Supplementary Information for

"*Computing Reliable Energetics for Conjugate Addition Reactions*"

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Contents:

I. Full reference 15; references for basis sets employed

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II. Additional computational details

The calculations for the present study were carried out with the Gaussian 03, NWChem and Turbomole packages as shown below:

- Gaussian 03: B3LYP/6-31G(d) geometry optimizations and frequency calculations, G3MP2B3 calculations
- NWChem: all single-point DFT calculations
- Turbomole: all single-point MP2 and SCS-MP2 calculations (both in RI approximation)

The 6-31G(d) and 6-311++G(3df,3pd) basis sets were used with cartesian harmonics (6*d*/10*f* functions), in the case of the TZVP (DFT orbital) and cc-pVTZ basis sets spherical harmonics (5*d*/7*f* functions) were employed. For DFT calculations, the default integration grid in Gaussian 03, and the built-in 'fine' grid in NWChem was used.

In the case of DFT methods, the energetics of the five conjugate addition reactions has been calculated using both the 6-311++G(3df,3pd) and the TZVP (DFT orbital) basis sets (see Table S1). Not only the statistics, but even the individual reaction energies are in remarkably good agreement, the largest difference being 1.2 kcal/mol. We therefore decided to use the TZVP (DFT orbital) basis set for the further DFT calculations, which has an outstanding performance/cost ratio.

The quality of approximated functionals and perturbation methods for reactions shown in Scheme 1 has been evaluated by comparing the predicted reaction energies to those obtained from G3MP2B3 calculations. To allow the comparison of electronic energies, the G3MP2B3 electronic energies are also needed, which can be obtained from Gaussian 03 output by subtracting the scaled zero-point energy value (given as 'E(ZPE)' at the end of output along with other G3MP2B3 results) from the 0 K energy (termed 'G3MP2(0 K)').

Accuracy of the G3 family of methods has been assessed on various test sets in the literature. G3MP2B3[17] (originally termed as G3(MP2)//B3LYP) has an average error of 1.25 kcal/mol on the G2/97 test set[S1,S2] of experimental enthalpies of formation, ionization potentials and electron affinities. G3(MP2) provides an average error of 1.31 kcal/mol on the extended G3/99 test set;[S3] the use of density functional geometries was reassured during the development of G3X methods.[S4] G3MP2B3 estimations of enthalpies of formation of C_1–C_{16} alkanes had absolute errors of less than 2 kcal/mol, with small accumulation of error (around 0.04 kcal/mol per bond).[S5] One may therefore expect G3MP2B3 to provide energetics with a mean absolute deviation of around 2 kcal/mol for the investigated molecules.

Geometries of all stable species and transition states were optimized at the B3LYP/6-31G(d) level of theory without constraints. Stationary points were characterized as true local minima and first-order saddle points by calculating and inspecting the harmonic vibrational frequencies (zero and one imaginary frequency, respectively).

Thermodynamic data given in the Supplementary Information have been obtained using standard formulae in the ideal gas approximation (temperature 298.15 K, pressure 1 atm) as implemented in Gaussian 03 based on unscaled B3LYP/6-31G(d) frequencies.

For each addition reaction in Scheme 1, the most stable tautomer of the product was chosen. In order to avoid biasing the results with tautomerization energies, those tautomers of the reactants were used that correspond to the products, i.e., *keto*-acetylacetone (acac) form was used in (5) although it is the less stable tautomer of acac. In the mechanistic studies of the model reaction we used the more stable *enol* form of acac.

Reaction (4) yields a product with two nonequivalent stereocentres; the (*S,S*) isomer was used for energy calculations.

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III. Notation of species and stationary points

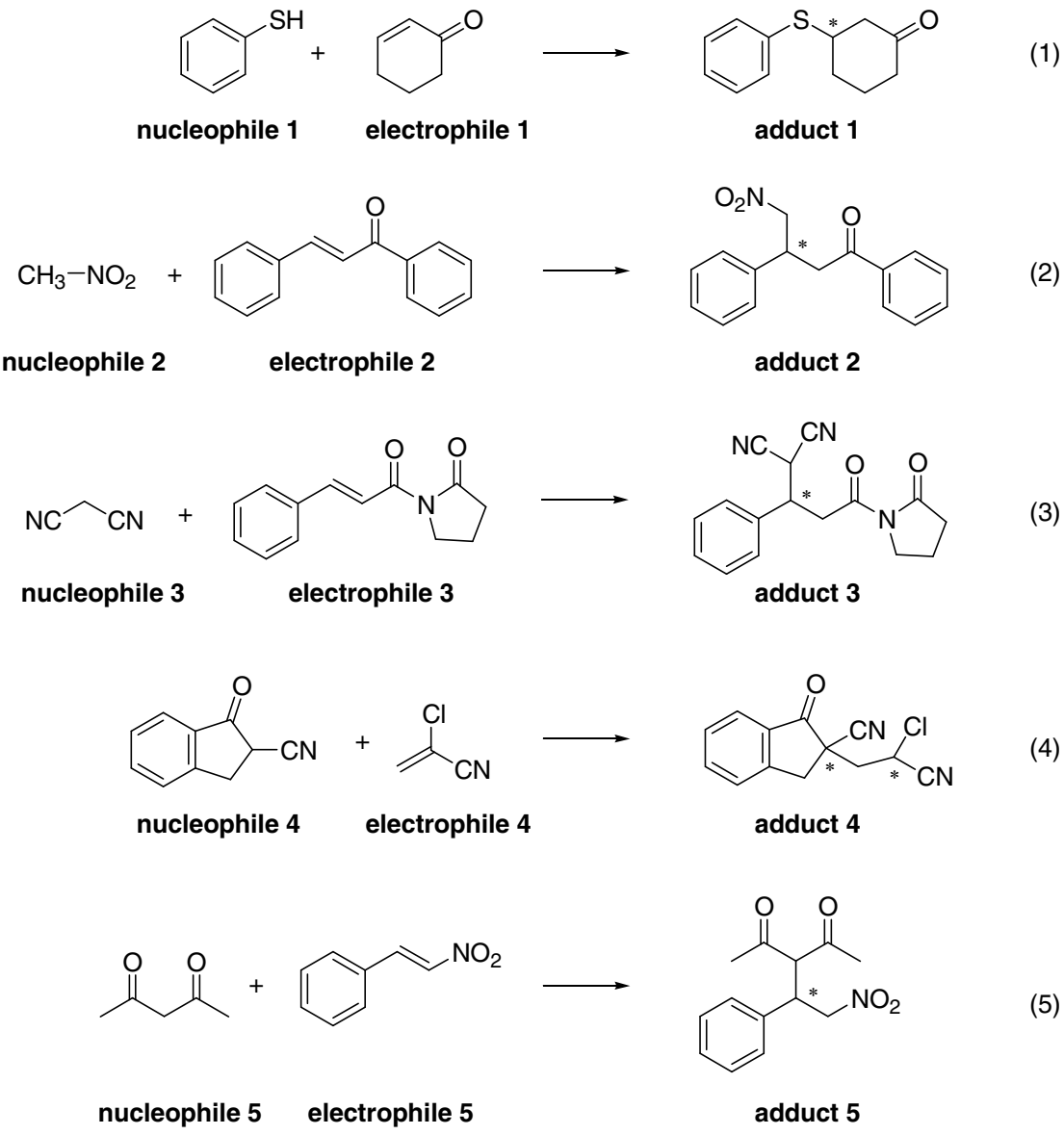


Figure S1. Notation of reactants and products of addition reactions.

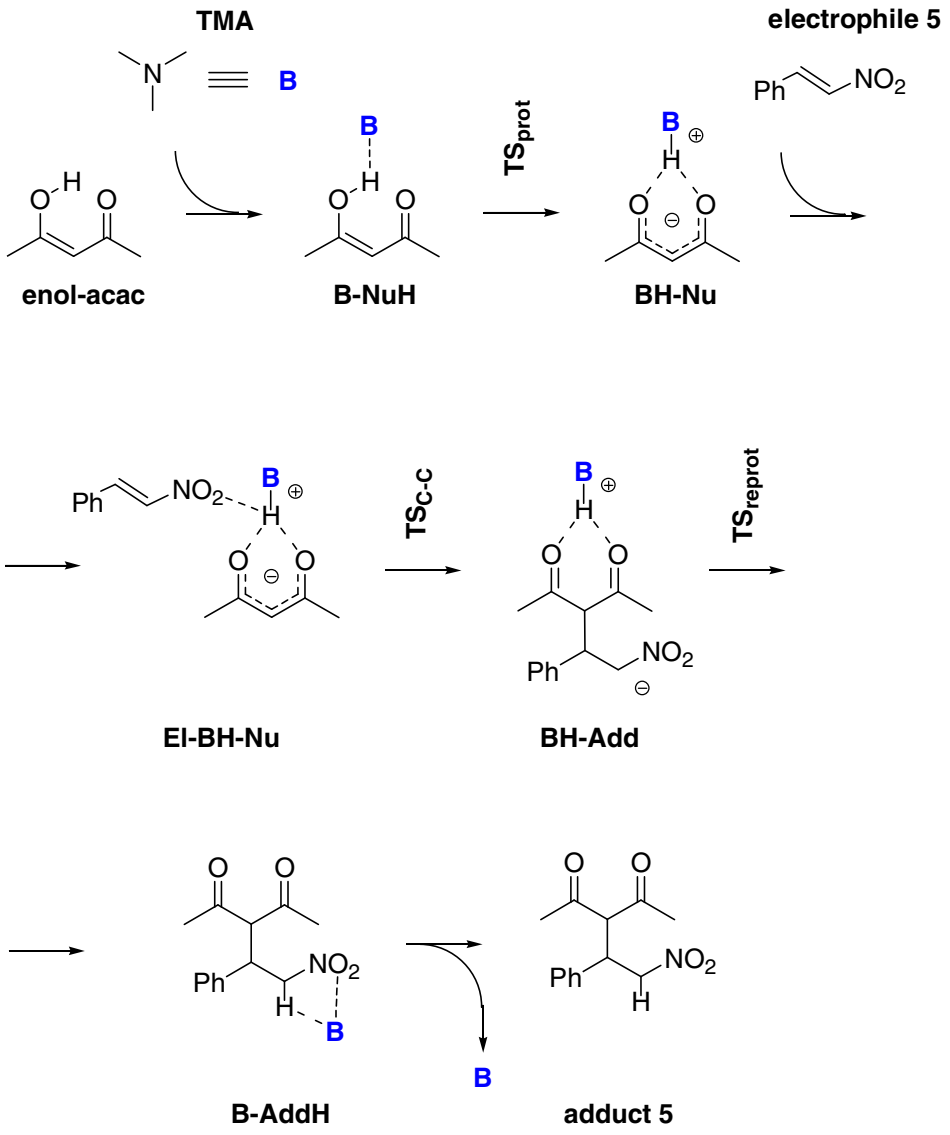


Figure S2. Full catalytic cycle of the trimethylamine-catalyzed reaction of *enol*-acac and β-nitrostyrene with notation of stationary points.

IV. 3D structures of stationary points of the model reaction

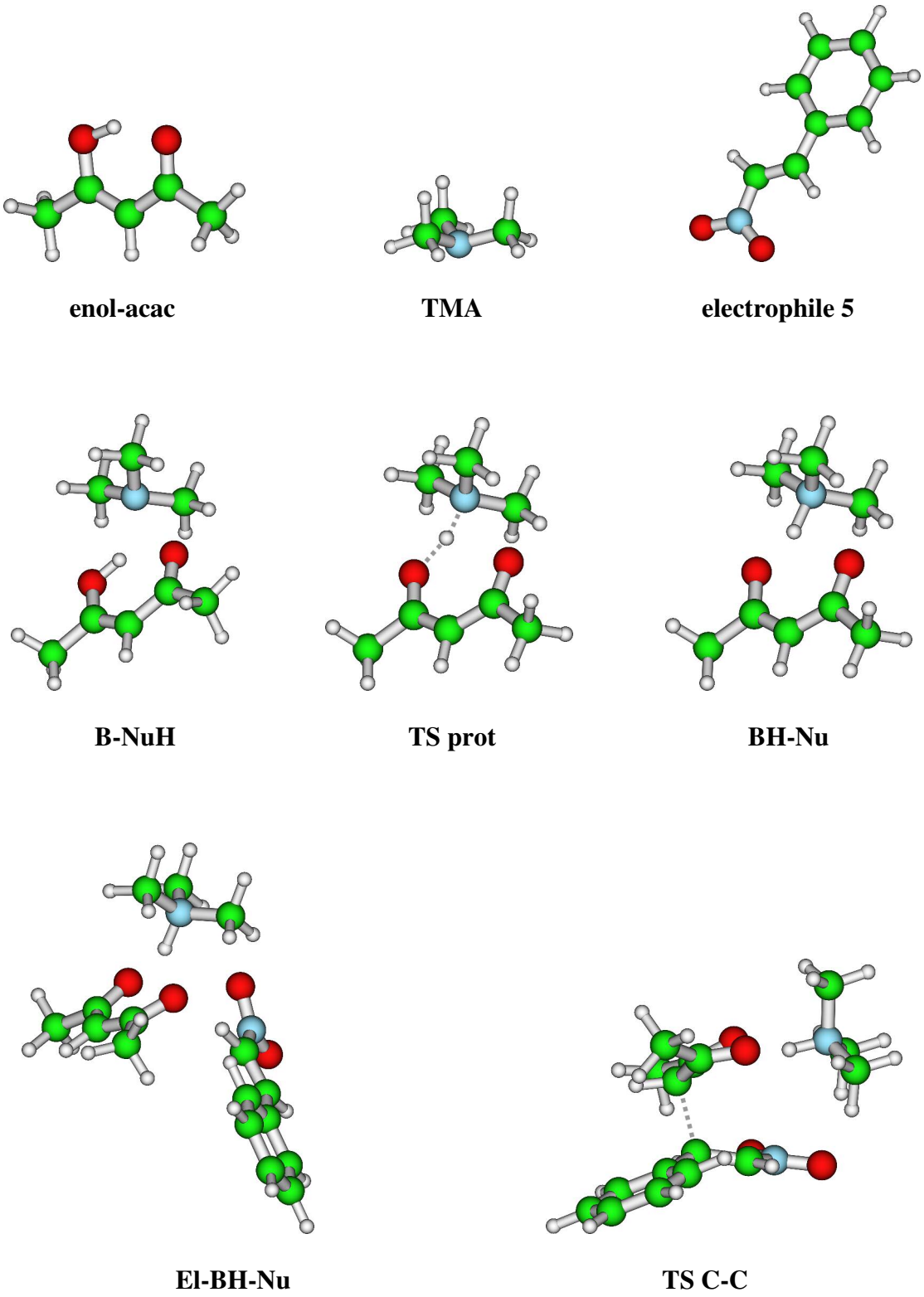
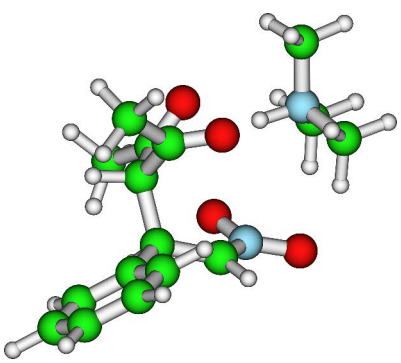
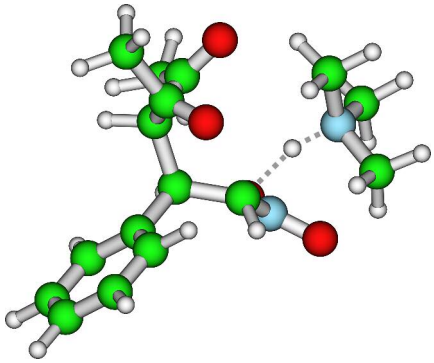


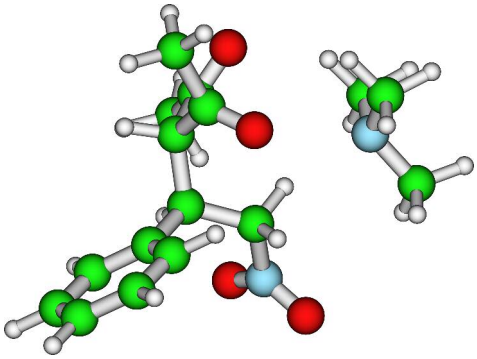
Figure S3/1. 3D structures of stationary points of the model reaction.



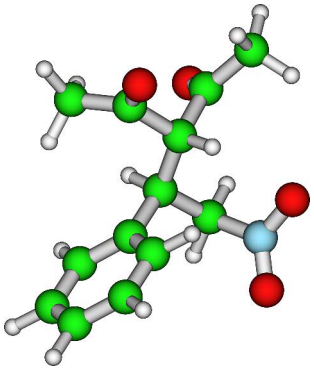
BH-Add



TS reprot



B-AddH



adduct 5

Figure S3/2. 3D structures of stationary points of the model reaction.

V. Description of reaction pathways referred to in Table 1

This paragraph is meant to give a brief summary of the results published in ref. 19d to aid understanding of data in Table 1 of the paper.

Recently, our research group published (ref. 19 (d): *J. Am. Chem. Soc.* **2006**, *128*, 13151–13160) studies concerning the mechanism of the enantioselective addition of acetylacetone to β-nitrostyrene catalyzed by a bifunctional organocatalyst developed by Takemoto et. al. (ref. 9 (d): *J. Am. Chem. Soc.* **2005**, *127*, 119–125). This catalyst, shown in Figure S4, has both basic (tertiary amine) and Lewis-acidic (thiourea) functionalities.

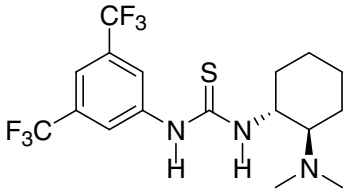


Figure S4. Takemoto's organocatalyst.

According to the concept proposed by Takemoto and co-workers, the amine functionality deprotonates the enol form of acetylacetone, thus enhancing its nucleophilicity. In their model, the deprotonated nucleophile remains bound to the protonated amine group, while the nitrostyrene electrophile is activated by two hydrogen bonds between its nitro group and the thiourea hydrogens. This is rationalized by the known affinity of the nitro group to bind to the thiourea moiety. C-C bond formation takes place from this ternary complex in which both reactants are activated. This mechanism was called 'route A'.

In our previous work, we first studied conformational properties of the catalyst. We identified 5 minima on the B3LYP/6-31G(d) potential energy surface of which one (earlier termed as $\mathbf{1a_1}$) corresponds to the solid phase X-ray structure. Although this is not the lowest lying conformer, it has the optimal arrangement of functional groups for double H-bonding and the dual activation concept; our calculations indeed showed that the most stable catalyst–reactant adducts are formed from $\mathbf{1a_1}$. This conformer is shown in Figure S5 for illustration.

We furthermore investigated the possible reaction routes. Besides 'route A', identification of a second pathway, termed 'route B', was possible. In the ternary complex of this mechanism, the roles of the protonated amine and thiourea hydrogens are interchanged: the nucleophile anion is bound to the thiourea, while the protonated amine provides activation of the electrophile.

Based on B3LYP/6-311++G(d,p)//B3LYP/6-31G(d) calculations, we concluded in our paper, that, for this reaction, route B is energetically favored over route A, and both pathways account qualitatively for the observed enantioselectivity.

Figure S6 illustrates a schematic representation of the C-C bond forming transition states (TSs) on both reaction routes, leading to both enantiomeric products. Relative energies of these TSs have been calculated using various methods in our present study,

and are shown in Table 1 of the present paper. Cartesian coordinates of the four TSs are given in section VIII of the Supplementary Information.

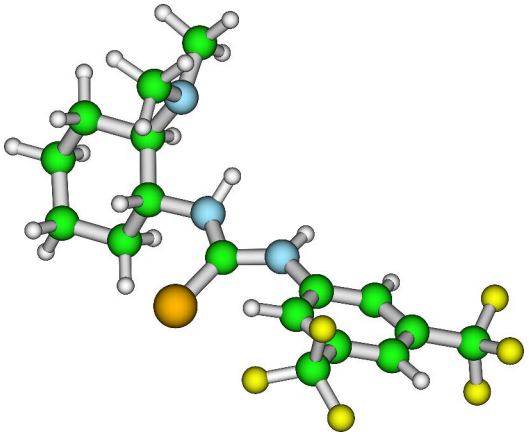


Figure S5. Conformer **1a**$_1$ of Takemoto's catalyst (see text above for details).

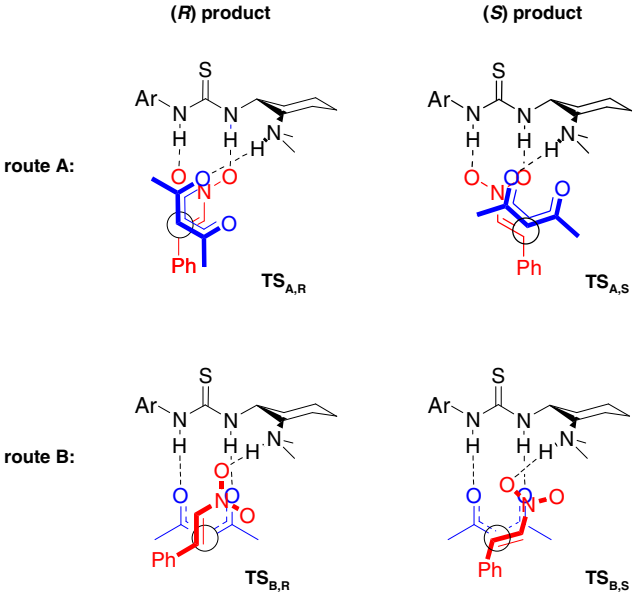


Figure S6. C-C bond forming transition states on both routes leading to both products. Electrophile is shown in red, deprotonated nucleophile in blue.

VI. Calculated energetics including Gibbs free energies of addition reactions

	(1)	(2)	(3)	(4)	(5)	MAD	MAX
B3LYP/6-31G(d)	-15.3	-14.0	-13.1	-18.6	-12.1	9.6	14.3
G3(MP2)//B3LYP	-21.4	-23.2	-24.3	-25.5	-26.4		
MP2/cc-pVTZ	-24.2	-24.8	-26.7	-29.0	-29.2	2.6	3.5
SCS-MP2/cc-pVTZ	-20.7	-21.8	-23.1	-25.4	-25.0	1.0	1.5
B3LYP/6-311++G(3df,3pd)	-9.3	-9.8	-9.5	-14.2	-7.2	14.1	19.2
B3LYP/TZVP (DFT orbital)	-9.8	-10.1	-9.7	-15.1	-7.5	13.7	18.9
TPSS/6-311++G(3df,3pd)	-11.3	-10.3	-10.4	-15.4	-8.7	12.9	17.7
TPSS/TZVP (DFT orbital)	-11.4	-10.0	-10.1	-15.8	-8.2	13.1	18.2
TPSSh/6-311++G(3df,3pd)	-12.8	-12.4	-12.4	-17.2	-10.8	11.0	15.6
TPSSh/TZVP (DFT orbital)	-12.9	-12.1	-12.2	-17.6	-10.4	11.1	16.0
MPW1K/6-311++G(3df,3pd)	-18.3	-20.2	-20.1	-23.6	-18.4	4.0	8.0
MPW1K/TZVP (DFT orbital)	-18.8	-20.2	-20.0	-24.3	-18.2	3.9	8.2
PWB6K/6-311++G(3df,3pd)	-18.1	-20.7	-20.4	-23.3	-20.1	3.6	6.3
PWB6K/TZVP (DFT orbital)	-18.8	-20.9	-20.7	-24.2	-20.1	3.2	6.3
M05/6-311++G(3df,3pd)	-15.7	-16.8	-16.4	-19.9	-15.0	7.4	11.4
M05/TZVP (DFT orbital)	-16.8	-17.5	-17.1	-21.1	-15.6	6.5	10.8
M05-2X/6-311++G(3df,3pd)	-21.5	-22.8	-23.5	-26.1	-23.8	0.9	2.6
M05-2X/TZVP (DFT orbital)	-22.0	-23.1	-23.5	-26.9	-24.0	1.1	2.4
M06/6-311++G(3df,3pd)	-19.0	-19.8	-20.0	-23.1	-20.6	3.7	5.8
M06/TZVP (DFT orbital)	-19.4	-19.6	-19.6	-23.3	-20.4	3.7	6.0
M06-2X/6-311++G(3df,3pd)	-20.9	-23.1	-23.4	-25.2	-24.2	0.8	2.2
M06-2X/TZVP (DFT orbital)	-21.5	-23.2	-23.4	-26.1	-24.2	0.8	2.2

Table S1. Net electronic energies of conjugate addition reactions (1)–(5) using various methods; mean (MAD) and maximum (MAX) absolute deviations from G3MP2B3 data. Values are given in kcal/mol. Note the good agreement between values obtained with 6-311++G(3df,3pd) and TZVP (DFT orbital) basis sets. Data for MP2, SCS-MP2, and DFT/6-311++G(3df,3pd) were used to obtain Figure 1 in the paper.

	(1)	(2)	(3)	(4)	(5)
B3LYP/6-31G(d)					
Reaction electronic energy	-15.3	-14.0	-13.1	-18.6	-12.1
Reaction enthalpy	-11.6	-11.5	-11.0	-15.9	-9.4
Reaction Gibbs free energy	1.4	2.8	2.1	-3.1	4.4
B3LYP/6-311++G(3df,3pd)//B3LYP/6-31G(d)					
Reaction electronic energy	-9.3	-9.8	-9.5	-14.2	-7.2
Reaction enthalpy	-5.6	-7.3	-7.4	-11.6	-4.6
Reaction Gibbs free energy	7.4	7.0	5.7	1.3	9.2

Table S2. Thermodynamic data for conjugate addition reactions (1)–(5) using B3LYP electronic energies obtained with different basis sets, and employing corrections from unscaled B3LYP/6-31G(d) harmonic frequencies. Values are given in kcal/mol. Note endergonic reactions (marked in red).

VII. Calculated reaction profile of the model reaction

	MP2/ cc-pVTZ	SCS-MP2/ cc-pVTZ	B3LYP/ TZVP (DFT orbital)	M06-2X/ TZVP (DFT orbital)
BH-Nu + electrophile 5	0.0	0.0	0.0	0.0
El-BH-Nu	-12.7	-10.7	-3.7	-9.7
TS C-C	-5.0	1.3	14.2	-1.0
BH-Add	-13.0	-8.9	9.8	-11.3
TS reprot	-8.7	-3.8	16.1	-3.2
B-AddH	-27.4	-27.0	-3.5	-19.4
TMA + adduct 5	-21.4	-22.1	-2.2	-14.8

Table S3. Calculated relative electronic energies of stationary points of the trimethyamine-catalyzed model reaction (data used to obtain Figure 2 in the paper). Values are given in kcal/mol. Isolated BH-Nu complex + electrophile 5 were used as reference.

VIII. Cartesian coordinates of all calculated stationary points

B3LYP/6-31G(d) optimized geometries of stationary points. Geometries are given in standard XYZ format: coordinates are Cartesian coordinates in the usual order, units are 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.

```
 13
nucleophile 1
C    -0.201628   -1.209382    0.000382
C    -1.595455   -1.201760    0.000091
C    -2.298272    0.004765   -0.000077
C    -1.591498    1.207702   -0.000122
C    -0.196189    1.210962   -0.000193
C     0.506769   -0.000115    0.000162
S     2.294135   -0.083571   -0.000570
H     2.517484    1.246462    0.007432
H     0.340265    2.156133   -0.000595
H    -2.124781    2.154790   -0.000227
H    -3.384405    0.006938   -0.000137
H    -2.133014   -2.146312    0.000226
H     0.335932   -2.153898    0.000951

 15
electrophile 1
C    -1.143328    0.022299    0.017947
C    -0.380700    1.289582   -0.052165
C     0.960633    1.326194    0.025091
C     1.819036    0.093843    0.132633
C     1.076271   -1.163504   -0.342504
C    -0.328557   -1.243478    0.270631
O    -2.361352    0.001651   -0.079856
H    -0.251929   -1.366220    1.362506
H    -0.898618   -2.098712   -0.104940
H     1.652991   -2.062915   -0.097749
H     0.989230   -1.130072   -1.436557
H     2.138645   -0.025431    1.181136
H     2.743886    0.236190   -0.441043
H     1.470713    2.289079    0.013662
H    -0.974228    2.195252   -0.147964

 28
adduct 1
C    -4.058006    0.617261    0.279343
C    -3.067033    1.462551   -0.223581
C    -1.809977    0.953410   -0.555123
C    -1.537743   -0.410994   -0.376285
C    -2.536485   -1.257250    0.125130
C    -3.791440   -0.742463    0.453190
S     0.054534   -1.089441   -0.856684
C     1.046744   -0.933897    0.718638
C     2.435150   -1.546474    0.460937
C     3.282692   -0.714514   -0.515253
C     3.394014    0.760023   -0.071379
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C 2.033617 1.361414 0.255379
C 1.173050 0.524734 1.195524
O 1.662896 2.432650 -0.185681
H 3.878906 1.379872 -0.830885
H 4.004072 0.813819 0.843981
H 2.838405 -0.754556 -1.516346
H 4.285472 -1.149688 -0.599291
H 1.661256 0.513435 2.183396
H 0.198780 1.003839 1.314259
H 2.328963 -2.572964 0.091312
H 2.951843 -1.612225 1.429694
H -4.561691 -1.404502 0.840091
H -5.036785 1.016233 0.532095
H -3.270812 2.520987 -0.361788
H 0.520215 -1.519851 1.479006
H -2.327417 -2.315919 0.247790
H -1.034414 1.608588 -0.940040

7
nucleophile 2
N 0.000000 0.174004 0.000000
O 1.070216 0.773221 0.000000
O -1.113895 0.688861 0.000000
C 0.041145 -1.324819 0.000000
H 1.081751 -1.640866 0.000000
H -0.489592 -1.662453 0.891315
H -0.489592 -1.662453 -0.891315

28
electrophile 2
O 2.465664 -0.186977 -0.110111
C 1.435664 0.484369 -0.077276
C 0.100822 -0.162577 -0.032539
C 1.521687 1.984304 -0.100696
H -0.784033 0.460404 -0.104735
C 0.002754 -1.503719 0.068389
H 0.945221 -2.046838 0.127338
C -1.209869 -2.319147 0.108310
C -2.508976 -1.782058 0.011240
H -2.643940 -0.710298 -0.100773
C -3.626050 -2.608867 0.053850
H -4.619755 -2.175935 -0.023593
C -3.475397 -3.992679 0.194530
H -4.350766 -4.635547 0.227453
C -2.196491 -4.542423 0.291542
H -2.070030 -5.616076 0.400320
C -1.077593 -3.713365 0.248044
H -0.081567 -4.142855 0.322807
C 0.443075 2.830652 0.199556
H -0.522003 2.419230 0.476757
C 0.602508 4.216436 0.175773
H -0.238578 4.860353 0.418167
C 1.838198 4.773536 -0.156134
H 1.959309 5.853358 -0.179771
C 2.920132 3.939406 -0.453946
H 3.884711 4.369537 -0.709938

C 2.763574 2.557632 -0.419958
H 3.591882 1.891481 -0.637253

35
adduct 2
C 2.986013 -0.995920 -0.907180
C 2.875963 -0.209606 0.250370
C 4.044961 0.202452 0.910913
C 5.296128 -0.164127 0.426142
C 5.396146 -0.947816 -0.727476
C 4.240722 -1.362347 -1.392605
C 1.558865 0.214649 0.822096
O 1.512901 0.913785 1.827421
C 0.277779 -0.256415 0.138734
C -1.005134 0.252965 0.823556
C -1.209988 1.783500 0.714020
N -1.543565 2.250897 -0.676910
O -0.686919 2.086411 -1.549701
C -2.245719 -0.528960 0.410479
C -2.583980 -0.727583 -0.936856
C -3.731224 -1.441039 -1.285163
C -4.560189 -1.970124 -0.294654
C -4.234437 -1.780131 1.048573
C -3.086662 -1.065742 1.394266
O -2.640703 2.763936 -0.860481
H 0.271122 -1.354502 0.149130
H -0.860990 0.108702 1.900726
H -2.837524 -0.924973 2.444077
H -4.870600 -2.189394 1.828907
H -5.452623 -2.526449 -0.568160
H -3.977590 -1.581130 -2.334260
H -1.954360 -0.319852 -1.722777
H 3.943297 0.810680 1.803631
H 6.194766 0.159614 0.944015
H 6.373235 -1.233920 -1.107610
H 4.316284 -1.969553 -2.290279
H 2.097147 -1.323109 -1.436964
H 0.306423 0.040704 -0.914037
H -0.295317 2.304800 0.999775
H -2.046007 2.106496 1.333003

7
nucleophile 3
C -1.223940 0.025677 -0.002030
C -0.000057 0.839553 0.000369
N -2.202598 -0.595162 0.000868
C 1.224481 0.026590 0.000130
N 2.202292 -0.595593 -0.000038
H 0.000693 1.493966 -0.880662
H -0.001458 1.490396 0.884042

29
electrophile 3
C 3.678763 -1.199915 -0.013411
C 2.640151 -0.250512 -0.008740
C 2.985677 1.115220 -0.042167

C 4.318752 1.508966 -0.079011
C 5.339052 0.551551 -0.083361
C 5.014490 -0.805218 -0.050305
C 1.258025 -0.725999 0.030042
C 0.136832 0.023148 0.038398
C -1.173535 -0.653453 0.077036
O -1.314515 -1.871123 0.104936
N -2.340668 0.146185 0.069456
C -3.644531 -0.541650 0.082845
C -4.645997 0.567271 -0.280860
C -3.968842 1.844650 0.228825
C -2.474833 1.539354 0.155720
H 2.205110 1.869989 -0.038910
H 4.566478 2.566715 -0.104430
H 6.379422 0.863949 -0.112207
H 5.800443 -1.555546 -0.053267
H 3.426767 -2.257379 0.012241
H -4.767650 0.615655 -1.368605
H -4.195468 2.749608 -0.339942
H 0.143651 1.104681 0.021802
H 1.126760 -1.806810 0.053436
H -5.631308 0.389613 0.157787
H -4.214766 2.047970 1.279983
O -1.579531 2.362375 0.187186
H -3.627919 -1.373378 -0.622689
H -3.829855 -0.960217 1.079883

36
adduct 3
C -3.830785 -0.244960 0.324272
N -2.510680 -0.181171 -0.331614
C -2.611337 -0.046846 -1.730446
C -4.096810 -0.018271 -2.070746
C -4.787564 -0.597645 -0.828709
C -1.358055 -0.166858 0.455718
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C -0.009060 -0.099753 -0.241613
C 1.178967 -0.196686 0.734338
C 1.233065 1.059622 1.689384
H 0.277552 1.069273 2.230185
C 2.497204 -0.455426 0.021112
C 2.901247 0.293216 -1.094606
C 4.120538 0.031626 -1.719997
C 4.953952 -0.981583 -1.243693
C 4.561843 -1.732657 -0.135395
C 3.343092 -1.469450 0.490090
C 1.343719 2.331868 0.957193
N 1.380660 3.322250 0.353791
H 2.270867 1.088764 -1.479853
H 4.417564 0.622564 -2.582011
H 5.902557 -1.183787 -1.733503
H 5.203042 -2.522878 0.245293
H 3.046487 -2.055357 1.356757
H -4.872721 -1.685835 -0.920190
H -4.280703 -0.563336 -2.999482
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H -4.376315 1.029497 -2.245279
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H 0.032555 0.810078 -0.850237
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19
nucleophile 4
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C -1.918377 -1.475909 -0.016499
C -3.051228 -0.679257 -0.198030
C -2.957561 0.720939 -0.253778
C -1.720828 1.344399 -0.124102
C -0.591693 0.540379 0.062574
H -2.008730 -2.558542 0.019807
H -4.024558 -1.151953 -0.299394
H -3.856075 1.314279 -0.396332
H -1.615602 2.424723 -0.160421
C 0.804297 0.986051 0.233291
C 1.643406 -0.301995 0.550752
C 0.685007 -1.498863 0.280679
O 1.246385 2.111475 0.184364
C 2.901666 -0.357986 -0.186000
N 3.894050 -0.422294 -0.784901
H 1.880543 -0.242979 1.621710
H 0.978653 -2.033626 -0.629806
H 0.705989 -2.226690 1.098570

7
electrophile 4
C -1.296691 -0.201031 -0.000461
C -0.012763 0.429282 -0.001677
N -2.340589 -0.713486 0.000591
Cl 1.349353 -0.677776 0.000277
C 0.147815 1.755687 -0.000172
H -0.719330 2.407734 0.003196
H 1.134285 2.205231 0.001825

26
adduct 4
C -0.496996 1.013596 1.420915
C -1.541453 0.221503 0.930400
C -1.679587 -0.064902 -0.431340
C -0.760754 0.455466 -1.341977
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C 0.414780 1.533073 0.508807
C -2.608942 -0.425193 1.703452
C -3.604488 -1.091715 0.661389
C -2.856405 -0.977133 -0.707447
O -2.752318 -0.489975 2.903922
C -3.922843 -2.524263 1.161772
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H -0.420081 1.212095 2.485736
H -2.514231 -1.965280 -1.034962
H -3.502930 -0.594983 -1.502602
H -4.160129 -2.456604 2.227286
H -3.026098 -3.143432 1.058799
N -4.662413 -3.662536 -2.085662

15
nucleophile 5
C 1.073660 0.035179 -0.862037
C 1.633234 1.035709 -1.886570
C 2.900342 1.756791 -1.482946
C 0.123401 0.805622 0.069246
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H 1.875345 -0.392693 -0.254435
H 0.539161 -0.748094 -1.405865
H -1.872296 1.584743 0.252676
H -1.368301 1.189943 -1.428522
H -1.783877 -0.108872 -0.311764
H 3.121162 2.557841 -2.191009
H 2.792499 2.158264 -0.468041
H 3.739290 1.049286 -1.458265

18
electrophile 5
C 7.779977 -2.149812 -1.031653
C 6.566314 -1.474072 -0.984732
C 5.447843 -2.052496 -0.352501
C 5.589952 -3.326290 0.227883
C 6.806729 -4.002726 0.180318
C 7.905051 -3.416195 -0.449651
C 4.147037 -1.395263 -0.269417
C 3.817270 -0.190971 -0.758045
N 2.472950 0.329450 -0.593957
O 2.268141 1.446801 -1.077893
O 1.629682 -0.346567 0.000472
H 4.450169 0.500808 -1.295251
H 3.355064 -1.936241 0.243346
H 4.734303 -3.783176 0.718642
H 6.897054 -4.985485 0.634097
H 8.855583 -3.940813 -0.488656
H 8.633192 -1.690578 -1.522752
H 6.484792 -0.491993 -1.440822

33
adduct 5

C -3.551427 -0.988572 0.892625
C -2.234299 -0.705811 1.254805
C -1.319359 -0.201802 0.318874
C -1.759669 0.016198 -0.994345
C -3.076815 -0.266406 -1.358989
C -3.976116 -0.769734 -0.418626
C 0.102435 0.123719 0.762710
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H -0.542822 1.907309 1.844417
C 1.188710 -0.357215 -0.228150
C 1.134794 -1.876659 -0.533343
O 1.375372 -2.266066 -1.658729
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O 2.848693 -0.101645 1.495094
C 3.676307 0.137760 -0.748493
C 0.865875 -2.828987 0.613016
H 1.230040 1.809373 1.579644
N 0.116491 2.543606 -0.026284
H -1.079328 0.409437 -1.744248
H -3.398297 -0.091222 -2.381818
H -5.000276 -0.991026 -0.705832
H -4.242266 -1.381988 1.633384
H -1.910129 -0.878662 2.279394
H 0.289313 -0.384984 1.715139
H 1.094384 0.135408 -1.196849
H 1.084889 -3.848458 0.289965
H -0.186165 -2.768393 0.915226
H 1.476242 -2.567980 1.485269
H 3.588826 -0.598274 -1.555476
H 4.669521 0.101323 -0.296566
H 3.510667 1.126608 -1.194598
O -0.918008 3.189057 -0.141003
O 1.063944 2.575882 -0.816725

15
enol-acac
C -3.531315 5.573384 -0.016035
C -2.782970 4.280524 -0.123155
O -2.608300 3.668729 1.042770
C -2.313496 3.758947 -1.302539
C -1.599360 2.503060 -1.319578
C -1.101040 1.969515 -2.646886
O -1.384651 1.852006 -0.274352
H -2.482080 4.297326 -2.227834
H -2.996642 6.258801 0.651878
H -3.656516 6.047719 -0.991797
H -4.517910 5.396787 0.428054
H -0.414269 2.685252 -3.115119
H -0.586658 1.019266 -2.491799
H -1.937785 1.823876 -3.341001
H -2.098439 2.823370 0.833582

13
tma
C -2.252238 -0.196642 -0.935847
N -2.076447 1.233744 -0.738440

C	-2.573866	1.992972	-1.875287
C	-2.685990	1.677945	0.505361
H	-1.813654	-0.743483	-0.093551
H	-3.315594	-0.499955	-1.023917
H	-1.735471	-0.510522	-1.849811
H	-3.663703	1.870387	-2.042060
H	-2.373264	3.059607	-1.724338
H	-2.055953	1.675779	-2.787461
H	-3.784742	1.527734	0.533276
H	-2.487717	2.745317	0.654540
H	-2.249159	1.130606	1.348259

28
B-NuH

C	1.834402	1.519835	-4.210556
C	1.162481	1.789242	-2.873590
O	0.006769	1.388068	-2.667632
C	1.920545	2.518179	-1.878515
C	1.426688	2.819580	-0.637975
O	0.220956	2.493851	-0.187173
C	2.221324	3.578061	0.386019
N	-2.303666	1.220425	-0.706912
C	-3.053203	1.918509	-1.746271
C	-2.217872	-0.209046	-0.988093
C	-2.856014	1.476543	0.617557
H	-1.619149	-0.699409	-0.212507
H	-3.210531	-0.699403	-1.016722
H	-1.721032	-0.356407	-1.950292
H	-4.102140	1.571486	-1.823206
H	-3.065578	2.992538	-1.529963
H	-2.558838	1.767129	-2.709347
H	-3.895893	1.112132	0.729454
H	-2.845883	2.553012	0.817890
H	-2.237123	0.984719	1.375360
H	-0.322962	1.986158	-0.853404
H	2.751869	0.934792	-4.070030
H	1.150310	0.971453	-4.861309
H	2.123932	2.460894	-4.694455
H	2.926535	2.843964	-2.120141
H	3.212326	3.845019	0.012741
H	2.330262	2.974883	1.295052
H	1.686567	4.491831	0.670784

28
TSprot

C	1.758292	1.534258	-4.215863
C	0.994201	1.730044	-2.905440
C	1.675926	2.400678	-1.840896
C	1.168651	2.680167	-0.575905
C	2.058966	3.406048	0.418132
O	-0.172876	1.292551	-2.850195
O	0.002464	2.402841	-0.098359
N	-2.120560	1.329706	-0.730508
C	-2.722315	1.595100	0.595333
C	-2.856849	2.028236	-1.808275
C	-2.011865	-0.122989	-0.994154

H -1.410128 -0.576949 -0.202348
H -3.007124 -0.585430 -1.005564
H -1.505732 -0.255333 -1.949012
H -3.892793 1.669373 -1.858878
H -2.854492 3.100238 -1.593966
H -2.332427 1.849317 -2.745510
H -3.748252 1.209897 0.642309
H -2.723071 2.672180 0.773878
H -2.111675 1.115647 1.362942
H -0.989120 1.803891 -0.651857
H 2.773649 1.940732 -4.195210
H 1.808184 0.463654 -4.446752
H 1.201171 2.009707 -5.031683
H 2.692272 2.726408 -2.035024
H 3.046759 3.640788 0.013057
H 2.179333 2.791332 1.318341
H 1.572230 4.336831 0.733518

28
BH-Nu
C 1.724083 1.529994 -4.189927
C 0.981398 1.738022 -2.868597
O -0.190919 1.300730 -2.801059
C 1.677993 2.409279 -1.823022
C 1.178983 2.694763 -0.546634
O 0.022827 2.415321 -0.075947
C 2.089189 3.424989 0.432147
N -2.131548 1.315769 -0.752939
C -2.868756 2.020703 -1.832722
C -2.025621 -0.142019 -1.017251
C -2.714130 1.592863 0.583768
H -1.424602 -0.593242 -0.224423
H -3.024324 -0.592481 -1.026667
H -1.517958 -0.269116 -1.971886
H -3.901656 1.658048 -1.876824
H -2.862163 3.090731 -1.612667
H -2.338925 1.841035 -2.766655
H -3.740577 1.215423 0.636502
H -2.698239 2.670191 0.754335
H -2.094801 1.110226 1.341084
H -1.084168 1.742407 -0.706619
H 2.738726 1.939156 -4.190175
H 1.773803 0.457017 -4.410942
H 1.152706 1.994975 -5.002165
H 2.692645 2.731235 -2.032858
H 3.072653 3.656491 0.013820
H 2.220653 2.814000 1.333475
H 1.609007 4.358382 0.750223

46
El-BH-Nu
C 3.313691 -1.974059 -1.520213
C 2.296962 -1.678796 -0.617359
C 2.480429 -1.929506 0.758229
C 3.699740 -2.485256 1.189096
C 4.715830 -2.772998 0.281149

C	4.524254	-2.518533	-1.077697
C	1.452277	-1.664776	1.759105
C	0.271327	-1.055728	1.561651
N	-0.671544	-0.978245	2.657866
O	-1.841983	-0.697125	2.355737
O	-0.300974	-1.207657	3.810193
C	0.234685	2.549158	-0.972698
C	-0.598209	2.812668	0.133562
O	-1.521442	2.067306	0.584782
C	0.289516	1.338059	-1.701857
O	-0.397867	0.300165	-1.473982
C	1.301637	1.259474	-2.845623
C	-0.392734	4.121493	0.888092
N	-3.144589	0.409985	-0.524963
C	-4.177437	0.724042	0.501371
C	-3.433627	1.072912	-1.824332
C	-2.951249	-1.055971	-0.693463
H	-2.696417	-1.475589	0.279287
H	-3.877890	-1.499292	-1.071987
H	-0.103620	-0.617214	0.643361
H	1.656453	-2.011558	2.769587
H	-2.128171	-1.204263	-1.390759
H	-4.384876	0.706996	-2.222241
H	-3.482471	2.150381	-1.658156
H	-2.611688	0.845344	-2.502495
H	-5.152403	0.354717	0.169169
H	-4.199966	1.805178	0.640045
H	-3.883970	0.251600	1.438455
H	-2.233426	0.886051	-0.163027
H	1.622316	2.243899	-3.200155
H	2.193477	0.714221	-2.510431
H	0.867202	0.695327	-3.677748
H	0.934809	3.328018	-1.257581
H	0.372344	4.762363	0.440770
H	-0.105124	3.896959	1.922255
H	-1.340109	4.671370	0.936255
H	3.845661	-2.687143	2.247546
H	5.652040	-3.197824	0.632411
H	5.311694	-2.746637	-1.791058
H	3.160048	-1.782371	-2.578667
H	1.362688	-1.256378	-0.979049

46
TScc

C	4.345801	-2.235616	-1.259072
C	3.202215	-1.642316	-0.726323
C	3.296278	-0.704003	0.315135
C	4.573250	-0.376335	0.797123
C	5.718705	-0.969222	0.266195
C	5.609446	-1.903137	-0.765200
C	2.095434	-0.063133	0.932702
C	0.908941	-0.824939	1.041385
N	-0.051462	-0.491088	1.960507
O	-1.122198	-1.182266	1.994246
O	0.118368	0.477560	2.747108
C	1.846711	1.593380	-0.167039

C 0.898475 2.439890 0.578161
O -0.320796 2.456088 0.362181
C 1.436874 1.114904 -1.492284
O 0.306019 0.663713 -1.716497
C 2.465064 1.171945 -2.610599
C 1.464507 3.327452 1.672524
N -2.255993 0.799368 -0.507737
C -2.953143 1.095652 0.784859
C -2.724946 1.678724 -1.614213
C -2.340177 -0.648728 -0.865504
H -1.958417 -1.220040 -0.015739
H -3.386020 -0.899507 -1.063546
H 0.657075 -1.669260 0.420297
H 2.327484 0.491491 1.838198
H -1.726485 -0.813832 -1.750356
H -3.784449 1.489091 -1.804032
H -2.569247 2.715994 -1.315459
H -2.126606 1.459966 -2.499077
H -4.022310 0.906503 0.655607
H -2.767762 2.139425 1.035146
H -2.529993 0.443447 1.553456
H -1.247242 1.059302 -0.381315
H 3.433888 0.779302 -2.285959
H 2.105879 0.605400 -3.473280
H 2.621335 2.216266 -2.913184
H 2.867049 1.972089 -0.130464
H 2.476265 3.683255 1.454271
H 1.492342 2.740037 2.598573
H 0.795586 4.176487 1.834131
H 4.665479 0.345005 1.606021
H 6.695637 -0.704523 0.662268
H 6.499431 -2.368549 -1.180025
H 4.249298 -2.960933 -2.062851
H 2.228479 -1.902004 -1.130871

46
BH-Add
C 5.741728 -2.048433 -0.673121
C 4.481303 -2.351046 -1.191536
C 3.340430 -1.734707 -0.674747
C 3.435529 -0.803655 0.371346
C 4.707630 -0.511628 0.881606
C 5.850979 -1.125051 0.367444
C 2.210896 -0.096014 0.936290
C 1.071801 -1.025479 1.165452
N 0.011208 -0.584505 1.822536
O -0.000354 0.655175 2.228263
O -1.017289 -1.321009 2.048264
C 1.846730 1.180199 0.036388
C 1.428374 0.794794 -1.370149
C 2.355213 1.178966 -2.504308
C 0.815427 2.143014 0.672985
C 1.323524 3.004664 1.811581
O -0.227625 2.444993 0.085654
O 0.377467 0.204674 -1.585290
N -2.269599 0.643121 -0.350101

C	-2.395462	-0.818042	-0.651090
C	-2.905045	0.994856	0.962281
C	-2.766499	1.495230	-1.466517
H	-1.975472	-1.362155	0.201293
H	-3.455487	-1.050604	-0.784278
H	1.046408	-2.053326	0.838618
H	2.496183	0.355944	1.895953
H	-1.834984	-1.026311	-1.561703
H	-3.836735	1.321497	-1.601127
H	-2.572545	2.537739	-1.213954
H	-2.219034	1.228818	-2.371642
H	-3.981249	0.820609	0.879525
H	-2.691170	2.043818	1.165541
H	-2.446386	0.362884	1.726633
H	-1.260302	0.881381	-0.268598
H	3.359574	0.775631	-2.331416
H	1.962639	0.807806	-3.453648
H	2.448905	2.272242	-2.549905
H	2.781314	1.756132	-0.020101
H	1.788983	3.904799	1.385805
H	2.058918	2.490994	2.433520
H	0.478607	3.309963	2.430865
H	4.801570	0.199768	1.699472
H	6.825575	-0.885774	0.785161
H	6.629281	-2.531116	-1.073470
H	4.383205	-3.072193	-1.999069
H	2.365854	-1.979035	-1.088336

46
TSreprot

C	5.211611	-2.449176	-0.498549
C	4.002197	-2.492392	-1.194259
C	2.945947	-1.655635	-0.831040
C	3.075784	-0.756358	0.238459
C	4.296860	-0.725899	0.928348
C	5.355524	-1.560581	0.567177
C	1.953499	0.184970	0.678840
C	0.592176	-0.490561	0.825325
N	0.091705	-0.538711	2.146878
O	0.452990	0.301047	3.005496
O	-0.811187	-1.377715	2.408762
C	1.969929	1.496657	-0.191328
C	1.607176	1.313922	-1.668306
C	2.150581	2.360028	-2.622227
C	1.063428	2.570736	0.430939
C	1.485813	3.157712	1.758083
O	0.020528	2.911623	-0.109580
O	0.924689	0.388249	-2.069162
N	-1.917707	0.102770	-0.218372
C	-2.420494	-1.291746	-0.336751
C	-2.587953	0.835729	0.892441
C	-2.049143	0.839162	-1.501465
H	-2.206231	-1.808263	0.599426
H	-3.495163	-1.282246	-0.548331
H	0.523575	-1.491383	0.405509
H	2.218029	0.522300	1.685774

H -1.891097 -1.782017 -1.156956
H -3.109865 0.918902 -1.765961
H -1.608009 1.827711 -1.379349
H -1.504046 0.301110 -2.276543
H -3.649593 0.968501 0.656722
H -2.106749 1.809711 0.997686
H -2.468111 0.258657 1.810113
H -0.785224 0.004453 0.103321
H 3.246618 2.306677 -2.648694
H 1.756276 2.188964 -3.625962
H 1.879758 3.366704 -2.283439
H 2.995823 1.890197 -0.147213
H 2.566357 3.328118 1.808772
H 1.220231 2.436236 2.541725
H 0.944781 4.090719 1.931890
H 4.416107 -0.046478 1.769950
H 6.287772 -1.521245 1.125004
H 6.031232 -3.104514 -0.781312
H 3.877037 -3.182654 -2.024862
H 2.016559 -1.694367 -1.388610

46
B-AddH
C 5.670179 -2.216396 -0.297172
C 4.597233 -2.285821 -1.187202
C 3.427127 -1.565620 -0.942637
C 3.308665 -0.761165 0.200939
C 4.393009 -0.703705 1.088082
C 5.564507 -1.421534 0.844299
C 2.059708 0.061279 0.510479
C 0.750909 -0.741917 0.435084
N 0.475711 -1.472986 1.733367
O 0.745619 -0.906240 2.793670
O -0.065238 -2.569425 1.646870
C 2.003234 1.387321 -0.310090
C 1.753322 1.208667 -1.816813
C 2.336317 2.259617 -2.734164
C 0.974763 2.396265 0.252759
C 0.991065 2.660592 1.745149
O 0.196906 2.972782 -0.486708
O 1.116340 0.262018 -2.240070
N -2.341163 0.505616 0.030204
C -3.067072 -0.696348 0.431229
C -2.860481 1.690000 0.707694
C -2.365331 0.680173 -1.420774
H -3.009587 -0.819075 1.517905
H -4.135894 -0.665938 0.143789
H 0.741491 -1.509200 -0.332907
H 2.150720 0.369755 1.554765
H -2.611738 -1.577274 -0.033007
H -3.391984 0.809205 -1.815122
H -1.773634 1.559032 -1.691568
H -1.917363 -0.193015 -1.905802
H -3.918186 1.898444 0.454292
H -2.260389 2.561367 0.428738
H -2.794683 1.552441 1.792863

H	-0.144030	-0.114169	0.306425
H	3.432396	2.241842	-2.672126
H	2.026475	2.066264	-3.762932
H	2.001285	3.255544	-2.425174
H	2.982261	1.873089	-0.177563
H	2.012311	2.805581	2.116301
H	0.571332	1.804085	2.286903
H	0.388235	3.546266	1.955173
H	4.314803	-0.098162	1.988696
H	6.388324	-1.365505	1.550879
H	6.578188	-2.781602	-0.489096
H	4.667493	-2.905714	-2.077140
H	2.606861	-1.626809	-1.650117

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TakemotoTS-A-R

C	4.317628	-4.148457	0.256112
C	4.275644	-2.913366	-0.413369
C	5.394575	-2.532913	-1.174550
C	6.512267	-3.361273	-1.261904
C	6.537841	-4.586084	-0.591033
C	5.434094	-4.977469	0.169354
C	3.048263	-2.085476	-0.311864
C	2.722266	-1.152568	-1.312134
N	1.461352	-0.652521	-1.387487
O	0.541568	-1.109684	-0.631280
O	1.208738	0.283038	-2.208130
C	3.346764	-1.031778	1.527060
C	4.322269	-0.021329	1.126204
C	5.776275	-0.261855	1.508254
C	2.018713	-0.634482	2.002145
C	1.164936	-1.714001	2.649347
O	1.544062	0.511950	1.937529
O	4.010241	0.985470	0.477947
N	1.861465	3.133532	1.307538
C	3.181133	3.380098	1.970681
C	1.819737	3.621030	-0.147441
C	0.397593	3.517901	-0.744358
C	0.424190	3.928695	-2.232555
C	0.986591	5.341812	-2.422463
C	2.377077	5.464199	-1.791181
C	2.367059	5.048044	-0.309086
N	-0.152538	2.183054	-0.576992
C	-1.462182	1.930667	-0.248813
S	-2.514448	3.139617	0.301144
N	-1.756424	0.604282	-0.394705
C	-2.934636	-0.141738	-0.239239
C	-4.191693	0.363461	0.122038
C	-5.281587	-0.505044	0.222368
C	-5.157737	-1.869664	-0.022261
C	-3.902390	-2.367831	-0.378094
C	-2.805144	-1.522574	-0.489843
C	-3.721741	-3.848451	-0.580445
F	-4.835493	-4.426416	-1.083162
C	-6.633409	0.076414	0.547609
F	-6.548250	1.072106	1.455778

F	-2.703687	-4.126698	-1.423735
F	-3.447452	-4.481089	0.586339
F	-7.228666	0.597999	-0.550550
F	-7.477341	-0.855350	1.046691
C	0.756483	3.627807	2.189354
H	3.424137	-0.659991	-1.965584
H	2.193818	-2.609010	0.102107
H	-0.943304	0.011337	-0.614144
H	0.315726	1.465909	-1.150095
H	-0.270293	4.206382	-0.219524
H	-0.600912	3.862703	-2.612143
H	1.024623	3.201022	-2.795622
H	1.031153	5.589320	-3.489604
H	0.307205	6.071207	-1.959072
H	3.085130	4.824598	-2.336502
H	2.754119	6.490398	-1.872813
H	3.384873	5.119855	0.086773
H	1.744715	5.752480	0.260597
H	2.481795	2.912428	-0.658072
H	3.273594	4.436847	2.223697
H	3.202336	2.777208	2.879732
H	3.978702	3.047603	1.309155
H	0.828971	4.712963	2.287581
H	0.882445	3.156378	3.165126
H	-0.213980	3.351092	1.779842
H	1.775557	2.085104	1.285756
H	6.085271	-1.290883	1.297906
H	6.421155	0.435094	0.966975
H	5.906516	-0.100231	2.587029
H	3.755828	-1.881152	2.068973
H	1.747220	-2.564348	3.016636
H	0.452139	-2.077913	1.899810
H	0.586910	-1.279132	3.469402
H	3.457753	-4.462024	0.843665
H	5.439738	-5.931030	0.690275
H	7.409240	-5.230925	-0.663314
H	7.365138	-3.049867	-1.858973
H	5.395833	-1.583877	-1.701712
H	-1.839059	-1.923630	-0.779378
H	-6.012996	-2.528875	0.059219
H	-4.311037	1.416834	0.329375

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TakemotoTS-A-S

C	4.333220	-3.956999	-0.074439
C	4.550331	-2.675439	-0.608905
C	5.787411	-2.407634	-1.217103
C	6.774097	-3.391188	-1.298432
C	6.544196	-4.659279	-0.763980
C	5.319562	-4.937504	-0.150552
C	3.510654	-1.613634	-0.576498
C	2.176764	-1.971820	-0.881312
N	1.286655	-1.013385	-1.255133
O	1.666428	0.193000	-1.394941
O	0.076483	-1.335785	-1.473037
C	3.729354	-0.855752	1.376596

C	4.654962	0.265209	1.160852
C	6.112885	0.023756	1.528068
C	2.383828	-0.623006	1.911050
C	1.671166	-1.842092	2.468687
O	1.772857	0.455711	1.916101
O	4.311929	1.345886	0.673996
N	1.715647	3.156343	1.415036
C	0.518607	3.623519	2.183611
C	1.760217	3.566200	-0.066910
C	2.297108	4.991344	-0.272761
C	2.425107	5.309825	-1.773111
C	1.092900	5.125183	-2.506984
C	0.521425	3.724061	-2.259982
C	0.381806	3.416959	-0.752457
N	-0.198963	2.099453	-0.539255
C	-1.537919	1.881704	-0.343781
N	-1.881015	0.576268	-0.562591
C	-3.063873	-0.148246	-0.320783
S	-2.589656	3.116823	0.154895
C	2.961275	3.514481	2.167847
H	-1.124642	-0.026479	-0.917530
H	0.371270	1.324138	-0.911288
H	-0.316478	4.141700	-0.324296
H	-0.471782	3.625745	-2.711146
H	1.162989	2.961531	-2.722503
H	1.619938	5.718355	0.197653
H	3.278027	5.106773	0.197868
H	0.373693	5.879026	-2.156690
H	1.224680	5.294295	-3.582236
H	2.796868	6.334314	-1.892244
H	3.182893	4.646840	-2.213409
H	2.466999	2.843718	-0.489724
H	0.590610	3.206790	3.189897
H	-0.401914	3.283312	1.711730
H	0.529218	4.714283	2.235253
H	2.962538	4.583657	2.382123
H	2.946219	2.949695	3.101706
H	3.829983	3.213542	1.586306
H	1.709003	2.108279	1.418544
H	6.487797	-0.892991	1.057680
H	6.719743	0.875326	1.211538
H	6.214994	-0.110696	2.612823
H	4.197290	-1.732811	1.817104
H	2.338728	-2.497284	3.037077
H	0.830831	-1.526430	3.090542
H	1.273818	-2.423686	1.624758
H	1.763446	-2.966764	-0.814693
H	3.802387	-0.662132	-1.009173
H	5.967537	-1.424293	-1.644648
H	7.720539	-3.165682	-1.782406
H	7.311495	-5.426055	-0.824394
H	5.132333	-5.922356	0.268792
H	3.388497	-4.185401	0.411719
C	-2.934234	-1.549769	-0.357228
C	-4.041037	-2.366490	-0.151064
C	-5.300792	-1.818826	0.095980

C	-5.425143	-0.432173	0.124470
C	-4.329085	0.407880	-0.083076
H	-1.963043	-1.992246	-0.553822
C	-3.861956	-3.860792	-0.119069
H	-6.160717	-2.457356	0.257563
C	-6.788043	0.184289	0.306977
H	-4.450402	1.480358	-0.053132
F	-3.599179	-4.304466	1.134822
F	-4.972779	-4.509078	-0.535410
F	-2.837478	-4.268025	-0.898995
F	-7.405219	0.386697	-0.881309
F	-7.603949	-0.608509	1.039733
F	-6.725559	1.382042	0.925241

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TakemotoTS-B-R

C	1.879055	-2.853204	0.050468
C	1.430906	-1.668081	-0.551446
C	2.379838	-0.703577	-0.938009
C	3.734929	-0.910618	-0.705842
C	4.189634	-2.089318	-0.113271
C	3.247302	-3.049323	0.250931
N	0.091138	-1.309363	-0.766620
C	-1.083280	-2.002563	-0.651608
S	-1.221952	-3.682382	-0.460988
C	4.700066	0.198573	-1.017582
C	3.712287	-4.358413	0.835684
N	-2.161277	-1.172011	-0.733888
C	-3.543982	-1.601492	-0.854571
C	-4.440671	-0.909880	0.200782
C	-5.900857	-1.363922	0.065517
C	-6.435277	-1.073125	-1.347657
C	-5.557678	-1.729286	-2.419673
C	-4.092782	-1.301697	-2.267416
N	-3.904055	-1.096959	1.619824
C	-3.748156	-2.514885	2.071522
C	-4.668686	-0.305151	2.633513
O	-1.482720	-0.045703	2.159421
N	-1.490429	1.210857	1.890672
O	-2.550383	1.883196	2.004822
C	-0.319162	1.779510	1.488156
C	-0.282293	3.135265	1.125204
C	1.001474	3.872557	1.060182
C	2.236991	3.238669	0.839241
C	3.418097	3.976872	0.795908
C	3.391127	5.361466	0.977338
C	2.172151	6.005128	1.201517
C	0.991021	5.266828	1.239389
C	-1.021984	3.331050	-0.896139
C	-2.374718	2.782806	-0.834561
O	-2.659015	1.591043	-1.021865
C	0.029737	2.652477	-1.642007
C	1.028955	3.519133	-2.391816
O	0.150220	1.419562	-1.683605
C	-3.487834	3.784034	-0.556911
H	-3.551464	-2.684247	-0.702666

H	-3.988706	-0.226832	-2.463586
H	-3.457809	-1.826052	-2.989735
H	-5.921482	-1.467440	-3.420380
H	-5.633394	-2.822846	-2.335361
H	-6.460368	0.013742	-1.507713
H	-7.470536	-1.426343	-1.421922
H	-5.976327	-2.442346	0.259498
H	-6.531792	-0.857606	0.804046
H	-4.366440	0.171553	0.041734
H	-0.014243	-0.324546	-1.028529
H	-2.008737	-0.170439	-0.899232
H	-3.296168	-2.495002	3.064952
H	-4.727121	-2.995429	2.121258
H	-3.085313	-3.050746	1.389286
H	-4.065128	-0.265259	3.540785
H	-4.796372	0.710244	2.262720
H	-5.627789	-0.784009	2.834923
H	-0.990363	4.417407	-0.951434
H	-4.427057	3.253505	-0.388851
H	-3.257554	4.395502	0.322593
H	-3.609817	4.464994	-1.408943
H	1.967187	2.975020	-2.527316
H	0.621440	3.752814	-3.385117
H	1.219801	4.467301	-1.881139
H	-2.927713	-0.671784	1.660906
H	0.503951	1.087074	1.416167
H	-1.120743	3.718567	1.490947
H	0.043983	5.771944	1.416147
H	2.140958	7.081233	1.349867
H	4.313715	5.934519	0.944906
H	4.356141	3.462715	0.612750
H	2.286860	2.164865	0.692451
H	2.037856	0.206509	-1.419609
H	5.245467	-2.252645	0.063266
H	1.168137	-3.605922	0.358250
F	4.804541	1.064770	0.031211
F	4.312536	0.935359	-2.082146
F	5.945061	-0.255697	-1.265849
F	3.855077	-5.306883	-0.118550
F	4.911860	-4.236904	1.449891
F	2.840750	-4.844353	1.745301

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C	1.182424	4.870628	1.291832
C	1.241252	3.513080	0.932116
C	2.480076	2.975939	0.545979
C	3.628344	3.767379	0.526754
C	3.556301	5.113287	0.888053
C	2.328613	5.662185	1.270116
C	0.047788	2.631535	0.964258
C	-0.842950	2.740302	2.051667
N	-1.723001	1.736095	2.335989
O	-2.513080	1.842393	3.307792
O	-1.721684	0.686104	1.594782
C	-0.872360	3.130891	-0.911582

C	0.057838	2.503761	-1.848579
O	0.139766	1.276956	-2.006657
C	-2.264572	2.684356	-0.836560
C	-3.227386	3.683607	-0.212974
O	-2.695701	1.591165	-1.229642
C	0.974821	3.419377	-2.640453
N	-4.079475	-0.638184	1.355636
C	-4.979104	0.274274	2.133139
C	-4.537572	-0.815674	-0.090280
C	-3.550434	-1.671234	-0.914108
C	-4.006912	-1.694406	-2.389060
C	-5.438209	-2.227088	-2.533099
C	-6.415668	-1.425585	-1.664959
C	-5.960358	-1.382990	-0.195249
N	-2.188065	-1.184485	-0.788804
C	-1.102384	-1.977954	-0.558735
N	0.069346	-1.291181	-0.723198
C	1.406749	-1.646346	-0.483017
S	-1.231889	-3.617470	-0.143435
C	-3.823110	-1.897862	2.121844
H	-3.548117	-2.699585	-0.541923
H	-3.934881	-0.678329	-2.800255
H	-3.301576	-2.319225	-2.947198
H	-5.748425	-2.191726	-3.584101
H	-5.465790	-3.284414	-2.233662
H	-6.488342	-0.397659	-2.047171
H	-7.423727	-1.853018	-1.718856
H	-5.988326	-2.399069	0.221231
H	-6.663594	-0.775988	0.385095
H	-4.509818	0.205482	-0.486226
H	-0.028492	-0.355309	-1.131412
H	-2.045861	-0.202257	-1.049634
H	-3.427951	-1.608584	3.097339
H	-4.756735	-2.449579	2.246614
H	-3.083489	-2.506636	1.598439
H	-4.404224	0.654696	2.978752
H	-5.266527	1.112277	1.495352
H	-5.866310	-0.268674	2.461329
H	-0.771769	4.211657	-0.839880
H	-2.970629	3.826505	0.845899
H	-3.157295	4.664785	-0.695945
H	-4.252734	3.314054	-0.290335
H	1.786381	2.839916	-3.086851
H	0.402255	3.902690	-3.443560
H	1.387331	4.213978	-2.010478
H	-3.146324	-0.131584	1.342691
H	0.207788	1.617205	0.615431
H	-0.900873	3.580558	2.727204
H	2.549871	1.928071	0.269282
H	4.572282	3.324958	0.223933
H	4.448792	5.732786	0.870834
H	2.264192	6.710175	1.550600
H	0.231507	5.312059	1.579089
C	2.374570	-0.835063	-1.102585
C	3.729744	-1.053909	-0.874953
C	4.159709	-2.094166	-0.050443

C	3.196696	-2.900144	0.553904
C	1.831222	-2.684715	0.358628
H	2.051814	-0.034200	-1.759542
C	4.735627	-0.101158	-1.458683
H	5.215085	-2.267668	0.120523
C	3.635031	-4.063990	1.405508
H	1.104575	-3.313211	0.851825
F	4.994462	0.924961	-0.599175
F	5.919197	-0.697767	-1.709635
F	4.306948	0.460815	-2.608877
F	3.751164	-5.197781	0.676986
F	4.840925	-3.840681	1.977309
F	2.758351	-4.322234	2.399181

IX. Total energies of all calculated stationary points

	Total electronic energy	Unscaled ZPE	Therm. corr. to *H*	Therm. corr. to *G*
nucleophile 1	-630.434123	0.099600	0.106838	0.068955
electrophile 1	-308.666132	0.127948	0.134976	0.098045
adduct 1	-939.124624	0.234144	0.247652	0.193654
nucleophile 2	-245.009333	0.050168	0.055491	0.022004
electrophile 2	-654.037938	0.225513	0.239533	0.183357
adduct 2	-899.069535	0.280755	0.298926	0.232076
nucleophile 3	-224.977147	0.044867	0.050664	0.017150
electrophile 3	-708.432995	0.236531	0.251270	0.193927
adduct 3	-933.431072	0.285340	0.305359	0.235331
nucleophile 4	-515.241677	0.144607	0.154823	0.109246
electrophile 4	-630.420047	0.041749	0.047630	0.013135
adduct 4	-1145.691337	0.190870	0.206669	0.147119
nucleophile 5	-345.794724	0.122664	0.131915	0.089124
electrophile 5	-514.151811	0.137098	0.147151	0.101332
adduct 5	-859.965752	0.264532	0.283249	0.216649
enol-acac	-345.799880	0.123533	0.132373	0.090379
TMA	-174.474400	0.121135	0.127488	0.093853
B-NuH	-520.279416	0.245713	0.262039	0.200194
TS prot	-520.271767	0.243253	0.258774	0.200332
BH-Nu	-520.272011	0.246232	0.262000	0.203763
El-BH-Nu	-1034.437046	0.386463	0.413003	0.327340
TS C-C	-1034.412188	0.387192	0.412381	0.331993
BH-Add	-1034.420169	0.389271	0.414161	0.335780
TS reprot	-1034.411246	0.384565	0.409350	0.330439
B-AddH	-1034.446250	0.386907	0.412973	0.328332
Takemoto TS A,R	-2681.928730	0.644320	0.689979	0.560439
Takemoto TS A,S	-2681.923461	0.643938	0.689825	0.557972
Takemoto TS B,R	-2681.937719	0.644067	0.689688	0.562596
Takemoto TS B,S	-2681.932271	0.643944	0.689603	0.561915

Table S4. Total B3LYP/6-31G(d) electronic energies, zero-point energies (ZPE), thermal corrections of electronic energy for enthalpies (*H*) and Gibbs free energies (*G*). Values are given in hartree. Single imaginary frequency of TSs was neglected in ZPE and thermal correction calculations.

	G3MP2(0 K)	Scaled E(ZPE)
nucleophile 1	-629.602791	0.095614
electrophile 1	-308.169681	0.122830
adduct 1	-937.800247	0.224778
nucleophile 2	-244.715742	0.048162
electrophile 2	-652.974411	0.216493
adduct 2	-897.722302	0.269525
nucleophile 3	-224.668896	0.043072
electrophile 3	-707.339883	0.227070
adduct 3	-932.043668	0.273927
nucleophile 4	-514.462981	0.138823
electrophile 4	-629.729623	0.040079
adduct 4	-1144.228886	0.183236
nucleophile 5	-345.286748	0.117759
electrophile 5	-513.408303	0.131614
adduct 5	-858.732544	0.253951

Table S5. Results of G3(MP2)//B3LYP calculations. Values are given in hartree.

	MP2/cc-pVTZ	SCS-MP2/cc-pVTZ
nucleophile 1	-629.447222	-629.426414
electrophile 1	-308.032646	-308.020373
adduct 1	-937.518508	-937.479746
nucleophile 2	-244.620859	-244.601704
electrophile 2	-652.659142	-652.600722
adduct 2	-897.319575	-897.237112
nucleophile 3	-224.553490	-224.537661
electrophile 3	-707.018986	-706.961943
adduct 3	-931.615034	-931.536405
nucleophile 4	-514.215204	-514.167046
electrophile 4	-629.592548	-629.577035
adduct 4	-1143.853939	-1143.784567
nucleophile 5	-345.141312	-345.127031
electrophile 5	-513.174130	-513.125005
adduct 5	-858.361960	-858.291884
enol-acac	-345.149092	-345.130566
TMA	-174.085923	-174.092111
B-NuH	-519.244272	-519.230644
TS prot	-519.239583	-519.223313
BH-Nu	-519.239638	-519.223804
El-BH-Nu	-1032.434030	-1032.365809
TS C-C	-1032.421704	-1032.346785
BH-Add	-1032.434451	-1032.362978
TS reprot	-1032.427580	-1032.354806
B-AddH	-1032.457399	-1032.391775
Takemoto TS A,R	-2677.473054	-2677.274919
Takemoto TS A,S	-2677.465210	-2677.268208
Takemoto TS B,R	-2677.484413	-2677.284569
Takemoto TS B,S	-2677.476785	-2677.277776

Table S6. Total electronic energies from perturbation methods. Values are given in hartree.

	B3LYP	TPSS	TPSSh
nucleophile 1	-630.555988	-630.598766	-630.566676
electrophile 1	-308.783075	-308.824871	-308.791808
adduct 1	-939.353899	-939.441623	-939.378865
nucleophile 2	-245.114745	-245.153923	-245.118077
electrophile 2	-654.267914	-654.368736	-654.294260
adduct 2	-899.398223	-899.539007	-899.432072
nucleophile 3	-225.062568	-225.095089	-225.064548
electrophile 3	-708.689583	-708.795508	-708.714875
adduct 3	-933.767369	-933.907131	-933.799212
nucleophile 4	-515.424694	-515.504786	-515.444087
electrophile 4	-630.520887	-630.553427	-630.524010
adduct 4	-1145.968274	-1146.082767	-1145.995438
nucleophile 5	-345.933962	-345.976202	-345.936340
electrophile 5	-514.345831	-514.430102	-514.363231
adduct 5	-860.291337	-860.420205	-860.316832

Table S7/1. Total electronic energies from density functional methods. Basis set: 6-311++G(3df,3pd). Values are given in hartree.

	MPW1K	PWB6K	M05
nucleophile 1	-630.481099	-630.868317	-630.341973
electrophile 1	-308.683415	-308.915829	-308.543266
adduct 1	-939.193715	-939.813054	-938.910214
nucleophile 2	-245.008431	-245.196276	-244.982670
electrophile 2	-654.046743	-654.572102	-653.732012
adduct 2	-899.087413	-899.801411	-898.741499
nucleophile 3	-224.964420	-225.154993	-224.904918
electrophile 3	-708.453658	-709.012192	-708.162790
adduct 3	-933.450068	-934.199737	-933.093917
nucleophile 4	-515.246637	-515.665911	-515.041326
electrophile 4	-630.453258	-630.823347	-630.391256
adduct 4	-1145.737561	-1146.526343	-1145.464340
nucleophile 5	-345.809250	-346.070517	-345.696849
electrophile 5	-514.150227	-514.560926	-513.982750
adduct 5	-859.988791	-860.663514	-859.703568

Table S7/2. Total electronic energies from density functional methods. Basis set: 6-311++G(3df,3pd). Values are given in hartree.

	M05-2X	M06	M06-2X
nucleophile 1	-630.501123	-630.331172	-630.410396
electrophile 1	-308.735681	-308.559298	-308.636951
adduct 1	-939.271023	-938.920708	-939.080641
nucleophile 2	-245.067793	-244.975510	-245.003651
electrophile 2	-654.184571	-653.772028	-653.972889
adduct 2	-899.288771	-898.779065	-899.013394
nucleophile 3	-225.031865	-224.906825	-224.971138
electrophile 3	-708.601106	-708.195292	-708.381796
adduct 3	-933.670357	-933.133927	-933.390247
nucleophile 4	-515.366738	-515.059659	-515.208959
electrophile 4	-630.473573	-630.361565	-630.417539
adduct 4	-1145.881901	-1145.458043	-1145.666732
nucleophile 5	-345.875766	-345.707386	-345.773410
electrophile 5	-514.270174	-513.994900	-514.117086
adduct 5	-860.183888	-859.735112	-859.929127

Table S7/3. Total electronic energies from density functional methods. Basis set: 6-311++G(3df,3pd). Values are given in hartree.

	B3LYP	TPSS	TPSSh
nucleophile 1	-630.513880	-630.549601	-630.515843
electrophile 1	-308.763182	-308.798566	-308.764335
adduct 1	-939.292731	-939.366276	-939.300786
nucleophile 2	-245.094661	-245.130411	-245.093489
electrophile 2	-654.227890	-654.315039	-654.237797
adduct 2	-899.338717	-899.461350	-899.350639
nucleophile 3	-225.045827	-225.072958	-225.041480
electrophile 3	-708.642990	-708.734695	-708.651091
adduct 3	-933.704324	-933.823740	-933.712010
nucleophile 4	-515.391103	-515.460095	-515.397239
electrophile 4	-630.480001	-630.506351	-630.475346
adduct 4	-1145.895127	-1145.991660	-1145.900679
nucleophile 5	-345.909714	-345.945280	-345.904088
electrophile 5	-514.310256	-514.385217	-514.316066
adduct 5	-860.231883	-860.343611	-860.236728
enol-acac	-345.920666		
TMA	-174.531251		
B-NuH	-520.453377		
TS prot	-520.448786		
BH-Nu	-520.449350		
El-BH-Nu	-1034.765533		
TS C-C	-1034.737050		
BH-Add	-1034.743958		
TS reprot	-1034.733896		
B-AddH	-1034.765159		
Takemoto TS A,R	-2682.682466		
Takemoto TS A,S	-2682.678257		
Takemoto TS B,R	-2682.686636		
Takemoto TS B,S	-2682.682296		

Table S8/1. Total electronic energies from density functional methods. Basis set: TZVP (DFT orbital). Values are given in hartree.

	MPW1K	PWB6K	M05
nucleophile 1	-630.431386	-630.817148	-630.291884
electrophile 1	-308.658221	-308.890534	-308.525901
adduct 1	-939.119489	-939.737672	-938.844489
nucleophile 2	-244.984102	-245.171176	-244.966266
electrophile 2	-653.995004	-654.519354	-653.692255
adduct 2	-899.011275	-899.723825	-898.686342
nucleophile 3	-224.943131	-225.133723	-224.888636
electrophile 3	-708.394187	-708.952044	-708.119613
adduct 3	-933.369206	-934.118704	-933.035543
nucleophile 4	-515.203463	-515.622482	-515.009196
electrophile 4	-630.404973	-630.774112	-630.343113
adduct 4	-1145.647106	-1146.435132	-1145.385952
nucleophile 5	-345.778927	-346.039952	-345.677236
electrophile 5	-514.105324	-514.514764	-513.949738
adduct 5	-859.913312	-860.586826	-859.651845

Table S8/2. Total electronic energies from density functional methods. Basis set: TZVP (DFT orbital). Values are given in hartree.

	M05-2X	M06	M06-2X
nucleophile 1	-630.465862	-630.288682	-630.376114
electrophile 1	-308.717578	-308.544875	-308.620518
adduct 1	-939.218425	-938.864424	-939.030921
nucleophile 2	-245.044133	-244.960043	-244.979630
electrophile 2	-654.155112	-653.742324	-653.945526
adduct 2	-899.236005	-898.733533	-898.962152
nucleophile 3	-225.016791	-224.894506	-224.956444
electrophile 3	-708.560013	-708.159522	-708.343180
adduct 3	-933.614329	-933.085256	-933.336874
nucleophile 4	-515.339817	-515.034775	-515.183125
electrophile 4	-630.437167	-630.319175	-630.381551
adduct 4	-1145.819833	-1145.391106	-1145.606212
nucleophile 5	-345.849806	-345.689218	-345.749216
electrophile 5	-514.237254	-513.967764	-514.084535
adduct 5	-860.125238	-859.689413	-859.872279
enol-acac			-345.758894
TMA			-174.432584
B-NuH			-520.199859
TS prot			-520.196760
BH-Nu			-520.196724
El-BH-Nu			-1034.296701
TS C-C			-1034.282779
BH-Add			-1034.299292
TS reprot			-1034.286402
B-AddH			-1034.312242
Takemoto TS A,R			-2681.755232
Takemoto TS A,S			-2681.748347
Takemoto TS B,R			-2681.765022
Takemoto TS B,S			-2681.757290

Table S8/3. Total electronic energies from density functional methods. Basis set: TZVP (DFT orbital). Values are given in hartree.