Supplementary Material (ESI) for Organic and Biomolecular Chemistry

The Mechanism of the Baeyer-Villiger Rearrangement: Quantum Chemistry and TST Study Supported by Experimental Kinetic Data.

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Supplementary Information (15 pages)

Table S1: Preliminary calculations of the BV reaction of propanone at four levels of theory.

Tables S2 and S3: Calculated $K_{eq(1)}$, $\kappa_{(2)}$, $k_{(2)}$ and k (for the catalyzed and uncatalyzed second step) values at different temperatures in the range of 280 to 320 K for the reactions of propanone and cyclohexanone with the corresponding Arrhenius plots.

Table S4: Comparison of the effect of diffuse functions on the thermodynamic calculations of the reaction of propanone.

Figure S1: Mulliken charge distribution of the stationary points of the reaction of propanone.

Figure S2: Plot of the energy change along the relaxed scan of the forced protonation of propanone by TFAA.

Figures and Cartesian coordinates of the optimized stationary points of the reactions of propanone and cyclohexanone at the MPWB1K/6-311G(d,p)-Onsager level of theory.

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Table S1. Gibbs free energies in kcal/mol (at 298.15 K) of the modelled stationary points relative to the reactant complex for the reaction of propanone with TFPAA using TFAA as catalyst.[a] Rate coefficients (without tunnelling correction, in L mol^{-1} s^{-1}) at 298.15 K are also reported.[b]

Method Species	B3LYP	MPWB1K	BH&HLYP	MP2
Isolated Reactants	1.89	1.67	2.06	1.02
Reactant Complex + TFPAA	0.00	0.00	0.00	0.00
TS1	14.36	14.05	14.49	18.71
Criegee + TFAA	4.95	-0.93	1.42	-3.36
TS2 + TFAA	16.92 [c]	20.66 [c]	24.87 [c]	19.70 [c]
TS2	15.88	21.85	25.42	15.59
Ester + 2 TFAA	-78.65	-83.59	-83.21	-81.46
k	1.47	1.07×10^{-3}	-	-

[a] Level of theory: Method/6-311++G(d,p)-IEF-PCM//Method/6-311G(d,p)
[b] Experimental value at 303 K: $k = 1.8 \times 10^{-3}$ L mol^{-1} s^{-1} (ref 11)
[c] Uncatalyzed values of the second step

Table S2: Calculated kinetic magnitudes at different temperatures for the reaction of propanone with its corresponding Arrhenius plots.

T(K)	$K_{eq(1)}$	$\kappa_{(2)}$	$k_{(2)}$	k	$\kappa_{(2)}^{a}$	$k_{(2)}^{a}$	k^{a}
280	8.53E-01	1.822	2.32E-05	1.98E-05	1.832	6.49E-05	5.53E-05
290	7.53E-01	1.763	6.85E-05	5.16E-05	1.771	2.73E-04	2.06E-04
298	6.85E-01	1.72	1.58E-04	1.08E-04	1.728	8.24E-04	5.64E-04
310	6.01E-01	1.666	4.92E-04	2.96E-04	1.672	3.70E-03	2.22E-03
320	5.43E-01	1.626	1.21E-03	6.58E-04	1.632	1.21E-02	6.57E-03

$\kappa_{(2)}$ is the tunnelling factor of the second step

[a] Uncatalyzed values of the second step

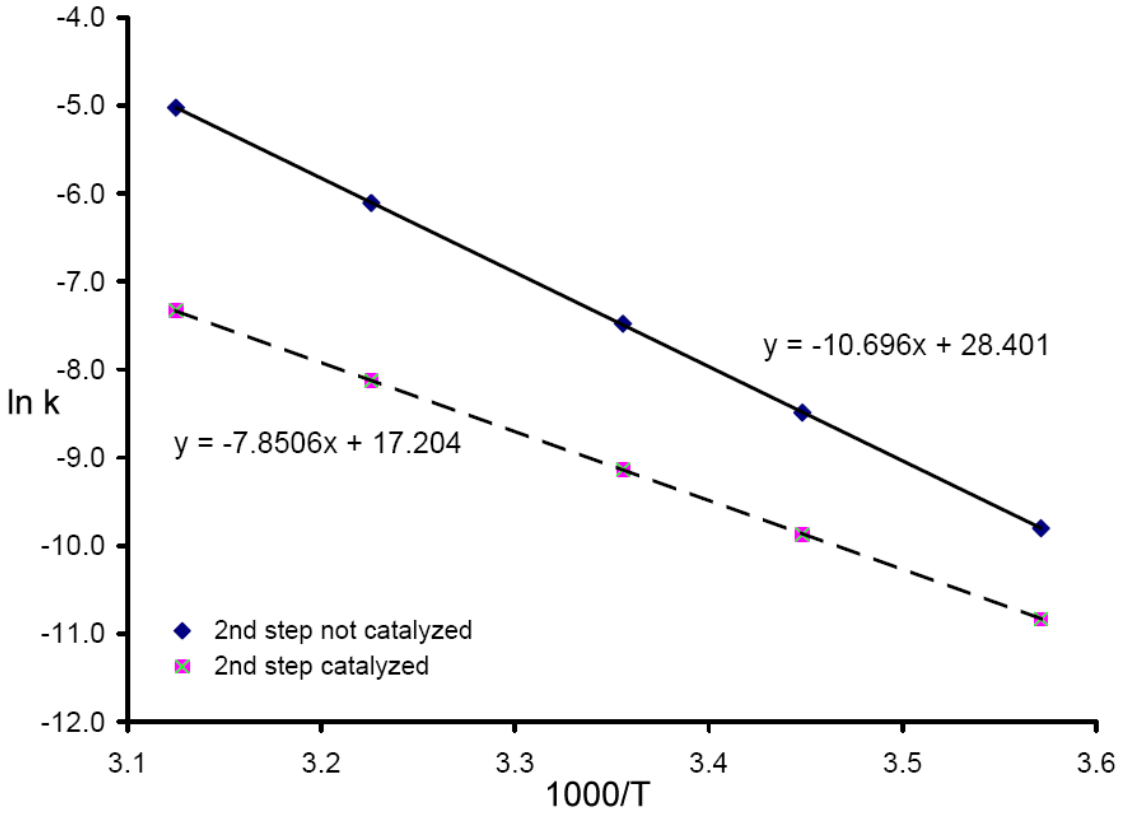


Table S3: Calculated kinetic magnitudes at different temperatures for the reaction of cyclohexanone with its corresponding Arrhenius plots.

T(K)	$K_{eq(1)}$	$\kappa_{(2)}$	$k_{(2)}$	k	$\kappa_{(2)}^{a}$	$k_{(2)}^{a}$	k^{a}
280	8.02E-01	1.711	1.04E-01	8.37E-02	1.680	2.02E-01	1.62E-01
290	6.81E-01	1.663	2.24E-01	1.53E-01	1.635	6.27E-01	4.27E-01
298	6.00E-01	1.629	4.04E-01	2.42E-01	1.602	1.49E+00	8.97E-01
310	5.06E-01	1.584	9.02E-01	4.57E-01	1.560	4.89E+00	2.48E+00
320	4.43E-01	1.551	1.70E+00	7.55E-01	1.528	1.24E+01	5.51E+00

$\kappa_{(2)}$ is the tunnelling factor of the second step
[a] Uncatalyzed values of the second step

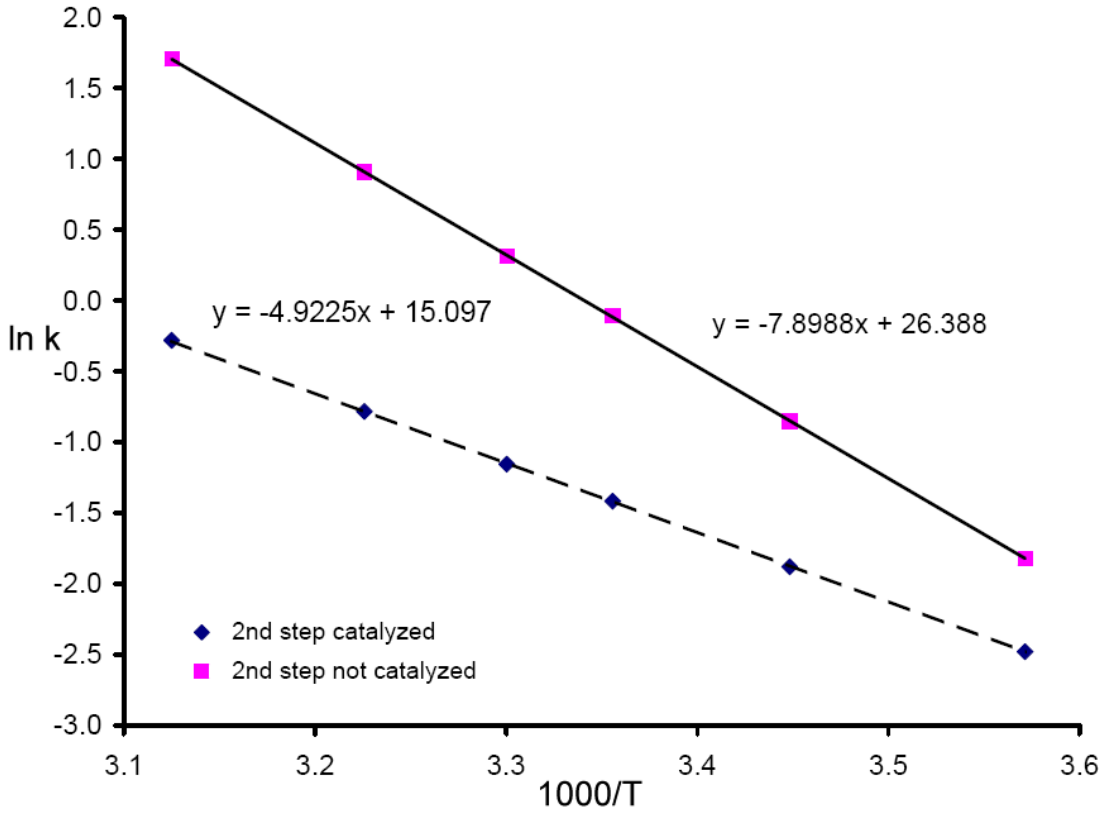


Table S4: Comparison of the effect of diffuse functions on the thermodynamic calculations of the reaction of propanone. Gibbs free energies in kcal/mol (at 298.15 K) of the modelled stationary points relative to the reactant complex (between propanone and TFAA) for the reaction of propanone with TFPAA using TFAA as catalyst.[a]

Basis Set	6-311G(d,p)	6-311++G(d,p)
Isolated Reactants	3.07	1.75
Reactant Complex + TFPAA	0	0
TS1	13.00	14.30
Criegee + TFAA	-0.03	0.54
TS2 + TFAA	23.73 [b]	22.94 [b]
TS2	22.36	23.76
Ester + 2 TFAA	-75.00	-76.69

[a] Level of theory: MPWB1K/Basis Set-IEF-PCM//MPWB1K/6-311G(d,p)-Onsager
[b] Uncatalyzed values of the second step

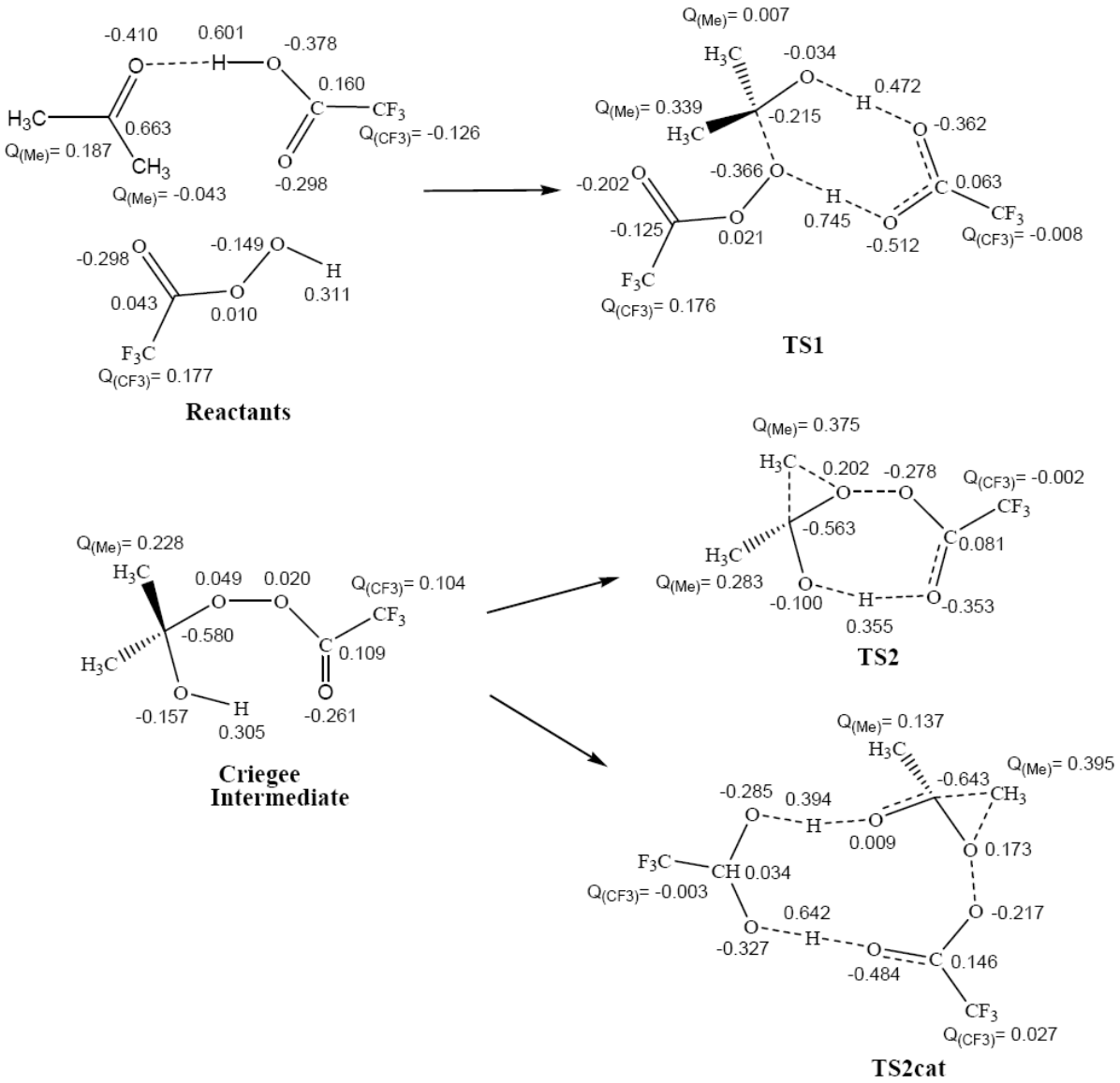


Figure S1: Mulliken charge distribution of the stationary points of the reaction of propanone.

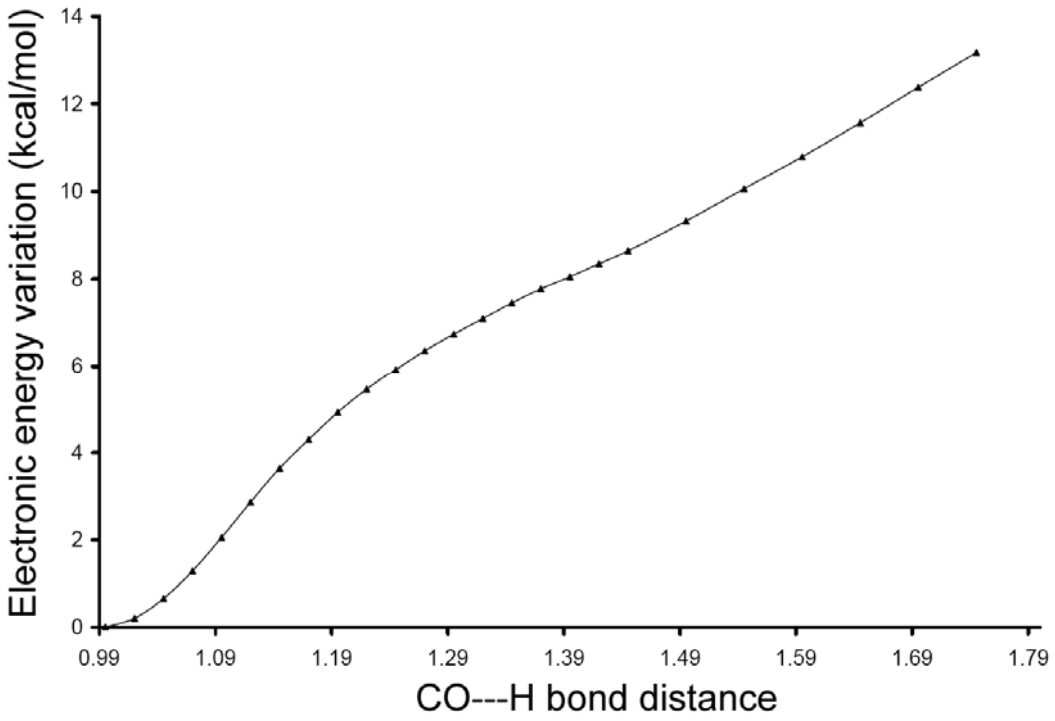
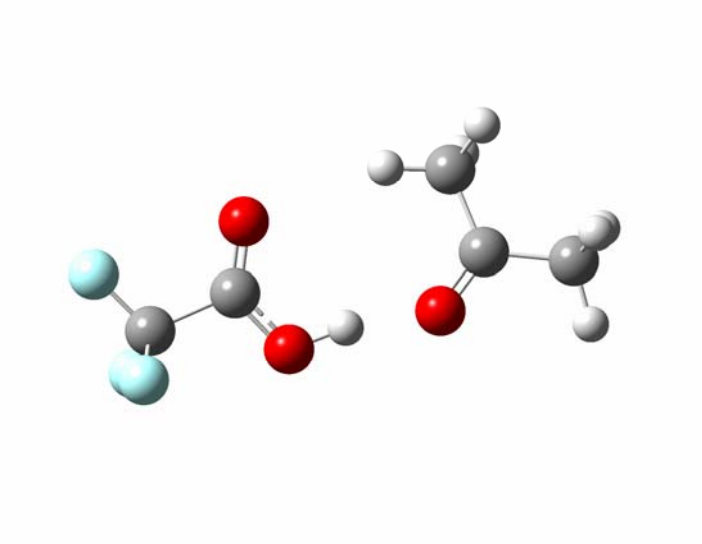


Figure S2. Energy variation during the forced protonation of propanone by TFAA in dichloromethane, modelled as a relaxed scan increasing the CO--H bond distance in the propanone-TFAA complex.

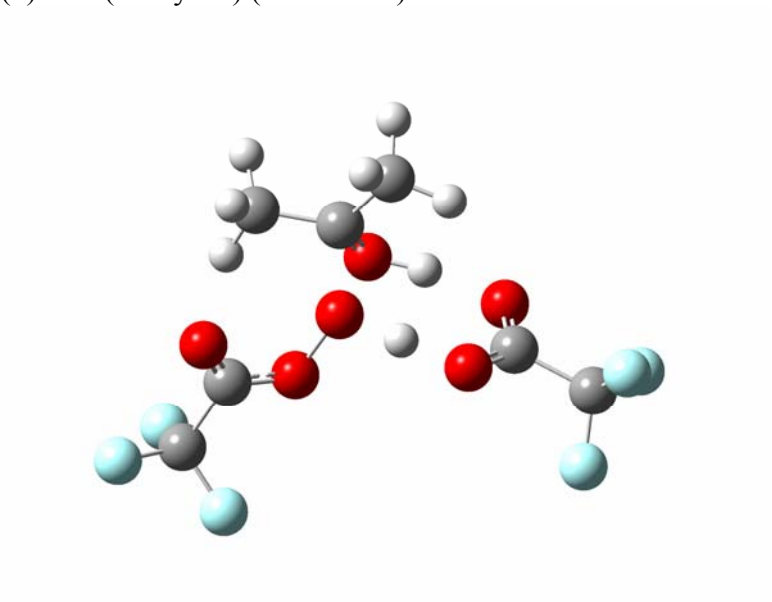
Cartesian coordinates of the optimized stationary points of the reaction of propanone with TFPAA at the MPWB1K/6-311G(d,p)-Onsager level of theory.

(a) Reactant Complex (propanone + TFAA)



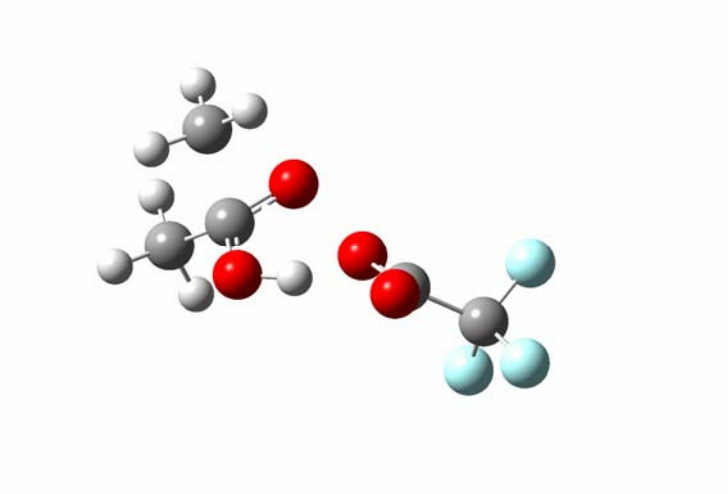
H	-0.67427300	-0.76555200	0.06160600
C	2.47012700	-0.05590500	0.00310900
C	0.96412900	0.21545000	-0.04545700
O	0.54963900	1.31935700	-0.19980400
O	0.31589800	-0.89084700	0.10045300
C	-4.58180800	-0.59467800	-0.10033000
C	-3.18590100	-0.09430600	0.01090100
O	-2.25312000	-0.86881300	-0.01149900
C	-2.98647100	1.37492500	0.15502900
H	-4.98539500	-0.30161900	-1.06770400
H	-3.29855600	1.66472300	1.15696200
H	-3.62632700	1.91685200	-0.53469500
H	-1.94804700	1.64393600	0.00847100
H	-4.60654000	-1.67230000	-0.01363800
H	-5.21857700	-0.13646400	0.65070600
F	2.83865500	-0.88670100	-0.96374500
F	2.82248700	-0.60578100	1.15733800
F	3.15862600	1.05914100	-0.13964000

(b) TS1 (catalyzed) (ν= 571.01*i*)



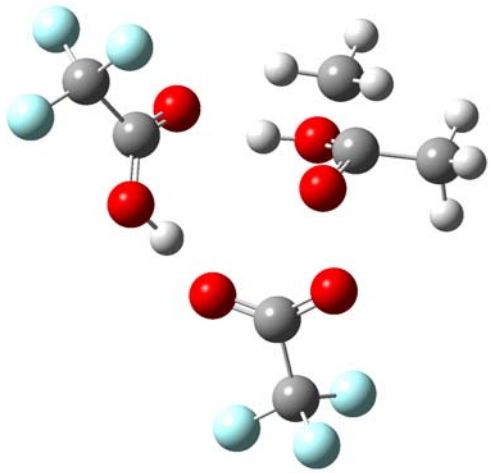
H	0.49151900	0.11778900	0.76778600
C	3.74185700	-0.95481900	0.01532400
C	2.46727000	-0.10906200	-0.06865100
O	2.43683300	0.79027700	-0.89725900
O	1.59769400	-0.45523400	0.75830400
H	1.14243400	1.53953200	-1.22978700
C	-3.37730300	-1.25629200	-0.24041500
C	-2.54592400	-0.31049500	0.63080300
O	-2.95709900	0.24165600	1.58404800
O	-1.33852700	-0.22274300	0.08409200
O	-0.52294800	0.64661300	0.80039100
C	0.59055800	2.91922000	0.76263500
C	-0.29217700	2.32268600	-0.26838900
O	0.19681300	1.86991000	-1.35031300
C	-1.71084800	2.72583100	-0.33564100
H	0.11121700	2.90353800	1.73235600
H	-1.74575500	3.74099200	-0.72647100
H	-2.16596900	2.71155400	0.64589700
H	-2.24624100	2.08293500	-1.02383600
F	3.46020400	-2.23164900	-0.20647000
F	4.27675600	-0.86350400	1.22367300
F	4.64510300	-0.57765200	-0.86312200
H	1.55173000	2.42172400	0.80169800
H	0.75751100	3.95572100	0.47431900
F	-2.76483700	-2.41518300	-0.40497100
F	-3.57027100	-0.71686700	-1.43206500
F	-4.54019400	-1.46848100	0.32183600

(c) TS2 (uncatalyzed) (ν= 630.688*i*)



O	-2.01514500	-0.89116100	-1.06086300
C	-2.29297700	0.05423900	-0.17170300
H	-2.01357600	1.79344000	-1.27365800
O	0.14902800	0.77154400	0.31255700
H	-3.23593000	1.96838200	-0.00958500
O	-1.52168900	0.13596200	0.86737900
H	-3.60807200	1.06858000	-1.49882600
H	-1.18220100	-1.32542100	-0.78263000
C	0.83592900	-0.22743300	-0.01783700
O	0.49330400	-1.34403700	-0.34360500
C	-2.84351800	1.30641100	-0.77015200
C	-3.36223400	-0.52865200	1.03285100
H	-2.99293600	-1.43852700	1.47653900
C	2.34283300	0.08240300	0.02569900
H	-3.64306300	0.22823200	1.74532500
H	-4.15270300	-0.73608800	0.31671600
F	2.73929000	0.28937500	1.27407300
F	3.06199100	-0.91109500	-0.46405500
F	2.63253100	1.17073600	-0.67343700

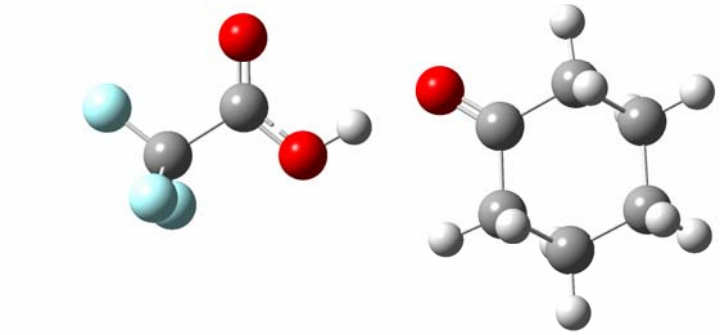
(d) TS2 (catalyzed) (ν= 629.246*i*)



O	-0.25491900	1.87610000	1.37534000
C	-0.43605100	2.26105500	0.12131000
H	-2.41903900	2.87772100	0.23090800
O	-1.97489600	0.46448600	-0.78745500
H	-1.50343900	3.70532700	-1.02881200
O	-0.33017200	1.37349000	-0.82020500
H	-1.26449600	4.13678100	0.68264700
H	0.38000400	1.14103900	1.40543000
C	-1.96923000	-0.61435300	-0.16052400
O	-1.05425900	-1.26169000	0.31469100
C	-1.46510200	3.33296300	-0.01401300
C	1.03412400	2.78051800	-0.61251200
H	1.81040700	2.03495900	-0.57246600
C	-3.39706400	-1.17019500	0.01166800
O	1.38238100	-1.49100000	-0.29355500
H	0.41670400	-1.32596500	-0.05926100
C	2.15294200	-0.67077100	0.31193600
C	3.62364800	-0.83349700	-0.07261100
O	1.85566700	0.20412400	1.08000900
F	4.39198500	-0.67648200	0.98266200
F	3.92922000	0.10934300	-0.95493800
F	3.88060000	-2.00496800	-0.61280600
H	0.86463400	3.19470300	-1.59139100
H	1.19694100	3.54216700	0.14524400
F	-3.94623800	-1.40456700	-1.16932500
F	-3.40071000	-2.29685100	0.69410900
F	-4.15838300	-0.29815700	0.65202800

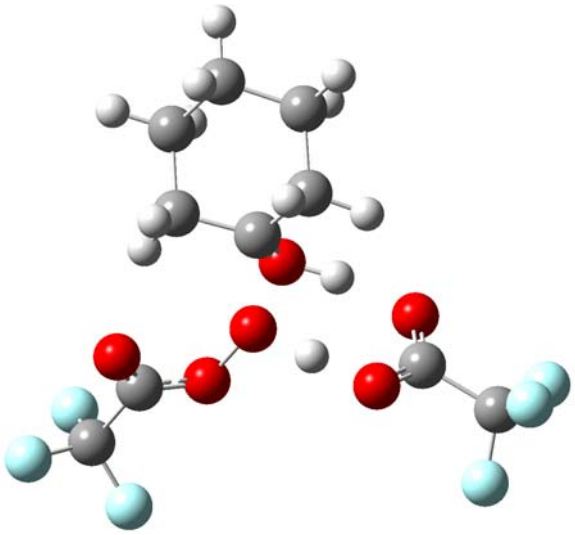
Cartesian coordinates of the optimized stationary points of the reaction of cyclohexanone with TFPAA at the MPWB1K/6-311G(d,p)-Onsager level of theory.

(a) Reactant Complex (cyclohexanone + TFAA)



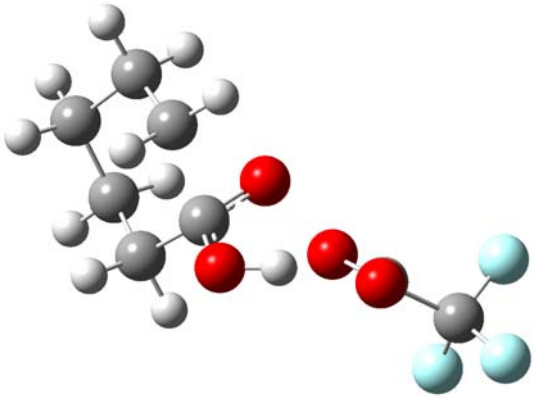
C	-2.25417500	0.58405300	-0.06809900
O	-1.20434700	-0.16201900	0.05713800
O	-2.33002500	1.76334600	-0.18958700
H	-0.35223000	0.35783300	0.05209900
C	2.28306300	-0.94583400	0.57619600
C	2.15136500	0.51672900	0.30246200
O	1.08547800	1.04882800	0.07382000
C	3.41704700	1.30481600	0.32323300
H	2.56053700	-1.04491800	1.62711400
H	3.75704400	1.33049000	1.36015000
H	1.32244100	-1.43181200	0.43712100
H	3.20070100	2.32093100	0.01421700
C	4.49670300	0.64439100	-0.52886200
H	5.42474700	1.19635500	-0.42030300
H	4.21497400	0.70965200	-1.57917400
C	3.38207100	-1.57138000	-0.27920700
H	3.50921400	-2.61051700	0.00779200
H	3.06713700	-1.56988100	-1.32219900
C	4.68389100	-0.80839600	-0.14478400
H	5.04163400	-0.87215800	0.88296100
H	5.44818100	-1.26365000	-0.76713000
C	-3.51374200	-0.28548500	-0.03682000
F	-4.59673900	0.45244900	-0.20651100
F	-3.49304100	-1.20035500	-0.99343100
F	-3.63028200	-0.91397400	1.12346000

(b) TS1 (ν= 512.569*i*)



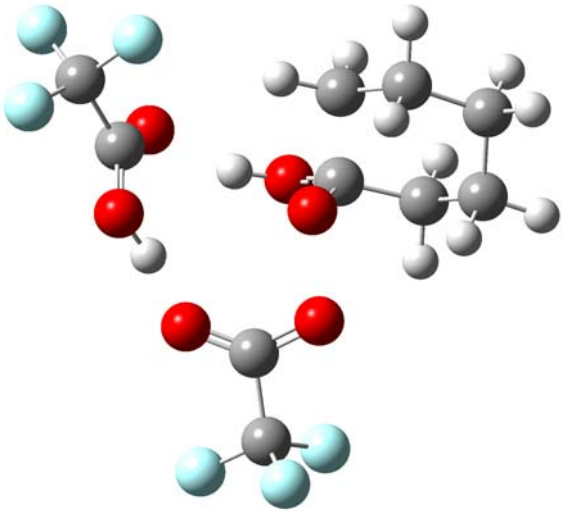
H	0.65151500	-0.40561300	0.79427800
C	4.01184200	-1.03289300	-0.00473100
C	2.62986900	-0.37487900	-0.07965800
O	2.45939100	0.48731800	-0.92947700
O	1.83314100	-0.82321500	0.77102300
H	1.04569800	1.04598200	-1.25869200
C	-3.02398300	-2.24205300	-0.21935200
C	-2.30738100	-1.22116000	0.66894800
O	-2.78333500	-0.73595300	1.62891700
O	-1.11916300	-0.98732200	0.12717300
O	-0.41801000	-0.02049000	0.84152800
C	0.34838000	2.44173400	0.69952400
C	-0.44839300	1.64357700	-0.26410900
O	0.06277600	1.22928700	-1.35503500
C	-1.90479100	1.89523600	-0.28464400
H	-0.03132900	2.26109200	1.70034500
H	-2.30454300	1.70776500	0.70717800
F	4.52329500	-0.90817800	1.21062000
F	4.86003400	-0.50682500	-0.86206100
F	3.91489300	-2.33067200	-0.26898500
F	-2.26238600	-3.29724300	-0.44993800
F	-4.12785200	-2.63845800	0.36323900
F	-3.32849500	-1.68984900	-1.38115200
H	1.39801700	2.17203100	0.65568700
H	-2.37676800	1.22948400	-1.00012300
C	-2.09998600	3.36725500	-0.65864500
H	-3.16130100	3.59224200	-0.64518900
H	-1.75206100	3.52816100	-1.67728400
C	0.13520500	3.91302200	0.32077300
H	0.67352800	4.53220200	1.03118000
H	0.57468000	4.09777300	-0.65803500
C	-1.33920700	4.26370700	0.29796900
H	-1.75301300	4.15753600	1.30054600
H	-1.46753800	5.30410600	0.01510800

(c) TS2 (uncatalyzed) (ν= 573.525*i*)



O	0.92603000	1.70019000	-1.01498100
C	1.42837600	0.62692300	-0.39812700
H	1.18206100	-0.75532600	-1.90932800
O	-0.78157600	-0.60586000	0.10945700
O	0.79834500	0.20123600	0.64465400
H	2.66955300	0.16446700	-2.03820200
H	0.07512500	1.91050700	-0.58697000
C	-1.66365500	0.29084300	0.04435200
O	-1.55745700	1.49309200	-0.04354000
C	2.03109000	-0.37521500	-1.34396500
C	2.63270600	1.09737100	0.74006600
H	3.14387100	1.71334100	0.00189000
H	2.17692200	1.73420700	1.48432300
C	3.45417400	-0.03297400	1.26772300
H	4.30401500	0.40691400	1.78951800
H	2.88012700	-0.58502200	2.00644000
C	2.77616100	-1.48925700	-0.64434100
H	3.13145400	-2.19613800	-1.38824100
H	2.08533400	-2.02666000	0.00281300
C	3.93682100	-0.95902400	0.17087600
H	4.49652300	-1.77883700	0.61011300
H	4.62760500	-0.42455500	-0.48143400
C	-3.07927100	-0.31180200	0.09954000
F	-3.33311800	-0.78518300	1.31187600
F	-4.00223800	0.58932500	-0.18220900
F	-3.21505900	-1.31007000	-0.75993300

(d) TS2 (catalyzed) (ν= 589.602*i*)



O	-0.27412900	0.92640300	1.89413200
C	-0.47441000	1.56351500	0.74162800
H	-2.47957400	1.95777900	1.03304900
O	-1.91813000	-0.03753400	-0.56554300
O	-0.33024900	0.89511200	-0.35687500
H	-1.41654600	3.18238900	1.70581000
H	0.40159200	0.24307200	1.77310200
C	-1.85396000	-1.22761300	-0.18389600
O	-0.90366500	-1.91582200	0.13114000
C	-1.59587900	2.55911900	0.83411700
C	0.94357700	2.40008900	0.21915300
H	1.06390700	2.87424700	1.19235200
H	1.74748700	1.69626400	0.06557200
C	-3.25185900	-1.87693500	-0.13785900
O	1.54552800	-1.81104300	-0.53284600
H	0.58241600	-1.78356000	-0.25378600
C	2.28176500	-1.14814300	0.27808600
C	3.74324200	-1.08898100	-0.16715200
O	1.95497000	-0.56064700	1.27195200
F	4.54364900	-1.12304600	0.87539000
F	3.93868300	0.05913000	-0.80438900
F	4.06584400	-2.07180900	-0.98041300
F	-3.21591800	-3.05348600	0.45214200
F	-3.71301600	-2.04773800	-1.36731400
F	-4.10570000	-1.11126100	0.51846000
C	0.70148600	3.35070700	-0.90809000
H	1.59170900	3.97397100	-0.99372100
H	0.61681000	2.79269100	-1.83612300
C	-1.75602700	3.37870200	-0.42380900
H	-2.62788700	4.01731900	-0.31910400
H	-1.94885300	2.70628200	-1.25773000
C	-0.52415100	4.21752600	-0.69647500
H	-0.67719400	4.84454000	-1.56934100
H	-0.35304000	4.88923500	0.14514500