Supporting Information for:

Computational Studies of Ene Reactions between Aminoborane $(F_3C)_2B{=}N(CH_3)_2$ and Substituted Propenes: Additive Effects on Barriers and Reaction Energies

Austin L. Gille,[1] Staci E. Hammer,[2] Jenna M. Lafferty,[2] Keaton R. Lawson,[2] James R. Gustafson,[2]
Brendan C. Dutmer[2,*] and Thomas M. Gilbert[1,*]
[1]Department of Chemistry and Biochemistry, Northern Illinois University, DeKalb, Illinois 60115 USA
[2]Department of Chemistry, Highland Community College, Freeport, Illinois 61032 USA

Table of Contents

Table of Contents (continued)

Table of Contents (continued)

Table S1. Optimized (MPW1K/6-311++G(d,p)) Cartesian coordinates of $(CF_3)_2BNMe_2$. **1**, of propene C_3H_6, and of the transition state and product for the ene reaction between propene and **1**

$(CF_3)_2BNMe_2$. 1

C	-1.492663	-0.341263	-0.009535
B	0.009878	0.245348	-0.002145
N	0.359172	1.569229	-0.003219
C	-0.554333	2.696760	0.053330
H	-0.489727	3.270376	-0.869889
H	-1.574628	2.381662	0.200412
H	-0.264303	3.347307	0.876376
C	1.734675	2.036005	-0.055380
H	1.843047	2.735155	-0.882418
H	1.983375	2.556438	0.867747
H	2.433458	1.225995	-0.198352
C	1.155520	-0.898977	0.010119
F	0.677472	-2.132289	0.126374
F	1.890122	-0.878260	-1.112747
F	2.013808	-0.732251	1.028096
F	-2.485238	0.544546	-0.149902
F	-1.638781	-1.210868	-1.012801
F	-1.741161	-1.000147	1.126332

C_3H_6

C	-1.223964	0.161858	-0.000001
C	0.132053	-0.451842	-0.000028
C	1.270872	0.219560	0.000006
H	2.224349	-0.286121	0.000076
H	1.288911	1.300591	-0.000058
H	0.166407	-1.534982	-0.000015
H	-1.792908	-0.152913	-0.874270
H	-1.792088	-0.151342	0.875378
H	-1.168435	1.247308	-0.000974

C_3H_6 + 1 ts

C	-0.623153	-0.273405	-1.767451
C	-1.975143	0.016580	-1.562747
C	-2.823960	-0.887672	-0.898269
H	-2.111449	-0.898796	0.105395
H	-3.839136	-0.573436	-0.704579
H	-2.730299	-1.931462	-1.182047
H	-2.296412	1.045106	-1.665054
B	0.023013	-0.071903	-0.106454
N	-0.722544	-0.973365	0.835395
C	-0.403226	-2.391746	0.788650
H	-0.314044	-2.736242	-0.236091
H	0.533649	-2.614529	1.298965
H	-1.198174	-2.957502	1.272384
C	-0.958975	-0.563577	2.213481
H	-1.686224	-1.235673	2.666537
H	-0.042173	-0.606408	2.802228
H	-1.353832	0.442389	2.261367
C	1.592415	-0.466594	-0.317981
F	2.279668	0.427406	-1.034708
F	2.229033	-0.576790	0.858448
F	1.780072	-1.646744	-0.941681
C	-0.102945	1.509960	0.263748
F	-1.380144	1.880178	0.535796
F	0.612360	1.878759	1.331108
F	0.278458	2.310976	-0.738970
H	-0.386435	-1.311291	-1.972710
H	-0.057812	0.425576	-2.368402

C_3H_6 + 1 product

C	-0.939809	-0.556862	-1.447222
C	-2.253178	-1.170358	-1.071684
C	-3.338272	-0.526340	-0.660539
H	-4.243120	-1.062268	-0.416438
H	-3.367113	0.550159	-0.578851
H	-2.319221	-2.251437	-1.140284
H	-0.394236	-1.259306	-2.074147
H	-1.114276	0.319046	-2.069246
B	0.010721	-0.081968	-0.208526
N	-0.319983	-1.001082	1.082208
H	-1.338418	-0.977646	1.080694
C	0.070908	-2.410704	0.896043
H	-0.238304	-2.751430	-0.083131
H	1.148243	-2.491541	0.972409
H	-0.394574	-3.020923	1.664529
C	0.130319	-0.532112	2.408579
H	-0.187639	-1.247355	3.162161
H	1.209509	-0.452238	2.410609
H	-0.302791	0.434653	2.622785
C	1.582222	-0.219093	-0.604818
F	1.962571	0.712694	-1.479744
F	2.430433	-0.123885	0.441447
F	1.880540	-1.404504	-1.178515
C	-0.322711	1.459698	0.208057
F	-1.501751	1.545784	0.878380
F	0.579897	2.038645	1.018030
F	-0.445986	2.271524	-0.841198

Table S2. Optimized (MPW1K/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1a, 1e, 2, 3a, 3e–C_3HMe_5** and **1**

1a, 1e, 2, 3a, 3e–C_3HMe_5 product

C	0.000784	-0.001732	0.002049
C	1.337304	-0.003565	-0.010090
C	2.159968	-1.273288	-0.006192
H	1.506043	-2.108629	-0.240247
C	-0.853883	-1.232295	0.077333
C	-0.828042	1.247092	-0.059377
C	2.144636	1.264585	-0.026209
C	2.770232	-1.541878	1.365811
C	3.238567	-1.256400	-1.083755
H	-0.313462	-2.136073	0.331570
H	-1.629149	-1.093711	0.831545
H	-1.371608	-1.402498	-0.868271
H	-0.266229	2.133863	-0.326885
H	-1.323301	1.432500	0.895553
H	-1.620329	1.127193	-0.798878
H	1.609319	2.108580	0.393164
H	3.057223	1.146704	0.554744
H	2.451577	1.532770	-1.037920
H	1.998517	-1.622467	2.128161
H	3.340429	-2.469947	1.359469
H	3.449667	-0.744839	1.664517
H	3.991011	-0.493056	-0.893853
H	3.751221	-2.216174	-1.119190
H	2.811286	-1.068317	-2.066900

1a, 1e, 2, 3a, 3e–C_3HMe_5 + 1 ts

B	-0.012694	-0.014157	-0.035075
N	1.519024	-0.049586	0.009940
C	-0.591239	1.524663	-0.061264
C	-0.643413	-0.692862	1.328893
C	2.252437	1.009421	-0.680728
C	2.226143	-0.305520	1.265133
F	-1.903456	1.609815	0.186928
F	0.008895	2.274903	0.880588
F	-0.406029	2.204586	-1.210389
F	-1.972028	-0.864633	1.307410
F	-0.395038	0.034552	2.426305
F	-0.147478	-1.925513	1.610162
H	1.725869	1.369684	-1.551089
H	2.406932	1.859102	-0.015788
H	3.229137	0.638205	-0.988141
H	1.875162	-1.208488	1.743365
H	2.109886	0.526515	1.957881
H	3.286563	-0.425383	1.048987
C	-0.573267	-0.880592	-1.526003
C	-0.000593	-2.192813	-1.264612
C	1.402728	-2.435062	-1.298594
H	1.615287	-1.358570	-0.648613
C	-0.052358	-0.160436	-2.776866
C	-2.097534	-0.861205	-1.644608
C	-0.914991	-3.249371	-0.751884
C	2.262125	-2.227421	-2.544762
C	1.930666	-3.643585	-0.546920
H	-0.609027	0.755287	-2.930378
H	0.995093	0.098496	-2.753572
H	-0.220245	-0.792775	-3.648498
H	-2.444447	0.160715	-1.755939
H	-2.623167	-1.281922	-0.799526
H	-2.402645	-1.402806	-2.541663
H	-1.642029	-2.900525	-0.030479
H	-1.483896	-3.579089	-1.627536
H	-0.397689	-4.108794	-0.350914
H	3.285277	-1.993914	-2.258453
H	2.294429	-3.165805	-3.099232
H	1.917183	-1.463954	-3.223129
H	3.009455	-3.549956	-0.438245
H	1.749586	-4.575014	-1.084857
H	1.511344	-3.735002	0.450286

1a, 1e, 2, 3a, 3e–C_3HMe_5 + 1

B	-0.054606	0.087013	-0.099258
N	1.451580	-0.397843	0.353857
C	0.102477	1.640515	-0.610893
C	-0.986033	0.158478	1.250085
C	2.546324	0.039392	-0.541105
C	1.878187	-0.157931	1.749280
F	-1.055875	2.294868	-0.682978
F	0.884055	2.374025	0.216997
F	0.678746	1.785307	-1.825053
F	-2.273107	0.380795	0.977109
F	-0.635839	1.118680	2.125098
F	-0.955230	-0.988797	1.974198
H	2.263892	-0.104303	-1.572473
H	2.753600	1.085943	-0.360871
H	3.432689	-0.548958	-0.321452
H	1.202929	-0.645429	2.437416
H	1.880147	0.907197	1.939470
H	2.880744	-0.555655	1.881252
C	-0.694801	-0.984593	-1.223763
C	0.395950	-1.726793	-2.015384
C	1.013810	-2.858511	-1.633817
H	1.396138	-1.400218	0.217736
C	-1.600909	-0.202732	-2.196965
C	-1.681573	-2.016910	-0.626669
C	0.759586	-1.118979	-3.346438
C	1.972378	-3.598540	-2.532498
C	0.876368	-3.578829	-0.317072
H	-2.076378	-0.890923	-2.895892
H	-2.392543	0.287568	-1.638135
H	-1.094253	0.560698	-2.774007
H	-1.916201	-2.755745	-1.391761
H	-2.609697	-1.527315	-0.350190
H	-1.341659	-2.547620	0.250146
H	0.824360	-0.037573	-3.276985
H	1.710603	-1.476904	-3.723109
H	0.001936	-1.332213	-4.100338
H	1.930959	-4.664030	-2.312639
H	1.752777	-3.482084	-3.587412
H	3.007329	-3.289087	-2.368696
H	1.856318	-3.942008	-0.003138
H	0.459898	-3.000465	0.500532
H	0.243783	-4.461161	-0.420806

Table S3. Optimized (MPW1K/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1a, 1e, 2, 3a–$C_3H_2Me_4$** and **1**

1a, 1e, 2, 3a–$C_3H_2Me_4$

C	1.337131	-0.002016	-0.010059
C	2.158795	-1.265434	-0.006518
H	1.644255	-2.069664	-0.526062
C	-0.821815	-1.254746	0.041822
C	-0.846411	1.232191	-0.022832
C	0.001692	-0.002698	0.001253
C	2.180329	1.237508	-0.009319
C	2.537306	-1.723511	1.396121
H	3.070744	-1.080945	-0.576038
H	-0.238093	-2.157892	0.174589
H	-1.538898	-1.202789	0.861907
H	-1.407012	-1.360795	-0.873209
H	-0.287105	2.147496	-0.172957
H	-1.410926	1.329543	0.905907
H	-1.582259	1.161782	-0.824819
H	1.630161	2.145900	0.204918
H	2.970532	1.152185	0.736880
H	2.677363	1.362967	-0.972771
H	1.651020	-1.982980	1.971346
H	3.187677	-2.595879	1.364588
H	3.061474	-0.939904	1.940035

1a, 1e, 2, 3a–$C_3H_2Me_4$ + 1 ts

B	0.039065	0.065627	-0.060669
N	1.545303	-0.029682	0.053120
C	-0.481355	1.596812	-0.352748
C	-0.715302	-0.399790	1.330620
C	2.403135	1.134338	-0.121680
C	2.119161	-0.888905	1.083840
F	-1.803682	1.690019	-0.543955
F	-0.206007	2.402259	0.685307
F	0.067722	2.208307	-1.423139
F	-2.019690	-0.118608	1.384028
F	-0.177253	0.206643	2.401710
F	-0.632866	-1.725574	1.605945
H	2.110394	1.716607	-0.983263
H	2.384558	1.783119	0.754797
H	3.428804	0.798890	-0.270124
H	1.591731	-1.834202	1.138824
H	2.083971	-0.424327	2.067214
H	3.160253	-1.094693	0.838265
C	-0.674132	-0.980422	-1.496713
C	0.311090	-2.010874	-1.570515
C	1.646323	-1.799324	-2.020910
H	1.836513	-1.063331	-1.073367
C	-0.798566	-0.106741	-2.751942
C	-2.080886	-1.455719	-1.146894
C	0.045524	-3.333714	-0.937155
C	2.104625	-0.976068	-3.214950
H	2.243916	-2.697280	-1.915703
H	-1.609547	0.600567	-2.625066
H	0.083103	0.457399	-3.009175
H	-1.056668	-0.743072	-3.598113
H	-2.732212	-0.604070	-0.987864
H	-2.138149	-2.076811	-0.262457
H	-2.486297	-2.025672	-1.984750
H	-0.468262	-3.257341	0.012320
H	-0.618702	-3.882874	-1.609970
H	0.952203	-3.917023	-0.817383
H	3.157883	-1.183149	-3.384932
H	1.568384	-1.237165	-4.123067
H	2.012785	0.093315	-3.062390

1a, 1e, 2, 3a–$C_3H_2Me_4$ + 1 product

B	-0.008405	-0.026914	-0.013454
N	1.618483	-0.102715	0.052685
C	-0.428828	1.559887	0.059814
C	-0.566837	-0.695077	1.386594
C	2.286029	0.776154	-0.925071
C	2.312465	0.005527	1.350819
F	-1.743816	1.733692	0.218155
F	0.159116	2.198635	1.095478
F	-0.090217	2.305847	-1.012238
F	-1.893236	-0.788636	1.453106
F	-0.210503	-0.030850	2.501791
F	-0.095378	-1.954813	1.581084
H	1.773880	0.723859	-1.875601
H	2.260996	1.797493	-0.566424
H	3.317801	0.458390	-1.046414
H	1.995921	-0.791584	2.008656
H	2.083213	0.959253	1.807335
H	3.382803	-0.073177	1.178870
C	-0.526519	-0.843026	-1.404450
C	0.558218	-1.763808	-1.999895
C	1.047356	-2.784896	-1.285813
H	1.766931	-1.051177	-0.300479
C	-1.032733	0.141694	-2.470716
C	-1.744404	-1.748853	-1.129928
C	0.972425	-1.552032	-3.426136
C	2.022678	-3.836749	-1.701725
H	0.647841	-2.928536	-0.289858
H	-1.432427	-0.399194	-3.326940
H	-1.845666	0.739120	-2.069562
H	-0.282017	0.834827	-2.835249
H	-2.023889	-2.255642	-2.053634
H	-2.599097	-1.166103	-0.798695
H	-1.549384	-2.512054	-0.384737
H	1.235225	-0.518975	-3.639741
H	1.814072	-2.174775	-3.705332
H	0.150253	-1.799541	-4.096896
H	2.751436	-4.020161	-0.913161
H	1.509633	-4.784276	-1.870978
H	2.568713	-3.596003	-2.607600

Table S4. Optimized (MPW1K/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1a, 1e, 2, 3e–$C_3H_2Me_4$** and **1**

1a, 1e, 2, 3e–$C_3H_2Me_4$

C	1.337131	-0.002016	-0.010059
C	2.158795	-1.265434	-0.006518
H	1.644255	-2.069664	-0.526062
C	-0.821815	-1.254746	0.041822
C	-0.846411	1.232191	-0.022832
C	0.001692	-0.002698	0.001253
C	2.180329	1.237508	-0.009319
C	2.537306	-1.723511	1.396121
H	3.070744	-1.080945	-0.576038
H	-0.238093	-2.157892	0.174589
H	-1.538898	-1.202789	0.861907
H	-1.407012	-1.360795	-0.873209
H	-0.287105	2.147496	-0.172957
H	-1.410926	1.329543	0.905907
H	-1.582259	1.161782	-0.824819
H	1.630161	2.145900	0.204918
H	2.970532	1.152185	0.736880
H	2.677363	1.362967	-0.972771
H	1.651020	-1.982980	1.971346
H	3.187677	-2.595879	1.364588
H	3.061474	-0.939904	1.940035

1a, 1e, 2, 3e–$C_3H_2Me_4$ + 1 ts

B	-0.004463	0.004596	0.000314
N	1.519838	-0.003351	-0.002060
C	-0.624278	1.526883	0.001390
C	-0.580997	-0.711952	1.366403
C	2.204430	1.043287	-0.753582
C	2.281525	-0.227944	1.224011
F	-1.917109	1.580332	0.342422
F	0.021157	2.303408	0.889696
F	-0.541404	2.196046	-1.166712
F	-1.903805	-0.928648	1.376229
F	-0.327496	0.006248	2.468001
F	-0.037140	-1.932484	1.610117
H	1.612017	1.400871	-1.582488
H	2.420671	1.896362	-0.110312
H	3.151595	0.662782	-1.138060
H	1.962732	-1.125676	1.734458
H	2.188201	0.615326	1.907596
H	3.333325	-0.341654	0.964897
C	-0.600042	-0.851632	-1.486764
C	-0.049293	-2.161650	-1.229823
C	1.344104	-2.351961	-1.386164
H	1.631831	-1.355838	-0.685425
C	-0.021276	-0.205152	-2.752957
C	-2.120144	-0.785254	-1.600391
C	-0.900917	-3.248035	-0.690670
H	1.736010	-1.926259	-2.305124
C	2.023177	-3.640442	-0.996052
H	-0.425118	0.788712	-2.898312
H	1.057609	-0.129189	-2.768590
H	-0.317974	-0.808316	-3.612147
H	-2.432229	0.240586	-1.768034
H	-2.646722	-1.137817	-0.724007
H	-2.453479	-1.367772	-2.460493
H	-1.723481	-2.894917	-0.083704
H	-1.336591	-3.739768	-1.567030
H	-0.337271	-3.993778	-0.145072
H	3.099332	-3.540902	-1.110513
H	1.833090	-3.904181	0.041288
H	1.708805	-4.477817	-1.617734

1a, 1e, 2, 3e–$C_3H_2Me_4$ + 1 product

B	-0.057465	0.116850	-0.105135
N	1.440442	-0.388977	0.347276
C	0.103196	1.680077	-0.581916
C	-1.004176	0.161182	1.236417
C	2.548508	0.084463	-0.514050
C	1.849110	-0.201276	1.756322
F	-1.054820	2.336827	-0.638260
F	0.886044	2.394422	0.260898
F	0.676031	1.848493	-1.793757
F	-2.288605	0.390093	0.954021
F	-0.660162	1.106725	2.129564
F	-0.985029	-0.996575	1.941811
H	2.279345	-0.008880	-1.554489
H	2.757358	1.119978	-0.280191
H	3.428658	-0.519367	-0.313030
H	1.164743	-0.712468	2.417564
H	1.849116	0.856514	1.984374
H	2.849873	-0.603941	1.886221
C	-0.691884	-0.925175	-1.256973
C	0.400041	-1.591229	-2.097347
C	1.080314	-2.703078	-1.787248
H	1.388664	-1.385784	0.171855
C	-1.649487	-0.139972	-2.170974
C	-1.590687	-2.026637	-0.655185
C	0.728045	-0.957705	-3.423145
H	1.795760	-3.026830	-2.533679
C	1.029846	-3.633148	-0.610867
H	-2.131055	-0.817560	-2.876215
H	-2.433583	0.318809	-1.576286
H	-1.168258	0.647084	-2.739685
H	-1.852575	-2.734976	-1.440062
H	-2.513657	-1.595795	-0.280802
H	-1.153889	-2.585736	0.160482
H	0.950903	0.102494	-3.329129
H	1.577494	-1.449048	-3.889188
H	-0.115445	-1.032288	-4.106943
H	2.017662	-4.056807	-0.437741
H	0.695057	-3.192637	0.324787
H	0.360316	-4.471893	-0.803303

Table S5. Optimized (MPW1K/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1a, 1e, 3a, 3e–$C_3H_2Me_4$** and **1**

1a, 1e, 3a, 3e–$C_3H_2Me_4$

C	0.004287	0.000823	-0.000016
C	1.333838	0.001805	-0.000002
C	2.275443	-1.160865	0.000017
H	1.707155	-2.089756	0.000038
C	-0.852415	-1.225066	-0.000006
C	-0.762883	1.286375	-0.000035
H	1.827086	0.969734	-0.000008
C	3.142766	-1.140620	1.253365
C	3.142767	-1.140667	-1.253333
H	-0.283718	-2.148114	-0.000002
H	-1.504593	-1.231180	0.873995
H	-1.504595	-1.231190	-0.874007
H	-0.103584	2.149703	-0.000033
H	-1.411103	1.351924	0.874728
H	-1.411082	1.351909	-0.874814
H	2.535476	-1.195751	2.153915
H	3.839822	-1.977296	1.259695
H	3.727547	-0.222150	1.302739
H	3.727548	-0.222200	-1.302744
H	3.839823	-1.977343	-1.259633
H	2.535475	-1.195834	-2.153879

1a, 1e, 3a, 3e–$C_3H_2Me_4$ + 1 ts

B	0.044494	0.089984	-0.019650
N	1.539221	-0.050219	0.116344
C	-0.436485	1.628540	-0.336270
C	-0.769040	-0.397734	1.322745
C	2.429653	0.901258	-0.536557
C	2.131210	-0.453246	1.389195
F	-1.749043	1.769484	-0.555338
F	-0.153327	2.410051	0.720027
F	0.155973	2.232392	-1.382806
F	-2.085449	-0.180660	1.276767
F	-0.348058	0.216411	2.438480
F	-0.637055	-1.723435	1.580055
H	2.117705	1.104020	-1.551427
H	2.471555	1.848877	0.001154
H	3.434422	0.483426	-0.564694
H	1.591512	-1.282570	1.828277
H	2.142133	0.367148	2.104780
H	3.158078	-0.771430	1.215277
C	-0.617566	-0.951135	-1.507860
C	0.129069	-2.107904	-1.206135
C	1.509231	-2.369507	-1.365285
H	1.697961	-1.391099	-0.627773
C	-0.336793	-0.172324	-2.786474
C	-2.120050	-1.173433	-1.369509
H	-0.360849	-2.759249	-0.492071
C	2.281598	-2.048012	-2.632058
C	2.010004	-3.644466	-0.716258
H	-1.053530	0.636034	-2.884414
H	0.647778	0.272250	-2.840317
H	-0.463181	-0.828596	-3.646597
H	-2.653332	-0.241176	-1.232941
H	-2.368139	-1.829508	-0.541437
H	-2.488438	-1.636020	-2.285461
H	3.348125	-2.045373	-2.419245
H	2.104457	-2.821030	-3.378972
H	2.027210	-1.094943	-3.073144
H	3.069747	-3.566965	-0.483075
H	1.891568	-4.494991	-1.387413
H	1.481181	-3.866878	0.206969

1a, 1e, 3a, 3e–$C_3H_2Me_4$ + 1 product

B	-0.055418	0.066175	0.039283
N	1.579594	-0.064766	0.038102
C	-0.443330	1.653590	-0.041647
C	-0.547317	-0.458495	1.516689
C	2.241169	0.706151	-1.032645
C	2.332357	0.139556	1.293076
F	-1.756020	1.857732	0.100772
F	0.157492	2.387262	0.920806
F	-0.101486	2.275941	-1.188183
F	-1.868797	-0.498402	1.674281
F	-0.099721	0.270941	2.555954
F	-0.100509	-1.716965	1.765826
H	1.696933	0.600250	-1.959678
H	2.261889	1.752559	-0.754882
H	3.257705	0.343851	-1.158082
H	2.029124	-0.588198	2.031816
H	2.140371	1.135737	1.669673
H	3.392270	0.022103	1.083834
C	-0.651256	-0.883329	-1.216099
C	0.395568	-1.876705	-1.690747
C	0.699095	-3.143677	-1.387079
H	1.680154	-1.046801	-0.221425
C	-0.992660	-0.055295	-2.471076
C	-1.975687	-1.576684	-0.864911
H	1.009019	-1.472086	-2.491680
C	1.784259	-3.839189	-2.156693
C	0.048196	-4.030896	-0.373275
H	-1.371816	-0.722329	-3.245374
H	-1.764172	0.680105	-2.262816
H	-0.141928	0.476632	-2.889729
H	-2.280035	-2.206172	-1.700561
H	-2.754663	-0.835815	-0.703752
H	-1.941605	-2.194820	0.021095
H	2.573398	-4.190644	-1.490784
H	1.386789	-4.723783	-2.655593
H	2.229044	-3.198106	-2.912594
H	0.810306	-4.583317	0.175910
H	-0.569200	-4.775391	-0.877789
H	-0.563182	-3.506901	0.343740

Table S6. Optimized (MPW1K/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1a, 2, 3a, 3e–$C_3H_2Me_4$** and **1**

1a, 2, 3a, 3e–$C_3H_2Me_4$

C	0.147729	-0.098303	0.113527
C	1.463810	-0.079832	-0.086294
C	2.279199	1.185754	-0.186576
H	1.602219	2.029999	-0.079580
H	-0.322546	-1.073907	0.168653
C	-0.795826	1.044354	0.276766
C	2.210673	-1.372716	-0.223192
C	3.306640	1.289113	0.935809
C	2.953765	1.321085	-1.547602
H	-0.316979	2.015938	0.216771
H	-1.572329	1.010406	-0.487593
H	-1.304636	0.985183	1.239081
H	1.539187	-2.221241	-0.128859
H	2.708230	-1.447700	-1.189550
H	2.982722	-1.472756	0.538901
H	4.068752	0.516162	0.854022
H	3.815003	2.251163	0.897862
H	2.835211	1.194653	1.911702
H	2.229666	1.245071	-2.356055
H	3.451782	2.285709	-1.630324
H	3.709290	0.552157	-1.698958

1a, 2, 3a, 3e–$C_3H_2Me_4$ + 1 ts

B	0.071063	0.009973	0.002184
N	1.581459	-0.096084	0.147093
C	-0.466377	1.543571	-0.214957
C	-0.713602	-0.577660	1.320499
C	2.409016	0.820266	-0.625822
C	2.180776	-0.237907	1.469729
F	-1.797375	1.619248	-0.359669
F	-0.158450	2.325230	0.832289
F	0.041782	2.187583	-1.284369
F	-2.034276	-0.719421	1.126809
F	-0.584926	0.173518	2.418886
F	-0.287381	-1.813653	1.690892
H	2.034070	0.943122	-1.631909
H	2.451237	1.807865	-0.163650
H	3.424777	0.431281	-0.680974
H	1.723275	-1.040271	2.031607
H	2.092543	0.683174	2.047106
H	3.239754	-0.465899	1.356315
C	-0.519545	-0.912336	-1.401780
C	0.072270	-2.207667	-1.191141
C	1.471064	-2.451149	-1.305055
H	1.682044	-1.522845	-0.516609
C	-0.357403	-0.185283	-2.740138
H	-1.584618	-0.979704	-1.202624
C	-0.807392	-3.258698	-0.615084
C	2.251486	-1.998459	-2.533247
C	2.012122	-3.772626	-0.796674
H	-1.131102	0.571105	-2.816425
H	0.584155	0.326718	-2.885633
H	-0.496548	-0.880604	-3.565398
H	-1.729626	-2.856690	-0.215018
H	-1.062925	-3.911761	-1.456651
H	-0.326483	-3.880031	0.129185
H	3.309477	-1.935225	-2.291901
H	2.143130	-2.738745	-3.325640
H	1.939075	-1.043308	-2.925705
H	3.098751	-3.752033	-0.821989
H	1.693228	-4.608657	-1.419493
H	1.717627	-3.983338	0.227013

1a, 2, 3a, 3e–$C_3H_2Me_4$ + 1 product

B	0.364544	-0.012211	0.007905
N	1.809214	0.712670	-0.244620
C	-0.706916	1.126466	0.485359
C	0.582094	-1.055018	1.252968
C	1.735405	1.884003	-1.140539
C	2.622446	1.071320	0.939465
F	-1.828621	0.582501	0.962371
F	-0.242797	1.942208	1.458046
F	-1.100031	1.970016	-0.493136
F	-0.403782	-1.942088	1.370786
F	0.697443	-0.478167	2.464157
F	1.721227	-1.780777	1.110078
H	1.105147	1.664363	-1.989661
H	1.310228	2.715956	-0.592827
H	2.735651	2.147210	-1.473573
H	2.859468	0.183717	1.507755
H	2.062628	1.758461	1.559370
H	3.541146	1.543706	0.602337
C	-0.188683	-0.859986	-1.282715
C	0.602490	-2.107174	-1.622512
C	0.100941	-3.344076	-1.551707
H	2.324120	-0.004029	-0.741103
C	-0.522725	-0.121716	-2.587460
H	-1.147278	-1.190026	-0.887666
C	2.016318	-1.875241	-2.093938
C	0.907034	-4.574509	-1.844126
C	-1.304501	-3.678168	-1.154533
H	-1.117199	-0.774620	-3.224400
H	-1.092078	0.787334	-2.422353
H	0.362350	0.137609	-3.168225
H	2.121740	-0.891561	-2.552718
H	2.737296	-1.957021	-1.275778
H	2.327685	-2.584366	-2.853878
H	0.772954	-5.299063	-1.040646
H	0.558320	-5.058697	-2.758195
H	1.970998	-4.393233	-1.940643
H	-1.699191	-4.446633	-1.819529
H	-1.330632	-4.090307	-0.145494
H	-1.987033	-2.837034	-1.183850

Table S7. Optimized (MPW1K/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1e, 2, 3a, 3e–$C_3H_2Me_4$** and **1**

1e, 2, 3a, 3e–$C_3H_2Me_4$

C	0.125897	-0.138751	0.182047
C	1.437467	-0.147869	-0.042158
C	2.191406	1.161214	-0.094801
H	1.456828	1.949775	0.072648
C	-0.812160	-1.292925	0.275911
H	-0.339738	0.831376	0.316836
C	2.241570	-1.392566	-0.251548
C	3.237831	1.268417	1.008701
C	2.824869	1.407058	-1.459480
H	-0.327484	-2.253556	0.137199
H	-1.305878	-1.308147	1.247700
H	-1.600338	-1.208575	-0.472393
H	1.640270	-2.292221	-0.189194
H	2.723653	-1.386698	-1.228400
H	3.034279	-1.475205	0.490951
H	4.043767	0.549845	0.868563
H	3.686634	2.260372	1.012609
H	2.796753	1.093753	1.987756
H	2.086215	1.336130	-2.255115
H	3.269809	2.399939	-1.499497
H	3.616449	0.689404	-1.668855

1e, 2, 3a, 3e–$C_3H_2Me_4$ + 1 ts

B	0.026899	-0.025092	0.000113
N	1.551556	0.021154	-0.006023
C	-0.645223	1.467398	0.001504
C	-0.542365	-0.848667	1.291172
C	2.161309	1.078140	-0.803721
C	2.301140	-0.114229	1.237741
F	-1.943200	1.484050	0.323795
F	-0.040955	2.286269	0.881134
F	-0.562554	2.100726	-1.188518
F	-1.847849	-1.145757	1.217642
F	-0.382261	-0.199725	2.451978
F	0.073019	-2.046914	1.464231
H	1.643249	1.208069	-1.746435
H	2.140030	2.032230	-0.278139
H	3.199869	0.826616	-1.010707
H	1.997422	-0.994530	1.787345
H	2.168727	0.758771	1.876635
H	3.360789	-0.207899	1.004425
C	-0.477263	-0.767277	-1.516326
C	0.133482	-2.064959	-1.462119
C	1.539445	-2.173753	-1.623490
H	1.719617	-1.265082	-0.759485
H	0.056186	-0.107681	-2.196126
C	-1.968561	-0.695127	-1.802512
C	-0.692177	-3.230386	-1.062614
C	2.189253	-1.539728	-2.849465
C	2.223031	-3.473517	-1.258103
H	-2.277922	0.338287	-1.909782
H	-2.574962	-1.131066	-1.017358
H	-2.202550	-1.203951	-2.736980
H	-1.534396	-2.961599	-0.437773
H	-1.097295	-3.642831	-1.992500
H	-0.119315	-4.015053	-0.586312
H	3.219243	-1.260227	-2.642632
H	2.208794	-2.269515	-3.659148
H	1.669722	-0.660101	-3.209971
H	3.301574	-3.333025	-1.269523
H	1.997734	-4.268127	-1.970318
H	1.954068	-3.820930	-0.264563

1e, 2, 3a, 3e–$C_3H_2Me_4$ + 1 product

B	-0.019253	-0.005238	0.031876
N	1.557067	-0.355879	0.301747
C	-0.117706	1.573738	-0.378190
C	-0.829287	-0.183603	1.445422
C	2.492650	0.255313	-0.665858
C	2.100354	-0.164993	1.661895
F	-1.369457	2.033335	-0.344500
F	0.604632	2.392759	0.417619
F	0.324394	1.833108	-1.629335
F	-2.145878	-0.029141	1.327842
F	-0.455327	0.679737	2.409240
F	-0.652457	-1.412932	1.996233
H	2.124964	0.119658	-1.671865
H	2.585171	1.312371	-0.451862
H	3.463118	-0.222404	-0.566166
H	1.550106	-0.765657	2.371909
H	2.018480	0.879461	1.933727
H	3.144886	-0.464355	1.666182
C	-0.610419	-0.947562	-1.201671
C	0.411939	-1.773452	-1.973491
C	0.987508	-2.901144	-1.529568
H	1.584709	-1.348775	0.090481
H	-0.947806	-0.210346	-1.929200
C	-1.874187	-1.773295	-0.914960
C	0.635085	-1.245729	-3.363109
C	1.908907	-3.762375	-2.341938
C	0.728445	-3.503430	-0.177194
H	-2.138762	-2.350048	-1.800050
H	-1.766449	-2.472146	-0.091844
H	-2.712220	-1.125266	-0.680322
H	0.765231	-0.164562	-3.347595
H	1.482034	-1.680138	-3.880886
H	-0.254953	-1.428740	-3.967884
H	2.871240	-3.879262	-1.840913
H	1.490094	-4.765662	-2.433263
H	2.095625	-3.396921	-3.343338
H	1.666581	-3.799788	0.297356
H	0.185182	-2.862070	0.505687
H	0.145397	-4.419655	-0.280662

Table S8. Optimized (MPW1K/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1a, 1e, 2–$C_3H_3Me_3$** and **1**

1a, 1e, 2–$C_3H_3Me_3$

C	-1.511123	1.239397	-0.012882
C	-0.668004	-0.000002	-0.000006
C	0.668004	-0.000002	0.000003
C	1.511128	-1.239396	-0.012883
H	0.949829	-2.157752	-0.130440
H	2.233669	-1.188867	-0.828250
H	2.091136	-1.315417	0.908189
C	1.511123	1.239397	0.012883
H	2.091075	1.315460	-0.908221
H	0.949823	2.157744	0.130514
H	2.233712	1.188842	0.828204
C	-1.511128	-1.239396	0.012883
H	-2.091169	-1.315397	-0.908169
H	-0.949824	-2.157756	0.130400
H	-2.233640	-1.188886	0.828278
H	-2.233715	1.188842	-0.828202
H	-2.091072	1.315459	0.908223
H	-0.949824	2.157744	-0.130515

1a, 1e, 2–$C_3H_3Me_3$ + 1 ts

C	1.671468	-0.425463	-0.645383
B	0.267428	-0.007666	0.099086
N	0.333800	-0.189151	1.610486
C	1.105596	-1.315465	2.125828
H	1.135408	-2.138928	1.428099
H	2.133734	-1.014101	2.325536
H	0.668300	-1.664315	3.061964
C	0.568364	0.945792	2.500998
H	0.441334	0.611807	3.529682
H	1.580576	1.332082	2.388782
H	-0.133562	1.747463	2.319645
C	0.013464	1.573727	-0.281941
F	-1.022694	2.135069	0.389970
F	1.071196	2.342954	0.005780
F	-0.259645	1.806520	-1.573402
F	1.767560	0.026288	-1.900795
F	2.725619	0.089575	0.011281
F	1.927007	-1.746764	-0.726415
C	-1.059781	-1.072646	-0.575043
C	-2.168608	-0.483610	0.125036
C	-2.317129	-0.738538	1.504801
H	-3.091870	-0.187010	2.019337
H	-2.241834	-1.769979	1.827956
C	-3.069058	0.492374	-0.533904
H	-2.587980	1.083705	-1.301731
H	-3.844503	-0.103519	-1.025027
H	-3.556831	1.142390	0.183850
C	-0.827462	-2.537865	-0.186501
H	0.051298	-2.935817	-0.677160
H	-0.723132	-2.709517	0.876581
H	-1.684696	-3.120087	-0.526774
C	-1.114687	-1.000038	-2.096470
H	-0.208995	-1.420885	-2.520912
H	-1.950612	-1.597538	-2.462696
H	-1.214454	0.003007	-2.488231
H	-1.140317	-0.408745	1.789972

1a, 1e, 2–$C_3H_3Me_3$ + 1 product

C	-1.252794	-0.020724	-0.788827
C	-2.403192	0.359479	0.152789
C	-2.436711	1.524361	0.803448
H	-3.281795	1.786688	1.422820
H	-1.665384	2.270739	0.692128
F	0.514585	2.456284	0.241707
C	1.123984	1.354811	-0.268560
B	0.250290	-0.019594	-0.012404
N	0.003417	-0.115674	1.596705
H	-0.812534	0.492794	1.694776
C	-0.454062	-1.444593	2.043317
H	-1.189780	-1.832908	1.352930
H	0.389491	-2.122612	2.076153
H	-0.890654	-1.358066	3.034236
C	1.032971	0.377393	2.533001
H	0.678974	0.221436	3.548581
H	1.956450	-0.164846	2.378554
H	1.205188	1.432023	2.371667
F	2.341864	1.352625	0.303923
C	1.240186	-1.257066	-0.439211
F	1.639601	-1.172775	-1.711290
F	2.366446	-1.298541	0.303688
F	0.717121	-2.493198	-0.303445
F	1.349985	1.624204	-1.552287
C	-3.577894	-0.563092	0.291840
H	-3.293246	-1.572892	0.579220
H	-4.280031	-0.181894	1.027283
H	-4.104918	-0.654426	-0.656770
C	-1.543066	-1.370501	-1.463210
H	-2.476480	-1.320620	-2.021293
H	-0.762637	-1.607946	-2.179035
H	-1.610319	-2.209862	-0.778007
C	-1.310484	1.000804	-1.943330
H	-2.300567	0.967501	-2.397832
H	-1.134742	2.019176	-1.615596
H	-0.582449	0.760795	-2.712938

Table S9. Optimized (MPW1K/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1a, 1e, 3a–$C_3H_3Me_3$** and **1**

1a, 1e, 3a–$C_3H_3Me_3$

C	0.000959	-0.000602	-0.001562
C	1.330826	-0.000734	-0.002931
C	2.262371	1.165136	-0.005465
H	1.717955	2.102800	0.073666
C	-0.854530	1.225704	0.009563
C	-0.765439	-1.286058	-0.008270
H	1.821977	-0.968361	-0.016138
C	3.150264	1.191898	-1.241803
H	2.896703	1.108060	0.881772
H	-0.284746	2.147704	-0.015060
H	-1.529466	1.223937	-0.846878
H	-1.483227	1.242219	0.900573
H	-0.105572	-2.148942	-0.014069
H	-1.414834	-1.346841	-0.882481
H	-1.412376	-1.357345	0.867020
H	2.554496	1.300424	-2.145631
H	3.858061	2.017499	-1.201093
H	3.721467	0.269541	-1.333595

1a, 1e, 3a–$C_3H_3Me_3$ + 1 ts

B	0.025699	-0.012789	0.005010
N	1.535856	0.036052	-0.002521
C	-0.668320	1.474832	-0.044481
C	-0.584066	-0.783876	1.322757
C	2.233545	1.190328	-0.557770
C	2.294629	-0.470506	1.139112
F	-2.003288	1.465578	-0.130062
F	-0.375948	2.141242	1.085500
F	-0.263223	2.283703	-1.040826
F	-1.913550	-0.726876	1.423926
F	-0.120263	-0.281986	2.476655
F	-0.281529	-2.106015	1.365376
H	1.807653	1.491929	-1.504410
H	2.200895	2.044971	0.117934
H	3.276875	0.926267	-0.720033
H	1.905207	-1.422951	1.475978
H	2.275401	0.225570	1.975412
H	3.330016	-0.616847	0.835080
C	-0.655660	-0.919402	-1.562864
C	0.264528	-1.981905	-1.487325
C	1.635712	-1.997145	-1.812073
H	1.793026	-1.116696	-0.938936
C	-0.588296	0.046904	-2.737191
C	-2.096647	-1.358789	-1.335184
H	-0.046324	-2.781552	-0.827360
C	2.268663	-1.453404	-3.077102
H	2.119222	-2.911007	-1.483888
H	-1.390138	0.773520	-2.662745
H	0.337681	0.601442	-2.810958
H	-0.729536	-0.504150	-3.666123
H	-2.726915	-0.533280	-1.029316
H	-2.178260	-2.142759	-0.589301
H	-2.491914	-1.747650	-2.273880
H	3.349727	-1.440625	-2.964386
H	2.039493	-2.095274	-3.925404
H	1.952886	-0.449132	-3.327016

1a, 1e, 3a–$C_3H_3Me_3$ + 1 product

B	-0.057291	0.076858	0.033003
N	1.579227	-0.028810	0.003780
C	-0.472859	1.658191	-0.018989
C	-0.514974	-0.480251	1.509684
C	2.209798	0.752908	-1.078128
C	2.349031	0.189624	1.246632
F	-1.787652	1.835840	0.137844
F	0.123005	2.388231	0.948553
F	-0.152310	2.302389	-1.159735
F	-1.832481	-0.544018	1.690307
F	-0.060472	0.239534	2.552652
F	-0.043089	-1.734770	1.728430
H	1.649468	0.641147	-1.994775
H	2.221433	1.798983	-0.798849
H	3.228519	0.404719	-1.223557
H	2.074550	-0.546564	1.988176
H	2.142038	1.180343	1.629375
H	3.407285	0.095550	1.018418
C	-0.665694	-0.858702	-1.226921
C	0.380831	-1.836036	-1.724436
C	0.703730	-3.092367	-1.410897
H	1.696615	-1.008826	-0.253862
C	-1.040834	-0.019302	-2.463706
C	-1.968496	-1.583228	-0.857953
H	0.978577	-1.431334	-2.536328
H	1.499795	-3.518373	-2.012453
C	0.143211	-4.043417	-0.409632
H	-1.423397	-0.680908	-3.240929
H	-1.819779	0.700875	-2.231782
H	-0.205457	0.531496	-2.888818
H	-2.284229	-2.197443	-1.700581
H	-2.756216	-0.862218	-0.655801
H	-1.894487	-2.223704	0.010066
H	0.953513	-4.533109	0.129032
H	-0.507971	-3.582438	0.317424
H	-0.410098	-4.833172	-0.918853

Table S10. Optimized (MPW1K/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1a, 1e, 3e–$C_3H_3Me_3$** and **1**

1a, 1e, 3e–$C_3H_3Me_3$

C	0.000959	-0.000602	-0.001562
C	1.330826	-0.000734	-0.002931
C	2.262371	1.165136	-0.005465
H	1.717955	2.102800	0.073666
C	-0.854530	1.225704	0.009563
C	-0.765439	-1.286058	-0.008270
H	1.821977	-0.968361	-0.016138
C	3.150264	1.191898	-1.241803
H	2.896703	1.108060	0.881772
H	-0.284746	2.147704	-0.015060
H	-1.529466	1.223937	-0.846878
H	-1.483227	1.242219	0.900573
H	-0.105572	-2.148942	-0.014069
H	-1.414834	-1.346841	-0.882481
H	-1.412376	-1.357345	0.867020
H	2.554496	1.300424	-2.145631
H	3.858061	2.017499	-1.201093
H	3.721467	0.269541	-1.333595

1a, 1e, 3e–$C_3H_3Me_3$ + 1 ts

B	0.030259	0.109357	-0.013245
N	1.529710	-0.015303	0.058306
C	-0.473960	1.648444	-0.288702
C	-0.732567	-0.408802	1.346423
C	2.392248	0.989334	-0.550155
C	2.165345	-0.519368	1.272686
F	-1.794910	1.786082	-0.445228
F	-0.145619	2.418946	0.762854
F	0.066733	2.266576	-1.354987
F	-2.048521	-0.184554	1.354864
F	-0.264515	0.176350	2.458858
F	-0.600677	-1.740974	1.566552
H	2.056939	1.247780	-1.544791
H	2.430730	1.902038	0.044519
H	3.402078	0.589023	-0.622586
H	1.640266	-1.384159	1.658986
H	2.197588	0.238698	2.052967
H	3.186219	-0.818144	1.039743
C	-0.675637	-0.921181	-1.486384
C	0.075166	-2.079584	-1.225848
C	1.438874	-2.230299	-1.534908
H	1.697148	-1.280820	-0.786199
C	-0.331923	-0.171325	-2.765405
C	-2.178246	-1.110401	-1.344170
H	-0.356695	-2.789003	-0.529454
H	1.747867	-1.791950	-2.479903
C	2.158087	-3.505781	-1.173962
H	-0.948694	0.713362	-2.871877
H	0.704392	0.143081	-2.825013
H	-0.533553	-0.819086	-3.619050
H	-2.694680	-0.169072	-1.205826
H	-2.432281	-1.760716	-0.513184
H	-2.559580	-1.568135	-2.257179
H	3.232052	-3.347637	-1.119966
H	1.830766	-3.884277	-0.208253
H	1.982210	-4.284133	-1.914061

1a, 1e, 3e–$C_3H_3Me_3$ + 1 product

B	-0.030466	-0.012200	0.013790
N	1.609272	-0.036861	-0.015064
C	-0.528138	1.543387	0.059119
C	-0.454303	-0.700205	1.445799
C	2.202322	0.801172	-1.074897
C	2.368758	0.179800	1.234504
F	-1.852527	1.641024	0.204142
F	0.013667	2.244507	1.077710
F	-0.227169	2.269730	-1.037762
F	-1.765483	-0.835694	1.629999
F	-0.023206	-0.040654	2.538467
F	0.074626	-1.945655	1.565317
H	1.656926	0.674915	-1.998731
H	2.152200	1.840576	-0.775957
H	3.240509	0.514888	-1.218306
H	2.141283	-0.599693	1.947018
H	2.103798	1.140203	1.656611
H	3.429998	0.158528	1.001964
C	-0.589434	-0.887938	-1.306357
C	0.479378	-1.837791	-1.804170
C	0.744765	-3.069220	-1.381199
H	1.766802	-1.003962	-0.297623
C	-0.977670	-0.009096	-2.506573
C	-1.856925	-1.688601	-0.975329
H	1.087729	-1.466518	-2.626411
C	1.795557	-3.953021	-1.960184
H	0.158184	-3.490964	-0.575428
H	-1.313638	-0.647730	-3.323716
H	-1.794182	0.662685	-2.258328
H	-0.162121	0.602040	-2.885162
H	-2.183711	-2.217940	-1.869666
H	-2.661263	-1.030501	-0.659050
H	-1.710416	-2.423274	-0.191652
H	2.503364	-4.280234	-1.198691
H	1.351748	-4.856194	-2.378254
H	2.348975	-3.453208	-2.751869

Table S11. Optimized (MPW1K/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1a, 2, 3a–$C_3H_3Me_3$** and **1**

1a, 2, 3a–$C_3H_3Me_3$

C	0.000959	-0.000602	-0.001562
C	1.330826	-0.000734	-0.002931
C	2.262371	1.165136	-0.005465
H	1.717955	2.102800	0.073666
C	-0.854530	1.225704	0.009563
C	-0.765439	-1.286058	-0.008270
H	1.821977	-0.968361	-0.016138
C	3.150264	1.191898	-1.241803
H	2.896703	1.108060	0.881772
H	-0.284746	2.147704	-0.015060
H	-1.529466	1.223937	-0.846878
H	-1.483227	1.242219	0.900573
H	-0.105572	-2.148942	-0.014069
H	-1.414834	-1.346841	-0.882481
H	-1.412376	-1.357345	0.867020
H	2.554496	1.300424	-2.145631
H	3.858061	2.017499	-1.201093
H	3.721467	0.269541	-1.333595

1a, 2, 3a–$C_3H_3Me_3$ + 1 ts

B	0.070926	-0.027081	-0.012605
N	1.583246	-0.161290	0.101380
C	-0.442914	1.521026	-0.178707
C	-0.702329	-0.636024	1.303178
C	2.408389	0.780115	-0.645384
C	2.201558	-0.360792	1.408773
F	-1.775411	1.622693	-0.283305
F	-0.090798	2.270684	0.877870
F	0.046320	2.182459	-1.246217
F	-2.026431	-0.763275	1.122056
F	-0.553867	0.096105	2.411924
F	-0.283260	-1.880421	1.647656
H	2.010488	0.961157	-1.633813
H	2.476886	1.741583	-0.134334
H	3.415783	0.378454	-0.744321
H	1.750990	-1.187003	1.940733
H	2.123264	0.534553	2.026166
H	3.258118	-0.584774	1.269140
C	-0.568023	-0.898312	-1.436809
C	0.039977	-2.186741	-1.285821
C	1.426090	-2.418694	-1.457255
H	1.671989	-1.547746	-0.603814
C	-0.405506	-0.144433	-2.757343
H	-1.628563	-0.965420	-1.213083
C	-0.768644	-3.282713	-0.690672
C	2.257541	-1.991021	-2.652924
H	1.719151	-3.406141	-1.114893
H	-1.120307	0.669985	-2.791492
H	0.570978	0.290299	-2.922150
H	-0.622560	-0.807505	-3.592456
H	-1.642005	-2.929244	-0.156974
H	-1.116170	-3.879578	-1.539581
H	-0.182147	-3.938748	-0.055438
H	3.310486	-2.141789	-2.429848
H	2.017259	-2.602431	-3.520498
H	2.124778	-0.954407	-2.928497

1a, 2, 3a–$C_3H_3Me_3$ + 1 product

B	0.118103	0.054772	-0.027187
N	1.736763	0.250349	-0.086121
C	-0.581618	1.525764	0.091054
C	-0.197983	-0.756097	1.363418
C	2.169735	1.252375	-1.080399
C	2.461907	0.501032	1.179661
F	-1.889001	1.435765	0.345559
F	-0.058482	2.293066	1.072978
F	-0.476193	2.290572	-1.015845
F	-1.448358	-1.220633	1.423762
F	-0.027175	-0.043836	2.491652
F	0.605583	-1.837335	1.512614
H	1.599186	1.146485	-1.991769
H	1.997516	2.240852	-0.672872
H	3.229426	1.126180	-1.284469
H	2.331478	-0.333972	1.852487
H	2.072151	1.400024	1.638420
H	3.518069	0.627514	0.957792
C	-0.419818	-0.838245	-1.305205
C	0.498058	-1.969975	-1.732511
C	0.371168	-3.235295	-1.327769
H	2.036407	-0.660972	-0.418520
C	-0.923185	-0.072556	-2.534966
H	-1.311167	-1.312219	-0.898544
C	1.548961	-1.677466	-2.772959
H	1.083350	-3.945529	-1.733650
C	-0.643201	-3.841219	-0.423255
H	-1.300838	-0.774655	-3.277523
H	-1.738123	0.594578	-2.273385
H	-0.161513	0.532830	-3.021357
H	2.255564	-0.895246	-2.494770
H	2.128244	-2.569832	-2.991814
H	1.091698	-1.344684	-3.703632
H	-1.123104	-4.682691	-0.923014
H	-0.173483	-4.235064	0.477012
H	-1.415144	-3.148706	-0.110142

Table S12. Optimized (MPW1K/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1a, 2, 3e–$C_3H_3Me_3$** and **1**

1a, 2, 3e–$C_3H_3Me_3$

C	0.200472	0.000923	0.072836
C	1.507203	-0.151117	-0.122252
C	2.471926	0.987869	-0.289586
H	1.954580	1.881905	-0.628244
H	-0.390133	-0.900880	0.187721
C	-0.571637	1.272332	0.161873
C	2.118101	-1.516842	-0.176122
C	3.243984	1.305686	0.985233
H	3.179632	0.729898	-1.079142
H	0.048965	2.155529	0.048967
H	-1.348416	1.308347	-0.602156
H	-1.077978	1.346910	1.124384
H	1.379381	-2.294263	-0.002217
H	2.578375	-1.695625	-1.148740
H	2.906143	-1.629323	0.568570
H	3.800645	0.441793	1.342177
H	3.957337	2.110506	0.819053
H	2.567152	1.612682	1.779594

1a, 2, 3e–$C_3H_3Me_3$ + 1 ts

B	0.010390	-0.017178	0.042463
N	1.524174	0.043788	0.047698
C	-0.715469	1.451395	-0.006400
C	-0.579896	-0.801266	1.358318
C	2.184861	1.067778	-0.746540
C	2.266518	-0.125209	1.290251
F	-2.052680	1.380148	-0.078440
F	-0.436892	2.172063	1.090459
F	-0.347852	2.238991	-1.037774
F	-1.889218	-1.080595	1.258886
F	-0.433692	-0.139716	2.510032
F	0.012365	-2.006302	1.569238
H	1.689609	1.216735	-1.696027
H	2.206239	2.028835	-0.230288
H	3.215340	0.767323	-0.937302
H	1.934249	-0.995121	1.839313
H	2.169557	0.748903	1.936097
H	3.322902	-0.256234	1.058152
C	-0.618559	-0.898146	-1.385635
C	0.108271	-2.127886	-1.342212
C	1.488145	-2.118471	-1.668974
H	1.737885	-1.307651	-0.794636
C	-0.527572	-0.102325	-2.687304
H	-1.662770	-1.055053	-1.132405
C	-0.530541	-3.349150	-0.801804
H	1.720598	-1.469022	-2.509293
C	2.322900	-3.373487	-1.632663
H	-1.160365	0.774953	-2.641963
H	0.472995	0.233012	-2.934870
H	-0.880292	-0.720263	-3.511931
H	-1.448260	-3.135472	-0.268143
H	-0.778516	-3.966361	-1.671178
H	0.132626	-3.936964	-0.176955
H	3.365243	-3.133860	-1.823501
H	2.010778	-4.091187	-2.389934
H	2.276971	-3.868588	-0.666385

1a, 2, 3e–$C_3H_3Me_3$ + 1 product

B	0.084669	0.080926	-0.091298
N	1.628872	-0.265062	0.307954
C	0.004963	1.643043	-0.544961
C	-0.825283	-0.126886	1.250993
C	2.635538	0.288570	-0.621550
C	2.069262	0.013086	1.691159
F	-1.238563	2.122715	-0.541940
F	0.719105	2.466633	0.258166
F	0.483792	1.877005	-1.786376
F	-2.134805	-0.126901	0.999114
F	-0.640969	0.775850	2.229207
F	-0.571438	-1.331710	1.828990
H	2.341346	0.101497	-1.642887
H	2.718254	1.355194	-0.456679
H	3.593695	-0.184696	-0.427364
H	1.475067	-0.552546	2.393766
H	1.956137	1.070964	1.890664
H	3.114004	-0.268393	1.790181
C	-0.450475	-1.024330	-1.194293
C	0.611597	-1.680367	-2.046092
C	1.186738	-2.813482	-1.630115
H	1.659555	-1.271272	0.159916
C	-1.625099	-0.524270	-2.037403
H	-0.844677	-1.831614	-0.574076
C	0.932669	-1.040376	-3.362999
C	2.234050	-3.628314	-2.312441
H	0.811666	-3.242786	-0.705072
H	-2.026524	-1.330854	-2.649829
H	-2.427848	-0.159209	-1.405578
H	-1.340754	0.287408	-2.701823
H	0.950023	0.044227	-3.290117
H	1.878199	-1.376978	-3.775643
H	0.156159	-1.283248	-4.087967
H	3.052642	-3.864103	-1.632615
H	1.822759	-4.582849	-2.642088
H	2.656375	-3.138584	-3.183842

Table S13. Optimized (MPW1K/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1a, 3a, 3e–$C_3H_3Me_3$** and **1**

1a, 3a, 3e–$C_3H_3Me_3$

C	0.031009	0.061490	-0.000121
C	1.336805	0.089876	-0.232413
C	2.250537	1.274405	-0.247672
H	1.678960	2.173508	-0.021809
H	-0.455571	-0.905820	-0.034732
C	-0.868736	1.209100	0.307455
H	1.825845	-0.856326	-0.441164
C	3.331654	1.122193	0.815563
C	2.873111	1.444212	-1.628330
H	-0.348104	2.160983	0.332865
H	-1.663776	1.282049	-0.434423
H	-1.354817	1.067193	1.272516
H	3.926822	0.227263	0.634847
H	4.007282	1.976093	0.808844
H	2.898333	1.037874	1.809461
H	3.546606	2.299596	-1.649227
H	3.450337	0.561264	-1.902313
H	2.110534	1.591679	-2.389547

1a, 3a, 3e–$C_3H_3Me_3$ + 1 ts

B	0.048433	-0.017657	0.019443
N	1.551899	0.074243	-0.005506
C	-0.721258	1.428187	0.015442
C	-0.529011	-0.877040	1.295415
C	2.175558	1.180480	-0.719097
C	2.318342	-0.190123	1.207027
F	-2.055346	1.321895	-0.032131
F	-0.438968	2.119809	1.130231
F	-0.394792	2.252549	-0.997999
F	-1.842020	-1.126175	1.206945
F	-0.344687	-0.275370	2.474481
F	0.042726	-2.102984	1.433543
H	1.681856	1.371470	-1.661940
H	2.151835	2.102182	-0.135798
H	3.217539	0.935644	-0.919641
H	2.003205	-1.108756	1.682803
H	2.220592	0.623612	1.926519
H	3.371535	-0.287747	0.947610
C	-0.618394	-0.854933	-1.483190
C	0.213256	-1.988087	-1.416151
C	1.580150	-2.105162	-1.759024
H	1.773864	-1.240075	-0.895802
C	-0.696468	0.031896	-2.715703
H	-1.613786	-1.086707	-1.119567
H	-0.128335	-2.746120	-0.723423
C	2.162974	-1.510343	-3.026782
C	2.249519	-3.408412	-1.376416
H	-1.534869	0.712321	-2.618308
H	0.180251	0.641641	-2.892415
H	-0.866181	-0.578524	-3.600079
H	3.241910	-1.418270	-2.927802
H	1.970844	-2.173662	-3.869048
H	1.764385	-0.535568	-3.271210
H	3.319867	-3.265661	-1.246278
H	2.117492	-4.156865	-2.157065
H	1.851094	-3.811325	-0.448975

1a, 3a, 3e–$C_3H_3Me_3$ + 1 product

B	0.079422	0.084161	0.054876
N	1.706080	0.087836	0.034148
C	-0.464184	1.618762	0.094031
C	-0.352479	-0.665264	1.445260
C	2.276541	0.874447	-1.075113
C	2.426879	0.413095	1.282136
F	-1.787049	1.674253	0.269988
F	0.075848	2.364775	1.081705
F	-0.211818	2.321953	-1.030112
F	-1.630907	-1.049249	1.460728
F	-0.176448	0.047709	2.570281
F	0.372310	-1.799228	1.634560
H	1.730964	0.676359	-1.987233
H	2.194150	1.928105	-0.839926
H	3.322939	0.612125	-1.204084
H	2.158491	-0.289606	2.057753
H	2.161988	1.414081	1.596615
H	3.496008	0.356570	1.095886
C	-0.479655	-0.809059	-1.213655
C	0.507227	-1.839910	-1.681377
C	0.556869	-3.147869	-1.423641
H	1.889327	-0.891586	-0.177334
C	-1.000858	-0.043533	-2.434290
H	-1.343398	-1.334496	-0.812016
H	1.260758	-1.471696	-2.374702
C	1.618983	-4.007166	-2.035954
C	-0.415575	-3.886981	-0.564407
H	-1.417105	-0.743133	-3.157350
H	-1.782522	0.660036	-2.163944
H	-0.221970	0.522242	-2.943064
H	2.199195	-4.518756	-1.267097
H	1.172598	-4.785508	-2.655658
H	2.301739	-3.431853	-2.655735
H	0.095143	-4.348420	0.280300
H	-1.204819	-3.259124	-0.169233
H	-0.871882	-4.696003	-1.135780

Table S14. Optimized (MPW1K/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1e, 2, 3a–$C_3H_3Me_3$** and **1**

1e, 2, 3a–$C_3H_3Me_3$

C	0.203751	-0.125913	0.071125
C	1.525045	-0.228192	-0.043464
C	2.372118	1.007997	-0.152990
H	1.722816	1.879400	-0.218215
C	-0.802700	-1.217488	0.195369
H	-0.210427	0.876089	0.077156
C	2.273360	-1.523527	-0.076823
C	3.349072	1.191302	1.000205
H	2.935028	0.969354	-1.089028
H	-0.361873	-2.208869	0.182455
H	-1.363258	-1.118224	1.125025
H	-1.530622	-1.165084	-0.614375
H	1.621402	-2.386618	-0.150847
H	2.954797	-1.544616	-0.927718
H	2.884069	-1.647353	0.817208
H	4.070771	0.379180	1.052051
H	3.908893	2.117408	0.887658
H	2.821957	1.230754	1.951570

1e, 2, 3a–$C_3H_3Me_3$ + 1 ts

B	0.015986	-0.059279	0.096426
N	1.538906	-0.123234	0.080635
C	-0.550344	1.467189	-0.071361
C	-0.597052	-0.685509	1.475775
C	2.213892	0.792385	-0.832023
C	2.289073	-0.169685	1.331153
F	-1.839392	1.611619	0.254694
F	0.121513	2.334548	0.706251
F	-0.440074	1.954044	-1.325802
F	-1.920662	-0.895443	1.437936
F	-0.381783	0.084419	2.550671
F	-0.065475	-1.893834	1.789173
H	1.692772	0.859212	-1.779627
H	2.272208	1.796326	-0.412879
H	3.227294	0.441484	-1.017650
H	1.933729	-0.962895	1.974377
H	2.219335	0.775267	1.869309
H	3.337918	-0.358193	1.106966
C	-0.572408	-0.927594	-1.331416
C	-0.030512	-2.237458	-1.140864
C	1.356846	-2.446239	-1.306065
H	1.622723	-1.496939	-0.513217
H	-0.015761	-0.379406	-2.088612
C	-2.063991	-0.804186	-1.592477
C	-0.870101	-3.323099	-0.578735
C	2.092595	-2.035022	-2.570044
H	1.694723	-3.408409	-0.935012
H	-2.334781	0.231860	-1.760323
H	-2.668469	-1.165372	-0.768943
H	-2.337690	-1.361970	-2.487250
H	3.152921	-1.898068	-2.375307
H	1.997528	-2.814014	-3.324430
H	1.713703	-1.113515	-2.998295
H	-0.272663	-4.055896	-0.046631
H	-1.672335	-2.968002	0.056238
H	-1.329354	-3.830922	-1.431973

1e, 2, 3a–$C_3H_3Me_3$ + 1 product

B	-0.028535	0.018730	0.030491
N	1.560715	-0.301614	0.248097
C	-0.177553	1.605413	-0.330224
C	-0.792502	-0.229299	1.458306
C	2.449739	0.352642	-0.735053
C	2.142776	-0.126063	1.594525
F	-1.439533	2.030004	-0.252950
F	0.543075	2.419269	0.472184
F	0.227185	1.911878	-1.583298
F	-2.115171	-0.101637	1.387825
F	-0.408329	0.605930	2.442448
F	-0.569232	-1.474236	1.954353
H	2.047739	0.237978	-1.730398
H	2.529330	1.405344	-0.495819
H	3.431676	-0.108675	-0.683886
H	1.630490	-0.755568	2.307973
H	2.045031	0.909855	1.892378
H	3.193626	-0.399862	1.557821
C	-0.629586	-0.898997	-1.217231
C	0.382535	-1.719215	-1.994672
C	1.002439	-2.823172	-1.569074
H	1.607881	-1.289333	0.015504
H	-0.980290	-0.156595	-1.933734
C	-1.870446	-1.754880	-0.919847
C	0.598756	-1.261746	-3.406899
H	1.662630	-3.312771	-2.275621
C	0.861781	-3.532072	-0.260400
H	-2.158934	-2.301910	-1.816109
H	-1.709565	-2.483459	-0.131572
H	-2.710129	-1.134506	-0.625625
H	0.846302	-0.201542	-3.456686
H	1.376938	-1.828901	-3.910907
H	-0.326785	-1.378656	-3.972564
H	1.837825	-3.779961	0.159794
H	0.300081	-2.974529	0.481290
H	0.345072	-4.482052	-0.400030

Table S15. Optimized (MPW1K/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1e, 2, 3e–$C_3H_3Me_3$** and **1**

1e, 2, 3e–$C_3H_3Me_3$

C	0.203751	-0.125913	0.071125
C	1.525045	-0.228192	-0.043464
C	2.372118	1.007997	-0.152990
H	1.722816	1.879400	-0.218215
C	-0.802700	-1.217488	0.195369
H	-0.210427	0.876089	0.077156
C	2.273360	-1.523527	-0.076823
C	3.349072	1.191302	1.000205
H	2.935028	0.969354	-1.089028
H	-0.361873	-2.208869	0.182455
H	-1.363258	-1.118224	1.125025
H	-1.530622	-1.165084	-0.614375
H	1.621402	-2.386618	-0.150847
H	2.954797	-1.544616	-0.927718
H	2.884069	-1.647353	0.817208
H	4.070771	0.379180	1.052051
H	3.908893	2.117408	0.887658
H	2.821957	1.230754	1.951570

1e, 2, 3e–$C_3H_3Me_3$ + 1 ts

B	-0.016457	0.015064	0.177574
N	1.500497	-0.011468	0.204081
C	-0.608564	1.524926	-0.029747
C	-0.645463	-0.624857	1.541427
C	2.188443	0.822942	-0.767200
C	2.221375	0.030262	1.469082
F	-1.909907	1.654562	0.252257
F	0.025285	2.413876	0.755408
F	-0.462713	1.993973	-1.287438
F	-1.961670	-0.872220	1.473777
F	-0.476120	0.138241	2.628478
F	-0.085257	-1.822976	1.851562
H	1.708545	0.773589	-1.739108
H	2.208089	1.868812	-0.461149
H	3.217540	0.481428	-0.876491
H	1.852002	-0.717000	2.158286
H	2.140324	1.009381	1.942078
H	3.275708	-0.171899	1.284295
C	-0.555582	-0.890250	-1.246209
C	-0.018284	-2.198226	-1.036909
C	1.384485	-2.359372	-1.159883
H	1.636757	-1.441600	-0.376790
H	0.029908	-0.359442	-1.995146
C	-2.037198	-0.771362	-1.562482
C	-0.883185	-3.298907	-0.556038
H	1.779304	-1.849581	-2.037282
C	2.069813	-3.669075	-0.863989
H	-2.285725	0.254222	-1.810130
H	-2.673209	-1.064610	-0.735679
H	-2.292260	-1.385587	-2.425308
H	3.146763	-3.552229	-0.949378
H	1.863928	-4.016726	0.145204
H	1.773246	-4.455244	-1.556899
H	-0.337903	-4.030590	0.027874
H	-1.740877	-2.945100	0.002723
H	-1.261519	-3.808949	-1.447314

1e, 2, 3e–$C_3H_3Me_3$ + 1 product

B	0.071835	-0.101280	0.066578
N	1.697060	-0.050987	0.128109
C	-0.498715	1.433545	0.100998
C	-0.440882	-0.844367	1.434203
C	2.284275	0.852808	-0.878925
C	2.358730	0.169753	1.429184
F	-1.799724	1.492187	0.393062
F	0.122947	2.226933	1.001718
F	-0.361483	2.085984	-1.073052
F	-1.729123	-1.175201	1.422755
F	-0.268514	-0.104236	2.546122
F	0.229733	-1.999643	1.687902
H	1.802970	0.699510	-1.835128
H	2.135312	1.878943	-0.566008
H	3.347971	0.651106	-0.966982
H	2.087427	-0.616278	2.119441
H	2.047343	1.124707	1.831378
H	3.435306	0.165584	1.281070
C	-0.340284	-0.813144	-1.355856
C	0.615761	-1.836447	-1.946206
C	1.117341	-2.850530	-1.237284
H	1.924568	-0.994652	-0.185122
H	-0.344650	0.011878	-2.071181
C	-1.765284	-1.379736	-1.404837
C	0.861160	-1.659613	-3.413869
C	1.990628	-3.964937	-1.709624
H	0.817410	-2.928711	-0.200204
H	-2.021904	-1.669603	-2.423125
H	-1.866893	-2.258659	-0.775859
H	-2.496804	-0.646858	-1.074460
H	1.343018	-0.703751	-3.622029
H	1.467046	-2.443802	-3.853488
H	-0.092152	-1.639986	-3.942169
H	2.849936	-4.089728	-1.051371
H	1.446796	-4.909744	-1.687096
H	2.364588	-3.822896	-2.717925

Table S16. Optimized (MPW1K/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1e, 3a, 3e–$C_3H_3Me_3$** and **1**

1e, 3a, 3e–$C_3H_3Me_3$

C	0.071256	-0.083706	0.198108
C	1.352727	-0.021733	-0.127504
C	2.191191	1.216493	-0.120478
H	1.559546	2.047474	0.198600
C	-0.758886	-1.320082	0.188226
H	-0.430311	0.830326	0.498351
H	1.861423	-0.933589	-0.429163
C	3.342884	1.082397	0.867924
C	2.714158	1.521381	-1.518679
H	-0.178594	-2.185116	-0.122826
H	-1.169977	-1.525149	1.176500
H	-1.606008	-1.218589	-0.489877
H	3.991430	0.250140	0.594464
H	3.952097	1.984841	0.882106
H	2.977397	0.901931	1.876125
H	3.319851	2.426235	-1.519803
H	3.337895	0.705709	-1.884287
H	1.897220	1.656935	-2.223577

1e, 3a, 3e–$C_3H_3Me_3$ + 1 ts

B	0.017234	-0.060152	0.059346
N	1.523641	-0.115331	0.063403
C	-0.562548	1.463757	-0.086284
C	-0.636082	-0.761203	1.381437
C	2.221658	0.812963	-0.815499
C	2.259253	-0.229564	1.316525
F	-1.852188	1.598749	0.238713
F	0.104069	2.310998	0.717112
F	-0.445994	1.979108	-1.326904
F	-1.958357	-0.944358	1.306074
F	-0.424858	-0.064972	2.506357
F	-0.128438	-1.997626	1.623290
H	1.712466	0.912252	-1.767038
H	2.293482	1.805321	-0.370373
H	3.231046	0.450339	-1.001660
H	1.875790	-1.035782	1.927141
H	2.210403	0.695702	1.890964
H	3.305230	-0.438300	1.096346
C	-0.573984	-0.890031	-1.447831
C	-0.018629	-2.163129	-1.225068
C	1.353543	-2.473435	-1.354908
H	1.613792	-1.543840	-0.583442
H	-0.037568	-0.296022	-2.182830
C	-2.075571	-0.818542	-1.652365
H	-0.637495	-2.861490	-0.670854
C	2.094408	-2.059727	-2.617037
C	1.801026	-3.815178	-0.819827
H	-2.447687	0.195177	-1.568934
H	-2.607588	-1.427590	-0.928929
H	-2.323626	-1.179958	-2.648593
H	3.158986	-1.956857	-2.421983
H	1.975253	-2.829649	-3.378536
H	1.738024	-1.122865	-3.030635
H	2.867618	-3.807379	-0.606453
H	1.281030	-4.072656	0.098874
H	1.624412	-4.606618	-1.547929

1e, 3a, 3e–$C_3H_3Me_3$ + 1 product

B	0.080585	-0.076090	0.109761
N	1.703820	0.095605	0.022374
C	-0.610543	1.401815	0.164218
C	-0.206373	-0.853763	1.515707
C	2.144286	0.954527	-1.092949
C	2.444249	0.476461	1.244362
F	-1.858945	1.369788	0.634707
F	0.053049	2.293899	0.934878
F	-0.689311	1.993572	-1.045817
F	-1.428462	-1.378432	1.611172
F	-0.058255	-0.085268	2.611208
F	0.652675	-1.889120	1.699411
H	1.633593	0.674207	-2.003851
H	1.910153	1.985586	-0.857490
H	3.217044	0.850059	-1.227770
H	2.285540	-0.260516	2.018017
H	2.094594	1.441205	1.586749
H	3.503757	0.531042	1.009473
C	-0.375268	-0.884626	-1.239478
C	0.575461	-1.988940	-1.639221
C	0.645095	-3.277859	-1.299681
H	1.977295	-0.856729	-0.211782
H	-0.258429	-0.140103	-2.029567
C	-1.859481	-1.253563	-1.319296
H	1.324734	-1.680892	-2.364881
C	1.693823	-4.158252	-1.908009
C	-0.269417	-3.995155	-0.361001
H	-2.076483	-1.702477	-2.286989
H	-2.181709	-1.945807	-0.552361
H	-2.476129	-0.363275	-1.221021
H	2.322393	-4.604117	-1.136287
H	1.232843	-4.986303	-2.447708
H	2.331458	-3.617371	-2.602156
H	0.312396	-4.556092	0.369643
H	-0.938011	-3.341535	0.178891
H	-0.867188	-4.723552	-0.911034

Table S17. Optimized (MPW1K/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **2, 3a, 3e–$C_3H_3Me_3$** and **1**

2, 3a, 3e–$C_3H_3Me_3$

C	-0.664214	-0.474000	-0.000884
C	0.800864	-0.123456	-0.000212
C	1.728456	-1.070537	-0.001871
H	2.782714	-0.832573	-0.001415
H	1.463515	-2.117632	-0.003744
C	1.179949	1.333810	0.002359
H	0.311709	1.986010	0.003805
H	1.773706	1.580144	0.879857
H	1.773187	1.583370	-0.874580
C	-1.363481	0.030539	1.255610
H	-2.407485	-0.277902	1.260129
H	-0.889967	-0.362134	2.152517
H	-1.345107	1.117785	1.315163
C	-1.363450	0.035291	-1.255476
H	-0.889967	-0.354045	-2.153853
H	-2.407478	-0.273048	-1.261151
H	-1.344986	1.122751	-1.310941
H	-0.728592	-1.562610	-0.002942

2, 3a, 3e–$C_3H_3Me_3$ + 1 ts

C	-0.469047	-0.044432	-1.459680
C	-1.732781	0.424357	-0.992040
C	-2.530618	-0.421377	-0.182064
C	-3.730591	0.166223	0.526217
H	-3.486199	1.056922	1.097909
H	-4.526672	0.422776	-0.173584
H	-4.139568	-0.562717	1.221830
C	-2.807256	-1.843354	-0.653986
H	-2.009262	-2.264674	-1.253193
H	-2.980260	-2.506129	0.189887
H	-3.713525	-1.845968	-1.259586
H	-1.535079	-0.605666	0.584751
N	-0.110840	-0.922492	1.013271
B	0.559086	-0.073638	-0.057228
C	1.964328	-0.694532	-0.615948
F	2.639457	0.146450	-1.407262
F	2.804503	-1.028209	0.378117
F	1.810257	-1.819389	-1.346898
C	0.834138	1.459691	0.428378
F	-0.243715	2.029744	1.026243
F	1.831526	1.579617	1.312627
F	1.135641	2.284155	-0.584682
C	0.058928	-2.365233	0.888220
H	-0.058828	-2.684621	-0.139679
H	1.047193	-2.678953	1.224357
H	-0.685344	-2.874381	1.497847
C	0.012824	-0.557802	2.419982
H	-0.653865	-1.184797	3.010207
H	1.030630	-0.711161	2.779638
H	-0.259881	0.475519	2.585001
C	-2.072996	1.857953	-1.172311
H	-1.229050	2.440816	-1.520211
H	-2.859570	1.899412	-1.930929
H	-2.479141	2.311718	-0.275723
H	-0.449525	-1.080242	-1.778788
H	0.007807	0.597507	-2.190394

2, 3a, 3e–$C_3H_3Me_3$ + 1 product

C	0.627086	0.115775	-1.158111
C	1.942534	0.636550	-0.646732
C	3.031187	-0.117369	-0.465159
C	4.313329	0.412715	0.103118
H	5.108835	0.382147	-0.643516
H	4.245019	1.424791	0.484138
H	4.639598	-0.222313	0.927153
C	3.119518	-1.579205	-0.775081
H	4.036410	-1.782824	-1.329206
H	3.171465	-2.161188	0.145205
H	2.288752	-1.961995	-1.354563
C	1.956190	2.113845	-0.346617
H	2.918747	2.574768	-0.541342
H	1.236334	2.640823	-0.973700
H	1.720700	2.325723	0.701288
H	0.341698	0.699710	-2.037497
H	0.744611	-0.897066	-1.532911
B	-0.628678	0.037879	-0.134360
N	-1.142770	1.530421	0.282447
H	-0.276624	1.997825	0.521676
C	-1.735240	2.280933	-0.840579
H	-1.108944	2.190208	-1.717509
H	-2.712629	1.869671	-1.060930
H	-1.836918	3.326474	-0.564067
C	-2.024373	1.646596	1.465022
H	-2.273730	2.693160	1.617484
H	-2.926561	1.075806	1.292049
H	-1.518082	1.264175	2.339791
C	-1.849923	-0.759512	-0.857261
F	-1.620205	-2.071483	-0.931907
F	-3.052038	-0.624509	-0.253471
F	-2.058684	-0.350643	-2.127012
C	-0.197459	-0.711071	1.244385
F	0.534035	0.113025	2.039560
F	-1.220177	-1.119984	2.019539
F	0.555625	-1.788382	1.040316

Table S18. Optimized (MPW1K/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1a, 1e–$C_3H_4Me_2$** and **1**, and between propene **1a, 2–$C_3H_4Me_2$** and **1**

1a, 1e–$C_3H_4Me_2$ = 1a, 2–$C_3H_4Me_2$

C	-2.093045	-0.078136	0.000000
C	-0.725987	-0.669905	-0.000005
C	0.445255	-0.040661	-0.000002
C	1.728096	-0.811216	0.000001
H	1.554434	-1.883582	-0.000007
H	2.330740	-0.563459	-0.874740
H	2.330730	-0.563470	0.874753
C	0.617154	1.444193	0.000000
H	1.187400	1.760178	-0.874178
H	-0.321965	1.985954	0.000016
H	1.187416	1.760169	0.874170
H	-0.699167	-1.753663	0.000003
H	-2.655191	-0.407578	-0.873892
H	-2.655008	-0.407141	0.874178
H	-2.088230	1.006945	-0.000273

1a, 1e–$C_3H_4Me_2$ + 1 ts

C	-1.328359	-0.781683	-0.886995
C	-2.195935	0.319956	-0.844253
C	-2.951183	0.678791	0.283057
H	-3.549980	1.575423	0.211356
H	-3.413020	-0.118034	0.853927
H	-1.904727	0.860429	0.938973
N	-0.472188	0.778630	1.341345
B	0.085548	0.078381	0.126445
C	1.125631	-1.134890	0.503124
F	1.553734	-1.851385	-0.541234
F	2.227267	-0.613145	1.069102
F	0.677946	-2.045687	1.386658
C	0.872943	1.085514	-0.904259
F	0.062036	1.993238	-1.501982
F	1.820851	1.812005	-0.294221
F	1.494582	0.460501	-1.906030
C	-0.470447	0.127977	2.646406
H	-0.826075	-0.890561	2.578596
H	0.525183	0.114215	3.088753
H	-1.131652	0.678946	3.312724
C	-0.251679	2.212162	1.520711
H	-0.961208	2.587794	2.256251
H	0.756159	2.421383	1.872652
H	-0.410087	2.749242	0.593876
H	-2.078664	1.058132	-1.626768
C	-1.755960	-2.008863	-0.097616
H	-1.004863	-2.787830	-0.154984
H	-1.943931	-1.810815	0.952199
H	-2.675030	-2.403945	-0.531335
C	-0.846765	-1.150981	-2.280274
H	0.063349	-1.736587	-2.255672
H	-1.616095	-1.752140	-2.765170
H	-0.669002	-0.275615	-2.897063

1a, 1e–$C_3H_4Me_2$ + 1 product

C	-1.363266	-0.716054	-0.507282
C	-2.396434	-0.643669	0.593989
C	-3.166960	0.385929	0.923553
H	-3.884655	0.302029	1.726053
H	-3.126384	1.328660	0.399768
F	-0.727356	2.301976	0.077773
C	0.248092	1.529196	-0.466566
B	0.089424	-0.038300	0.001900
N	0.095934	-0.008456	1.640629
H	-0.867406	0.271292	1.823195
C	0.259287	-1.337725	2.260617
H	-0.347143	-2.068359	1.744978
H	1.298407	-1.634769	2.195021
H	-0.037554	-1.284243	3.304244
C	0.965661	0.951857	2.352777
H	0.851192	0.793712	3.421684
H	1.995823	0.789147	2.064527
H	0.679839	1.964222	2.106539
F	1.399219	2.116002	-0.088137
C	1.422516	-0.834703	-0.506365
F	1.559943	-0.784891	-1.833996
F	2.565437	-0.334308	0.008665
F	1.461866	-2.144242	-0.183737
F	0.186041	1.724691	-1.781134
H	-2.522707	-1.553173	1.174811
C	-1.247380	-2.197903	-0.897082
H	-2.225974	-2.564652	-1.207503
H	-0.566594	-2.336862	-1.731661
H	-0.900379	-2.835952	-0.088243
C	-1.927544	-0.016093	-1.753394
H	-2.856942	-0.505565	-2.041241
H	-2.143218	1.034691	-1.595430
H	-1.235139	-0.087547	-2.587027

1a, 2–$C_3H_4Me_2$ + 1 ts

C	-0.893573	-0.842906	-1.081606
C	-2.152148	-0.673547	-0.433340
C	-2.421649	-1.395815	0.750464
H	-3.371836	-1.213155	1.233306
H	-2.121261	-2.437518	0.765960
C	-3.095465	0.376896	-0.880446
H	-2.618769	1.145528	-1.476353
H	-3.825029	-0.133753	-1.515919
H	-3.641787	0.823623	-0.055838
B	0.225000	-0.016224	0.057732
N	0.056972	-0.512356	1.480829
C	0.723230	-1.746387	1.868336
H	0.671371	-2.487360	1.082787
H	1.776271	-1.581566	2.099609
H	0.242323	-2.150749	2.758985
C	0.123929	0.419996	2.599897
H	-0.219706	-0.084521	3.502065
H	1.144971	0.762749	2.772649
H	-0.506023	1.283466	2.438271
C	1.718887	-0.268249	-0.565655
F	1.825060	0.101256	-1.850052
F	2.651557	0.425823	0.102936
F	2.148533	-1.545758	-0.527820
C	-0.090297	1.588457	-0.075705
F	-1.268527	1.946344	0.497652
F	0.823599	2.381696	0.489821
F	-0.194210	1.997594	-1.349939
C	-0.490134	-2.279117	-1.407871
H	0.470119	-2.305993	-1.906501
H	-0.427168	-2.928201	-0.541592
H	-1.225378	-2.710050	-2.085877
H	-0.824067	-0.230895	-1.975952
H	-1.458612	-0.922559	1.342114

1a, 2–$C_3H_4Me_2$ + 1 product

C	1.064126	-0.076980	-1.110325
C	2.376414	-0.522705	-0.523140
C	2.707520	-1.814090	-0.489233
H	3.639170	-2.150323	-0.058314
H	2.081679	-2.568014	-0.949368
F	-1.374200	-1.887613	-1.241967
C	-1.508814	-0.575385	-0.912682
B	-0.214455	-0.052127	-0.063659
N	0.044393	-1.118963	1.143172
H	0.636932	-1.812277	0.691598
C	0.859271	-0.591803	2.258016
H	1.723588	-0.072710	1.873626
H	0.256359	0.090259	2.843543
H	1.182182	-1.420355	2.881471
C	-1.126473	-1.818239	1.713821
H	-0.784898	-2.492860	2.493915
H	-1.803309	-1.086091	2.135275
H	-1.635927	-2.382418	0.946550
F	-2.693576	-0.490492	-0.285827
C	-0.561482	1.395653	0.595968
F	-1.129257	2.239349	-0.264963
F	-1.414921	1.308724	1.642837
F	0.517690	2.043274	1.086921
F	-1.664482	0.064120	-2.072573
C	3.322223	0.518129	-0.009388
H	2.824336	1.257560	0.614551
H	4.141045	0.070417	0.547053
H	3.749069	1.068659	-0.846718
C	1.208612	1.209768	-1.923567
H	1.969314	1.092407	-2.694325
H	0.276263	1.462597	-2.416527
H	1.490001	2.057526	-1.304639
H	0.796062	-0.863351	-1.818278

Table S19. Optimized (MPW1K/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1a, 3a–$C_3H_4Me_2$** and **1**, and between propene **1a, 3e–$C_3H_4Me_2$** and **1**

1a, 3a–$C_3H_4Me_2$ = 1a, 3e–$C_3H_4Me_2$

C	0.088941	0.035259	0.032611
C	1.403499	-0.056782	-0.122347
C	2.390531	1.051624	-0.277792
H	1.890199	2.016641	-0.304833
H	-0.461937	-0.891647	0.136629
C	-0.741032	1.271911	0.079272
H	1.832681	-1.052489	-0.128169
C	3.439414	1.047239	0.825316
H	2.891194	0.940669	-1.241870
H	-0.152587	2.180115	-0.001948
H	-1.472401	1.273978	-0.728805
H	-1.304666	1.319791	1.010675
H	3.969541	0.096822	0.858171
H	4.176321	1.832721	0.670973
H	2.979592	1.200889	1.799197

1a, 3a–$C_3H_4Me_2$ + 1 ts

B	0.097593	-0.017381	0.019638
N	1.600606	-0.110544	0.119132
C	-0.473832	1.502137	-0.194996
C	-0.681416	-0.651102	1.319715
C	2.412471	0.844385	-0.624743
C	2.228155	-0.349408	1.415124
F	-1.802254	1.553500	-0.352734
F	-0.191863	2.269992	0.868862
F	0.034797	2.167652	-1.248630
F	-2.005870	-0.738715	1.142107
F	-0.503634	0.050497	2.443740
F	-0.292907	-1.915118	1.629295
H	2.023582	1.000503	-1.621592
H	2.454238	1.812993	-0.125201
H	3.428650	0.462101	-0.706571
H	1.773378	-1.187202	1.926465
H	2.160483	0.527835	2.058655
H	3.281487	-0.578563	1.261557
C	-0.561976	-0.928110	-1.447221
C	0.129142	-2.126654	-1.197662
C	1.493436	-2.402468	-1.422625
H	1.742241	-1.490344	-0.611987
C	-0.429537	-0.180317	-2.763286
H	-1.602877	-1.003446	-1.151482
H	-0.336772	-2.771563	-0.465091
C	2.270632	-2.065137	-2.677359
H	1.800534	-3.348876	-0.991288
H	-1.148291	0.630232	-2.798190
H	0.546139	0.254707	-2.938854
H	-0.649579	-0.853194	-3.589511
H	3.335493	-2.172445	-2.488250
H	2.012420	-2.751068	-3.481462
H	2.097861	-1.057262	-3.031466

1a, 3a–$C_3H_4Me_2$ + 1 product

B	0.071061	0.092748	0.050039
N	1.697370	0.082959	0.011182
C	-0.459811	1.632130	0.083753
C	-0.351802	-0.642738	1.450425
C	2.261267	0.856219	-1.111087
C	2.433767	0.414940	1.248713
F	-1.780123	1.699077	0.273437
F	0.096710	2.380306	1.060226
F	-0.213893	2.325109	-1.048040
F	-1.633105	-1.015286	1.482766
F	-0.156728	0.077239	2.567584
F	0.365398	-1.781269	1.639340
H	1.702607	0.657271	-2.015108
H	2.191526	1.912190	-0.882315
H	3.303392	0.583132	-1.251222
H	2.170036	-0.279805	2.033094
H	2.178128	1.420066	1.557385
H	3.500320	0.350368	1.050919
C	-0.513224	-0.803265	-1.206250
C	0.462203	-1.837591	-1.686869
C	0.517586	-3.135844	-1.399292
H	1.874816	-0.899140	-0.191338
C	-1.053616	-0.040545	-2.419871
H	-1.368612	-1.328810	-0.786285
H	1.198078	-1.483046	-2.404300
H	1.298767	-3.711709	-1.882073
C	-0.393264	-3.915867	-0.518274
H	-1.483674	-0.740703	-3.134197
H	-1.829358	0.664715	-2.137580
H	-0.281944	0.522600	-2.942184
H	0.155449	-4.353523	0.314547
H	-1.196751	-3.316967	-0.104627
H	-0.832156	-4.742852	-1.076016

1a, 3e–$C_3H_4Me_2$ + 1 ts

B	0.047460	-0.017050	-0.007280
N	1.547907	0.079305	-0.070047
C	-0.731149	1.423805	0.016860
C	-0.500184	-0.892432	1.269236
C	2.159850	1.190640	-0.785142
C	2.350989	-0.221549	1.109885
F	-2.063863	1.310063	-0.040646
F	-0.458993	2.092025	1.147804
F	-0.404804	2.273604	-0.975963
F	-1.815677	-1.134590	1.206631
F	-0.284510	-0.312353	2.453516
F	0.070131	-2.122483	1.371862
H	1.633011	1.407757	-1.703983
H	2.171917	2.100011	-0.183065
H	3.190215	0.934339	-1.028930
H	2.044431	-1.150353	1.571435
H	2.280692	0.573780	1.852373
H	3.394655	-0.318216	0.814447
C	-0.643065	-0.846653	-1.504579
C	0.155564	-1.999433	-1.443856
C	1.501993	-2.036471	-1.852771
H	1.760588	-1.186822	-0.994908
C	-0.587592	0.009489	-2.757313
H	-1.661051	-1.020213	-1.174031
H	-0.177484	-2.797173	-0.792754
H	1.731852	-1.455405	-2.741966
C	2.302543	-3.305680	-1.709663
H	-1.219654	0.883247	-2.663721
H	0.411514	0.352103	-3.005114
H	-0.951762	-0.573401	-3.601992
H	3.368420	-3.094256	-1.696606
H	2.116434	-3.987858	-2.536694
H	2.056253	-3.823915	-0.785795

1a, 3e–$C_3H_4Me_2$ + 1 product

B	0.032650	0.049823	-0.011199
N	1.654697	-0.008630	0.026924
C	-0.447756	1.606199	0.027978
C	-0.494756	-0.697174	1.345142
C	2.287261	0.798751	-1.032612
C	2.343886	0.235897	1.309874
F	-1.766152	1.722992	0.201707
F	0.124644	2.320246	1.022535
F	-0.160518	2.303164	-1.091264
F	-1.797677	-0.980148	1.313137
F	-0.296256	-0.031752	2.495310
F	0.134762	-1.890120	1.517501
H	1.762229	0.655119	-1.967319
H	2.236496	1.845104	-0.758720
H	3.326576	0.501978	-1.142039
H	2.025984	-0.491758	2.042938
H	2.101939	1.229948	1.661944
H	3.416115	0.150138	1.155192
C	-0.508081	-0.817883	-1.311020
C	0.507876	-1.787414	-1.846269
C	0.711568	-3.033434	-1.432519
H	1.811481	-0.984249	-0.223580
C	-1.100142	-0.024165	-2.476967
H	-1.324814	-1.418473	-0.912633
H	1.118660	-1.433449	-2.674459
C	1.709080	-3.973136	-2.016771
H	0.099732	-3.419297	-0.625720
H	-1.509011	-0.704787	-3.222400
H	-1.903174	0.630166	-2.151105
H	-0.358945	0.599349	-2.973994
H	2.402264	-4.339338	-1.259597
H	1.215001	-4.850197	-2.434041
H	2.285243	-3.502458	-2.810002

Table S20. Optimized (MPW1K/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1e, 2–$C_3H_4Me_2$** and **1**

1e, 2–$C_3H_4Me_2$

C	-2.093045	-0.078136	0.000000
C	-0.725987	-0.669905	-0.000005
C	0.445255	-0.040661	-0.000002
C	1.728096	-0.811216	0.000001
H	1.554434	-1.883582	-0.000007
H	2.330740	-0.563459	-0.874740
H	2.330730	-0.563470	0.874753
C	0.617154	1.444193	0.000000
H	1.187400	1.760178	-0.874178
H	-0.321965	1.985954	0.000016
H	1.187416	1.760169	0.874170
H	-0.699167	-1.753663	0.000003
H	-2.655191	-0.407578	-0.873892
H	-2.655008	-0.407141	0.874178
H	-2.088230	1.006945	-0.000273

1e, 2–$C_3H_4Me_2$ + 1 ts

C	0.924041	-0.366938	-1.294593
C	2.130654	0.246042	-0.848543
C	2.223150	1.653969	-0.914295
H	3.107581	2.113225	-0.494716
H	1.903962	2.101861	-1.850457
C	3.185281	-0.543948	-0.173577
H	2.790888	-1.390347	0.376588
H	3.832700	-0.942266	-0.959628
H	3.796093	0.072482	0.477136
B	-0.247982	0.101947	-0.040386
N	-0.305894	1.617540	0.011329
C	-0.986784	2.285694	-1.086226
H	-0.743044	1.826792	-2.038624
H	-2.069635	2.252867	-0.969685
H	-0.679497	3.330519	-1.122120
C	-0.613049	2.306644	1.257757
H	-0.430958	3.372611	1.127635
H	-1.657060	2.170975	1.540678
H	0.013184	1.954947	2.066173
C	-1.662794	-0.558719	-0.526887
F	-1.779044	-1.867247	-0.275776
F	-2.709938	0.024407	0.082242
F	-1.898045	-0.421920	-1.848710
C	0.166407	-0.528623	1.406790
F	1.249250	0.085025	1.947486
F	-0.796663	-0.431459	2.331595
F	0.497881	-1.826953	1.362302
H	0.490792	0.200047	-2.116773
C	0.952100	-1.848009	-1.627056
H	-0.012285	-2.169591	-2.002507
H	1.687699	-2.045725	-2.405848
H	1.187868	-2.469311	-0.771050
H	1.177880	1.855031	-0.286650

1e, 2–$C_3H_4Me_2$ + 1 product

C	-1.249360	-0.056707	-0.835369
C	-2.507415	0.115707	-0.010477
C	-2.679689	1.061036	0.911400
H	-3.621777	1.163268	1.430045
H	-1.919936	1.795039	1.131355
F	0.245217	2.221868	1.028983
C	0.896271	1.433710	0.133659
B	0.188646	-0.032724	-0.042646
N	-0.068451	-0.620616	1.452740
H	-0.918360	-0.120729	1.713376
C	-0.432663	-2.049954	1.454445
H	-1.172955	-2.241872	0.689554
H	0.450663	-2.642527	1.250431
H	-0.833380	-2.318205	2.427655
C	0.938346	-0.370085	2.503369
H	0.599514	-0.827118	3.429130
H	1.884116	-0.802526	2.204797
H	1.059973	0.693530	2.651087
F	2.159631	1.369747	0.595649
C	1.256123	-1.007706	-0.810484
F	1.783385	-0.438053	-1.895980
F	2.300420	-1.386011	-0.041395
F	0.714422	-2.168369	-1.237590
F	0.963201	2.145561	-0.987995
C	-3.623113	-0.823591	-0.349646
H	-3.333190	-1.862021	-0.186843
H	-4.518990	-0.621270	0.230346
H	-3.872744	-0.738464	-1.407204
H	-1.315676	-1.064874	-1.249042
C	-1.329305	0.875286	-2.052405
H	-2.234614	0.675703	-2.624093
H	-1.348708	1.918545	-1.754108
H	-0.479665	0.732589	-2.714450

Table S21. Optimized (MPW1K/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1e, 3a–$C_3H_4Me_2$** and **1**, and between propene **1e, 3e–$C_3H_4Me_2$** and **1**

1e, 3a–$C_3H_4Me_2$ = 1e, 3e–$C_3H_4Me_2$

C	0.135115	-0.096361	0.080558
C	1.445426	-0.136892	-0.104597
C	2.340644	1.053431	-0.185893
H	1.742202	1.961835	-0.124944
C	-0.757085	-1.285363	0.167410
H	-0.343249	0.872766	0.175570
H	1.928259	-1.105127	-0.196981
C	3.408402	1.060198	0.898132
H	2.828202	1.068885	-1.162931
H	-0.196084	-2.210895	0.064672
H	-1.284068	-1.312348	1.120961
H	-1.518433	-1.262470	-0.612076
H	4.024973	0.164153	0.847176
H	4.066591	1.920700	0.797085
H	2.956866	1.093497	1.887348

1e, 3a–$C_3H_4Me_2$ + 1 ts

B	0.008792	-0.063937	0.059342
N	1.516897	-0.121093	0.074851
C	-0.566340	1.460792	-0.095617
C	-0.654963	-0.758563	1.379683
C	2.222041	0.807762	-0.799171
C	2.240688	-0.232635	1.335848
F	-1.857483	1.598747	0.220587
F	0.096825	2.308656	0.709912
F	-0.440607	1.972298	-1.336683
F	-1.977237	-0.937533	1.295954
F	-0.449175	-0.056179	2.502007
F	-0.152574	-1.994037	1.630735
H	1.719676	0.906386	-1.754318
H	2.289999	1.799540	-0.352949
H	3.232539	0.444543	-0.977178
H	1.854451	-1.041683	1.940923
H	2.180932	0.691962	1.909648
H	3.289367	-0.436761	1.125106
C	-0.579535	-0.895484	-1.453089
C	-0.014107	-2.161004	-1.217564
C	1.359949	-2.442992	-1.350613
H	1.626987	-1.524013	-0.558029
H	-0.041476	-0.301584	-2.187236
C	-2.080176	-0.827883	-1.659527
H	-0.622458	-2.862405	-0.658405
C	2.132408	-2.069040	-2.602533
H	1.649686	-3.406132	-0.946700
H	-2.456366	0.184238	-1.574926
H	-2.611299	-1.440979	-0.938925
H	-2.324014	-1.188052	-2.657235
H	3.195518	-1.989030	-2.392547
H	2.005112	-2.835706	-3.364040
H	1.805650	-1.124763	-3.024999

1e, 3a–$C_3H_4Me_2$ + 1 product

B	0.077715	-0.071971	0.103414
N	1.702408	0.081659	0.009474
C	-0.599218	1.413329	0.132090
C	-0.212821	-0.821934	1.523786
C	2.147744	0.908788	-1.127876
C	2.447651	0.487013	1.221085
F	-1.847665	1.400363	0.603336
F	0.072606	2.312381	0.886701
F	-0.673181	1.984140	-1.088119
F	-1.438703	-1.333854	1.632912
F	-0.053948	-0.034507	2.604247
F	0.637886	-1.860854	1.722831
H	1.634935	0.608172	-2.031186
H	1.919742	1.946913	-0.918941
H	3.219728	0.794421	-1.260350
H	2.283058	-0.228973	2.013049
H	2.107282	1.463160	1.539405
H	3.507266	0.525663	0.983695
C	-0.394857	-0.899719	-1.228886
C	0.542667	-2.018918	-1.610200
C	0.600859	-3.294144	-1.231178
H	1.970637	-0.877807	-0.198637
H	-0.286788	-0.170699	-2.034374
C	-1.877493	-1.279035	-1.278255
H	1.291971	-1.740808	-2.346734
H	1.377704	-3.889941	-1.697352
C	-0.263028	-4.047564	-0.281355
H	-2.112317	-1.723340	-2.243811
H	-2.171540	-1.981787	-0.509487
H	-2.500831	-0.396311	-1.158177
H	0.352628	-4.581505	0.440919
H	-0.949530	-3.419546	0.268974
H	-0.840094	-4.800816	-0.818861

1e, 3e–$C_3H_4Me_2$ + 1 ts

B	-0.009490	0.017007	0.134090
N	1.492360	0.001806	0.179879
C	-0.619259	1.521842	-0.066039
C	-0.678992	-0.682993	1.445975
C	2.198317	0.872567	-0.745945
C	2.198786	-0.035101	1.453242
F	-1.920156	1.638697	0.218126
F	0.008051	2.399089	0.736832
F	-0.473784	2.010503	-1.313832
F	-1.992586	-0.906245	1.335463
F	-0.520627	0.028786	2.569548
F	-0.139549	-1.900918	1.710021
H	1.724850	0.874616	-1.721959
H	2.229953	1.901719	-0.388558
H	3.223053	0.522177	-0.864706
H	1.811332	-0.813831	2.096440
H	2.123243	0.917982	1.977216
H	3.252503	-0.240407	1.269496
C	-0.547395	-0.860424	-1.376721
C	0.030348	-2.115146	-1.131606
C	1.419107	-2.348723	-1.214327
H	1.664628	-1.442697	-0.434179
H	0.011550	-0.266719	-2.096486
C	-2.041203	-0.814714	-1.631826
H	-0.589103	-2.858638	-0.639899
H	1.882307	-1.900031	-2.091821
C	1.982857	-3.692706	-0.827807
H	-2.431128	0.194114	-1.576373
H	-2.587659	-1.420551	-0.916530
H	-2.250614	-1.194136	-2.630307
H	3.051958	-3.626060	-0.644643
H	1.516374	-4.065334	0.080775
H	1.832636	-4.431520	-1.612649

1e, 3e–$C_3H_4Me_2$ + 1 product

B	0.139855	-0.117065	0.081068
N	1.745072	0.200615	0.011191
C	-0.678492	1.287926	0.213023
C	-0.052716	-1.012646	1.434505
C	2.122230	1.086668	-1.105820
C	2.430630	0.654809	1.241996
F	-1.912972	1.121771	0.691387
F	-0.092627	2.205439	1.015716
F	-0.823010	1.918782	-0.971065
F	-1.197408	-1.687969	1.497817
F	0.009234	-0.300145	2.576958
F	0.929966	-1.942404	1.551507
H	1.684631	0.730316	-2.028360
H	1.756160	2.085560	-0.901778
H	3.204170	1.111487	-1.199217
H	2.297840	-0.072894	2.028963
H	2.014787	1.602921	1.553109
H	3.490039	0.769115	1.029301
C	-0.268871	-0.901658	-1.295813
C	0.670332	-2.027109	-1.619577
C	0.441700	-3.327212	-1.500165
H	2.116239	-0.720573	-0.197850
H	-0.141489	-0.163815	-2.092426
C	-1.736760	-1.315737	-1.370179
H	1.646072	-1.743192	-2.013592
C	1.423637	-4.397223	-1.826705
H	-0.522486	-3.659267	-1.136860
H	-1.953831	-1.732430	-2.352386
H	-2.000783	-2.058630	-0.625958
H	-2.391686	-0.462945	-1.216447
H	1.641498	-5.006560	-0.949704
H	1.031592	-5.071736	-2.587501
H	2.360356	-3.983328	-2.193528

Table S22. Optimized (MPW1K/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **2, 3a–$C_3H_4Me_2$** and **1**, and between propene **2, 3e–$C_3H_4Me_2$** and **1**

2, 3a–$C_3H_4Me_2$ = 2, 3e–$C_3H_4Me_2$

C	-0.808206	-0.442853	0.546502
C	0.583796	-0.115750	0.092538
C	1.448411	-1.066829	-0.233017
H	2.451923	-0.832328	-0.556352
H	1.180246	-2.112016	-0.184423
C	0.948217	1.333146	0.034312
H	0.332235	1.868008	-0.687450
H	0.787191	1.810044	1.001578
H	1.988571	1.470129	-0.245205
H	-0.960937	-0.020407	1.542391
C	-1.895621	0.077822	-0.382909
H	-1.768016	-0.318432	-1.388208
H	-2.879552	-0.219488	-0.027034
H	-1.887515	1.163458	-0.448119
H	-0.903728	-1.522181	0.648264

2, 3a–$C_3H_4Me_2$ + 1 ts

C	-0.800413	0.055363	-1.379719
C	-1.985194	0.587769	-0.798852
C	-2.767308	-0.222042	0.050633
H	-3.530503	0.326345	0.593254
C	-3.233022	-1.607195	-0.357666
H	-2.505517	-2.132999	-0.966036
H	-3.443706	-2.221069	0.513663
H	-4.152752	-1.531128	-0.934676
H	-1.746774	-0.467649	0.763331
N	-0.322762	-0.888758	1.061931
B	0.324592	-0.078595	-0.051881
C	1.627864	-0.799181	-0.726496
F	2.300773	-0.002452	-1.563754
F	2.515012	-1.208130	0.195395
F	1.329903	-1.899708	-1.449722
C	0.756766	1.421806	0.422607
F	-0.219440	2.065572	1.111284
F	1.829877	1.449005	1.221357
F	1.038453	2.235003	-0.605790
C	-0.272187	-2.339041	0.916681
H	-0.485436	-2.637812	-0.102038
H	0.710421	-2.729702	1.180773
H	-1.008650	-2.796800	1.574592
C	-0.065981	-0.550109	2.457559
H	-0.727164	-1.137844	3.092531
H	0.963249	-0.776063	2.737296
H	-0.255231	0.496992	2.650406
C	-2.263804	2.042210	-0.885941
H	-1.387737	2.627939	-1.137011
H	-2.994631	2.166202	-1.689422
H	-2.718577	2.423350	0.023270
H	-0.879708	-0.971682	-1.719180
H	-0.332433	0.685112	-2.126628

2, 3a–$C_3H_4Me_2$ + 1 product

C	0.904986	0.189701	-1.106988
C	2.168987	0.806942	-0.581005
C	3.317412	0.154291	-0.421586
H	4.160817	0.731478	-0.059008
C	3.607282	-1.285507	-0.661073
H	4.431414	-1.398381	-1.365524
H	3.915626	-1.769196	0.265516
H	2.756148	-1.836944	-1.044495
C	2.113952	2.270269	-0.248839
H	3.110045	2.693545	-0.154897
H	1.586101	2.839374	-1.016372
H	1.621311	2.450248	0.711514
H	0.611637	0.738918	-2.006066
H	1.116186	-0.815444	-1.464412
B	-0.379227	0.037128	-0.130799
N	-1.037605	1.493547	0.201579
H	-0.226147	2.044865	0.452853
C	-1.646119	2.146895	-0.972773
H	-0.973913	2.089396	-1.817943
H	-2.569709	1.637848	-1.219199
H	-1.857463	3.186363	-0.739019
C	-1.973017	1.573090	1.345236
H	-2.324440	2.596458	1.443920
H	-2.810177	0.912824	1.163805
H	-1.468865	1.274237	2.253244
C	-1.494400	-0.891094	-0.869361
F	-1.155755	-2.181124	-0.871325
F	-2.730838	-0.830054	-0.326010
F	-1.673910	-0.556843	-2.164797
C	0.058974	-0.622887	1.290098
F	0.687817	0.288709	2.077220
F	-0.953885	-1.090574	2.044064
F	0.907955	-1.637477	1.151600

2, 3e–$C_3H_4Me_2$ + 1 ts

C	0.543701	-0.018541	-1.521056
C	1.884563	-0.166693	-1.070438
C	2.495717	0.950277	-0.455034
C	3.884464	0.884186	0.124339
H	3.984852	0.082209	0.851135
H	4.640710	0.733873	-0.644862
H	4.121811	1.813435	0.634729
H	2.279881	1.882000	-0.975468
H	1.574592	1.070786	0.364558
N	0.075758	1.216414	0.779233
B	-0.437151	0.083493	-0.085026
C	-1.943101	0.325331	-0.667467
F	-2.464904	-0.747789	-1.272784
F	-2.808781	0.667303	0.300975
F	-2.015395	1.318322	-1.579292
C	-0.383932	-1.356387	0.678129
F	0.805236	-1.570354	1.299414
F	-1.312892	-1.513380	1.627693
F	-0.525665	-2.397867	-0.154675
C	-0.244644	2.564874	0.341719
H	-0.112253	2.668032	-0.730183
H	-1.274641	2.835005	0.575316
H	0.414362	3.275520	0.839861
C	-0.027408	1.137544	2.229472
H	0.550454	1.946662	2.674311
H	-1.062044	1.236593	2.560145
H	0.364198	0.199950	2.600309
C	2.527238	-1.500592	-1.061551
H	1.815481	-2.299986	-1.228541
H	3.253814	-1.508265	-1.878437
H	3.080115	-1.686495	-0.146696
H	0.343344	0.936581	-1.996796
H	0.162800	-0.844350	-2.109545

2, 3e–$C_3H_4Me_2$ + 1 product

C	0.734735	0.547246	-1.161662
C	2.145207	0.650042	-0.626457
C	2.916328	-0.430180	-0.519906
C	4.314830	-0.532566	-0.018244
H	4.975945	-0.908519	-0.799280
H	4.721246	0.409582	0.334983
H	4.370760	-1.246736	0.803305
H	2.485692	-1.370855	-0.838845
C	2.619386	2.032837	-0.287194
H	3.662650	2.062069	0.006006
H	2.497656	2.688297	-1.149986
H	2.046115	2.489413	0.521943
H	0.454163	1.503052	-1.605055
H	0.719888	-0.160431	-1.989886
B	-0.430990	0.060655	-0.144988
N	-0.314623	0.884951	1.250638
H	0.681040	0.820572	1.439635
C	-0.652009	2.313473	1.101320
H	-0.193834	2.711923	0.206747
H	-1.727795	2.408219	1.017247
H	-0.308371	2.862312	1.973599
C	-1.014963	0.343726	2.435687
H	-0.841489	1.004063	3.280916
H	-2.074357	0.289824	2.223238
H	-0.641303	-0.643720	2.664816
C	-1.895803	0.320380	-0.810073
F	-2.177822	-0.564407	-1.767041
F	-2.925443	0.268905	0.065263
F	-2.004606	1.534533	-1.389862
C	-0.279328	-1.522767	0.225892
F	0.688861	-1.742083	1.151358
F	-1.385785	-2.082349	0.748003
F	0.049130	-2.275728	-0.824952

Table S23. Optimized (MPW1K/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **3a, 3e–$C_3H_4Me_2$** and **1**

3a, 3e–$C_3H_4Me_2$

C	0.368999	0.000001	-0.309208
C	-0.940365	-0.000003	0.412059
C	-2.131774	0.000000	-0.160845
H	-3.040267	-0.000004	0.422150
H	-2.240066	0.000005	-1.236669
H	-0.876936	-0.000009	1.495863
C	1.165565	1.254014	0.028253
H	2.118039	1.261550	-0.498976
H	0.618095	2.153512	-0.243134
H	1.377498	1.300622	1.096192
C	1.165569	-1.254012	0.028250
H	0.618110	-2.153510	-0.243159
H	2.118053	-1.261535	-0.498960
H	1.377482	-1.300633	1.096192
H	0.162028	0.000001	-1.380555

3a, 3e–$C_3H_4Me_2$ + 1 ts

C	-0.463099	-0.277461	-1.581062
C	-1.646206	0.409280	-1.271666
C	-2.643961	-0.091328	-0.406671
C	-3.734659	0.868468	0.010214
H	-3.350579	1.875953	0.146356
H	-4.531062	0.902501	-0.732419
H	-4.183579	0.553856	0.949536
C	-3.133340	-1.519233	-0.572941
H	-2.356870	-2.198343	-0.906529
H	-3.532760	-1.900235	0.363474
H	-3.938306	-1.543941	-1.306269
H	-1.767223	-0.206268	0.459593
N	-0.345267	-0.593738	1.085360
B	0.455265	-0.054905	-0.068661
C	1.832461	-0.875061	-0.381070
F	2.613218	-0.281968	-1.289658
F	2.582847	-1.017553	0.723033
F	1.632993	-2.125428	-0.845170
C	0.793998	1.536528	0.059875
F	-0.289014	2.280587	0.407902
F	1.727662	1.819151	0.974072
F	1.218512	2.075408	-1.089912
C	-0.333343	-2.036960	1.278318
H	-0.411468	-2.558778	0.332206
H	0.583539	-2.367681	1.767808
H	-1.175285	-2.328013	1.904112
C	-0.289838	0.063648	2.384944
H	-1.060155	-0.355796	3.030343
H	0.676766	-0.089791	2.866471
H	-0.466073	1.127285	2.297165
H	-1.646154	1.477819	-1.450674
H	-0.529106	-1.354106	-1.678241
H	0.160822	0.177169	-2.339186

3a, 3e–$C_3H_4Me_2$ + 1 product

C	0.652140	0.381012	-1.266648
C	1.929313	0.942020	-0.722370
C	3.069066	0.311305	-0.440129
C	4.248046	1.059502	0.096579
H	5.102317	0.965090	-0.574579
H	4.034813	2.117489	0.225582
H	4.562385	0.652373	1.058249
C	3.298105	-1.149898	-0.642181
H	4.154726	-1.306369	-1.298611
H	3.536617	-1.630713	0.306345
H	2.442822	-1.662650	-1.064908
H	1.935527	2.016360	-0.554404
H	0.265535	1.077055	-2.012000
H	0.837371	-0.542457	-1.810492
B	-0.506890	0.079687	-0.168389
N	-0.429835	1.222456	0.980595
H	0.567181	1.219747	1.183442
C	-0.763244	2.567368	0.476661
H	-0.262000	2.742232	-0.466099
H	-1.833394	2.630723	0.321717
H	-0.457812	3.314274	1.203911
C	-1.137042	0.979810	2.254263
H	-0.967009	1.821679	2.919899
H	-2.195797	0.874872	2.057555
H	-0.765654	0.074788	2.713568
C	-1.978567	0.079177	-0.860014
F	-2.178511	-1.005258	-1.610841
F	-3.008740	0.127587	0.012738
F	-2.176948	1.134141	-1.679041
C	-0.241058	-1.345636	0.577119
F	0.785367	-1.255694	1.461917
F	-1.276270	-1.817113	1.294860
F	0.091224	-2.324561	-0.265309

Table S24. Optimized (MPW1K/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1a–C_3H_5Me** and **1**, and between propene **1e–$C_3H_4Me_2$** and **1**

1a–C_3H_5Me

C	1.574273	-0.519017	-0.000001
C	0.663239	0.659655	-0.000003
C	-0.663239	0.659655	-0.000003
H	-1.156845	1.623724	0.000009
C	-1.574273	-0.519017	-0.000001
H	-2.224998	-0.501259	-0.874008
H	-1.042094	-1.464832	-0.000187
H	-2.224731	-0.501460	0.874211
H	1.156845	1.623724	0.000008
H	2.225019	-0.501242	-0.873992
H	2.224710	-0.501477	0.874227
H	1.042094	-1.464832	-0.000218

1a–C_3H_5Me + 1 ts

C	-0.992452	-0.530999	-1.420572
C	-2.015419	0.409948	-1.236502
C	-3.013844	0.271413	-0.257555
H	-2.149007	0.298122	0.638154
N	-0.778332	0.048086	1.297249
B	0.032393	0.005910	0.026886
C	1.256141	-1.081070	0.028335
F	1.871250	-1.189390	-1.155410
F	2.201811	-0.731382	0.912754
F	0.911932	-2.337842	0.366029
C	0.667122	1.458973	-0.395060
F	-0.248040	2.461314	-0.445490
F	1.612362	1.895234	0.442561
F	1.223683	1.446352	-1.612477
C	-0.943846	-1.171400	2.077712
H	-1.128460	-2.025764	1.441372
H	-0.061953	-1.385620	2.681724
H	-1.792697	-1.050457	2.749257
C	-0.643316	1.178476	2.211378
H	-1.449551	1.140282	2.941956
H	0.305059	1.144853	2.747291
H	-0.709167	2.121928	1.686419
H	-3.727754	1.076465	-0.160035
H	-3.434430	-0.714969	-0.100704
H	-1.860206	1.396383	-1.649797
C	-1.348383	-2.005637	-1.393208
H	-0.466915	-2.625634	-1.495293
H	-1.861710	-2.309677	-0.487017
H	-2.007597	-2.225594	-2.231479
H	-0.322249	-0.283279	-2.235901

1a–C_3H_5Me + 1 product

C	-1.261110	-0.633443	-0.945607
C	-2.544095	-0.729246	-0.179218
C	-3.411272	0.256610	0.022838
H	-4.319808	0.097946	0.584071
H	-3.254332	1.241182	-0.395837
F	-0.697645	2.312277	-0.381454
C	0.329109	1.461235	-0.647728
B	0.008182	-0.028175	-0.061603
N	-0.447288	0.152989	1.485687
H	-1.419784	0.439249	1.375530
C	-0.487404	-1.121365	2.227840
H	-0.941648	-1.889603	1.616623
H	0.524059	-1.419384	2.473812
H	-1.060533	-0.989204	3.140948
C	0.225828	1.178242	2.308299
H	-0.201698	1.161645	3.307161
H	1.284395	0.959993	2.358474
H	0.079372	2.155215	1.869868
F	1.421857	2.066255	-0.155357
C	1.377274	-0.911828	-0.099315
F	1.980148	-0.874866	-1.288600
F	2.298391	-0.490085	0.797350
F	1.204912	-2.218626	0.185676
F	0.472387	1.475437	-1.973473
H	-2.779857	-1.701126	0.244787
C	-1.006756	-1.947587	-1.683357
H	-1.841014	-2.175699	-2.344910
H	-0.108362	-1.896283	-2.291267
H	-0.888647	-2.783667	-0.997602
H	-1.431937	0.120450	-1.713233

1e–C_3H_5Me

C	-1.945047	-0.078753	0.000003
C	-0.532581	0.392820	-0.000007
C	0.532581	-0.392820	-0.000003
C	1.945047	0.078753	0.000004
H	1.999807	1.164579	0.000021
H	2.481231	-0.288080	0.874998
H	2.481233	-0.288052	-0.875002
H	0.383807	-1.467490	-0.000011
H	-0.383806	1.467490	-0.000008
H	-2.481183	0.287947	0.875084
H	-2.481281	0.288184	-0.874917
H	-1.999808	-1.164579	-0.000138

1e–C_3H_5Me + 1 ts

C	0.623577	-0.710211	-1.540271
C	1.972195	-0.812341	-1.173099
C	2.824360	0.307009	-1.123402
H	2.087610	0.925773	-0.357797
N	0.714364	1.404995	0.158994
B	-0.013408	0.100778	-0.025012
C	-1.603352	0.306912	-0.350487
F	-2.351213	-0.787979	-0.185993
F	-2.135437	1.235989	0.462818
F	-1.857367	0.737361	-1.601600
C	0.162196	-0.898323	1.251723
F	1.459204	-1.036100	1.625081
F	-0.483319	-0.477203	2.347000
F	-0.266061	-2.145155	1.029925
C	0.362066	2.497269	-0.734881
H	0.215902	2.141495	-1.749087
H	-0.553726	2.996071	-0.419810
H	1.165987	3.232145	-0.743223
C	0.974853	1.927138	1.494351
H	1.667783	2.763761	1.418956
H	0.058965	2.281549	1.966919
H	1.423377	1.174622	2.129044
H	3.824057	0.154923	-0.743113
H	2.775695	0.979573	-1.974432
H	2.289574	-1.732258	-0.695996
H	0.429682	0.105442	-2.233389
C	-0.106595	-1.981087	-1.922220
H	-1.180178	-1.840880	-1.946067
H	0.206752	-2.293841	-2.916511
H	0.106956	-2.787636	-1.228763

1e–C_3H_5Me + 1 product

C	-1.171669	0.780746	-0.873836
C	-2.281107	-0.158786	-1.233342
C	-3.504689	-0.188858	-0.729092
H	-4.227145	-0.916723	-1.064617
H	-3.827578	0.504135	0.032457
F	-1.036482	-1.710351	1.228560
C	-0.312880	-0.567702	1.347169
B	0.074949	0.032415	-0.121286
N	0.492399	-1.277285	-1.013459
H	-0.398288	-1.754449	-1.099231
C	0.942612	-0.944885	-2.377882
H	0.220953	-0.301536	-2.862522
H	1.894239	-0.430897	-2.319094
H	1.061009	-1.858744	-2.952828
C	1.426947	-2.263212	-0.423097
H	1.535491	-3.095393	-1.113135
H	2.386870	-1.793258	-0.261594
H	1.038730	-2.623813	0.518013
F	0.750850	-0.908547	2.100487
C	1.358912	1.032258	-0.008254
F	1.259895	1.883271	1.013997
F	2.546252	0.405387	0.148410
F	1.521773	1.793307	-1.110476
F	-1.042322	0.245218	2.105665
H	-2.062614	-0.885005	-2.014405
H	-0.757282	1.133734	-1.822500
C	-1.672039	2.034121	-0.161589
H	-2.426657	2.529646	-0.770267
H	-2.112238	1.815545	0.805121
H	-0.863236	2.739019	0.004982

Table S25. Optimized (MPW1K/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **2–C_3H_5Me** and **1**

2–C_3H_5Me

C	-1.264959	-0.673314	0.000003
C	0.000000	0.121930	-0.000017
C	-0.000003	1.447333	-0.000002
H	0.921050	2.011061	0.000002
H	-0.921057	2.011057	0.000033
C	1.264961	-0.673310	0.000002
H	1.312335	-1.322459	-0.874675
H	2.142888	-0.034251	-0.000115
H	1.312431	-1.322257	0.874828
H	-1.312420	-1.322302	-0.874791
H	-1.312336	-1.322422	0.874712
H	-2.142887	-0.034259	0.000087

2–C_3H_5Me + 1 ts

C	0.801377	0.333805	-1.478464
C	2.105458	0.558436	-0.965913
C	2.342872	1.760694	-0.267782
H	1.409778	1.578806	0.528225
N	-0.069301	1.269342	0.856333
B	-0.210447	0.083083	-0.074903
C	-1.703990	-0.080902	-0.714458
F	-1.880034	-1.226058	-1.382940
F	-2.659460	-0.046066	0.228693
F	-2.027565	0.894994	-1.588672
C	0.226767	-1.320352	0.629891
F	1.403616	-1.219857	1.298675
F	-0.652056	-1.785802	1.523999
F	0.418945	-2.312245	-0.252533
C	-0.744849	2.493606	0.456778
H	-0.605936	2.687696	-0.601703
H	-1.816780	2.447281	0.647891
H	-0.334795	3.333674	1.016404
C	-0.199482	1.088750	2.295994
H	0.104751	2.005016	2.799996
H	-1.230270	0.870756	2.577000
H	0.431907	0.284619	2.648971
H	3.315522	1.892424	0.185739
H	1.948441	2.661716	-0.727398
C	3.116746	-0.523195	-0.971821
H	2.671432	-1.507328	-1.060164
H	3.742153	-0.358005	-1.852831
H	3.764312	-0.480362	-0.101774
H	0.344009	1.213027	-1.921237
H	0.692407	-0.539867	-2.109273

2–C_3H_5Me + 1 product

C	-1.183079	-0.144280	-1.072834
C	-2.531686	0.190301	-0.490051
C	-2.790018	1.297981	0.203763
H	-3.784651	1.499170	0.573367
H	-2.046428	2.064721	0.360576
F	0.190653	2.405817	0.394706
C	0.861889	1.431838	-0.276209
B	0.141799	-0.027304	-0.127950
N	-0.290720	-0.210283	1.418076
H	-1.113675	0.390209	1.468111
C	-0.774864	-1.569672	1.719302
H	-1.470781	-1.885389	0.953463
H	0.065797	-2.252154	1.739033
H	-1.268429	-1.570975	2.686719
C	0.655852	0.225866	2.463185
H	0.206787	0.059449	3.438491
H	1.569717	-0.347345	2.377700
H	0.878012	1.276877	2.343490
F	2.116502	1.491584	0.199951
C	1.216811	-1.183461	-0.536211
F	1.821760	-0.921080	-1.695635
F	2.200835	-1.368967	0.369839
F	0.657390	-2.403644	-0.684804
F	0.927867	1.849801	-1.539680
C	-3.621384	-0.794484	-0.777411
H	-3.356065	-1.795752	-0.437067
H	-4.563160	-0.509065	-0.317623
H	-3.772933	-0.870111	-1.854343
H	-1.235468	-1.152976	-1.478988
H	-1.018865	0.495729	-1.940312

Table S26. Optimized (MPW1K/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **3a–C_3H_5Me** and **1**, and between propene **3e-$C_3H_4Me_2$** and **1**

3a–C_3H_5Me = 3e–C_3H_5Me

C	0.535362	0.515111	0.306387
C	-0.713676	-0.298728	0.330858
C	-1.845131	0.020811	-0.274043
H	-2.714520	-0.616396	-0.221365
H	-1.941499	0.935497	-0.842421
H	-0.662903	-1.228337	0.887491
H	0.785089	0.811082	1.327286
C	1.712307	-0.241277	-0.291219
H	1.513365	-0.515209	-1.324953
H	2.617482	0.361475	-0.268911
H	1.911196	-1.158147	0.261206
H	0.358611	1.434538	-0.250230

3a–C_3H_5Me + 1 ts

C	-0.740868	-0.003986	-1.581836
C	-1.706623	0.956275	-1.250419
C	-2.785946	0.693199	-0.384457
H	-3.341073	1.576724	-0.091708
C	-3.658089	-0.536158	-0.540312
H	-3.097935	-1.403664	-0.872575
H	-4.140270	-0.791158	0.399213
H	-4.441309	-0.346597	-1.271212
H	-1.969701	0.374168	0.498626
N	-0.703883	-0.346895	1.093002
B	0.206454	-0.040245	-0.066696
C	1.307246	-1.203572	-0.388707
F	2.213240	-0.843454	-1.302441
F	1.997641	-1.545756	0.710738
F	0.772666	-2.352254	-0.850728
C	0.964831	1.399215	0.059415
F	0.126402	2.410417	0.404537
F	1.939283	1.416154	0.974968
F	1.522226	1.798981	-1.090100
C	-1.067261	-1.743468	1.292833
H	-1.291253	-2.226923	0.349762
H	-0.262201	-2.300728	1.772526
H	-1.948028	-1.802388	1.929627
C	-0.471466	0.278238	2.389622
H	-1.323624	0.081275	3.038244
H	0.421257	-0.124873	2.868709
H	-0.359432	1.349949	2.295594
H	-1.442284	1.993391	-1.410497
H	-1.082024	-1.026824	-1.686108
H	-0.021276	0.281880	-2.337332

3a–C_3H_5Me + 1 product

C	0.825036	0.704582	-1.215715
C	1.945836	1.494756	-0.616782
C	3.177950	1.091201	-0.320974
H	3.848436	1.826448	0.107770
C	3.762058	-0.259450	-0.537978
H	4.656175	-0.188449	-1.156869
H	4.067842	-0.702238	0.409165
H	3.069311	-0.945112	-1.012750
H	1.731334	2.539899	-0.412101
H	0.307869	1.338475	-1.936280
H	1.212979	-0.131576	-1.793145
B	-0.256723	0.107586	-0.158648
N	-0.429546	1.170173	1.054368
H	0.542565	1.363597	1.282985
C	-1.032974	2.443610	0.620450
H	-0.572771	2.775330	-0.300797
H	-2.091110	2.289955	0.447943
H	-0.897058	3.193045	1.394844
C	-1.086468	0.709152	2.294885
H	-1.108007	1.527714	3.009067
H	-2.095915	0.394759	2.065092
H	-0.537511	-0.121805	2.714655
C	-1.689638	-0.152541	-0.883453
F	-1.652056	-1.204525	-1.702632
F	-2.716774	-0.372675	-0.034046
F	-2.092888	0.889181	-1.642025
C	0.290674	-1.276109	0.508709
F	1.260468	-1.031404	1.427302
F	-0.634644	-1.997801	1.164932
F	0.836056	-2.107262	-0.380394

3e–C_3H_5Me + 1 ts

C	-0.496663	-0.234219	-1.685067
C	-1.805269	0.165057	-1.390879
C	-2.686355	-0.653897	-0.656484
C	-4.057217	-0.153780	-0.280600
H	-4.022052	0.887774	0.029343
H	-4.753940	-0.235706	-1.112264
H	-4.466586	-0.729653	0.544887
H	-2.647168	-1.704890	-0.938456
H	-1.890807	-0.711750	0.271448
N	-0.433940	-0.911168	0.914876
B	0.295953	-0.071071	-0.090910
C	1.811974	-0.576197	-0.422109
F	2.502385	0.265218	-1.198019
F	2.532362	-0.730788	0.699901
F	1.864282	-1.767648	-1.050705
C	0.309553	1.517394	0.273793
F	-0.915724	1.975431	0.640432
F	1.128246	1.841016	1.279702
F	0.665111	2.288273	-0.761710
C	-0.231178	-2.349087	0.851325
H	-0.253346	-2.700014	-0.174918
H	0.724439	-2.644578	1.284997
H	-1.024790	-2.852025	1.402448
C	-0.526344	-0.484621	2.303987
H	-1.263644	-1.098754	2.819189
H	0.428575	-0.597087	2.819239
H	-0.837593	0.548820	2.378087
H	-2.046799	1.217614	-1.483303
H	-0.359452	-1.287822	-1.900998
H	0.070017	0.414184	-2.339489

3e–C_3H_5Me + 1 product

C	-0.780725	-0.488240	-1.309883
C	-2.140907	-0.839578	-0.793841
C	-3.167974	-0.009355	-0.671257
C	-4.510487	-0.379825	-0.146962
H	-5.284134	-0.199645	-0.892919
H	-4.553704	-1.429123	0.136286
H	-4.771075	0.220784	0.724325
H	-3.038505	1.022041	-0.978670
H	-2.303902	-1.873944	-0.497676
H	-0.402060	-1.316759	-1.908575
H	-0.858200	0.354344	-1.994562
B	0.312973	-0.084960	-0.180956
N	0.119395	-1.056799	1.103887
H	-0.878218	-0.956727	1.272391
C	0.367937	-2.477121	0.798303
H	-0.137441	-2.749508	-0.118684
H	1.432568	-2.628912	0.670290
H	0.009090	-3.093916	1.617274
C	0.809414	-0.690419	2.358096
H	0.541951	-1.405124	3.131606
H	1.878484	-0.710652	2.193251
H	0.512473	0.302437	2.664778
C	1.820450	-0.224417	-0.772972
F	2.091351	0.724402	-1.670982
F	2.802467	-0.159670	0.150980
F	2.026501	-1.399828	-1.406252
C	0.050373	1.435281	0.353565
F	-0.985363	1.478681	1.231969
F	1.082949	1.992731	1.010236
F	-0.266398	2.289144	-0.619488

Table S27. Optimized (M11/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1a, 1e, 2, 3a, 3e–$C_3H(CF_3)_5$** and **1**

1a, 1e, 2, 3a, 3e–$C_3H(CF_3)_5$ product			
C	0.013410	-0.028980	0.008834
C	1.337379	-0.049478	-0.120771
C	2.169225	1.221665	-0.064763
H	1.534523	2.049475	0.257202
C	-0.777390	1.276278	-0.069205
C	-0.861420	-1.250904	0.290084
C	2.103114	-1.355633	-0.364325
C	2.760277	1.668410	-1.421908
C	3.228066	1.183250	1.048654
F	-0.233431	2.116678	-0.976859
F	-2.034949	1.050532	-0.457851
F	-0.796716	1.915494	1.113698
F	-0.173657	-2.232180	0.885029
F	-1.433615	-1.730578	-0.819266
F	-1.835125	-0.887979	1.148047
F	1.371971	-2.222334	-1.079242
F	3.202151	-1.080331	-1.089480
F	2.489426	-1.942616	0.773886
F	2.109654	1.073371	-2.436715
F	2.605529	2.997308	-1.556125
F	4.065645	1.399339	-1.540644
F	4.167664	0.247295	0.904567
F	3.834435	2.381185	1.108198
F	2.605052	0.963512	2.223244

1a, 1e, 2, 3a, 3e–$C_3H(CF_3)_5$ + 1 ts			
B	0.369037	-0.328384	0.290688
N	1.758094	-0.073494	-0.141165
C	-0.782504	3.081356	-0.337555
C	0.129033	2.923274	-1.325407
C	1.536762	2.520457	-1.089660
H	1.646885	1.130319	-0.569216
C	0.072042	-1.253677	1.580345
C	-0.779419	-0.354803	-0.848026
C	2.771944	-0.057338	0.951646
C	2.191273	-1.038516	-1.200982
F	-1.233968	-1.509388	1.770743
F	0.696155	-2.450035	1.363262
F	0.560372	-0.758729	2.739560
F	-1.931355	0.207330	-0.432605
F	-1.034105	-1.643151	-1.180721
F	-0.420477	0.284368	-1.994974
H	2.429684	0.574725	1.772508
H	2.936492	-1.080123	1.311857
H	3.701719	0.352882	0.544505
H	1.492559	-1.034788	-2.038942
H	2.250611	-2.041673	-0.760608
H	3.177839	-0.730989	-1.559027
C	-0.660389	2.537728	1.066736
C	-2.065527	3.915837	-0.426750
C	-0.320063	3.304954	-2.752835
C	2.248912	3.463570	-0.110306
C	2.477198	2.180139	-2.228348
F	-1.828333	2.115220	1.531453
F	0.159688	1.346606	1.088967
F	-0.090995	3.310561	1.970428
F	-2.286186	4.479790	0.788153
F	-3.151367	3.194183	-0.731468
F	-1.961317	4.933261	-1.288444
F	-1.639923	3.125407	-2.920271
F	-0.007119	4.584941	-3.009788
F	0.275142	2.552807	-3.683973
F	1.483174	4.499725	0.287648
F	3.371033	4.006418	-0.616799
F	2.623774	2.814605	1.032893
F	3.661276	1.761024	-1.672385
F	2.776825	3.164577	-3.089811
F	2.055275	1.118008	-2.952258

1a, 1e, 2, 3a, 3e–$C_3H(CF_3)_5$ + 1			
B	-0.074464	0.123826	0.123469
N	1.506790	0.007403	0.412836
C	-0.458546	1.735632	0.032007
C	-0.844455	-0.366820	1.536653
C	2.323418	0.850166	-0.515185
C	2.026001	0.226259	1.808041
F	-1.774404	1.945448	0.249513
F	0.215367	2.424783	1.017133
F	-0.136431	2.403979	-1.097920
F	-2.176323	-0.498811	1.514013
F	-0.594870	0.551111	2.522058
F	-0.345106	-1.544975	2.035004
H	1.923364	0.810705	-1.527980
H	2.280499	1.883964	-0.161874
H	3.356468	0.489670	-0.504153
H	1.601736	-0.516011	2.483045
H	1.758624	1.230257	2.136889
H	3.114538	0.114305	1.768646
C	-0.441373	-0.862009	-1.293669
C	0.507058	-0.985226	-2.567094
C	1.394440	-1.955139	-2.884429
H	1.725506	-0.968002	0.206032
C	-1.854339	-0.433564	-1.832209
C	-0.649318	-2.335840	-0.807792
C	0.366230	0.097041	-3.696247
C	1.604659	-2.438258	-4.348627
C	2.310117	-2.816168	-1.993473
F	-2.264288	-1.287019	-2.795836
F	-2.777020	-0.439550	-0.872501
F	-1.853795	0.803707	-2.342085
F	-0.749834	-3.227096	-1.812605
F	-1.727076	-2.495651	-0.047186
F	0.424286	-2.706861	-0.064988
F	0.408552	1.307144	-3.125094
F	1.444016	0.071885	-4.508936
F	-0.719498	0.010326	-4.457459
F	1.647951	-3.788608	-4.283209
F	0.558867	-2.136944	-5.125996
F	2.724447	-2.028780	-4.946754
F	3.461730	-3.008059	-2.664213
F	2.683655	-2.137348	-0.870839
F	1.848842	-4.007143	-1.638626

Table S28. Optimized (M11/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1a, 1e, 2, 3a–$C_3H_2(CF_3)_4$** and **1**

1a, 1e, 2, 3a–$C_3H_2(CF_3)_4$ product

C	0.064380	-0.013229	-0.017609
C	1.387299	-0.043136	0.105294
C	2.276773	1.180755	0.135122
H	1.726966	2.059762	0.473730
C	-0.673296	1.270496	-0.372639
C	-0.866925	-1.197749	0.220357
C	2.166571	-1.349880	0.246436
C	2.912879	1.507712	-1.225707
H	3.093850	0.998337	0.841644
F	0.090978	2.090942	-1.118638
F	-1.771876	0.999531	-1.089639
F	-1.040123	1.950164	0.730085
F	-0.348893	-2.069974	1.097247
F	-1.158625	-1.848888	-0.912240
F	-2.019876	-0.750696	0.756194
F	1.619734	-2.355479	-0.444114
F	3.410926	-1.161636	-0.242184
F	2.296140	-1.715802	1.532748
F	2.386764	0.765076	-2.221112
F	2.727176	2.802935	-1.542306
F	4.241048	1.288540	-1.218649

1a, 1e, 2, 3a–$C_3H_2(CF_3)_4$ + 1 ts

C	0.025435	0.082435	0.031741
B	1.004120	0.719676	-1.101572
N	1.905496	-0.152797	-1.878025
C	1.947559	-1.611120	-1.564429
H	2.191479	-1.772893	-0.516866
H	0.973728	-2.057849	-1.796781
H	2.722033	-2.069131	-2.186721
C	1.979538	0.040685	-3.359348
H	2.035924	1.105185	-3.600935
H	1.101921	-0.401207	-3.837860
H	2.889148	-0.456886	-3.714339
C	0.158051	1.831161	-1.952691
F	-0.814325	2.447074	-1.268018
F	-0.467068	1.194482	-2.991756
F	0.934810	2.795303	-2.518653
F	-0.430798	0.992602	0.912673
F	-1.060181	-0.379980	-0.664647
F	0.481999	-0.974434	0.742103
C	2.533029	2.010434	0.205362
C	3.450095	2.119395	-0.852344
C	4.232540	1.090594	-1.442768
C	5.252053	0.140937	-0.835051
F	4.851368	-1.157325	-0.865416
F	6.369270	0.191493	-1.600212
F	5.626184	0.431268	0.415128
H	4.651632	1.396229	-2.398933
C	3.585566	3.405712	-1.717696
F	2.700840	4.370531	-1.530015
F	4.809482	3.906021	-1.453560
F	3.557501	3.095857	-3.036710
C	2.844250	0.987192	1.304634
F	1.834814	0.708559	2.125096
F	3.204010	-0.194505	0.744067
F	3.861315	1.428342	2.064859
C	1.921963	3.292678	0.816586
F	1.435139	3.075979	2.044786
F	0.924494	3.796638	0.085700
F	2.882698	4.236405	0.953796
H	3.103805	0.327620	-1.653654

1a, 1e, 2, 3a–$C_3H_2(CF_3)_4$ + 1

B	0.135505	0.032139	-0.001643
N	1.755131	0.069738	0.193953
C	-0.585011	1.620610	-0.021823
C	-0.672074	2.197973	-1.463739
C	-1.676271	2.371696	-2.327775
C	-0.415876	-1.002729	1.162411
C	-0.214951	-0.707616	-1.442613
C	2.241143	0.086949	1.614520
C	2.537997	-0.971737	-0.551229
F	-1.684199	-1.409494	0.966045
F	0.355606	-2.145728	1.144686
F	-0.324552	-0.561644	2.446638
F	-1.521886	-0.661390	-1.755160
F	0.133214	-2.021934	-1.473519
F	0.438961	-0.137501	-2.514990
H	1.650475	0.774435	2.217882
H	2.158488	-0.921533	2.024451
H	3.289583	0.401553	1.606938
H	2.378861	-0.852824	-1.623695
H	2.214913	-1.962057	-0.227845
H	3.596777	-0.823502	-0.315300
H	2.051044	0.957891	-0.204528
C	0.152748	2.656444	0.881282
C	-2.026634	1.575276	0.571485
C	0.651857	2.713405	-2.077564
H	-1.369760	2.775513	-3.288564
C	-3.184194	2.158486	-2.445719
F	-0.298798	3.903697	0.721390
F	0.041394	2.340879	2.183016
F	1.494206	2.710043	0.631568
F	-2.560965	2.811471	0.623581
F	-2.072650	1.091099	1.817101
F	-2.823143	0.806857	-0.177582
F	1.733310	1.948722	-1.755176
F	0.639678	2.748630	-3.417180
F	0.925782	3.959365	-1.652676
F	-3.554136	2.789442	-3.594122
F	-3.521346	0.872996	-2.597141
F	-3.931146	2.694602	-1.476544

Table S29. Optimized (M11/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1a, 1e, 2, 3e–$C_3H_2(CF_3)_4$** and **1**

1a, 1e, 2, 3e–$C_3H_2(CF_3)_4$ product

C	0.064380	-0.013229	-0.017609
C	1.387299	-0.043136	0.105294
C	2.276773	1.180755	0.135122
H	1.726966	2.059762	0.473730
C	-0.673296	1.270496	-0.372639
C	-0.866925	-1.197749	0.220357
C	2.166571	-1.349880	0.246436
C	2.912879	1.507712	-1.225707
H	3.093850	0.998337	0.841644
F	0.090978	2.090942	-1.118638
F	-1.771876	0.999531	-1.089639
F	-1.040123	1.950164	0.730085
F	-0.348893	-2.069974	1.097247
F	-1.158625	-1.848888	-0.912240
F	-2.019876	-0.750696	0.756194
F	1.619734	-2.355479	-0.444114
F	3.410926	-1.161636	-0.242184
F	2.296140	-1.715802	1.532748
F	2.386764	0.765076	-2.221112
F	2.727176	2.802935	-1.542306
F	4.241048	1.288540	-1.218649

1a, 1e, 2, 3e–$C_3H_2(CF_3)_4$ + 1 ts

C	0.022649	0.019537	0.003787
B	0.902867	0.648046	-1.214524
N	1.766576	-0.191085	-2.059769
C	1.889655	-1.648098	-1.789719
H	1.960738	-1.850942	-0.724970
H	1.013660	-2.161925	-2.204170
H	2.790845	-2.017093	-2.293406
C	1.759218	0.025277	-3.539059
H	1.846022	1.091008	-3.769817
H	0.838359	-0.374861	-3.969877
H	2.624323	-0.496443	-3.959585
C	-0.033651	1.726641	-2.015570
F	-0.982748	2.322607	-1.281139
F	-0.705974	1.062429	-3.006900
F	0.680987	2.706019	-2.637161
F	-0.314224	0.955773	0.917475
F	-1.136766	-0.434293	-0.553872
F	0.536414	-1.027945	0.693850
C	2.422088	1.916455	0.005193
C	3.291116	2.149469	-1.080224
C	4.086229	1.092306	-1.593006
H	4.491117	0.410444	-0.849274
C	5.085035	1.154526	-2.734984
F	5.881314	0.060781	-2.626552
F	5.886706	2.229079	-2.716976
F	4.525130	1.083669	-3.962614
C	3.365768	3.491725	-1.845695
F	2.364341	4.341614	-1.671604
F	4.496807	4.103413	-1.455820
F	3.448975	3.240507	-3.166745
C	2.917642	0.869265	1.027593
F	2.103122	0.640759	2.047656
F	3.130922	-0.348311	0.452512
F	4.108311	1.267058	1.531336
C	1.793937	3.149462	0.703605
F	1.393649	2.900536	1.953462
F	0.738801	3.628769	0.042469
F	2.725840	4.130794	0.799903
H	3.016918	0.339815	-1.887183

1a, 1e, 2, 3e–$C_3H_2(CF_3)_4$ + 1

B	0.128776	-0.015971	0.026805
N	1.752453	0.071568	0.156573
C	-0.619423	1.544107	-0.047943
C	-0.724374	2.092551	-1.503685
C	-0.354267	-1.001870	1.259815
C	-0.254166	-0.821422	-1.370225
C	2.288782	0.175140	1.555074
C	2.535398	-0.989399	-0.560934
F	-1.617221	-1.452836	1.132492
F	0.447006	-2.123111	1.278749
F	-0.237504	-0.483833	2.512988
F	-1.571717	-0.813676	-1.657074
F	0.117230	-2.129029	-1.356582
F	0.361299	-0.278145	-2.475857
H	1.704971	0.881139	2.143186
H	2.243923	-0.811577	2.020566
H	3.328760	0.510729	1.492193
H	2.338836	-0.930437	-1.631959
H	2.247320	-1.968369	-0.175505
H	3.597450	-0.805412	-0.369343
C	-1.882301	2.213701	-2.144527
H	2.008562	0.944958	-0.300045
C	0.098566	2.643098	0.791424
C	-2.062382	1.482188	0.567897
C	0.540622	2.564218	-2.229510
C	-2.165947	2.843570	-3.494312
H	-2.809515	1.876814	-1.697949
F	-0.425704	3.858040	0.594400
F	0.068400	2.389624	2.109777
F	1.419279	2.748533	0.466008
F	-2.685756	2.680982	0.496632
F	-2.047630	1.136636	1.858398
F	-2.852414	0.596517	-0.059164
F	1.663607	1.875583	-1.864223
F	0.447463	2.395689	-3.549673
F	0.794243	3.858222	-1.980989
F	-3.483213	3.148585	-3.532984
F	-1.496672	3.992580	-3.698673
F	-1.925024	2.018706	-4.525514

Table S30. Optimized (M11/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1a, 1e, 3a, 3e–$C_3H_2(CF_3)_4$** and **1**

1a, 1e, 3a, 3e–$C_3H_2(CF_3)_4$ product

C	-0.026360	0.042976	-0.049977
C	1.286425	0.098633	-0.197123
C	2.108944	1.361158	-0.144596
H	1.505401	2.264995	-0.014107
C	-0.865412	1.282703	0.186058
C	-0.762021	-1.276053	-0.113640
H	1.842410	-0.824480	-0.366140
C	2.857177	1.517331	-1.470628
C	3.052740	1.280473	1.058603
F	-0.733248	2.153530	-0.839157
F	-2.163430	0.996281	0.319978
F	-0.462248	1.930963	1.300570
F	0.086765	-2.295108	-0.334214
F	-1.669777	-1.275911	-1.105603
F	-1.410046	-1.523777	1.038168
F	1.964075	1.577152	-2.475783
F	3.593053	2.635039	-1.502912
F	3.669977	0.470976	-1.707746
F	3.834476	0.186142	1.002043
F	3.844912	2.355953	1.148789
F	2.322607	1.203454	2.185629

1a, 1e, 3a, 3e–$C_3H_2(CF_3)_4$ + 1 ts

C	0.022983	0.037029	0.012337
B	1.025844	0.731345	-1.068430
N	1.892648	-0.144628	-1.871856
C	1.990877	-1.589828	-1.506425
H	2.279612	-1.707704	-0.464714
H	1.022643	-2.071540	-1.685383
H	2.754277	-2.046182	-2.143253
C	1.785977	-0.040287	-3.363282
H	1.804907	1.000574	-3.685693
H	0.853246	-0.512163	-3.689229
H	2.642359	-0.566096	-3.798509
C	0.323437	1.984777	-1.837981
F	-0.386444	2.798947	-1.044430
F	-0.537193	1.498793	-2.776780
F	1.211990	2.773974	-2.511863
F	-0.629910	0.881920	0.818531
F	-0.922591	-0.559741	-0.791991
F	0.521219	-0.950706	0.787509
C	2.613948	2.019651	0.318835
C	3.434260	2.124181	-0.784074
C	4.224891	1.163202	-1.479932
C	5.226277	0.218631	-0.816609
F	4.793558	-1.067130	-0.817439
F	6.400100	0.217506	-1.475692
F	5.490863	0.562855	0.450808
C	4.725312	1.658822	-2.826269
F	3.772756	2.395863	-3.444902
F	5.821149	2.433420	-2.751925
F	5.006832	0.618744	-3.642521
H	3.244795	3.030407	-1.361208
C	2.829668	1.035090	1.450813
F	1.742128	0.922633	2.224898
F	3.102940	-0.192838	0.942810
F	3.844172	1.387487	2.251857
C	1.973348	3.321738	0.801000
F	0.760299	3.149585	1.330843
F	1.865942	4.215247	-0.200367
F	2.751071	3.878591	1.757089
H	3.093697	0.384283	-1.725601

1a, 1e, 3a, 3e–$C_3H_2(CF_3)_4$ + 1

B	-0.052513	0.057882	0.068445
N	1.514943	-0.256614	0.403319
C	-0.133827	1.594308	-0.505616
C	-0.915883	0.081261	1.487546
C	2.527574	0.344652	-0.533458
C	1.980044	0.047962	1.798782
F	-1.371746	2.117907	-0.448185
F	0.675827	2.427936	0.222827
F	0.293330	1.736765	-1.800874
F	-2.241625	0.221360	1.333922
F	-0.519732	1.142076	2.259659
F	-0.745865	-1.021462	2.277858
H	2.169541	0.348606	-1.560060
H	2.717063	1.372819	-0.218769
H	3.449137	-0.243328	-0.463261
H	1.400358	-0.527676	2.520336
H	1.854921	1.117331	1.979972
H	3.038058	-0.225819	1.864409
C	-0.586451	-1.105595	-1.062689
C	0.300355	-1.102581	-2.304758
C	1.321329	-1.790900	-2.808481
H	1.601117	-1.270445	0.306172
C	-1.985331	-0.782800	-1.696963
C	-0.726895	-2.504179	-0.403527
H	-0.015193	-0.304562	-2.974816
C	1.848341	-1.354105	-4.167666
C	2.153034	-2.903850	-2.216789
F	-2.313790	-1.788727	-2.545355
F	-2.986634	-0.636331	-0.842042
F	-1.927321	0.347513	-2.431815
F	-0.527951	-3.498579	-1.288179
F	-1.935231	-2.675616	0.142203
F	0.168914	-2.692619	0.600138
F	2.217690	-2.416704	-4.902678
F	0.938258	-0.663115	-4.870696
F	2.931469	-0.553395	-4.029555
F	3.449972	-2.742919	-2.553824
F	2.116244	-2.882165	-0.859598
F	1.775624	-4.117752	-2.618425

Table S31. Optimized (M11/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1a, 2, 3a, 3e–$C_3H_2(CF_3)_4$** and **1**

1a, 2, 3a, 3e–$C_3H_2(CF_3)_4$ product

C	0.031521	0.005781	-0.135236
C	1.345500	-0.015478	0.018339
C	2.195687	1.236871	0.091776
H	1.538491	2.095611	0.258429
C	-0.760999	1.282903	-0.237002
H	-0.546329	-0.911778	-0.217988
C	2.031810	-1.366969	0.077272
C	2.930119	1.551895	-1.232453
C	3.151785	1.279358	1.287607
F	-0.282672	2.088025	-1.212847
F	-2.047226	1.025117	-0.509796
F	-0.715298	1.993601	0.912467
F	1.235321	-2.349480	-0.380615
F	3.148297	-1.356464	-0.670697
F	2.372424	-1.684621	1.339075
F	2.288111	0.993053	-2.272480
F	2.948669	2.882933	-1.427045
F	4.198700	1.123359	-1.246896
F	3.767237	2.475481	1.321147
F	2.442731	1.136413	2.423069
F	4.095130	0.332350	1.269045

1a, 2, 3a, 3e–$C_3H_2(CF_3)_4$ + 1 ts

C	-0.002016	0.000369	-0.037715
B	1.070387	0.702834	-1.053895
N	1.865268	-0.232564	-1.874122
C	2.027640	-1.644919	-1.432646
H	2.336324	-1.702468	-0.392340
H	1.075924	-2.174529	-1.565342
H	2.794510	-2.109653	-2.060888
C	1.616286	-0.245419	-3.346051
H	1.537224	0.760520	-3.751749
H	0.682414	-0.790316	-3.532773
H	2.449310	-0.763686	-3.834904
C	0.347277	1.933204	-1.843639
F	-0.180432	2.862953	-1.018459
F	-0.649248	1.506677	-2.654708
F	1.228629	2.611241	-2.652574
F	-0.709117	0.860663	0.717210
F	-0.899663	-0.612504	-0.879105
F	0.447343	-0.978968	0.779803
C	2.412483	1.856804	0.118751
C	3.308132	2.170805	-0.903715
C	4.123945	1.221548	-1.621046
C	5.184749	0.397829	-0.863323
F	4.904846	-0.923429	-0.890678
F	6.401314	0.555987	-1.412442
F	5.294724	0.776054	0.414896
C	4.614122	1.508648	-3.041142
F	3.603111	1.883466	-3.846336
F	5.585382	2.423735	-3.131899
F	5.082799	0.344686	-3.557258
C	3.326051	3.673657	-1.271989
F	3.494180	3.968548	-2.555051
F	2.243142	4.327000	-0.834886
F	4.397448	4.155995	-0.599278
C	2.684379	0.988703	1.332846
F	1.578982	0.909573	2.088794
F	3.078278	-0.266127	1.032889
F	3.626815	1.553482	2.107889
H	1.800915	2.695464	0.454970
H	3.129261	0.381741	-1.814532

1a, 2, 3a, 3e–$C_3H_2(CF_3)_4$ + 1

B	0.151856	0.140991	-0.237981
N	1.751352	0.001752	-0.033130
C	-0.421266	1.707635	-0.096645
C	-0.646248	2.468821	-1.403457
C	-1.840897	2.774137	-1.916134
H	2.136941	0.880367	-0.382334
C	-0.299670	-0.440425	-1.711398
C	-0.592314	-0.832833	0.851989
C	2.406116	-1.095009	-0.813869
C	2.185621	-0.107717	1.397889
F	-1.604671	-0.192872	-1.982528
F	-0.136286	-1.783873	-1.841472
F	0.398331	0.123001	-2.752949
F	-0.578019	-0.360290	2.132052
F	-1.892937	-1.039387	0.548632
F	-0.005343	-2.072793	0.914972
H	2.268784	-0.918790	-1.882140
H	1.950347	-2.046280	-0.529543
H	3.473521	-1.100149	-0.570405
H	1.958099	-1.115564	1.752549
H	3.264813	0.068934	1.444556
H	1.661226	0.620649	2.015330
H	-1.397023	1.580567	0.373518
C	0.267843	2.640800	0.897657
C	0.633085	2.940437	-2.117645
C	-2.047555	3.645650	-3.166364
C	-3.195980	2.312126	-1.370112
F	1.618171	2.746551	0.720551
F	-0.222987	3.892867	0.824251
F	0.091307	2.220157	2.165475
F	1.693911	2.152416	-1.771892
F	0.966754	4.186433	-1.755757
F	0.555030	2.871137	-3.446255
F	-3.265823	4.214766	-3.148682
F	-1.956340	2.924835	-4.292818
F	-1.163433	4.655004	-3.225831
F	-3.945431	1.865672	-2.393241
F	-3.840886	3.338513	-0.784562
F	-3.146119	1.322046	-0.468170

Table S32. Optimized (M11/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1e, 2, 3a, 3e–$C_3H_2(CF_3)_4$** and **1**

1e, 2, 3a, 3e–$C_3H_2(CF_3)_4$ product

C	0.093578	-0.030641	0.021703
C	1.416342	-0.092476	-0.036426
C	2.203420	1.203667	-0.054600
H	1.480160	2.025413	-0.091463
H	-0.408510	0.935637	0.023363
C	-0.874868	-1.189106	0.108543
C	2.168475	-1.418200	-0.050380
C	3.103667	1.418090	-1.290199
C	2.980090	1.428403	1.245857
F	1.530291	-2.330057	-0.800330
F	3.399154	-1.257891	-0.566755
F	2.305894	-1.915576	1.188967
F	2.647248	0.701837	-2.332326
F	3.063710	2.719877	-1.642037
F	4.385598	1.102254	-1.081726
F	3.674462	2.576575	1.182346
F	2.109734	1.522156	2.270138
F	3.830530	0.433051	1.520574
F	-2.043954	-0.733307	0.609187
F	-1.134863	-1.715424	-1.099976
F	-0.447628	-2.170902	0.915281

1e, 2, 3a, 3e–$C_3H_2(CF_3)_4$ + 1 ts

C	-0.003961	-0.007086	0.010430
N	0.022843	0.947087	1.149140
B	0.894790	2.140020	1.045102
C	2.207183	1.929747	0.095758
F	3.177905	2.838823	0.260334
F	2.752933	0.725208	0.470882
F	1.956024	1.825649	-1.237090
C	1.259976	2.876830	2.436276
F	1.765411	4.111967	2.273312
F	2.180874	2.146837	3.124561
F	0.175910	3.005217	3.256473
C	0.014728	0.192603	2.435342
H	-0.245009	0.849889	3.267055
H	1.007755	-0.242730	2.598950
H	-0.734692	-0.601484	2.360507
H	0.059355	0.520332	-0.943593
H	0.838479	-0.701560	0.091882
H	-0.947523	-0.564954	0.049202
C	-0.344448	3.501087	0.019435
C	-1.473441	3.530207	0.827229
C	-2.241615	2.318661	0.986255
C	-2.944041	1.794025	-0.254605
F	-3.448399	0.563135	-0.048648
F	-3.961695	2.591614	-0.620823
F	-2.112323	1.706938	-1.321358
C	-3.059122	2.062552	2.244818
F	-4.353289	2.394962	2.161679
F	-2.508779	2.680132	3.304784
F	-3.018839	0.730061	2.521555
C	-1.901635	4.833349	1.541366
F	-1.098379	5.191110	2.539113
F	-1.933042	5.821776	0.629039
F	-3.154074	4.721860	2.008648
H	-0.311687	2.732144	-0.757856
C	0.366089	4.754203	-0.474338
F	0.582757	5.676973	0.467048
F	1.556822	4.424082	-1.001692
F	-0.356057	5.322524	-1.464393
H	-1.176620	1.500243	1.121720

1e, 2, 3a, 3e–$C_3H_2(CF_3)_4$ + 1

B	0.260850	0.026220	0.001980
N	1.840304	-0.159482	0.265268
C	-0.066376	1.635958	-0.006261
C	-0.587156	-0.585682	1.272855
C	2.685250	0.783317	-0.538743
C	2.285853	-0.108708	1.695807
F	-1.348940	1.927077	0.275160
F	0.685243	2.314089	0.921379
F	0.223093	2.241283	-1.205285
F	-1.909669	-0.688708	0.999593
F	-0.483791	0.198698	2.385077
F	-0.183467	-1.832470	1.666243
H	2.242202	0.949736	-1.521616
H	2.732490	1.736899	-0.008794
H	3.688520	0.360363	-0.646744
H	1.835615	-0.933420	2.249940
H	1.977833	0.844653	2.128667
H	3.377134	-0.197642	1.714418
C	-0.287139	-0.731550	-1.389158
C	-0.052727	-0.074251	-2.747892
C	0.947349	-0.216234	-3.627394
H	2.043580	-1.105703	-0.063202
H	-1.366407	-0.626973	-1.232083
C	-0.138178	-2.265249	-1.369673
C	-1.263889	0.797362	-3.163117
C	1.033849	0.475649	-4.998880
C	2.202188	-1.034882	-3.386763
F	1.906822	-0.177628	-5.791732
F	-0.129278	0.497047	-5.656593
F	1.485903	1.735355	-4.872682
F	3.295242	-0.271769	-3.612136
F	2.305998	-1.457862	-2.104749
F	2.278766	-2.118121	-4.159303
F	-2.057517	0.091604	-3.991603
F	-2.023948	1.135202	-2.108293
F	-0.901481	1.935627	-3.761150
F	0.068512	-2.793312	-2.593534
F	0.874238	-2.720288	-0.576465
F	-1.258071	-2.824487	-0.877565

Table S33. Optimized (M11/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1a, 1e, 2–$C_3H_3(CF_3)_3$** and **1**

1a, 1e, 2–$C_3H_3(CF_3)_3$

C	-0.028838	-0.026448	-0.041392
C	1.301658	0.023358	-0.019398
C	2.126233	1.279647	0.064754
H	1.562033	2.109011	0.491723
C	-0.850638	1.241126	-0.211788
C	-0.872451	-1.277387	0.156525
C	2.155161	-1.242850	-0.073841
H	2.496677	1.565861	-0.926513
H	2.997931	1.079436	0.697683
F	-0.220385	2.141366	-0.994256
F	-2.025095	0.974519	-0.804889
F	-1.102002	1.841000	0.968188
F	-0.231278	-2.207618	0.880943
F	-1.252259	-1.831451	-1.004913
F	-1.986690	-0.957817	0.847116
F	1.604486	-2.209783	-0.821409
F	3.347138	-0.948508	-0.640045
F	2.411249	-1.727803	1.152773

1a, 1e, 2–$C_3H_3(CF_3)_3$ + 1 ts

C	0.018534	0.010989	0.016152
B	0.980559	0.656916	-1.132950
N	1.822259	-0.226403	-1.958108
C	1.873370	-1.681043	-1.682656
H	2.014223	-1.877940	-0.622831
H	0.940227	-2.151402	-2.019484
H	2.709781	-2.111634	-2.245687
C	1.902960	0.000579	-3.426701
H	1.959723	1.068830	-3.649224
H	1.029080	-0.428379	-3.925851
H	2.812388	-0.486940	-3.798477
C	0.077382	1.732643	-1.981462
F	-0.902880	2.333805	-1.289735
F	-0.553544	1.075184	-3.004188
F	0.817940	2.715215	-2.575250
F	-0.398672	0.931660	0.912795
F	-1.094898	-0.459785	-0.620180
F	0.498842	-1.035691	0.735511
C	2.387139	1.865614	0.063580
C	3.351834	2.048498	-0.954781
C	4.175054	1.004053	-1.417422
H	4.603937	0.312189	-0.696323
H	4.822583	1.239453	-2.259177
C	3.527116	3.315703	-1.819047
F	2.661665	4.302449	-1.658917
F	4.759042	3.798881	-1.547340
F	3.516479	2.970030	-3.128925
C	2.843795	0.869462	1.151529
F	1.975065	0.663309	2.132993
F	3.112791	-0.357896	0.628635
F	3.995315	1.308703	1.711812
C	1.786802	3.144214	0.695909
F	1.242820	2.933663	1.897648
F	0.850029	3.710854	-0.065340
F	2.783423	4.049864	0.885650
H	3.157431	0.290654	-1.746777

1a, 1e, 2–$C_3H_3(CF_3)_3$ + 1 product

B	0.031931	0.094135	-0.014319
N	1.664953	0.042626	-0.043101
C	-0.570964	1.710556	0.077210
C	-0.719029	2.345203	-1.331208
C	-1.866748	2.500018	-1.978696
H	1.946969	0.915600	-0.488061
C	-0.522278	-0.600330	-1.415636
C	-0.423137	-0.916511	1.207158
C	2.295589	-1.041409	-0.868724
C	2.332111	0.025713	1.302340
F	-1.848115	-0.478314	-1.621494
F	-0.262521	-1.936972	-1.477620
F	0.073515	-0.065072	-2.536403
F	-0.172868	-0.465651	2.466737
F	-1.724890	-1.263757	1.163490
F	0.285465	-2.095813	1.119296
H	2.019448	-0.918835	-1.915789
H	1.960760	-2.011375	-0.498568
H	3.381214	-0.950496	-0.759691
H	2.263189	-0.985933	1.707976
H	3.382227	0.300891	1.162268
H	1.852890	0.722303	1.986260
C	-1.978511	1.737064	0.760667
C	0.296942	2.661548	0.943478
C	0.505920	2.852384	-2.080818
H	-1.870604	2.920642	-2.979820
H	-2.825073	2.206894	-1.568404
F	-1.927199	1.354511	2.043471
F	-2.861535	0.928792	0.154404
F	-2.515224	2.978269	0.747200
F	1.591506	2.686636	0.506132
F	-0.133328	3.927830	0.907353
F	0.359877	2.291384	2.234334
F	1.592191	2.022127	-1.979118
F	0.913538	4.056700	-1.634877
F	0.277120	2.981381	-3.396457

Table S34. Optimized (M11/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1a, 1e, 3a–$C_3H_3(CF_3)_3$** and **1** and between propene **1a, 1e, 3e–$C_3H_3(CF_3)_3$** and **1**

1a, 1e, 3a–$C_3H_3(CF_3)_3$ = 1a, 1e, 3e– $C_3H_3(CF_3)_3$			
C	-0.109589	0.035686	-0.075402
C	1.203318	0.158126	-0.201294
C	1.944887	1.463882	-0.248892
H	1.362644	2.264107	-0.716746
C	-1.017265	1.240907	0.008576
C	-0.774274	-1.316802	-0.029514
H	1.800737	-0.752553	-0.261276
C	3.233967	1.309451	-1.021278
H	2.208309	1.783712	0.767910
F	-1.059234	1.905710	-1.167853
F	-2.271740	0.910405	0.336606
F	-0.566548	2.121502	0.932838
F	0.118446	-2.306499	-0.216150
F	-1.714716	-1.427167	-0.987330
F	-1.375892	-1.533506	1.155963
F	3.006141	0.922332	-2.293887
F	3.923645	2.463634	-1.059630
F	4.034495	0.373066	-0.460430

1a, 1e, 3a–$C_3H_3(CF_3)_3$ + 1 ts			
C	0.007150	-0.067226	0.010377
B	1.033116	0.660088	-1.035531
N	1.854628	-0.239618	-1.870511
C	1.944282	-1.683658	-1.519579
H	2.238973	-1.815394	-0.481348
H	0.973121	-2.162332	-1.695085
H	2.700666	-2.144289	-2.162282
C	1.764911	-0.114875	-3.352709
H	1.830620	0.929169	-3.663026
H	0.818257	-0.538246	-3.705239
H	2.600745	-0.671472	-3.791604
C	0.270299	1.864076	-1.838302
F	-0.472518	2.669463	-1.063931
F	-0.570751	1.340914	-2.773397
F	1.128961	2.683375	-2.533695
F	-0.669877	0.754840	0.824737
F	-0.925554	-0.672080	-0.800622
F	0.511231	-1.057214	0.785248
C	2.473281	1.860114	0.246339
C	3.353686	2.020773	-0.820598
C	4.173761	1.088645	-1.499789
C	5.190756	0.132960	-0.902897
F	4.773667	-1.158213	-0.896615
F	6.305803	0.157601	-1.671629
F	5.565550	0.443971	0.345400
H	4.587269	1.492187	-2.423731
H	3.158919	2.925696	-1.396399
C	2.792832	0.914814	1.390889
F	1.756924	0.774734	2.226812
F	3.109972	-0.307853	0.901270
F	3.835654	1.337991	2.122335
C	1.840897	3.160319	0.756348
F	0.648482	2.987682	1.325736
F	1.705331	4.061264	-0.236179
F	2.649393	3.718125	1.688239
H	3.121942	0.328909	-1.755915

1a, 1e, 3a–$C_3H_3(CF_3)_3$ + 1 product			
B	0.010354	0.005506	0.028432
N	1.635762	0.152769	0.057144
C	-0.611053	1.516973	0.161582
C	-0.449076	-0.802146	1.401374
C	2.190945	1.350960	-0.660267
C	2.303745	0.123575	1.403827
F	-1.913888	1.525026	0.502061
F	0.045876	2.237489	1.127984
F	-0.490361	2.274885	-0.974532
F	-1.742640	-1.149556	1.463652
F	-0.221699	-0.033805	2.512704
F	0.268792	-1.953225	1.610746
H	1.663791	1.527267	-1.593976
H	2.078185	2.220932	-0.009821
H	3.250822	1.164487	-0.859504
H	2.105836	-0.822646	1.904716
H	1.919830	0.954024	1.999600
H	3.379908	0.240769	1.240619
C	-0.456519	-0.776274	-1.421846
C	0.246818	-0.188147	-2.637799
C	1.345811	-0.450937	-3.343387
H	1.986915	-0.669757	-0.440866
C	-1.968791	-0.595114	-1.756390
C	-0.199565	-2.289647	-1.331748
H	-0.301262	0.671591	-3.024814
H	1.530834	0.196933	-4.198945
C	2.487442	-1.423159	-3.182221
F	-2.287504	-1.299982	-2.867582
F	-2.790834	-0.984224	-0.786169
F	-2.253408	0.694237	-2.033969
F	-0.298755	-2.913914	-2.514332
F	-1.031611	-2.903214	-0.486341
F	1.074334	-2.502073	-0.886414
F	3.127898	-1.266023	-1.974509
F	2.180269	-2.715754	-3.295567
F	3.419331	-1.150187	-4.120588

Table S34. (continued)

1a, 1e, 3e–$C_3H_3(CF_3)_3$ + 1 ts			
C	0.021440	0.001672	0.023785
B	0.976729	0.742465	-1.081584
N	1.778571	-0.140770	-1.944588
C	1.884320	-1.589473	-1.645453
H	2.089548	-1.760025	-0.591220
H	0.949070	-2.092926	-1.920681
H	2.703133	-2.004610	-2.244353
C	1.730439	0.049730	-3.420731
H	1.815975	1.106328	-3.681043
H	0.790435	-0.346827	-3.819271
H	2.574702	-0.490965	-3.864639
C	0.151033	1.923805	-1.855415
F	-0.599205	2.698696	-1.054383
F	-0.695209	1.374412	-2.770571
F	0.959147	2.779686	-2.563525
F	-0.649843	0.822083	0.845737
F	-0.919184	-0.671022	-0.716469
F	0.602344	-0.935075	0.816469
C	2.414481	1.966070	0.090304
C	3.267745	2.167911	-0.990535
C	4.104993	1.162995	-1.515522
H	4.648087	0.503864	-0.835471
C	4.884385	1.493366	-2.753935
F	4.184293	2.304473	-3.580715
F	6.054718	2.105965	-2.490455
F	5.171975	0.365886	-3.446644
H	3.088263	3.057830	-1.596317
C	2.901179	1.029324	1.185503
F	2.033156	0.941269	2.194272
F	3.122367	-0.222113	0.703573
F	4.084037	1.441097	1.690765
C	1.789476	3.235966	0.671774
F	0.630121	3.036795	1.295092
F	1.601678	4.161196	-0.286592
F	2.642130	3.769207	1.581899
H	3.098057	0.407926	-1.800638

1a, 1e, 3e–$C_3H_3(CF_3)_3$ + 1 product			
B	-0.033675	-0.000763	-0.006842
N	1.591927	0.162603	-0.160241
C	-0.647158	1.502833	0.221360
C	-0.355193	-0.836977	1.386519
C	2.073851	1.405456	-0.860172
C	2.395019	0.051183	1.104280
F	-1.917205	1.489673	0.666613
F	0.087604	2.191708	1.154672
F	-0.625044	2.301634	-0.891140
F	-1.645632	-1.168491	1.546570
F	-0.018856	-0.106197	2.493374
F	0.357812	-2.004363	1.502252
H	1.469064	1.633228	-1.734407
H	2.015620	2.236795	-0.154552
H	3.113064	1.242893	-1.163629
H	2.245055	-0.925488	1.562226
H	2.072301	0.840226	1.786602
H	3.449961	0.186399	0.845110
C	-0.629343	-0.761665	-1.415707
C	0.052198	-0.130015	-2.609557
C	1.039439	-0.636787	-3.334174
H	1.872196	-0.627470	-0.747124
C	-2.149437	-0.571844	-1.649488
C	-0.343600	-2.271360	-1.381785
H	-0.291851	0.880998	-2.830105
C	1.729220	0.196335	-4.368239
H	1.450131	-1.638385	-3.225581
F	-2.548889	-1.285697	-2.727054
F	-2.906918	-0.946645	-0.619937
F	-2.429489	0.718977	-1.916857
F	-0.501929	-2.881575	-2.569495
F	-1.100979	-2.918350	-0.497013
F	0.972056	-2.477718	-1.037336
F	1.709656	-0.375564	-5.584667
F	1.204505	1.432821	-4.483841
F	3.039388	0.357393	-4.029483

Table S35. Optimized (M11/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1a, 2, 3a–$C_3H_3(CF_3)_3$** and **1** and between propene **1a, 2, 3e–$C_3H_3(CF_3)_3$** and **1**

1a, 2, 3a–$C_3H_3(CF_3)_3$ = 1a, 2, 3e– $C_3H_3(CF_3)_3$

C	0.030880	-0.066337	-0.191420
C	1.343287	0.010393	-0.038315
C	2.135111	1.285590	0.097643
H	1.473754	2.145827	0.223872
C	-0.846712	1.152430	-0.282183
H	-0.485609	-1.021696	-0.249341
C	2.123247	-1.289629	0.002485
C	3.012621	1.567741	-1.109865
H	2.797451	1.225999	0.968936
F	-0.441640	2.000830	-1.249980
F	-2.117348	0.806052	-0.545369
F	-0.847049	1.854778	0.876584
F	1.353820	-2.328118	0.382075
F	3.152346	-1.204755	0.868729
F	2.629274	-1.589500	-1.207445
F	2.331577	1.444666	-2.264032
F	3.498350	2.824394	-1.049229
F	4.068760	0.731176	-1.168585

1a, 2, 3a–$C_3H_3(CF_3)_3$ + 1 ts

C	0.032064	-0.019704	0.025702
B	1.090077	0.694750	-0.999579
N	1.889755	-0.221467	-1.838232
C	2.026980	-1.639120	-1.419709
H	2.318702	-1.714252	-0.374769
H	1.072143	-2.158830	-1.575142
H	2.799606	-2.109917	-2.035608
C	1.714763	-0.175945	-3.314070
H	1.807012	0.842068	-3.693953
H	0.727693	-0.573501	-3.581686
H	2.490111	-0.798938	-3.773343
C	0.309724	1.886289	-1.801825
F	-0.254374	2.812165	-0.994882
F	-0.672658	1.405411	-2.602152
F	1.152770	2.588738	-2.631278
F	-0.646505	0.852157	0.801076
F	-0.896072	-0.640331	-0.769635
F	0.506973	-0.987809	0.845608
C	2.313580	1.826368	0.193409
C	3.280645	2.136021	-0.761039
C	4.151506	1.246155	-1.457983
C	5.174006	0.311981	-0.817086
F	4.768913	-0.977428	-0.778351
F	6.298163	0.330895	-1.568394
F	5.519711	0.671465	0.425880
H	4.631283	1.720427	-2.314749
C	3.303699	3.576473	-1.288958
F	3.491989	3.657621	-2.614427
F	2.221921	4.284807	-0.959899
F	4.371427	4.162808	-0.699818
C	2.676415	0.996884	1.407691
F	1.636146	0.876927	2.240886
F	3.114457	-0.238845	1.087440
F	3.659264	1.606297	2.102566
H	1.667541	2.652899	0.497431
H	3.212814	0.462641	-1.797034

1a, 2, 3a–$C_3H_3(CF_3)_3$ + 1 product

B	0.137430	0.091794	-0.160203
N	1.751038	0.024435	-0.059638
C	-0.488811	1.637625	-0.085822
C	-0.691201	2.319842	-1.432425
C	-1.835395	2.505267	-2.075892
H	2.075700	0.900424	-0.473824
C	-0.383021	-0.575971	-1.571809
C	-0.499487	-0.858566	1.016093
C	2.396762	-1.083180	-0.831798
C	2.278240	-0.003740	1.343163
F	-1.710843	-0.374691	-1.763429
F	-0.190029	-1.919226	-1.658149
F	0.234523	-0.043995	-2.681145
F	-0.405779	-0.360222	2.281045
F	-1.814856	-1.099397	0.810395
F	0.119317	-2.085015	1.066440
H	2.187164	-0.960905	-1.895757
H	1.994474	-2.035441	-0.478040
H	3.476757	-1.041280	-0.656727
H	2.110198	-1.002029	1.754231
H	3.351091	0.211318	1.313325
H	1.766388	0.733249	1.960876
H	-1.483822	1.492871	0.345095
C	0.168775	2.616911	0.872449
C	0.532416	2.881656	-2.144950
H	-1.833574	2.980579	-3.055346
C	-3.233122	2.136920	-1.663351
F	1.507355	2.776693	0.620815
F	-0.381171	3.843117	0.799757
F	0.075531	2.219363	2.155454
F	1.635354	2.096036	-1.962921
F	0.856767	4.101412	-1.678671
F	0.360681	2.991720	-3.470010
F	-3.795593	1.352893	-2.602213
F	-3.981859	3.261826	-1.584986
F	-3.349317	1.503207	-0.483645

Table S35. (continued)

1a, 2, 3e–$C_3H_3(CF_3)_3$ + 1 ts			
C	0.067708	0.011721	0.155664
B	1.016134	0.690671	-0.996244
N	1.759552	-0.223924	-1.881674
C	1.872467	-1.658772	-1.534766
H	2.127204	-1.795637	-0.486784
H	0.919989	-2.164932	-1.743275
H	2.654752	-2.108194	-2.156969
C	1.609988	-0.086509	-3.354027
H	1.780213	0.942781	-3.672378
H	0.605119	-0.401453	-3.660736
H	2.354655	-0.726878	-3.839767
C	0.152662	1.860819	-1.744486
F	-0.393212	2.762109	-0.897246
F	-0.861690	1.339886	-2.479545
F	0.907035	2.598050	-2.623334
F	-0.457084	0.916981	1.012705
F	-0.982436	-0.580622	-0.485655
F	0.618888	-0.962231	0.925273
C	2.314279	1.818155	0.072692
C	3.202895	2.176752	-0.941243
C	4.061803	1.189091	-1.505089
H	4.551174	0.540903	-0.771747
C	4.993223	1.451751	-2.665968
F	4.335989	1.537354	-3.842555
F	5.729365	2.567118	-2.526915
F	5.850207	0.410972	-2.774862
C	3.170861	3.618983	-1.450933
F	3.263108	3.718088	-2.778722
F	2.084404	4.279989	-1.036292
F	4.244042	4.233927	-0.909772
C	2.873691	0.948702	1.184747
F	2.029895	0.866261	2.213428
F	3.187853	-0.311504	0.787810
F	4.028956	1.482344	1.652632
H	1.673161	2.603509	0.477498
H	3.141141	0.396643	-1.824141

1a, 2, 3e–$C_3H_3(CF_3)_3$ + 1 product			
B	0.153644	0.170766	-0.106231
N	1.760825	0.002473	-0.042473
C	-0.373119	1.746528	0.008807
C	-0.546999	2.509562	-1.303182
C	-1.764214	2.813341	-1.731823
H	2.128691	0.873168	-0.430154
C	-0.444345	-0.412365	-1.523455
C	-0.513256	-0.775487	1.058450
C	2.320520	-1.108000	-0.874574
C	2.315545	-0.108899	1.344919
F	-1.766681	-0.131012	-1.657152
F	-0.329017	-1.758624	-1.674859
F	0.163880	0.137778	-2.626075
F	-0.349500	-0.336106	2.337575
F	-1.850029	-0.921583	0.889994
F	0.021010	-2.040780	1.041598
H	2.092816	-0.927700	-1.926727
H	1.870605	-2.049256	-0.549959
H	3.405017	-1.137171	-0.727384
H	2.089635	-1.106288	1.729650
H	3.399602	0.034108	1.295385
H	1.869253	0.641841	1.996742
H	-1.387411	1.653735	0.423133
C	0.337835	2.655937	1.000225
C	0.684946	2.956520	-2.073135
C	-2.148253	3.613701	-2.952261
H	-2.629711	2.472893	-1.166162
F	1.676916	2.759450	0.734957
F	-0.150550	3.910079	0.978186
F	0.237359	2.215574	2.268803
F	1.751115	2.130468	-1.832090
F	1.075358	4.187861	-1.706458
F	0.503239	2.944367	-3.395608
F	-3.421323	4.045117	-2.800513
F	-2.108697	2.891179	-4.085312
F	-1.380524	4.705845	-3.126156

Table S36. Optimized (M11/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1a, 3a, 3e–$C_3H_3(CF_3)_3$** and **1**

1a, 3a, 3e–$C_3H_3(CF_3)_3$

C	0.031812	0.123891	0.205603
C	1.327847	0.236103	0.448062
C	2.219262	1.424450	0.168012
H	1.694431	2.378653	0.261454
C	-0.884677	1.160791	-0.375281
H	-0.481420	-0.812577	0.417363
H	1.842970	-0.636643	0.851406
C	3.360465	1.446176	1.179576
C	2.722747	1.336107	-1.274683
F	-0.375228	2.412327	-0.368152
F	-1.205822	0.865741	-1.649773
F	-2.038203	1.200520	0.326173
F	4.148142	0.358119	1.075081
F	2.846863	1.452147	2.427967
F	4.133695	2.532614	1.050551
F	1.676241	1.445699	-2.115032
F	3.593454	2.312894	-1.568900
F	3.321729	0.156709	-1.522386

1a, 3a, 3e–$C_3H_3(CF_3)_3$ + 1 ts

C	0.070311	0.045452	-0.002780
B	1.135075	0.722651	-1.046276
N	1.885611	-0.214697	-1.899666
C	1.970786	-1.643419	-1.507340
H	2.284831	-1.741454	-0.469395
H	0.995893	-2.128383	-1.646694
H	2.713797	-2.131123	-2.147255
C	1.717530	-0.114578	-3.373685
H	1.799364	0.920146	-3.710344
H	0.737301	-0.513837	-3.662883
H	2.506439	-0.704644	-3.854533
C	0.406148	1.989758	-1.789441
F	-0.115855	2.890473	-0.921885
F	-0.606907	1.569433	-2.584582
F	1.237113	2.722533	-2.600946
F	-0.561412	0.926837	0.798773
F	-0.894468	-0.528359	-0.790214
F	0.527708	-0.950210	0.792223
C	2.465938	1.792997	0.228161
C	3.342850	2.025995	-0.813056
C	4.216100	1.118122	-1.505169
C	5.234087	0.209529	-0.802473
F	4.808845	-1.072794	-0.756417
F	6.409468	0.198534	-1.457236
F	5.486509	0.609542	0.450510
C	4.758928	1.672437	-2.816402
F	3.814537	2.407497	-3.445180
F	5.832493	2.465631	-2.662944
F	5.093566	0.668174	-3.651558
H	3.097066	2.914449	-1.394755
C	2.770972	0.945034	1.440930
F	1.703905	0.864792	2.248530
F	3.147640	-0.310063	1.111184
F	3.761389	1.495113	2.171277
H	1.808381	2.621945	0.496620
H	3.230505	0.348366	-1.807289

1a, 3a, 3e–$C_3H_3(CF_3)_3$ + 1 product

B	0.045930	0.133168	-0.143575
N	1.669744	0.136840	-0.136528
C	-0.634168	1.633318	0.132070
C	-0.738008	2.428630	-1.144505
C	-1.801560	2.741453	-1.870237
H	1.940146	1.049265	-0.512089
C	-0.458773	-0.381930	-1.618258
C	-0.492760	-0.959992	0.943068
C	2.335328	-0.904850	-0.987151
C	2.263844	0.044222	1.238870
F	-1.778316	-0.187995	-1.828403
F	-0.226720	-1.701645	-1.852596
F	0.191694	0.293886	-2.635067
F	-0.403089	-0.553708	2.241646
F	-1.793186	-1.265935	0.732665
F	0.201934	-2.143904	0.884907
H	2.093610	-0.743837	-2.037497
H	1.979594	-1.887364	-0.669416
H	3.416728	-0.828512	-0.834502
H	2.173450	-0.992521	1.572526
H	3.319759	0.326308	1.182708
H	1.737787	0.692746	1.935914
H	-1.621817	1.447854	0.564598
C	0.070428	2.551847	1.109853
H	0.216985	2.777687	-1.544985
C	-1.600796	3.426226	-3.204847
C	-3.249392	2.440676	-1.561275
F	1.371061	2.790979	0.714100
F	-0.517882	3.759503	1.184044
F	0.135611	2.070899	2.363473
F	-0.405980	4.051902	-3.270759
F	-2.554374	4.343979	-3.445043
F	-1.635597	2.535228	-4.215066
F	-3.867875	1.934306	-2.643620
F	-3.904379	3.568244	-1.212841
F	-3.411821	1.567765	-0.551103

Table S37. Optimized (M11/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1e, 2, 3a–$C_3H_3(CF_3)_3$** and **1** and between propene **1e, 2, 3e–$C_3H_3(CF_3)_3$** and **1**

1e, 2, 3a–$C_3H_3(CF_3)_3$ = 1e, 2, 3e– $C_3H_3(CF_3)_3$			
C	0.119485	-0.004298	0.099621
C	1.435617	-0.067210	-0.041740
C	2.264167	1.193364	-0.086793
H	1.636967	2.050942	-0.348043
H	-0.370942	0.965550	0.169879
C	-0.844679	-1.161781	0.186388
C	2.183984	-1.388666	-0.157987
C	2.886770	1.493055	1.262941
H	3.077284	1.112493	-0.814393
F	-0.366665	-2.199226	0.889773
F	-1.975027	-0.744463	0.798093
F	-1.195971	-1.611228	-1.033903
F	1.527888	-2.256102	-0.949457
F	3.402256	-1.190275	-0.707839
F	2.372136	-1.972293	1.034121
F	3.667298	0.481174	1.687420
F	1.940715	1.697436	2.203838
F	3.647007	2.604258	1.203492

1e, 2, 3a–$C_3H_3(CF_3)_3$ + 1 ts			
C	-0.002795	0.004359	-0.018406
B	1.090701	0.560718	-1.094024
N	1.861831	-0.494659	-1.795629
C	2.102304	-1.763277	-1.071906
H	2.371213	-1.580836	-0.030158
H	1.197223	-2.383673	-1.096361
H	2.923961	-2.300029	-1.559355
C	1.604991	-0.785218	-3.227341
H	1.638321	0.125930	-3.825873
H	0.620537	-1.256504	-3.340089
H	2.380942	-1.473976	-3.580989
C	0.465648	1.672604	-2.104562
F	-0.124575	2.733628	-1.542708
F	-0.455873	1.109742	-2.935678
F	1.459793	2.175155	-2.923558
F	-0.817417	0.944586	0.492308
F	-0.802468	-0.895505	-0.670336
F	0.529871	-0.666774	1.042041
C	2.426689	1.440310	0.093019
C	3.355301	1.874788	-0.852193
C	4.127446	0.942773	-1.604924
C	5.045971	-0.038794	-0.918627
F	4.562946	-0.520063	0.249067
F	5.264166	-1.107120	-1.723656
F	6.245138	0.507397	-0.653090
H	4.642535	1.360406	-2.470793
C	3.465275	3.341509	-1.272298
F	2.345577	4.027745	-1.046252
F	4.465857	3.901716	-0.565795
F	3.782841	3.460926	-2.572714
H	2.656957	0.477241	0.553335
C	1.861268	2.373337	1.165975
F	1.522999	1.629871	2.238481
F	0.790715	3.085655	0.820273
F	2.816734	3.245671	1.567168
H	3.147508	0.190085	-1.908880

1e, 2, 3a–$C_3H_3(CF_3)_3$ + 1 product			
B	0.235800	0.020297	-0.010477
N	1.819313	-0.170152	0.236099
C	-0.090739	1.627460	-0.031862
C	-0.602184	-0.585475	1.271425
C	2.657831	0.784092	-0.557573
C	2.272970	-0.133874	1.663563
F	-1.393582	1.900272	0.175124
F	0.602642	2.303636	0.942856
F	0.258264	2.250756	-1.203259
F	-1.927266	-0.690493	1.010558
F	-0.492787	0.194657	2.386129
F	-0.194694	-1.834263	1.658838
H	2.225573	0.938352	-1.546259
H	2.678211	1.740790	-0.030197
H	3.670540	0.379419	-0.647621
H	1.827840	-0.964438	2.212734
H	1.963382	0.814988	2.106202
H	3.364652	-0.218995	1.676739
C	-0.328398	-0.733473	-1.384676
C	-0.047914	-0.116313	-2.745425
C	0.975082	-0.199186	-3.586721
H	2.021499	-1.110688	-0.110751
H	-1.411857	-0.611634	-1.245726
C	-0.174020	-2.265402	-1.365736
C	-1.274620	0.590684	-3.316132
H	0.922189	0.303809	-4.550332
C	2.248014	-0.960521	-3.421442
F	0.011540	-2.794793	-2.592292
F	-1.271260	-2.838808	-0.842109
F	0.871351	-2.706009	-0.602506
F	-2.140231	-0.351920	-3.760398
F	-1.929471	1.315371	-2.397356
F	-0.989018	1.399436	-4.350252
F	3.315874	-0.147448	-3.608423
F	2.396761	-1.508537	-2.188840
F	2.343883	-1.956075	-4.313551

Table S37. (continued)

1e, 2, 3e–$C_3H_3(CF_3)_3$ + 1 ts			
C	0.143149	0.033095	0.116514
N	0.150305	0.992291	1.236149
B	0.912876	2.245966	1.075772
C	2.210656	2.137641	0.096049
F	2.975284	3.241671	0.043714
F	3.005742	1.128445	0.565463
F	1.913375	1.807557	-1.195991
C	1.214308	3.002888	2.481141
F	1.795528	4.205824	2.398377
F	2.006044	2.242419	3.288082
F	0.033467	3.190888	3.170334
C	0.114809	0.281194	2.536785
H	1.082494	-0.198764	2.728897
H	-0.668630	-0.484449	2.491283
H	-0.117019	0.968402	3.351417
H	-0.058845	0.541373	-0.831942
H	1.110645	-0.477675	0.032321
H	-0.642946	-0.710511	0.291914
C	-0.298660	3.434989	-0.019879
C	-1.435659	3.474791	0.784140
C	-2.185856	2.261690	0.872642
H	-2.395208	1.816274	-0.105336
C	-3.351359	2.034602	1.802421
F	-4.290457	2.995331	1.746065
F	-2.965741	1.898406	3.086186
F	-3.949777	0.869159	1.449947
C	-1.799871	4.715490	1.601033
F	-0.744761	5.513016	1.784496
F	-2.738727	5.395628	0.916250
F	-2.306603	4.407296	2.798000
H	-0.334504	2.667895	-0.799503
C	0.341353	4.691723	-0.612870
F	1.235432	5.318793	0.146422
F	0.956836	4.345654	-1.763212
F	-0.623121	5.588669	-0.933390
H	-1.230113	1.527006	1.202443

1e, 2, 3e–$C_3H_3(CF_3)_3$ + 1 product			
B	-0.250431	0.005682	-0.003410
N	1.248080	0.048256	-0.632767
C	-0.695883	1.581712	0.245956
C	-0.471431	2.490104	-0.954023
C	-1.209255	2.400942	-2.055592
H	1.199346	0.750004	-1.378939
C	-1.181626	-0.827181	-1.050204
C	-0.197853	-0.823709	1.412883
C	1.744627	-1.204560	-1.293825
C	2.277570	0.521481	0.344930
F	-2.503836	-0.640961	-0.865475
F	-0.963398	-2.170121	-1.002785
F	-0.928032	-0.465202	-2.363180
F	0.181801	-0.033996	2.464199
F	-1.366422	-1.399068	1.749390
F	0.725965	-1.846183	1.392293
H	1.119373	-1.437219	-2.155891
H	1.709211	-2.023931	-0.575630
H	2.775340	-1.030696	-1.619367
H	2.453140	-0.276866	1.070076
H	3.200449	0.750944	-0.195982
H	1.932553	1.417826	0.864713
C	-2.071742	1.870814	0.836954
H	-0.048862	1.925940	1.060637
C	0.687659	3.468219	-0.851127
C	-1.026044	3.166355	-3.344069
H	-2.031489	1.689578	-2.097200
F	-2.349676	1.048023	1.859996
F	-3.091299	1.789128	-0.041093
F	-2.095723	3.141141	1.320825
F	1.828086	2.898535	-1.356141
F	0.965762	3.776574	0.431472
F	0.484744	4.611343	-1.503399
F	-1.672704	2.518536	-4.333989
F	0.272644	3.249589	-3.709375
F	-1.522682	4.413097	-3.290398

Table S38. Optimized (M11/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1e, 3a, 3e–$C_3H_3(CF_3)_3$** and **1**

1e, 3a, 3e–$C_3H_3(CF_3)_3$

C	0.032973	0.031680	-0.100289
C	1.326247	0.071713	0.161951
C	2.139786	1.330057	0.006098
H	1.498496	2.212981	-0.098191
H	-0.539436	0.897825	-0.430125
C	-0.762424	-1.231945	0.030635
H	1.860556	-0.824375	0.480857
C	2.978279	1.235368	-1.271491
C	3.009753	1.549028	1.242579
F	-0.016160	-2.273284	0.443184
F	-1.770888	-1.076666	0.915793
F	-1.323183	-1.573418	-1.149308
F	2.161989	1.298042	-2.342042
F	3.866233	2.236092	-1.372446
F	3.651287	0.073821	-1.338762
F	3.967769	0.608889	1.342683
F	2.247004	1.476063	2.350883
F	3.603158	2.751778	1.236330

1e, 3a, 3e–$C_3H_3(CF_3)_3$ + 1 ts

C	-0.177903	0.168219	-0.204664
B	0.986487	0.794690	-1.171013
N	1.808130	-0.202030	-1.883647
C	2.045582	-1.503741	-1.218708
H	2.074506	-1.389152	-0.131811
H	1.244777	-2.204655	-1.479032
H	3.006538	-1.909463	-1.557976
C	1.585185	-0.420387	-3.335334
H	1.597364	0.522520	-3.883518
H	0.620245	-0.922150	-3.485099
H	2.392043	-1.057411	-3.716216
C	0.434674	2.014253	-2.082222
F	-0.001415	3.067017	-1.361230
F	-0.584585	1.618354	-2.884272
F	1.412037	2.512431	-2.916894
F	-1.221927	0.987618	0.005214
F	-0.696767	-0.931841	-0.838963
F	0.252299	-0.271028	1.010964
C	2.281486	1.683542	0.166712
C	3.146819	2.176236	-0.788451
C	3.990098	1.339080	-1.588468
C	4.958691	0.399850	-0.896981
F	4.344268	-0.310664	0.078596
F	5.456676	-0.487344	-1.783543
F	5.991929	1.032611	-0.322935
C	4.593946	1.962667	-2.841698
F	4.111876	3.195259	-3.071317
F	5.934909	2.055012	-2.786821
F	4.293968	1.204936	-3.923262
H	3.015549	3.214079	-1.097808
H	2.477449	0.736914	0.671888
C	1.653545	2.703475	1.099063
F	2.351836	2.712712	2.259936
F	1.702603	3.953099	0.598744
F	0.380686	2.433474	1.407636
H	3.059941	0.523525	-1.915567

1e, 3a, 3e–$C_3H_3(CF_3)_3$ + 1 product

B	0.200997	-0.034948	-0.016797
N	1.793787	-0.129638	0.213305
C	-0.230702	1.541669	-0.128509
C	-0.594624	-0.631177	1.295140
C	2.579280	0.825875	-0.632109
C	2.247136	0.011892	1.634715
F	-1.571457	1.701352	-0.034361
F	0.331046	2.314857	0.849292
F	0.133269	2.146117	-1.306374
F	-1.911538	-0.827671	1.045151
F	-0.532308	0.198287	2.377047
F	-0.108194	-1.835175	1.729096
H	2.183332	0.856018	-1.647285
H	2.496611	1.821542	-0.187809
H	3.625853	0.506462	-0.645599
H	1.852800	-0.811108	2.231816
H	1.880369	0.964123	2.024904
H	3.341721	-0.005664	1.649343
C	-0.322445	-0.866290	-1.356454
C	-0.028598	-0.218975	-2.684182
C	0.939786	-0.345966	-3.587220
H	2.043951	-1.075992	-0.086637
H	-1.412284	-0.772818	-1.251274
C	-0.108407	-2.382422	-1.277339
H	-0.779468	0.525429	-2.949606
C	0.922642	0.536281	-4.815224
C	2.163703	-1.214929	-3.501288
F	0.063328	-2.950305	-2.488590
F	-1.174135	-2.972108	-0.705576
F	0.966858	-2.757094	-0.521941
F	1.366489	-0.132446	-5.897240
F	-0.310507	0.995986	-5.090869
F	1.721940	1.615236	-4.656588
F	3.260411	-0.521067	-3.879958
F	2.390851	-1.614886	-2.220519
F	2.098859	-2.311759	-4.260242

Table S39. Optimized (M11/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **2, 3a, 3e–$C_3H_3(CF_3)_3$** and **1**

2, 3a, 3e–$C_3H_3(CF_3)_3$

C	0.055462	0.055190	-0.068443
C	1.376736	-0.004119	-0.017800
C	2.226122	1.248182	-0.023797
H	1.538995	2.101561	-0.006218
H	-0.463701	1.011085	-0.102578
H	-0.545449	-0.851102	-0.083839
C	2.050478	-1.355707	0.059050
C	3.071505	1.446818	-1.300382
C	3.087455	1.415402	1.229193
F	1.270049	-2.328817	-0.450035
F	3.211456	-1.359702	-0.622747
F	2.325099	-1.700291	1.334533
F	2.515225	0.805961	-2.342925
F	3.113795	2.760933	-1.608986
F	4.336500	1.028133	-1.175812
F	3.975794	0.428925	1.396737
F	2.294082	1.445620	2.317725
F	3.762926	2.579328	1.174434

2, 3a, 3e–$C_3H_3(CF_3)_3$ + 1 ts

C	0.070394	-0.028176	-0.064356
N	0.008983	0.900654	1.089303
B	0.786388	2.167176	0.976608
C	2.107275	2.115930	0.018941
F	2.888943	3.210274	0.135215
F	2.872763	1.042902	0.370345
F	1.850623	1.975471	-1.315655
C	1.140478	2.891670	2.381835
F	1.465454	4.197249	2.237642
F	2.182083	2.284297	3.008704
F	0.091086	2.860455	3.260293
C	0.079282	0.115970	2.350285
H	-0.198110	0.728359	3.208441
H	1.098520	-0.268446	2.484488
H	-0.621448	-0.722504	2.272944
H	0.061925	0.515012	-1.010525
H	0.989059	-0.624559	-0.005663
H	-0.799974	-0.694348	-0.030359
C	-0.312467	3.369268	-0.038332
C	-1.418613	3.460304	0.788146
C	-2.263894	2.310377	0.996201
C	-2.985843	1.778967	-0.231063
F	-3.631653	0.632586	0.050664
F	-3.892106	2.654124	-0.699934
F	-2.138042	1.513999	-1.255352
C	-3.157457	2.218878	2.223886
F	-4.433432	2.571274	1.995480
F	-2.685228	2.967781	3.231503
F	-3.174574	0.935415	2.665020
C	-1.701435	4.821576	1.461021
F	-1.172289	5.010048	2.665058
F	-1.233221	5.801342	0.660942
F	-3.036396	4.976675	1.545434
H	-0.335445	2.651603	-0.858585
H	0.269453	4.270888	-0.225114
H	-1.254234	1.437510	1.128888

2, 3a, 3e–$C_3H_3(CF_3)_3$ + 1 product

B	0.057139	0.105554	-0.308584
N	1.664659	-0.085958	-0.159309
C	-0.324190	1.698822	-0.084407
C	-0.615940	2.505140	-1.325854
C	-1.815169	2.770454	-1.851097
H	2.042662	0.699755	-0.692571
C	-0.358192	-0.434066	-1.789700
C	-0.677425	-0.811606	0.824355
C	2.272736	-1.321888	-0.744438
C	2.124442	0.072183	1.252114
F	-1.621134	-0.138943	-2.164056
F	-0.222914	-1.779667	-1.954837
F	0.463161	0.147091	-2.741056
F	-0.670756	-0.219411	2.063158
F	-1.967208	-1.074395	0.536960
F	-0.069689	-2.031272	1.012774
H	2.139961	-1.315315	-1.827259
H	1.782545	-2.197779	-0.315938
H	3.340603	-1.328934	-0.501329
H	1.859501	-0.832344	1.805796
H	3.210411	0.209236	1.263557
H	1.631774	0.930321	1.715010
H	-1.163243	1.765513	0.607225
H	0.512090	2.200587	0.421941
C	0.644324	3.089439	-1.973527
C	-2.051314	3.632277	-3.091753
C	-3.126359	2.221654	-1.303392
F	1.757401	2.388843	-1.574321
F	0.859536	4.351893	-1.569262
F	0.649508	3.044478	-3.304049
F	-3.308059	4.112247	-3.109073
F	-1.875987	2.930216	-4.222978
F	-1.236030	4.702854	-3.128685
F	-3.855548	1.703938	-2.308528
F	-3.850323	3.205575	-0.727396
F	-2.981315	1.260448	-0.382412

Table S40. Optimized (M11/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1a, 1e–$C_3H_4(CF_3)_2$** and **1** and between propene **1a, 2–$C_3H_4(CF_3)_2$** and **1**

1a, 1e–$C_3H_4(CF_3)_2$

C	-0.060095	0.024764	-0.021416
C	1.260894	0.068051	0.106784
C	2.117356	1.292518	0.120637
H	1.553286	2.221475	0.023471
C	-0.889285	1.276737	-0.175702
C	-0.808823	-1.281382	-0.018651
H	1.776366	-0.887062	0.212767
H	2.845012	1.231716	-0.698298
H	2.690088	1.320575	1.055920
F	-0.518198	1.986567	-1.266753
F	-2.198000	1.005956	-0.298269
F	-0.743638	2.102463	0.886759
F	0.027878	-2.328862	0.130893
F	-1.485547	-1.472265	-1.169858
F	-1.706275	-1.340443	0.986786

1a, 1e–$C_3H_4(CF_3)_2$ + 1 ts

B	2.798255	1.076210	0.116369
N	3.402666	0.064131	1.004126
C	0.737253	1.239714	0.627931
C	0.926262	1.197220	2.018004
C	1.257415	0.026013	2.723464
H	2.320779	-0.097992	2.072081
C	2.876822	0.721747	-1.486784
C	3.326786	2.609037	0.366086
C	3.729864	-1.285015	0.495088
C	4.440690	0.469647	1.980979
C	0.050833	0.021684	0.021040
C	0.091890	2.530329	0.117956
F	2.397912	1.667561	-2.311953
F	4.215179	0.602360	-1.773696
F	2.313538	-0.448129	-1.890138
F	3.062821	3.072937	1.636935
F	4.681662	2.669091	0.230872
F	2.821599	3.531931	-0.470224
H	2.956806	-1.657428	-0.172586
H	4.687819	-1.258297	-0.040686
H	3.821453	-1.967723	1.349158
H	4.565787	-0.340453	2.710084
H	5.395943	0.644418	1.472231
H	4.149519	1.378170	2.511835
F	0.353364	2.800843	-1.159609
F	-1.257696	2.432566	0.232074
F	0.470591	3.587642	0.861316
F	-0.227701	0.194818	-1.273374
F	0.807254	-1.096815	0.148627
F	-1.113221	-0.251820	0.655254
H	1.057212	2.160958	2.511122
H	1.434342	0.137008	3.791451
H	0.774171	-0.908470	2.432275

1a, 1e–$C_3H_4(CF_3)_2$ + 1 product

B	0.003564	-0.001709	-0.007757
N	1.640739	0.089989	-0.099958
C	-0.556036	1.533810	0.139991
C	-0.404050	-0.761373	1.409528
C	2.190944	1.294239	-0.809372
C	2.394801	-0.028607	1.191428
F	-1.843600	1.589757	0.529370
F	0.164516	2.230363	1.081541
F	-0.453727	2.291139	-0.997031
F	-1.713000	-1.027366	1.539702
F	-0.072522	0.003038	2.497482
F	0.249520	-1.952743	1.606710
H	1.642559	1.487208	-1.727237
H	2.109125	2.153968	-0.141418
H	3.243874	1.100441	-1.039237
H	2.183007	-0.985399	1.666521
H	2.087785	0.790711	1.845011
H	3.463561	0.050477	0.967237
C	-0.553726	-0.787922	-1.409287
C	0.189791	-0.252204	-2.625731
C	1.161090	-0.840391	-3.313306
H	1.901075	-0.721183	-0.667610
C	-2.055059	-0.551416	-1.707266
C	-0.339418	-2.305092	-1.293391
H	-0.135977	0.746119	-2.919669
H	1.608716	-0.317910	-4.156976
H	1.529874	-1.842483	-3.104704
F	-2.451443	-1.294155	-2.766765
F	-2.866533	-0.848635	-0.690214
F	-2.278158	0.737400	-2.038043
F	-0.489156	-2.974722	-2.448742
F	0.952764	-2.552820	-0.888463
F	-1.154590	-2.875171	-0.402360

1a, 2–$C_3H_4(CF_3)_2$

C	0.011392	-0.011983	-0.181464
C	1.324243	0.064422	-0.026396
C	2.155220	1.294407	0.186689
H	1.545559	2.198027	0.230399
C	-0.863438	1.207934	-0.160553
H	-0.502631	-0.957753	-0.331623
C	2.124108	-1.216404	-0.061701
H	2.880253	1.391587	-0.630513
H	2.718301	1.197418	1.122784
F	-0.529268	2.095032	-1.126760
F	-2.154218	0.874823	-0.350477
F	-0.787442	1.873053	1.015977
F	1.372353	-2.312946	-0.261250
F	2.794853	-1.389259	1.099146
F	3.048104	-1.171658	-1.047280

1a, 2–$C_3H_4(CF_3)_2$ + 1 ts

B	0.060263	0.060994	0.022549
N	1.535541	0.031365	-0.000488
C	-0.599484	1.939809	0.013986
C	0.286195	2.509454	-0.904218
C	1.656305	2.717192	-0.620165
H	1.866405	1.523459	-0.371512
C	-0.658109	-0.631608	1.327855
C	-0.691654	-0.525232	-1.312333
C	2.277594	-0.306045	1.231008
C	2.225820	-0.517864	-1.191158
C	-0.496737	2.487290	1.424253
H	-1.642024	1.828539	-0.291060
F	-2.005980	-0.509342	1.313281
F	-0.385377	-1.970403	1.285197
F	-0.256080	-0.225928	2.561153
F	-0.212271	0.011116	-2.479732
F	-0.528619	-1.867700	-1.434575
F	-2.026038	-0.288924	-1.336297
H	1.872938	0.228373	2.088635
H	2.224510	-1.386658	1.423111
H	3.328190	-0.021976	1.098998
H	3.306854	-0.425824	-1.040023
H	1.973333	-1.575614	-1.337530
H	1.950131	0.040180	-2.090005
F	-1.499823	2.062187	2.195688
F	0.675223	2.178255	2.036985
F	-0.554380	3.843363	1.408554
C	-0.168157	2.797975	-2.328555
H	2.264576	3.115757	-1.431179
H	1.898298	3.120006	0.366208
F	0.703072	2.340902	-3.244768
F	-1.386527	2.327787	-2.603851
F	-0.211197	4.144484	-2.462232

1a, 2–$C_3H_4(CF_3)_2$ + 1 product

B	0.135357	0.106045	-0.065053
N	1.752426	0.023557	-0.066228
C	-0.460953	1.659406	-0.002268
C	-0.676454	2.344446	-1.348151
C	-1.878316	2.530875	-1.871417
H	2.053684	0.893104	-0.511068
C	-0.480809	-0.585421	-1.427082
C	-0.427439	-0.826727	1.166038
C	2.341845	-1.094430	-0.866372
C	2.366395	0.007064	1.300286
F	-1.817560	-0.374517	-1.536530
F	-0.310137	-1.935814	-1.493482
F	0.070382	-0.092679	-2.584766
F	-0.250438	-0.325000	2.420071
F	-1.756806	-1.066370	1.051808
F	0.186544	-2.057357	1.185395
H	2.067532	-0.978412	-1.916123
H	1.956540	-2.041193	-0.480477
H	3.431002	-1.058500	-0.759206
H	2.224767	-0.987818	1.729418
H	3.435252	0.221862	1.202012
H	1.893922	0.749611	1.942373
H	-1.468087	1.543328	0.424326
C	0.232094	2.629785	0.936632
C	0.508991	2.865179	-2.125910
H	-2.006997	2.992042	-2.847511
H	-2.768892	2.195709	-1.343891
F	1.561242	2.772640	0.624166
F	-0.303231	3.863498	0.888070
F	0.191518	2.237452	2.225651
F	1.603597	2.043274	-2.016002
F	0.914132	4.074982	-1.687652
F	0.257189	2.984070	-3.438436

Table S41. Optimized (M11/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1a, 3a–$C_3H_4(CF_3)_2$** and **1** and between propene **1a, 3e–$C_3H_4(CF_3)_2$** and **1**

1a, 3a–$C_3H_4(CF_3)_2$ = 1a, 3e–$C_3H_4(CF_3)_2$

C	-0.046715	-0.022520	-0.143315
C	1.263375	0.118211	-0.272563
C	2.003481	1.427588	-0.217656
H	1.386019	2.275152	-0.531605
C	-0.960102	1.148514	0.067504
H	-0.534723	-0.992901	-0.180507
H	1.871110	-0.776190	-0.415178
C	3.220557	1.387854	-1.109136
H	2.358427	1.623233	0.802780
F	-1.036437	1.946435	-1.026200
F	-2.211982	0.747218	0.357142
F	-0.544841	1.944269	1.085481
F	2.891315	1.164627	-2.399321
F	4.070486	0.397263	-0.743397
F	3.908659	2.545296	-1.059189

1a, 3a–$C_3H_4(CF_3)_2$ + 1 ts

B	0.055825	0.097924	-0.029550
N	1.534180	0.044715	0.040165
C	-0.671568	1.962634	0.179324
C	0.200467	2.475818	-0.774620
C	1.611296	2.686684	-0.710420
H	1.826323	1.478186	-0.437744
C	-0.731725	-0.719101	1.146113
C	-0.593221	-0.327962	-1.479386
C	2.178127	-0.206635	1.350616
C	2.258751	-0.727285	-0.997253
C	-0.684858	2.440473	1.613231
H	-1.696118	1.796304	-0.159197
F	-2.078918	-0.618819	1.070279
F	-0.427014	-2.044122	0.989649
F	-0.389271	-0.418263	2.422860
F	-0.007232	0.306507	-2.559600
F	-0.464906	-1.650774	-1.728588
F	-1.913695	-0.032026	-1.585362
H	1.761766	0.434449	2.124816
H	2.046626	-1.259752	1.636529
H	3.247999	0.009193	1.258110
H	3.331955	-0.531949	-0.891043
H	2.078102	-1.802327	-0.860329
H	1.948292	-0.439292	-2.002363
F	-1.656042	1.837331	2.313947
F	0.487691	2.239098	2.249806
F	-0.945790	3.765694	1.659860
H	-0.170545	2.386235	-1.795232
C	2.348617	3.457739	0.371991
H	2.043989	2.944199	-1.677242
F	1.578669	4.351531	1.012195
F	2.908904	2.655999	1.307165
F	3.368433	4.143255	-0.196927

1a, 3a–$C_3H_4(CF_3)_2$ + 1 product

B	0.067894	0.073360	-0.073957
N	1.680188	0.320284	-0.103520
C	-0.649918	1.475620	0.338260
C	-0.204038	-1.058838	1.078362
C	2.092156	1.606390	-0.747063
C	2.402517	0.223633	1.208481
F	-1.946536	1.324057	0.670646
F	-0.035693	2.063274	1.421196
F	-0.603512	2.428399	-0.645640
F	-1.437135	-1.592256	1.063870
F	0.012696	-0.636507	2.356688
F	0.663279	-2.121071	0.881958
H	1.530059	1.778767	-1.663073
H	1.890331	2.418779	-0.043917
H	3.163975	1.561575	-0.966162
H	2.333601	-0.791052	1.598706
H	1.948608	0.926118	1.910245
H	3.451890	0.485358	1.037614
C	-0.416297	-0.579075	-1.530498
C	0.355581	-0.085120	-2.725920
C	1.318856	-0.728533	-3.375821
H	2.038005	-0.444419	-0.684247
C	-1.885407	-0.392490	-1.903763
H	-0.294074	-1.667698	-1.435963
H	0.063209	0.900050	-3.097705
H	1.813000	-0.304653	-4.246656
C	1.773158	-2.106015	-3.000390
F	-2.157791	-1.080193	-3.046080
F	-2.747290	-0.821266	-0.977512
F	-2.181021	0.903880	-2.164943
F	2.822135	-2.496977	-3.744656
F	2.183871	-2.163744	-1.687126
F	0.811654	-3.038084	-3.123956

1a, 3e–$C_3H_4(CF_3)_2$ + 1 ts

B	0.041868	0.063596	-0.010366
N	1.521002	0.029991	0.036525
C	-0.638168	1.930517	0.027692
C	0.243280	2.415366	-0.931712
C	1.604304	2.683840	-0.628829
H	1.824664	1.497460	-0.281675
C	-0.750558	-0.620755	1.252043
C	-0.650051	-0.502441	-1.391515
C	2.217323	-0.357667	1.281547
C	2.254985	-0.498333	-1.137689
C	-0.507348	2.504099	1.422844
H	-1.678956	1.765052	-0.256621
F	-2.084035	-0.385501	1.245998
F	-0.590882	-1.973808	1.162248
F	-0.318906	-0.281540	2.495219
F	-0.276710	0.171879	-2.534557
F	-0.324883	-1.799605	-1.615068
F	-2.003492	-0.431982	-1.378856
H	1.848236	0.214454	2.130959
H	2.077994	-1.429344	1.480593
H	3.287837	-0.159085	1.156034
H	3.309956	-0.210803	-1.050913
H	2.181367	-1.592040	-1.180132
H	1.858666	-0.079679	-2.065949
F	-1.501922	2.119038	2.224589
F	0.670016	2.172244	2.017168
F	-0.526340	3.861082	1.382201
H	-0.035395	2.304788	-1.979366
H	1.843018	3.222732	0.291410
C	2.496586	3.075246	-1.770367
F	2.167367	2.415579	-2.906423
F	2.444557	4.393814	-2.047961
F	3.785420	2.776388	-1.492441

1a, 3e–$C_3H_4(CF_3)_2$ + 1 product

B	0.061727	0.163105	-0.038972
N	1.681553	0.147092	-0.133870
C	-0.566636	1.684603	0.171177
C	-0.631784	2.475079	-1.116951
C	-1.754767	2.779744	-1.741776
H	1.934253	1.047160	-0.550224
C	-0.556996	-0.411202	-1.447052
C	-0.415869	-0.890163	1.120052
C	2.278535	-0.926049	-0.994347
C	2.354850	0.086952	1.206033
F	-1.886493	-0.182426	-1.557669
F	-0.385901	-1.750408	-1.627430
F	0.026585	0.181305	-2.547035
F	-0.232431	-0.473751	2.403331
F	-1.734297	-1.181022	1.005940
F	0.254270	-2.088410	1.034955
H	1.967899	-0.792728	-2.030504
H	1.932515	-1.893852	-0.624633
H	3.368725	-0.861260	-0.916526
H	2.277292	-0.939842	1.572590
H	3.407467	0.359640	1.081669
H	1.872955	0.758782	1.913777
H	-1.587067	1.545203	0.556802
C	0.131063	2.595763	1.159520
H	0.314798	2.810807	-1.547092
C	-1.759910	3.544549	-3.025752
H	-2.737540	2.473172	-1.387063
F	1.430706	2.833033	0.757572
F	-0.454865	3.803519	1.247205
F	0.207010	2.109749	2.412202
F	-2.487311	4.681368	-2.918464
F	-2.313571	2.825409	-4.027870
F	-0.520477	3.901337	-3.428076

Table S42. Optimized (M11/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1e, 2–$C_3H_4(CF_3)_2$** and **1** and between propene **3a, 3e–$C_3H_4(CF_3)_2$** and **1**

1e, 2–$C_3H_4(CF_3)_2$

C	0.013130	-0.034832	0.012542
C	1.337680	-0.001142	-0.038255
C	2.121682	1.279326	-0.017532
H	1.456485	2.135797	0.117284
H	-0.545659	0.898683	0.044230
C	-0.869199	-1.254015	0.071817
C	2.189742	-1.256037	-0.070025
H	2.684719	1.398717	-0.949876
H	2.849480	1.259494	0.803560
F	-0.410604	-2.193673	0.920106
F	-2.095915	-0.886621	0.512993
F	-1.045162	-1.835078	-1.131080
F	1.616543	-2.273076	-0.729579
F	2.476299	-1.674173	1.180500
F	3.371097	-1.003190	-0.679675

1e, 2–$C_3H_4(CF_3)_2$ + 1 ts

B	0.034659	0.173891	-0.254550
N	1.477568	-0.082281	-0.062731
C	-0.190680	2.116691	-0.071605
C	0.678810	2.599284	-1.053346
C	2.080906	2.445732	-0.886327
H	2.063951	1.236125	-0.730060
C	-0.908417	-0.379341	0.955943
C	-0.490292	-0.285125	-1.725336
C	2.007449	-0.027436	1.306999
C	2.173590	-1.124996	-0.843871
F	-2.233187	-0.298717	0.729781
F	-0.622817	-1.704457	1.144540
F	-0.683141	0.222940	2.162557
F	-1.752437	0.030252	-2.044561
F	-0.376966	-1.632800	-1.898102
F	0.305205	0.292175	-2.698352
H	1.627123	0.848098	1.843435
H	1.724344	-0.922788	1.877303
H	3.101853	0.036347	1.265545
H	1.977900	-1.014782	-1.911197
H	1.848177	-2.123340	-0.521156
H	3.252394	-1.027461	-0.672538
H	0.252961	2.111003	0.928194
C	-1.623927	2.632671	0.054769
C	0.188844	3.154003	-2.387029
H	2.451897	2.728749	0.104057
H	2.713345	2.769574	-1.710627
F	-1.043091	2.748631	-2.696909
F	0.190380	4.501114	-2.308489
F	1.016105	2.814405	-3.390034
F	-1.995369	2.544407	1.349627
F	-2.550085	2.010231	-0.670060
F	-1.668372	3.948192	-0.281011

1e, 2–$C_3H_4(CF_3)_2$ + 1 product

B	-0.130796	-0.087184	-0.048078
N	1.450269	-0.037135	-0.437299
C	-0.640152	1.484455	0.038202
C	-0.469002	2.277478	-1.250696
C	-1.170570	2.113743	-2.363824
H	1.506044	0.666875	-1.179507
C	-0.867111	-0.990700	-1.195050
C	-0.270242	-0.867171	1.385086
C	2.058831	-1.287704	-1.000265
C	2.318296	0.444540	0.682189
F	-2.207211	-0.849565	-1.237234
F	-0.624053	-2.325012	-1.051972
F	-0.418157	-0.678025	-2.466611
F	0.030928	-0.068788	2.454167
F	-1.498580	-1.377447	1.598443
F	0.600060	-1.930979	1.492594
H	1.581885	-1.539187	-1.946982
H	1.920449	-2.100640	-0.286388
H	3.126417	-1.103302	-1.159396
H	2.421530	-0.367032	1.406793
H	3.298022	0.715914	0.277204
H	1.873892	1.313254	1.168775
C	-2.034430	1.776460	0.583248
H	-0.009173	1.954739	0.807126
C	0.579152	3.352806	-1.193766
H	-1.000151	2.750679	-3.228802
H	-1.940824	1.349209	-2.431848
F	-2.254660	1.172090	1.763672
F	-3.035256	1.422253	-0.246326
F	-2.172139	3.112479	0.794359
F	1.822258	2.783112	-0.981245
F	0.392989	4.199438	-0.166384
F	0.682652	4.075840	-2.315835

3a, 3e–$C_3H_4(CF_3)_2$

C	0.046627	0.012463	0.045818
C	1.369038	0.037581	0.046575
C	2.159507	1.320047	-0.037231
H	1.495498	2.189429	-0.114237
H	-0.542027	0.927587	-0.017244
H	-0.496317	-0.928021	0.108964
H	1.957498	-0.878630	0.110371
C	3.029293	1.315320	-1.292807
C	2.984369	1.505542	1.235353
F	3.809329	0.463274	1.452267
F	3.731808	2.622360	1.210258
F	2.158173	1.597803	2.296739
F	2.246178	1.192102	-2.383156
F	3.895246	0.283544	-1.295779
F	3.738809	2.447969	-1.435051

3a, 3e–$C_3H_4(CF_3)_2$ + 1 ts

B	0.039729	0.012530	0.026016
N	1.524897	-0.045730	0.097819
C	-0.668543	1.833942	0.265480
C	0.344008	2.473308	-0.412528
C	1.661024	2.621943	0.134046
H	1.849497	1.349382	0.195725
C	-0.750681	-0.681029	1.275766
C	-0.632903	-0.408524	-1.404435
C	2.197192	-0.767689	1.200350
C	2.269183	-0.227705	-1.171632
H	-0.679157	1.841810	1.355263
H	-1.641600	1.750326	-0.217235
F	-2.094404	-0.531819	1.217492
F	-0.503213	-2.018660	1.319103
F	-0.388187	-0.185343	2.499250
F	-0.268806	0.418007	-2.440850
F	-0.261171	-1.664014	-1.776828
F	-1.985833	-0.392706	-1.402858
H	1.732961	-0.531936	2.157526
H	2.152647	-1.850520	1.028696
H	3.247244	-0.452817	1.231901
H	3.336435	-0.070719	-0.976663
H	2.115223	-1.233157	-1.578565
H	1.937809	0.507751	-1.912660
H	0.233030	2.642652	-1.484476
C	2.701866	3.282198	-0.742626
C	1.776055	3.013914	1.594658
F	2.395218	3.134638	-2.051088
F	2.821663	4.601767	-0.501858
F	3.919500	2.726846	-0.561270
F	3.049455	3.273385	1.935573
F	1.039881	4.098369	1.901184
F	1.343180	2.005489	2.392884

3a, 3e–$C_3H_4(CF_3)_2$ + 1 product

B	0.161633	0.042258	-0.041920
N	1.766878	0.103300	0.145563
C	-0.469846	1.533760	0.122612
C	-0.429405	-0.925520	1.134808
C	2.403946	1.195617	-0.649612
C	2.268605	0.174560	1.554424
F	-1.807605	1.494809	0.322885
F	0.059492	2.252007	1.163558
F	-0.277546	2.325699	-0.985189
F	-1.699470	-1.331963	0.911189
F	-0.416549	-0.385479	2.386344
F	0.324837	-2.081743	1.220249
H	2.009933	1.199121	-1.666454
H	2.176152	2.149360	-0.165141
H	3.486742	1.036568	-0.671011
H	2.004427	-0.738896	2.087928
H	1.811337	1.035672	2.046194
H	3.357225	0.289269	1.528554
C	-0.267686	-0.668488	-1.452576
C	0.086327	0.017286	-2.725247
C	1.018555	-0.350774	-3.605191
H	2.095150	-0.782790	-0.247720
H	-1.365576	-0.713239	-1.408120
H	0.084794	-1.707992	-1.441079
H	-0.474591	0.921891	-2.962671
C	1.295154	0.451938	-4.845375
C	1.885755	-1.558580	-3.385621
F	1.200298	-0.293082	-5.964872
F	0.437007	1.481103	-4.969927
F	2.545085	0.976718	-4.824308
F	2.836490	-1.691303	-4.317967
F	2.538505	-1.475881	-2.174413
F	1.185768	-2.707297	-3.344492

Table S43. Optimized (M11/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1e, 3a–$C_3H_4(CF_3)_2$** and **1** and between propene **1e, 3e–$C_3H_4(CF_3)_2$** and **1**

1e, 3a–$C_3H_4(CF_3)_2$ = 1e, 3e–$C_3H_4(CF_3)_2$

C	-0.051392	0.012679	-0.063765
C	1.264956	0.107291	0.014658
C	2.001615	1.409180	-0.105964
H	1.326879	2.242571	-0.327266
H	-0.703996	0.867881	-0.234673
C	-0.764656	-1.294572	0.081074
H	1.863541	-0.789450	0.180909
C	3.036728	1.349334	-1.206644
H	2.544052	1.632461	0.821519
F	0.075081	-2.328418	0.285882
F	-1.628965	-1.265309	1.122767
F	-1.495256	-1.578690	-1.020320
F	2.475332	1.136679	-2.414098
F	3.923770	0.349690	-0.996314
F	3.737682	2.500063	-1.283205

1e, 3a–$C_3H_4(CF_3)_2$ + 1 ts

B	0.014428	-0.044236	-0.203417
N	1.489410	-0.057013	-0.054157
C	-0.549702	1.807021	0.164373
C	0.177552	2.424684	-0.848565
C	1.598412	2.522148	-0.854381
H	1.783877	1.299456	-0.620034
C	-0.773148	-0.944195	0.921726
C	-0.512209	-0.395579	-1.697873
C	2.032632	-0.097851	1.320155
C	2.298070	-0.924938	-0.936883
H	-0.164799	1.819216	1.185845
C	-2.047232	2.058414	0.145101
F	-1.965544	-1.422816	0.522244
F	-0.010673	-2.053181	1.191918
F	-0.963945	-0.324391	2.121340
F	0.183802	0.300858	-2.668206
F	-0.358098	-1.709937	-1.999173
F	-1.811126	-0.089373	-1.896038
H	1.364915	0.410303	2.021373
H	2.154564	-1.137595	1.645582
H	3.008914	0.402432	1.338690
H	3.358383	-0.697326	-0.772992
H	2.115021	-1.980244	-0.692037
H	2.057448	-0.752321	-1.987551
F	-2.492987	2.416230	-1.077052
F	-2.775647	1.015993	0.556694
F	-2.324196	3.090657	0.980292
H	-0.349280	2.615222	-1.784784
H	2.039093	2.862299	-1.792163
C	2.322040	3.164175	0.299408
F	1.789233	2.857630	1.505101
F	3.615877	2.762478	0.327976
F	2.331735	4.508470	0.205216

1e, 3a–$C_3H_4(CF_3)_2$ + 1 product

B	0.172510	-0.044192	-0.017501
N	1.773192	-0.123645	0.169448
C	-0.277329	1.530328	-0.100190
C	-0.577366	-0.654160	1.315876
C	2.519688	0.844960	-0.693977
C	2.269437	0.009324	1.575837
F	-1.615255	1.679032	0.047847
F	0.313549	2.302228	0.864369
F	0.034830	2.151663	-1.283206
F	-1.900317	-0.860388	1.107374
F	-0.489267	0.170340	2.401768
F	-0.069039	-1.856074	1.730995
H	2.084053	0.875503	-1.692583
H	2.444500	1.836089	-0.238215
H	3.567759	0.534599	-0.748898
H	1.899676	-0.821232	2.178282
H	1.908243	0.955526	1.985503
H	3.364209	-0.000360	1.556757
C	-0.373299	-0.866258	-1.347498
C	-0.127563	-0.224029	-2.695632
C	0.818202	-0.349446	-3.620376
H	2.021558	-1.064385	-0.149211
H	-1.461440	-0.790479	-1.213541
C	-0.140864	-2.380510	-1.279316
H	-0.908100	0.491416	-2.954688
H	0.746293	0.222967	-4.543279
C	2.065228	-1.162818	-3.550071
F	0.006566	-2.950547	-2.492476
F	-1.183496	-2.987596	-0.678550
F	0.959354	-2.746119	-0.552098
F	2.050737	-2.247155	-4.339961
F	3.130430	-0.410528	-3.932416
F	2.346082	-1.588771	-2.286059

1e, 3e–$C_3H_4(CF_3)_2$ + 1 ts

B	0.008650	-0.092946	-0.054973
N	1.474886	-0.150730	-0.225827
C	-0.647265	1.849180	-0.183306
C	0.371770	2.385354	-0.953491
C	1.679189	2.518497	-0.418106
H	1.835228	1.291999	-0.238374
C	-0.484881	-0.397788	1.467655
C	-0.844740	-0.914490	-1.172571
C	2.339937	-0.798358	0.782430
C	1.989936	-0.389008	-1.590614
H	-0.602498	2.020031	0.894766
C	-2.044634	2.059699	-0.727486
F	-1.802219	-0.226374	1.679619
F	-0.183239	-1.664448	1.852612
F	0.144230	0.436459	2.373510
F	-0.660488	-0.486724	-2.454030
F	-0.422292	-2.218895	-1.149830
F	-2.175230	-0.942804	-0.966663
H	2.071950	-0.484539	1.791405
H	2.252122	-1.890103	0.711255
H	3.379133	-0.508490	0.585947
H	3.074324	-0.225042	-1.592842
H	1.771985	-1.410291	-1.924176
H	1.527243	0.310881	-2.295565
F	-2.145391	1.708224	-2.023669
F	-2.989925	1.422023	-0.034850
F	-2.343093	3.387866	-0.663965
H	0.211384	2.500547	-2.030302
C	2.758182	3.066344	-1.304277
H	1.756129	2.883054	0.610425
F	2.566892	2.714497	-2.597710
F	2.835327	4.411841	-1.265527
F	3.970477	2.589452	-0.935901

1e, 3e–$C_3H_4(CF_3)_2$ + 1 product

B	0.059014	-0.000552	0.003789
N	1.682442	0.076701	-0.038369
C	-0.533870	1.518824	0.158304
C	-0.425278	-0.799463	1.354056
C	2.238298	1.249445	-0.793491
C	2.365844	0.041718	1.296111
F	-1.834770	1.522419	0.523437
F	0.140819	2.249207	1.101410
F	-0.467347	2.274586	-0.986108
F	-1.741637	-1.102756	1.323075
F	-0.230634	-0.078894	2.498956
F	0.245306	-1.980007	1.555302
H	1.709159	1.394327	-1.733096
H	2.125886	2.138928	-0.168881
H	3.299033	1.064785	-0.991180
H	2.151877	-0.898762	1.803096
H	1.994333	0.879473	1.891468
H	3.443572	0.144677	1.133562
C	-0.547619	-0.729327	-1.362292
C	-0.012238	-0.086670	-2.613250
C	0.919180	-0.577236	-3.421671
H	1.962135	-0.770278	-0.542793
H	-1.636425	-0.576071	-1.319328
C	-0.345221	-2.232694	-1.399402
H	-0.400908	0.908656	-2.824914
C	1.470299	0.236215	-4.546119
H	1.374917	-1.560554	-3.321969
F	-0.642030	-2.778294	-2.599258
F	-1.074357	-2.890245	-0.493774
F	0.978387	-2.549983	-1.161561
F	2.786897	0.515177	-4.324318
F	1.410555	-0.412951	-5.725930
F	0.845742	1.421628	-4.700049

Table S44. Optimized (M11/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **2, 3a–$C_3H_4(CF_3)_2$** and **1** and between propene **2, 3e–$C_3H_4(CF_3)_2$** and **1**

2, 3a–$C_3H_4(CF_3)_2$ = 2, 3e–$C_3H_4(CF_3)_2$

C	0.223035	-0.113364	-0.585707
C	1.451871	-0.090814	-0.095534
C	2.309607	1.146165	0.040884
H	1.765701	1.948834	0.549965
H	-0.255330	0.801770	-0.929048
H	-0.331079	-1.045655	-0.663830
C	2.106617	-1.354845	0.387825
C	2.738195	1.684122	-1.306978
H	3.220866	0.936597	0.611764
F	1.342776	-2.446533	0.218213
F	3.281310	-1.570357	-0.244333
F	2.396383	-1.263287	1.711611
F	1.674493	2.096853	-2.037557
F	3.391509	0.765245	-2.040518
F	3.556256	2.748870	-1.161598

2, 3a–$C_3H_4(CF_3)_2$ + 1 ts

B	0.047972	-0.027220	0.007862
N	1.535579	-0.018967	-0.023081
C	-0.562899	1.768305	-0.069896
C	0.102241	2.229695	-1.197022
C	1.517591	2.365726	-1.280737
H	1.748060	1.183114	-0.820460
C	-0.624863	-0.497607	1.419697
C	-0.644133	-0.804743	-1.239269
C	2.233136	0.199719	1.262994
C	2.255000	-1.044477	-0.812617
H	-0.143793	2.033514	0.901562
H	-1.650356	1.693921	-0.111071
F	-1.970689	-0.614270	1.365263
F	-0.136727	-1.723644	1.768231
F	-0.368690	0.324467	2.482257
F	-0.144000	-0.349542	-2.441471
F	-0.402917	-2.143176	-1.216475
F	-1.981845	-0.652187	-1.315815
H	1.762419	1.006075	1.828063
H	2.207424	-0.717496	1.865881
H	3.275499	0.471354	1.061259
H	3.318339	-0.779221	-0.841000
H	2.140415	-2.028202	-0.338603
H	1.873072	-1.092341	-1.833512
C	-0.675055	2.432109	-2.492613
H	1.913004	2.539234	-2.282675
C	2.272395	3.223806	-0.299354
F	0.022902	2.067649	-3.580132
F	-1.849613	1.797891	-2.503297
F	-0.922187	3.758764	-2.603711
F	1.740914	3.229055	0.944157
F	3.551940	2.791783	-0.178120
F	2.330136	4.506883	-0.704795

2, 3a–$C_3H_4(CF_3)_2$ + 1 product

B	0.060523	0.018332	-0.222019
N	1.681777	-0.046327	-0.209999
C	-0.491443	1.559904	-0.102123
C	-0.726780	2.327591	-1.375821
C	-1.839508	2.506010	-2.077315
H	1.957294	0.691324	-0.862283
C	-0.445733	-0.695601	-1.593873
C	-0.509950	-0.809763	1.060768
C	2.304296	-1.312684	-0.708403
C	2.259342	0.293437	1.122547
F	-1.743875	-0.458344	-1.878397
F	-0.293378	-2.051286	-1.619825
F	0.273180	-0.220942	-2.676198
F	-0.401611	-0.096844	2.230862
F	-1.820474	-1.109823	0.925925
F	0.138823	-1.994147	1.308256
H	2.068058	-1.445096	-1.765002
H	1.909041	-2.152186	-0.133118
H	3.389188	-1.241695	-0.576111
H	2.092059	-0.551050	1.796926
H	3.333687	0.473398	1.013895
H	1.769387	1.179383	1.531554
H	-1.427225	1.516575	0.459945
H	0.192460	2.155306	0.520683
C	0.490560	3.071133	-1.876220
H	-1.827006	3.101658	-2.987824
C	-3.219495	2.016646	-1.750204
F	0.355406	3.625813	-3.085109
F	1.585933	2.246052	-1.945719
F	0.835074	4.052620	-1.011932
F	-4.049294	3.086605	-1.638654
F	-3.325209	1.320404	-0.607488
F	-3.708405	1.253059	-2.746985

2, 3e–$C_3H_4(CF_3)_2$ + 1 ts

B	0.053188	-0.035270	0.006420
N	1.534456	-0.072758	-0.013629
C	-0.611633	1.796235	-0.029184
C	0.418048	2.504364	-0.630489
C	1.656155	2.597260	0.065021
H	1.853361	1.330532	0.083546
C	-0.615790	-0.515794	1.413592
C	-0.708958	-0.658993	-1.291070
C	2.296719	-0.749386	1.057574
C	2.195444	-0.275368	-1.323353
H	-0.657544	1.876478	1.057321
H	-1.574587	1.733729	-0.533117
F	-1.953892	-0.338701	1.474439
F	-0.374501	-1.824626	1.680458
F	-0.113652	0.190722	2.489130
F	-0.483780	0.054618	-2.436071
F	-0.294310	-1.932674	-1.547841
F	-2.054242	-0.713436	-1.155504
H	1.909631	-0.486737	2.042053
H	2.241388	-1.837611	0.928472
H	3.344790	-0.434045	0.991762
H	3.262942	-0.047269	-1.218759
H	2.073759	-1.311315	-1.660301
H	1.764983	0.392766	-2.073225
C	0.255768	2.990943	-2.071415
C	2.863513	3.336897	-0.433059
H	1.548154	2.729799	1.146506
F	0.961349	2.283015	-2.968807
F	-1.030290	2.952617	-2.447662
F	0.669841	4.271234	-2.144882
F	3.140939	3.075339	-1.725387
F	2.762645	4.673012	-0.298814
F	3.944025	2.949674	0.291876

2, 3e–$C_3H_4(CF_3)_2$ + 1 product

B	-0.009554	0.060388	-0.137036
N	1.587279	0.028764	-0.388708
C	-0.599167	1.561779	0.111315
C	-0.581967	2.492598	-1.070362
C	-1.661548	2.747606	-1.800455
H	1.771915	0.766830	-1.073316
C	-0.733996	-0.594536	-1.441772
C	-0.372213	-0.826747	1.184185
C	2.126138	-1.230240	-0.995673
C	2.356399	0.359094	0.847066
F	-2.055671	-0.296926	-1.516041
F	-0.643593	-1.952732	-1.524280
F	-0.173548	-0.113151	-2.605849
F	-0.115251	-0.157449	2.354088
F	-1.686974	-1.150831	1.220777
F	0.319249	-2.006675	1.292905
H	1.726529	-1.347159	-2.003968
H	1.826264	-2.078244	-0.377560
H	3.218070	-1.157288	-1.034368
H	2.304398	-0.499276	1.522780
H	3.398595	0.559886	0.579211
H	1.919845	1.234256	1.331525
H	-1.646445	1.413402	0.404382
H	-0.106395	2.038413	0.967438
C	0.764413	3.091119	-1.424253
C	-1.741166	3.589142	-3.044887
H	-2.610009	2.290300	-1.524998
F	1.409123	2.348219	-2.369306
F	1.595811	3.074592	-0.342301
F	0.709544	4.349580	-1.858035
F	-0.685006	3.421361	-3.866085
F	-1.836494	4.908792	-2.772769
F	-2.846744	3.251889	-3.743448

Table S45. Optimized (M11/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1a–$C_3H_5(CF_3)$** and **1** and between propene **1e–$C_3H_5(CF_3)$** and **1**

1a–$C_3H_5(CF_3)$

C	0.003286	-0.026009	0.112613
C	1.326955	-0.016671	0.022761
C	2.206912	1.186064	-0.131041
H	1.647017	2.123383	-0.164412
C	-0.818357	1.225792	0.069440
H	-0.568406	-0.943903	0.223043
H	1.833605	-0.982621	0.064498
H	2.918484	1.232494	0.702884
H	2.796287	1.097325	-1.052318
F	-0.514248	2.088614	1.072198
F	-0.655828	1.921267	-1.084839
F	-2.135575	0.946016	0.177626

1a–$C_3H_5(CF_3)$ + 1 ts

B	0.554880	-0.000700	0.104605
N	0.658236	0.776327	1.366412
C	-0.971066	0.515691	-0.948601
C	-0.807594	1.904340	-0.849469
C	-1.150602	2.631487	0.314308
H	-0.337950	1.997007	0.992898
C	0.374938	-1.622818	0.280302
C	1.786071	0.229305	-0.966462
C	0.242031	0.165723	2.643074
C	1.849296	1.620206	1.588075
F	1.531934	-2.129106	0.803620
F	-0.613546	-2.035011	1.119137
F	0.162447	-2.275221	-0.888583
F	1.933302	1.540745	-1.381167
F	2.990791	-0.118167	-0.450864
F	1.637177	-0.472241	-2.117896
H	-0.743175	-0.289318	2.559686
H	0.964472	-0.600676	2.960254
H	0.205565	0.949115	3.409816
H	1.654276	2.293013	2.432365
H	2.727843	1.004268	1.822683
H	2.072413	2.226538	0.707007
C	-2.254305	-0.042959	-0.373506
H	-0.735211	0.047103	-1.906628
H	-0.144025	2.374404	-1.574501
H	-0.934880	3.698491	0.304267
H	-2.075548	2.361304	0.828986
F	-2.439628	-1.324251	-0.707574
F	-2.318068	0.052939	0.980223
F	-3.330486	0.646282	-0.839207

1a–$C_3H_5(CF_3)$ + 1 product

B	-0.017335	0.038497	-0.004317
N	1.534846	0.431450	-0.233408
C	-0.772262	1.281686	0.745903
C	-0.036576	-1.238821	1.018380
C	1.671190	1.752739	-0.912866
C	2.461305	0.363683	0.937838
F	-1.933881	0.912339	1.324960
F	0.008604	1.798595	1.760404
F	-1.045931	2.354505	-0.048642
F	-1.231998	-1.868317	1.076317
F	0.307890	-0.954333	2.303301
F	0.870325	-2.199485	0.596846
H	0.943174	1.828906	-1.724646
H	1.469079	2.538378	-0.179309
H	2.691145	1.857660	-1.297363
H	2.523349	-0.664933	1.295687
H	2.084083	1.009115	1.732065
H	3.450502	0.703509	0.612349
C	-0.661769	-0.500988	-1.443481
C	0.381486	-0.882563	-2.473238
C	0.979225	-2.067123	-2.539772
H	1.850623	-0.285534	-0.897930
C	-1.678279	0.381177	-2.132758
H	-1.235760	-1.403085	-1.193070
H	0.650772	-0.109642	-3.199830
H	1.724767	-2.274221	-3.305569
H	0.728608	-2.870720	-1.847562
F	-2.210473	-0.245395	-3.214026
F	-2.704798	0.718120	-1.335064
F	-1.130721	1.535141	-2.612050

1e–$C_3H_5(CF_3)$

C	0.042890	-0.021666	0.087928
C	1.356623	-0.032291	-0.081437
C	2.222701	1.186472	-0.019233
H	1.636690	2.088303	0.184125
H	-0.523859	0.886558	0.289286
C	-0.782785	-1.262704	0.017729
H	1.847330	-0.986920	-0.279657
H	2.980898	1.074759	0.765770
H	2.758637	1.320984	-0.967011
F	-0.052878	-2.370413	-0.233916
F	-1.451346	-1.482598	1.176868
F	-1.725912	-1.179543	-0.953194

1e–$C_3H_5(CF_3)$ + 1 ts

B	-0.620761	0.000233	-0.058004
N	-1.675476	0.792011	-0.724244
C	-0.639334	-1.589843	-0.480501
C	-0.587105	0.175990	1.554560
C	-1.958755	0.491566	-2.132462
C	-2.912065	1.135060	-0.004416
F	-1.944190	-1.974556	-0.668129
F	-0.002966	-1.871545	-1.658194
F	-0.151945	-2.436142	0.446409
F	-0.602437	1.510552	1.913382
F	-1.663358	-0.388394	2.164375
F	0.511428	-0.344904	2.140529
H	-2.355902	1.390471	-2.624761
H	-1.049098	0.179742	-2.657902
H	-2.696146	-0.316286	-2.225999
H	-3.477907	1.864086	-0.598924
H	-3.532984	0.238997	0.141901
H	-2.691321	1.576634	0.969538
C	1.078886	0.655011	-0.720737
C	0.977036	2.011819	-0.407053
C	0.078937	2.867847	-1.095704
H	0.033154	3.903431	-0.764055
H	0.062241	2.745947	-2.184359
H	-0.906994	2.230108	-0.816606
H	0.903661	0.371318	-1.762527
C	2.313097	-0.044565	-0.187701
H	1.447909	2.352255	0.517496
F	2.139206	-1.348413	0.049908
F	3.309489	0.055608	-1.109215
F	2.778270	0.526413	0.943385

1e–$C_3H_5(CF_3)$ + 1 product

B	0.100263	-0.004041	-0.010883
N	1.725527	0.007621	0.042291
C	-0.435690	1.543264	0.063107
C	-0.475136	-0.731610	1.345613
C	2.356303	1.101110	-0.764563
C	2.336062	0.044037	1.410254
F	-1.755004	1.606457	0.355255
F	0.211728	2.282383	1.021439
F	-0.276084	2.262947	-1.094203
F	-1.792736	-1.018763	1.258874
F	-0.331321	0.035293	2.469676
F	0.165962	-1.911204	1.637932
H	1.894025	1.157125	-1.748336
H	2.215363	2.043617	-0.229556
H	3.426227	0.889108	-0.862216
H	2.061993	-0.850239	1.968820
H	1.966731	0.933039	1.926955
H	3.424154	0.098519	1.300260
C	-0.469634	-0.754521	-1.374093
C	0.042131	-0.149937	-2.665812
C	0.955401	-0.656471	-3.487209
H	1.992284	-0.883329	-0.387717
H	-1.561159	-0.613382	-1.338084
C	-0.273169	-2.258581	-1.367566
H	-0.396907	0.816289	-2.910947
H	1.239617	-0.111173	-4.385542
H	1.433788	-1.621304	-3.325454
F	-0.562216	-2.848964	-2.546078
F	1.046954	-2.580657	-1.101166
F	-1.013586	-2.887914	-0.445291

Table S46. Optimized (M11/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **2–$C_3H_5(CF_3)$** and **1**

2–$C_3H_5(CF_3)$

C	-0.024329	0.022173	0.138459
C	1.293889	-0.021141	0.020166
C	2.211352	1.159914	-0.116048
H	1.638598	2.091215	-0.104798
H	-0.545209	0.977860	0.143466
H	-0.616421	-0.884799	0.232798
C	1.999212	-1.350138	0.014825
H	2.936441	1.178440	0.706724
H	2.775329	1.100509	-1.054917
F	1.171109	-2.404103	0.139584
F	2.699476	-1.524647	-1.133849
F	2.900153	-1.426713	1.026089

2–$C_3H_5(CF_3)$ + 1 ts

B	-0.820962	0.101648	-0.014584
N	-0.930191	1.343346	0.792580
C	-2.134635	-0.245595	-0.920203
C	-0.357775	-1.198043	0.842653
C	-1.685653	2.454449	0.198447
C	-1.174978	1.259559	2.243855
F	-2.073248	-1.447410	-1.539360
F	-3.249915	-0.265423	-0.132825
F	-2.398563	0.665729	-1.910867
F	0.785087	-0.918094	1.563804
F	-1.285619	-1.601001	1.752966
F	-0.061320	-2.281270	0.091342
H	-1.389484	2.606195	-0.845329
H	-2.767117	2.260326	0.222584
H	-1.476823	3.373757	0.760220
H	-1.055609	2.258127	2.682132
H	-2.196423	0.903368	2.439825
H	-0.465940	0.581089	2.721174
C	0.460702	0.330707	-1.346190
C	1.559296	0.818848	-0.641842
C	1.551107	2.094727	-0.028090
H	2.431062	2.381413	0.545220
H	1.122219	2.899752	-0.632897
H	0.551355	1.853314	0.665885
H	-0.094851	1.076728	-1.920028
H	0.544433	-0.647434	-1.821921
C	2.747225	-0.087061	-0.357579
F	2.482819	-1.380908	-0.557966
F	3.739272	0.265314	-1.213270
F	3.226448	0.068781	0.886922

2–$C_3H_5(CF_3)$ + 1 product

B	-0.032234	-0.050360	-0.122137
N	1.549421	-0.058258	-0.448586
C	-0.636802	1.455838	-0.023983
C	-0.530190	2.327415	-1.253916
C	-1.324393	2.290660	-2.316104
H	1.653062	0.618059	-1.210320
C	-0.777010	-0.893703	-1.305447
C	-0.302029	-0.800834	1.303627
C	2.127705	-1.350857	-0.929461
C	2.354923	0.453419	0.698430
F	-2.110516	-0.653055	-1.379354
F	-0.642074	-2.247912	-1.203178
F	-0.271349	-0.571230	-2.550424
F	-0.024060	-0.003342	2.384408
F	-1.598757	-1.171228	1.436285
F	0.444760	-1.936267	1.505971
H	1.681791	-1.618182	-1.888278
H	1.913744	-2.128610	-0.194152
H	3.209935	-1.227116	-1.043731
H	2.376635	-0.318871	1.472760
H	3.371600	0.670866	0.355771
H	1.896601	1.360168	1.097232
H	-1.702151	1.331153	0.212736
H	-0.210349	1.986322	0.837866
C	0.585697	3.332509	-1.227092
H	-1.175450	2.960381	-3.159452
H	-2.145624	1.578468	-2.362868
F	1.808264	2.695166	-1.111191
F	0.669538	4.103840	-2.320027
F	0.510812	4.150760	-0.155844

Table S47. Optimized (M11/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **3a–$C_3H_5(CF_3)$** and **1** and between propene **3e–$C_3H_5(CF_3)$** and **1**

3a–$C_3H_5(CF_3)$ = 3e–$C_3H_5(CF_3)$

C	0.030852	-0.082471	-0.034946
C	1.354453	-0.050570	-0.070446
C	2.156820	1.215171	0.055609
H	1.511564	2.086986	0.209436
H	-0.556697	0.826287	0.097829
H	-0.514163	-1.018642	-0.136702
H	1.924859	-0.971983	-0.198501
C	3.115366	1.148798	1.220512
H	2.769554	1.387468	-0.838614
F	2.476180	1.015568	2.401606
F	3.964248	0.098742	1.108376
F	3.875255	2.265405	1.302199

3a–$C_3H_5(CF_3)$ + 1 ts

B	0.017492	0.020043	-0.038512
N	1.510176	0.097025	-0.050736
C	-0.739891	1.439387	0.227162
C	-0.579703	-1.106785	0.979321
C	2.091285	1.310995	-0.657581
C	2.242972	-0.231743	1.189000
F	-2.065370	1.299778	0.475598
F	-0.201661	2.058371	1.319050
F	-0.642572	2.339152	-0.796149
F	0.129040	-2.292736	0.931570
F	-0.563997	-0.718953	2.277412
F	-1.860909	-1.457046	0.686599
H	1.548414	1.595554	-1.561178
H	2.052084	2.148263	0.053531
H	3.137237	1.114607	-0.924498
H	3.318408	-0.227108	0.974761
H	2.030502	0.520327	1.962499
H	1.963606	-1.218025	1.563021
C	-0.596803	-0.380498	-1.734486
C	0.013781	-1.629822	-1.799392
C	1.417176	-1.827932	-1.959624
H	1.768263	-2.850407	-1.815053
C	2.169154	-1.200700	-3.099323
H	1.719774	-1.053382	-0.983862
H	-0.175978	0.452379	-2.296719
H	-1.681134	-0.361964	-1.618038
H	-0.557154	-2.478813	-1.418676
F	1.730528	0.037888	-3.425026
F	3.484686	-1.080612	-2.793887
F	2.099451	-1.944641	-4.225004

3a–$C_3H_5(CF_3)$ + 1 product

B	0.154425	0.047006	-0.077688
N	1.760246	0.056136	0.129343
C	-0.427942	1.559295	0.087760
C	-0.480098	-0.898660	1.095055
C	2.433940	1.137578	-0.648740
C	2.253715	0.092321	1.540862
F	-1.768107	1.567209	0.279551
F	0.117306	2.256115	1.137834
F	-0.201955	2.352685	-1.012526
F	-1.763851	-1.256410	0.865902
F	-0.454087	-0.361871	2.349703
F	0.228078	-2.083909	1.185687
H	2.038698	1.163735	-1.664911
H	2.236514	2.091200	-0.150689
H	3.511101	0.942561	-0.670302
H	1.959010	-0.820422	2.059524
H	1.817297	0.958580	2.042573
H	3.345569	0.175878	1.524886
C	-0.267340	-0.646354	-1.492400
C	0.109466	0.027428	-2.773267
C	1.042182	-0.358297	-3.641876
H	2.062561	-0.833099	-0.277958
H	-1.365813	-0.692214	-1.463987
H	0.077063	-1.690172	-1.481061
H	-0.450255	0.929530	-3.025067
H	1.240020	0.177615	-4.566540
C	1.904256	-1.554562	-3.413629
F	2.863586	-1.664421	-4.351377
F	2.565200	-1.489095	-2.199794
F	1.231965	-2.724614	-3.387607

3e–$C_3H_5(CF_3)$ + 1 ts

B	0.074131	-0.020273	-0.044157
N	1.563521	0.038527	-0.076418
C	-0.661562	1.423641	0.131417
C	-0.519541	-1.088331	1.031871
C	2.153153	1.174374	-0.800776
C	2.308024	-0.213470	1.172545
F	-1.991618	1.329435	0.371976
F	-0.119309	2.099809	1.185775
F	-0.533257	2.256543	-0.947816
F	0.173042	-2.279681	1.007208
F	-0.468321	-0.649177	2.313659
F	-1.813480	-1.427786	0.783939
H	1.660959	1.314351	-1.769456
H	2.052818	2.107354	-0.228061
H	3.218655	0.977759	-0.973622
H	3.379487	-0.264011	0.944079
H	2.134426	0.601496	1.890400
H	2.004993	-1.158427	1.626175
C	-0.584045	-0.520208	-1.703417
C	0.042066	-1.757507	-1.765921
C	1.440619	-1.849168	-2.019304
C	2.061292	-3.213054	-2.020425
H	1.831926	-1.221398	-2.826528
H	1.772307	-1.166697	-1.021455
H	-0.181560	0.286930	-2.319433
H	-1.663692	-0.496145	-1.554606
H	-0.473639	-2.634722	-1.366510
F	1.867112	-3.868533	-3.190580
F	3.398380	-3.138067	-1.834103
F	1.555004	-3.994017	-1.043966

3e–$C_3H_5(CF_3)$ + 1 product

B	0.009486	0.125289	-0.025681
N	1.630933	0.196337	-0.122330
C	-0.568080	1.597466	0.351355
C	-0.397590	-0.929818	1.149082
C	2.147955	1.427717	-0.800744
C	2.364938	0.037112	1.172360
F	-1.849449	1.548884	0.780377
F	0.144849	2.238606	1.336061
F	-0.560947	2.461821	-0.717300
F	-1.702622	-1.279429	1.100795
F	-0.156430	-0.519239	2.426508
F	0.310022	-2.111953	1.000963
H	1.582828	1.631874	-1.709262
H	2.040339	2.266539	-0.108354
H	3.204456	1.277992	-1.046076
H	2.176093	-0.951850	1.590200
H	2.007137	0.804433	1.863522
H	3.436035	0.168457	0.986346
C	-0.645582	-0.458410	-1.403397
C	-0.019336	0.069672	-2.646117
C	0.858597	-0.609100	-3.379528
H	1.879897	-0.596706	-0.721378
H	-1.715156	-0.208561	-1.377034
H	-0.571590	-1.555473	-1.389542
H	-0.252483	1.098820	-2.930504
C	1.586909	0.007511	-4.523482
H	1.121734	-1.648522	-3.180472
F	1.430753	-0.683222	-5.673706
F	1.210176	1.281852	-4.762352
F	2.929791	0.039051	-4.278907

Table S48. Optimized (M06-2X/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1a, 1e, 2, 3a, 3e–C_3HF_5** and **1** and between propene **1a, 1e, 2, 3a–$C_3H_2F_4$** and **1**

1a, 1e, 2, 3a, 3e–C_3HF_5

C	0.003573	0.001061	-0.000713
C	0.001918	0.003141	1.488968
C	1.098780	-0.002250	2.227670
F	1.110638	0.000358	3.531582
F	2.311413	-0.010279	1.723464
F	-1.193264	0.011660	2.074821
H	1.014131	-0.006718	-0.410151
F	-0.669294	-1.083419	-0.457528
F	-0.653728	1.093814	-0.460653

1a, 1e, 2, 3a, 3e–C_3HF_5 + 1 ts

C	0.006184	0.030827	-0.018230
C	0.860347	0.797538	-0.891610
C	2.245027	0.428783	-1.014760
F	2.409556	-0.876589	-1.315137
F	2.945767	1.173792	-1.869915
F	0.547372	2.031761	-1.122473
H	0.770629	-0.010346	0.952727
F	-1.183835	0.579767	0.224641
F	-0.138683	-1.269760	-0.338273
B	2.888889	0.674782	0.684043
N	2.152784	-0.235241	1.615258
C	2.508002	-1.668710	1.591445
H	2.672091	-2.013021	0.575408
H	3.418598	-1.833863	2.175924
H	1.693821	-2.243629	2.036164
C	1.926227	0.186752	3.013306
H	1.257242	-0.531023	3.490863
H	2.878149	0.199362	3.552377
H	1.475686	1.173427	3.062804
C	4.477482	0.326943	0.516213
F	5.167206	1.288495	-0.111929
F	5.020690	0.210005	1.754042
F	4.757506	-0.828140	-0.117354
C	2.686054	2.249192	1.045524
F	1.370686	2.527823	1.309330
F	3.367471	2.625071	2.143425
F	3.038545	3.087472	0.062304

1a, 1e, 2, 3a, 3e–C_3HF_5 + 1 product

B	0.028544	0.032696	-0.012294
N	1.633319	0.106322	-0.197677
H	1.784293	0.846211	-0.888003
C	2.268839	-1.131340	-0.752925
H	1.895987	-1.318583	-1.755078
H	2.023770	-1.967006	-0.102165
H	3.347829	-0.980808	-0.780215
C	2.371749	0.507352	1.043351
H	2.344630	-0.330212	1.737182
H	3.404004	0.729948	0.774399
H	1.898795	1.374086	1.491988
C	-0.599287	1.553434	-0.022503
C	-0.622710	2.213423	-1.369361
C	-1.653255	2.596944	-2.102520
F	-1.515081	3.108448	-3.300936
F	-2.904629	2.510274	-1.750684
F	0.617589	2.351103	-1.891206
F	0.140880	2.395390	0.792260
F	-1.855793	1.539818	0.485060
C	-0.615763	-0.781358	-1.267907
F	-1.934786	-0.575127	-1.393657
F	-0.435064	-2.117740	-1.213291
F	-0.063595	-0.385737	-2.455586
C	-0.335493	-0.719105	1.384017
F	-0.161958	0.064141	2.472216
F	-1.598257	-1.159865	1.422945
F	0.453836	-1.812271	1.600921

1a, 1e, 2, 3a–$C_3H_2F_4$

C	0.002923	0.001775	-0.001549
C	0.000063	0.009178	1.479785
C	1.079193	-0.006695	2.245035
F	2.306181	-0.025890	1.773922
F	1.062273	-0.016637	3.552219
F	-1.200917	0.035123	2.073211
H	1.001818	-0.219993	-0.377032
F	-0.388165	1.236927	-0.489367
H	-0.711649	-0.738070	-0.368373

1a, 1e, 2, 3a–$C_3H_2F_4$ + 1 ts

C	0.009598	0.025886	-0.013051
C	0.882516	0.796108	-0.839881
C	2.256473	0.437673	-1.014167
F	2.452189	-0.856819	-1.319724
F	2.951093	1.202633	-1.855409
F	0.580575	2.046905	-1.042970
H	0.703517	0.054436	0.982764
F	-0.021934	-1.311596	-0.301588
H	-0.985513	0.441109	0.124329
B	2.888997	0.691402	0.719514
N	2.153516	-0.208278	1.651692
C	2.488871	-1.644574	1.614267
H	2.622934	-1.986599	0.592883
H	3.409730	-1.829617	2.177492
H	1.675841	-2.211396	2.071725
C	1.953288	0.206843	3.053295
H	1.264812	-0.493274	3.530606
H	2.907336	0.183675	3.589429
H	1.535393	1.206973	3.118235
C	4.476932	0.340624	0.541577
F	5.166300	1.295548	-0.099275
F	5.026569	0.235582	1.777968
F	4.755393	-0.820769	-0.080821
C	2.699079	2.270340	1.074941
F	1.393248	2.563469	1.370045
F	3.408227	2.645439	2.156505
F	3.036467	3.104366	0.082440

1a, 1e, 2, 3a–$C_3H_2F_4$ + 1 product

B	0.142881	0.072098	-0.073644
N	1.750208	0.181225	-0.226078
H	1.895502	0.933026	-0.904757
C	2.423445	-1.035397	-0.781762
H	2.074762	-1.219599	-1.793061
H	2.183425	-1.883503	-0.145286
H	3.499358	-0.861676	-0.785546
C	2.457291	0.583763	1.032307
H	2.437666	-0.262585	1.715572
H	3.488667	0.833199	0.784063
H	1.956939	1.433779	1.482645
C	-0.513222	1.581168	-0.090030
C	-0.542161	2.244538	-1.437054
C	-1.544060	2.637019	-2.202791
H	-1.384883	3.062790	-3.185208
F	-2.814380	2.530915	-1.838980
F	0.717452	2.391683	-1.926473
F	0.212691	2.435125	0.728454
F	-1.769157	1.547519	0.414138
C	-0.458742	-0.757128	-1.340475
F	-1.779679	-0.589200	-1.486511
F	-0.240971	-2.089218	-1.282400
F	0.101625	-0.348453	-2.519952
C	-0.229406	-0.691724	1.314194
F	-0.090014	0.090071	2.408392
F	-1.482391	-1.160277	1.331708
F	0.580126	-1.769005	1.540438

Table S49. Optimized (M06-2X/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1a, 1e, 2, 3e–$C_3H_2F_4$** and **1** and between propene **1a, 1e, 3a, 3e–$C_3H_2F_4$** and **1**

1a, 1e, 2, 3e–$C_3H_2F_4$

C	0.003130	-0.002030	-0.001785
C	0.001019	-0.011020	1.479548
C	1.080457	0.007572	2.244301
F	2.307144	0.031357	1.772604
F	1.064144	0.016012	3.551504
F	-1.199604	-0.041600	2.073491
H	1.001124	0.223383	-0.377505
H	-0.714014	0.735889	-0.367473
F	-0.384182	-1.237926	-0.490716

1a, 1e, 2, 3e–$C_3H_2F_4$ + 1 ts

C	0.007914	0.036389	-0.017152
C	0.906804	0.810287	-0.822855
C	2.257434	0.355287	-0.950772
F	2.292880	-0.985050	-1.169406
F	3.000893	0.982468	-1.861429
F	0.630641	2.032109	-1.126949
H	0.723463	-0.166349	0.918774
F	-1.146701	0.673775	0.287274
H	-0.162795	-0.968834	-0.415156
B	2.936412	0.609827	0.732384
N	2.233487	-0.315791	1.661546
C	2.649317	-1.727742	1.679744
H	2.923052	-2.071282	0.687114
H	3.508443	-1.860753	2.345988
H	1.825040	-2.340676	2.054234
C	1.931695	0.115056	3.038200
H	1.261736	-0.615461	3.497229
H	2.852118	0.163946	3.629574
H	1.447521	1.087024	3.056615
C	4.525441	0.287250	0.505087
F	5.197492	1.280504	-0.094109
F	5.108930	0.107661	1.715649
F	4.790049	-0.832504	-0.201612
C	2.729305	2.183631	1.084883
F	1.415857	2.471643	1.346220
F	3.415745	2.574614	2.173320
F	3.076899	3.008218	0.084070

1a, 1e, 2, 3e–$C_3H_2F_4$ + 1 product

B	0.026759	0.026479	-0.013558
N	1.632250	0.089503	-0.205614
H	1.784050	0.822815	-0.902991
C	2.261393	-1.154702	-0.752806
H	1.885477	-1.347520	-1.752787
H	2.014659	-1.984854	-0.095709
H	3.340869	-1.008249	-0.783846
C	2.376270	0.498801	1.029019
H	2.345436	-0.330929	1.732121
H	3.409316	0.711844	0.755411
H	1.909911	1.373399	1.469434
C	-0.584928	1.551923	-0.035358
C	-0.576882	2.231004	-1.372275
C	-1.635810	2.635187	-2.046801
H	-2.643736	2.525434	-1.675737
F	-1.517391	3.193893	-3.247588
F	0.670045	2.356554	-1.872853
F	0.126807	2.378162	0.818075
F	-1.865642	1.544638	0.425594
C	-0.623512	-0.796938	-1.259841
F	-1.945390	-0.606429	-1.377119
F	-0.431330	-2.132695	-1.197982
F	-0.082010	-0.404649	-2.451959
C	-0.335889	-0.713039	1.389683
F	-0.155429	0.076034	2.472343
F	-1.601541	-1.146865	1.436158
F	0.447752	-1.809031	1.612005

1a, 1e, 3a, 3e–$C_3H_2F_4$

C	0.002595	0.001892	0.001677
C	-0.007487	0.004719	1.487868
C	1.109561	-0.003945	2.186237
F	2.321160	-0.015754	1.676164
F	1.174551	-0.002192	3.494160
H	-0.955981	0.014103	2.005673
H	1.002360	-0.006254	-0.432691
F	-0.675411	-1.083353	-0.463439
F	-0.659375	1.095316	-0.467298

1a, 1e, 3a, 3e–$C_3H_2F_4$ + 1 ts

C	-0.003794	-0.002106	-0.007223
N	-0.370643	1.430414	0.005694
B	0.367877	2.340732	-0.900094
C	1.946315	1.979412	-1.112111
F	2.629014	2.941658	-1.745089
F	2.510505	1.855668	0.117743
F	2.212829	0.827451	-1.753188
C	0.182782	3.921993	-0.561066
F	-1.118783	4.247044	-0.287796
F	0.886935	4.296588	0.523235
F	0.542269	4.737484	-1.563221
C	-0.669088	1.854953	1.390946
H	-1.364221	1.140231	1.834099
H	0.255556	1.865477	1.974130
H	-1.117691	2.843524	1.412106
H	0.186153	-0.341656	-1.020501
H	0.892243	-0.157167	0.600275
H	-0.827019	-0.580281	0.415093
C	-0.316779	2.065511	-2.680010
C	-1.640122	2.465484	-2.443725
C	-2.481885	1.657477	-1.639338
F	-3.677197	2.171406	-1.316180
F	-2.632983	0.356393	-1.965288
H	-1.842811	3.530284	-2.478407
F	0.436598	2.813256	-3.485517
F	-0.101892	0.769546	-2.956922
H	-1.686214	1.595789	-0.653680

1a, 1e, 3a, 3e–$C_3H_2F_4$ + 1 product

B	0.044035	0.057264	-0.007321
N	1.629814	0.189620	-0.325423
H	1.672967	0.910123	-1.051165
C	2.303280	-1.018004	-0.901493
H	1.868492	-1.254489	-1.867516
H	2.164016	-1.851605	-0.218636
H	3.364391	-0.795979	-1.014916
C	2.430072	0.677295	0.841166
H	2.487811	-0.130582	1.568286
H	3.431519	0.935570	0.497505
H	1.942541	1.535557	1.293136
C	-0.587792	1.574182	0.034232
C	-0.315676	2.454842	-1.157960
C	-1.039062	2.469710	-2.262429
F	-0.788862	3.258314	-3.284464
F	-2.082953	1.730548	-2.507818
H	0.501155	3.161146	-1.091461
F	-0.077343	2.282025	1.112835
F	-1.930622	1.493350	0.255950
C	-0.632611	-0.800179	-1.220668
F	-1.963254	-0.739467	-1.265414
F	-0.312129	-2.115752	-1.184216
F	-0.189043	-0.359741	-2.442400
C	-0.171518	-0.739236	1.397818
F	0.086837	-0.003458	2.500492
F	-1.418487	-1.207630	1.532652
F	0.655394	-1.823272	1.501128

Table S50. Optimized (M06-2X/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1a, 2, 3a, 3e–$C_3H_2F_4$** and **1** and between propene **1e, 2, 3a, 3e–$C_3H_2F_4$** and **1**

1a, 2, 3a, 3e–$C_3H_2F_4$

C	0.005057	0.001344	0.001680
C	0.000631	0.003356	1.495267
C	1.074975	-0.002893	2.264759
F	2.296653	-0.012137	1.722849
H	1.056028	-0.001236	3.345684
F	-1.213293	0.012528	2.049073
H	1.016672	-0.005669	-0.403522
F	-0.666132	-1.084794	-0.455413
F	-0.652124	1.094852	-0.458200

1a, 2, 3a, 3e–$C_3H_2F_4$ + 1 ts

C	-0.016158	0.001564	-0.010609
N	-0.345291	1.442701	0.021043
B	0.424416	2.340802	-0.900757
C	1.999347	1.959724	-1.086855
F	2.644653	2.818358	-1.901478
F	2.618554	2.026865	0.114898
F	2.258245	0.726565	-1.561948
C	0.278764	3.923164	-0.542413
F	-1.006319	4.263159	-0.236340
F	1.019752	4.305537	0.512050
F	0.625629	4.723918	-1.570361
C	-0.553374	1.866760	1.421433
H	-1.247228	1.172384	1.898581
H	0.397831	1.844372	1.961431
H	-0.969128	2.868463	1.473762
H	0.102616	-0.342467	-1.033851
H	0.910625	-0.185686	0.540096
H	-0.827339	-0.555011	0.462365
C	-0.215128	2.153767	-2.605436
C	-1.590284	2.441880	-2.447248
C	-2.446356	1.590313	-1.665216
F	-3.688744	2.034940	-1.473933
F	-2.468334	0.287636	-1.997186
F	-1.967483	3.685957	-2.558258
H	0.352769	2.857894	-3.211148
F	0.022311	0.854847	-2.963585
H	-1.689793	1.606926	-0.646251

1a, 2, 3a, 3e–$C_3H_2F_4$ + 1 product

B	0.019390	0.052083	0.000301
N	1.621431	0.150287	-0.194991
H	1.746591	0.859962	-0.920544
C	2.289725	-1.093014	-0.689389
H	1.913869	-1.343486	-1.676863
H	2.077511	-1.902569	0.004343
H	3.363703	-0.912674	-0.737155
C	2.335517	0.639308	1.024875
H	2.309014	-0.151154	1.772967
H	3.369428	0.860161	0.760167
H	1.837649	1.524537	1.408389
C	-0.674277	1.533297	0.000723
C	-0.582490	2.249089	-1.293127
C	-1.584691	2.713780	-2.018463
F	-2.841857	2.638997	-1.654439
F	-1.447998	3.286024	-3.187354
F	0.671400	2.403039	-1.790686
H	-1.732137	1.422441	0.252370
F	-0.099801	2.367769	0.981306
C	-0.604490	-0.766507	-1.263643
F	-1.927488	-0.564222	-1.404476
F	-0.424977	-2.103291	-1.218979
F	-0.042102	-0.361805	-2.442182
C	-0.327784	-0.721732	1.387787
F	-0.136508	0.036235	2.491524
F	-1.613891	-1.115715	1.423349
F	0.419824	-1.841350	1.591183

1e, 2, 3a, 3e–$C_3H_2F_4$

C	0.002201	0.000432	-0.002845
C	0.008668	0.002121	1.487657
C	1.126672	-0.001166	2.194287
H	2.110785	-0.005733	1.747029
F	1.114688	0.000613	3.520523
F	-1.190518	0.007503	2.057838
H	1.013444	-0.004913	-0.414055
F	-0.665458	-1.085423	-0.464635
F	-0.654846	1.091752	-0.467143

1e, 2, 3a, 3e–$C_3H_2F_4$ + 1 ts

C	-0.012325	-0.001871	-0.008156
N	-0.340319	1.436293	0.054057
B	0.434215	2.332534	-0.879203
C	2.001652	1.928200	-1.059881
F	2.747836	2.884991	-1.623332
F	2.559514	1.666755	0.148063
F	2.191131	0.806887	-1.801172
C	0.251475	3.905053	-0.516924
F	-1.067530	4.193482	-0.285112
F	0.910649	4.266405	0.603184
F	0.639693	4.746478	-1.481317
C	-0.512291	1.845643	1.464183
H	-1.190816	1.142733	1.950700
H	0.451901	1.827687	1.979047
H	-0.934222	2.844406	1.529773
H	0.064520	-0.338280	-1.040800
H	0.939030	-0.197404	0.493360
H	-0.802357	-0.570700	0.484450
C	-0.217101	2.090566	-2.551944
C	-1.592595	2.410839	-2.439896
C	-2.420534	1.606274	-1.592806
F	-3.677571	2.019186	-1.431559
F	-2.398120	0.280996	-1.889849
F	-2.002237	3.597249	-2.766539
H	-0.024955	1.027705	-2.715910
F	0.471529	2.863245	-3.425010
H	-1.638603	1.627090	-0.563562

1e, 2, 3a, 3e–$C_3H_2F_4$ + 1 product

B	0.029857	0.033053	-0.002810
N	1.631550	0.133595	-0.232912
H	1.734594	0.803361	-0.999554
C	2.310430	-1.123508	-0.680379
H	1.900379	-1.437956	-1.634978
H	2.147004	-1.895548	0.065980
H	3.376420	-0.920785	-0.784931
C	2.360354	0.696482	0.939985
H	2.318825	-0.026972	1.752069
H	3.397408	0.880743	0.660789
H	1.894660	1.625494	1.257458
C	-0.609314	1.540704	0.082299
C	-0.521674	2.304360	-1.200999
C	-1.458740	2.682457	-2.051310
F	-2.740177	2.476496	-1.901918
F	-1.191858	3.325841	-3.167186
F	0.769514	2.584929	-1.528281
H	-0.105896	2.144907	0.847256
F	-1.934892	1.444194	0.466487
C	-0.591167	-0.751932	-1.283353
F	-1.897478	-0.532748	-1.463468
F	-0.422098	-2.093642	-1.253591
F	0.020477	-0.336314	-2.440106
C	-0.286981	-0.740882	1.392686
F	-0.152740	0.078360	2.468935
F	-1.523941	-1.243584	1.445354
F	0.557523	-1.783356	1.643982

Table S51. Optimized (M06-2X/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1a, 1e, 2–$C_3H_3F_3$** and **1** and between propene **1a, 1e, 3a–$C_3H_3F_3$** and **1**

1a, 1e, 2–$C_3H_3F_3$

C	0.001250	-0.000102	-0.000457
C	-0.002405	-0.000122	1.482702
C	1.051757	-0.001462	2.278392
F	2.297127	-0.003047	1.839560
F	1.003163	-0.000502	3.591284
F	-1.216469	0.002331	2.062132
H	1.023037	-0.005491	-0.376251
H	-0.511515	0.888146	-0.375503
H	-0.520759	-0.883134	-0.375002

1a, 1e, 2–$C_3H_3F_3$ + 1 ts

C	0.006037	0.036615	-0.011901
C	0.919321	0.799869	-0.789281
C	2.267645	0.358903	-0.945018
F	2.339620	-0.972316	-1.184068
F	3.012788	1.015974	-1.834473
F	0.672798	2.041261	-1.078705
H	0.680927	-0.133793	0.944390
H	-0.933896	0.538567	0.192311
H	-0.094432	-0.986532	-0.379163
B	2.931259	0.620354	0.760340
N	2.232704	-0.296181	1.698368
C	2.629390	-1.712080	1.701244
H	2.859080	-2.059170	0.698335
H	3.511968	-1.861950	2.333273
H	1.810944	-2.314145	2.105655
C	1.968264	0.133073	3.080880
H	1.288478	-0.583130	3.548968
H	2.898704	0.156780	3.658915
H	1.508538	1.116500	3.114226
C	4.522281	0.298606	0.537116
F	5.196315	1.283997	-0.074394
F	5.103404	0.138039	1.752379
F	4.792790	-0.831351	-0.150472
C	2.734658	2.198332	1.109627
F	1.429830	2.501149	1.397526
F	3.444320	2.585497	2.186155
F	3.072534	3.020873	0.104053

1a, 1e, 2–$C_3H_2F_3$ + 1 product

B	0.131779	0.067865	-0.079303
N	1.738168	0.178525	-0.245150
H	1.874361	0.923982	-0.932925
C	2.412889	-1.040312	-0.793001
H	2.056447	-1.237052	-1.799273
H	2.183030	-1.882992	-0.145663
H	3.487751	-0.860610	-0.808275
C	2.451994	0.598771	1.003170
H	2.438352	-0.238173	1.698163
H	3.481378	0.847087	0.745630
H	1.952447	1.453902	1.444907
C	-0.521698	1.575962	-0.107041
C	-0.531009	2.258029	-1.447734
C	-1.564402	2.656063	-2.154607
H	-1.426649	3.112755	-3.124986
H	-2.557386	2.509664	-1.755403
F	0.743282	2.397454	-1.902143
F	0.170793	2.423056	0.744870
F	-1.798095	1.534840	0.357647
C	-0.474541	-0.777608	-1.333132
F	-1.800172	-0.634403	-1.465365
F	-0.236402	-2.107083	-1.266245
F	0.066966	-0.371202	-2.520423
C	-0.227774	-0.685608	1.317672
F	-0.086280	0.104981	2.405099
F	-1.479370	-1.159869	1.347054
F	0.587112	-1.757873	1.548359

1a, 1e, 3a–$C_3H_3F_3$

C	0.002936	0.004067	0.000280
C	-0.006628	0.012420	1.490483
C	1.101362	-0.006760	2.204003
F	2.323138	-0.049368	1.715411
F	1.150783	-0.001814	3.517044
H	-0.944653	0.051231	2.026736
H	1.013024	-0.116980	-0.391440
H	-0.638528	-0.787390	-0.391201
F	-0.500754	1.206995	-0.480673

1a, 1e, 3a–$C_3H_3F_3$ + 1 ts

C	0.004768	0.030227	-0.017152
C	0.870485	0.841564	-0.783275
C	2.184204	0.449273	-1.070361
F	2.422875	-0.832650	-1.371208
F	2.926776	1.221958	-1.863756
H	0.691146	1.910841	-0.801463
H	0.734026	0.038663	0.999532
F	-0.017119	-1.309431	-0.317303
H	-0.993569	0.405324	0.184326
B	2.842031	0.728515	0.734594
N	2.101535	-0.168721	1.650736
C	2.439944	-1.606219	1.613823
H	2.579771	-1.941382	0.590573
H	3.356105	-1.788711	2.183708
H	1.621790	-2.172838	2.061390
C	1.861858	0.249471	3.046198
H	1.156902	-0.446799	3.504356
H	2.801020	0.224564	3.606365
H	1.446335	1.251802	3.093227
C	4.421294	0.365772	0.530185
F	5.107769	1.318622	-0.115653
F	4.983870	0.260049	1.762866
F	4.690541	-0.795943	-0.092026
C	2.666625	2.313540	1.070544
F	1.370634	2.644395	1.372213
F	3.393092	2.693637	2.138034
F	3.004674	3.127539	0.058938

1a, 1e, 3a–$C_3H_2F_3$ + 1 product

B	0.106127	0.119488	-0.067231
N	1.730576	0.088415	-0.108180
H	1.985915	0.860616	-0.726315
C	2.348287	-1.151416	-0.673077
H	2.054665	-1.271545	-1.711242
H	2.001867	-2.001699	-0.090581
H	3.432103	-1.061985	-0.599064
C	2.379426	0.381251	1.211750
H	2.260820	-0.494186	1.846283
H	3.438716	0.571981	1.039990
H	1.907805	1.241756	1.672465
C	-0.383151	1.698661	-0.132101
C	-0.697733	2.283988	-1.476531
C	-1.895183	2.470956	-2.004490
F	-3.033366	2.150995	-1.397261
H	-2.055824	2.891906	-2.989255
H	0.152522	2.568242	-2.084422
F	0.652971	2.497523	0.375600
F	-1.433500	1.887137	0.711119
C	-0.475078	-0.693237	-1.352419
F	-1.784357	-0.487788	-1.542462
F	-0.305859	-2.033705	-1.287251
F	0.143441	-0.310480	-2.513080
C	-0.401731	-0.609151	1.297391
F	-0.205551	0.122872	2.417019
F	-1.700490	-0.926455	1.265737
F	0.269017	-1.780695	1.520891

Table S52. Optimized (M06-2X/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1a, 1e, 3e–$C_3H_3F_3$** and **1** and between propene **1a, 2, 3a–$C_3H_3F_3$** and **1**

1a, 1e, 3e–$C_3H_3F_3$

C	0.002383	-0.002690	0.000331
C	-0.007099	-0.007947	1.490544
C	1.101097	0.003773	2.203909
F	2.323118	0.035552	1.715130
F	1.150629	0.001057	3.516951
H	-0.945334	-0.038146	2.026986
H	1.013304	0.110056	-0.391718
H	-0.633226	0.792718	-0.392691
F	-0.510263	-1.202805	-0.478200

1a, 1e, 3e–$C_3H_3F_3$ + 1 ts

C	-0.000595	0.037455	-0.018006
C	0.872682	0.856814	-0.769732
C	2.168200	0.377424	-1.002222
F	2.257559	-0.957366	-1.205261
F	2.956519	1.008998	-1.871751
H	0.698570	1.924116	-0.858537
H	0.780636	-0.189930	0.917968
F	-1.148760	0.638267	0.400924
H	-0.185759	-0.970477	-0.397618
B	2.874326	0.657832	0.735706
N	2.161603	-0.271415	1.642525
C	2.590096	-1.681927	1.674946
H	2.885533	-2.021974	0.687416
H	3.435419	-1.799540	2.359420
H	1.761326	-2.297261	2.033210
C	1.794848	0.161991	3.005035
H	1.118583	-0.576877	3.439588
H	2.692307	0.229168	3.627152
H	1.295766	1.126349	2.992228
C	4.455458	0.316246	0.489654
F	5.130669	1.308549	-0.105279
F	5.043941	0.127335	1.698638
F	4.711873	-0.800438	-0.220904
C	2.696275	2.238487	1.079019
F	1.404923	2.580959	1.371493
F	3.424724	2.616581	2.145508
F	3.042148	3.043787	0.059256

1a, 1e, 3e–$C_3H_2F_3$ + 1 product

B	0.027067	0.036233	-0.042480
N	1.645918	0.033194	-0.167784
H	1.859998	0.776994	-0.834883
C	2.248922	-1.222035	-0.719231
H	1.902554	-1.383624	-1.735159
H	1.943894	-2.052595	-0.087423
H	3.333850	-1.118672	-0.705902
C	2.360221	0.381304	1.104653
H	2.281931	-0.471056	1.775685
H	3.407675	0.571513	0.871300
H	1.903306	1.253380	1.558440
C	-0.511682	1.587990	-0.102975
C	-0.608429	2.236036	-1.449163
C	-1.770750	2.530302	-1.999339
H	-2.741022	2.342371	-1.559484
F	-1.838773	3.098474	-3.207316
H	0.311954	2.451470	-1.980734
F	-1.731681	1.647528	0.511710
F	0.330928	2.399563	0.657043
C	-0.605821	-0.792691	-1.293127
F	-1.919824	-0.575057	-1.445272
F	-0.448614	-2.133110	-1.205092
F	-0.024317	-0.439791	-2.479869
C	-0.403027	-0.677947	1.355653
F	-0.208775	0.102530	2.442284
F	-1.686932	-1.054382	1.375157
F	0.324483	-1.810748	1.598006

1a, 2, 3a–$C_3H_3F_3$

C	0.004802	0.002117	0.000608
C	-0.000849	0.009086	1.485665
C	1.053593	-0.008080	2.283665
F	2.291896	-0.013831	1.776164
H	1.008009	-0.022189	3.363659
F	-1.222248	0.022016	2.044373
H	1.022300	-0.126341	-0.367660
H	-0.639169	-0.797569	-0.372288
F	-0.496032	1.199909	-0.479303

1a, 2, 3a–$C_3H_3F_3$ + 1 ts

C	0.009197	0.011644	-0.013592
C	0.885024	0.866280	-0.742523
C	2.255796	0.602672	-0.946521
H	2.811309	1.324663	-1.541710
F	2.523558	-0.684324	-1.313645
F	0.514546	2.123680	-0.813272
H	0.702618	0.082705	1.019235
F	0.082032	-1.317658	-0.315286
H	-1.015524	0.355114	0.096864
B	2.877591	0.794047	0.781408
N	2.108266	-0.095335	1.707095
C	2.426377	-1.537293	1.666749
H	2.535582	-1.877600	0.641002
H	3.354152	-1.738428	2.212147
H	1.612496	-2.091398	2.138635
C	1.925416	0.323929	3.109756
H	1.223012	-0.359333	3.591654
H	2.879796	0.280156	3.644127
H	1.529827	1.333208	3.174447
C	4.453406	0.408700	0.592713
F	5.101781	1.262198	-0.226643
F	5.074433	0.480901	1.793733
F	4.712198	-0.827111	0.125014
C	2.750884	2.380903	1.138103
F	1.480433	2.742033	1.478717
F	3.523510	2.755532	2.173699
F	3.083519	3.178315	0.101965

1a, 2, 3a–$C_3H_2F_3$ + 1 product

B	0.018908	0.048522	-0.003349
N	1.622177	0.146830	-0.199957
H	1.744430	0.862930	-0.919856
C	2.289076	-1.093058	-0.703652
H	1.912305	-1.337197	-1.692263
H	2.076647	-1.906991	-0.014971
H	3.363288	-0.913568	-0.750741
C	2.340784	0.625577	1.021432
H	2.318053	-0.171738	1.762289
H	3.373541	0.849131	0.754192
H	1.844491	1.507138	1.414598
C	-0.668892	1.531875	-0.003544
C	-0.599086	2.241829	-1.305416
C	-1.590490	2.692356	-2.053080
F	-2.855324	2.579989	-1.642755
H	-1.465842	3.157332	-3.021254
F	0.666704	2.403997	-1.783630
H	-1.723202	1.436453	0.268261
F	-0.064978	2.371152	0.955679
C	-0.605957	-0.776952	-1.261793
F	-1.928740	-0.581724	-1.398942
F	-0.419778	-2.113868	-1.211023
F	-0.047628	-0.377681	-2.444796
C	-0.323027	-0.721468	1.387536
F	-0.133345	0.042547	2.487803
F	-1.606263	-1.123029	1.428415
F	0.431678	-1.836478	1.594861

Table S53. Optimized (M06-2X/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1a, 2, 3e–$C_3H_3F_3$** and **1** and between propene **1a, 3a, 3e–$C_3H_3F_3$** and **1**

1a, 2, 3e–$C_3H_3F_3$

C	0.004777	-0.001629	0.000410
C	-0.000431	-0.007591	1.485466
C	1.054299	0.006858	2.283137
F	2.292455	0.008367	1.775254
H	1.009087	0.021864	3.363134
F	-1.221699	-0.016299	2.044566
H	1.022519	0.123709	-0.368249
H	-0.637049	0.799639	-0.372794
F	-0.499577	-1.198313	-0.478581

1a, 2, 3e–$C_3H_3F_3$ + 1 ts

C	-0.003369	0.037690	-0.011162
C	0.872221	0.911201	-0.720414
C	2.230375	0.551044	-0.886517
H	2.829054	1.165063	-1.556055
F	2.338409	-0.792618	-1.173996
F	0.522994	2.149621	-0.898003
H	0.726105	-0.080921	0.975217
F	-1.233645	0.541167	0.245939
H	-0.035947	-0.982939	-0.396707
B	2.900516	0.741866	0.793183
N	2.152744	-0.169819	1.716765
C	2.536368	-1.592643	1.726396
H	2.699184	-1.958680	0.716961
H	3.454563	-1.740135	2.305063
H	1.736563	-2.172605	2.193845
C	1.892561	0.268575	3.100784
H	1.203444	-0.436533	3.570715
H	2.824260	0.282896	3.675873
H	1.445136	1.257614	3.127241
C	4.476154	0.372743	0.582901
F	5.129301	1.279744	-0.171688
F	5.103937	0.344836	1.781336
F	4.722960	-0.825883	0.012524
C	2.756657	2.323447	1.152920
F	1.472169	2.671666	1.453929
F	3.497351	2.706410	2.207746
F	3.106200	3.122383	0.122768

1a, 2, 3e–$C_3H_2F_3$ + 1 product

B	0.019173	0.046463	-0.000732
N	1.617912	0.112042	-0.234487
H	1.737481	0.809405	-0.972997
C	2.254425	-1.148819	-0.725175
H	1.853601	-1.405941	-1.701128
H	2.043759	-1.945714	-0.016514
H	3.329977	-0.987207	-0.798291
C	2.367414	0.609329	0.960167
H	2.344559	-0.167161	1.722922
H	3.398647	0.807948	0.668701
H	1.893190	1.509803	1.338446
C	-0.645004	1.540861	-0.006579
C	-0.548196	2.257936	-1.302297
C	-1.559823	2.718613	-2.016908
H	-2.589611	2.644208	-1.698813
F	-1.375028	3.292860	-3.202945
F	0.716917	2.394322	-1.772873
H	-1.704138	1.449592	0.250894
F	-0.052291	2.365333	0.971408
C	-0.646438	-0.781504	-1.236817
F	-1.972210	-0.573234	-1.344067
F	-0.476811	-2.120030	-1.178248
F	-0.112313	-0.397969	-2.433803
C	-0.309978	-0.703092	1.404916
F	-0.077603	0.061254	2.496045
F	-1.603538	-1.069823	1.475359
F	0.418259	-1.836150	1.603579

1a, 3a, 3e–$C_3H_3F_3$

C	0.003913	0.002077	0.003603
C	-0.007787	0.005345	1.493139
C	1.092216	-0.003207	2.222908
F	2.310459	-0.015653	1.667553
H	1.131934	-0.001226	3.304183
H	-0.972496	0.015296	1.983877
H	1.002597	-0.006647	-0.431291
F	-0.676359	-1.084272	-0.458875
F	-0.659303	1.096984	-0.463386

1a, 3a, 3e–$C_3H_3F_3$ + 1 ts

C	-0.014420	0.002079	-0.010040
N	-0.353933	1.441095	0.008305
B	0.409523	2.343296	-0.893772
C	1.977174	1.960099	-1.122704
F	2.600735	2.804145	-1.968670
F	2.626451	2.054224	0.062567
F	2.228361	0.719684	-1.578553
C	0.270158	3.931143	-0.556779
F	-1.013686	4.304107	-0.272644
F	1.003952	4.323043	0.497353
F	0.633634	4.711196	-1.597363
C	-0.633992	1.873661	1.393065
H	-1.350766	1.182497	1.839900
H	0.288964	1.857824	1.979618
H	-1.053064	2.875468	1.414982
H	0.111592	-0.344719	-1.031729
H	0.908419	-0.176320	0.549277
H	-0.828116	-0.554485	0.458152
C	-0.263752	2.145648	-2.649409
C	-1.595865	2.465546	-2.399245
C	-2.448912	1.580251	-1.692101
F	-3.687369	2.013764	-1.413359
F	-2.509048	0.284755	-2.050878
H	-1.849178	3.517678	-2.322487
H	0.355783	2.844267	-3.205497
F	-0.004261	0.852071	-2.995055
H	-1.672829	1.566495	-0.674347

1a, 3a, 3e–$C_3H_2F_3$ + 1 product

B	0.009132	0.011280	-0.011584
N	1.602126	0.095456	-0.286336
H	1.660350	0.426632	-1.252103
C	2.281935	-1.233275	-0.255142
H	1.718609	-1.947471	-0.851741
H	2.317229	-1.574821	0.777677
H	3.294130	-1.125816	-0.645047
C	2.355537	1.068477	0.558344
H	2.240461	0.786751	1.601569
H	3.406755	1.039159	0.269771
H	1.951273	2.066805	0.420603
C	-0.660798	1.484728	0.113215
C	-0.424794	2.390343	-1.053061
C	-1.402938	2.864150	-1.801057
F	-1.230098	3.629616	-2.857614
F	-2.682471	2.638227	-1.620210
H	0.576638	2.685507	-1.344135
H	-1.736012	1.353547	0.250535
F	-0.194612	2.133360	1.279372
C	-0.626620	-0.707199	-1.342025
F	-1.911182	-0.370987	-1.549820
F	-0.579195	-2.053837	-1.375738
F	0.050532	-0.306406	-2.468080
C	-0.278076	-0.847554	1.342106
F	0.474834	-0.431159	2.395552
F	-1.562376	-0.744001	1.727767
F	-0.023810	-2.175254	1.241635

Table S54. Optimized (M06-2X/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1e, 2, 3a–$C_3H_3F_3$** and **1** and between propene **1e, 2, 3e–$C_3H_3F_3$** and **1**

1e, 2, 3a–$C_3H_3F_3$

C	0.001151	0.001018	-0.003888
C	0.007330	0.006061	1.479830
C	1.104350	-0.006002	2.220292
H	2.102102	0.002613	1.805581
F	1.052481	-0.030778	3.549148
F	-1.200527	0.010448	2.052408
H	1.011977	-0.155366	-0.383612
F	-0.469877	1.208971	-0.487893
H	-0.662686	-0.782946	-0.375135

1e, 2, 3a–$C_3H_3F_3$ + 1 ts

C	-0.014498	-0.003131	-0.011781
N	-0.340193	1.434374	0.049681
B	0.431111	2.324687	-0.887120
C	2.001248	1.924972	-1.067259
F	2.745462	2.882869	-1.634069
F	2.560105	1.671281	0.142120
F	2.198351	0.801815	-1.803496
C	0.259991	3.900095	-0.524895
F	-1.049623	4.201219	-0.255884
F	0.951393	4.260104	0.576837
F	0.627025	4.739136	-1.500507
C	-0.494274	1.841283	1.460235
H	-1.178473	1.146216	1.951138
H	0.472277	1.807830	1.971329
H	-0.901465	2.845468	1.535683
H	0.065394	-0.340182	-1.043447
H	0.933505	-0.202615	0.496195
H	-0.808434	-0.571827	0.475152
C	-0.205574	2.075859	-2.574228
C	-1.571403	2.402929	-2.421051
C	-2.417553	1.590057	-1.622516
F	-2.298951	0.244568	-1.897981
H	-3.451730	1.901598	-1.518231
F	-1.963403	3.612237	-2.713022
H	-0.014656	1.014022	-2.734155
F	0.485334	2.848632	-3.445270
H	-1.694753	1.653111	-0.586355

1e, 2, 3a–$C_3H_2F_3$ + 1 product

B	0.028389	0.033685	-0.003723
N	1.630138	0.136801	-0.235181
H	1.727344	0.805197	-1.003680
C	2.313745	-1.118722	-0.678307
H	1.905632	-1.437390	-1.632288
H	2.152365	-1.889542	0.069780
H	3.379233	-0.912638	-0.782275
C	2.358279	0.707596	0.933970
H	2.323656	-0.013601	1.748361
H	3.393466	0.897666	0.651501
H	1.887207	1.634364	1.249881
C	-0.617607	1.540000	0.073592
C	-0.545724	2.298956	-1.211353
C	-1.459779	2.717252	-2.068099
F	-2.762037	2.522199	-1.879479
H	-1.203199	3.241682	-2.979004
F	0.759927	2.552454	-1.535932
H	-0.108694	2.147330	0.832851
F	-1.937621	1.435825	0.472538
C	-0.591162	-0.767964	-1.274387
F	-1.899006	-0.565465	-1.451316
F	-0.407527	-2.108885	-1.230919
F	0.013783	-0.360136	-2.437659
C	-0.282139	-0.730712	1.399077
F	-0.147188	0.095654	2.469752
F	-1.515836	-1.239764	1.460551
F	0.568925	-1.767954	1.654362

1e, 2, 3e–$C_3H_3F_3$

C	0.001360	-0.000712	-0.004019
C	0.007885	-0.005501	1.479711
C	1.105055	0.005528	2.219970
H	2.102720	-0.004068	1.805069
F	1.053438	0.030584	3.548827
F	-1.199865	-0.008557	2.052519
H	1.012223	0.154715	-0.384035
H	-0.661923	0.783736	-0.375223
F	-0.470839	-1.208368	-0.487658

1e, 2, 3e–$C_3H_3F_3$ + 1 ts

C	0.011922	-0.024349	-0.005226
C	-1.366910	0.310821	0.090358
C	-2.236047	-0.463631	0.910937
H	-1.471445	-0.543494	1.896493
F	-3.443691	0.103775	1.150057
H	-2.328083	-1.510796	0.615621
F	-1.754709	1.473354	-0.326690
B	0.659190	0.234640	1.640284
N	-0.095778	-0.674326	2.576838
C	0.237030	-2.103642	2.509974
H	0.296129	-2.444657	1.475260
H	1.201278	-2.309577	2.984142
H	-0.537008	-2.679157	3.023568
C	-0.278187	-0.266944	3.981859
H	-0.962299	-0.967474	4.465872
H	0.678427	-0.281789	4.512878
H	-0.703087	0.731103	4.044007
C	2.235287	-0.141908	1.466939
F	2.975127	0.815451	0.895110
F	2.797067	-0.390241	2.676078
F	2.438075	-1.269941	0.733885
C	0.450454	1.804651	1.995575
F	-0.876161	2.075000	2.207684
F	1.090594	2.193776	3.117095
F	0.834836	2.641939	1.023203
H	0.192165	-1.091454	-0.152274
F	0.698934	0.711007	-0.917117

1e, 2, 3e–$C_3H_2F_3$ + 1 product

B	0.022498	0.028039	0.000206
N	1.624160	0.125489	-0.233374
H	1.725171	0.788915	-1.005824
C	2.305630	-1.133549	-0.670328
H	1.900290	-1.452721	-1.625403
H	2.139139	-1.902371	0.078676
H	3.371928	-0.930418	-0.770954
C	2.352519	0.702553	0.932740
H	2.311201	-0.010692	1.753862
H	3.389500	0.883980	0.651460
H	1.886518	1.635665	1.237689
C	-0.609099	1.538751	0.073702
C	-0.491653	2.321784	-1.193441
C	-1.466730	2.730306	-1.982491
F	-1.211697	3.406559	-3.105669
H	-2.507807	2.537794	-1.772936
F	0.805204	2.570413	-1.513120
H	-0.141556	2.125418	0.873840
F	-1.957002	1.444584	0.394523
C	-0.598200	-0.776083	-1.269230
F	-1.911006	-0.589929	-1.441685
F	-0.402872	-2.115540	-1.224421
F	-0.002973	-0.363179	-2.432840
C	-0.292411	-0.734885	1.403033
F	-0.157753	0.091543	2.474010
F	-1.530733	-1.235823	1.461144
F	0.550708	-1.776168	1.661616

Table S55. Optimized (M06-2X/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1e, 3a, 3e–$C_3H_3F_3$** and **1** and between propene **2, 3a, 3e–$C_3H_3F_3$** and **1**

1e, 3a, 3e–$C_3H_3F_3$

C	0.001295	0.000347	-0.000297
C	-0.000915	0.001189	1.484893
C	1.141451	-0.000896	2.145088
H	2.128218	-0.003872	1.696009
F	1.186323	0.000072	3.476515
H	-0.957267	0.003725	1.994070
H	1.001723	-0.005663	-0.437398
F	-0.672461	-1.085667	-0.471904
F	-0.659846	1.093497	-0.473367

1e, 3a, 3e–$C_3H_3F_3$ + 1 ts

C	-0.011904	0.001933	-0.009842
N	-0.341852	1.440308	0.035898
B	0.421399	2.329384	-0.889152
C	1.981606	1.912927	-1.111646
F	2.719008	2.867904	-1.688320
F	2.560172	1.654984	0.088454
F	2.159373	0.790588	-1.850986
C	0.266195	3.907836	-0.534455
F	-1.041879	4.242753	-0.304265
F	0.933624	4.246199	0.589205
F	0.681592	4.741694	-1.494525
C	-0.576621	1.859740	1.433631
H	-1.278561	1.162487	1.894283
H	0.364747	1.841805	1.988793
H	-0.996176	2.860855	1.473532
H	0.094090	-0.335842	-1.038881
H	0.924020	-0.187417	0.521851
H	-0.816659	-0.564087	0.461208
C	-0.258987	2.077950	-2.611627
C	-1.601904	2.418985	-2.424358
C	-2.403451	1.573347	-1.626820
F	-3.678734	1.927330	-1.420075
F	-2.349223	0.242991	-1.903229
H	-1.921286	3.444742	-2.584963
H	-0.005962	1.030064	-2.778674
F	0.455140	2.887815	-3.433517
H	-1.640277	1.615404	-0.590496

1e, 3a, 3e–$C_3H_2F_3$ + 1 product

B	0.016509	0.033747	-0.002719
N	1.589988	0.184651	-0.381327
H	1.565458	0.832813	-1.174470
C	2.305988	-1.038461	-0.859201
H	1.837786	-1.400048	-1.769160
H	2.251721	-1.801654	-0.087990
H	3.345378	-0.774328	-1.056389
C	2.381313	0.830861	0.702214
H	2.449267	0.137449	1.538809
H	3.379758	1.063214	0.332095
H	1.886661	1.741505	1.032186
C	-0.595077	1.547527	0.124513
C	-0.214671	2.497780	-0.980232
C	-0.834593	2.570189	-2.145565
F	-1.844221	1.835912	-2.523800
F	-0.523635	3.434872	-3.091646
H	0.570928	3.226665	-0.821315
H	-0.261927	2.000356	1.063360
F	-1.983526	1.466516	0.227125
C	-0.661708	-0.819461	-1.212339
F	-1.988423	-0.754380	-1.286348
F	-0.348105	-2.140726	-1.170246
F	-0.185786	-0.383648	-2.426060
C	-0.139627	-0.750508	1.415622
F	0.095734	0.059142	2.484695
F	-1.362017	-1.263204	1.594161
F	0.735847	-1.784883	1.572888

2, 3a, 3e–$C_3H_3F_3$

C	0.003080	0.000948	-0.001059
C	0.006153	0.003069	1.496289
C	1.085848	-0.002263	2.253374
H	2.064007	-0.008994	1.793874
H	1.007690	-0.000008	3.331881
F	-1.226375	0.011472	2.009307
H	1.014786	-0.006197	-0.409156
F	-0.665649	-1.084807	-0.462498
F	-0.651421	1.094130	-0.465512

2, 3a, 3e–$C_3H_3F_3$ + 1 ts

C	0.008964	-0.016356	-0.011653
C	-1.361985	0.247255	0.118143
C	-2.192772	-0.621217	0.897592
F	-3.475080	-0.278999	1.029863
F	-2.095200	-1.934776	0.577274
F	-1.826925	1.447394	-0.102113
B	0.656004	0.167280	1.653203
N	-0.131035	-0.718842	2.591297
C	0.199661	-2.156792	2.545852
H	0.276561	-2.501446	1.516402
H	1.149863	-2.347950	3.052413
H	-0.590741	-2.721339	3.043518
C	-0.301084	-0.296097	3.996321
H	-0.991600	-0.983784	4.488320
H	0.660097	-0.324043	4.517408
H	-0.708391	0.709312	4.053667
C	2.215679	-0.257186	1.470674
F	2.939404	0.660521	0.804500
F	2.817768	-0.426583	2.670079
F	2.394150	-1.424569	0.801018
C	0.525025	1.744778	2.019484
F	-0.770730	2.088461	2.279892
F	1.230759	2.107822	3.108725
F	0.916206	2.557921	1.020732
H	0.224486	-1.063834	-0.219180
H	0.552243	0.687762	-0.636394
H	-1.435606	-0.566053	1.950016

2, 3a, 3e–$C_3H_2F_3$ + 1 product

B	0.012621	0.032359	0.009216
N	1.614035	0.130587	-0.245344
H	1.694474	0.775913	-1.034764
C	2.301171	-1.132234	-0.652384
H	1.876334	-1.493034	-1.584258
H	2.163325	-1.876006	0.127502
H	3.362635	-0.923142	-0.787893
C	2.342481	0.751991	0.894506
H	2.322955	0.062091	1.736605
H	3.373452	0.946205	0.599271
H	1.856641	1.682836	1.175115
C	-0.661606	1.512584	0.080392
C	-0.492429	2.314330	-1.154134
C	-1.417777	2.759274	-1.984207
F	-2.707919	2.583972	-1.795309
F	-1.172389	3.426441	-3.089927
F	0.803187	2.580709	-1.495376
H	-1.732383	1.374629	0.251838
H	-0.289687	2.087845	0.934939
C	-0.613953	-0.781274	-1.253709
F	-1.929950	-0.571470	-1.414687
F	-0.444841	-2.123137	-1.211416
F	-0.027339	-0.380304	-2.425508
C	-0.283496	-0.741100	1.407969
F	-0.069053	0.051813	2.493130
F	-1.562342	-1.145827	1.493338
F	0.481135	-1.843981	1.627402

Table S56. Optimized (M06-2X/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1a, 1e–$C_3H_4F_2$** and **1** and between propene **1a, 2–$C_3H_4F_2$** and **1**

1a, 1e–$C_3H_4F_2$

C	0.001447	-0.000016	0.001384
C	-0.008876	0.000199	1.499402
C	1.081033	-0.000405	2.236378
F	2.319013	-0.001550	1.772789
F	1.107535	-0.000018	3.557199
H	-0.946437	0.001070	2.039834
H	1.020083	-0.004925	-0.384925
H	-0.508791	0.883445	-0.388001
H	-0.517303	-0.878610	-0.387656

1a, 1e–$C_3H_4F_2$ + 1 ts

C	0.000221	0.031755	-0.018680
C	0.889495	0.857753	-0.745352
C	2.183263	0.391956	-1.010303
F	2.303533	-0.930905	-1.249582
F	2.968534	1.059689	-1.858800
H	0.749476	1.930744	-0.822851
H	0.743809	-0.132920	0.953747
H	-0.058897	-1.002168	-0.362256
H	-0.947328	0.474357	0.265069
B	2.862260	0.671807	0.742774
N	2.147118	-0.244419	1.664687
C	2.540396	-1.664168	1.667684
H	2.764022	-2.007750	0.662206
H	3.423555	-1.811694	2.297140
H	1.718678	-2.259542	2.073452
C	1.854634	0.186255	3.043428
H	1.166744	-0.530152	3.498020
H	2.776400	0.211802	3.632993
H	1.394440	1.169787	3.061676
C	4.445371	0.326876	0.516488
F	5.128427	1.306552	-0.092286
F	5.024233	0.162134	1.734650
F	4.708073	-0.805055	-0.166699
C	2.694177	2.255301	1.087560
F	1.407592	2.604139	1.401839
F	3.438230	2.633115	2.144082
F	3.028143	3.062252	0.065266

1a, 1e–$C_3H_4F_2$ + 1 product

B	0.029124	0.030432	-0.020532
N	1.649934	0.070388	-0.134047
H	1.846822	0.836620	-0.780658
C	2.289254	-1.154453	-0.710683
H	1.953333	-1.301423	-1.732302
H	2.002299	-2.007435	-0.100567
H	3.371086	-1.023224	-0.687630
C	2.347513	0.406184	1.150646
H	2.288043	-0.463783	1.800662
H	3.390956	0.629243	0.928283
H	1.865488	1.255056	1.621825
C	-0.544153	1.570721	-0.054914
C	-0.657949	2.239160	-1.393751
C	-1.813795	2.535324	-1.967100
H	-1.849137	3.012831	-2.938133
H	-2.752306	2.298652	-1.480751
H	0.286276	2.466193	-1.882103
F	0.294257	2.387985	0.709759
F	-1.755318	1.598432	0.573005
C	-0.573273	-0.793331	-1.289378
F	-1.891520	-0.615562	-1.443458
F	-0.373630	-2.130913	-1.226292
F	0.003124	-0.401522	-2.467195
C	-0.388768	-0.722024	1.361159
F	-0.217204	0.039899	2.464775
F	-1.662594	-1.131437	1.369049
F	0.366459	-1.841817	1.583392

1a, 2–$C_3H_4F_2$

C	0.002789	0.000173	0.001407
C	-0.003709	0.001493	1.484313
C	1.028922	-0.000061	2.309531
F	2.283205	-0.004098	1.825248
H	0.960406	0.000740	3.387563
F	-1.235571	0.004275	2.036161
H	1.027096	-0.005564	-0.366972
H	-0.510994	0.887341	-0.375194
H	-0.520479	-0.882151	-0.373441

1a, 2–$C_3H_4F_2$ + 1 ts

C	-0.002104	0.029253	-0.013004
C	0.883259	0.897619	-0.691438
C	2.245124	0.568893	-0.883640
H	2.833849	1.211825	-1.534106
F	2.397957	-0.761552	-1.196380
F	0.552448	2.153554	-0.848892
H	0.686133	-0.052264	0.989734
H	-1.001175	0.415953	0.153540
H	0.048207	-1.001479	-0.361854
B	2.893863	0.762462	0.810656
N	2.147015	-0.139976	1.744171
C	2.504876	-1.567726	1.732965
H	2.631711	-1.927919	0.715628
H	3.436197	-1.741580	2.283374
H	1.707127	-2.137644	2.216866
C	1.931328	0.293337	3.135003
H	1.236195	-0.398408	3.616862
H	2.874622	0.282363	3.691956
H	1.508232	1.292588	3.179253
C	4.471941	0.392299	0.609723
F	5.125982	1.281510	-0.166647
F	5.097443	0.397932	1.810418
F	4.725897	-0.820263	0.073615
C	2.763262	2.347022	1.170882
F	1.488950	2.709783	1.496867
F	3.525975	2.723082	2.213973
F	3.104847	3.145478	0.137320

1a, 2–$C_3H_4F_2$ + 1 product

B	0.018193	0.043734	-0.003765
N	1.618774	0.145842	-0.217577
H	1.729242	0.866286	-0.935430
C	2.285421	-1.089239	-0.731654
H	1.899956	-1.331574	-1.717403
H	2.083655	-1.906884	-0.044154
H	3.358336	-0.904969	-0.789270
C	2.347982	0.626407	0.996293
H	2.333156	-0.169473	1.738975
H	3.377967	0.850891	0.719177
H	1.854422	1.508557	1.391810
C	-0.672051	1.525823	0.009863
C	-0.596684	2.263850	-1.282820
C	-1.577335	2.690040	-2.052845
H	-1.372595	3.164123	-3.003104
H	-2.600539	2.546898	-1.736932
F	0.698920	2.451957	-1.678298
H	-1.726616	1.423504	0.277800
F	-0.076015	2.348684	0.987191
C	-0.616363	-0.782695	-1.256817
F	-1.944661	-0.605155	-1.374245
F	-0.415785	-2.118771	-1.212031
F	-0.079434	-0.375406	-2.445132
C	-0.307187	-0.734361	1.387296
F	-0.105858	0.020597	2.491478
F	-1.590983	-1.136411	1.440243
F	0.448718	-1.851300	1.578940

Table S57. Optimized (M06-2X/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1a, 3a–$C_3H_4F_2$** and **1** and between propene **1a, 3e–$C_3H_4F_2$** and **1**

1a, 3a–$C_3H_4F_2$

C	0.004026	0.003149	0.002544
C	-0.007507	0.008414	1.495304
C	1.080062	-0.006707	2.244546
F	2.311025	-0.030659	1.708582
H	1.105040	-0.009222	3.326236
H	-0.967159	0.024874	1.997483
H	1.015020	0.112984	-0.389386
H	-0.444532	-0.911696	-0.391784
F	-0.760858	1.064409	-0.467016

1a, 3a–$C_3H_4F_2$ + 1 ts

C	0.011121	0.008800	-0.013339
C	0.895654	0.884405	-0.681765
C	2.220397	0.576056	-0.978839
H	2.830362	1.289742	-1.526072
F	2.499735	-0.705067	-1.343216
H	0.668195	1.941650	-0.590710
H	0.724759	0.050532	1.026032
H	-1.008964	0.336601	0.160665
F	0.055294	-1.319333	-0.342269
B	2.859867	0.783733	0.795857
N	2.098535	-0.106565	1.711918
C	2.419572	-1.547829	1.674642
H	2.527386	-1.885911	0.647622
H	3.346450	-1.747859	2.221200
H	1.603856	-2.100866	2.144279
C	1.875124	0.319709	3.105666
H	1.153958	-0.356367	3.569738
H	2.812440	0.274748	3.668789
H	1.483177	1.331984	3.151411
C	4.431346	0.404325	0.582543
F	5.065659	1.252560	-0.253100
F	5.068142	0.495259	1.775528
F	4.690130	-0.834192	0.126337
C	2.725186	2.375621	1.125156
F	1.448175	2.750857	1.443119
F	3.485957	2.778814	2.155554
F	3.057327	3.151878	0.069935

1a, 3a–$C_3H_4F_2$ + 1 product

B	0.014077	0.010725	-0.019587
N	1.609117	0.122842	-0.279581
H	1.665240	0.499110	-1.228838
C	2.305363	-1.197018	-0.306011
H	1.754392	-1.890518	-0.937251
H	2.340698	-1.585556	0.709997
H	3.317824	-1.059112	-0.685784
C	2.349034	1.063984	0.611269
H	2.240248	0.728921	1.639342
H	3.400333	1.064240	0.321176
H	1.929071	2.061209	0.524242
C	-0.672872	1.476156	0.123266
C	-0.423268	2.408969	-1.020676
C	-1.352547	2.828392	-1.863882
H	-1.183517	3.479448	-2.712039
F	-2.634624	2.469478	-1.746474
H	0.583144	2.776598	-1.198652
H	-1.749378	1.338666	0.242818
F	-0.221609	2.107678	1.305378
C	-0.597101	-0.699894	-1.365846
F	-1.877388	-0.369909	-1.593503
F	-0.541953	-2.047505	-1.405776
F	0.098990	-0.291313	-2.478439
C	-0.273684	-0.874936	1.316300
F	0.435014	-0.446656	2.394806
F	-1.570612	-0.824341	1.668651
F	0.032452	-2.191904	1.206176

1a, 3e–$C_3H_4F_2$

C	0.003643	-0.002566	0.002779
C	-0.008078	-0.006728	1.495540
C	1.079454	0.005285	2.244892
F	2.310556	0.024655	1.709059
H	1.104326	0.008507	3.326584
H	-0.967830	-0.019583	1.997635
H	1.014350	-0.115727	-0.388944
H	-0.442115	0.913350	-0.392237
F	-0.764369	-1.061851	-0.466138

1a, 3e–$C_3H_4F_2$ + 1 ts

C	-0.002897	0.030022	-0.013867
C	0.874974	0.925490	-0.662995
C	2.183626	0.520148	-0.919615
H	2.834143	1.118020	-1.551716
F	2.306397	-0.823143	-1.181750
H	0.653477	1.987809	-0.646014
H	0.772506	-0.139569	0.959844
F	-1.208789	0.544614	0.359710
H	-0.100120	-0.980819	-0.410932
B	2.879579	0.733002	0.801764
N	2.136997	-0.188595	1.704439
C	2.550561	-1.603662	1.736956
H	2.732077	-1.973824	0.732314
H	3.462359	-1.723265	2.330682
H	1.754053	-2.192442	2.197663
C	1.794411	0.257353	3.068354
H	1.099626	-0.459383	3.510906
H	2.695799	0.302555	3.687456
H	1.321910	1.235208	3.056550
C	4.451039	0.363745	0.565356
F	5.095257	1.275956	-0.189811
F	5.092044	0.332239	1.758049
F	4.694875	-0.829945	-0.012704
C	2.744919	2.320306	1.144644
F	1.470724	2.705878	1.450117
F	3.501466	2.708239	2.185039
F	3.093180	3.098756	0.095514

1a, 3e–$C_3H_4F_2$ + 1 product

B	0.004053	0.008430	-0.004982
N	1.593489	0.133824	-0.279067
H	1.638077	0.539411	-1.217194
C	2.302294	-1.177590	-0.350612
H	1.758622	-1.854138	-1.005910
H	2.342045	-1.601153	0.650972
H	3.312955	-1.016619	-0.725994
C	2.331059	1.055596	0.634167
H	2.257350	0.672183	1.648482
H	3.374409	1.097361	0.319827
H	1.882520	2.043791	0.602206
C	-0.689290	1.471355	0.132497
C	-0.414113	2.414986	-0.995044
C	-1.363991	2.806762	-1.825447
H	-2.408771	2.525028	-1.768440
F	-1.099987	3.602890	-2.869028
H	0.596623	2.780261	-1.161216
H	-1.768743	1.321389	0.219382
F	-0.284360	2.091871	1.335693
C	-0.618525	-0.712280	-1.341306
F	-1.910321	-0.397510	-1.551898
F	-0.554432	-2.058966	-1.374099
F	0.053398	-0.302192	-2.464033
C	-0.275231	-0.875222	1.332803
F	0.402446	-0.423837	2.419586
F	-1.580308	-0.856512	1.662494
F	0.066313	-2.184364	1.233329

Table S58. Optimized (M06-2X/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1e, 2–$C_3H_4F_2$** and **1** and between propene **1e, 3a–$C_3H_4F_2$** and **1**

1e, 2–$C_3H_4F_2$

C	-0.000009	-0.000233	-0.002464
C	0.004895	-0.000160	1.482600
C	1.071747	-0.000534	2.265066
H	2.085460	-0.001163	1.892962
F	0.965089	-0.000790	3.598522
F	-1.218081	0.000031	2.037778
H	1.019457	-0.001898	-0.386718
H	-0.518179	0.885301	-0.376627
H	-0.521007	-0.884138	-0.376559

1e, 2–$C_3H_4F_2$ + 1 ts

C	0.011435	-0.025371	-0.007781
C	-1.366559	0.294901	0.111611
C	-2.240876	-0.481637	0.905589
H	-1.513703	-0.527360	1.902941
H	-3.220900	-0.046611	1.067593
H	-2.252803	-1.539744	0.646522
F	-1.737723	1.479465	-0.286223
B	0.644074	0.234539	1.649611
N	-0.108612	-0.664540	2.596545
C	0.206182	-2.095873	2.519450
H	0.242935	-2.432946	1.482387
H	1.175102	-2.318253	2.977355
H	-0.567116	-2.665050	3.041852
C	-0.257594	-0.260273	4.004222
H	-0.944007	-0.951834	4.498699
H	0.706926	-0.291706	4.520983
H	-0.665491	0.744060	4.078928
C	2.221747	-0.144494	1.482550
F	2.967106	0.809693	0.910638
F	2.779209	-0.389329	2.695045
F	2.428090	-1.275563	0.755095
C	0.449510	1.808268	2.006198
F	-0.869315	2.093483	2.246817
F	1.115132	2.189764	3.117077
F	0.823273	2.646768	1.030717
H	0.203043	-1.087505	-0.166424
F	0.701266	0.730897	-0.901185

1e, 2–$C_3H_4F_2$ + 1 product

B	0.022409	0.029296	-0.000662
N	1.623734	0.127992	-0.237119
H	1.717951	0.792768	-1.009248
C	2.308370	-1.128711	-0.673367
H	1.902514	-1.450775	-1.627222
H	2.145824	-1.897443	0.076650
H	3.373968	-0.922434	-0.776021
C	2.352962	0.710111	0.925521
H	2.318152	-0.001779	1.748102
H	3.388150	0.896206	0.640403
H	1.883131	1.641374	1.229976
C	-0.615306	1.538328	0.066046
C	-0.516679	2.318274	-1.205312
C	-1.465637	2.750507	-2.006280
H	-1.223846	3.294519	-2.908526
H	-2.493999	2.542522	-1.749180
F	0.803085	2.544606	-1.499001
H	-0.138167	2.130063	0.856893
F	-1.955594	1.435583	0.409371
C	-0.598952	-0.789012	-1.260449
F	-1.913286	-0.616147	-1.427403
F	-0.392297	-2.127687	-1.205196
F	-0.012022	-0.383331	-2.431008
C	-0.285094	-0.726573	1.408198
F	-0.149050	0.104667	2.475151
F	-1.520172	-1.234180	1.475279
F	0.564503	-1.763409	1.668304

1e, 3a–$C_3H_4F_2$

C	0.000467	0.002205	-0.001398
C	-0.001590	0.005686	1.488897
C	1.130549	-0.004788	2.168268
H	2.125387	-0.004949	1.737347
F	1.155002	-0.024450	3.505114
H	-0.949645	0.016993	2.014704
H	1.016356	-0.068583	-0.396406
H	-0.598588	-0.819775	-0.398783
F	-0.561323	1.179305	-0.482832

1e, 3a–$C_3H_4F_2$ + 1 ts

C	-0.014691	0.000837	-0.014477
N	-0.344388	1.438207	0.030287
B	0.413863	2.320739	-0.904414
C	1.978359	1.911943	-1.120730
F	2.713825	2.869947	-1.697863
F	2.554745	1.662698	0.082611
F	2.168688	0.788518	-1.854780
C	0.269331	3.902484	-0.549914
F	-1.030691	4.247715	-0.282151
F	0.969075	4.243647	0.552878
F	0.658285	4.734357	-1.524178
C	-0.547622	1.857602	1.430408
H	-1.247310	1.166036	1.904169
H	0.401643	1.830188	1.972859
H	-0.957577	2.862273	1.482533
H	0.097806	-0.336537	-1.042391
H	0.915963	-0.191733	0.526758
H	-0.824316	-0.566375	0.447390
C	-0.241678	2.063672	-2.641368
C	-1.569789	2.424478	-2.404428
C	-2.396712	1.564469	-1.654193
F	-2.230653	0.218890	-1.925084
H	-3.443772	1.811811	-1.521283
H	-1.854078	3.465484	-2.526905
H	-0.000955	1.016396	-2.817252
F	0.480062	2.873906	-3.457159
H	-1.692995	1.640692	-0.602697

1e, 3a–$C_3H_4F_2$ + 1 product

B	0.011811	0.031854	-0.000782
N	1.582955	0.189155	-0.390037
H	1.547339	0.830214	-1.188617
C	2.305766	-1.031601	-0.862654
H	1.834421	-1.404214	-1.766461
H	2.262684	-1.789303	-0.085404
H	3.341838	-0.760575	-1.068444
C	2.374431	0.849295	0.684298
H	2.456776	0.160231	1.523250
H	3.367620	1.091903	0.306367
H	1.870710	1.754797	1.014751
C	-0.609369	1.543197	0.127829
C	-0.215066	2.490352	-0.972730
C	-0.802675	2.601123	-2.155895
F	-1.838763	1.849766	-2.515628
H	-0.519369	3.314031	-2.920826
H	0.600028	3.183784	-0.788117
H	-0.292484	1.990750	1.075393
F	-1.997677	1.453486	0.210853
C	-0.666264	-0.829396	-1.205435
F	-1.992452	-0.777994	-1.276990
F	-0.341191	-2.150111	-1.152767
F	-0.193589	-0.401637	-2.421401
C	-0.129439	-0.751351	1.420170
F	0.113824	0.059159	2.487318
F	-1.349089	-1.266455	1.610587
F	0.749723	-1.783900	1.571877

Table S59. Optimized (M06-2X/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1e, 3e–$C_3H_4F_2$** and **1** and between propene **2, 3a–$C_3H_4F_2$** and **1**

1e, 3e–$C_3H_4F_2$

C	0.000263	-0.001282	-0.001588
C	-0.001831	-0.003446	1.488873
C	1.130546	0.001504	2.168004
H	2.125166	-0.002393	1.736673
F	1.155428	0.022295	3.504725
H	-0.949606	-0.009787	2.015198
H	1.016403	0.067009	-0.396129
H	-0.597205	0.821217	-0.399988
F	-0.563561	-1.177935	-0.481585

1e, 3e–$C_3H_4F_2$ + 1 ts

C	-0.004677	0.027542	-0.018047
C	0.851364	0.823738	-0.809359
C	2.194437	0.459972	-0.968773
H	2.437057	-0.595136	-1.100720
F	2.915770	1.220306	-1.837920
H	0.556509	1.840331	-1.061694
H	0.759952	-0.057042	0.971634
F	-1.217117	0.581828	0.273331
H	-0.111875	-1.024619	-0.289036
B	2.859669	0.741149	0.722416
N	2.119773	-0.165739	1.650763
C	2.460777	-1.593942	1.598219
H	2.546029	-1.935616	0.566264
H	3.413633	-1.789205	2.098379
H	1.676240	-2.169784	2.094666
C	1.873319	0.248849	3.043847
H	1.168821	-0.449464	3.500801
H	2.807147	0.236569	3.613474
H	1.447196	1.247457	3.081569
C	4.432289	0.361452	0.514002
F	5.159311	1.321216	-0.068215
F	5.010985	0.120541	1.717813
F	4.632830	-0.766901	-0.215536
C	2.671134	2.316066	1.071225
F	1.357492	2.626407	1.299655
F	3.334569	2.687086	2.186729
F	3.065415	3.145920	0.095404

1e, 3e–$C_3H_4F_2$ + 1 product

B	0.025072	0.035605	-0.000553
N	1.612228	0.151089	-0.325016
H	1.631999	0.756404	-1.150566
C	2.320294	-1.106493	-0.720195
H	1.835244	-1.540535	-1.588655
H	2.283347	-1.804667	0.110611
H	3.355095	-0.859051	-0.958663
C	2.376350	0.829762	0.757817
H	2.361768	0.192229	1.640408
H	3.404479	0.986836	0.431953
H	1.914099	1.784423	0.997454
C	-0.581702	1.549561	0.121297
C	-0.285040	2.438680	-1.050027
C	-1.147534	2.643075	-2.029739
F	-0.845722	3.444335	-3.063141
H	-2.140461	2.217421	-2.093790
H	0.673578	2.951106	-1.088656
H	-0.219038	2.038340	1.031881
F	-1.964514	1.440219	0.283578
C	-0.627279	-0.773273	-1.258457
F	-1.935703	-0.578046	-1.441931
F	-0.448368	-2.115699	-1.184255
F	-0.027388	-0.401685	-2.435926
C	-0.210465	-0.759440	1.400275
F	-0.001541	0.037982	2.483326
F	-1.453360	-1.239796	1.518661
F	0.627195	-1.819109	1.591029

2, 3a–$C_3H_4F_2$

C	0.002612	0.001296	-0.001846
C	0.004479	0.007642	1.488445
C	1.059055	-0.008272	2.283268
H	2.052221	0.010868	1.858369
H	0.942755	-0.037820	3.358107
F	-1.239264	0.003860	1.998668
H	1.024321	-0.057322	-0.377653
H	-0.585945	-0.840276	-0.375261
F	-0.580358	1.161067	-0.480832

2, 3a–$C_3H_4F_2$ + 1 ts

C	0.010441	-0.022197	-0.011852
C	-1.355581	0.231880	0.160700
C	-2.202724	-0.648466	0.883832
F	-2.002217	-1.975936	0.587859
H	-3.255271	-0.397298	0.962288
F	-1.811895	1.450965	-0.013989
B	0.641906	0.161413	1.665324
N	-0.143772	-0.718634	2.607580
C	0.188727	-2.155351	2.567472
H	0.275900	-2.502463	1.540251
H	1.132927	-2.346783	3.086712
H	-0.606873	-2.721072	3.056107
C	-0.298078	-0.295421	4.012094
H	-0.990216	-0.977704	4.510393
H	0.665458	-0.331875	4.529777
H	-0.696482	0.713179	4.076258
C	2.203792	-0.263243	1.483296
F	2.928831	0.655077	0.817006
F	2.806573	-0.431135	2.682926
F	2.386594	-1.430497	0.814709
C	0.529507	1.742163	2.034205
F	-0.753179	2.106302	2.329776
F	1.267038	2.095831	3.106496
F	0.906301	2.553685	1.027675
H	0.229753	-1.067461	-0.220589
H	0.548163	0.689004	-0.632498
H	-1.505323	-0.550557	1.941811

2, 3a–$C_3H_4F_2$ + 1 product

B	0.012363	0.032448	0.006978
N	1.613871	0.119444	-0.258781
H	1.689672	0.760265	-1.052264
C	2.293498	-1.148352	-0.661542
H	1.865302	-1.510697	-1.591221
H	2.152895	-1.888448	0.121385
H	3.355981	-0.945578	-0.799314
C	2.352794	0.745682	0.871394
H	2.338455	0.060736	1.717633
H	3.381910	0.935619	0.566831
H	1.871382	1.679209	1.150454
C	-0.652053	1.517558	0.061985
C	-0.499156	2.308162	-1.180418
C	-1.413979	2.788189	-2.003914
F	-2.716301	2.617484	-1.738729
H	-1.201195	3.329339	-2.914570
F	0.806772	2.540764	-1.532496
H	-0.260704	2.097403	0.904908
H	-1.722441	1.394406	0.247217
C	-0.624781	-0.803502	-1.235375
F	-1.942637	-0.607562	-1.384251
F	-0.444616	-2.144661	-1.172694
F	-0.052642	-0.419462	-2.420150
C	-0.273417	-0.718288	1.420895
F	-0.051923	0.091298	2.492310
F	-1.549677	-1.125871	1.523730
F	0.496863	-1.816045	1.651686

Table S60. Optimized (M06-2X/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **2, 3e–$C_3H_4F_2$** and **1** and between propene **3a, 3e–$C_3H_4F_2$** and **1**

2, 3e–$C_3H_4F_2$

C	0.002450	-0.000817	-0.001883
C	0.004262	-0.005396	1.488553
C	1.058811	0.005597	2.283494
H	2.051890	-0.018746	1.858650
H	0.942417	0.036423	3.358288
F	-1.239493	0.005088	1.998525
H	1.024374	0.052936	-0.377878
H	-0.582553	0.842807	-0.376234
F	-0.585613	-1.158633	-0.479191

2, 3e–$C_3H_4F_2$ + 1 ts

C	0.008070	-0.017570	-0.012338
C	-1.370085	0.249908	0.105271
C	-2.226115	-0.599081	0.859824
H	-1.490227	-0.611315	1.877811
F	-3.489617	-0.145509	1.048821
H	-2.204902	-1.650478	0.568307
F	-1.822945	1.431400	-0.210301
B	0.652618	0.180711	1.631144
N	-0.118631	-0.711378	2.575936
C	0.197066	-2.144440	2.515018
H	0.245371	-2.486831	1.480325
H	1.160582	-2.362366	2.986163
H	-0.582203	-2.708270	3.034179
C	-0.286539	-0.294870	3.978934
H	-0.986934	-0.975158	4.468985
H	0.670161	-0.331323	4.509630
H	-0.685887	0.713876	4.039015
C	2.218742	-0.225407	1.456535
F	2.941009	0.686450	0.780061
F	2.823477	-0.382564	2.656328
F	2.404355	-1.401600	0.797551
C	0.501711	1.756509	1.994045
F	-0.803253	2.084354	2.231386
F	1.185344	2.137644	3.091678
F	0.897423	2.571442	0.996961
H	0.225859	-1.065390	-0.214086
H	0.543023	0.666671	-0.666195

2, 3e–$C_3H_4F_2$ + 1 product

B	0.003398	0.022455	0.011549
N	1.597975	0.119470	-0.278417
H	1.661987	0.753479	-1.078463
C	2.280864	-1.147614	-0.677940
H	1.837763	-1.526062	-1.594230
H	2.162433	-1.878382	0.117302
H	3.338408	-0.937285	-0.839688
C	2.346711	0.764273	0.835203
H	2.346181	0.090227	1.690247
H	3.370713	0.956286	0.515305
H	1.863105	1.699231	1.105582
C	-0.671246	1.502675	0.073946
C	-0.471353	2.321586	-1.146470
C	-1.374873	2.738846	-2.016442
H	-2.430880	2.535536	-1.918649
F	-1.030115	3.439622	-3.102682
F	0.838739	2.624385	-1.389025
H	-0.316231	2.068221	0.942071
H	-1.745653	1.363800	0.222514
C	-0.648441	-0.816594	-1.222412
F	-1.971449	-0.618585	-1.355226
F	-0.473217	-2.157399	-1.156593
F	-0.093761	-0.438645	-2.414691
C	-0.262212	-0.731385	1.427897
F	-0.023269	0.074172	2.498403
F	-1.540586	-1.131987	1.546770
F	0.503970	-1.833363	1.645524

3a, 3e–$C_3H_4F_2$

C	0.001889	0.000691	0.000858
C	-0.002185	0.002032	1.491468
C	1.120534	-0.001340	2.194238
H	2.090304	-0.005616	1.707022
H	1.112618	0.000030	3.276916
H	-0.983572	0.006088	1.955243
H	1.003825	-0.006375	-0.433029
F	-0.674336	-1.085480	-0.469557
F	-0.659752	1.094991	-0.471560

3a, 3e–$C_3H_4F_2$ + 1 ts

C	-0.012647	0.004231	-0.011934
N	-0.346351	1.440705	0.017402
B	0.423911	2.324503	-0.913568
C	1.980270	1.899847	-1.130077
F	2.686506	2.810919	-1.824000
F	2.605281	1.756778	0.061980
F	2.155895	0.723497	-1.780351
C	0.303450	3.908342	-0.563372
F	-0.986632	4.282421	-0.304711
F	1.015513	4.274687	0.519537
F	0.700396	4.707621	-1.573056
C	-0.575112	1.874768	1.409049
H	-1.285241	1.191918	1.879459
H	0.364389	1.851855	1.968926
H	-0.983487	2.881018	1.441778
H	0.079449	-0.345907	-1.037902
H	0.929383	-0.181394	0.512178
H	-0.810608	-0.557357	0.476817
C	-0.239691	2.130047	-2.612267
C	-1.589639	2.433890	-2.414563
C	-2.402919	1.522310	-1.701921
F	-3.695853	1.823506	-1.516423
F	-2.295766	0.209023	-2.018757
H	-1.944007	3.460235	-2.452147
H	-0.005552	1.086201	-2.816103
H	0.344407	2.846722	-3.181492
H	-1.676175	1.585819	-0.652514

3a, 3e–$C_3H_4F_2$ + 1 product

B	-0.002047	0.029144	0.011343
N	1.561349	0.190777	-0.397915
H	1.507563	0.820585	-1.204334
C	2.284518	-1.031987	-0.855909
H	1.799868	-1.428147	-1.743277
H	2.258287	-1.773682	-0.061919
H	3.316210	-0.763341	-1.085934
C	2.352075	0.881592	0.655225
H	2.487059	0.195777	1.490136
H	3.323528	1.168732	0.252358
H	1.811419	1.759960	1.001070
C	-0.685870	1.504161	0.098280
C	-0.222308	2.471373	-0.958488
C	-0.812489	2.629720	-2.128197
F	-0.412025	3.464498	-3.071475
F	-1.894364	1.996546	-2.522367
H	0.640006	3.108238	-0.791001
H	-0.508009	1.951721	1.079425
H	-1.768339	1.371070	0.022596
C	-0.694011	-0.846506	-1.174803
F	-2.030426	-0.754393	-1.202271
F	-0.409447	-2.171809	-1.143862
F	-0.261119	-0.418305	-2.404097
C	-0.125586	-0.739461	1.438179
F	0.201664	0.055438	2.494565
F	-1.378512	-1.164825	1.671948
F	0.678709	-1.829836	1.568886

Table S61. Optimized (M06-2X/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **1a–C_3H_5F** and **1** and between propene **1e–C_3H_5F** and **1**

1a–C_3H_5F

C	0.002755	-0.001184	0.003281
C	-0.009650	-0.005059	1.500950
C	1.066309	0.002629	2.266915
F	2.309575	0.015221	1.746075
H	1.078543	0.000006	3.348599
H	-0.962512	-0.014952	2.018186
H	1.022103	0.008162	-0.380233
H	-0.521790	0.875609	-0.383729
H	-0.507328	-0.884531	-0.388119

1a–C_3H_5F + 1 ts

C	-0.002372	0.027687	-0.013160
C	0.891422	0.924809	-0.639590
C	2.201666	0.537814	-0.923538
H	2.844799	1.158350	-1.541570
F	2.354673	-0.794161	-1.214216
H	0.702451	1.993066	-0.615617
H	0.738457	-0.085753	0.989404
H	-0.985875	0.404279	0.241922
H	0.021052	-1.001191	-0.370356
B	2.866639	0.756185	0.805136
N	2.123191	-0.153533	1.725222
C	2.508704	-1.575504	1.732658
H	2.655712	-1.938174	0.719143
H	3.433627	-1.723821	2.299679
H	1.712272	-2.153941	2.207332
C	1.849137	0.289288	3.103066
H	1.150473	-0.410537	3.567324
H	2.773010	0.303088	3.690484
H	1.406051	1.281000	3.118323
C	4.441915	0.387799	0.592686
F	5.094805	1.290596	-0.168060
F	5.069778	0.375651	1.793685
F	4.696299	-0.814261	0.037431
C	2.738678	2.345886	1.146931
F	1.469969	2.735432	1.475806
F	3.512814	2.737457	2.173581
F	3.070022	3.124069	0.091534

1a–C_3H_5F + 1 product

B	-0.024144	0.019353	0.025410
N	1.535788	0.167386	-0.371169
H	1.491535	0.707970	-1.240725
C	2.249206	-1.104350	-0.686618
H	1.701434	-1.656519	-1.445330
H	2.312347	-1.700243	0.220632
H	3.250322	-0.867052	-1.047847
C	2.336974	0.961793	0.604426
H	2.457127	0.372919	1.510982
H	3.312746	1.178119	0.168544
H	1.811081	1.879624	0.852200
C	-0.711174	1.494024	0.156731
C	-0.335654	2.456075	-0.934689
C	-0.901262	2.515711	-2.135572
H	-1.728470	1.868129	-2.406608
H	-0.552543	3.216133	-2.884465
H	0.480991	3.133220	-0.687201
F	-0.359686	2.101520	1.380142
H	-1.795924	1.365426	0.185019
C	-0.733077	-0.773503	-1.224174
F	-2.039323	-0.477980	-1.367970
F	-0.660445	-2.119286	-1.165678
F	-0.148566	-0.441670	-2.418573
C	-0.196203	-0.828729	1.402708
F	0.398269	-0.258863	2.477770
F	-1.497585	-0.971433	1.716849
F	0.319840	-2.086178	1.352732

1e–C_3H_5F

C	-0.000285	-0.000225	-0.001011
C	-0.002066	-0.000201	1.497360
C	1.104537	-0.000017	2.216101
C	1.075800	-0.000356	3.561977
H	2.116292	0.000178	1.827994
H	-0.952007	-0.000427	2.022700
H	-0.516744	0.879766	-0.391211
H	1.017278	0.000354	-0.395190
H	-0.515765	-0.880786	-0.391233

1e–C_3H_5F + 1 ts

C	-0.002346	0.024860	-0.016669
C	0.863987	0.843644	-0.778651
C	2.200883	0.475580	-0.967439
H	2.438259	-0.578027	-1.114062
F	2.932787	1.248237	-1.818971
H	0.606685	1.876323	-1.003848
H	0.728231	-0.016320	0.993333
H	-0.992784	0.414758	0.185850
H	0.014858	-1.038516	-0.258595
B	2.844806	0.759347	0.733328
N	2.105525	-0.136559	1.675411
C	2.430269	-1.567035	1.614821
H	2.495859	-1.906267	0.580776
H	3.387327	-1.776663	2.101711
H	1.645402	-2.136273	2.119001
C	1.900539	0.277934	3.073090
H	1.196961	-0.411323	3.545960
H	2.846017	0.251389	3.623468
H	1.489822	1.282481	3.124325
C	4.419763	0.378752	0.538279
F	5.152460	1.335163	-0.044528
F	4.990990	0.146042	1.748055
F	4.627871	-0.754243	-0.181554
C	2.669500	2.337917	1.082850
F	1.362736	2.660362	1.340524
F	3.357907	2.706218	2.184824
F	3.048034	3.168093	0.100658

1e–C_3H_5F + 1 product

B	0.020404	0.042441	0.007432
N	1.612991	0.148095	-0.303714
H	1.643639	0.741768	-1.136451
C	2.320318	-1.116339	-0.677445
H	1.842701	-1.557670	-1.546311
H	2.271647	-1.805607	0.160018
H	3.358763	-0.875463	-0.907041
C	2.369382	0.837822	0.777364
H	2.340422	0.213520	1.668998
H	3.402392	0.982701	0.461124
H	1.910743	1.798897	0.996741
C	-0.590933	1.556924	0.103399
C	-0.327242	2.415981	-1.094871
C	-1.235735	2.732676	-2.008944
H	-2.255428	2.377323	-1.918670
H	-0.984709	3.354869	-2.858672
H	0.689194	2.801091	-1.189357
F	-1.965468	1.441054	0.307670
H	-0.206412	2.066676	0.994830
C	-0.621878	-0.782521	-1.243356
F	-1.928828	-0.598061	-1.433736
F	-0.434966	-2.125003	-1.155106
F	-0.014687	-0.420315	-2.420311
C	-0.226466	-0.732261	1.418390
F	-0.033818	0.081250	2.492055
F	-1.465918	-1.221793	1.531784
F	0.617723	-1.783671	1.633795

Table S62. Optimized (M06-2X/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **2–C_3H_5F** and **1** and between propene **3a–C_3H_5F** and **1**

2–C_3H_5F

C	0.000929	-0.000015	-0.000855
C	0.001624	0.000589	1.486732
C	1.026820	-0.000500	2.320675
H	2.035047	-0.002329	1.933080
H	0.868869	0.000712	3.390261
F	-1.255914	0.003581	1.985949
H	-0.520038	0.884403	-0.374372
H	1.020255	-0.003744	-0.382815
H	-0.526294	-0.881039	-0.373540

2–C_3H_5F + 1 ts

C	0.008666	-0.022003	-0.013942
C	-1.371343	0.226275	0.126855
C	-2.242237	-0.612694	0.856537
H	-1.532566	-0.605213	1.879014
H	-3.255454	-0.249828	0.985536
H	-2.159997	-1.668906	0.605522
F	-1.804280	1.428992	-0.177146
B	0.634552	0.180146	1.636942
N	-0.135673	-0.706890	2.588665
C	0.170531	-2.140334	2.519447
H	0.207580	-2.478258	1.482873
H	1.135995	-2.368972	2.982404
H	-0.608924	-2.702291	3.041101
C	-0.274832	-0.294403	3.994074
H	-0.974021	-0.969407	4.494001
H	0.688945	-0.341824	4.511859
H	-0.663079	0.718076	4.065354
C	2.204182	-0.222899	1.475290
F	2.930997	0.687845	0.800497
F	2.801440	-0.373518	2.680410
F	2.399540	-1.401593	0.823630
C	0.490304	1.758205	2.000923
F	-0.807895	2.094800	2.262756
F	1.194407	2.136910	3.087830
F	0.873538	2.573714	0.999006
H	0.238076	-1.066222	-0.216299
H	0.539484	0.674748	-0.657236

2–C_3H_5F + 1 product

B	0.004513	0.023630	0.009228
N	1.600440	0.121382	-0.277472
H	1.662330	0.765659	-1.069546
C	2.284550	-1.140876	-0.687821
H	1.845935	-1.508957	-1.610404
H	2.161927	-1.880774	0.098408
H	3.343156	-0.929512	-0.841756
C	2.347981	0.755943	0.842464
H	2.348425	0.073615	1.690926
H	3.371898	0.952242	0.524644
H	1.863272	1.687658	1.121423
C	-0.669819	1.503752	0.071123
C	-0.492989	2.321599	-1.155679
C	-1.368528	2.761724	-2.039042
H	-2.417132	2.541522	-1.901449
H	-1.048501	3.326140	-2.903863
F	0.839387	2.608200	-1.370239
H	-0.290197	2.069235	0.928826
H	-1.740794	1.370285	0.241326
C	-0.644242	-0.822132	-1.221499
F	-1.968331	-0.637728	-1.350991
F	-0.456455	-2.162573	-1.152774
F	-0.094920	-0.444116	-2.416330
C	-0.258490	-0.730251	1.426727
F	-0.027592	0.077236	2.497558
F	-1.532677	-1.143477	1.545559
F	0.518198	-1.825736	1.646243

3a–C_3H_5F

C	0.001250	0.001448	-0.000086
C	-0.002490	0.004785	1.493657
C	1.104872	-0.004298	2.223936
H	2.086059	0.013068	1.759909
H	1.071819	-0.034115	3.306148
H	-0.981180	-0.002579	1.965419
H	1.012996	0.117858	-0.394381
H	-0.439845	-0.917620	-0.395383
F	-0.770793	1.054979	-0.477583

3a–C_3H_5F + 1 ts

C	0.005842	0.014406	-0.008575
C	0.846234	0.934975	-0.669882
C	2.186659	0.627513	-0.915981
H	2.414651	-0.413908	-1.131836
H	2.771954	1.349888	-1.476390
H	0.520452	1.971551	-0.671100
H	0.670608	0.114017	1.054764
F	0.222950	-1.311066	-0.313278
H	-1.052784	0.222689	0.102919
B	2.823612	0.821734	0.795436
N	2.057190	-0.055393	1.736682
C	2.389969	-1.490943	1.707238
H	2.486818	-1.840754	0.682078
H	3.327724	-1.680679	2.239223
H	1.587808	-2.053769	2.188526
C	1.864284	0.378607	3.131312
H	1.159046	-0.299160	3.617487
H	2.813432	0.347742	3.675722
H	1.464186	1.387901	3.176976
C	4.384243	0.402202	0.586464
F	5.091989	1.315977	-0.105164
F	5.005452	0.263790	1.781554
F	4.570577	-0.773800	-0.060858
C	2.715020	2.408823	1.146994
F	1.433198	2.794262	1.436822
F	3.453258	2.774777	2.212436
F	3.091339	3.207586	0.127722

3a–C_3H_5F + 1 product

B	-0.002915	0.032239	0.010922
N	1.561536	0.195727	-0.399891
H	1.503942	0.826303	-1.205689
C	2.287366	-1.024427	-0.859738
H	1.802376	-1.421664	-1.746334
H	2.264729	-1.766757	-0.066268
H	3.318065	-0.752615	-1.091084
C	2.351316	0.886144	0.653752
H	2.492031	0.197274	1.485232
H	3.320534	1.179905	0.249973
H	1.806805	1.759858	1.005038
C	-0.687142	1.507838	0.105699
C	-0.212037	2.479067	-0.938061
C	-0.764417	2.654745	-2.129206
F	-1.856629	1.972600	-2.499351
H	-0.429597	3.347098	-2.890829
H	0.650816	3.108245	-0.733130
H	-1.767617	1.372780	0.008620
H	-0.518322	1.940078	1.095402
C	-0.691357	-0.846212	-1.175392
F	-2.026830	-0.759718	-1.207198
F	-0.402696	-2.172629	-1.133328
F	-0.252564	-0.428079	-2.404272
C	-0.120880	-0.741026	1.436562
F	0.207877	0.050047	2.495661
F	-1.371758	-1.170588	1.672904
F	0.686786	-1.830334	1.562065

Table S63. Optimized (M06-2X/6-311++G(d,p)) Cartesian coordinates of the propene, transition state and product for the ene reaction between propene **3e–C_3H_5F** and **1**

3e–C_3H_5F

C	0.001151	-0.002012	-0.000170
C	-0.002261	-0.005657	1.493572
C	1.105230	0.005014	2.223633
H	2.086355	-0.010735	1.759416
H	1.072344	0.034575	3.305858
H	-0.980866	0.000095	1.965534
H	1.012983	-0.116818	-0.394713
H	-0.441416	0.916473	-0.395178
F	-0.769408	-1.056606	-0.477710

3e–C_3H_5F + 1 ts

C	-0.002784	0.013107	-0.015275
C	0.851212	0.890431	-0.718874
C	2.202536	0.564923	-0.897282
H	2.429727	-0.486932	-1.065366
H	2.790667	1.242977	-1.508528
H	0.514071	1.916614	-0.849377
H	0.727082	-0.027820	0.995338
F	-1.261643	0.473360	0.243841
H	-0.022105	-1.036338	-0.315035
B	2.858733	0.786939	0.780483
N	2.107907	-0.109104	1.716514
C	2.443949	-1.537966	1.678602
H	2.516368	-1.889771	0.649301
H	3.399951	-1.735547	2.173578
H	1.660995	-2.105051	2.188030
C	1.869792	0.319834	3.104668
H	1.155313	-0.362783	3.570410
H	2.802368	0.299630	3.677611
H	1.457817	1.324812	3.136183
C	4.424829	0.390604	0.574588
F	5.125002	1.302863	-0.124348
F	5.049697	0.260017	1.768096
F	4.617196	-0.790622	-0.068559
C	2.711786	2.367980	1.128209
F	1.414471	2.721556	1.376443
F	3.411383	2.753851	2.213255
F	3.102343	3.169470	0.116077

3e–C_3H_5F + 1 product

B	-0.006065	0.020995	0.010151
N	1.553938	0.187049	-0.404602
H	1.495393	0.809147	-1.217235
C	2.281839	-1.037624	-0.848939
H	1.788569	-1.457321	-1.720621
H	2.275230	-1.762641	-0.039294
H	3.307346	-0.764458	-1.100263
C	2.342998	0.891818	0.640753
H	2.481658	0.214886	1.482304
H	3.312610	1.178930	0.233553
H	1.799127	1.771550	0.977495
C	-0.698281	1.491207	0.101306
C	-0.238548	2.464102	-0.953286
C	-0.797037	2.578787	-2.146696
F	-0.325716	3.447352	-3.061168
H	-1.652103	2.019348	-2.507933
H	0.608093	3.116726	-0.745811
H	-0.529216	1.932965	1.086779
H	-1.779514	1.347884	0.025287
C	-0.700205	-0.861088	-1.174078
F	-2.037102	-0.730648	-1.226683
F	-0.455670	-2.191320	-1.110654
F	-0.246394	-0.474339	-2.408814
C	-0.126515	-0.752786	1.434954
F	0.204480	0.037127	2.493146
F	-1.381871	-1.174015	1.668216
F	0.672590	-1.847315	1.562148

Table S64. Raw molecular energies (hartree) and resulting barrier heights and reaction energies (kJ mol^{-1}) for ene reactions between **1** and methyl–substituted propenes using various model chemistries.

	HF	HF	M062X	M11	MP2//M11	MPW1K/
	6-31++G(d,p)	6-31++G(d,p)	6-311++G(d,p)	6-311++G(d,p)	6-311++G(d,p)	6-311++G(d,p)
	ZPE					
$(F_3C)_2BNMe_2$	0.126179	-830.814074	-834.722503	-834.756104	-833.088392	-834.722557
1a,1e,2,3a,3e-C_3HMe_5	0.234740	-312.270418	-314.396029	-314.331634	-313.535127	-314.489042
BN + 1a,1e,2,3a,3e- TS	0.360266	-1142.977459	-1149.078995	-1149.054487	-1146.590704	-1149.157405
BN + 1a,1e,2,3a,3e-	0.368091	-1143.043639	-1149.127880	-1149.104658	-1146.638779	-1149.204166
Barrier	**2**	**279**	**102**	**86**	**85**	**141**
Reaction	**-19**	**125**	**-7**	**-27**	**-23**	**37**
1a,1e,2,3a-$C_3H_2Me_4$	0.204861	-273.235774	-275.092430	-275.035947	-274.337816	-275.175018
BN + 1a,1e,2,3a TS	0.330498	-1103.950188	-1109.777897	-1109.760035	-1107.393035	-1109.846535
BN + 1a,1e,2,3a	0.338368	-1104.007555	-1109.826858	-1109.810998	-1107.443860	-1109.892853
Barrier	**1**	**260**	**96**	**83**	**86**	**133**
Reaction	**-19**	**129**	**-14**	**-32**	**-29**	**30**
1a,1e,2,3e-$C_3H_2Me_4$	0.204861	-273.235774	-275.092430	-275.035947	-274.337816	-275.175018
BN + 1a,1e,2,3e TS	0.329330	-1103.960416	-1109.787963	-1109.771507	-1107.404898	-1109.857951
BN + 1a,1e,2,3e	0.337516	-1104.021508	-1109.832736	-1109.817242	-1107.449311	-1109.895591
Barrier	**4**	**231**	**67**	**50**	**52**	**100**
Reaction	**-17**	**90**	**-31**	**-50**	**-45**	**21**
1a,1e,3a,3e-$C_3H_2Me_4$	0.204875	-273.240986	-275.093755	-275.036133	-274.340208	-275.177393
BN + 1a,1e,3a,3e TS	0.329688	-1103.952686	-1109.777658	-1109.758298	-1107.396211	-1109.847785
BN + 1a,1e,3a,3e	0.337396	-1104.023023	-1109.828845	-1109.811344	-1107.446137	-1109.898564
Barrier	**4**	**265**	**98**	**86**	**82**	**134**
Reaction	**-17**	**99**	**-18**	**-35**	**-31**	**19**
1a,2,3a,3e-$C_3H_2Me_4$	0.205186	-273.236700	-275.092257	-275.035693	-274.338087	-275.174382
BN + 1a,2,3a,3e TS	0.329850	-1103.961168	-1109.784394	-1109.765714	-1107.400086	-1109.856874
BN + 1a,2,3a,3e	0.337124	-1104.036200	-1109.841668	-1109.825518	-1107.457873	-1109.907251
Barrier	**4**	**232**	**76**	**65**	**66**	**102**
Reaction	**-15**	**52**	**-57**	**-75**	**-69**	**-13**
1e,2,3a,3e-$C_3H_2Me_4$	0.204946	-273.237417	-275.092573	-275.035865	-274.338621	-275.175071
BN + 1e,2,3a,3e TS	0.329540	-1103.972443	-1109.797239	-1109.779867	-1107.414554	-1109.869386
BN + 1e,2,3a,3e	0.336565	-1104.031715	-1109.834772	-1109.817669	-1107.451277	-1109.907251
Barrier	**4**	**204**	**43**	**28**	**29**	**70**
Reaction	**-14**	**65**	**-39**	**-54**	**-51**	**-12**
1a,1e,2-$C_3H_3Me_3$	0.174177	-234.199096	-235.788809	-235.740484	-235.141128	-235.856819
BN + 1a,1e,2 TS	0.299603	-1064.926151	-1070.485079	-1070.476120	-1068.208345	-1070.534398
BN + 1a,1e,2	0.308088	-1064.986786	-1070.529392	-1070.521561	-1068.252858	-1070.570940
Barrier	**2**	**227**	**67**	**52**	**54**	**116**
Reaction	**-20**	**88**	**-29**	**-47**	**-43**	**41**
1a,1e,3a-$C_3H_3Me_3$	0.175110	-234.202843	-235.788414	-235.739637	-235.140660	-235.860788
BN + 1a,1e,3a TS	0.300287	-1064.915728	-1070.472770	-1070.461892	-1068.196481	-1070.531848
BN + 1a,1e,3a	0.307824	-1064.984033	-1070.521095	-1070.511973	-1068.244329	-1070.579459
Barrier	**3**	**263**	**98**	**86**	**83**	**133**
Reaction	**-17**	**102**	**-11**	**-27**	**-24**	**26**
1a,1e,3e-$C_3H_3Me_3$	0.175110	-234.202843	-235.788414	-235.739637	-235.140660	-235.860788
BN + 1a,1e,3e TS	0.299559	-1064.924854	-1070.479972	-1070.469640	-1068.203836	-1070.540058
BN + 1a,1e,3e	0.307309	-1064.996839	-1070.532563	-1070.523667	-1068.255986	-1070.581945
Barrier	**5**	**238**	**77**	**64**	**62**	**109**
Reaction	**-16**	**67**	**-42**	**-59**	**-56**	**18**
1a,2,3a-$C_3H_3Me_3$	0.175204	-234.201279	-235.788214	-235.739700	-235.140480	-235.859625
BN + 1a,2,3a TS	0.300158	-1064.929385	-1070.482073	-1070.471180	-1068.203934	-1070.544194
BN + 1a,2,3a	0.307599	-1065.003045	-1070.538337	-1070.529879	-1068.261131	-1070.591299
Barrier	**3**	**223**	**72**	**62**	**63**	**97**
Reaction	**-16**	**47**	**-58**	**-74**	**-70**	**-9**

Table S64. (continued)

	HF	HF	M062X	M11	MP2//M11	MPW1K/
	6-31++G(d,p)	6-31++G(d,p)	6-311++G(d,p)	6-311++G(d,p)	6-311++G(d,p)	6-311++G(d,p)
	ZPE					
1a,2,3e-$C_3H_3Me_3$	0.175204	-234.201279	-235.788214	-235.739700	-235.140480	-235.859625
BN + 1a,2,3e TS	0.299201	-1064.939249	-1070.488661	-1070.477762	-1068.210021	-1070.552682
BN + 1a,2,3e	0.307245	-1065.003547	-1070.536912	-1070.527733	-1068.259966	-1070.598653
Barrier	6	195	53	42	44	72
Reaction	-15	45	-55	-70	-67	-29
1a,3a,3e-$C_3H_3Me_3$	0.175322	-234.200451	-235.785608	-235.736425	-235.138860	-235.857229
BN + 1a,3a,3e TS	0.299761	-1064.927246	-1070.477818	-1070.465838	-1068.201739	-1070.540857
BN + 1a,3a,3e	0.306951	-1065.008829	-1070.538772	-1070.528877	-1068.262324	-1070.600988
Barrier	5	225	75	66	63	98
Reaction	-14	28	-67	-82	-79	-43
1e,2,3a-$C_3H_3Me_3$	0.175078	-234.201290	-235.788063	-235.739522	-235.140374	-235.859821
BN + 1e,2,3a TS	0.299910	-1064.939165	-1070.493501	-1070.483779	-1068.216308	-1070.555352
BN + 1e,2,3a	0.307620	-1064.997011	-1070.531592	-1070.522199	-1068.254748	-1070.591299
Barrier	4	197	42	28	29	68
Reaction	-17	64	-40	-54	-53	-8
1e,2,3e-$C_3H_3Me_3$	0.175078	-234.201290	-235.788063	-235.739522	-235.140374	-235.859821
BN + 1e,2,3e TS	0.299117	-1064.944995	-1070.496718	-1070.487138	-1068.218266	-1070.560078
BN + 1e,2,3e	0.307245	-1065.003547	-1070.534115	-1070.524318	-1068.258315	-1070.598653
Barrier	6	180	31	17	22	53
Reaction	-16	45	-47	-61	-63	-28
1e,3a,3e-$C_3H_3Me_3$	0.175032	-234.203242	-235.787594	-235.738140	-235.141021	-235.859346
BN + 1e,3a,3e TS	0.299367	-1064.935082	-1070.486436	-1070.475535	-1068.210720	-1070.549477
BN + 1e,3a,3e	0.306898	-1065.008147	-1070.534273	-1070.524356	-1068.257448	-1070.600988
Barrier	5	211	58	45	45	81
Reaction	-15	38	-50	-65	-60	-36
2,3a,3e-$C_3H_3Me_3$	0.174842	-234.197530	-235.785409	-235.736833	-235.138933	-235.851604
BN + 2,3a,3e TS	0.299420	-1064.944512	-1070.496389	-1070.485571	-1068.220064	-1070.550929
BN + 2,3a,3e	0.306109	-1065.008680	-1070.538755	-1070.529239	-1068.261622	-1070.593418
Barrier	4	172	26	15	15	57
Reaction	-13	20	-69	-83	-78	-38
1a,1e-$C_3H_4Me_2$	0.144586	-195.165133	-196.485352	-196.444992	-195.944608	-196.542484
BN + 1a,1e TS	0.269991	-1025.887118	-1031.176241	-1031.173856	-1029.006736	-1031.215409
BN + 1a,1e	0.277629	-1025.956213	-1031.225411	-1031.224872	-1029.055566	-1031.257016
Barrier	2	240	81	70	67	128
Reaction	-18	77	-30	-46	-43	38
1a,2-$C_3H_4Me_2$	0.144586	-195.165133	-196.485352	-196.444992	-195.944608	-196.542484
BN + 1a,2 TS	0.269497	-1025.903517	-1031.185686	-1031.182642	-1029.013918	-1031.228785
BN + 1a,2	0.277644	-1025.967079	-1031.232875	-1031.231655	-1029.062833	-1031.273109
Barrier	3	196	55	45	47	92
Reaction	-18	48	-49	-64	-62	-5
1a,3a-$C_3H_4Me_2$	0.145506	-195.162258	-196.480192	-196.439655	-195.939632	-196.540583
BN + 1a,3a TS	0.270383	-1025.889507	-1031.172414	-1031.168729	-1029.002264	-1031.224291
BN + 1a,3a	0.277459	-1025.968512	-1031.230383	-1031.228932	-1029.060036	-1031.280646
Barrier	3	225	76	68	64	99
Reaction	-15	34	-59	-73	-70	-32
1a,3e-$C_3H_4Me_2$	0.145506	-195.162258	-196.480192	-196.439655	-195.939632	-196.540583
BN + 1a,3e TS	0.269644	-1025.897605	-1031.178019	-1031.174370	-1029.007703	-1031.231474
BN + 1a,3e	0.277153	-1025.971347	-1031.231223	-1031.228818	-1029.061361	-1031.282086
Barrier	5	202	60	51	48	78
Reaction	-14	26	-62	-74	-74	-37
1e,2-$C_3H_4Me_2$	0.144586	-195.165133	-196.485352	-196.444992	-195.944608	-196.542484
BN + 1e,2 TS	0.269346	-1025.909572	-1031.193656	-1031.191790	-1029.022077	-1031.236294
BN + 1e,2	0.277644	-1025.967079	-1031.230239	-1031.228270	-1029.061368	-1031.273109
Barrier	4	179	34	21	25	72
Reaction	-18	48	-42	-55	-58	-5

Table S64. (continued)

	HF	HF	M062X	M11	MP2//M11	MPW1K/
	6-31++G(d,p)	6-31++G(d,p)	6-311++G(d,p)	6-311++G(d,p)	6-311++G(d,p)	6-311++G(d,p)
	ZPE					
1e,3a-$C_3H_4Me_2$	0.145236	-195.164908	-196.482098	-196.441310	-195.941838	-196.542618
BN + 1e,3a TS	0.270074	-1025.896837	-1031.180444	-1031.177698	-1029.010517	-1031.232311
BN + 1e,3a	0.277397	-1025.967607	-1031.226161	-1031.224540	-1029.055582	-1031.280646
Barrier	4	212	60	49	49	83
Reaction	-16	44	-42	-57	-52	-26
1e,3e-$C_3H_4Me_2$	0.145236	-195.164908	-196.482098	-196.441310	-195.941838	-196.542618
BN + 1e,3e TS	0.269239	-1025.902400	-1031.182967	-1031.179972	-1029.012557	-1031.236599
BN + 1e,3e	0.276998	-1025.969248	-1031.229450	-1031.227675	-1029.058120	-1031.282086
Barrier	6	196	52	41	41	70
Reaction	-15	39	-52	-66	-60	-31
2,3a-$C_3H_4Me_2$	0.145320	-195.163931	-196.483356	-196.442800	-195.943210	-196.539339
BN + 2,3a TS	0.269853	-1025.910467	-1031.192274	-1031.189268	-1029.021422	-1031.236731
BN + 2,3a	0.276970	-1025.975443	-1031.237703	-1031.235857	-1029.067028	-1031.278690
Barrier	4	173	32	21	23	62
Reaction	-14	20	-70	-84	-80	-31
2,3e-$C_3H_4Me_2$	0.145320	-195.163931	-196.483356	-196.442800	-195.943210	-196.539339
BN + 2,3e TS	0.269017	-1025.916378	-1031.195513	-1031.192632	-1029.023706	-1031.241577
BN + 2,3e	0.276615	-1025.974816	-1031.235341	-1031.232814	-1029.065219	-1031.278339
Barrier	7	156	21	10	15	47
Reaction	-13	21	-65	-77	-76	-31
3a,3e-$C_3H_4Me_2$	0.145239	-195.161892	-196.480297	-196.439164	-195.941298	-196.535898
BN + 3a,3e TS	0.269454	-1025.904998	-1031.185148	-1031.181593	-1029.015760	-1031.230030
BN + 3a,3e	0.276543	-1025.980781	-1031.238950	-1031.236579	-1029.068600	-1031.284334
Barrier	5	182	42	31	32	70
Reaction	-13	0	-83	-96	-90	-56
1a-C_3H_5Me	0.114934	-156.124557	-157.177249	-157.145319	-156.743575	-157.222822
BN + 1a TS	0.240072	-986.859319	-991.874208	-991.878624	-989.810934	-991.906744
BN + 1a	0.247455	-986.930386	-991.924029	-991.929963	-989.861170	-991.953212
Barrier	3	206	65	57	53	99
Reaction	-17	37	-48	-60	-61	-5
1e-C_3H_5Me	0.114757	-156.126994	-157.179006	-157.146819	-156.745751	-157.224649
BN + 1e TS	0.239661	-986.864263	-991.879144	-991.884217	-989.815606	-991.911833
BN + 1e	0.247274	-986.928711	-991.922430	-991.928974	-989.858097	-991.953212
Barrier	3	199	56	46	46	90
Reaction	-17	48	-40	-53	-48	0
2-C_3H_5Me	0.114741	-156.127674	-157.180771	-157.148467	-156.747731	-157.225497
BN + 2 TS	0.239292	-986.880398	-991.892116	-991.897055	-989.827226	-991.926617
BN + 2	0.246967	-986.938331	-991.931162	-991.936535	-989.867957	-991.964536
Barrier	4	157	25	16	19	52
Reaction	-16	24	-59	-69	-69	-29
3a-C_3H_5Me	0.115372	-156.123499	-157.174772	-157.142305	-156.742187	-157.219631
BN + 3a TS	0.240138	-986.866532	-991.879079	-991.883782	-989.815665	-991.913208
BN + 3a	0.247007	-986.940063	-991.930461	-991.936468	-989.866516	-991.964311
Barrier	4	183	44	35	36	73
Reaction	-14	7	-74	-87	-81	-45
3e-C_3H_5Me	0.115372	-156.123499	-157.174772	-157.142305	-156.742187	-157.219631
BN + 3e TS	0.239365	-986.871811	-991.881420	-991.885743	-989.817709	-991.917279
BN + 3e	0.246461	-986.941723	-991.929675	-991.935007	-989.866498	-991.965045
Barrier	6	167	36	28	29	60
Reaction	-13	1	-73	-84	-82	-48
C_3H_6	0.084795	-117.085599	-117.871746	-117.847870	-117.546263	-117.904752
BN + C_3H_6 TS	0.209766	-947.833373	-952.577387	-952.589934	-950.620715	-952.608951
BN + C_3H_6	0.216686	-947.900023	-952.626877	-952.640283	-950.671381	-952.649839
Barrier	3	171	41	34	34	45
Reaction	-15	13	-72	-82	-83	-45

Table S65. Energy differences between barriers and reactions for differing substitution patterns, and associated averages and standard deviations (M11/6-311++G(,dp), kJ mol^{-1}) for ene reactions between **1** and methyl-substituted propenes. The data are organized as (# – #'), where # and #' represent the substitution patterns involved. The individual calculation sets are denoted "Change by placing <substituent(s)> at position(s) #". Averaged data are denoted "Average Substitution Correction" in the manuscript text.

M11 values					
Change by Placing Me at Position 1a			**Change by Placing Me at Position 1e**		
Subst. Pattern	**Barrier**	**Reaction**	**Subst. Pattern**	**Barrier**	**Reaction**
1a–0	23	22	**1e–0**	12	28
1a,1e–1e	24	7	**1a,1e–1a**	12	14
1a,2–2	30	6	**1e,2–2**	5	15
1a,3a–3a	33	14	**1e,3a–3a**	14	30
1a,3e–3e	23	11	**1e,3e–3e**	13	18
1a,1e,2–1e,2	31	8	**1a,1e,2–1a,2**	7	17
1a,1e,3a–1e,3a	38	30	**1a,1e,3a–1a,3a**	19	46
1a,1e,3e–1e,3e	24	7	**1a,1e,3e–1a,3e**	13	15
1a,2,3a–2,3a	40	9	**1e,2,3a–2,3a**	7	29
1a,2,3e–2,3e	32	7	**1e,2,3e–2,3e**	7	16
1a,3a,3e–3a,3e	35	14	**1e,3a,3e–3a,3e**	14	31
1a,1e,2,3a–1e,2,3a	55	22	**1a,1e,2,3a–1a,2,3a**	21	42
1a,1e,2,3e–1e,2,3e	33	10	**1a,1e,2,3e–1a,2,3e**	8	19
1a,1e,3a,3e–1e,3a,3e	41	30	**1a,1e,3a,3e–1a,3a,3e**	20	47
1a,2,3a,3e–2,3a,3e	49	8	**1e,2,3a,3e–2,3a,3e**	12	29
1a,1e,2,3a,3e–1e,2,3a,3e	58	27	**1a,1e,2,3a,3e–1a,2,3a,3e**	21	48
Avg(StdDev)	**35.5 (10.9)**	**14.6 (8.8)**	**Avg(StdDev)**	**12.7 (5.3)**	**27.8 (12.4)**
Change by Placing Me at Position 2			**Change by Placing Me at Position 3a**		
Subst. Pattern	**Barrier**	**Reaction**	**Subst. Pattern**	**Barrier**	**Reaction**
2–0	-18	12	**3a-0**	1	-5
1a,2–1a	-12	-4	**1a,3a-1a**	10	-14
1e,2–1e	-25	-2	**1e,3a-1e**	2	-4
2,3a–3a	-14	3	**2,3a-2**	6	-14
2,3e–3e	-18	8	**3a,3e-3e**	3	-12
1a,1e,2–1a,1e	-18	-1	**1a,1e,3a-1a,1e**	17	19
1a,2,3a–1a,3a	-6	-1	**1a,2,3a-1a,2**	16	-11
1a,2,3e–1a,3e	-9	4	**1a,3a,3e-1a,3e**	15	-9
1e,2,3a–1e,3a	-21	2	**1e,2,3a-1e,2**	7	0
1e,2,3e–1e,3e	-23	5	**1e,3a,3e-1e,3e**	4	1
2,3a,3e–3a,3e	-16	13	**2,3a,3e-2,3e**	5	-6
1a,1e,2,3a–1a,1e,3a	-4	-5	**1a,1e,2,3a-1a,1e,2**	31	15
1a,1e,2,3e–1a,2,3e	8	19	**1a,1e,3a,3e-1a,1e,3e**	21	24
1a,2,3a,3e–1a,3a,3e	-1	8	**1a,2,3a,3e-1a,2,3e**	23	-5
1e,2,3a,3e–1e,3a,3e	-17	11	**1e,2,3a,3e-1e,2,3e**	11	7
1a,1e,2,3a,3e–1a,1e,3a,3e	0	8	**1a,1e,2,3a,3e-1a,1e,2,3e**	36	23
Avg(StdDev)	**-12.1 (9.2)**	**5.0 (6.8)**	**Avg(StdDev)**	**13.0 (10.4)**	**0.6 (13.1)**
Change by Placing Me at Position 3e					
Subst. Pattern	**Barrier**	**Reaction**			
3e–0	-6	-3			
1a,3e–1a	-6	-14			
1e,3e–1e	-5	-13			
2,3e–2	-5	-7			
3a,3e–3a	-4	-9			
1a,1e,3e–1a,1e	-5	-13			
1a,2,3e–1a,2	-3	-6			
1a,3a,3e–1a,3a	-2	-9			
1e,2,3e–1e,2	-4	-6			
1e,3a,3e–1e,3a	-4	-9			
2,3a,3e–2,3a	-6	1			
1a,1e,2,3e–1a,1e,2	-2	-4			
1a,1e,3a,3e–1a,1e,3a	-1	-8			
1a,2,3a,3e–1a,2,3a	3	0			
1e,2,3a,3e–1e,2,3a	0	0			
1a,1e,2,3a,3e–1a,1e,2,3a	3	5			
Avg(StdDev)	**-3.0 (3.0)**	**-5.9 (5.4)**			

Table S65 (continued)

M11 values					
Change by Placing Mes at Positions 1a,1e			Change by Placing Mes at Positions 1a,2		
Subst. Pattern	Barrier	Reaction	Subst. Pattern	Barrier	Reaction
1a,1e–0	36	36	1a,2–0	11	18
1a,1e,2–2	36	22	1a,1e,2–1e	6	6
1a,1e,3a–3a	51	60	1a,2,3a–3a	27	12
1a,1e,3e–3e	36	25	1a,2,3e–3e	14	15
1a,1e,2,3a–2,3a	61	52	1a,1e,2,3a–1e,3a	34	25
1a,1e,2,3e–2,3e	39	26	1a,1e,2,3e–1e,3e	9	15
1a,1e,3a,3e–3a,3e	55	61	1a,2,3a,3e–3a,3e	34	21
1a,1e,2,3a,3e–2,3a,3e	70	56	1a,1e,2,3a,3e–1e,3a,3e	41	38
Avg(StdDev)	48.2 (13.3)	42.3 (16.6)	Avg(StdDev)	22.0 (13.4)	18.9 (9.6)
Change by Placing Mes at Positions 1a,3a			Change by Placing Mes at Positions 1a,3e		
Subst. Pattern	Barrier	Reaction	Subst. Pattern	Barrier	Reaction
1a,3a–0	34	8	1a,3e–0	17	8
1a,1e,3a–1e	40	26	1a,1e,3e–1e	18	-6
1a,2,3a–2	46	-5	1a,2,3e–2	26	0
1a,3a,3e–3e	38	2	1a,3a,3e–3a	31	4
1a,1e,2,3a–1e,2	62	23	1a,1e,2,3e–1e,2	29	4
1a,1e,3a,3e–1e,3e	45	31	1a,1e,3a,3e–1e,3a	37	22
1a,2,3a,3e–2,3e	54	2	1a,2,3a,3e–2,3a	43	9
1a,1e,2,3a,3e–1e,2,3e	69	34	1a,1e,2,3a,3e–1e,2,3a	58	27
Avg(StdDev)	48.5 (12.1)	15.1 (15.0)	Avg(StdDev)	32.5 (13.5)	8.6 (11.0)
Change by Placing Mes at Positions 1e,2			Change by Placing Mes at Positions 1e,3a		
Subst. Pattern	Barrier	Reaction	Subst. Pattern	Barrier	Reaction
1e,2–0	-13	27	1e,3a–0	15	25
1a,1e,2–1a	-5	13	1a,1e,3a–1a	29	33
1e,2,3a–3a	-7	32	1e,2,3a–2	12	15
1e,2,3e–3e	-11	23	1e,3a,3e–3e	17	19
1a,1e,2,3a–1a,3a	15	41	1a,1e,2,3a–1a,2	37	32
1a,1e,2,3e–1a,3e	-1	23	1a,1e,3a,3e–1a,3e	35	39
1e,2,3a,3e–3a,3e	-3	42	1e,2,3a,3e–2,3e	17	22
1a,1e,2,3a,3e–1a,3a,3e	20	55	1a,1e,2,3a,3e–1a,2,3e	44	43
Avg(StdDev)	-0.8 (11.9)	32.0 (13.5)	Avg(StdDev)	25.7 (12.0)	28.3 (9.7)
Change by Placing Mes at Positions 1e,3e			Change by Placing Mes at Positions 2,3a		
Subst. Pattern	Barrier	Reaction	Subst. Pattern	Barrier	Reaction
1e,3e–0	7	16	2,3a–0	-13	-2
1a,1e,3e–1a	7	1	1a,2,3a–1a	4	-15
1e,2,3e–2	1	8	1e,2,3a–1e	-18	-1
1e,3a,3e–3a	10	21	2,3a,3e–3e	-13	1
1a,1e,2,3e–1a,2	4	13	1a,1e,2,3a–1a,1e	13	14
1a,1e,3a,3e–1a,3a	18	38	1a,2,3a,3e–1a,3e	14	-1
1e,2,3a,3e–2,3a	7	29	1e,2,3a,3e–1e,3e	-13	12
1a,1e,2,3a,3e–1a,2,3a	24	47	1a,1e,2,3a,3e–1a,1e,3e	21	32
Avg(StdDev)	9.7 (7.5)	21.8 (15.7)	Avg(StdDev)	-0.4 (15.3)	4.9 (14.0)
Change by Placing Mes at Positions 2,3e			Change by Placing Mes at Positions 3a,3e		
Subst. Pattern	Barrier	Reaction	Subst. Pattern	Barrier	Reaction
2,3e–0	-23	5	3a,3e–0	-3	-15
1a,2,3e–1a	-15	-10	1a,3a,3e–1a	9	-23
1e,2,3e–1e	-29	-8	1e,3a,3e–1e	-1	-12
2,3a,3e–3a	-20	4	2,3a,3e–2	0	-14
1a,1e,2,3e–1a,1e	-20	-5	1a,1e,3a,3e–1a,1e	16	11
1a,2,3a,3e–1a,3a	-3	-1	1a,2,3a,3e–1a,2	19	-11
1e,2,3a,3e–1e,3a	-21	2	1e,2,3a,3e–1e,2	7	0
1a,1e,2,3a,3e–1a,1e,3a	-1	0	1a,1e,2,3a,3e–1a,1e,2	34	20
Avg(StdDev)	-16.4 (9.8)	-1.7 (5.4)	Avg(StdDev)	10.0 (12.6)	-5.4 (14.5)

Table S65 (continued)

M11 values						
Change by Placing Mes at Positions 1a,1e,2			Change by Placing Mes at Positions 1a,1e,3a			
Subst. Pattern	Barrier	Reaction	Subst. Pattern		Barrier	Reaction
1a,1e,2–0	18	35	1a,1e,3a–0		53	55
1a,1e,2,3a–3a	48	55	1a,1e,2,3a–2		67	37
1a,1e,2,3e–3e	22	34	1a,1e,3a,3e–3e		58	49
1a,1e,2,3a,3e–2,3a,3e	70	56	1a,1e,2,3a,3e–2,3e		75	50
Avg(StdDev)	39.5 (24.4)	44.7 (12.2)	Avg(StdDev)		63.1 (10.0)	47.7 (7.4)
Change by Placing Mes at Positions 1a,1e,3e			Change by Placing Mes at Positions 1a,2,3a			
Subst. Pattern	Barrier	Reaction	Subst. Pattern		Barrier	Reaction
1a,1e,3e–0	30	23	1a,2,3a–0		28	7
1a,1e,2,3e–2	34	19	1a,1e,2,3a–1e		37	21
1a,1e,3a,3e–3a	51	52	1a,2,3a,3e–3e		37	10
1a,1e,2,3a,3e–2,3a	64	57	1a,1e,2,3a,3e–1e,3e		45	39
Avg(StdDev)	44.9 (15.7)	37.5 (19.5)	Avg(StdDev)		36.6 (7.1)	19.1 (14.5)
Change by Placing Mes at Positions 1a,2,3e			Change by Placing Mes at Positions 1a,3a,3e			
Subst. Pattern	Barrier	Reaction	Subst. Pattern		Barrier	Reaction
1a,2,3e–0	8	12	1a,3a,3e–0		32	-1
1a,1e,2,3e–1e	4	3	1a,1e,3a,3e–1e		40	18
1a,2,3a,3e–3a	30	12	1a,2,3a,3e–2		49	-5
1a,1e,2,3a,3e–1e,3a	37	30	1a,1e,2,3a,3e–1e,2		65	28
Avg(StdDev)	19.7 (16.3)	14.1 (11.3)	Avg(StdDev)		46.4 (14.1)	10.0 (15.6)
Change by Placing Mes at Positions 1e,2,3a			Change by Placing Mes at Positions 1e,2,3e			
Subst. Pattern	Barrier	Reaction	Subst. Pattern		Barrier	Reaction
1e,2,3a–0	-6	27	1e,2,3e–0		-17	21
1a,1e,2,3a–1a	25	28	1a,1e,2,3e–1a		-8	9
1e,2,3a,3e–3e	0	30	1e,2,3a,3e–3a		-7	32
1a,1e,2,3a,3e–1a,3e	34	46	1a,1e,2,3a,3e–1a,3a		18	46
Avg(StdDev)	13.4 (19.6)	32.8 (9.2)	Avg(StdDev)		-3.4 (14.9)	27.1 (15.8)
Change by Placing Mes at Positions 1e,3a,3e			Change by Placing Mes at Positions 2,3a,3e			
Subst. Pattern	Barrier	Reaction	Subst. Pattern		Barrier	Reaction
1e,3a,3e–0	11	16	2,3a,3e–0		-18	-1
1a,1e,3a,3e–1a	28	25	1a,2,3a,3e–1a		7	-15
1e,2,3a,3e–2	12	15	1e,2,3a,3e–1e		-18	-1
1a,1e,2,3a,3e–1a,2	40	37	1a,1e,2,3a,3e–1a,1e		16	19
Avg(StdDev)	22.9 (14.1)	23.1 (9.9)	Avg(StdDev)		-3.3 (17.7)	0.2 (13.9)
Change by Placing Mes at Positions 1a,1e,2,3a			Change by Placing Mes at Positions 1a,1e,2,3e			
Subst. Pattern	Barrier	Reaction	Subst. Pattern		Barrier	Reaction
1a,1e,2,3a–0	49	49	1a,1e,2,3e–0		16	31
1a,1e,2,3a,3e–3e	58	57	1a,1e,2,3a,3e–3a		51	60
Avg(StdDev)	53.3 (6.3)	53.3 (5.4)	Avg(StdDev)		33.3 (24.7)	45.3 (20.2)
Change by Placing Mes at Positions 1a,1e,3a,3e			Change by Placing Mes at Positions 1a,2,3a,3e			
Subst. Pattern	Barrier	Reaction	Subst. Pattern		Barrier	Reaction
1a,1e,3a,3e–0	52	47	1a,2,3a,3e–0		31	7
1a,1e,2,3a,3e–2	70	42	1a,1e,2,3a,3e–1e		40	26
Avg(StdDev)	60.9 (12.8)	44.5 (3.2)	Avg(StdDev)		35.3 (6.2)	16.4 (13.5)
Change by Placing Mes at Positions 1e,2,3a,3e						
Subst. Pattern	Barrier	Reaction				
1e,2,3a,3e–0	-6	27				
1a,1e,2,3a,3e–1a	28	33				
Avg(StdDev)	11.2 (24.3)	29.9 (3.8)				

Table S66. Raw molecular energies (hartree) and resulting barrier heights and reaction energies (kJ mol^{-1}) for ene reactions between **1** and trifluoromethyl–substituted propenes using various model chemistries.

	M062X		M062X	M11	MP2//M11	
	6-311++G(d,p)		6-311++G(d,p)	6-311++G(d,p)	6-311++G(d,p)	
	ZPE					
$(F_3C)_2BNMe_2$	0.118846		-834.722504	-834.756104	-833.088392	
1a,1e,2,3a,3e-$C_3H(CF_3)_5$	0.108442		-1803.083392	-1803.209310	-1799.786045	
BN + 1a,1e,2,3a,3e- TS	0.222974		-2637.741215	-2637.908377	-2632.815112	
BN + 1a,1e,2,3a,3e-	0.232023		-2637.779175	-2637.946155	-2632.849933	
Barrier	**11**		**159**	**139**	**145**	
Reaction	**-12**		**82**	**63**	**76**	
1a,1e,2,3a-$C_3H_2(CF_3)_4$	0.103365		-1466.048633	-1466.145183	-1463.343807	
BN + 1a,1e,2,3a TS	0.219664		-2300.702701	-2300.834816	-2296.371574	
BN + 1a,1e,2,3a	0.227542		-2300.771518	-2300.908814	-2296.435526	
Barrier	**7**		**173**	**168**	**153**	
Reaction	**-14**		**13**	**-6**	**5**	
1a,1e,2,3e-$C_3H_2(CF_3)_4$	0.103365		-1466.048633	-1466.145183	-1463.343807	
BN + 1a,1e,2,3e TS	0.219544		-2300.707958	-2300.840204	-2296.376424	
BN + 1a,1e,2,3e	0.227388		-2300.784691	-2300.922226	-2296.450055	
Barrier	**7**		**159**	**154**	**140**	
Reaction	**-14**		**-22**	**-42**	**-34**	
1a,1e,3a,3e-$C_3H_2(CF_3)_4$	0.103104		-1466.061102	-1466.156582	-1463.358759	
BN + 1a,1e,3a,3e TS	0.219534		-2300.728824	-2300.861602	-2296.396198	
BN + 1a,1e,3a,3e	0.227046		-2300.788343	-2300.924199	-2296.456127	
Barrier	**6**		**138**	**128**	**128**	
Reaction	**-13**		**1**	**-17**	**-11**	
1a,2,3a,3e-$C_3H_2(CF_3)_4$	0.103272		-1466.057532	-1466.153802	-1463.354123	
BN + 1a,2,3a,3e TS	0.219744		-2300.716874	-2300.849613	-2296.388187	
BN + 1a,2,3a,3e	0.227067		-2300.797395	-2300.933172	-2296.464821	
Barrier	**6**		**160**	**152**	**137**	
Reaction	**-13**		**-33**	**-48**	**-46**	
1e,2,3a,3e-$C_3H_2(CF_3)_4$	0.103222		-1466.052519	-1466.148324	-1463.349444	
BN + 1e,2,3a,3e TS	0.218940		-2300.727143	-2300.858731	-2296.400454	
BN + 1e,2,3a,3e	0.227659		-2300.793288	-2300.929811	-2296.456850	
Barrier	**8**		**118**	**112**	**90**	
Reaction	**-15**		**-34**	**-52**	**-36**	
1a,1e,2-$C_3H_3(CF_3)_3$	0.097239		-1129.005390	-1129.071614	-1126.894398	
BN + 1a,1e,2 TS	0.214065		-1963.671313	-1963.774598	-1959.933957	
BN + 1a,1e,2	0.222103		-1963.749074	-1963.857332	-1960.007110	
Barrier	**5**		**143**	**134**	**123**	
Reaction	**-16**		**-40**	**-62**	**-49**	
1a,1e,3a-$C_3H_3(CF_3)_3$	0.097821		-1129.020863	-1129.086959	-1126.910429	
BN + 1a,1e,3a TS	0.214721		-1963.685069	-1963.787907	-1959.946324	
BN + 1a,1e,3a	0.221763		-1963.748362	-1963.854969	-1960.008408	
Barrier	**5**		**148**	**140**	**133**	
Reaction	**-13**		**0**	**-18**	**-12**	
1a,1e,3e-$C_3H_3(CF_3)_3$	0.097821		-1129.020863	-1129.086959	-1126.910429	
BN + 1a,1e,3e TS	0.214098		-1963.699561	-1963.802489	-1959.961959	
BN + 1a,1e,3e	0.221524		-1963.761098	-1963.867832	-1960.021811	
Barrier	**7**		**108**	**100**	**90**	
Reaction	**-13**		**-34**	**-53**	**-48**	
1a,2,3a-$C_3H_3(CF_3)_3$	0.098084		-1129.021537	-1129.087720	-1126.911555	
BN + 1a,2,3a TS	0.214838		-1963.690285	-1963.792636	-1959.954864	
BN + 1a,2,3a	0.222276		-1963.770867	-1963.876685	-1960.031408	
Barrier	**5**		**136**	**129**	**113**	
Reaction	**-14**		**-57**	**-73**	**-69**	

Table S66 (continued).

	M062X		M062X	M11	MP2//M11	
	6-311++G(d,p)		6-311++G(d,p)	6-311++G(d,p)	6-311++G(d,p)	
	ZPE					
1a,2,3e-$C_3H_3(CF_3)_3$	0.098084		-1129.021537	-1129.087720	-1126.911555	
BN + 1a,2,3e TS	0.214355		-1963.697340	-1963.799766	-1959.961989	
BN + 1a,2,3e	0.221899		-1963.767655	-1963.873077	-1960.028701	
Barrier	7		116	109	93	
Reaction	-13		-49	-64	-63	
1a,3a,3e-$C_3H_3(CF_3)_3$	0.098017		-1129.018122	-1129.084122	-1126.908311	
BN + 1a,3a,3e TS	0.214453		-1963.695339	-1963.797947	-1959.957376	
BN + 1a,3a,3e	0.221903		-1963.768589	-1963.872840	-1960.031081	
Barrier	6		113	105	97	
Reaction	-13		-61	-73	-77	
1e,2,3a-$C_3H_3(CF_3)_3$	0.097997		-1129.017054	-1129.082868	-1126.907565	
BN + 1e,2,3a TS	0.214709		-1963.699383	-1963.801650	-1959.965809	
BN + 1e,2,3a	0.222583		-1963.767453	-1963.873608	-1960.026573	
Barrier	6		100	93	74	
Reaction	-15		-59	-76	-66	
1e,2,3e-$C_3H_3(CF_3)_3$	0.097997		-1129.017054	-1129.082868	-1126.907565	
BN + 1e,2,3e TS	0.214340		-1963.694568	-1963.796354	-1959.960042	
BN + 1e,2,3e	0.221846		-1963.766363	-1963.871253	-1960.028577	
Barrier	7		112	106	88	
Reaction	-13		-58	-72	-73	
1e,3a,3e-$C_3H_3(CF_3)_3$	0.097537		-1129.020904	-1129.086169	-1126.912050	
BN + 1e,3a,3e TS	0.214396		-1963.708746	-1963.811130	-1959.971175	
BN + 1e,3a,3e	0.222275		-1963.767693	-1963.873455	-1960.026069	
Barrier	5		86	77	72	
Reaction	-15		-49	-67	-52	
2,3a,3e-$C_3H_3(CF_3)_3$	0.097685		-1129.014387	-1129.080880	-1126.904999	
BN + 2,3a,3e TS	0.213691		-1963.698392	-1963.800562	-1959.965944	
BN + 2,3a,3e	0.221534		-1963.756621	-1963.861080	-1960.017186	
Barrier	7		94	88	65	
Reaction	-13		-39	-51	-50	
1a,1e-$C_3H_4(CF_3)_2$	0.091809		-791.971248	-792.007777	-790.454612	
BN + 1a,1e TS	0.209119		-1626.648874	-1626.722482	-1623.503415	
BN + 1a,1e	0.216080		-1626.707988	-1626.784977	-1623.562412	
Barrier	4		114	105	100	
Reaction	-14		-24	-42	-37	
1a,2-$C_3H_4(CF_3)_2$	0.091751		-791.975884	-792.012416	-790.459812	
BN + 1a,2 TS	0.209227		-1626.656748	-1626.729187	-1623.513299	
BN + 1a,2	0.216675		-1626.727100	-1626.803232	-1623.581257	
Barrier	4		106	100	88	
Reaction	-16		-60	-76	-71	
1a,3a-$C_3H_4(CF_3)_2$	0.092530		-791.976494	-792.012911	-790.460062	
BN + 1a,3a TS	0.210053		-1626.653273	-1626.725651	-1623.507784	
BN + 1a,3a	0.216559		-1626.722838	-1626.797496	-1623.578755	
Barrier	3		117	110	103	
Reaction	-14		-49	-62	-66	
1a,3e-$C_3H_4(CF_3)_2$	0.092530		-791.976494	-792.012911	-790.460062	
BN + 1a,3e TS	0.209296		-1626.666709	-1626.739593	-1623.521689	
BN + 1a,3e	0.216204		-1626.725851	-1626.800318	-1623.580444	
Barrier	5		79	72	65	
Reaction	-13		-58	-70	-72	
1e,2-$C_3H_4(CF_3)_2$	0.091847		-791.969288	-792.005304	-790.453637	
BN + 1e,2 TS	0.209181		-1626.653567	-1626.726026	-1623.510378	
BN + 1e,2	0.216432		-1626.726875	-1626.802494	-1623.581740	
Barrier	4		97	89	79	
Reaction	-15		-77	-93	-90	

Table S66 (continued).

	M062X		M062X	M11	MP2//M11	
	6-311++G(d,p)		6-311++G(d,p)	6-311++G(d,p)	6-311++G(d,p)	
	ZPE					
1e,3a-$C_3H_4(CF_3)_2$	0.092426		-791.979120	-792.014854	-790.463708	
BN + 1e,3a TS	0.209573		-1626.665913	-1626.738611	-1623.521369	
BN + 1e,3a	0.216923		-1626.722641	-1626.798646	-1623.574426	
Barrier	4		89	81	76	
Reaction	-15		-41	-58	-44	
1e,3e-$C_3H_4(CF_3)_2$	0.092426		-791.979120	-792.014854	-790.463708	
BN + 1e,3e TS	0.208936		-1626.664635	-1626.736116	-1623.520816	
BN + 1e,3e	0.216310		-1626.727988	-1626.803154	-1623.581213	
Barrier	6		91	86	76	
Reaction	-13		-56	-72	-64	
2,3a-$C_3H_4(CF_3)_2$	0.092438		-791.978121	-792.014753	-790.462355	
BN + 2,3a TS	0.209415		-1626.668510	-1626.740463	-1623.528075	
BN + 2,3a	0.216658		-1626.727000	-1626.801107	-1623.582121	
Barrier	5		80	75	55	
Reaction	-14		-56	-66	-69	
2,3e-$C_3H_4(CF_3)_2$	0.092438		-791.978121	-792.014753	-790.462355	
BN + 2,3e TS	0.208827		-1626.663638	-1626.734992	-1623.523652	
BN + 2,3e	0.216114		-1626.725679	-1626.800324	-1623.580829	
Barrier	6		91	88	65	
Reaction	-13		-53	-65	-67	
3a,3e-$C_3H_4(CF_3)_2$	0.091889		-791.971246	-792.007037	-790.457003	
BN + 3a,3e TS	0.208945		-1626.669325	-1626.742080	-1623.527570	
BN + 3a,3e	0.216144		-1626.728112	-1626.802091	-1623.582228	
Barrier	5		60	51	42	
Reaction	-14		-76	-88	-83	
1a-$C_3H_5(CF_3)$	0.086309		-454.924352	-454.930994	-454.002631	
BN + 1a TS	0.204298		-1289.616354	-1289.659175	-1287.063611	
BN + 1a	0.210621		-1289.674570	-1289.719264	-1287.124505	
Barrier	2		78	71	70	
Reaction	-14		-59	-71	-74	
1e-$C_3H_5(CF_3)$	0.086196		-454.927479	-454.933695	-454.006398	
BN + 1e TS	0.203738		-1289.618138	-1289.660490	-1287.065309	
BN + 1e	0.211033		-1289.673003	-1289.718427	-1287.120578	
Barrier	3		80	74	74	
Reaction	-16		-45	-60	-52	
2-$C_3H_5(CF_3)$	0.086251		-454.928203	-454.934720	-454.007154	
BN + 2 TS	0.203777		-1289.621678	-1289.663821	-1287.072788	
BN + 2	0.210578		-1289.683130	-1289.727840	-1287.131433	
Barrier	3		73	68	56	
Reaction	-14		-71	-83	-80	
3a-$C_3H_5(CF_3)$	0.086639		-454.927036	-454.933055	-454.006598	
BN + 3a TS	0.204274		-1289.626591	-1289.669415	-1287.077064	
BN + 3a	0.210822		-1289.680498	-1289.724837	-1287.128436	
Barrier	3		57	49	44	
Reaction	-14		-68	-80	-74	
3e-$C_3H_5(CF_3)$	0.086639		-454.927036	-454.933055	-454.006598	
BN + 3e TS	0.203567		-1289.628444	-1289.670637	-1287.078662	
BN + 3e	0.210424		-1289.678769	-1289.721992	-1287.127265	
Barrier	5		51	44	38	
Reaction	-13		-64	-74	-72	
C_3H_6	0.080137		-117.871746	-117.847870	-117.546263	
BN + C_3H_6 TS	0.198239		-952.577387	-952.589934	-950.620715	
BN + C_3H_6	0.204545		-952.626877	-952.640283	-950.671381	
Barrier	2		42	35	35	
Reaction	-15		-72	-82	-83	

Table S67. Energy differences between barriers and reactions for differing substitution patterns, and associated averages and standard deviations (M11/6-311++G(,dp), kJ mol^{-1}) for ene reactions between **1** and trifluoromethyl-substituted propenes. The data are organized as (# – #'), where # and #' represent the substitution patterns involved. The individual calculation sets are denoted "Change by placing <substituent(s)> at position(s) #". Averaged data are denoted "Average Substitution Correction" in the manuscript text.

M11 values						
Change by Placing CF_3 at Position 1a			Change by Placing CF_3 at Position 1e			
Subst. Pattern	Barrier	Reaction	Subst. Pattern		Barrier	Reaction
1a–0	36	11	1e–0		39	22
1a,1e–1e	31	18	1a,1e–1a		34	29
1a,2–2	32	8	1e,2–2		22	-10
1a,3a–3a	62	19	1e,3a–3a		32	22
1a,3e–3e	28	4	1e,3e–3e		42	2
1a,1e,2–1e,2	45	31	1a,1e,2–1a,2		35	13
1a,1e,3a–1e,3a	59	40	1a,1e,3a–1a,3a		29	43
1a,1e,3e–1e,3e	14	19	1a,1e,3e–1a,3e		28	17
1a,2,3a–2,3a	54	-7	1e,2,3a–2,3a		18	-11
1a,2,3e–2,3e	21	1	1e,2,3e–2,3e		18	-7
1a,3a,3e–3a,3e	54	16	1e,3a,3e–3a,3e		26	22
1a,1e,2,3a–1e,2,3a	75	70	1a,1e,2,3a–1a,2,3a		39	66
1a,1e,2,3e–1e,2,3e	48	30	1a,1e,2,3e–1a,2,3e		44	22
1a,1e,3a,3e–1e,3a,3e	51	50	1a,1e,3a,3e–1a,3a,3e		23	56
1a,2,3a,3e–2,3a,3e	64	2	1e,2,3a,3e–2,3a,3e		24	-2
1a,1e,2,3a,3e–1e,2,3a,3e	27	115	1a,1e,2,3a,3e–1a,2,3a,3e		-13	111
Avg(StdDev)	43.9 (17.3)	26.6 (30.8)	Avg(StdDev)		27.3 (13.7)	24.8 (32.1)
Change by Placing CF_3 at Position 2			Change by Placing CF_3 at Position 3a			
Subst. Pattern	Barrier	Reaction	Subst. Pattern		Barrier	Reaction
2–0	32	-1	3a-0		14	2
1a,2–1a	29	-5	1a,3a-1a		39	9
1e,2–1e	15	-33	1e,3a-1e		7	2
2,3a–3a	26	14	2,3a-2		8	17
2,3e–3e	44	9	3a,3e-3e		7	-15
1a,1e,2–1a,1e	30	-21	1a,1e,3a-1a,1e		35	23
1a,2,3a–1a,3a	19	-11	1a,2,3a-1a,2		29	3
1a,2,3e–1a,3e	37	6	1a,3a,3e-1a,3e		33	-3
1e,2,3a–1e,3a	12	-18	1e,2,3a-1e,2		4	17
1e,2,3e–1e,3e	20	0	1e,3a,3e-1e,3e		-9	5
2,3a,3e–3a,3e	38	38	2,3a,3e-2,3e		0	15
1a,1e,2,3a–1a,1e,3a	28	12	1a,1e,2,3a-1a,1e,2		34	56
1a,1e,2,3e–1a,2,3e	44	22	1a,1e,3a,3e-1a,1e,3e		28	35
1a,2,3a,3e–1a,3a,3e	47	24	1a,2,3a,3e-1a,2,3e		43	16
1e,2,3a,3e–1e,3a,3e	35	14	1e,2,3a,3e-1e,2,3e		6	20
1a,1e,2,3a,3e–1a,1e,3a,3e	11	80	1a,1e,2,3a,3e-1a,1e,2,3e		-15	104
Avg(StdDev)	29.3 (11.6)	8.1 (26.5)	Avg(StdDev)		16.5 (18.0)	19.1 (28.0)
Change by Placing CF_3 at Position 3e						
Subst. Pattern	Barrier	Reaction				
3e–0	9	8				
1a,3e–1a	1	1				
1e,3e–1e	12	-12				
2,3e–2	20	18				
3a,3e–3a	2	-8				
1a,1e,3e–1a,1e	-5	-11				
1a,2,3e–1a,2	9	12				
1a,3a,3e–1a,3a	-6	-11				
1e,2,3e–1e,2	16	21				
1e,3a,3e–1e,3a	-4	-9				
2,3a,3e–2,3a	13	15				
1a,1e,2,3e–1a,1e,2	19	21				
1a,1e,3a,3e–1a,1e,3a	-12	1				
1a,2,3a,3e–1a,2,3a	23	24				
1e,2,3a,3e–1e,2,3a	19	24				
1a,1e,2,3a,3e–1a,1e,2,3a	-29	69				
Avg(StdDev)	5.6 (14.2)	10.2 (20.7)				

Table S67 (continued).

M11 values					
Change by Placing CF_3 at Positions 1a,1e			Change by Placing CF_3 at Positions 1a,2		
Subst. Pattern	Barrier	Reaction	Subst. Pattern	Barrier	Reaction
1a,1e–0	70	40	1a,2–0	65	6
1a,1e,2–2	67	21	1a,1e,2–1e	61	-3
1a,1e,3a–3a	91	62	1a,2,3a–3a	80	7
1a,1e,3e–3e	56	21	1a,2,3e–3e	65	9
1a,1e,2,3a–2,3a	93	60	1a,1e,2,3a–1e,3a	87	52
1a,1e,2,3e–2,3e	66	23	1a,1e,2,3e–1e,3e	68	30
1a,1e,3a,3e–3a,3e	77	71	1a,2,3a,3e–3a,3e	102	40
1a,1e,2,3a,3e–2,3a,3e	50	113	1a,1e,2,3a,3e–1e,3a,3e	62	129
Avg(StdDev)	71.3 (15.2)	51.4 (32.0)	Avg(StdDev)	73.8 (14.6)	34.0 (42.9)
Change by Placing CF_3 at Positions 1a,3a			Change by Placing CF_3 at Positions 1a,3e		
Subst. Pattern	Barrier	Reaction	Subst. Pattern	Barrier	Reaction
1a,3a–0	75	20	1a,3e–0	37	12
1a,1e,3a–1e	66	42	1a,1e,3e–1e	26	7
1a,2,3a–2	62	11	1a,2,3e–2	42	19
1a,3a,3e–3e	61	1	1a,3a,3e–3a	56	7
1a,1e,2,3a–1e,2	79	87	1a,1e,2,3e–1e,2	65	51
1a,1e,3a,3e–1e,3e	42	54	1a,1e,3a,3e–1e,3a	47	41
1a,2,3a,3e–2,3e	64	17	1a,2,3a,3e–2,3a	77	17
1a,1e,2,3a,3e–1e,2,3e	33	135	1a,1e,2,3a,3e–1e,2,3a	46	139
Avg(StdDev)	60.4 (15.5)	45.8 (45.4)	Avg(StdDev)	49.5 (16.1)	36.8 (44.3)
Change by Placing CF_3 at Positions 1e,2			Change by Placing CF_3 at Positions 1e,3a		
Subst. Pattern	Barrier	Reaction	Subst. Pattern	Barrier	Reaction
1e,2–0	54	-11	1e,3a–0	46	24
1a,1e,2–1a	63	8	1a,1e,3a–1a	69	52
1e,2,3a–3a	44	4	1e,2,3a–2	25	7
1e,2,3e–3e	62	2	1e,3a,3e–3e	33	7
1a,1e,2,3a–1a,3a	58	55	1a,1e,2,3a–1a,2	68	69
1a,1e,2,3e–1a,3e	82	28	1a,1e,3a,3e–1a,3e	56	53
1e,2,3a,3e–3a,3e	61	36	1e,2,3a,3e–2,3e	24	13
1a,1e,2,3a,3e–1a,3a,3e	34	135	1a,1e,2,3a,3e–1a,2,3e	30	127
Avg(StdDev)	57.1 (14.2)	32.1 (47.0)	Avg(StdDev)	43.8 (18.6)	43.9 (41.1)
Change by Placing CF_3 at Positions 1e,3e			Change by Placing CF_3 at Positions 2,3a		
Subst. Pattern	Barrier	Reaction	Subst. Pattern	Barrier	Reaction
1e,3e–0	50	10	2,3a–0	40	16
1a,1e,3e–1a	29	18	1a,2,3a–1a	58	-2
1e,2,3e–2	38	11	1e,2,3a–1e	19	-16
1e,3a,3e–3a	28	13	2,3a,3e–3e	45	23
1a,1e,2,3e–1a,2	54	34	1a,1e,2,3a–1a,1e	63	35
1a,1e,3a,3e–1a,3a	17	44	1a,2,3a,3e–1a,3e	80	21
1e,2,3a,3e–2,3a	37	13	1e,2,3a,3e–1e,3e	26	19
1a,1e,2,3a,3e–1a,2,3a	10	135	1a,1e,2,3a,3e–1a,1e,3e	39	115
Avg(StdDev)	32.9 (15.1)	34.9 (42.4)	Avg(StdDev)	46.3 (20.1)	26.5 (39.3)
Change by Placing CF_3 at Positions 2,3e			Change by Placing CF_3 at Positions 3a,3e		
Subst. Pattern	Barrier	Reaction	Subst. Pattern	Barrier	Reaction
2,3e–0	53	17	3a,3e–0	16	-7
1a,2,3e–1a	38	6	1a,3a,3e–1a	34	-2
1e,2,3e–1e	32	-12	1e,3a,3e–1e	3	-7
2,3a,3e–3a	40	30	2,3a,3e–2	21	33
1a,1e,2,3e–1a,1e	49	0	1a,1e,3a,3e–1a,1e	23	24
1a,2,3a,3e–1a,3a	42	13	1a,2,3a,3e–1a,2	52	27
1e,2,3a,3e–1e,3a	31	6	1e,2,3a,3e–1e,2	23	41
1a,1e,2,3a,3e–1a,1e,3a	-1	81	1a,1e,2,3a,3e–1a,1e,2	4	125
Avg(StdDev)	35.4 (16.5)	17.5 (28.4)	Avg(StdDev)	22.1 (15.9)	29.3 (43.0)

Table S67 (continued).

M11 values					
Change by Placing CF_3 at Positions 1a,1e,2			Change by Placing CF_3 at Positions 1a,1e,3a		
Subst. Pattern	Barrier	Reaction	Subst. Pattern	Barrier	Reaction
1a,1e,2–0	99	19	1a,1e,3a–0	105	64
1a,1e,2,3a–3a	119	74	1a,1e,2,3a–2	100	77
1a,1e,2,3e–3e	110	32	1a,1e,3a,3e–3e	84	56
1a,1e,2,3a,3e–2,3a,3e	50	113	1a,1e,2,3a,3e–2,3e	51	128
Avg(StdDev)	94.7 (30.7)	59.6 (42.6)	Avg(StdDev)	85.1 (24.5)	81.2 (32.2)
Change by Placing CF_3 at Positions 1a,1e,3e			Change by Placing CF_3 at Positions 1a,2,3a		
Subst. Pattern	Barrier	Reaction	Subst. Pattern	Barrier	Reaction
1a,1e,3e–0	65	29	1a,2,3a–0	94	9
1a,1e,2,3e–2	86	41	1a,1e,2,3a–1e	94	54
1a,1e,3a,3e–3a	79	63	1a,2,3a,3e–3e	109	25
1a,1e,2,3a,3e–2,3a	64	128	1a,1e,2,3a,3e–1e,3e	53	134
Avg(StdDev)	73.5 (10.9)	65.5 (44.2)	Avg(StdDev)	87.5 (23.8)	55.6 (55.6)
Change by Placing CF_3 at Positions 1a,2,3e			Change by Placing CF_3 at Positions 1a,3a,3e		
Subst. Pattern	Barrier	Reaction	Subst. Pattern	Barrier	Reaction
1a,2,3e–0	74	18	1a,3a,3e–0	70	9
1a,1e,2,3e–1e	80	18	1a,1e,3a,3e–1e	54	43
1a,2,3a,3e–3a	104	32	1a,2,3a,3e–2	85	35
1a,1e,2,3a,3e–1e,3a	58	121	1a,1e,2,3a,3e–1e,2	50	156
Avg(StdDev)	78.9 (18.8)	47.1 (49.6)	Avg(StdDev)	64.6 (15.9)	60.6 (65.1)
Change by Placing CF_3 at Positions 1e,2,3a			Change by Placing CF_3 at Positions 1e,2,3e		
Subst. Pattern	Barrier	Reaction	Subst. Pattern	Barrier	Reaction
1e,2,3a–0	57	6	1e,2,3e–0	70	10
1a,1e,2,3a–1a	97	64	1a,1e,2,3e–1a	82	29
1e,2,3a,3e–3e	68	21	1e,2,3a,3e–3a	63	28
1a,1e,2,3a,3e–1a,3e	67	133	1a,1e,2,3a,3e–1a,3a	28	124
Avg(StdDev)	72.4 (17.0)	55.9 (56.8)	Avg(StdDev)	61.1 (23.3)	47.6 (51.8)
Change by Placing CF_3 at Positions 1e,3a,3e			Change by Placing CF_3 at Positions 2,3a,3e		
Subst. Pattern	Barrier	Reaction	Subst. Pattern	Barrier	Reaction
1e,3a,3e–0	42	15	2,3a,3e–0	53	31
1a,1e,3a,3e–1a	57	53	1a,2,3a,3e–1a	81	22
1e,2,3a,3e–2	44	31	1e,2,3a,3e–1e	38	8
1a,1e,2,3a,3e–1a,2	39	138	1a,1e,2,3a,3e–1a,1e	34	104
Avg(StdDev)	45.5 (7.9)	59.4 (54.9)	Avg(StdDev)	51.7 (21.3)	41.3 (43.1)
Change by Placing CF_3 at Positions 1a,1e,2,3a			Change by Placing CF_3 at Positions 1a,1e,2,3e		
Subst. Pattern	Barrier	Reaction	Subst. Pattern	Barrier	Reaction
1a,1e,2,3a–0	133	76	1a,1e,2,3e–0	119	40
1a,1e,2,3a,3e–3e	95	136	1a,1e,2,3a,3e–3a	90	143
Avg(StdDev)	114.0 (26.8)	106.0 (42.8)	Avg(StdDev)	104.3 (20.2)	91.4 (72.5)
Change by Placing CF_3 at Positions 1a,1e,3a,3e			Change by Placing CF_3 at Positions 1a,2,3a,3e		
Subst. Pattern	Barrier	Reaction	Subst. Pattern	Barrier	Reaction
1a,1e,3a,3e–0	93	65	1a,2,3a,3e–0	117	33
1a,1e,2,3a,3e–2	71	146	1a,1e,2,3a,3e–1e	65	123
Avg(StdDev)	82.1 (15.3)	105.2 (57.4)	Avg(StdDev)	91.2 (36.8)	78.0 (63.0)
Change by Placing CF3 at Positions 1e,2,3a,3e					
Subst. Pattern	Barrier	Reaction			
1e,2,3a,3e–0	77	29			
1a,1e,2,3a,3e–1a	68	133			
Avg(StdDev)	72.3 (6.6)	81.3 (73.3)			

Table S68. Raw molecular energies (hartree) and resulting barrier heights and reaction energies (kJ mol^{-1}) for ene reactions between **1** and fluoro–substituted propenes using various model chemistries.

	WB97XD	WB97XD	M062X	M11	MP2/M11	
	6-311++G(d,p)	6-311++G(d,p)	6-311++G(d,p)	6-311++G(d,p)	6-311++G(d,p)	
	ZPE					
$(F_3C)_2BNF_2$	0.117841	-834.768239	-834.722406	-834.755843	-833.088639	
1a,1e,2,3a,3e-C_3HF_5	0.043098	-614.090318	-614.064780	-614.105784	-612.924862	
BN + 1a,1e,2,3a,3e- TS	0.158042	-1448.797259	-1448.729068	-1448.805695	-1445.959122	
BN + 1a,1e,2,3a,3e-	0.165427	-1448.881296	-1448.816389	-1448.896390	-1446.045117	
Barrier	**8**	**154**	**146**	**140**	**136**	
Reaction	**-12**	**-49**	**-66**	**-80**	**-72**	
1a,1e,2,3a-$C_3H_2F_4$	0.050743	-514.846125	-514.819907	-514.848641	-513.841620	
BN + 1a,1e,2,3a TS	0.166346	-1349.561682	-1349.494577	-1349.558708	-1346.885589	
BN + 1a,1e,2,3a	0.172489	-1349.640928	-1349.576364	-1349.644094	-1346.967232	
Barrier	**6**	**133**	**120**	**115**	**112**	
Reaction	**-10**	**-60**	**-80**	**-95**	**-88**	
1a,1e,2,3e-$C_3H_2F_4$	0.050639	-514.846128	-514.819909	-514.848641	-513.841620	
BN + 1a,1e,2,3e TS	0.166529	-1349.568336	-1349.500295	-1349.564551	-1346.889528	
BN + 1a,1e,2,3e	0.172542	-1349.647202	-1349.582206	-1349.649974	-1346.973254	
Barrier	**5**	**116**	**106**	**100**	**102**	
Reaction	**-11**	**-76**	**-95**	**-110**	**-103**	
1a,1e,3a,3e-$C_3H_2F_4$	0.050940	-514.868953	-514.843585	-514.871887	-513.866725	
BN + 1a,1e,3a,3e TS	0.166367	-1349.568909	-1349.500777	-1349.564758	-1346.894338	
BN + 1a,1e,3a,3e	0.173091	-1349.650909	-1349.585469	-1349.651697	-1346.977571	
Barrier	**6**	**173**	**165**	**160**	**154**	
Reaction	**-11**	**-26**	**-41**	**-53**	**-48**	
1a,2,3a,3e-$C_3H_2F_4$	0.050686	-514.851525	-514.826319	-514.855253	-513.848748	
BN + 1a,2,3a,3e TS	0.166256	-1349.568019	-1349.499118	-1349.563274	-1346.891720	
BN + 1a,2,3a,3e	0.173657	-1349.645017	-1349.576964	-1349.643887	-1346.968218	
Barrier	**6**	**130**	**125**	**120**	**114**	
Reaction	**-13**	**-54**	**-62**	**-74**	**-69**	
1e,2,3a,3e-$C_3H_2F_4$	0.050910	-514.852864	-514.827233	-514.855520	-513.850384	
BN + 1e,2,3a,3e TS	0.166403	-1349.571426	-1349.506027	-1349.566304	-1346.894757	
BN + 1e,2,3a,3e	0.172909	-1349.633099	-1349.566081	-1349.632639	-1346.956665	
Barrier	**6**	**125**	**109**	**113**	**111**	
Reaction	**-11**	**-21**	**-33**	**-46**	**-36**	
1a,1e,2-$C_3H_3F_3$	0.057484	-415.615062	-415.589028	-415.604999	-414.772754	
BN + 1a,1e,2 TS	0.173961	-1250.345553	-1250.278254	-1250.329972	-1247.830002	
BN + 1a,1e,2	0.179918	-1250.416219	-1250.351864	-1250.406727	-1247.905849	
Barrier	**4**	**96**	**84**	**78**	**79**	
Reaction	**-12**	**-75**	**-95**	**-109**	**-106**	
1a,1e,3a-$C_3H_3F_3$	0.058748	-415.619205	-415.593435	-415.609266	-414.778437	
BN + 1a,1e,3a TS	0.174389	-1250.331162	-1250.264132	-1250.315747	-1247.819013	
BN + 1a,1e,3a	0.180269	-1250.404665	-1250.340190	-1250.394424	-1247.893809	
Barrier	**6**	**142**	**130**	**124**	**121**	
Reaction	**-10**	**-36**	**-55**	**-68**	**-61**	
1a,1e,3e-$C_3H_3F_3$	0.058680	-415.619196	-415.593435	-415.609266	-414.778437	
BN + 1a,1e,3e TS	0.173946	-1250.336159	-1250.268076	-1250.319630	-1247.821692	
BN + 1a,1e,3e	0.180772	-1250.410220	-1250.345099	-1250.399777	-1247.898728	
Barrier	**7**	**128**	**119**	**113**	**113**	
Reaction	**-11**	**-50**	**-67**	**-81**	**-73**	
1a,2,3a-$C_3H_3F_3$	0.058367	-415.606670	-415.580722	-415.597203	-414.764993	
BN + 1a,2,3a TS	0.174349	-1250.330896	-1250.263174	-1250.314680	-1247.816860	
BN + 1a,2,3a	0.181194	-1250.404738	-1250.337118	-1250.391866	-1247.890594	
Barrier	**5**	**111**	**100**	**96**	**92**	
Reaction	**-13**	**-66**	**-77**	**-90**	**-85**	

Table S68 (continued).

	WB97XD	WB97XD	M062X	M11	MP2/M11	
	6-311++G(d,p)	6-311++G(d,p)	6-311++G(d,p)	6-311++G(d,p)	6-311++G(d,p)	
	ZPE					
1a,2,3e-$C_3H_3F_3$	0.058240	-415.606663	-415.580722	-415.597203	-414.764993	
BN + 1a,2,3e TS	0.174677	-1250.338764	-1250.269553	-1250.321116	-1247.822590	
BN + 1a,2,3e	0.181264	-1250.407044	-1250.338967	-1250.393271	-1247.893067	
Barrier	4	91	85	80	78	
Reaction	-14	-72	-82	-93	-91	
1a,3a,3e-$C_3H_3F_3$	0.058637	-415.624510	-415.599052	-415.615228	-414.784986	
BN + 1a,3a,3e TS	0.174849	-1250.339050	-1250.269920	-1250.321335	-1247.825505	
BN + 1a,3a,3e	0.181176	-1250.410914	-1250.342607	-1250.395906	-1247.896921	
Barrier	4	137	131	127	122	
Reaction	-12	-36	-44	-54	-50	
1e,2,3a-$C_3H_3F_3$	0.058537	-415.607913	-415.581561	-415.597510	-414.766500	
BN + 1e,2,3a TS	0.174234	-1250.336213	-1250.267619	-1250.319780	-1247.822470	
BN + 1e,2,3a	0.180507	-1250.393393	-1250.326598	-1250.380655	-1247.879721	
Barrier	6	100	90	83	81	
Reaction	-11	-35	-49	-62	-55	
1e,2,3e-$C_3H_3F_3$	0.058526	-415.607904	-415.581561	-415.597510	-414.766500	
BN + 1e,2,3e TS	0.174265	-1250.339043	-1250.268568	-1250.319783	-1247.822783	
BN + 1e,2,3e	0.181108	-1250.399511	-1250.332403	-1250.386654	-1247.885525	
Barrier	6	92	88	83	80	
Reaction	-12	-50	-63	-76	-68	
1e,3a,3e-$C_3H_3F_3$	0.058479	-415.624827	-415.599188	-415.614780	-414.785571	
BN + 1e,3a,3e TS	0.174202	-1250.337909	-1250.268609	-1250.320403	-1247.823753	
BN + 1e,3a,3e	0.181007	-1250.401957	-1250.334783	-1250.387954	-1247.889094	
Barrier	6	140	134	127	127	
Reaction	-12	-12	-23	-34	-28	
2,3a,3e-$C_3H_3F_3$	0.058090	-415.622297	-415.597258	-415.612670	-414.783488	
BN + 2,3a,3e TS	0.174383	-1250.354182	-1250.284075	-1250.336057	-1247.840282	
BN + 2,3a,3e	0.181045	-1250.413432	-1250.344594	-1250.397942	-1247.898726	
Barrier	4	92	90	81	80	
Reaction	-13	-48	-53	-65	-57	
1a,1e-$C_3H_4F_2$	0.065318	-316.384005	-316.358346	-316.361108	-315.705606	
BN + 1a,1e TS	0.181434	-1151.107210	-1151.040283	-1151.079150	-1148.756716	
BN + 1a,1e	0.187770	-1151.169616	-1151.104930	-1151.146172	-1148.821896	
Barrier	5	114	102	95	94	
Reaction	-12	-34	-52	-66	-61	
1a,2-$C_3H_4F_2$	0.065004	-316.376609	-316.350631	-316.354098	-315.697268	
BN + 1a,2 TS	0.182100	-1151.114997	-1151.046635	-1151.085495	-1148.762371	
BN + 1a,2	0.188640	-1151.174553	-1151.107210	-1151.148676	-1148.824264	
Barrier	2	77	68	62	60	
Reaction	-15	-64	-76	-88	-87	
1a,3a-$C_3H_4F_2$	0.066179	-316.374194	-316.348294	-316.351846	-315.696094	
BN + 1a,3a TS	0.182635	-1151.099523	-1151.031400	-1151.070329	-1148.748476	
BN + 1a,3a	0.188776	-1151.164887	-1151.096579	-1151.137501	-1148.813784	
Barrier	4	109	100	95	92	
Reaction	-12	-47	-56	-67	-65	
1a,3e-$C_3H_4F_2$	0.066255	-316.374218	-316.348294	-316.351846	-315.696094	
BN + 1a,3e TS	0.182119	-1151.105230	-1151.036005	-1151.074923	-1148.752417	
BN + 1a,3e	0.188447	-1151.166543	-1151.097919	-1151.138433	-1148.815233	
Barrier	5	93	86	81	80	
Reaction	-11	-53	-61	-70	-70	
1e,2-$C_3H_4F_2$	0.065350	-316.376539	-316.350214	-316.353296	-315.697371	
BN + 1e,2 TS	0.181842	-1151.116260	-1151.046767	-1151.085403	-1148.763990	
BN + 1e,2	0.188089	-1151.169301	-1151.102735	-1151.143930	-1148.819063	
Barrier	4	72	65	59	55	
Reaction	-13	-53	-67	-80	-75	

Table S68 (continued).

	WB97XD	WB97XD	M062X	M11	MP2/M11	
	6-311++G(d,p)	6-311++G(d,p)	6-311++G(d,p)	6-311++G(d,p)	6-311++G(d,p)	
	ZPE					
1e,3a-$C_3H_4F_2$	0.066101	-316.374454	-316.348253	-316.351263	-315.696702	
BN + 1e,3a TS	0.182490	-1151.099750	-1151.031680	-1151.071181	-1148.748723	
BN + 1e,3a	0.188701	-1151.155547	-1151.088284	-1151.128934	-1148.805395	
Barrier	4	109	99	91	93	
Reaction	-12	-22	-35	-46	-41	
1e,3e-$C_3H_4F_2$	0.066172	-316.374462	-316.348253	-316.351263	-315.696702	
BN + 1e,3e TS	0.181894	-1151.101787	-1151.031457	-1151.069660	-1148.747693	
BN + 1e,3e	0.188038	-1151.160016	-1151.092131	-1151.132889	-1148.808700	
Barrier	6	102	98	93	94	
Reaction	-11	-36	-47	-58	-52	
2,3a-$C_3H_4F_2$	0.065710	-316.376038	-316.350229	-316.353173	-315.698369	
BN + 2,3a TS	0.182720	-1151.117515	-1151.048442	-1151.087795	-1148.766442	
BN + 2,3a	0.188601	-1151.174268	-1151.105604	-1151.146478	-1148.822305	
Barrier	2	68	62	54	52	
Reaction	-13	-67	-74	-86	-80	
2,3e-$C_3H_4F_2$	0.065704	-316.376025	-316.350229	-316.353173	-315.698369	
BN + 2,3e TS	0.181842	-1151.121308	-1151.050238	-1151.088661	-1148.768176	
BN + 2,3e	0.188850	-1151.175426	-1151.106576	-1151.147237	-1148.823575	
Barrier	4	56	55	49	45	
Reaction	-14	-69	-76	-88	-83	
3a,3e-$C_3H_4F_2$	0.065816	-316.385337	-316.359936	-316.362214	-315.709691	
BN + 3a,3e TS	0.182376	-1151.115719	-1151.045921	-1151.084900	-1148.764130	
BN + 3a,3e	0.188875	-1151.176667	-1151.108218	-1151.148201	-1148.825538	
Barrier	3	96	93	84	87	
Reaction	-14	-48	-55	-67	-59	
1a-C_3H_5F	0.072875	-217.139548	-217.113489	-217.103679	-216.624019	
BN + 1a TS	0.190113	-1051.875008	-1051.806864	-1051.832960	-1049.686320	
BN + 1a	0.196657	-1051.925249	-1051.857469	-1051.884857	-1049.735267	
Barrier	2	85	75	68	68	
Reaction	-16	-31	-42	-52	-45	
1e-C_3H_5F	0.072769	-217.138624	-217.112393	-217.102217	-216.623282	
BN + 1e TS	0.189732	-1051.872218	-1051.803176	-1051.828767	-1049.682781	
BN + 1e	0.195599	-1051.919421	-1051.851906	-1051.878992	-1049.731877	
Barrier	2	89	81	75	74	
Reaction	-13	-21	-33	-43	-40	
2-C_3H_5F	0.072468	-217.145305	-217.119274	-217.109180	-216.629860	
BN + 2 TS	0.189403	-1051.896383	-1051.826252	-1051.852007	-1049.707440	
BN + 2	0.195778	-1051.943810	-1051.875415	-1051.903022	-1049.755748	
Barrier	2	43	38	32	27	
Reaction	-14	-66	-75	-87	-85	
3a-C_3H_5F	0.073307	-217.133743	-217.107771	-217.097334	-216.619549	
BN + 3a TS	0.190494	-1051.876169	-1051.807444	-1051.833920	-1049.687439	
BN + 3a	0.196598	-1051.931297	-1051.862802	-1051.890254	-1049.743145	
Barrier	2	66	58	49	53	
Reaction	-14	-64	-72	-84	-79	
3e-C_3H_5F	0.073334	-217.133761	-217.107771	-217.097334	-216.619549	
BN + 3e TS	0.190219	-1051.878577	-1051.807726	-1051.833034	-1049.687516	
BN + 3e	0.196160	-1051.931957	-1051.862879	-1051.890083	-1049.743179	
Barrier	3	59	57	51	52	
Reaction	-13	-67	-74	-85	-80	
C_3H_6	0.079968	-117.897914	-117.871746	-117.847870	-117.546263	
BN + C_3H_6 TS	0.198102	-952.647116	-952.577387	-952.589934	-950.621679	
BN + C_3H_6	0.204197	-952.690549	-952.626877	-952.640283	-950.671381	
Barrier	-1	51	45	37	35	
Reaction	-17	-49	-70	-81	-80	

Table S69. Energy differences between barriers and reactions for differing substitution patterns, and associated averages and standard deviations (M11/6-311++G(,dp), kJ mol^{-1}) for ene reactions between **1** and fluoro-substituted propenes. The data are organized as (# – #'), where # and #' represent the substitution patterns involved. The individual calculation sets are denoted "Change by placing <substituent(s)> at position(s) #". Averaged data are denoted "Average Substitution Correction" in the manuscript text.

M11 values					
Change by Placing F at Position 1a			**Change by Placing F at Position 1e**		
Subst. Pattern	**Barrier**	**Reaction**	**Subst. Pattern**	**Barrier**	**Reaction**
1a–0	31	28	**1e–0**	38	38
1a,1e–1e	20	-23	**1a,1e–1a**	27	-13
1a,2–2	30	-1	**1e,2–2**	27	7
1a,3a–3a	46	17	**1e,3a–3a**	42	38
1a,3e–3e	31	15	**1e,3e–3e**	43	27
1a,1e,2–1e,2	19	-30	**1a,1e,2–1a,2**	15	-22
1a,1e,3a–1e,3a	33	-22	**1a,1e,3a–1a,3a**	30	-1
1a,1e,3e–1e,3e	20	-23	**1a,1e,3e–1a,3e**	32	-11
1a,2,3a–2,3a	43	-4	**1e,2,3a–2,3a**	29	24
1a,2,3e–2,3e	31	-6	**1e,2,3e–2,3e**	34	12
1a,3a,3e–3a,3e	43	13	**1e,3a,3e–3a,3e**	43	32
1a,1e,2,3a–1e,2,3a	32	-33	**1a,1e,2,3a–1a,2,3a**	19	-5
1a,1e,2,3e–1e,2,3e	17	-34	**1a,1e,2,3e–1a,2,3e**	20	-17
1a,1e,3a,3e–1e,3a,3e	33	-18	**1a,1e,3a,3e–1a,3a,3e**	33	1
1a,2,3a,3e–2,3a,3e	39	-9	**1e,2,3a,3e–2,3a,3e**	31	19
1a,1e,2,3a,3e–1e,2,3a,3e	27	-35	**1a,1e,2,3a,3e–1a,2,3a,3e**	20	-7
Avg(StdDev)	**30.9 (8.8)**	**-10.2 (20.2)**	**Avg(StdDev)**	**30.1 (8.7)**	**7.7 (19.9)**
Change by Placing F at Position 2			**Change by Placing F at Position 3a**		
Subst. Pattern	**Barrier**	**Reaction**	**Subst. Pattern**	**Barrier**	**Reaction**
2–0	-5	-6	**3a-0**	12	-4
1a,2–1a	-6	-36	**1a,3a-1a**	26	-15
1e,2–1e	-16	-37	**1e,3a-1e**	16	-3
2,3a–3a	5	-2	**2,3a-2**	22	0
2,3e–3e	-1	-3	**3a,3e-3e**	33	18
1a,1e,2–1a,1e	-17	-44	**1a,1e,3a-1a,1e**	29	-2
1a,2,3a–1a,3a	1	-23	**1a,2,3a-1a,2**	34	-2
1a,2,3e–1a,3e	-1	-23	**1a,3a,3e-1a,3e**	45	16
1e,2,3a–1e,3a	-8	-16	**1e,2,3a-1e,2**	24	18
1e,2,3e–1e,3e	-10	-18	**1e,3a,3e-1e,3e**	34	24
2,3a,3e–3a,3e	-2	2	**2,3a,3e-2,3e**	32	23
1a,1e,2,3a–1a,1e,3a	-10	-26	**1a,1e,2,3a-1a,1e,2**	37	15
1a,1e,2,3e–1a,2,3e	20	-17	**1a,1e,3a,3e-1a,1e,3e**	46	28
1a,2,3a,3e–1a,3a,3e	-7	-20	**1a,2,3a,3e-1a,2,3e**	40	19
1e,2,3a,3e–1e,3a,3e	-14	-12	**1e,2,3a,3e-1e,2,3e**	30	30
1a,1e,2,3a,3e–1a,1e,3a,3e	-20	-28	**1a,1e,2,3a,3e-1a,1e,2,3e**	40	29
Avg(StdDev)	**-5.6 (9.7)**	**-19.2 (13.1)**	**Avg(StdDev)**	**31.2 (9.6)**	**12.2 (14.2)**
Change by Placing F at Position 3e					
Subst. Pattern	**Barrier**	**Reaction**			
3e–0	14	-4			
1a,3e–1a	13	-18			
1e,3e–1e	18	-15			
2,3e–2	17	-1			
3a,3e–3a	35	18			
1a,1e,3e–1a,1e	18	-15			
1a,2,3e–1a,2	18	-5			
1a,3a,3e–1a,3a	32	13			
1e,2,3e–1e,2	24	4			
1e,3a,3e–1e,3a	36	12			
2,3a,3e–2,3a	28	21			
1a,1e,2,3e–1a,1e,2	22	0			
1a,1e,3a,3e–1a,1e,3a	35	16			
1a,2,3a,3e–1a,2,3a	24	16			
1e,2,3a,3e–1e,2,3a	30	16			
1a,1e,2,3a,3e–1a,1e,2,3a	25	14			
Avg(StdDev)	**24.3 (7.6)**	**4.3 (13.1)**			

Table S69 (continued).

M11 values					
Change by Placing F at Positions 1a,1e			Change by Placing F at Positions 1a,2		
Subst. Pattern	Barrier	Reaction	Subst. Pattern	Barrier	Reaction
1a,1e–0	58	15	1a,2–0	25	-7
1a,1e,2–2	46	-23	1a,1e,2–1e	3	-66
1a,1e,3a–3a	75	16	1a,2,3a–3a	47	-6
1a,1e,3e–3e	63	4	1a,2,3e–3e	30	-8
1a,1e,2,3a–2,3a	61	-8	1a,1e,2,3a–1e,3a	24	-49
1a,1e,2,3e–2,3e	51	-22	1a,1e,2,3e–1e,3e	7	-52
1a,1e,3a,3e–3a,3e	76	14	1a,2,3a,3e–3a,3e	36	-7
1a,1e,2,3a,3e–2,3a,3e	58	-16	1a,1e,2,3a,3e–1e,3a,3e	13	-46
Avg(StdDev)	61.0 (10.5)	-2.4 (16.8)	Avg(StdDev)	23.2 (15.0)	-30.2 (25.4)
Change by Placing F at Positions 1a,3a			Change by Placing F at Positions 1a,3e		
Subst. Pattern	Barrier	Reaction	Subst. Pattern	Barrier	Reaction
1a,3a–0	58	14	1a,3e–0	44	10
1a,1e,3a–1e	49	-25	1a,1e,3e–1e	38	-38
1a,2,3a–2	64	-3	1a,2,3e–2	48	-7
1a,3a,3e–3e	76	31	1a,3a,3e–3a	78	30
1a,1e,2,3a–1e,2	56	-15	1a,1e,2,3e–1e,2	41	-30
1a,1e,3a,3e–1e,3e	66	5	1a,1e,3a,3e–1e,3a	69	-7
1a,2,3a,3e–2,3e	71	14	1a,2,3a,3e–2,3a	66	12
1a,1e,2,3a,3e–1e,2,3e	57	-4	1a,1e,2,3a,3e–1e,2,3a	57	-19
Avg(StdDev)	62.2 (8.8)	2.0 (17.9)	Avg(StdDev)	55.2 (14.4)	-5.8 (22.9)
Change by Placing F at Positions 1e,2			Change by Placing F at Positions 1e,3a		
Subst. Pattern	Barrier	Reaction	Subst. Pattern	Barrier	Reaction
1e,2–0	22	1	1e,3a–0	54	35
1a,1e,2–1a	9	-57	1a,1e,3a–1a	56	-16
1e,2,3a–3a	34	22	1e,2,3a–2	51	25
1e,2,3e–3e	32	9	1e,3a,3e–3e	76	51
1a,1e,2,3a–1a,3a	20	-28	1a,1e,2,3a–1a,2	52	-7
1a,1e,2,3e–1a,3e	19	-39	1a,1e,3a,3e–1a,3e	78	18
1e,2,3a,3e–3a,3e	29	21	1e,2,3a,3e–2,3e	63	42
1a,1e,2,3a,3e–1a,3a,3e	13	-27	1a,1e,2,3a,3e–1a,2,3e	59	13
Avg(StdDev)	22.4 (8.8)	-12.2 (29.6)	Avg(StdDev)	61.3 (10.6)	19.9 (23.1)
Change by Placing F at Positions 1e,3e			Change by Placing F at Positions 2,3a		
Subst. Pattern	Barrier	Reaction	Subst. Pattern	Barrier	Reaction
1e,3e–0	56	23	2,3a–0	17	-6
1a,1e,3e–1a	45	-29	1a,2,3a–1a	28	-38
1e,2,3e–2	51	11	1e,2,3a–1e	8	-19
1e,3a,3e–3a	78	50	2,3a,3e–3e	31	20
1a,1e,2,3e–1a,2	38	-22	1a,1e,2,3a–1a,1e	20	-29
1a,1e,3a,3e–1a,3a	65	14	1a,2,3a,3e–1a,3e	39	-3
1e,2,3a,3e–2,3a	59	40	1e,2,3a,3e–1e,3e	19	12
1a,1e,2,3a,3e–1a,2,3a	44	9	1a,1e,2,3a,3e–1a,1e,3e	27	0
Avg(StdDev)	54.4 (12.9)	12.1 (27.2)	Avg(StdDev)	23.6 (9.5)	-7.8 (19.7)
Change by Placing F at Positions 2,3e			Change by Placing F at Positions 3a,3e		
Subst. Pattern	Barrier	Reaction	Subst. Pattern	Barrier	Reaction
2,3e–0	12	-7	3a,3e–0	47	14
1a,2,3e–1a	12	-41	1a,3a,3e–1a	58	-2
1e,2,3e–1e	8	-33	1e,3a,3e–1e	52	9
2,3a,3e–3a	32	19	2,3a,3e–2	49	22
1a,1e,2,3e–1a,1e	5	-44	1a,1e,3a,3e–1a,1e	64	13
1a,2,3a,3e–1a,3a	25	-7	1a,2,3a,3e–1a,2	58	14
1e,2,3a,3e–1e,3a	22	0	1e,2,3a,3e–1e,2	54	34
1a,1e,2,3a,3e–1a,1e,3a	16	-12	1a,1e,2,3a,3e–1a,1e,2	62	29
Avg(StdDev)	16.6 (9.2)	-15.6 (22.0)	Avg(StdDev)	55.6 (6.1)	16.6 (11.3)

Table S69 (continued).

M11 values					
Change by Placing F at Positions 1a,1e,2			Change by Placing F at Positions 1a,1e,3a		
Subst. Pattern	Barrier	Reaction	Subst. Pattern	Barrier	Reaction
1a,1e,2–0	41	-29	1a,1e,3a–0	87	13
1a,1e,2,3a–3a	66	-10	1a,1e,2,3a–2	83	-8
1a,1e,2,3e–3e	50	-25	1a,1e,3a,3e–3e	109	32
1a,1e,2,3a,3e–2,3a,3e	58	-16	1a,1e,2,3a,3e–2,3e	91	7
Avg(StdDev)	53.7 (10.8)	-19.9 (8.4)	Avg(StdDev)	92.4 (11.5)	11.0 (16.7)
Change by Placing F at Positions 1a,1e,3e			Change by Placing F at Positions 1a,2,3a		
Subst. Pattern	Barrier	Reaction	Subst. Pattern	Barrier	Reaction
1a,1e,3e–0	76	0	1a,2,3a–0	59	-9
1a,1e,2,3e–2	68	-23	1a,1e,2,3a–1e	40	-52
1a,1e,3a,3e–3a	111	32	1a,2,3a,3e–3e	69	11
1a,1e,2,3a,3e–2,3a	86	6	1a,1e,2,3a,3e–1e,3e	47	-22
Avg(StdDev)	85.3 (18.4)	3.5 (22.5)	Avg(StdDev)	53.9 (13.2)	-18.1 (26.3)
Change by Placing F at Positions 1a,2,3e			Change by Placing F at Positions 1a,3a,3e		
Subst. Pattern	Barrier	Reaction	Subst. Pattern	Barrier	Reaction
1a,2,3e–0	44	-13	1a,3a,3e–0	90	27
1a,1e,2,3e–1e	25	-67	1a,1e,3a,3e–1e	85	-10
1a,2,3a,3e–3a	71	10	1a,2,3a,3e–2	88	13
1a,1e,2,3a,3e–1e,3a	49	-35	1a,1e,2,3a,3e–1e,2	81	-1
Avg(StdDev)	47.3 (18.8)	-25.8 (32.9)	Avg(StdDev)	85.8 (4.0)	7.3 (15.9)
Change by Placing F at Positions 1e,2,3a			Change by Placing F at Positions 1e,2,3e		
Subst. Pattern	Barrier	Reaction	Subst. Pattern	Barrier	Reaction
1e,2,3a–0	46	19	1e,2,3e–0	46	5
1a,1e,2,3a–1a	46	-42	1a,1e,2,3e–1a	32	-57
1e,2,3a,3e–3e	62	39	1e,2,3a,3e–3a	64	38
1a,1e,2,3a,3e–1a,3e	59	-10	1a,1e,2,3a,3e–1a,3a	45	-14
Avg(StdDev)	53.3 (8.2)	1.3 (35.5)	Avg(StdDev)	46.7 (13.0)	-7.0 (39.9)
Change by Placing F at Positions 1e,3a,3e			Change by Placing F at Positions 2,3a,3e		
Subst. Pattern	Barrier	Reaction	Subst. Pattern	Barrier	Reaction
1e,3a,3e–0	90	46	2,3a,3e–0	45	16
1a,1e,3a,3e–1a	91	0	1a,2,3a,3e–1a	52	-22
1e,2,3a,3e–2	81	41	1e,2,3a,3e–1e	38	-3
1a,1e,2,3a,3e–1a,2	77	7	1a,1e,2,3a,3e–1a,1e	45	-15
Avg(StdDev)	84.8 (6.8)	23.5 (23.5)	Avg(StdDev)	44.7 (5.7)	-5.9 (16.3)
Change by Placing F at Positions 1a,1e,2,3a			Change by Placing F at Positions 1a,1e,2,3e		
Subst. Pattern	Barrier	Reaction	Subst. Pattern	Barrier	Reaction
1a,1e,2,3a–0	78	-14	1a,1e,2,3e–0	63	-29
1a,1e,2,3a,3e–3e	89	4	1a,1e,2,3a,3e–3a	91	4
Avg(StdDev)	83.6 (8.0)	-4.8 (13.0)	Avg(StdDev)	77.1 (19.5)	-12.6 (23.2)
Change by Placing F at Positions 1a,1e,3a,3e			Change by Placing F at Positions 1a,2,3a,3e		
Subst. Pattern	Barrier	Reaction	Subst. Pattern	Barrier	Reaction
1a,1e,3a,3e–0	123	28	1a,2,3a,3e–0	83	7
1a,1e,2,3a,3e–2	108	6	1a,1e,2,3a,3e–1e	65	-38
Avg(StdDev)	115.2 (10.4)	17.1 (15.5)	Avg(StdDev)	74.1 (12.8)	-15.3 (31.4)
Change by Placing F at Positions 1e,2,3a,3e					
Subst. Pattern	Barrier	Reaction			
1e,2,3a,3e–0	76	35			
1a,1e,2,3a,3e–1a	72	-28			
Avg(StdDev)	73.7 (3.0)	3.3 (44.6)			

Table S70. Data used to generate scatter plots in Figures 3, 6, and 11. All data are based on M11/6-311++G(d,p) optimizations.

Notes: $\Delta E^{\ddagger}$ and ΔE are the M11-predicted barriers and exothermicities for the ene reaction involving each substituted propene.
$\Delta E^{\ddagger}_{ASC\#}$ and $\Delta E^{\ddagger}_{ASC\#}$ are calculated as in Tables S65, S67, and S69.
$\Sigma\Delta E^{\ddagger}_{ASC\#}$ and $\Sigma\Delta E_{ASC\#}$ are the appropriate sums of $\Delta E^{\ddagger}_{ASC(1-5)}$ and $\Sigma\Delta E_{ASC(1-5)}$.
$\Delta E^{\ddagger}_{P\#} = \Delta E^{\ddagger}$ (**1** + C_3H_6) + $\Delta E^{\ddagger}_{ASC\#}$, except for $\Delta E^{\ddagger}_{P12345} = \Delta E^{\ddagger}$ (**1** + C_3H_6) + $\Sigma\Delta E^{\ddagger}_{ASC12345}$
$\Delta E_{P\#} = \Delta E$ (**1** + C_3H_6) + $\Delta E_{ASC\#}$, except for $\Delta E_{P12345} = \Delta E$ (**1** + C_3H_6) + $\Sigma\Delta E_{ASC12345}$

Ene Me	$\Delta E^{\ddagger}$	$\Delta E^{\ddagger}_{ASC\#}$	$\Sigma\Delta E^{\ddagger}_{ASC\#}$	$\Delta E^{\ddagger}_{P\#}$	ΔE	$\Delta E_{ASC\#}$	$\Sigma\Delta E_{ASC\#}$	$\Delta E_{P\#}$
C_3H_6	34				-82			
1	57	36		70	-60	15		-67
2	46	13		47	-53	28		-54
3	16	-12		22	-69	5		-77
4	35	13		47	-87	1		-81
5	28	-3		31	-84	-6		-88
12	70	48	49	82	-46	42	43	-40
13	45	22	24	56	-64	19	20	-63
14	68	49	49	83	-73	15	16	-67
15	51	33	33	67	-74	9	9	-73
23	21	-1	1	33	-55	32	33	-50
24	49	26	26	60	-57	28	29	-54
25	41	10	10	44	-66	22	22	-60
34	21	0	1	34	-84	5	6	-77
35	10	-16	-15	18	-77	-2	-1	-84
45	31	10	10	44	-96	-5	-5	-87
123	52	40	37	74	-47	45	48	-37
124	86	63	62	97	-27	48	44	-34
125	64	45	46	79	-59	38	37	-44
134	62	37	37	71	-74	19	21	-63
135	42	20	21	54	-70	14	14	-68
145	66	46	46	80	-82	10	10	-72
234	28	13	14	47	-54	33	34	-49
235	17	-3	-2	31	-61	27	27	-55
245	45	23	23	57	-65	23	23	-59
345	15	-3	-2	31	-83	0	0	-82
1234	83	53	50	87	-32	53	49	-29
1235	50	33	34	67	-50	45	42	-37
1245	86	61	59	95	-35	45	38	-37
1345	65	35	34	69	-75	16	15	-66
2345	28	11	11	45	-54	30	28	-52
12345	86		47	81	-27		43	-39

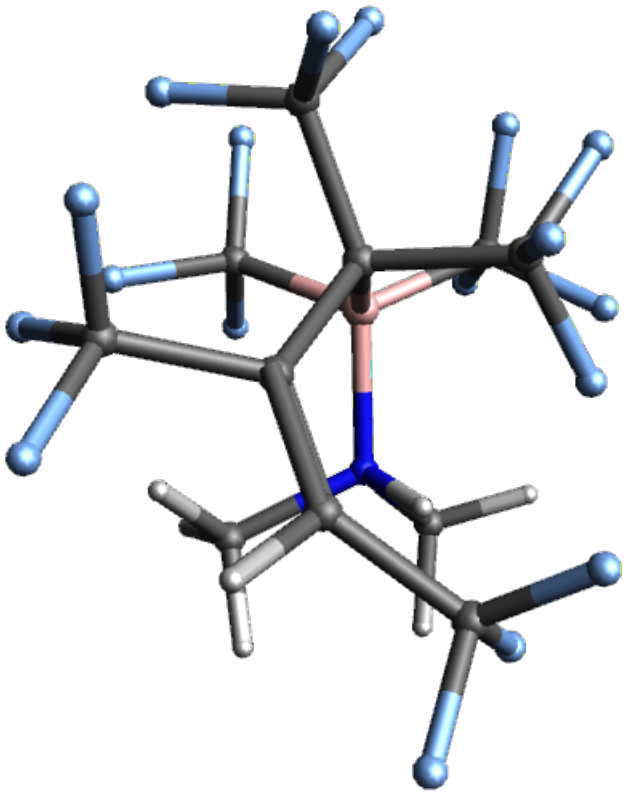
Ene CF_3	$\Delta E^{\ddagger}$	$\Delta E^{\ddagger}_{ASC\#}$	$\Sigma\Delta E^{\ddagger}_{ASC\#}$	$\Delta E^{\ddagger}_{P\#}$	ΔE	$\Delta E_{ASC\#}$	$\Sigma\Delta E_{ASC\#}$	$\Delta E_{P\#}$
1	71	44		78	-71	27		-55
2	74	27		61	-60	25		-57
3	68	29		63	-83	8		-74
4	49	17		51	-80	19		-63
5	44	6		40	-74	10		-72
12	105	71	71	105	-42	51	52	-31
13	100	74	73	108	-76	34	35	-48
14	110	60	61	94	-62	46	46	-36
15	72	50	50	84	-70	37	37	-45
23	89	57	56	91	-93	32	33	-50
24	81	44	44	78	-58	44	44	-38
25	86	33	33	67	-72	35	35	-47
34	75	46	46	80	-66	27	27	-55
35	88	35	35	69	-65	18	18	-64
45	51	22	23	56	-88	29	29	-53
123	134	95	100	129	-62	60	60	-22
124	140	85	88	119	-18	81	71	-1
125	100	74	77	108	-53	66	62	-16
134	129	88	90	122	-73	56	54	-26
135	109	79	79	113	-64	47	45	-35
145	105	65	67	99	-73	61	56	-21
234	93	72	73	106	-76	56	52	-26
235	106	61	62	95	-72	48	43	-34
245	77	46	50	80	-67	59	54	-23
345	88	52	52	86	-51	41	37	-41
1234	168	114	117	148	-6	106	79	24
1235	154	104	106	138	-42	91	70	9
1245	128	82	94	116	-17	105	81	23
1345	152	91	96	125	-48	78	64	-4
2345	112	72	79	106	-52	81	62	-1
12345	139		123	157	63		89	7

Table S70. (continued)

Ene F	$\Delta E^{\ddagger}$	$\Delta E^{\ddagger}_{ASC\#}$	$\Sigma\Delta E^{\ddagger}_{ASC\#}$	$\Delta E^{\ddagger}_{P\#}$	ΔE	$\Delta E_{ASC\#}$	$\Sigma\Delta E_{ASC\#}$	$\Delta E_{P\#}$
1	68	31		65	-52	-10		-92
2	75	30		64	-43	8		-74
3	32	-6		28	-87	-19		-101
4	49	31		65	-84	12		-70
5	51	24		58	-85	4		-78
12	95	61	61	95	-66	-2	-2	-84
13	62	23	25	57	-88	-30	-29	-112
14	95	62	62	96	-67	2	2	-80
15	81	55	55	89	-70	-6	-6	-88
23	59	22	24	56	-80	-12	-11	-94
24	91	61	61	95	-46	20	20	-62
25	93	54	54	88	-58	12	12	-70
34	54	24	25	58	-86	-8	-7	-90
35	49	17	18	51	-88	-16	-15	-98
45	84	56	55	90	-67	17	16	-65
123	78	54	55	88	-109	-20	-21	-102
124	124	92	92	126	-68	11	10	-71
125	113	85	85	119	-81	3	2	-79
134	96	54	56	88	-90	-18	-17	-100
135	80	47	49	81	-93	-26	-25	-108
145	127	86	86	120	-54	7	6	-75
234	83	53	55	87	-62	1	1	-81
235	83	47	48	81	-76	-7	-7	-89
245	127	85	85	119	-34	24	24	-58
345	81	45	49	79	-65	-6	-3	-88
1234	115	84	86	118	-95	-5	-9	-87
1235	100	77	79	111	-110	-13	-17	-95
1245	160	115	116	149	-53	17	14	-65
1345	120	74	80	108	-74	-15	-13	-97
2345	113	74	79	108	-46	3	5	-79
12345	140		110	144	-80		-5	-87

Graphic SF1. Ball and stick models of two conformers (a) and (b) of the product of reaction **1** + **1a, 1e, 2, 3e-$C_3H_2(CF_3)_4$**. Conformer (b) is of lower energy by 39 kJ mol^{-1} (M06-2X/6-311++G(d,p).

(a)



(b)