Supporting Information

Concerted Attack of Frustrated Lewis Acid–Base Pairs on Olefinic Double Bonds: A Theoretical Study

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Contents:

I. Computational details

The calculations were carried out with the Gaussian 03[S1] and Turbomole[S2] packages. The geometries of all stationary points were fully optimized in the gas phase at the B3LYP/6-31G(d) level of density functional theory.[S3,S4] We used ultra-fine integration grid in all DFT calculations to reduce numerical uncertainty in flat regions of the potential energy surface. The located stationary points were characterized as minima or first-order saddle-points according to the calculated harmonic vibrational frequencies. For each optimized structure, we carried out single point spin-component scaled (SCS) MP2/cc-pVTZ calculations[S5,S6] using the resolution-of-identity (RI) integral approximation.[S7] Solvent effects were taken into account by single-point IEF-PCM calculations[S8] using the UA0 atomic radii[S9] and B3LYP/6-31G(d) wavefunction, with all other parameters left at their default values. Experiments were done in bromobenzene solution, for which the solvent model in Gaussian was not parametrized; we chose therefore chlorobenzene which is expected to give similar results. All energy values reported in this paper refer to solvent-corrected but zero-point uncorrected SCS-MP2/cc-pVTZ electronic energies. Computed total electronic energies, thermochemistry and solvation data are given below in Section VII.

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[S7] a) M. Feyereisen, G. Fitzgerald, A. Komornicki, *Chem. Phys. Lett.* **1993**, *208*, 359; b) F. Weigend, M. Häser, *Theor. Chem. Acc.* **1997**, *97*, 331. c) F. Weigend, A. Kohn, C. Hattig, *J. Chem. Phys.* **2002**, *116*, 3175.

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II. On the asynchronous nature of addition (Figure S1)

The progress of the addition on the two C atoms was monitored by the planarity of the CCH_2 units defined as the angle (ϕ) between the C–C bond and the sum of the C–H vectors of a given C atom. The reaction has been followed using the IRC and steepest descent algorithms from the TS in both directions of the transition vector. As seen in Figure S1, the transition from sp^2 to sp^3 hybrid states occurs asymmetrically, as the degree of planarity at the boron site (φ_B) is always smaller than that at the phosphorous side (φ_P).

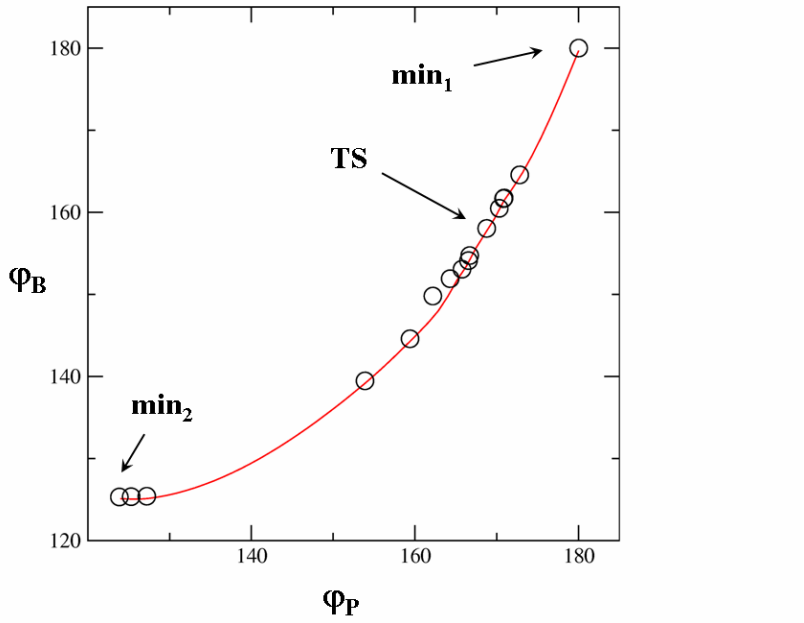


Figure S1. Comparison of the degrees of planarity (φ_B and φ_P) along the addition pathway (points selected from initial IRC and subsequent steepest descent pathways). Points corresponding to TS and related minima (min_1 and min_2) are shown for clarity (for structures, see Figure S2).

III. Energy minima related to TS (Figure S2)

Intrinsic reaction coordinate (IRC) calculations were initiated from the TS in both directions defined by the transition vector. Due to the flat nature of the potential energy surface in this region, the IRC algorithm failed to reach the respective minima. For this reason, we performed subsequent geometry optimizations to locate the minima related to the TS. The optimized structures of the three stationary points are shown in Figure S3 along with their relative stabilities.

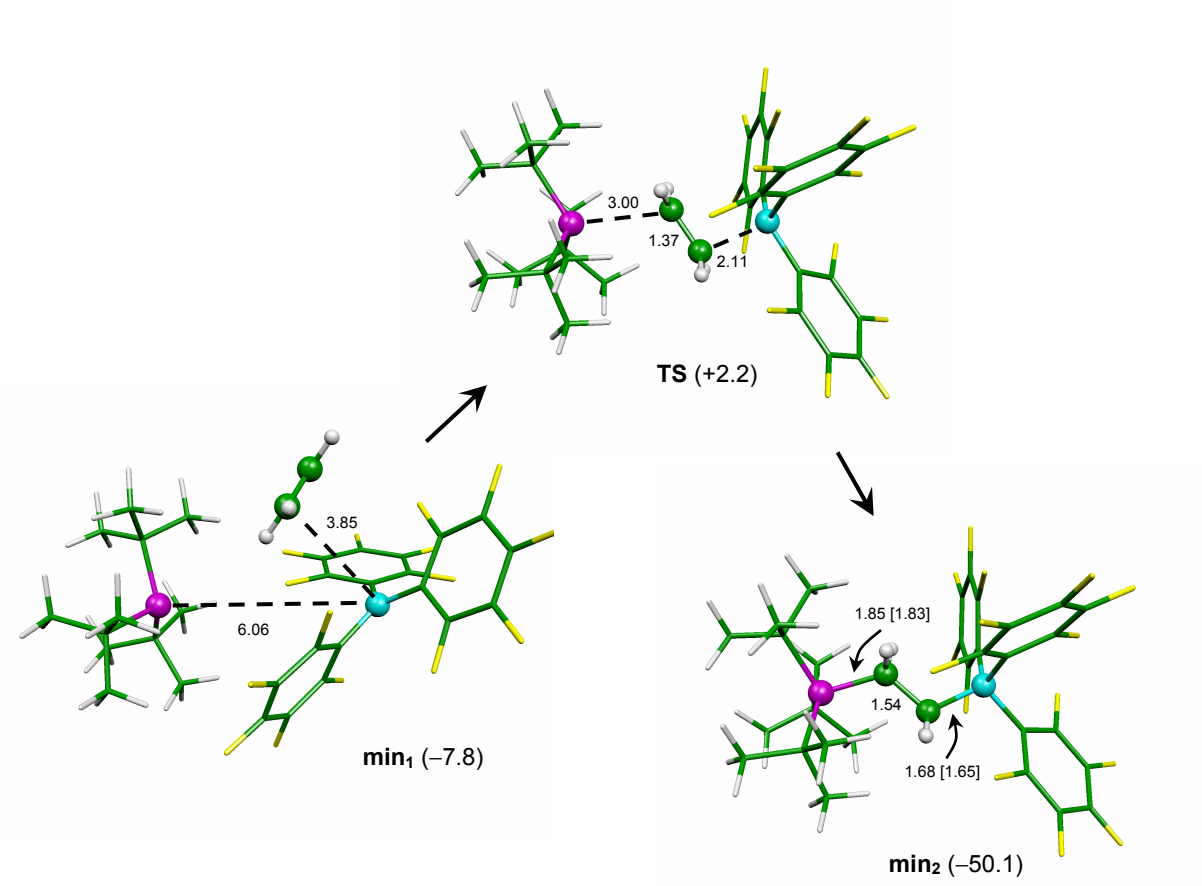


Figure S2. Optimized structures of the stationary points located for $P(tBu)_3/B(C_6F_5)_3 + C_2H_4$ addition. Selected bond distances are given in Å, relative stabilities (in kcal/mol) with respect to $P(tBu)_3 + B(C_6F_5)_3 + C_2H_4$ are given in parentheses. Experimental B–C and P–C bond distances of the product molecule are shown in brackets (X-ray data from Ref. 9 of the paper).

IV. Binary $(C_6F_5)_3B\cdots C_2H_4$ and $(t\text{Bu})_3P\cdots C_2H_4$ interactions (Figures S3, S4)

To explore the nature of $(C_6F_5)_3B\cdots C_2H_4$ and $(t\text{Bu})_3P\cdots C_2H_4$ interactions, we first derived potential energy curves with respect to B–C and P–C distances without symmetry constraints. Potential energy scans, allowing 8 relaxation steps for each value of the scanned variable, were performed at the B3LYP/6-31G(d) level. For each partially optimized structure, single point SCS-MP2/cc-pVTZ energy calculations were carried out. The obtained gas-phase potential energy curves are depicted in Figure S3 and reveal repulsive interactions for $(t\text{Bu})_3P\cdots C_2H_4$, whereas weak attractive forces are observed for $(C_6F_5)_3B\cdots C_2H_4$.

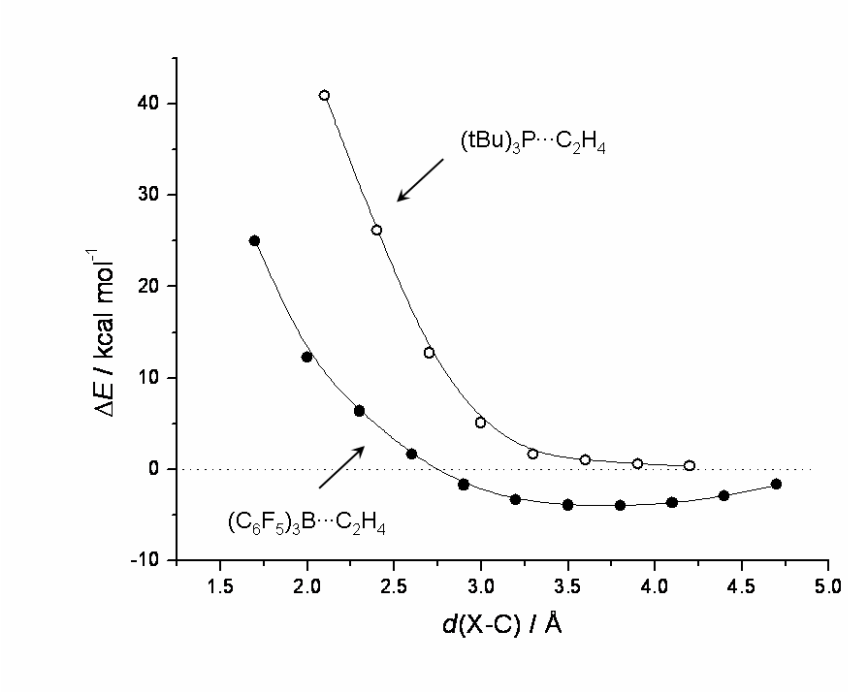


Figure S3. Gas-phase interaction energy of C_2H_4 with $B(C_6F_5)_3$ and $P(t\text{Bu})_3$ as a function of X–C distance.

For $(C_6F_5)_3B\cdots C_2H_4$, full geometry optimization was performed and the structure identified as an energy minimum is shown in Figure S4. The association energy of the $(C_6F_5)_3B\cdots C_2H_4$ adduct is predicted to be –4.0 kcal/mol (–3.5 kcal/mol in solution). The ethylene molecule in this adduct does not directly interact with B center as revealed from long B–C distances; the stabilization is rather due to van der Waals and C–H···F contacts.

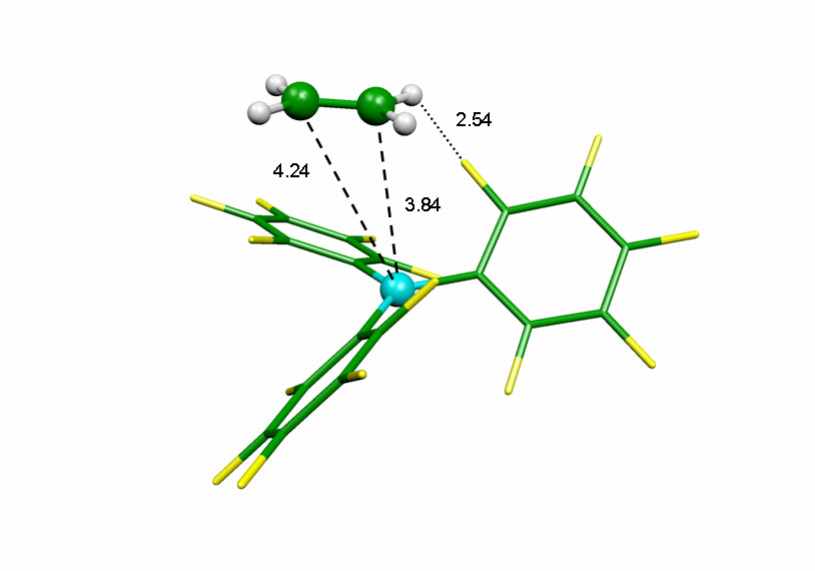
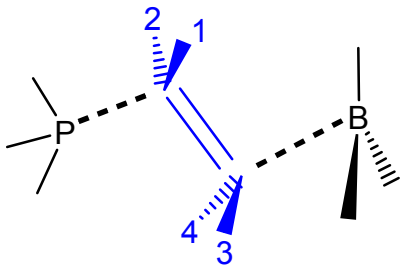


Figure S4. Optimized structure of the $(C_6F_5)_3B\cdots C_2H_4$ adduct. Selected bond distances are given in Å.

V. P(*t*Bu)$_3$/B(C$_6$F$_5$)$_3$ addition to propylene (Scheme S1)

Four different transition states have been located for the reaction of P(*t*Bu)$_3$/B(C$_6$F$_5$)$_3$ with propylene. The initial structures in these transition state optimizations were constructed from the TS identified for addition to C_2H_4 (TS in Figure S2) by corresponding methyl substitutions. The relative energies of the optimized TSs are: 0.0 (TS_1), 1.8 (TS_2), 3.5 (TS_3) and 9.6 (TS_4) kcal/mol relative to the most stable structure (TS_1) and the labelling is defined in Scheme S1.



Scheme S1. Labelling of transition states for P(*t*Bu)$_3$/B(C$_6$F$_5$)$_3$ + propylene addition.

VI. Cartesian coordinates of calculated structures

B3LYP/6-31G(d) optimized geometries, given in standard XYZ format: coordinates are Cartesian coordinates in the usual order (units are in ångstroms), first line indicates total number of atoms, second line is molecule name. Page numbers are omitted in this section to ease copying and pasting.

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  40
(tBu)3P
 C   -3.115802    1.066753   -3.054350
 C   -3.616068   -0.138263   -2.226944
 P   -3.198354    0.147441   -0.341319
 C   -4.252985   -1.127725    0.695535
 C   -3.599012   -1.196766    2.098882
 C   -5.087628   -0.401263   -2.600662
 C   -2.748216   -1.335741   -2.689455
 C   -3.808476    1.939682    0.132736
 C   -3.844278    2.081509    1.670462
 C   -5.168205    2.403481   -0.424683
 C   -2.702209    2.917380   -0.338048
 C   -4.081583   -2.543349    0.100836
 C   -5.760917   -0.850369    0.850538
 H   -3.162456    0.805259   -4.120408
 H   -5.174267   -0.514173   -3.691152
 H   -2.863305   -1.466528   -3.774637
 H   -3.724072    1.963624   -2.918187
 H   -2.073696    1.314590   -2.824783
 H   -5.744953    0.420786   -2.304434
 H   -5.176396    2.460963   -1.516184
 H   -5.475632   -1.319895   -2.153208
 H   -1.687573   -1.155519   -2.483872
 H   -2.601941    2.969091   -1.422658
 H   -3.023944   -2.279897   -2.219019
 H   -5.393181    3.412433   -0.049090
 H   -5.988683    1.749544   -0.116697
 H   -2.941099    3.930253    0.015873
 H   -4.606994   -2.677331   -0.847434
 H   -1.727586    2.638516    0.076809
 H   -6.278616   -0.813340   -0.112060
 H   -3.026521   -2.798792   -0.046162
 H   -4.499806   -3.274473    0.806284
 H   -5.963300    0.085579    1.377431
 H   -6.222544   -1.655923    1.440110
 H   -3.982752    3.141889    1.922680
 H   -4.667307    1.532373    2.133468
 H   -2.905379    1.755909    2.131492
 H   -2.531131   -1.429050    2.025103
 H   -3.702218   -0.275018    2.672298
 H   -4.078007   -1.997225    2.680145

  34
B(C6F5)3
 C    0.712060   -1.264193    4.322972
 C    0.233284   -0.073099    3.781200
 C    0.596968    0.278752    2.486517
 C    1.416352   -0.521554    1.674882
 C    1.863323   -1.714649    2.264284
 C    1.537368   -2.089964    3.562427
```

B	1.805132	-0.111396	0.211261
C	2.081395	1.393828	-0.134594
C	1.699439	1.965532	-1.358449
C	1.926761	3.299048	-1.678417
C	2.581709	4.117388	-0.760379
C	2.990134	3.596356	0.465663
C	2.727618	2.263059	0.758365
F	1.527035	3.800156	-2.851367
F	1.055294	1.227450	-2.277462
F	2.816404	5.394905	-1.053906
F	3.625853	4.378492	1.343632
F	3.153790	1.813283	1.950165
F	0.097100	1.432268	2.013480
F	2.670450	-2.544272	1.582724
F	-0.565314	0.715622	4.507059
F	2.003976	-3.228677	4.084235
F	0.381703	-1.612490	5.565081
C	1.917534	-1.206322	-0.906895
C	2.893914	-1.153207	-1.914059
C	3.015227	-2.118645	-2.906765
C	2.120614	-3.186610	-2.930726
C	1.126143	-3.280623	-1.959320
C	1.048565	-2.306928	-0.970298
F	2.215923	-4.115603	-3.880019
F	3.974907	-2.032346	-3.833207
F	0.262163	-4.300187	-1.986617
F	3.790306	-0.153000	-1.934196
F	0.063460	-2.443112	-0.067334

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[(tBu)3P]...[B(C6F5)3] (SCS-MP2 minimum, see Ref. 8 in the paper)

C	-1.674960	-2.393416	-3.663834
C	-0.946747	-1.206471	-3.634109
C	-0.932463	-0.448324	-2.470319
C	-1.582724	-0.831512	-1.288263
C	-2.301595	-2.034781	-1.371922
C	-2.364501	-2.807411	-2.526473
B	-1.507115	0.022933	0.029398
C	-1.518678	1.593016	-0.051328
C	-0.819701	2.397422	0.860457
C	-0.777975	3.783766	0.785475
C	-1.496540	4.432890	-0.215690
C	-2.232828	3.684316	-1.131052
C	-2.225686	2.296665	-1.039741
F	-0.057993	4.492547	1.662024
F	-0.113096	1.836563	1.857866
F	-1.481449	5.762376	-0.296336
F	-2.935576	4.303115	-2.085556
F	-2.962804	1.636045	-1.947986
F	-0.219437	0.691173	-2.514124
F	-2.994865	-2.486660	-0.313650
F	-0.271076	-0.806210	-4.716855
F	-3.076066	-3.939122	-2.554006
F	-1.713405	-3.128010	-4.774343
C	-1.523061	-0.691875	1.429779
C	-2.186608	-0.158743	2.546634
C	-2.196277	-0.773617	3.793948
C	-1.507348	-1.971370	3.970426
C	-0.833463	-2.543548	2.894102
C	-0.871802	-1.913048	1.657041

F	-1.494938	-2.567240	5.161680
F	-2.856428	-0.227422	4.820456
F	-0.159063	-3.687260	3.055828
F	-2.877016	0.988959	2.442761
F	-0.210151	-2.525734	0.659219
C	2.538430	-0.329895	2.748484
C	3.420015	0.388409	1.697189
P	2.653392	-0.038020	-0.052031
C	3.341771	-1.795660	-0.567418
C	2.421318	-2.310459	-1.701577
C	3.266517	1.897610	1.994498
C	4.896287	0.010640	1.932482
C	3.376120	1.258227	-1.327467
C	3.156862	0.762300	-2.775036
C	4.862662	1.640446	-1.180571
C	2.507988	2.533719	-1.193919
C	3.163976	-2.800680	0.593605
C	4.809529	-1.870765	-1.033991
H	3.529594	2.072026	3.046804
H	5.195163	0.333054	2.940253
H	2.883949	-0.055766	3.754969
H	3.931179	2.522477	1.394260
H	2.239633	2.245359	1.857923
H	5.569692	0.497376	1.222540
H	5.081361	2.130452	-0.229047
H	5.071112	-1.066365	1.879114
H	1.493165	-0.019367	2.659511
H	2.591276	3.015005	-0.218512
H	2.578751	-1.417715	2.677463
H	5.132935	2.350770	-1.975125
H	5.526833	0.777760	-1.276267
H	2.827537	3.266691	-1.947704
H	3.848357	-2.620398	1.425275
H	1.452949	2.308180	-1.375526
H	5.509053	-1.526433	-0.268015
H	2.140966	-2.814625	0.977503
H	3.381014	-3.809071	0.215445
H	4.994589	-1.294383	-1.943363
H	5.062730	-2.916224	-1.261610
H	3.397709	1.584099	-3.463238
H	3.803655	-0.075569	-3.043654
H	2.118495	0.478687	-2.963707
H	1.378644	-2.345585	-1.372149
H	2.472469	-1.707445	-2.609147
H	2.721046	-3.332563	-1.971796

6

C_2H_4

C	0.701970	0.283848	-1.744645
C	0.262293	1.511930	-2.010818
H	-0.612204	1.928398	-1.516386
H	0.756725	2.154156	-2.735896
H	0.206913	-0.358195	-1.019905
H	1.576160	-0.132336	-2.239748

9

C_3H_6

C	0.027702	0.000000	-0.041609
C	-0.045528	0.000000	1.468918

H	1.063843	0.000000	-0.393498
H	-0.464900	-0.882531	-0.468056
H	-0.464900	0.882531	-0.468056
C	-1.173455	0.000000	2.180120
H	0.905178	0.000000	2.002181
H	-1.162765	0.000000	3.266769
H	-2.153608	0.000000	1.705733

40

$B(C_6F_5)_3$-C_2H_4 binary complex

C	-0.385531	3.351148	1.173238
C	-0.703881	2.279174	0.347740
C	0.093354	1.882060	-0.736391
C	1.244197	2.655407	-0.950058
C	1.584512	3.747198	-0.159415
C	0.764958	4.092917	0.912789
F	2.066667	2.374492	-1.974626
B	-0.276865	0.657231	-1.645806
C	-0.988160	-1.520363	1.441004
C	0.264388	-1.619984	1.884221
F	2.684566	4.462414	-0.415583
F	-1.823175	1.598918	0.650529
F	1.080502	5.129702	1.687342
F	-1.169099	3.677233	2.206469
C	0.852524	-0.282600	-2.196220
C	0.791340	-0.861404	-3.474198
C	1.783102	-1.692131	-3.982630
C	2.891606	-1.990802	-3.193150
C	2.997662	-1.448150	-1.914593
C	1.996650	-0.603422	-1.448086
F	1.684933	-2.203299	-5.213953
F	3.847359	-2.792138	-3.659986
F	-0.245715	-0.599511	-4.286827
F	4.057347	-1.739684	-1.152957
F	2.155384	-0.117313	-0.206974
C	-1.779025	0.394116	-2.022933
C	-2.679987	1.440837	-2.273356
C	-4.011347	1.234039	-2.617465
C	-4.497426	-0.068358	-2.706177
C	-3.646399	-1.143529	-2.457907
C	-2.316386	-0.896948	-2.139068
F	-5.772007	-0.285931	-3.025465
F	-4.823444	2.266831	-2.863307
F	-4.112659	-2.394068	-2.533809
F	-2.266673	2.717690	-2.215459
F	-1.547743	-1.975654	-1.901807
H	-1.353575	-2.132163	0.620825
H	0.972401	-2.324087	1.454264
H	-1.692362	-0.813051	1.870918
H	0.635375	-1.006857	2.701969

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ternary complex (min1)

F	-1.478710	-1.161252	-3.825288
F	-2.194986	-3.373475	-2.400421
C	-0.804805	-1.491371	-2.718011
C	-1.168393	-2.623454	-1.994576
F	1.193251	5.629466	-0.814527
F	3.681416	4.623445	-1.301358
F	0.533484	0.395537	-2.979355

C	1.403686	4.315645	-0.752171
C	0.235599	-0.696487	-2.253769
C	2.674521	3.798694	-0.996118
C	-0.474462	-2.959980	-0.835961
F	-0.849122	-4.028274	-0.122031
F	-0.866770	3.946453	-0.200531
C	0.354919	3.453214	-0.440841
F	4.119224	1.983094	-1.172755
C	2.876660	2.425209	-0.918380
C	0.970099	-0.994199	-1.097423
C	0.587543	-2.163292	-0.424853
C	0.590894	2.084457	-0.392250
C	1.853108	1.513991	-0.619116
F	-0.461669	1.306202	-0.081468
F	3.418019	-2.481728	-1.455667
B	2.091944	-0.038189	-0.555107
F	1.222857	-2.534947	0.700092
C	3.985961	-1.818426	-0.435768
F	5.664951	-3.493571	-0.419316
C	3.417189	-0.624562	0.039013
C	5.156099	-2.362884	0.080676
C	4.114256	-0.006864	1.091128
C	5.801134	-1.716553	1.132683
F	3.657520	1.131725	1.634531
H	0.858372	1.574272	3.089876
C	5.274701	-0.533322	1.646265
F	6.918592	-2.227891	1.645734
C	1.088807	0.561375	3.411174
H	-0.313615	-0.394232	2.145703
F	5.889897	0.083992	2.660340
H	1.859781	0.463929	4.171757
H	-2.991828	0.307701	-2.182596
C	0.457844	-0.497397	2.904890
H	0.685100	-1.509974	3.227583
H	-4.178796	-2.586623	-1.057995
H	-3.076688	-2.921786	1.167102
H	-4.387800	-0.766402	-2.319948
C	-4.085168	0.269518	-2.163284
H	-4.451125	0.849419	-3.021986
H	-3.008738	2.372771	-0.753982
C	-5.118744	-2.437791	-0.518107
H	-5.549412	-3.433061	-0.342218
H	-1.951598	1.532037	2.133616
C	-4.031585	-2.726426	1.667172
H	-4.557953	-3.686643	1.760439
H	-5.812166	-1.901494	-1.169586
H	-3.815579	-2.376373	2.677216
P	-3.854019	-0.117943	0.616885
C	-4.099315	2.338428	-0.839177
C	-4.639230	0.890853	-0.857961
H	-4.369882	2.825178	-1.786265
H	-2.848095	-0.467864	3.393586
C	-4.908867	-1.746587	0.847508
H	-3.022435	2.750381	1.443975
C	-2.931642	2.007234	2.235973
H	-4.528365	2.943557	-0.037132
H	-2.945126	2.546116	3.193579
C	-3.799112	0.069347	3.474311
C	-4.068360	0.954796	2.236882
H	-6.631199	-0.030139	-1.083858

C	-6.177374	0.952913	-0.935376
H	-6.475159	1.575746	-1.791320
H	-4.593300	-0.655411	3.666280
H	-3.732375	0.714870	4.360525
C	-6.286161	-1.606861	1.525195
H	-6.775113	-2.590934	1.565998
H	-6.951936	-0.934472	0.977238
H	-6.213803	-1.244423	2.553476
H	-6.620804	1.396097	-0.039897
H	-5.613248	2.418824	1.665593
C	-5.416800	1.673121	2.440184
H	-6.261423	0.979709	2.462324
H	-5.404753	2.206301	3.401885

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TS with ethylene (TS)

P	4.153017	-0.324792	0.384733
B	-1.435099	0.122442	-0.015922
C	4.504000	-2.125579	1.036962
C	5.971870	-2.594363	0.987967
H	6.360580	-2.648977	-0.031867
H	6.636587	-1.950638	1.569761
H	6.040673	-3.605866	1.411871
C	3.630223	-3.099353	0.207764
H	3.740581	-4.110406	0.621714
H	3.914241	-3.151013	-0.843390
H	2.568465	-2.839911	0.259871
C	5.168005	-0.045887	-1.255437
C	4.976359	-1.253466	-2.199543
H	5.494724	-2.151673	-1.857815
H	5.392811	-0.996039	-3.182129
H	3.919499	-1.497680	-2.350127
C	4.525342	1.157605	-1.988609
H	5.023742	1.291613	-2.957858
H	3.462902	0.981641	-2.189380
H	4.615731	2.098701	-1.446053
C	6.680486	0.203769	-1.092126
H	7.138520	0.307134	-2.085725
H	7.185950	-0.621242	-0.583582
H	6.897925	1.123372	-0.543577
C	3.999979	-2.252808	2.491804
H	4.031216	-3.311882	2.778832
H	2.963342	-1.917462	2.599231
H	4.619139	-1.709033	3.208468
C	4.767122	0.954221	1.719182
C	4.827818	2.365923	1.094614
H	3.889324	2.638861	0.600422
H	5.644874	2.485811	0.380231
C	3.674474	1.034155	2.813879
H	2.700748	1.295289	2.387908
H	3.946214	1.822101	3.528838
H	3.556693	0.110377	3.380156
C	6.127952	0.657225	2.379834
H	6.942284	0.598240	1.653034
H	6.119646	-0.271466	2.955668
H	6.371993	1.467225	3.081281
H	4.994154	3.094880	1.898288
F	0.034850	-2.614104	-0.529243
C	-1.117609	-2.331586	-1.186899
C	-1.583231	-3.350146	-2.019337

F -0.896890 -4.496186 -2.133662
C -2.767687 -3.176980 -2.723215
F -3.228821 -4.143479 -3.523759
C -3.469960 -1.982729 -2.581995
F -4.618044 -1.798453 -3.246010
C -2.966131 -0.997510 -1.742165
F -3.693012 0.134067 -1.628645
C -1.767332 -1.108761 -1.024857
C -1.197161 1.592641 -0.653152
C -1.117337 1.860906 -2.025743
F -1.248906 0.877834 -2.937859
C -0.876425 3.129375 -2.554325
F -0.818629 3.309920 -3.880579
C -0.678806 4.206748 -1.699889
F -0.437858 5.426906 -2.189042
C -0.723046 3.994149 -0.325131
F -0.518977 5.015890 0.517339
C -0.972430 2.714622 0.157805
F -0.974859 2.587512 1.504319
C -2.428791 0.001634 1.266648
C -2.477699 -1.152621 2.062755
F -1.628877 -2.181132 1.832198
C -3.366312 -1.339226 3.116792
F -3.335163 -2.463850 3.844364
C -4.304100 -0.352029 3.400427
F -5.172384 -0.511357 4.403011
C -4.330117 0.797195 2.619431
F -5.242476 1.746677 2.862315
C -3.415813 0.948761 1.578044
F -3.556349 2.072296 0.853322
C 1.207181 -0.025669 -0.102235
C 0.389270 -0.181586 0.988994
H 1.408114 -0.849386 -0.772519
H 1.495412 0.958495 -0.451478
H 0.208334 -1.174972 1.375684
H 0.282821 0.638947 1.690795

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Product with ethylene (min2)
F -4.600407 -1.576482 -2.959151
F -3.507491 -4.073173 -3.241746
C -3.436891 -1.870621 -2.359326
C -2.885778 -3.140756 -2.506628
F -5.064352 0.510351 4.195920
F -4.782979 2.511469 2.348561
F -3.356493 0.289461 -1.507115
C -4.128528 0.424045 3.239810
C -2.769290 -0.923059 -1.591670
C -3.977601 1.438095 2.302352
C -1.676645 -3.420009 -1.886006
F -1.115385 -4.634898 -2.020074
F -3.430452 -1.688667 4.048820
C -3.295046 -0.685276 3.164425
F -2.961011 2.355641 0.439831
C -2.997348 1.330450 1.315828
C -1.550253 -1.145282 -0.936112
C -1.051029 -2.431067 -1.126277
C -2.330970 -0.746833 2.161346
C -2.109898 0.254070 1.207694
F -1.593795 -1.888722 2.145466

F	-0.690719	0.484764	-3.004677
B	-0.936497	0.053763	0.039260
F	0.143465	-2.816764	-0.583298
C	-0.477686	1.550291	-2.199549
F	-0.004355	2.731897	-4.208831
C	-0.601260	1.446464	-0.810261
C	-0.100880	2.717332	-2.869332
C	-0.267123	2.628715	-0.139218
C	0.197903	3.863000	-2.144627
F	-0.283356	2.663507	1.219344
H	0.381631	-1.288246	1.339171
C	0.120635	3.813555	-0.755959
F	0.573685	4.989386	-2.767002
C	0.488245	-0.330375	0.834157
H	1.606078	-1.171374	-0.807748
F	0.426777	4.901323	-0.028435
H	0.616945	0.423135	1.614632
H	1.637544	-2.887864	1.188494
C	1.717028	-0.354430	-0.089853
H	1.763090	0.568251	-0.679083
H	3.157963	-2.738890	-1.472718
H	2.955575	-0.391279	-2.496716
H	3.096513	-3.681915	0.590336
C	2.665230	-3.149707	1.437192
H	2.631323	-3.854707	2.276357
H	1.893241	-1.057928	3.108428
C	4.219861	-2.492183	-1.385334
H	4.673824	-2.664923	-2.368217
H	2.011952	2.049700	1.645736
C	3.990297	-0.172934	-2.222914
H	4.616674	-0.448573	-3.079575
H	4.687769	-3.191245	-0.689683
H	4.089433	0.902844	-2.083658
P	3.441789	-0.540446	0.562667
C	2.913123	-1.430539	3.223801
C	3.514289	-1.935939	1.890536
H	2.874809	-2.282697	3.912446
H	3.327623	2.301913	-0.495260
C	4.467583	-1.011940	-1.009369
H	2.625752	1.124634	3.020045
C	2.914017	1.768637	2.190377
H	3.524189	-0.661476	3.700696
H	3.328459	2.688100	2.622028
C	4.216837	2.182986	0.130423
C	4.006717	1.163046	1.274211
H	5.406645	-2.902278	1.286446
C	4.957434	-2.417874	2.156375
H	4.918810	-3.167860	2.955540
H	5.073245	1.951500	-0.505541
H	4.411750	3.158279	0.591367
C	5.985918	-0.804429	-0.821559
H	6.494644	-1.174489	-1.719885
H	6.390176	-1.356763	0.030184
H	6.258194	0.247564	-0.711173
H	5.624018	-1.620395	2.491980
H	5.193051	0.482862	3.005710
C	5.320110	1.047591	2.079246
H	6.138433	0.600621	1.510124
H	5.634091	2.059398	2.362064

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TS with propylene 1:

C	-2.771839	0.740864	2.119555
C	-2.029074	-0.214562	1.412535
C	-2.063791	-1.493506	1.984497
C	-2.716828	-1.804943	3.173310
C	-3.415546	-0.809620	3.847508
C	-3.445068	0.471670	3.310757
B	-1.312370	0.059680	-0.040481
C	-1.006138	1.633884	-0.390138
C	-1.200281	2.239475	-1.635040
C	-0.889187	3.571741	-1.910947
C	-0.330855	4.367330	-0.918642
C	-0.079405	3.807043	0.330759
C	-0.413128	2.476913	0.558023
F	-1.669686	1.532070	-2.688439
F	-1.107570	4.080478	-3.131412
F	-0.016340	5.643695	-1.165250
F	0.486383	4.546708	1.295254
F	-0.095371	1.991255	1.783647
F	-1.444707	-2.532721	1.374873
F	-2.688061	-3.053500	3.661525
F	-4.054669	-1.083931	4.989601
F	-4.127872	1.440011	3.936496
F	-2.893525	2.003340	1.668853
C	-2.207062	-0.765955	-1.140200
C	-1.972080	-2.016879	-1.713626
C	-2.878894	-2.675631	-2.545665
C	-4.108595	-2.094149	-2.821720
C	-4.409083	-0.857024	-2.258334
C	-3.472620	-0.239234	-1.438588
F	-0.812401	-2.691841	-1.503077
F	-2.569069	-3.870403	-3.070588
F	-4.991025	-2.711967	-3.614437
F	-5.593768	-0.281211	-2.501985
F	-3.836344	0.945459	-0.904256
C	0.418788	-0.699470	0.195126
C	1.188587	-0.130659	-0.825558
P	4.085954	-0.576631	-0.022927
C	4.522607	0.596514	1.472597
C	5.730150	0.170535	2.332612
C	4.230057	-2.425107	0.574674
C	3.487355	-2.598911	1.919019
C	5.394575	-0.276797	-1.437502
C	6.866304	-0.152288	-0.994561
C	5.658966	-2.981176	0.737735
C	3.456380	-3.299160	-0.442884
C	5.299300	-1.412450	-2.481029
C	4.984528	1.016301	-2.184876
C	4.777679	2.030821	0.958674
C	3.269298	0.700615	2.376670
H	6.205077	-3.023738	-0.207922
H	6.255158	-2.403415	1.448566
H	5.600340	-4.009921	1.119234
H	3.457859	-4.338569	-0.089164
H	3.894536	-3.297675	-1.441128
H	2.411894	-2.984192	-0.527519
H	5.688775	-2.364066	-2.113757
H	5.903212	-1.134070	-3.354450
H	4.274313	-1.570262	-2.831936

H	5.641111	1.146407	-3.055222
H	3.956278	0.961312	-2.557329
H	5.072733	1.916345	-1.576958
H	7.499237	-0.026862	-1.884115
H	7.220493	-1.039727	-0.464540
H	7.039709	0.716471	-0.355151
H	3.430637	-3.671448	2.145647
H	2.460456	-2.223471	1.876149
H	3.999101	-2.122170	2.757490
H	3.968156	2.390594	0.314690
H	5.722793	2.133266	0.421317
H	2.416933	1.139352	1.848959
H	3.500205	1.366511	3.218654
H	2.953061	-0.253177	2.799018
H	6.649615	0.078729	1.749186
H	5.562161	-0.775785	2.852160
H	5.905877	0.932583	3.104381
H	4.824963	2.705234	1.823274
C	1.209390	-0.588077	-2.243369
H	1.568478	0.872179	-0.662312
H	0.225924	-1.762069	0.143758
H	0.633668	-0.324839	1.191867
H	2.106725	-0.247553	-2.762817
H	1.093727	-1.666580	-2.346344
H	0.348612	-0.113964	-2.742848

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TS with propylene 2:

C	-3.090392	-0.119728	1.970738
C	-1.940893	-0.593213	1.323352
C	-1.479908	-1.816338	1.829927
C	-2.040771	-2.485446	2.913623
C	-3.160391	-1.948996	3.538551
C	-3.689807	-0.758611	3.056180
B	-1.250774	0.099180	-0.010436
C	-1.695744	1.647633	-0.301793
C	-2.050465	2.167365	-1.552531
C	-2.395176	3.502895	-1.772668
C	-2.370573	4.403788	-0.716367
C	-1.998338	3.949629	0.545654
C	-1.670062	2.609860	0.717430
F	-2.058422	1.389614	-2.655953
F	-2.729567	3.922526	-3.001362
F	-2.686238	5.689293	-0.909266
F	-1.951909	4.804990	1.577339
F	-1.302959	2.254957	1.971338
F	-0.421272	-2.445798	1.255246
F	-1.521079	-3.645162	3.344039
F	-3.722655	-2.573471	4.579426
F	-4.782421	-0.236239	3.630165
F	-3.712253	1.001689	1.561807
C	-1.547341	-0.961663	-1.232402
C	-0.679403	-1.867137	-1.838856
C	-1.067103	-2.807025	-2.794549
C	-2.398992	-2.886614	-3.176236
C	-3.318557	-2.019302	-2.591957
C	-2.880501	-1.101564	-1.645004
F	0.647289	-1.892782	-1.530500
F	-0.160917	-3.635471	-3.337208
F	-2.793499	-3.781041	-4.089991

F	-4.610523	-2.082074	-2.941581
F	-3.824538	-0.300322	-1.108578
C	0.523826	0.232594	0.473577
C	1.339914	0.720649	-0.576208
P	4.055171	0.089020	0.124009
C	4.781460	1.491248	1.268773
C	6.061242	1.130896	2.050255
C	4.144010	-1.606239	1.084250
C	3.548511	-1.422599	2.498787
C	5.153068	-0.049969	-1.479849
C	6.677340	0.030345	-1.259045
C	5.552879	-2.218870	1.223103
C	3.232421	-2.632112	0.367548
C	4.838298	-1.371181	-2.216565
C	4.720286	1.077266	-2.448691
C	5.072012	2.757445	0.431655
C	3.675359	1.893095	2.275317
H	5.979128	-2.507474	0.259117
H	6.260227	-1.553990	1.723583
H	5.480032	-3.134177	1.826261
H	3.198715	-3.544604	0.976831
H	3.596236	-2.920267	-0.618024
H	2.205828	-2.280657	0.255583
H	5.246508	-2.247870	-1.710050
H	5.301283	-1.330520	-3.210982
H	3.763935	-1.523034	-2.364069
H	5.316145	1.000784	-3.367536
H	3.669129	0.972742	-2.736913
H	4.869567	2.081289	-2.050034
H	7.184671	-0.111612	-2.223190
H	7.043157	-0.744163	-0.580812
H	6.996411	1.000331	-0.870458
H	3.439780	-2.413235	2.957870
H	2.554198	-0.966644	2.474795
H	4.188544	-0.833565	3.159025
H	4.202724	3.082440	-0.147370
H	5.918325	2.638570	-0.247945
H	2.761352	2.213579	1.767560
H	4.034446	2.741238	2.872819
H	3.410648	1.097037	2.970702
H	6.884427	0.832924	1.396020
H	5.897254	0.332937	2.778061
H	6.393107	2.014032	2.613340
H	5.325374	3.574420	1.119419
H	1.571145	0.035747	-1.381926
C	1.463460	2.169491	-0.900690
H	0.724352	-0.799012	0.735012
H	0.463694	0.886338	1.342916
H	2.334334	2.389365	-1.519021
H	0.571768	2.435995	-1.490693
H	1.460517	2.807933	-0.013980

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TS with propylene 3:

C	3.140033	1.661670	-1.241128
C	2.444097	0.446113	-1.148125
C	2.942758	-0.548590	-2.005055
C	3.959197	-0.350783	-2.934864
C	4.575597	0.892459	-3.017639
C	4.165193	1.901351	-2.155946

B	1.303280	0.090245	-0.030804
C	0.728444	1.337141	0.865666
C	0.534771	1.292280	2.254476
C	0.011229	2.344997	3.006676
C	-0.379859	3.518180	2.375236
C	-0.241249	3.611642	0.994623
C	0.296045	2.540779	0.287685
F	0.820920	0.184912	2.968340
F	-0.133719	2.220760	4.333328
F	-0.894936	4.532478	3.077833
F	-0.631619	4.724145	0.355986
F	0.369450	2.721239	-1.052795
F	2.447588	-1.804102	-1.954480
F	4.357456	-1.351659	-3.733162
F	5.555792	1.107804	-3.900636
F	4.772397	3.095475	-2.191850
F	2.885544	2.686698	-0.407712
C	1.875817	-1.186717	0.819098
C	1.520324	-2.533098	0.764543
C	2.175435	-3.540266	1.474545
C	3.260016	-3.221937	2.280242
C	3.671932	-1.894509	2.360470
C	2.986534	-0.928079	1.635109
F	0.496077	-2.965772	-0.013290
F	1.767447	-4.814493	1.372195
F	3.900938	-4.174766	2.966840
F	4.718992	-1.563394	3.128444
F	3.436207	0.340218	1.751082
C	-0.357335	-0.258882	-1.196687
C	-1.183632	-0.656782	-0.142181
P	-3.902255	-0.552520	-0.555168
C	-4.425118	0.910610	-1.727088
C	-5.882463	0.877484	-2.230324
C	-4.594522	-2.226226	-1.274497
C	-4.300798	-2.317068	-2.787874
C	-4.693587	-0.256374	1.204273
C	-6.161425	0.218802	1.201354
C	-6.103337	-2.469418	-1.064563
C	-3.793910	-3.380561	-0.622813
C	-4.599735	-1.547928	2.047326
C	-3.832670	0.789206	1.956618
C	-4.183085	2.260410	-1.014915
C	-3.470932	0.905994	-2.945858
H	-6.374811	-2.553459	-0.010052
H	-6.719754	-1.686400	-1.513401
H	-6.379852	-3.418704	-1.543178
H	-4.143256	-4.332013	-1.044520
H	-3.916659	-3.443087	0.458551
H	-2.724277	-3.302356	-0.841443
H	-5.274244	-2.335865	1.706709
H	-4.882735	-1.306660	3.079953
H	-3.581412	-1.949225	2.078243
H	-4.291453	0.978491	2.935692
H	-2.820993	0.418816	2.147397
H	-3.753275	1.748500	1.446152
H	-6.515161	0.285390	2.239236
H	-6.826761	-0.468146	0.673250
H	-6.278603	1.212081	0.761395
H	-4.539786	-3.334329	-3.123558
H	-3.244987	-2.141849	-3.016261

H	-4.907395	-1.632765	-3.384796
H	-3.162738	2.348227	-0.627388
H	-4.885135	2.449371	-0.200302
H	-2.426868	1.006098	-2.638154
H	-3.711292	1.768591	-3.580937
H	-3.560683	0.014222	-3.565868
H	-6.610963	0.887248	-1.416319
H	-6.088174	0.008917	-2.860593
H	-6.065447	1.769453	-2.844966
H	-4.318421	3.065678	-1.748063
H	-1.319196	-1.707148	0.076343
H	-1.384298	0.022247	0.672844
C	-0.247458	-1.143207	-2.424429
H	-0.396922	0.797649	-1.445069
H	0.528472	-0.793085	-3.107821
H	-0.042131	-2.184038	-2.171896
H	-1.198023	-1.103330	-2.974483

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TS with propylene 4:

C	3.740586	0.667334	-1.107272
C	2.580600	-0.123685	-1.113803
C	2.685312	-1.263123	-1.926177
C	3.784046	-1.560246	-2.727300
C	4.887970	-0.715612	-2.712509
C	4.864733	0.402542	-1.888491
B	1.317486	0.115341	-0.101944
C	1.120539	1.610598	0.519369
C	0.632195	1.848598	1.810999
C	0.430098	3.118546	2.348043
C	0.700611	4.241376	1.575166
C	1.153386	4.066545	0.271644
C	1.340631	2.778813	-0.222204
F	0.265442	0.822226	2.612865
F	-0.041790	3.261760	3.594660
F	0.506409	5.469030	2.068156
F	1.394644	5.134774	-0.500628
F	1.740885	2.703247	-1.509854
F	1.687139	-2.177646	-1.965101
F	3.790788	-2.660973	-3.492267
F	5.957690	-0.983209	-3.467456
F	5.930997	1.211248	-1.833626
F	3.854302	1.735937	-0.299931
C	1.378650	-1.102797	0.995618
C	0.603996	-2.256531	1.114310
C	0.833240	-3.258902	2.057164
C	1.899958	-3.144725	2.937841
C	2.715262	-2.018888	2.861817
C	2.443202	-1.045693	1.907457
F	-0.476918	-2.473337	0.316131
F	0.026612	-4.328991	2.112721
F	2.137148	-4.096068	3.847083
F	3.749748	-1.884550	3.701320
F	3.272489	0.018893	1.886044
C	-0.285907	-0.153142	-1.384740
C	-1.146545	0.250324	-0.378702
P	-3.934595	-0.199869	-0.607439
C	-4.913893	1.389368	-1.160136
C	-6.393124	1.178688	-1.541211
C	-4.390277	-1.669707	-1.797763

C	-4.308081	-1.193037	-3.264619
C	-4.465389	-0.673511	1.207765
C	-5.977743	-0.605922	1.501244
C	-5.771481	-2.318255	-1.576031
C	-3.288464	-2.746907	-1.645916
C	-3.967065	-2.099426	1.537396
C	-3.724219	0.268164	2.191525
C	-4.848759	2.455372	-0.043940
C	-4.157495	2.000207	-2.365502
H	-5.855757	-2.799719	-0.598878
H	-6.592276	-1.603058	-1.674712
H	-5.924594	-3.100212	-2.332547
H	-3.475660	-3.545233	-2.376242
H	-3.262179	-3.210100	-0.660190
H	-2.295460	-2.336957	-1.850036
H	-4.530286	-2.877266	1.017333
H	-4.102309	-2.271669	2.613002
H	-2.903624	-2.237222	1.317979
H	-3.985350	-0.026603	3.216321
H	-2.635776	0.190702	2.107288
H	-3.996696	1.317612	2.081325
H	-6.158373	-0.941848	2.531637
H	-6.562434	-1.250268	0.840164
H	-6.373859	0.409682	1.422809
H	-4.386686	-2.071102	-3.918433
H	-3.352180	-0.707458	-3.487303
H	-5.117477	-0.514353	-3.541860
H	-3.822826	2.646661	0.288400
H	-5.454061	2.200118	0.828261
H	-3.110805	2.208135	-2.120072
H	-4.630016	2.954380	-2.633441
H	-4.174838	1.369848	-3.254484
H	-6.979174	0.755819	-0.721269
H	-6.514197	0.531755	-2.413423
H	-6.839669	2.149456	-1.797369
H	-5.240871	3.399955	-0.442425
H	-1.312129	-0.369530	0.487050
H	-1.426679	1.292510	-0.280316
H	-0.139706	-1.219415	-1.491506
C	-0.174132	0.639598	-2.669420
H	0.782053	0.471601	-3.171096
H	-0.968238	0.323301	-3.360245
H	-0.281274	1.714956	-2.505202

VII. Computed electronic energies, thermochemistry and solvation data

Table S1. Total energies of calculated structures at the B3LYP/6-31G(d) and SCS-MP2/cc-pVTZ levels; zero-point energy values and thermal corrections to the enthalpy at the B3LYP/6-31G(d) level; solvation Gibbs free energies at the IEFPCM-UA0/B3LYP/6-31G(d) level. All values are given in hartree except solvation free energies which are in kcal/mol.

	Electronic energies		Corrections		Solvation free energy
	B3LYP	SCS-MP2	Zero-point	Enthalpy	
$(t\text{Bu})_3\text{P}$	-814.875650	-813.333907	0.371379	0.390146	9.4
$\text{B}(\text{C}_6\text{F}_5)_3$	-2208.231110	-2204.840245	0.153557	0.183577	13.6
C_2H_4	-78.5874586	-78.404708	0.051219	0.054261	2.9
C_3H_6	-117.904239	-117.628482	0.079630	0.083170	not calculated
$(t\text{Bu})_3\text{P}\cdots\text{B}(\text{C}_6\text{F}_5)_3$	published earlier, see Ref. 8 of the paper				26.5
$\text{B}(\text{C}_6\text{F}_5)_3\cdots\text{C}_2\text{H}_4$	-2286.822200	-2283.250935	0.205644	0.239808	17.0
ternary complex	-3101.704604	-3096.597991	0.577956	0.632145	30.1
TS	-3101.675550	-3096.576015	0.579954	0.631510	26.3
product	-3101.725196	-3096.646977	0.584886	0.635221	18.5
TS, propylene 1	-3140.993258	-3135.805426	0.609101	0.661472	23.5
TS, propylene 2	-3140.992852	-3135.805129	0.608582	0.661193	25.1
TS, propylene 3	-3140.987413	-3135.803404	0.608620	0.661446	25.7
TS, propylene 4	-3140.980033	-3135.796479	0.609184	0.660725	27.3