825349	0.203828	0.023740
H	-1.232060	1.999531	2.437569	0.152735	-0.065579
H	0.438560	2.007360	1.837109	0.159962	-0.036372
H	-1.654399	3.661491	-0.913851	0.157667	-0.032406
H	-1.962029	3.820881	0.824119	0.142755	-0.071896
H	4.795939	0.619867	0.353099	0.144197	0.011869
C	3.860499	0.090058	0.191489	-0.013722	-0.062274
H	2.815160	1.849139	-0.453311	0.137876	0.026903
H	4.656238	-1.827402	0.773579	0.137056	0.017290
C	2.734460	0.781039	-0.258501	0.140684	-0.041313
C	3.782458	-1.281132	0.427209	-0.081852	-0.036438
C	1.506919	0.133189	-0.469411	-1.052077	-0.404120
C	2.575438	-1.946871	0.214359	-0.060008	-0.052717
H	0.737250	2.342670	-1.703591	-0.139890	-0.409050
Si	0.035050	1.162780	-1.083201	0.916211	1.606352
C	1.450088	-1.248621	-0.223071	0.076400	-0.056898
H	-0.701461	0.507840	-2.187701	-0.003302	-0.344702
H	2.503057	-3.015911	0.396109	0.160150	0.019067
H	0.508448	-1.773440	-0.359101	0.116639	0.106440
H	-1.210541	-0.721409	-0.065191	-1.527997	-0.523484

P

Electronic energy: -785.907722

Electronic energy + zero-point energy: -785.581364

Electronic energy + thermal energy correction: -785.553777

Electronic energy + thermal enthalpy correction: -785.552596

Electronic energy + thermal free energy correction: -785.646516

Table S35. Cartesian coordinates, Mulliken and APT charges of all atoms at **P** in the reaction of propene with phenylsilane.

Symbol	X	Y	Z	Mulliken	APT
C	-1.623473	3.179318	-0.043250	-0.523711	0.101641
C	-0.746052	2.002709	0.398300	-0.689166	-0.322673
C	-0.244042	2.187959	1.834500	-0.399808	0.083065
H	-1.349671	1.085058	0.367860	0.218236	0.064023

H	-1.060244	4.122778	-0.042920	0.160475	-0.042412
H	-2.775659	-1.170293	-2.191600	0.116871	-0.101044
H	-1.193939	-0.613472	-1.659460	0.196359	-0.101373
B	-2.558099	-1.389733	0.066950	0.365473	0.703938
H	-4.550840	-0.304685	0.474380	0.146870	-0.090477
C	-2.260579	-0.637933	-1.374140	-0.892284	-0.142314
H	-2.597527	-3.514253	-0.781040	0.132780	-0.101866
H	-2.189827	-3.494273	0.940220	0.134365	-0.096541
C	-4.169049	-1.335705	0.398250	-0.816572	-0.131253
C	-2.041867	-2.954553	-0.008810	-0.846890	-0.134268
H	-4.757468	-1.832345	-0.393080	0.127562	-0.104021
H	-2.623220	0.403677	-1.411010	0.214326	-0.089753
H	-4.422488	-1.840005	1.344260	0.123876	-0.097286
H	-0.974727	-3.053252	-0.270440	0.172322	-0.096305
H	0.336039	1.321950	2.170230	0.167743	-0.007532
H	-1.090822	2.303438	2.522430	0.162853	-0.050891
H	0.389147	3.081030	1.927530	0.166574	-0.036646
H	-2.028323	3.024197	-1.048820	0.134968	-0.011191
H	-2.473283	3.300987	0.640040	0.167221	-0.059200
H	4.959391	-0.841536	-0.164300	0.145804	0.011848
C	3.876891	-0.867887	-0.068310	-0.108520	-0.071127
H	3.622329	1.136193	-0.794740	0.133192	0.019951
H	3.831273	-2.882737	0.696040	0.141083	0.019512
C	3.116490	0.245442	-0.425700	0.080665	-0.033066
C	3.243462	-2.012398	0.415990	-0.158433	-0.019000
C	1.718290	0.237961	-0.313020	-0.474025	-0.392268
C	1.854982	-2.035739	0.540460	-0.189380	-0.058354
H	1.601967	2.921901	-0.749110	-0.064540	-0.371020
Si	0.685439	1.737780	-0.794950	0.988564	1.461892
C	1.096541	-0.920790	0.181190	-0.199097	-0.069788
H	0.200649	1.631209	-2.196000	-0.099082	-0.363579
H	1.348603	-2.921390	0.914040	0.182580	0.037206
H	0.012671	-0.964501	0.295260	-0.049788	0.141038
H	-1.949249	-0.810233	0.991990	-0.069468	-0.448867

Dissociation of $NaHBEt_3$ and addition of NaH to styrene

As it was not possible to compute dissociation energy of $NaHBEt_3$ using the same protocol as for other reactions (this molecular system only features one potential energy hypersurface minimum corresponding to NaHBEt3 complex), free energy change of this reaction ΔG was calculated using a different protocol:

$$\Delta G = \Delta G_{NaHBEt_3} - \Delta G_{NaH} - \Delta G_{BEt_3} + E_{BSSE}$$

Where ΔG_{NaHBEt_3}, ΔG_{NaH} and ΔG_{BEt_3} are Gibbs free energies calculated for individual reagents and E_{BSSE} is basis set superposition error as described by Boys and Bernardi (S. F. Boys and F. Bernardi, Mol. Phys., 19 (1970) 553). All other computation parameters, including functional, basis set, solvation model and temperature were the same as in the rest of the study.
Similar approach was employed to calculate activation free energy and free energy change for the addition of NaH to styrene.

NaHBEt$_3$

Electronic energy: -307.393616

Electronic energy + zero-point energy: -307.269298

Electronic energy + thermal energy correction: -307.257551

Electronic energy + thermal enthalpy correction: -307.256370

Electronic energy + thermal free energy correction: -307.310854

Electronic energy of NaH fragment in NaHBEt$_3$ basis set: -162.801139

Electronic energy of BEt$_3$ fragment in NaHBEt$_3$ basis set: -144.484965

Electronic energy of NaH fragment in NaH basis set: -162.800168

Electronic energy of BEt$_3$ fragment in BEt$_3$ basis set: -144.484655

Table S36. Cartesian coordinates, Mulliken and APT charges of all atoms at **NaHBEt$_3$**.

Symbol	X	Y	Z	Mulliken	APT
Na	-1.913548	-0.000179	-0.481753	0.668252	0.787259
H	2.582000	-0.000202	0.481034	0.132040	-0.048813
H	0.560497	-1.393140	1.541381	0.163687	-0.024803
C	2.038621	-0.000267	-0.475733	-0.749740	-0.160555
H	0.560358	1.393924	1.541108	0.163666	-0.024848
H	2.376944	-0.883129	-1.033913	0.152491	-0.049389
C	-0.007371	-1.366351	0.601846	-0.632129	-0.148150
H	2.377453	0.882143	-1.034316	0.152507	-0.049379

B	0.437309	0.000127	-0.233251	0.157416	0.629738
C	-0.007211	1.366775	0.601399	-0.632033	-0.148041
H	0.244272	-2.284458	0.055694	0.170748	-0.041502
H	-1.060788	-1.498927	0.937766	0.057756	-0.139631
H	0.244463	2.284772	0.055071	0.170749	-0.041510
H	-1.060748	1.499364	0.936950	0.057751	-0.139652
H	-0.106204	0.000050	-1.380308	-0.033161	-0.400724

NaH

Electronic energy: -144.531111

Electronic energy + zero-point energy: -144.418178

Electronic energy + thermal energy correction: -144.410190

Electronic energy + thermal enthalpy correction: -144.409008

Electronic energy + thermal free energy correction: -144.455016

Table S37. Cartesian coordinates, Mulliken and APT charges of all atoms at **NaH**.

Symbol	X	Y	Z	Mulliken	APT
B	2.632584	0.546426	-0.005786	0.616620	0.884320
C	1.817826	1.895195	0.000989	-0.731687	-0.309523
H	2.271966	2.647933	0.655852	0.175063	0.007416
H	1.879118	2.316962	-1.013905	0.184349	0.019375
H	0.757574	1.792558	0.250031	0.166183	-0.014664
C	1.864448	-0.829086	0.043705	-0.732082	-0.308145
H	2.489744	-1.716983	-0.085667	0.164497	-0.018949
H	1.357583	-0.908633	1.016117	0.182478	0.018583
H	1.058802	-0.851480	-0.701129	0.178027	0.012771
C	4.207256	0.574335	-0.051982	-0.728865	-0.307131
H	4.580115	0.187157	0.907999	0.182723	0.021786
H	4.598364	-0.113669	-0.811134	0.176589	0.009154
H	4.647411	1.563937	-0.205091	0.166105	-0.014991

BEt_3

Electronic energy: -162.828589

Electronic energy + zero-point energy: -162.826226

Electronic energy + thermal energy correction: -162.823184

Electronic energy + thermal enthalpy correction: -162.822002

Electronic energy + thermal free energy correction: -162.849838

Table S38. Cartesian coordinates, Mulliken and APT charges of all atoms at **BEt_3**.

Symbol	X	Y	Z	Mulliken	APT
Na	-0.701776	3.627907	0.000000	0.731737	0.815975
H	-2.672643	3.627907	0.000000	-0.731737	-0.815975

Styrene

Electronic energy: -309.521892

Electronic energy + zero-point energy: -309.387645

Electronic energy + thermal energy correction: -309.377329

Electronic energy + thermal enthalpy correction: -309.376148

Electronic energy + thermal free energy correction: -309.430291

Table S39. Cartesian coordinates, Mulliken and APT charges of all atoms at **styrene**.

Symbol	X	Y	Z	Mulliken	APT
C	-0.984006	-1.196003	0.054260	-0.849686	-0.082906
C	-2.320981	-1.589501	0.055152	0.326770	-0.018802
C	-3.329262	-0.630753	-0.012401	-0.504735	-0.071712
C	-2.989101	0.721859	-0.084107	0.390014	-0.040398
C	-1.654229	1.111731	-0.084851	-1.397639	-0.082747
C	-0.628963	0.157455	-0.008103	1.218970	0.046837
H	-0.199922	-1.947223	0.107025	0.116839	0.044245
H	-2.573067	-2.644180	0.107357	0.164381	0.040364
H	-4.372001	-0.932180	-0.014340	0.145855	0.045563
H	-3.768889	1.474793	-0.146025	0.174579	0.038583
H	-1.408159	2.166920	-0.155375	0.054118	0.048304
C	0.801573	0.521981	0.004970	0.013082	0.122730
C	1.310138	1.751293	0.129518	-0.273426	-0.210232
H	1.488762	-0.318262	-0.087191	0.122552	0.018786
H	2.383106	1.909368	0.126994	0.161260	0.047252
H	0.685736	2.632470	0.244580	0.137065	0.054134

Addition of NaH to styrene – transition state

Electronic energy: -472.345798

Electronic energy + zero-point energy: -472.207861

Electronic energy + thermal energy correction: -472.194467

Electronic energy + thermal enthalpy correction: -472.193286

Electronic energy + thermal free energy correction: -472.253903

Electronic energy of NaH fragment in $CH_3CHNaPh$ basis set: -162.800762

Electronic energy of styrene fragment in $CH_3CHNaPh$ basis set: -309.514530

Electronic energy of NaH fragment in NaH basis set: -162.800032

Electronic energy of styrene fragment in styrene basis set: -309.514036

Table S40. Cartesian coordinates, Mulliken and APT charges of all atoms at **transition state of addition of NaH to styrene**.

Symbol	X	Y	Z	Mulliken	APT
C	2.194422	0.885174	0.371478	0.094343	0.141819
C	0.883282	1.332824	0.287960	-0.549262	-0.313916
C	2.537563	-0.397299	-0.071812	-0.246361	-0.220213
C	-0.140190	0.526862	-0.261915	0.093055	0.561766
C	0.222910	-0.771979	-0.688940	-0.338411	-0.174964
C	1.542941	-1.217539	-0.598230	-0.125969	0.050057
H	2.957792	1.538264	0.784785	0.156393	0.032308
H	3.562902	-0.746270	-0.007247	0.147649	0.042150
H	1.790985	-2.216489	-0.945996	0.155908	0.031439
H	-0.528091	-1.429704	-1.119443	0.118664	0.046693
H	0.630922	2.333475	0.631412	0.128365	0.035784
C	-1.514862	1.002072	-0.295612	0.558078	-0.897818
C	-2.559558	0.285522	-0.816210	-0.905899	0.889774
H	-1.723279	1.916487	0.256552	0.148532	0.006427
H	-2.402866	-0.505371	-1.538674	0.222384	-0.036359
H	-3.562168	0.695745	-0.796282	0.164977	0.017360
Na	-1.601920	-0.941367	1.497909	0.695089	0.685989

H	-3.186595	-1.260553	0.279170	-0.517536	-0.898296

$CH_3CHNaPh$

Electronic energy: -472.396303

Electronic energy + zero-point energy: -472.252349

Electronic energy + thermal energy correction: -472.238747

Electronic energy + thermal enthalpy correction: -472.237565

Electronic energy + thermal free energy correction: -472.297926

Electronic energy of NaH fragment in $CH_3CHNaPh$ basis set: -162.707032

Electronic energy of styrene fragment in $CH_3CHNaPh$ basis set: -309.385259

Electronic energy of NaH fragment in NaH basis set: -162.705211

Electronic energy of styrene fragment in styrene basis set: -309.383982

Table S41. Cartesian coordinates, Mulliken and APT charges of all atoms at **CH3CHNaPh**.

Symbol	X	Y	Z	Mulliken	APT
C	-0.469024	-1.288903	-0.579017	0.137233	-0.406090
C	-1.796159	-0.940060	-0.446307	-0.072941	0.385429
C	-2.202684	0.403580	-0.226409	-0.336174	-0.762295
C	-1.203655	1.394429	-0.356620	-0.064311	0.467158
C	0.139292	1.078749	-0.487086	-0.294733	-0.501182
C	0.601041	-0.306002	-0.424911	-0.619862	0.634054
H	-0.191983	-2.327537	-0.741509	0.122910	0.008915
H	-2.553789	-1.717687	-0.520141	0.150315	0.024725
H	-3.251155	0.668195	-0.167862	0.134959	0.042721
H	-1.495862	2.442894	-0.358629	0.156149	0.018538
H	0.869924	1.873674	-0.595838	0.116443	0.031915
C	1.901466	-0.656854	-0.135437	0.081730	-0.719637
C	3.016462	0.348726	-0.040724	-0.735447	0.261811
H	2.166122	-1.711699	-0.159755	0.102192	-0.015566
H	3.270987	0.801070	-1.012239	0.159733	-0.110998
H	2.768225	1.185712	0.628831	0.137995	-0.054431
Na	-0.493796	-0.118491	1.705458	0.669591	0.731125

H	3.928856	-0.113220	0.346169	0.154217	-0.036191

Percentage contributions of particular transitions associated with five longest electronic excitation wavelengths for the intermediates identified in the reaction of 1,1-diphenylethene with phenylsilane

Transitions whose contribution is smaller than 10% are not listed.

I1

Excitation wavelength [nm]	Oscillator strength	Orbitals involved	CI coefficient	Percentage contribution [%]
535.93	0.0044	HOMO→LUMO	0.64289	82.66
471.17	0.0074	HOMO→LUMO+1	0.37425	28.01
		HOMO→LUMO+2	0.57310	65.69
469.25	0.0045	HOMO→LUMO+1	0.56704	64.31
		HOMO→LUMO+2	-0.35062	24.59
444.69	0.5337	HOMO→LUMO+8	0.63905	81.68
428.26	0.0773	HOMO→LUMO+3	0.50209	50.42
		HOMO→LUMO+9	-0.29383	17.27
		HOMO→LUMO+10	-0.28339	16.06

I2

Excitation wavelength [nm]	Oscillator strength	Orbitals involved	CI coefficient	Percentage contribution [%]
258.73	0.0043	HOMO→LUMO	0.62932	79.21
		HOMO→LUMO+1	0.22968	10.55
251.09	0.0212	HOMO→LUMO+8	0.57735	66.67
247.00	0.1654	HOMO→LUMO+6	0.23874	11.40
		HOMO→LUMO+9	0.53161	56.52
241.75	0.0013	HOMO→LUMO+1	0.60276	72.66
240.10	0.0304	HOMO→LUMO+2	0.50130	50.26
		HOMO→LUMO+3	0.36322	26.39

I3

Excitation wavelength [nm]	Oscillator strength	Orbitals involved	CI coefficient	Percentage contribution
405.06	0.0230	HOMO→LUMO	0.62165	77.29
385.60	0.3344	HOMO→LUMO+2	0.23559	11.10
		HOMO→LUMO+10	0.25317	12.82
		HOMO→LUMO+13	0.41373	34.23
372.95	0.1043	HOMO→LUMO+1	0.37901	28.73
		HOMO→LUMO+2	0.29375	17.26
		HOMO→LUMO+3	-0.23383	10.94
368.73	0.0099	HOMO→LUMO+2	0.46513	43.27
		HOMO→LUMO+3	0.25679	13.19
		HOMO→LUMO+4	-0.27464	15.09
361.44	0.0803	HOMO→LUMO+3	0.53949	58.21

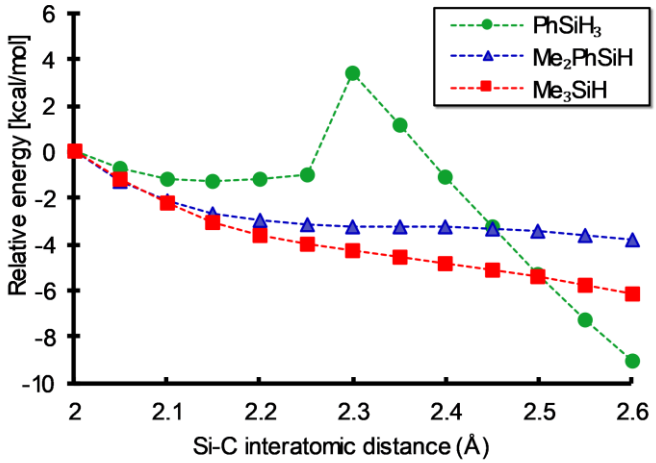

Figure S01. Relaxed potential energy hypersurface scan of Si-C interatomic distance corresponding to I2→I3 step for the reaction of styrene with different hydrosilanes.

This figure is intended to barely illustrate the fact that no extrema are present on the potential energy hypersurfaces for Me_2PHSiH and Me_3SiH that could correspond to **TS2** or **I3**. Due to the discontinuity on the curve for $PhSiH_3$, neither Si-C distances nor Gibbs energies corresponding to **TS2** and **I3** should be read from this figure (they were identified precisely and described on pages 9-11).