Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

On the mechanism of carboxylate elimination from carbohydrate monoester-derived radicals

Supporting Information

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Table of Contents

1.0 Computational Information

Geometry optimizations of all species have been performed with the (U)M06-2X functional suitable for open shell systems in combination with the def2-TZVP basis set.[1–3] Gas phase free energies ($G_{298,qh}$) with quasi-harmonic corrections (cutoff: 100 cm^{-1}) and a scaling factor of 0.971 for harmonic frequencies were calculated using GoodVibes v3.0.1[4] and refer to a standard state of 1 atm. Solution phase results were calculated at the SMD(AcCN)/(U)M06-2X/def2-TZVP level of theory.[5] Free energies in solution have been corrected to the standard state of 1 mol/l by addition of +7.908 kJ/mol. The NPA charge parameters have been computed with Gaussian 16, rev. A.3, using the build-in NBO 3.1 program. Conformational searching was performed on Schrödinger's Maestro software.[6] Relative energies are computed relative to the most stable conformer in the conformational stack of energies. For each model system used, a full conformational analysis has been performed for the closed-shell reference system (ex, Ac-I-H, Piv-I-H, etc) and radical conformers have been generated after formal H abstraction.

For benchmarking studies single point energies were calculated using DLPNO-CCSD(T)/CBS(cc-pVTZ/cc-pVQZ) level of theory (ORCA),[7] ROB2PLYP-D3/cc-pVTZ, and G3B3 based on (U)M06-2X/def2-TZVP geometries.

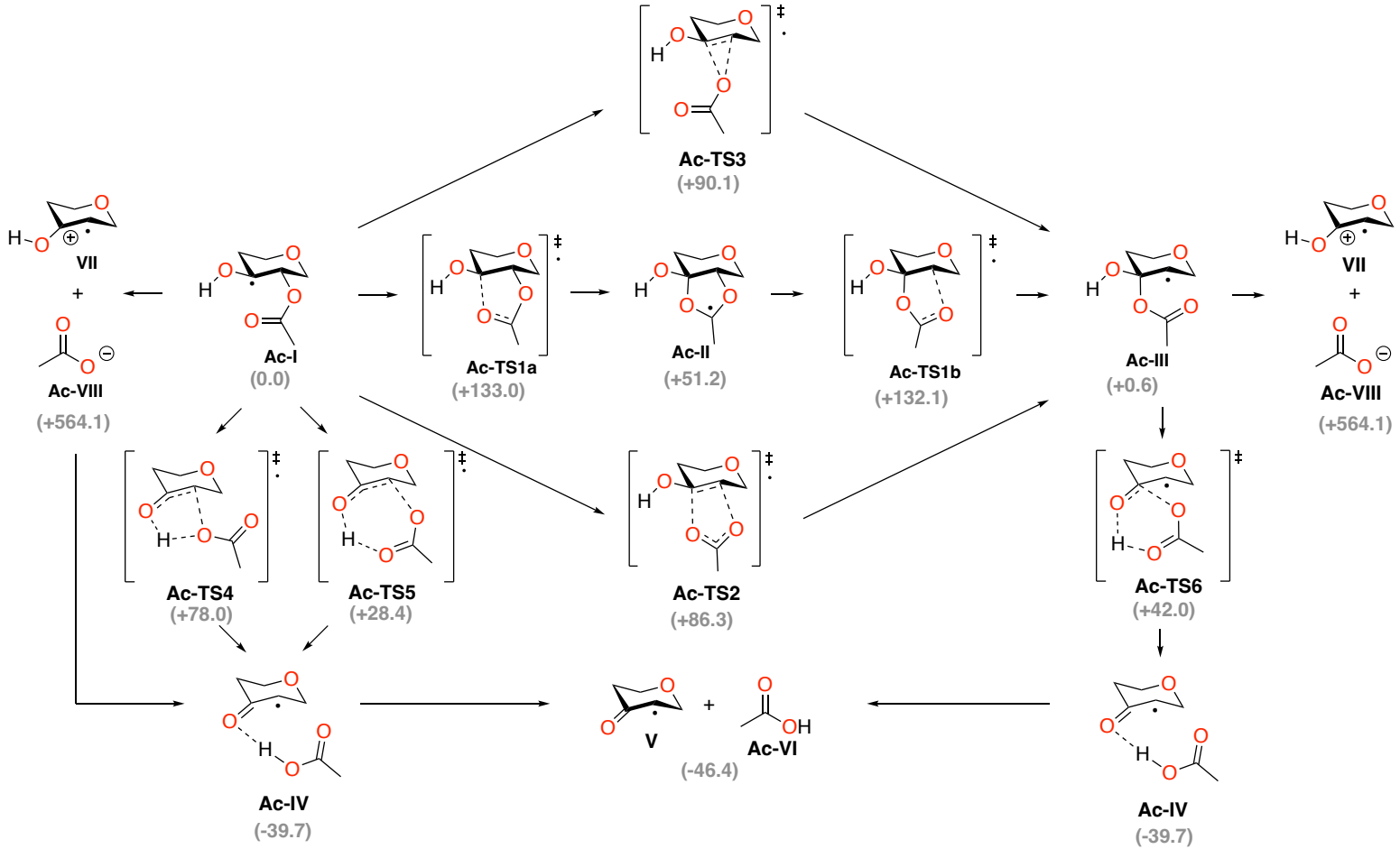
details for correction of enthalpies and free energies with GoodVibes 3.0.1
for gas phase calculations and gas phase standard state of 1 atm:
python -m goodvibes <file>.log > <file>.qh
cutoff: 100 cm^{-1}; scaling factor: 0.971; use Grimme entropic qh treatment

for solution phase calculations and solution phase standard state of 1 mol/l:
python -m goodvibes -c 1.0 <file>.log > <file>.qh
cutoff: 100 cm^{-1}; scaling factor: 0.971; use Grimme entropic qh treatment;
add entropy correction of +7.908 kJ/mol or +1.89 kcal/mol or +0.003012 Hartree.

2.0 Reaction Pathways

Following earlier theoretical studies[8] on small model systems, and more recent studies[9] on systems closely similar to carbohydrate radical substrates, acyloxy group migration reactions in model substrate **Ac-I** can, in principle, involve the reaction pathways outlined in Scheme S01. Starting from radical **Ac-I**, a stepwise pathway for formation of product radical **Ac-III** can lead through cyclic intermediate **Ac-II** together with the associated transition states for ring closure (**Ac-TS1a**) and ring opening (**Ac-TS1b**). The same product radical **Ac-III** can also be formed through the concerted (single step) pathways involving either the three-membered ring transition state **Ac-TS3** or the five-membered ring transition state **Ac-TS2**. In addition to acyloxy group migration we may also expect acetic acid elimination from radical **1** through transition states such as **Ac-TS4** or **Ac-TS5**. A final pathway involves C-O bond heterolysis to acetate (**Ac-VIII**) and radical cation **VII**, whose interchange of the hydroxyl group proton also leads to product complex **Ac-IV** and (ultimately) radical **V** and acetic acid (**Ac-VI**).

Gas phase results obtained at the (U)M06-2X/def2-TZVP level of theory as summarized in Table S01 and illustrated in Scheme S01 indicate that acyloxy group migration from **Ac-I** to **Ac-III** is without notable driving force (ΔG_{298} = +0.6 kJ/mol). The most facile pathway for this rearrangement involves 5-membered ring transition state **Ac-TS2** with a barrier of ΔG_{298} = +86.3 kJ/mol. This is substantially less than the stepwise ring-closure/ring-opening sequence through **Ac-TS1a** with a barrier of ΔG_{298} = +133.0 kJ/mol. Transition state **Ac-TS2** is significantly polarized as indicated by the charge of the migrating acyloxy group of -0.55e (Figure S01). A much lower barrier of only ΔG_{298} = +28.4 kJ/mol is found for elimination of acetic acid through transition state **Ac-TS5** that is exergonic by ΔG_{298} = -46.4 kJ/mol. Formation of the same products (radical **V** and acetic acid (**Ac-VI**)) through C-O bond heterolysis and the formation of radical cation **VII** and acetate **Ac-VIII** is, at least in the gas phase, much less favorable.



Scheme S01. Acyloxy group migration and elimination pathways for model substrate **Ac-I**. Gas phase Gibbs free energy differences (ΔG_{298}) relative to radical **Ac-I** ((U)M06-2X/def2-TZVP results in kJ/mol) are given in brackets.

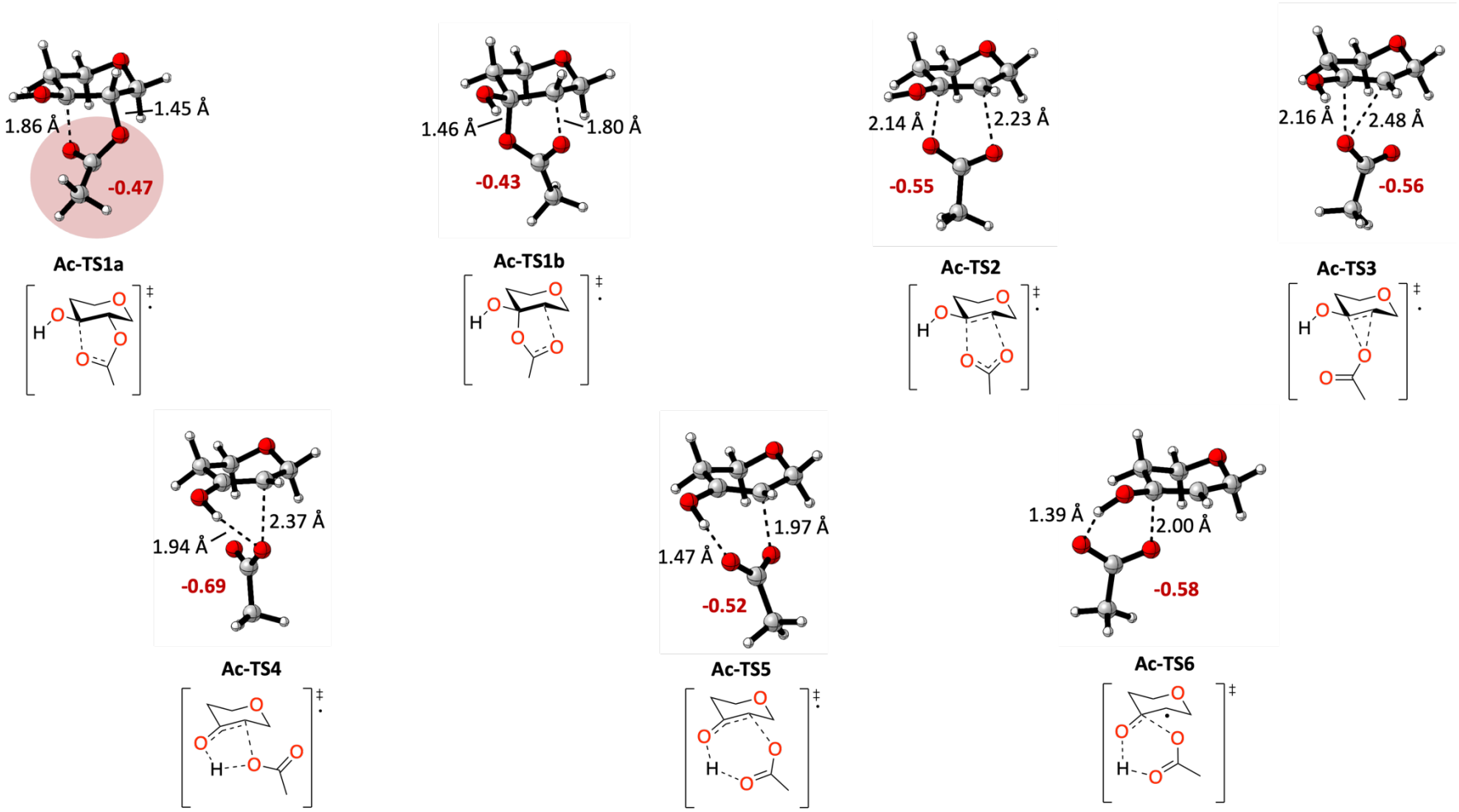
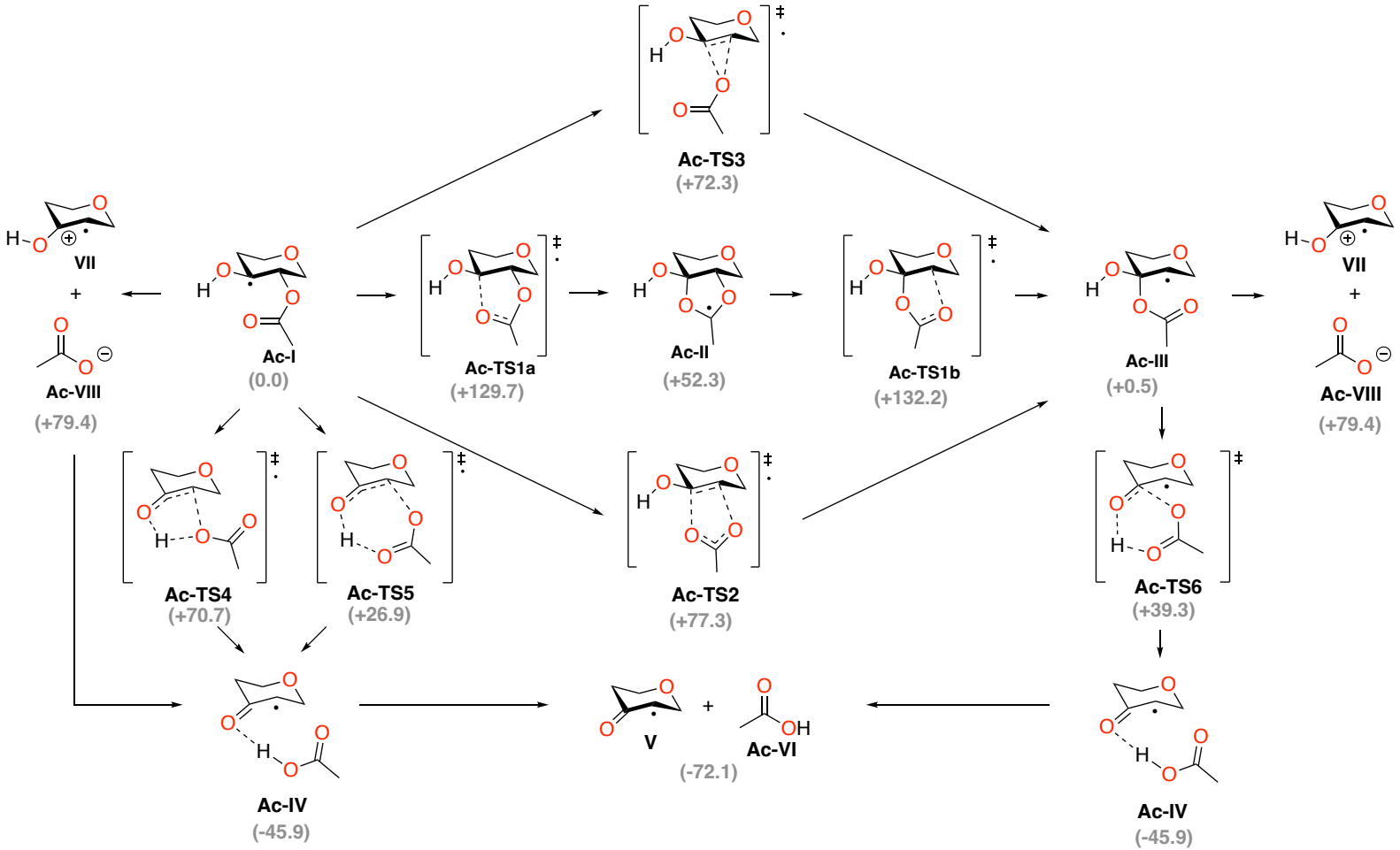


Figure S01. Selected transition states for the reactions shown in Scheme S01 (gas phase (U)M06-2X/def2-TZVP results). Acyloxy group (-O_2CCH_3) charges are shown in red type (NPA/(U)M06-2X/def2-TZVP results) and distances are shown in Angstrom (Å).

3.0 Solvent Effects and Benchmarking

The influence of acetonitrile as a bulk solvent can be assessed through addition of solvation free energies with aid of the SMD continuum solvation model and a standard state of 1 mol/l. Reaction free energies calculated in this manner deviate surprisingly little from the gas phase free energies discussed before (Table S01/Scheme S01). The largest difference is, as expected, seen for the energetics of ions **VII** and **Ac-VIII**, whose formation is now endergonic by only 79.4 kJ/mol (as compared to +564.1 kJ/mol in the gas phase). The energetically most favorable pathway still involves elimination of acetate through transition state **Ac-TS5** with a barrier of +26.9 kJ/mol. From the 1,2-acyloxy group migration pathways it is now 3-membered ring transition state **Ac-TS3** that is preferred.

Reoptimizing all ground and transition states at the SMD(AcCN)/(U)M06-2X/def2-TZVP level of theory we find very similar reaction energies as obtained already with the single point SMD approach (Table S01). For the 1,2-acyloxy group migration reaction transition states **Ac-TS2** and **Ac-TS3** continue to be quite close at around 70 kJ/mol, and elimination of acetate through **Ac-TS5** again shows the lowest overall barrier at +28.0 kJ/mol. Given this rather low barrier we must conclude that the chemistry of radical **Ac-I** will be dominated by acetic acid elimination and rapid formation of radical **V** unless an extraordinarily fast bimolecular process traps radical **Ac-I** (e.g. by hydrogen atom transfer).



Scheme S02. Acyloxy group migration and elimination pathways for model substrate **Ac-I**. Gibbs free energy differences ($\Delta G_{298,qh,sol}$) relative to radical **Ac-I** (UM06-2X/def2-TZVP//SMD(acetonitrile) results in kJ/mol) are given in brackets.

Benchmarking studies were conducted by calculating single point energies for species in Scheme S01 at ROB2PLYP-D3/cc-pVTZ, DLPNO-CCSD(T)/CBS, and G3B3 levels of theory. These results vary little from those calculated at (U)M06-2X/def2-TZVP with single point energies in acetonitrile (Table S01).

Table S01. Summary of reaction energies for the species shown in Scheme S01 (in kJ/mol).[a]

System	ΔH_{298}[b] ((U)M06-2X/ def2-TZVP)	$\Delta G_{298,qh}$[b] ((U)M06-2X/ def2-TZVP)	$\Delta G_{298,qh,sol}$[b] ((U)M06-2X/ def2-TZVP)	$\Delta G_{298,qh,sol}$[c] ((U)M06-2X/ def2-TZVP)	ΔG_{298}[b] (ROB2PLYP-D3/cc-pVTZ)	ΔG_{298}[b] (DLPNO-CCSD(T)/CBS)	$\Delta G_{298,qh,sol}$[b] (DLPNO-CCSD(T)/CBS)	ΔG_{298}[b] (G3B3)
Ac-I	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ac-TS1a	+127.9	+133.0	+129.7	+129.8	+127.5	+129.9	+126.6	+122.3
Ac-II	+43.8	+51.2	+52.3	+53.0	+66.0	+50.6	+52.2	+47.1
Ac-TS1b	+125.5	+132.1	+132.2	+132.0	+129.3	+127.2	+127.3	+119.7
Ac-III	+0.3	+0.6	+0.5	-0.4	+5.1	+0.4	+0.3	-3.3
Ac-TS2	+86.7	+86.3	+77.3	+69.4	+62.3	+85.8	+76.8	+74.1
Ac-TS3	+93.5	+90.1	+72.3	+67.3	+69.3	+93.1	+78.9	+86.8
Ac-TS4	+79.6	+78.0	+70.7	+67.5	+59.5	+85.1	+77.8	+74.3
Ac-TS5	**+27.7**	**+28.4**	**+26.9**	**+28.0**	**+9.5**	**+33.1**	**+31.5**	**+29.0**
Ac-TS6	+41.3	+42.0	+39.3	+39.2	+31.3	+49.0	+45.8	+43.0
Ac-IV	-31.2	-39.7	-45.9	-52.6	-51.4	-41.4	-46.7	-42.8
V + Ac-VI	+10.0	-46.4	-72.1	-64.6	-57.5	-55.2	-80.8	-49.5
VII + Ac-VIII	+621.6	+564.1	+79.4	+89.2	+556.0	+562.9	+78.3	+567.0

[a] Calculated with reference to the best conformer of each species. [b] Using gas phase (U)M06-2X/def2-TZVP geometries.
[c] Using solution phase SMD(AcCN)/(U)M06-2X/def2-TZVP geometries.

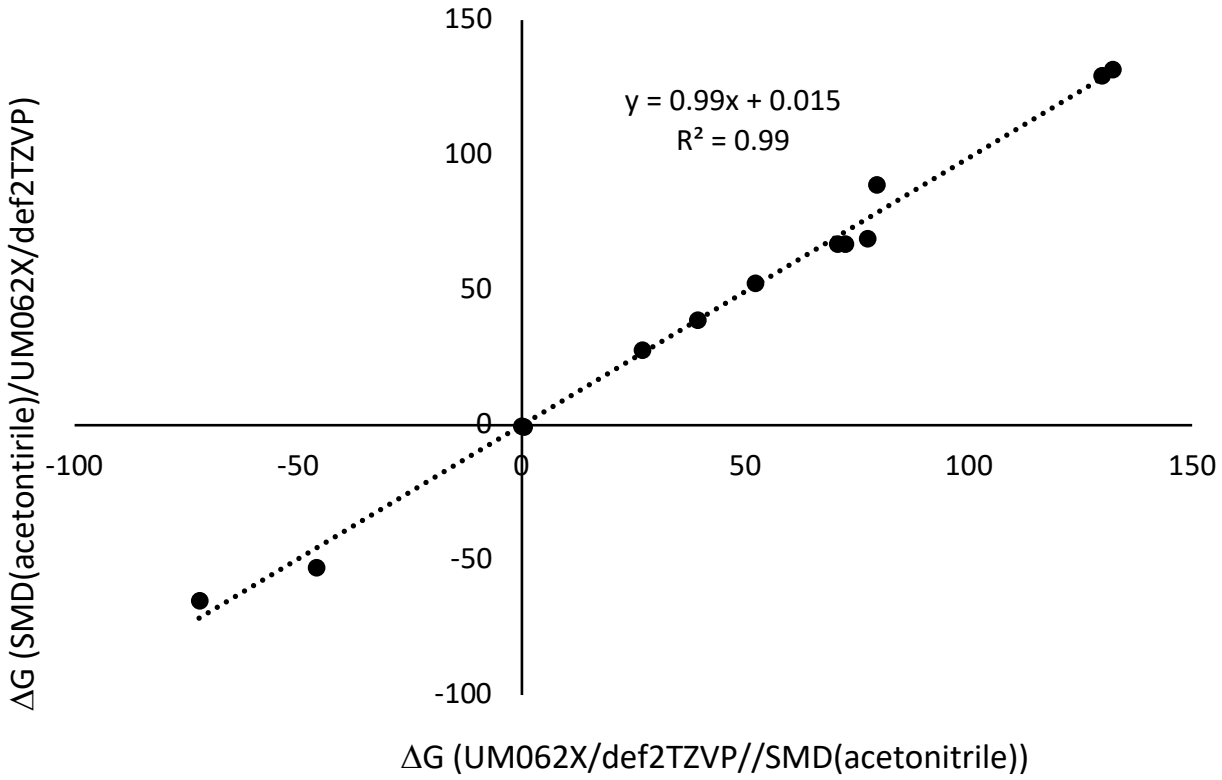


Figure S02. Plot of ΔG for calculated using (U)M06-2X/def2-TZVP level of theory with gas phase geometry geometry optimization and single point energies at (U)M06-2X/def2-TZVP//SMD(acetonitrile) vs ΔG calculated using SMD(acetonitrile)/(U)M06-2X/def2-TZVP level of theory with solution phase geometry optimization for stationary points in Scheme S01.

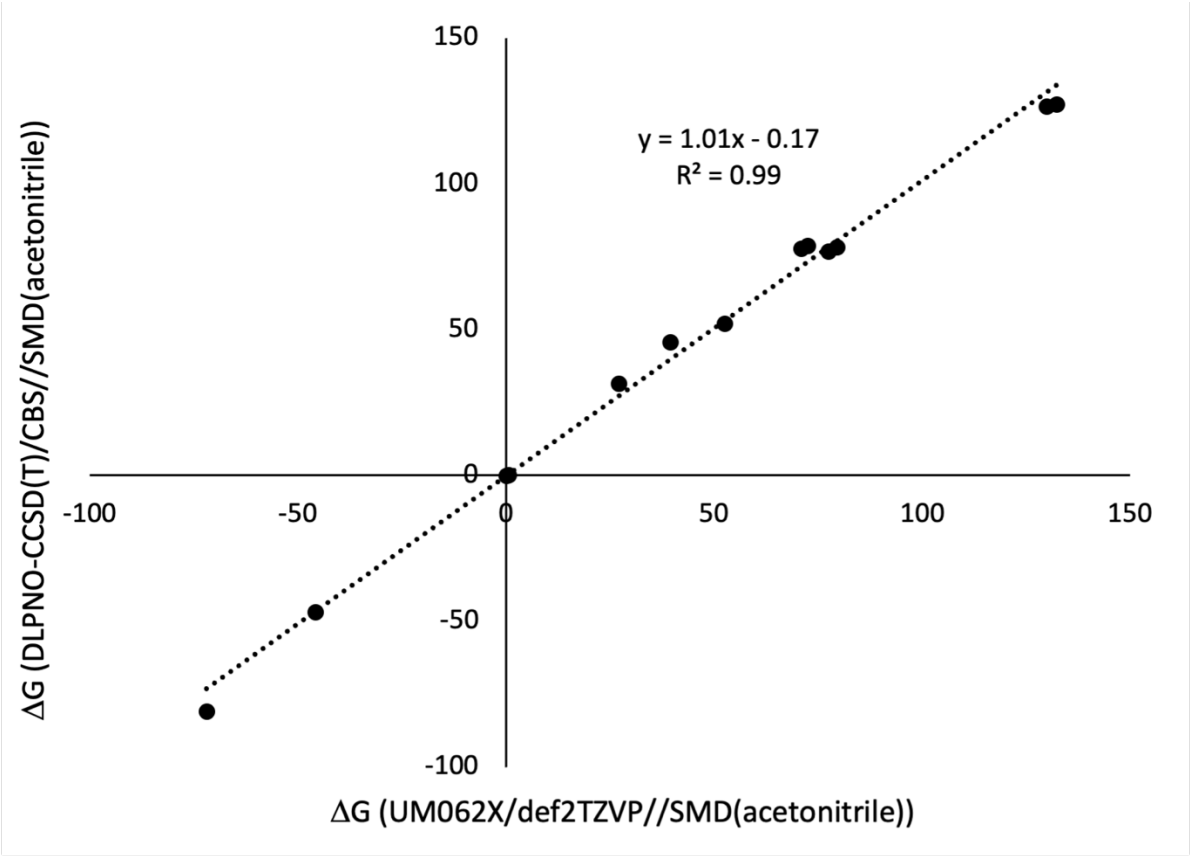


Figure S03. Plot of ΔG for calculated using (U)M06-2X/def2-TZVP level of theory with gas phase geometry geometry optimization and single point energies at (U)M06-2X/def2-TZVP//SMD(acetonitrile) vs ΔG calculated using DLPNO-CCSD(T)/CBS//SMD(acetonitrile) level of theory for stationary points in Scheme S01.

Table S02. Energy values for the species shown in Scheme S01 (gas phase (U)M06-2X/def2-TZVP results).

System	E_{tot} **((U)M06-2X/ def2-TZVP)**	H_{298} **((U)M06-2X/ def2-TZVP)**	$G_{298,qh}$ **((U)M06-2X/ def2-TZVP)**	E_{tot} **(SMD(AcCN)/ (U)M06-2X/ def2-TZVP)**	**q(NPA,AcO)**	$\Delta G_{298,qh}$ **((U)M06-2X/ def2-TZVP) [kJ/mol]**	$\Delta G_{298,qh.sol}$ **((U)M06-2X/ def2-TZVP)[a] [kJ/mol]**
Ac-I							
aco_024f	**-574.2128353**	**-574.0239376**	**-574.0727460**	**-574.2270709**	-0.3035	0.0	0.0
aco_005	-574.2093757	-574.0206377	-574.0698982	-574.2250949	-0.3089	+7.5	+3.6
aco_002	-574.2055086	-574.0168421	-574.0663809	-574.2236632	-0.2949	+16.7	+6.4
aco_006	-574.2042959	-574.0156706	-574.0649547	-574.2207620	-0.3100	+20.5	+14.6
aco_003	-574.2033567	-574.0148340	-574.0641671	-574.2204886	-0.2943	+22.5	+14.9
Ac-TS1a							
aco_014	**-574.1615865**	**-573.9752299 (imag=-950 cm^{-1})**	**-574.0221055**	**-574.1770666**	-0.4693	**+133.0**	**+129.7**
aco_025	-574.1610416	-573.9747270 (imag=-937 cm^{-1})	-574.0215835	-574.1761851	-0.5020	+134.3	+131.9
Ac-II							
aco_015r	**-574.1965273**	**-574.0072482**	**-574.0532410**	-574.2099272	-0.5516	+51.2	+53.4
aco_012	-574.1962317	-574.0069472	-574.0529055	**-574.2101639**	-0.5502	+52.1	+52.9
aco_008	-574.1954873	-574.0063332	-574.0526034	-574.2099443	-0.5350	+52.9	**+52.3**
aco_026r	-574.1944476	-574.0053106	-574.0515740	-574.2094460	-0.5353	+55.6	+53.6
aco_013	-574.1908903	-574.0018311	-574.0484196	-574.2072539		+63.9	+58.3
aco_027	-574.1900824	-574.0011160	-574.0478958	-574.2062771		+65.2	+60.1
Ac-TS1b							
aco_015	-574.1619790	-573.9761218 (imag=-950 cm^{-1})	-574.0224481	-574.1761732	-0.4250	**+132.1**	**+132.2**
aco_026	-574.1596395	-573.9739862 (imag=-1033 cm^{-1})	-574.0205680	-574.1752776	-0.4072	+137.0	+133.3

Ac-III							
aco_016	**-574.2110687**	**-574.0238378**	**-574.0725182**	-574.2253361	-0.3484	+0.6	**+0.5**
aco_021f	-574.2092998	-574.0221980	-574.0709712	-574.2234206	-0.3556	+4.7	+5.0
aco_004	-574.2040081	-574.0171445	-574.0662997	-574.2214907	-0.3308	+16.9	+8.4
aco_023r	-574.2017108	-574.0146827	-574.0641254	-574.2176988		+22.6	+18.0
aco_011r	-574.2006972	-574.0137314	-574.0631133	-574.2163413		+25.3	+21.6
aco_028f	-574.1979759	-574.0111355	-574.0604803	-574.2150130		+32.2	+24.8
Ac-TS2							
aco_010	**-574.1769633**	**-573.9909321** (imag=-278 cm^{-1})	**-574.0398695**	**-574.1946458**	-0.5509	**+86.3**	**+77.3**
aco_028	-574.1726703	-573.9867366 (imag=-297 cm^{-1})	-574.0358433	-574.1911628	-0.5159	+96.9	+85.7
Ac-TS3							
aco_023	-574.1738495	**-573.9883179 (imag=-157 cm^{-1})**	**-574.0384235**	**-574.1935054**	-0.5589	**+90.1**	**+75.9**
aco_011	-574.1714675	-573.9854670 (imag=-55 cm^{-1})	-574.0352964	-574.1928538	-0.5063	+98.3	+79.5
Ac-TS4							
aco_022	-574.1795821	-573.9936341 (imag=-205 cm^{-1})	-574.0430295	-574.1966063	-0.6923	+78.0	+70.7
Ac-TS5							
aco_024	**-574.1989292**	**-574.0134021** (imag=-193 cm^{-1})	**-574.0619162**	**-574.2137499**	-0.5242	+28.4	+26.9
Ac-TS6							

aco_021	-574.1906569	-574.0074599 (imag=-452 cm^{-1})	-574.0557474	-574.2060893	-0.5766	+44.6	+41.5
Ac-IV							
aco_021r	**-574.2224544**	**-574.0358361**	-574.0878664	**-574.2386047**	-0.5518	**-39.7**	**-44.7**
aco_022f	-574.2223135	-574.0356896	**-574.0882660**	-574.2384912	-0.5507	-40.7	-45.8
V							
aco_007	-345.1158220	-344.9975398	-345.0354352	-345.1303555	-		
Ac-VI							
aco_009	-229.0887384	-229.0226012	-229.0549932	-229.0982225	-0.4923		
V + AcVI	-574.2045604	-574.020141	-574.0904284	-574.228578	-	**-46.4**	**-72.1**
VII							
aco_019	-345.4496196	-345.3188634	-345.3569734	-345.5527916	-		
Ac-VIII							
aco_018	-228.5209366	-228.4683132	-228.5009275	-228.6165958	-1.0000		
VII + AcVIII	-573.9705562	-573.7871766	-573.8579009	-574.1693874	-	+564.1	+79.4

[a] Using gas phase M06-2X/def2-TZVP geometries.

Table S03. Energy values for the species shown in Scheme S01 at the SMD(AcCN)/(U)M06-2X/def2-TZVP level of theory.

System	E_{tot} (SMD(AcCN)/	H_{298} (SMD(AcCN)/	$G_{298,qh}$ (SMD(AcCN)/	$\Delta G_{298,qh}$ (SMD(AcCN)/

	(U)M06-2X/ def2-TZVP)	(U)M06-2X/ def2-TZVP)	(U)M06-2X/ def2-TZVP)	(U)M06-2X/ def2-TZVP) [kJ/mol]
Ac-I				
aco_024fsol	**-574.2272928**	**-574.0390635**	**-574.0848058**	0.0
aco_023solf	-574.2211109	-574.0331646	-574.0794205	+14.1
aco_022solr	-574.2210470	-574.0330286	-574.0792833	+14.5
aco_014solr	-574.2208350	-574.0327621	-574.0790434	+15.1
aco_028solr	-574.2201426	-574.0322116	-574.0785821	+16.3
Ac-TS1a				
aco_014sol	**-574.1772364**	**-573.9914380** (imag=-985 cm^{-1})	**-574.0353714**	**+129.8**
aco_025sol	-574.1764948	-573.9908689 (imag=-992 cm^{-1})	-574.0347166	+131.5
Ac-II				
aco_025solf	-574.2103614	-574.0216902	-574.0645866	+53.1
aco_014solf	-574.2102243	-574.0215528	-574.0646078	**+53.0**
aco_015solr	-574.2101209	-574.0213791	-574.0644223	+53.5
aco_026solr	-574.2099147	-574.0212272	-574.0642907	+53.9
Ac-TS1b				
aco_015sol	**-574.1763449**	**-573.9910110** (imag=-1103 cm^{-1})	**-574.0345308**	**132.0**
aco_026sol	-574.1756222	-573.9903400 (imag=-1116 cm^{-1})	-574.0339111	+133.6
Ac-III				
aco_015solf	**-574.2255370**	**-574.0390585**	**-574.0849449**	-0.4

aco_021solf	-574.2236443	-574.0372876	-574.0830968	+4.5
aco_010solf	-574.2218053	-574.0354739	-574.0818405	+7.8
aco_011solr	-574.2168136	-574.0306418	-574.0771707	+20.0
aco_028solf	-574.2155529	-574.0293511	-574.0758827	+23.4
Ac-TS2				
aco_010sol	**-574.1967379**	**-574.0115294** (imag=-189 cm^{-1})	**-574.0583923**	**+69.4**
aco_028sol	-574.1943482	-574.0092215 (imag=-155 cm^{-1})	-574.0563277	+74.8
Ac-TS3				
aco_023sol	**-574.1953412**	**-574.0105058** (imag=-58 cm^{-1})	**-574.0580900**	**+70.1**
aco_011sol	-574.1945222	-574.0094768 (imag=-58 cm^{-1})	-574.0568769	+73.3
Ac-TS4				
aco_022sol	-574.1976621	-574.0122772 (imag=-161 cm^{-1})	-574.0590799	**+67.5**
Ac-TS5				
aco_024sol	**-574.2139489**	**-574.0286752** (imag=-217 cm^{-1})	**-574.0741509**	**+28.0**
Ac-TS6				
aco_021sol	-574.2065578	-574.0234399 (imag=-352 cm^{-1})	-574.0689469	**+41.6**
Ac-IV				
aco_021solr	**-574.2407610**	**-574.0549576**	-574.1045295	-51.8

aco_022solf	-574.2404534	-574.0546750	**-574.1048372**	**-52.6**
aco_024solr	-574.2404462	-574.0546345	-574.1045980	-52.0
V				
aco_007sol	-345.1305303	-345.0124047	-345.0472302	
Ac-VI				
aco_009sol	-229.0984248	-229.0327659	-229.0621870	
V + Ac-VI			-574.1094172	-64.6
VII				
aco_019sol	**-345.5531468**	**-345.4224408**	**-345.4574849**	
aco_020sol	-345.5523892	-345.4216836	-345.4567290	
Ac-VIII				
aco_018sol	-228.6170295	-228.5641993	-228.5933670	
VII +Ac-VIII			-574.0508519	+89.2

Table S04. Energy values for the species shown in Scheme S01 at ROB2PLYP-D3/cc-pVTZ level.[a]

System	E_{tot} (ROB2PLYP-D3/ cc-pVTZ)	H_{298} (ROB2PLYP-D3/ cc-pVTZ)	G_{298} (ROB2PLYP-D3/ cc-pVTZ)	ΔG_{298} (ROB2PLYP-D3/ cc-pVTZ) [kJ/mol]
Ac-I				
aco_024f	**-574.0024571**	**-573.8135594**	**-573.8623678**	**0.0**
aco_005	-573.9981015	-573.8092277	-573.858624	+9.8
aco_002	-573.9943647	-573.8056982	-573.855237	+18.7

aco_006	-573.9927087	-573.8040834	-573.8533675	+23.6
aco_003	-573.9914839	-573.8029612	-573.8522943	+26.4
Ac-TS1a				
aco_014	**-573.9532856**	**-573.766929**	**-573.8138046**	**+127.5**
aco_025	-573.9529734	-573.7666588	-573.8135153	+128.3
Ac-II				
aco_015r	**-573.9805221**	**-573.791243**	**-573.8372358**	**+66.0**
aco_012	-573.980322	-573.7910375	-573.8369958	+66.6
aco_008	-573.9797084	-573.7905543	-573.8368245	+67.1
aco_026r				
aco_013	**-573.975017**	**-573.7859578**	**-573.8325463**	**+78.3**
aco_027	-573.9745344	-573.785568	-573.8323478	+78.8
Ac-TS1b				
aco_015	**-573.952666**	**-573.76184**	**-573.808042**	**+129.3**
aco_026	-573.9504625	-573.7598495	-573.8062985	+133.8
Ac-III				
aco_016	**-573.9989888**	**-573.8117579**	**-573.8604383**	**+5.1**
aco_021f	-573.9972895	-573.8101877	-573.8589609	+8.9
aco_004	-573.9920242	-573.8051606	-573.8543158	+21.1
aco_023r	-573.9892405	-573.8022124	-573.8514551	+28.7
aco_011r	-573.9883327	-573.8013369	-573.8507488	+30.5
aco_028f	-573.9862239	-573.7993835	-573.8487283	+35.8
Ac-TS2				
aco_010	**-573.9757419**	**-573.7897107**	**-573.8386481**	**+62.3**
aco_028	-573.9719098	-573.7859761	-573.8350828	+71.6

Ac-TS3				
aco_029	**-573.9714725**	-573.7854156	-573.8353949	+70.8
aco_023	-573.9713799	**-573.7858483**	**-573.8359539**	**+69.3**
aco_011	-573.9699425	-573.783942	-573.8337714	+75.1
Ac-TS4				
aco_022	-573.9762456	-573.7902976	-573.839693	**+59.5**
Ac-TS5				
aco_024	-573.9957751	-573.810248	-573.8587621	**+9.5**
Ac-TS6				
aco_021	-573.9853675	-573.8021705	-573.850458	**+31.3**
Ac-IV				
aco_021r	**-574.0165365**	**-573.8299182**	**-573.8819485**	**-51.4**
aco_022f	-574.0164979	-573.829874	-573.8824504	-52.7
V				
aco_007	-344.9842656	-344.8659834	-344.9038788	
Ac-VI				
aco_009	-229.0141332	-229.007996	-228.980388	
V + AcVI			-573.8842856	**-57.5**
VII				
aco_019	-345.32368	-345.1929238	-345.2310338	

Ac-VIII				
aco_018	-228.4395757	-228.3869523	-228.4195748	
VII + AcVIII			-573.6506086	**+556.0**

[a] Using gas phase (U)M06-2X/def2-TZVP geometries.

Table S05. Energy values for the species shown in Scheme S01 at DLPNO-CCSD(T)/CBS level.[a]

System	E_{tot} (DLPNO-CCSD(T)/CBS)	H_{298} (DLPNO-CCSD(T)/CBS)	G_{298} (DLPNO-CCSD(T)/CBS)	ΔG_{298} (DLPNO-CCSD(T)/CBS) [kJ/mol]	$\Delta G_{298,qh,sol}$ (DLPNO-CCSD(T)/CBS) [kJ/mol]
Ac-I					
aco_024f	**-573.6027267**	**-573.413829**	**-573.4626374**	**0.0**	**0.0**
aco_005	-573.5993231	-573.4104493	-573.4598456	+7.3	+3.4
aco_002	-573.5957068	-573.4070403	-573.4565791	+15.9	+5.6
aco_006	-573.5935945	-573.4049692	-573.4542533	+22.0	+16.2
aco_003	-573.5925121	-573.4039894	-573.4533225	+24.5	+16.9
Ac-TS1a					
aco_014	**-573.5526571**	**-573.3663005**	**-573.4131761**	**+129.9**	**+126.6**
aco_025	-573.5523974	-573.3660828	-573.4129393	+130.5	+128.1
Ac-II					
aco_015r	**-573.5866482**	**-573.3973691**	**-573.4433619**	**+50.6**	+52.8
aco_012	-573.5862836	-573.3969991	-573.4429574	+51.7	+52.5
aco_008	-573.5854133	-573.3962592	-573.4425294	+52.8	**+52.2**
aco_026r	-573.5845233	-573.3953863	-573.4416497	+55.1	+53.1
aco_013	-573.581099	-573.3920398	-573.4386283	+63.0	+57.4
aco_027	-573.5797266	-573.3907602	-573.43754	+65.9	+60.7

Ac-TS1b					
aco_015	**-573.5537356**	**-573.3678784**	**-573.4142047**	**+127.2**	**+127.3**
aco_026	-573.5512673	-573.365614	-573.4121958	+132.4	+128.8
Ac-III					
aco_016	**-573.6010316**	**-573.4138007**	**-573.4624811**	**+0.4**	**+0.3**
aco_021f	-573.5993607	-573.4122589	-573.4610321	+4.2	+4.5
aco_004	-573.5940455	-573.4071819	-573.4563371	+16.5	+8.0
aco_023r	-573.5914636	-573.4044355	-573.4536782	+23.5	+18.4
aco_011r	-573.5903847	-573.4033889	-573.4528008	+25.8	+22.1
aco_028f	-573.5880906	-573.4012502	-573.450595	+31.6	+24.3
Ac-TS2					
aco_010	**-573.5670426**	**-573.3810114**	**-573.4299488**	**+85.8**	**+76.8**
aco_028	-573.5631769	-573.3772432	-573.4263499	+95.3	+84.1
Ac-TS3					
aco_029					
aco_023	**-573.5625897**	**-573.3770581**	**-573.4271637**	**+93.1**	**+78.9**
aco_011	-573.5587237	-573.3727232	-573.4225526	+105.2	+86.5
Ac-TS4					
aco_022	-573.5667764	-573.3808284	-573.4302238	**+85.1**	**+77.8**
Ac-TS5					
aco_024	-573.5870526	-573.4015255	-573.4500396	**+33.1**	**+31.5**
Ac-TS6					
aco_021	-573.5788909	-573.3956939	-573.4439814	**+49.0**	**+45.8**

Ac-IV					
aco_021r	**-573.6131139**	**-573.4264956**	**-573.4785259**	**-41.7**	**-46.7**
aco_022f	-573.6124497	-573.4258258	-573.4784022	-41.4	-46.5
V					
aco_007	-344.7313273	-344.6130451	-344.6509405		
Ac-VI					
aco_009	-228.8664334	-228.8602962	-228.8326882		
V + AcVI			-573.4836475	-55.2	**-80.8**
VII					
aco_019	-345.0628669	-344.9321107	-344.9702207		
Ac-VIII					
aco_018	-228.2980208	-228.2453974	-228.2780199		
VII + AcVIII			-573.2482323	**+562.9**	**+78.3**

[a] Using gas phase (U)M06-2X/def2-TZVP geometries.

Table S06. Energy values for the species shown in Scheme S01 at G3B3 level.[a]

System	E_{tot} **(G3B3)**	H_{298} **(G3B3)**	G_{298} **(G3B3)**	ΔG_{298} **(G3B3) [kJ/mol]**
Ac-I				
aco_024f	-574.0055819	-573.81668	-573.86549	**0.0**
aco_005	-574.0023254	-573.81345	-573.86285	**+6.9**
aco_002	-573.9984928	-573.80983	-573.85937	**+16.1**

aco_006	-573.9970527	-573.80843	-573.85771	**+20.4**
aco_003	-573.996128	-573.80761	-573.85694	**+22.5**
Ac-TS1a				
aco_014	-573.9583971	-573.77204	-573.81892	**+122.3**
aco_025	-573.9581932	-573.77188	-573.81874	**+122.8**
Ac-II				
aco_015r	-573.9908544	-573.80158	-573.84757	**+47.1**
aco_012	-573.9905827	-573.8013	-573.84726	**+47.9**
aco_008	-573.9896809	-573.80053	-573.8468	**+49.1**
aco_026r	-573.9886182	-573.79948	-573.84574	**+51.8**
aco_013	-573.9851772	-573.79612	-573.84271	**+59.8**
aco_027	-573.9840734	-573.79511	-573.84189	**+62.0**
Ac-TS1b				
aco_015	-573.9594506	-573.77359	-573.81992	**+119.7**
aco_026	-573.9569883	-573.77134	-573.81792	**+124.9**
Ac-III				
aco_016	-574.0052918	-573.81806	-573.86674	**-3.3**
aco_021f	-574.0033269	-573.81623	-573.865	**+1.3**
aco_004	-573.9986142	-573.81175	-573.86091	**+12.0**
aco_023r	-573.9954238	-573.8084	-573.85764	**+20.6**
aco_011r	-573.9942018	-573.80721	-573.85662	**+23.3**
aco_028f	-573.9924977	-573.80566	-573.855	**+27.5**
Ac-TS2				
aco_010	-573.9743744	-573.78834	-573.83728	**+74.1**
aco_028	-573.9700306	-573.7841	-573.8332	**+84.8**

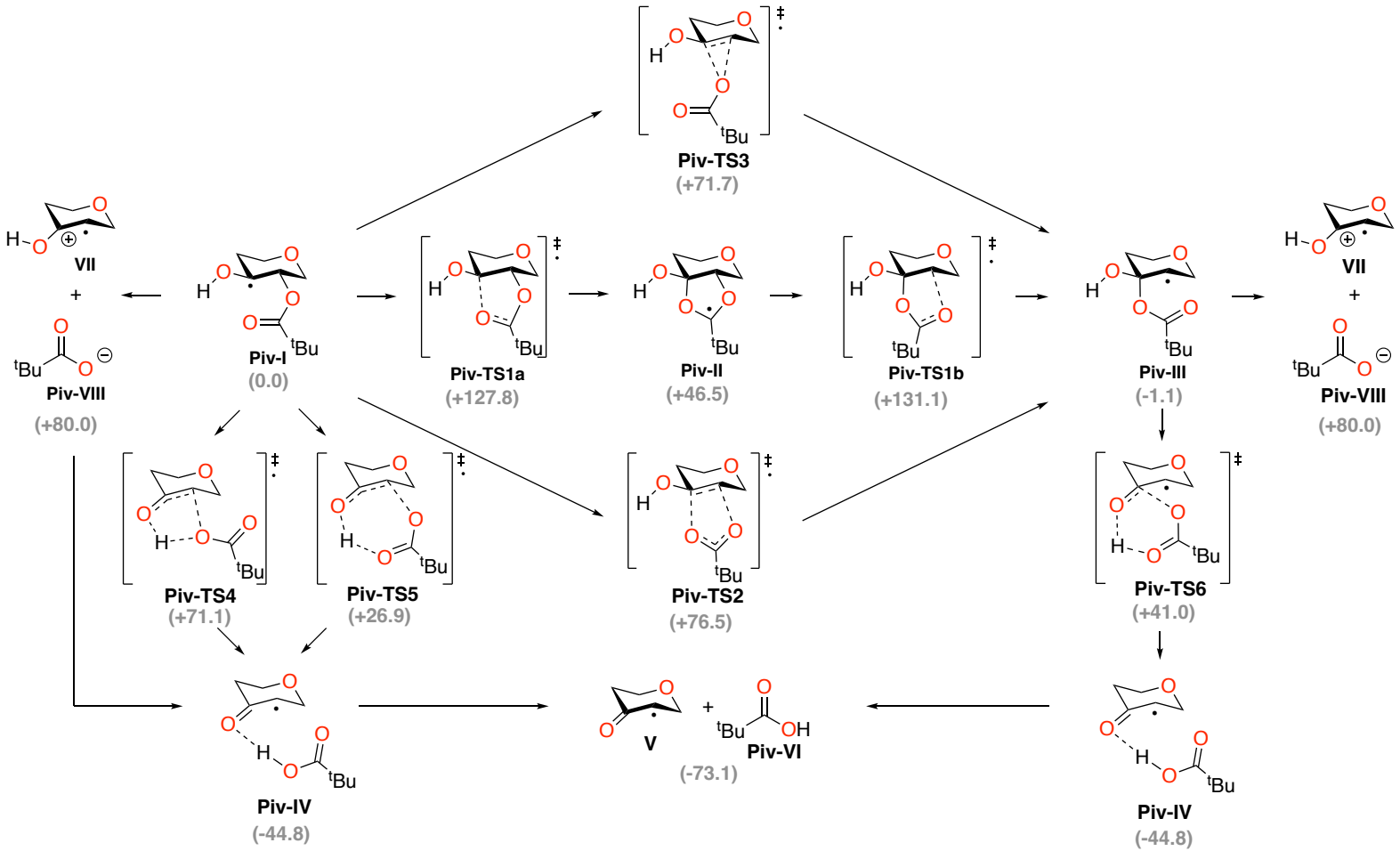
Ac-TS3				
aco_029	-573.9657565	-573.7797	-573.82968	**+94.0**
aco_023	-573.9678518	-573.78232	-573.83243	**+86.8**
aco_011	-573.9633045	-573.7773	-573.82713	**+100.7**
Ac-TS4				
aco_022	-573.9737462	-573.7878	-573.83719	**+74.3**
Ac-TS5				
aco_024	-573.9914608	-573.80593	-573.85445	**+29.0**
Ac-TS6				
aco_021	-573.9840421	-573.80085	-573.84913	**+43.0**
Ac-IV				
aco_021r	-574.0162405	-573.82962	-573.88165	**-42.4**
aco_022f	-574.0158263	-573.8292	-573.88178	**-42.8**
V				
aco_007	-344.8623419	-344.74406	-344.78196	
Ac-VI				
aco_009	-228.9233183	-228.91718	-228.88957	
V + Ac-VI	-573.9984532	-573.81403	-573.88434	**-49.5**
VII				
aco_019	-345.1917599	-345.061	-345.09911	

Ac-VIII				
aco_018	-228.3576195	-228.305	-228.33762	
VI + Ac-VIII	-573.7621724	-573.57879	-573.64952	+**567.0**

[a] Using gas phase (U)M06-2X/def2-TZVP geometries.

4.0 Evaluation of Leaving groups

4.1 Pivaloyl



Scheme S03. Pivaloxy group migration and elimination pathways for model substrate **Piv-I**. Gibbs free energy differences ($\Delta G_{298,qh,sol}$) relative to radical **Piv-I** ((U)M06-2X/def2-TZVP//SMD(acetonitrile) results in kJ/mol) are given in brackets.

Table S07. Reaction energies for the species shown in Scheme S03 (in kJ/mol).[a]

System	ΔH_{298}[b] ((U)M06-2X/ def2-TZVP)	$\Delta G_{298,qh}$[b] ((U)M06-2X/ def2-TZVP)	$\Delta G_{298,qh,sol}$[b] ((U)M06-2X/ def2-TZVP)
Piv-I	0.0	0.0	0.0
Piv-TS1a	+123.3	+130.2	+127.8
Piv-II	+37.3	+45.4	+46.5
Piv-TS1b	+123.8	+131.4	+131.1
Piv-III	-1.1	-1.0	-1.1
Piv-TS2	+85.3	+85.1	+76.5
Piv-TS3	+93.1	+90.2	+71.7
Piv-TS4	+77.8	+77.4	+71.1
Piv-TS5	**+27.7**	**+28.3**	**+26.9**
Piv-TS6	+43.1	+44.2	+41.0
Piv-IV	-30.9	-39.4	-44.8
V + Piv-VI	+10.4	-47.4	-73.1
VII + Piv-VIII	+605.1	+547.6	+80.0

[a] Calculated with reference to the best conformer of each species. [b] Using gas phase (U)M06-2X/def2-TZVP geometries.

Table S08. Energy values for the species shown in Scheme S03.

System	E_{tot} ((U)M06-2X/ def2-TZVP)	H_{298} ((U)M06-2X/ def2-TZVP)	$G_{298,qh}$ ((U)M06-2X/ def2-TZVP)	E_{tot} (SMD(AcCN)/ (U)M06-2X/ def2-TZVP)[a]
Piv-I				
pivo_024f	-692.1378245	-691.8623286	-691.9193282	-692.152686

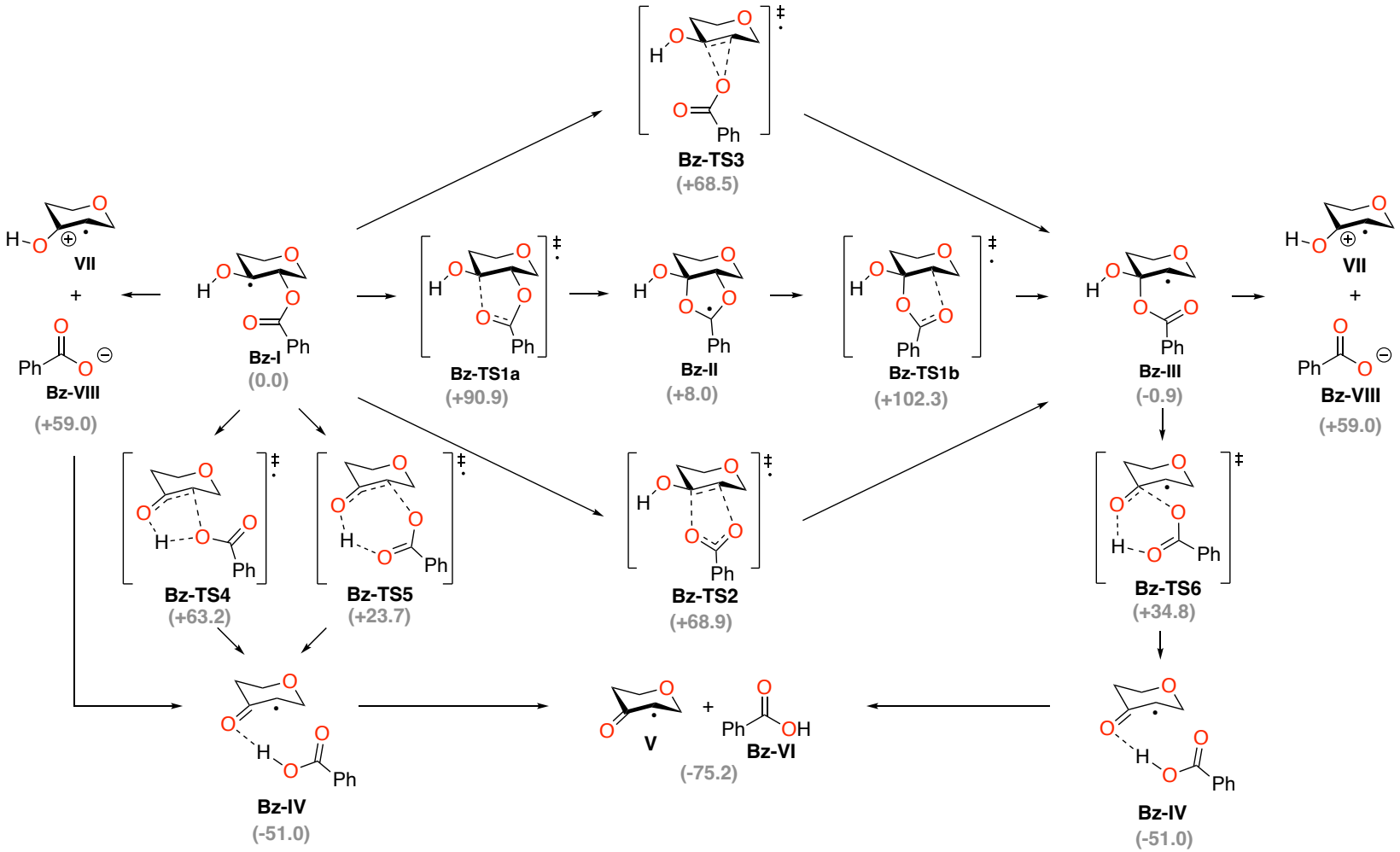
pivo_005	-692.1345645	-691.8591817	-691.9163862	-692.1510244
pivo_002	-692.1306495	-691.8554489	-691.9131089	-692.1492834
pivo_006	-692.1299528	-691.8547468	-691.911963	-692.1469051
pivo_003	-692.1284874	-691.8533197	-691.9106593	-692.1462119
Piv-TS1a				
pivo_014	-692.0873726	-691.8143261 (imag=-982 cm^{-1})	-691.8692363	-692.1036378
pivo_025	-692.0884449	-691.8153778 (imag=-945cm^{-1})	-691.8697205	-692.1038399
Piv-II				
pivo_015r	-692.1232578	-691.8473452	-691.9014022	-692.1373992
pivo_012	-692.1240628	-691.8481277	-691.9020402	-692.1384856
pivo_008	-692.1223452	-691.8465518	-691.9009082	-692.1376208
pivo_026r	-692.1210242	-691.8452497	-691.8996284	-692.1368019
pivo_013	-692.117978	-691.8423385	-691.8973139	-692.1347778
pivo_027	-692.116933	-691.8414128	-691.8965329	-692.1341568
Piv-TS1a				
pivo_015	-692.0877439	-691.8151613 (imag=-954 cm^{-1})	-691.8692986	-692.1027021
pivo_026	-692.0854672	-691.8131097 (imag=-977cm^{-1})	-691.8675308	-692.1018074
Piv-III				
pivo_016	-692.1364834	-691.8627483	-691.9196954	-692.1514009
pivo_021f	-692.1347582	-691.8610261	-691.9176746	-692.1494821
pivo_004	-692.1292988	-691.8558593	-691.9132417	-692.1474753
pivo_023r	-692.1267681	-691.8531113	-691.9107757	-692.143399
pivo_011r	-692.1256486	-691.8520699	-691.9096095	-692.1420397

pivo_028f	-692.1233047	-691.8498356	-691.9073656	-692.1409952
Piv-TS2				
pivo_010	-692.1024191	-691.8298437 (imag=-234 cm^{-1})	-691.8869095	-692.1205559
pivo_028	-692.0979952	-691.8264992 (imag=-259 cm^{-1})	-691.8814736	
Piv-TS3				
pivo_029	-692.0993457	-691.8268279 (imag=-84 cm^{-1})	-691.8846353	-692.1215944
pivo_023	-692.0989374	-691.8268578 (imag=-146 cm^{-1})	-691.8849716	-692.1193044
pivo_011	-692.0966512	-691.8241486 (imag=-53 cm^{-1})	-691.8824554	-692.1185544
Piv-TS4				
pivo_022	-692.1051248	-691.8326902 (imag=-181 cm^{-1})	-691.8898428	-692.1223861
Piv-TS5				
pivo_024	-692.1238643	-691.851784 (imag=-173 cm^{-1})	-691.9085328	-692.1392881
Piv-TS6				
pivo_021	-692.1156835	-691.8458952 (imag=-437 cm^{-1})	-691.9025089	-692.1317623
Piv-IV				
pivo_021r	-692.1472291	-691.8741067	-691.9343485	-692.1641491
pivo_022f	-692.1471	-691.8738413	-691.9341821	-692.1639583

V				
pivo_007	-345.1158220	-344.9975398	-345.0354352	-345.1303555
Piv-VI				
pivo_009	-347.0136253	-346.8608407	-346.9019646	-347.0237316
VII				
pivo_019	-345.4496196	-345.3188634	-345.3569734	-345.5527916
Piv-VIII				
pivo_018	-346.451875	-346.313001	-346.3537822	-346.5416612

[a] Using gas phase (U)M06-2X/def2-TZVP geometries.

4.2 Benzoyl



Scheme S04. Benzoyloxy group migration and elimination pathways for model substrate **Bz-I**. Gibbs free energy differences ($\Delta G_{298,qh,sol}$) relative to radical **Bz-I** ((U)M06-2X/def2-TZVP//SMD(acetonitrile) results in kJ/mol) are given in brackets.

Table S09. Reaction energies for the species shown in Scheme S04 (in kJ/mol).[a]

System	ΔH_{298}[b] ((U)M06-2X/ def2-TZVP)	$\Delta G_{298,qh}$[b] ((U)M06-2X/ def2-TZVP)	$\Delta G_{298,qh,sol}$[b] ((U)M06-2X/ def2-TZVP)
Bz-I	0.0	0.0	0.0
Bz-TS1a	+100.2	+104.9	+90.9
Bz-II	+10.0	+15.0	+8.0
Bz-TS1b	+98.2	+104.7	+102.3
Bz-III	-0.2	-0.4	-0.9
Bz-TS2	+84.1	+83.2	+68.9
Bz-TS3	+96.0	+88.4	+68.5
Bz-TS4	+75.3	+74.7	+63.2
Bz-TS5	**+25.7**	**+26.9**	**+23.7**
Bz-TS6	+38.8	+39.7	+34.8
Bz-IV	-33.8	-43.5	-51.0
V + Bz-VI	+9.8	-49.1	-75.2
VII + Bz-VIII	+585.3	+526.5	+59.0

[a] Calculated with reference to the best conformer of each species. [b] Using gas phase (U)M06-2X/def2-TZVP geometries.

Table S10. Energy values for the species shown in Scheme S04.

System	E_{tot} ((U)M06-2X/ def2-TZVP)	H_{298} ((U)M06-2X/ def2-TZVP)	$G_{298,qh}$ ((U)M06-2X/ def2-TZVP)	E_{tot} (SMD(AcCN)/ (U)M06-2X/ def2-TZVP)[a]
Bz-I				

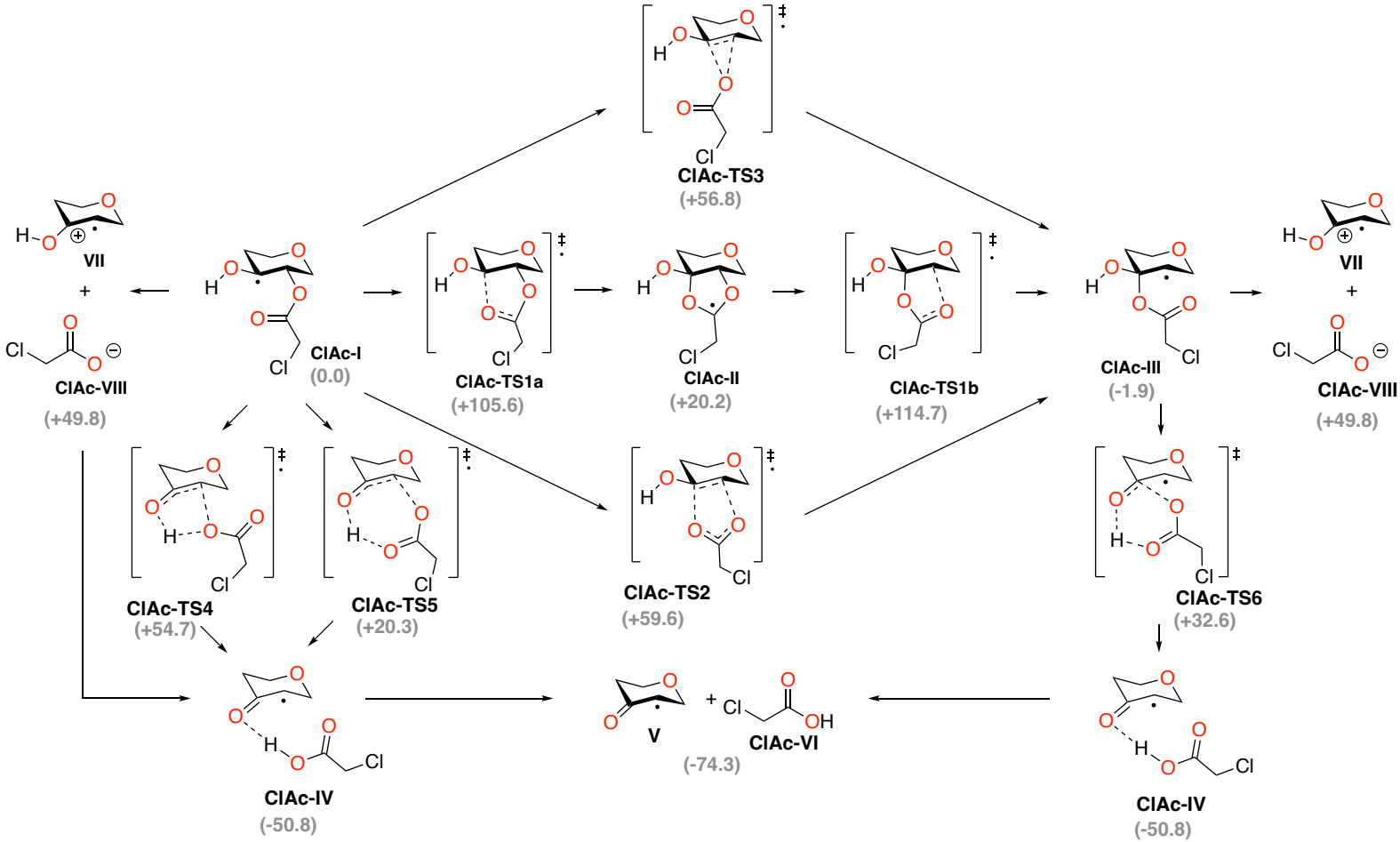
acob_024fx	-765.9440732	-765.6997800	-765.7551451	-765.9621550
acob_005	-765.9408350	-765.6966932	-765.7524975	-765.9603275
acob_022f	-765.9359106	-765.6918939	-765.7478955	-765.9560205
acob_028r	-765.9342066	-765.6903396	-765.7464355	-765.9553574
acob_010r	-765.9338503	-765.6899009	-765.7463851	-765.9537579
acob_029f	-765.9333355	-765.6895186	-765.7463312	-765.9554004
Bz-TS1a				
acob_014	-765.9032670	-765.6616262 (imag=-867 cm^{-1})	-765.7151871	-765.9266752
acob_025	-765.9046970	-765.6631017 (imag=-794 cm^{-1})	-765.7166388	-765.9254175
Bz-II				
acob_015f	-765.9399376	-765.6959602	-765.7494254	-765.9606935
acob_014f	-765.9390733	-765.6951097	-765.7486223	-765.9612714
Bz-TS1b				
acob_015	-765.9035788	-765.6623722 (imag=-967 cm^{-1})	-765.7152649	-765.9225759
acob_026	-765.9011302	-765.6600780 (imag=-988 cm^{-1})	-765.7132273	-765.9218181
Bz-III				
acob_015r	-765.9424662	-765.6998707	-765.7552771	-765.9607414
aco0b_021f	-765.9407028	-765.6981030	-765.7533507	-765.9588192
acob_010f	-765.9353186	-765.6930305	-765.7488493	-765.9570118
acob_023f	-765.9333348	-765.6908637	-765.7468646	-765.9532113
acob_011f	-765.9320992	-765.6897599	-765.7458798	-765.9519337
acob_028f	-765.9289920	-765.6867795	-765.7429219	-765.9506040

Bz-TS2				
acob_010	-765.9091424	-765.6677533 (imag=-247 cm^{-1})	-765.7234517	-765.9326739
acob_028	-765.9044520	-765.6632199 (imag=-271 cm^{-1})	-765.7190224	-765.9290241
Bz-TS3				
acob_023	**-765.9060200**	**-765.6650035** (imag=-119 cm^{-1})	**-765.7214810**	-765.9316827
acob_029	-765.9057507	-765.6643709 (imag=-97 cm^{-1})	-765.7206672	**-765.9334879**
acob_011	-765.9036389	-765.6621798 (imag=-62 cm^{-1})	-765.7184788	-765.9308943
Bz-TS4				
acob_022	-765.9125327	-765.6711196 (imag=-168 cm^{-1})	-765.7266840	-765.9350232
acob_031	-765.9065197	-765.6662931 (imag=-251 cm^{-1})	-765.7228686	-765.9323352
Bz-TS5				
acob_024	-765.9310681	-765.6899828 (imag=-185 cm^{-1})	-765.7448970	-765.9503879
Bz-TS6				
acob_032	-765.9242916	-765.6850058 (imag=-316 cm^{-1})	-765.7400154	-765.9442450
acob_021	-765.9229836	-765.6841752 (imag=-404 cm^{-1})	-765.7389737	-765.9431057

Bz-IV				
acob_031r	**-765.9546494**	**-765.7126471**	**-765.7717267**	**-765.9755767**
acob_021r	-765.9541307	-765.7121530	-765.7706226	-765.9745463
acob_022r	-765.9540757	-765.7121078	-765.7708915	-765.9745663
acob_024f	-765.9540757	-	-	-
acob_032f	-765.9540757	-	-	-
V				
aco_007	-345.1158220	-344.9975398	-345.0354352	-345.1303555
Bz-VI				
acob_009	-420.8199897	-420.6984864	-420.7384047	-420.8334702
VII				
aco_019	-345.4496196	-345.3188634	-345.3569734	-345.5527916
aco_020	-345.4473655	-345.3167618	-345.3549276	-345.5519952
Bz-VIII				
acob_018	-420.2657923	-420.1579989	-420.1976276	-420.3587779

[a] Using gas phase (U)M06-2X/def2-TZVP geometries.

4.3 Chloromethyl



Scheme S05. Chloroacetyloxy group migration and elimination pathways for model substrate **ClAc-I**. Gibbs free energy differences ($\Delta G_{298,qh,sol}$) relative to radical **ClAc-I** ((U)M06-2X/def2-TZVP//SMD(acetonitrile) results in kJ/mol) are given in brackets.

Table S11. Reaction energies for the species shown in Scheme S05 (in kJ/mol).[a]

System	ΔH_{298}[b] ((U)M06-2X/ def2-TZVP)	$\Delta G_{298,qh}$[b] ((U)M06-2X/ def2-TZVP)	$\Delta G_{298,qh,sol}$[b] ((U)M06-2X/ def2-TZVP)
ClAc-I	0.0	0.0	0.0
ClAc-TS1a	+105.1	+110.4	+105.6
ClAc-II	+7.4	+15.4	+20.2
ClAc-TS1b	+103.6	+111.4	+114.7
ClAc-III	-2.6	-1.8	-1.9
ClAc-TS2	+73.1	+72.7	+59.6
ClAc-TS3	+80.3	+77.8	+56.8
ClAc-TS4	+65.7	+65.6	+54.7
ClAc-TS5	**+20.8**	**+21.8**	**+20.3**
ClAc-TS6	+34.6	+36.5	+32.6
ClAc-IV	-37.1	-45.3	-50.8
V + ClAc-VI	+9.3	-47.6	-74.3
VII + ClAc-VIII	+991.2	+932.9	+49.8

[a] Calculated with reference to the best conformer of each species. [b] Using gas phase (U)M06-2X/def2-TZVP geometries.

Table S12. Energy values for the species shown in Scheme S05.

System	E_{tot} ((U)M06-2X/ def2-TZVP)	H_{298} ((U)M06-2X/ def2-TZVP)	$G_{298,qh}$ ((U)M06-2X/ def2-TZVP)	E_{tot} (SMD(AcCN)/ (U)M06-2X/ def2-TZVP)[a]
ClAc-I				

mcl_024f-b	-1033.805972	-1033.624257	-1033.676031	-1033.822682
mcl_024f-c	-1033.805971	-1033.624255	-1033.676047	
mcl_024f-a	-1033.806229	-1033.624818	-1033.676468	-1033.824326
mcl_005-a	-1033.802851	-1033.621641	-1033.673794	-1033.822904
mcl_005-b	-1033.804418	-1033.622863	-1033.674621	-1033.821635
mcl_005-c	-1033.802557	-1033.622034	-1033.671916	-1033.821139
mcl_002-a	-1033.800046	-1033.618838	-1033.671005	-1033.822039
mcl_002-b	-1033.798806	-1033.617264	-1033.669834	-1033.820219
mcl_002-c	-1033.7997	-1033.618191	-1033.670663	-1033.82044
mcl_006-a	-1033.798201	-1033.617051	-1033.668949	-1033.819023
mcl_006-b	-1033.797886	-1033.616432	-1033.668537	-1033.81733
mcl_006-c	-1033.80066	-1033.619155	-1033.67056	-1033.817783
mcl_003-a	-1033.798407	-1033.617305	-1033.669239	-1033.819298
mcl_003-b	-1033.797077	-1033.615749	-1033.66807	-1033.817517
mcl_003-c	-1033.797651	-1033.616245	-1033.668588	-1033.817566
ClAc-TS1a				
mcl_014-a	-1033.760861	-1033.581755 (imag=-868 cm^{-1})	-1033.631436	-1033.781923
mcl_014-b	-1033.763964	-1033.584795 (imag=-886 cm^{-1})	-1033.634415	-1033.783889
ClAc-II				
mcl_015r-a	-1033.801725	-1033.619704	-1033.668605	-1033.81904
mcl_015r-b	-1033.793112	-1033.611246	-1033.660343	-1033.810989
mcl_015r-c	-1033.793178	-1033.611349	-1033.660528	-1033.810983
mcl_012-a	-1033.793083	-1033.611142	-1033.660187	-1033.811364
mcl_012-b	-1033.792753	-1033.61081	-1033.659874	-1033.811272
mcl_012-c	-1033.803953	-1033.622012	-1033.670598	-1033.819929

mcl_008-a	-1033.803953	-1033.622013	-1033.6706	-1033.819932
mcl_008-b	-1033.793346	-1033.611477	-1033.660581	-1033.811738
mcl_008-c	-1033.792847	-1033.610992	-1033.660168	-1033.811684
mcl_026r-a	-1033.791122	-1033.609319	-1033.658602	-1033.810912
mcl_026r-b	-1033.791996	-1033.610195	-1033.659381	-1033.810997
mcl_026r-c	-1033.801106	-1033.619185	-1033.668262	-1033.819697
mcl_013-a	-1033.793346	-1033.611479	-1033.660586	-1033.811739
mcl_013-b	-1033.803953	-1033.622012	-1033.670597	-1033.819932
mcl_013-c	-1033.788485	-1033.606778	-1033.656513	-1033.808763
mcl_027-a	-1033.787473	-1033.605808	-1033.655632	-1033.808306
mcl_027-b	-1033.787951	-1033.60631	-1033.656087	-1033.808196
mcl_027-c	-1033.795349	-1033.613766	-1033.663813	-1033.815462
ClAc-TS1b				
mcl_015-a	-1033.764165	-1033.585345 (imag=-996 cm^{-1})	-1033.63405	-1033.78089
mcl_015-b	-1033.758696	-1033.580329 (imag=-957 cm^{-1})	-1033.62966	-1033.774436
mcl_015-c	-1033.764165	-1033.585343 (imag=-996 cm^{-1})	-1033.634044	-1033.780889
mcl_026-a	-1033.762649	-1033.584018 (imag=-234 cm^{-1})	-1033.632969	-1033.780574
mcl_026-c	-1033.762649	-1033.584019 (imag=-1011 cm^{-1})	-1033.632966	-1033.780569
ClAc-III				
mcl_016-a	-1033.805169	-1033.625533	-1033.676974	-1033.823496
mcl_016-b	-1033.805857	-1033.62582	-1033.677138	-1033.822376
mcl_016-c	-1033.805857	-1033.62582	-1033.67714	-1033.822375

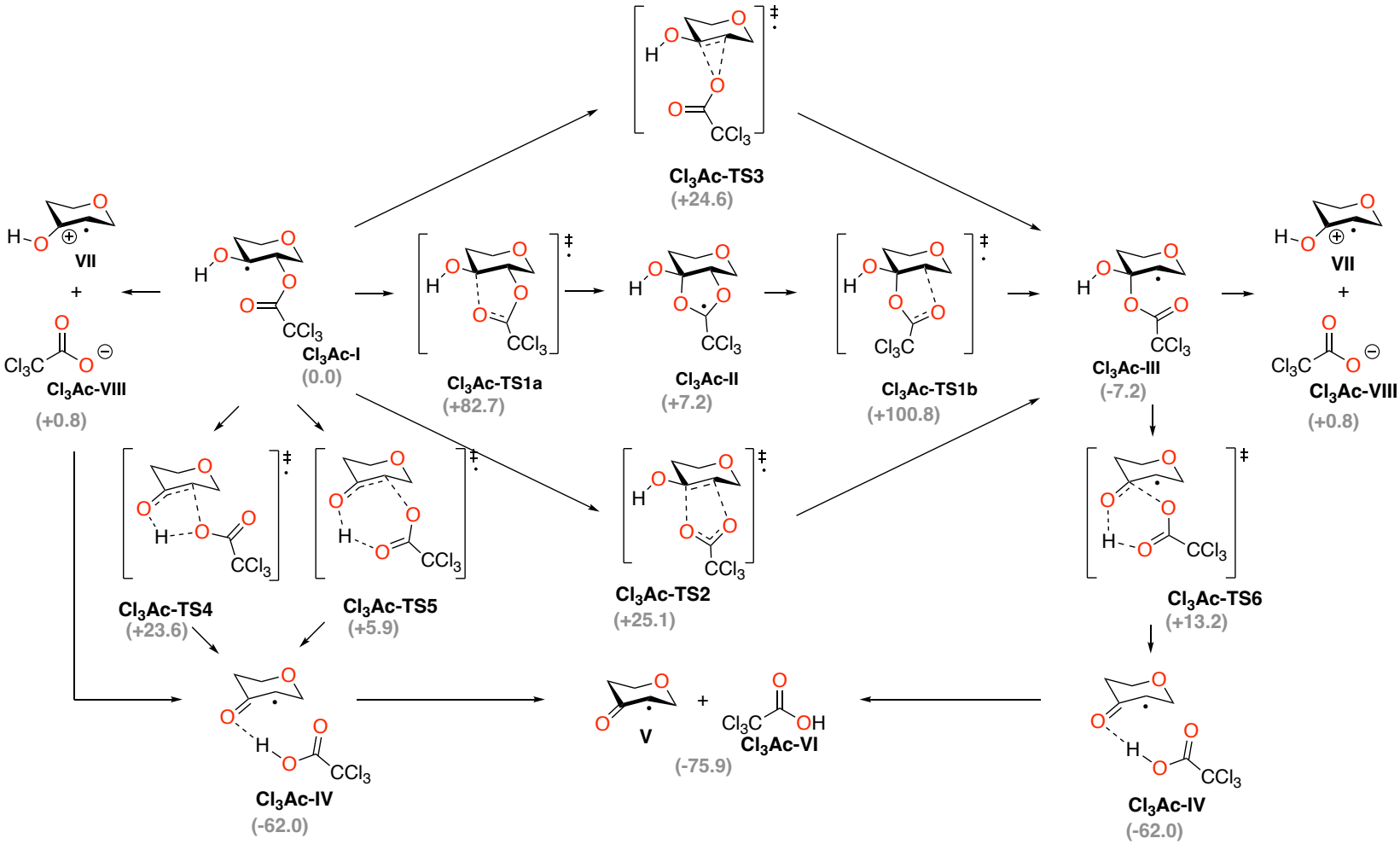
mcl_021f-a	-1033.804073	-1033.624983	-1033.674161	-1033.820344
mcl_021f-b	-1033.804073	-1033.624984	-1033.674163	-1033.820344
mcl_021f-c	-1033.80347	-1033.62382	-1033.675391	-1033.821568
mcl_004-a	-1033.79955	-1033.61982	-1033.671658	-1033.819317
mcl_004-b	-1033.798804	-1033.619109	-1033.671206	-1033.818567
mcl_004-c	-1033.798554	-1033.619162	-1033.671049	-1033.820366
mcl_023r-a	-1033.796206	-1033.616676	-1033.668813	-1033.816351
mcl_023r-b	-1033.795621	-1033.615763	-1033.667984	-1033.814694
mcl_023r-c	-1033.796359	-1033.61649	-1033.668487	-1033.814798
mcl_011r-a	-1033.79526	-1033.615804	-1033.668273	-1033.815147
mcl_011r-b	-1033.795491	-1033.615663	-1033.667951	-1033.813581
mcl_011r-c	-1033.794399	-1033.615607	-1033.665622	-1033.81333
mcl_028f-a	-1033.792153	-1033.61252	-1033.664678	-1033.812683
mcl_028f-b	-1033.793007	-1033.613322	-1033.665694	-1033.812334
mcl_028f-c	-1033.79288	-1033.613524	-1033.665763	-1033.814156
ClAc-TS-2				
mcl_010-a	-1033.774829	-1033.596232 (imag=-247 cm^{-1})	-1033.648196	-1033.798504
mcl_010-b	-1033.775559	-1033.596967 (imag=-246 cm^{-1})	-1033.648779	-1033.798539
mcl_028-a	-1033.770457	-1033.591991 (imag=-266 cm^{-1})	-1033.6438	-1033.795121
mcl_028-c	-1033.77101	-1033.592552 (imag=-268 cm^{-1})	-1033.644383	-1033.794901
ClAc-TS3				
mcl_029-a	-1033.77288	-1033.594191	-1033.646658	-1033.799005

		(imag=-96 cm^{-1})		
mcl_029-c	-1033.771951	-1033.593243 (imag=-94 cm^{-1})	-1033.645391	-1033.799495
mcl_023-a	-1033.771999	-1033.593796 (imag=-120 cm^{-1})	-1033.646407	-1033.79756
mcl_023-b	-1033.772423	-1033.594219 (imag=-125 cm^{-1})	-1033.646854	-1033.79664
mcl_011-a	-1033.769649	-1033.590992 (imag=-66 cm^{-1})	-1033.643266	-1033.796995
mcl_011-c	-1033.768639	-1033.589753 (imag=-65 cm^{-1})	-1033.642278	-1033.794983
ClAc-TS4				
mcl_022-a	-1033.777839	-1033.598824 (imag=-181 cm^{-1})	-1033.650755	-1033.798793
mcl_022-b	-1033.778523	-1033.5998 (imag=-162 cm^{-1})	-1033.651475	-1033.800788
mcl_022-c	-1033.778162	-1033.599202 (imag=-156 cm^{-1})	-1033.651096	-1033.79934
ClAc-TS5				
mcl_024-a	-1033.795231	-1033.616628 (imag=-163 cm^{-1})	-1033.667592	-1033.814454
mcl_024-b	-1033.795539	-1033.616879 (imag=-177 cm^{-1})	-1033.668166	-1033.813891
mcl_024-c	-1033.795539	-1033.61688 (imag=-177 cm^{-1})	-1033.668165	-1033.813891
ClAc-TS6				
mcl_021-a	-1033.788067	-1033.611653 (imag=-342 cm^{-1})	-1033.662576	-1033.807225

mcl_021-b	-1033.787057	-1033.610665 (imag=-343 cm^{-1})	-1033.661939	-1033.807283
mcl_021-c	-1033.786055	-1033.609393 (imag=-356 cm^{-1})	-1033.660559	-1033.805435
ClAc-IV				
mcl_021r-a	-1033.817873	-1033.638959	-1033.6936	-1033.83775
mcl_021r-b	-1033.816961	-1033.637605	-1033.691974	-1033.836226
mcl_021r-c	-1033.816201	-1033.637855	-1033.690433	-1033.835767
mcl_022f-a	-1033.817791	-1033.638834	-1033.693718	-1033.83797
mcl_022f-b	-1033.816033	-1033.636749	-1033.69223	-1033.836133
mcl_022f-c	-1033.817253	-1033.638846	-1033.691056	-1033.835619
V				
mcl_007	-345.1158220	-344.9975398	-345.0354352	-345.1303555
ClAc-VI				
(mcl_009)-a	-688.6816379	-688.6236986	-688.6574387	-688.6941852
(mcl_009)-b	-688.6816379	-688.6236986	-688.6574387	-688.6941852
(mcl_009)-c	-688.6823292	-688.6237543	-688.6591453	-688.6960723
VII				
mcl_019	-345.4496196	-345.3188634	-345.3569734	-345.5527916
ClAc-VIII				
mcl_018-a	-687.9743041	-687.9284094	-687.9641289	-688.2255878
mcl_018-b	-687.9743041	-687.9284094	-687.9641289	-688.2255878
mcl_018-c	-687.9742846	-687.9284096	-687.9641609	-688.2255755

[a] Using gas phase (U)M06-2X/def2-TZVP geometries.

4.4 Trichloromethyl



Scheme S06. Trichloroacetyloxy group migration and elimination pathways for model substrate **Cl₃Ac-I**. Gibbs free energy differences ($\Delta G_{298,qh,sol}$) relative to radical **Cl₃Ac-I** ((U)M06-2X/def2-TZVP//SMD(acetonitrile) results in kJ/mol) are given in brackets.

Table S13. Reaction energies for the species shown in Scheme S06 (in kJ/mol).[a]

System	ΔH_{298}[b] ((U)M06-2X/ def2-TZVP)	$\Delta G_{298,qh}$[b] ((U)M06-2X/ def2-TZVP)	$\Delta G_{298,qh,sol}$[b] ((U)M06-2X/ def2-TZVP)
Cl_3Ac-I	0.0	0.0	0.0
Cl_3Ac-TS1a	+92.5	+97.8	+82.7
Cl_3Ac-II	+0.1	+8.3	+7.2
Cl_3Ac-TS1b	+97.3	+104.7	+100.8
Cl_3Ac-III	-9.5	-8.6	-7.2
Cl_3Ac-TS2	+54.5	+54.1	+25.1
Cl_3Ac-TS3	+59.6	+58.3	+24.6
Cl_3Ac-TS4	+45.4	+45.2	+23.6
Cl_3Ac-TS5	**+11.0**	**+11.9**	**+5.9**
Cl_3Ac-TS6	+21.8	+24.0	+13.2
Cl_3Ac-IV	-44.4	-53.0	-62.0
V + Cl_3Ac-VI	+6.8	-51.0	-75.9
VII + Cl_3Ac-VIII	+986.7	+927.6	+0.8

[a] Calculated with reference to the best conformer of each species. [b] Using gas phase (U)M06-2X/def2-TZVP geometries.

Table S14. Energy values for the species shown in Scheme S06.

System	E_{tot} ((U)M06-2X/ def2-TZVP)	H_{298} ((U)M06-2X/ def2-TZVP)	$G_{298,qh}$ ((U)M06-2X/ def2-TZVP)	E_{tot} (SMD(AcCN)/ (U)M06-2X/ def2-TZVP)[a]
Cl_3Ac-I				

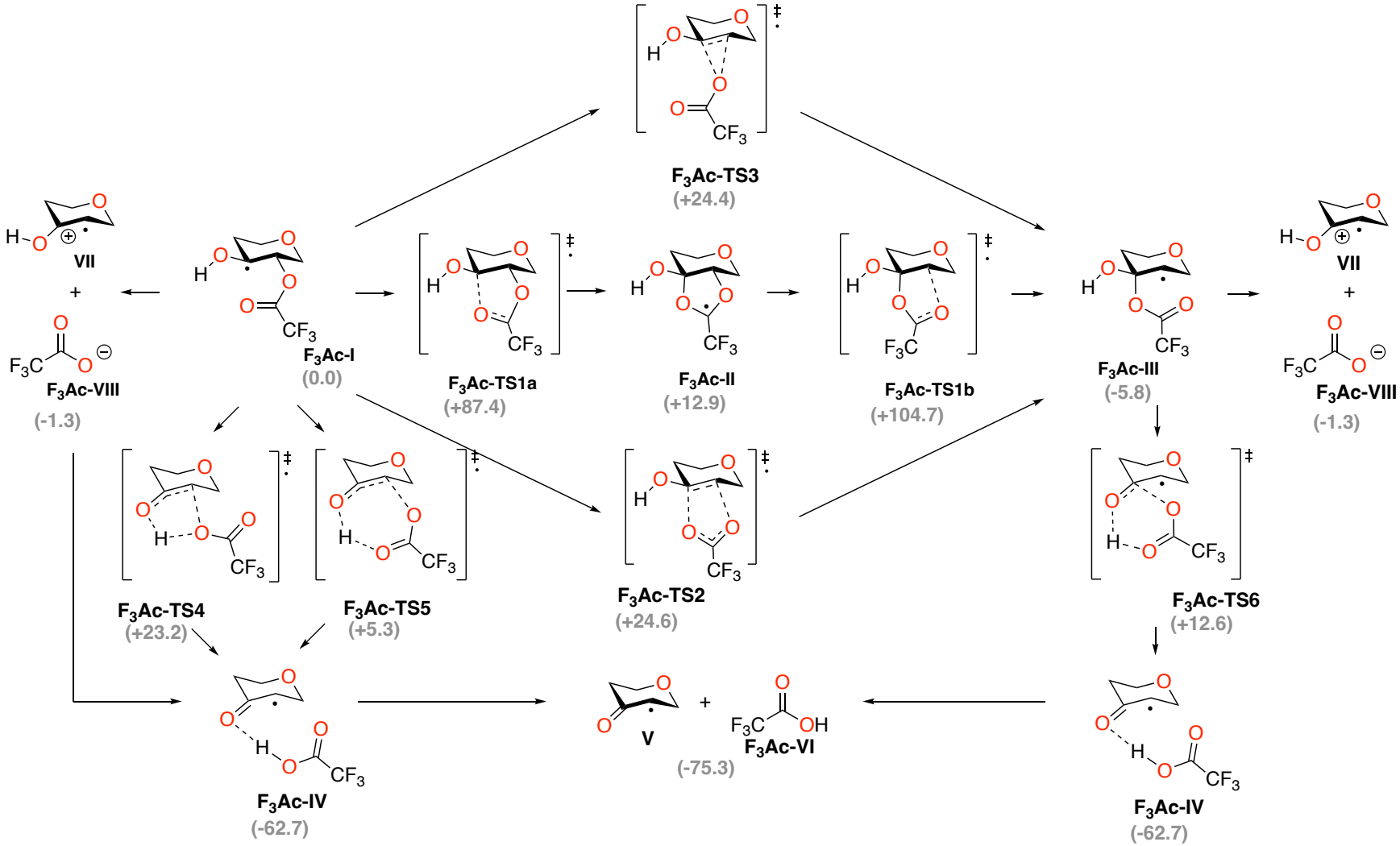
ccl3o_024f	-1952.981988	-1952.818536	-1952.874048	-1952.996947
ccl3o_005	-1952.986414	-1952.821939	-1952.879142	-1953.001933
ccl3o_002	-1952.982276	-1952.817857	-1952.875514	-1953.001664
ccl3o_006	-1952.982818	-1952.818432	-1952.875465	-1952.998119
ccl3o_003	-1952.980907	-1952.81659	-1952.874225	-1952.999716
Cl_3Ac-TS1a				
ccl3o_014	-1952.94886	-1952.78669 (imag=-861 cm^{-1})	-1952.841888	-1952.970391
Cl_3Ac-II				
ccl3o_015r	-1952.984732	-1952.819636	-1952.873959	-1953.0018
ccl3o_012	-1952.98697	-1952.821919	-1952.875985	-1953.002762
ccl3o_008	-1952.984194	-1952.819211	-1952.873673	-1953.002695
ccl3o_026r	-1952.984439	-1952.819377	-1952.873803	-1953.002716
ccl3o_013	-1952.984194	-1952.819211	-1952.873673	-1953.002692
ccl3o_027	-1952.980062	-1952.815321	-1952.870575	-1953.000562
Cl_3Ac-TS1b				
ccl3o_015	-1952.946547	-1952.784871 (imag=-970 cm^{-1})	-1952.839277	-1952.963312
ccl3o_026	-1952.945265	-1952.783763 (imag=-1005 cm^{-1})	-1952.838597	-1952.963163
Cl_3Ac-III				
ccl3o_016	-1952.988426	-1952.82556	-1952.882424	-1953.003649
ccl3o_021f	-1952.986579	-1952.823746	-1952.880699	-1953.001583
ccl3o_004	-1952.983312	-1952.820645	-1952.877835	-1953.001733
ccl3o_023r	-1952.979296	-1952.816562	-1952.8742	-1952.996642

ccl3o_011r	-1952.978478	-1952.815888	-1952.873931	-1952.995559
ccl3o_028f	-1952.976545	-1952.814001	-1952.871644	-1952.995369
Cl_3Ac-TS2				
ccl3o_010	-1952.962914	-1952.801182 (imag=-195 cm^{-1})	-1952.858526	-1952.989716
ccl3o_028	-1952.957438	-1952.795899 (imag=-219 cm^{-1})	-1952.854013	-1952.985641
Cl_3Ac-TS3				
ccl3o_029	-1952.960897	-1952.79902 (imag=-95 cm^{-1})	-1952.856485	-1952.989925
ccl3o_023	-1952.960585	-1952.799231 (imag=-50 cm^{-1})	-1952.856922	-1952.987971
ccl3o_011	-1952.958766	-1952.79676 (imag=-42 cm^{-1})	-1952.853821	-1952.987459
Cl_3Ac-TS4				
ccl3o_022	-1952.96669	-1952.804659 (imag=-115 cm^{-1})	-1952.861914	-1952.990705
Cl_3Ac-TS5				
ccl3o_024	-1952.98004	-1952.81775 (imag=-152 cm^{-1})	-1952.874613	-1952.998082
Cl_3Ac-TS6				
ccl3o_021	-1952.973926	-1952.813626 (imag=-256 cm^{-1})	-1952.870014	-1952.993804
Cl_3Ac-IV				

ccl3o_022f	-1953.000732	-1952.838844	-1952.899331	-1953.019908
V				
ccl3o_007	-345.1158220	-344.9975398	-345.0354352	-345.1303555
Cl_3Ac-VI				
ccl3o_009	-1607.863585	-1607.821802	-1607.863141	-1607.874287
VII				
ccl3o_019	-345.4496196	-345.3188634	-345.3569734	-345.5527916
Cl_3Ac-VIII				
ccl3o_018	-1607.156186	-1607.127257	-1607.168872	-1607.421771

[a] Using gas phase (U)M06-2X/def2-TZVP geometries.

4.5 Trifluoromethyl



Scheme S07. Trifluoroacetyloxy group migration and elimination pathways for model substrate **F$_3$Ac-I**. Gibbs free energy differences ($\Delta G_{298,qh,sol}$) relative to radical **F$_3$Ac-I** ((U)M06-2X/def2-TZVP//SMD(acetonitrile) results in kJ/mol) are given in brackets.

Table S15. Reaction energies for the species shown in Scheme S07 (in kJ/mol).[a]

System	ΔH_{298}[b] ((U)M06-2X/ def2-TZVP)	$\Delta G_{298,qh}$[b] ((U)M06-2X/ def2-TZVP)	$\Delta G_{298,qh,sol}$[b] ((U)M06-2X/ def2-TZVP)
F_3Ac-I	0.0	0.0	0.0
F_3Ac-TS1a	+96.2	+98.0	+87.4
F_3Ac-II	+9.8	+17.8	+12.9
F_3Ac-TS1b	+101.9	+108.9	+104.7
F_3Ac-III	-5.3	-5.0	-5.8
F_3Ac-TS2	+55.6	+54.5	+24.6
F_3Ac-TS3	+61.9	+59.2	+24.4
F_3Ac-TS4	+47.0	+46.6	+23.2
F_3Ac-TS5	**+12.1**	**+12.0**	**+5.3**
F_3Ac-TS6	+25.1	+26.0	+12.6
F_3Ac-IV	-42.9	-51.8	-62.7
V + F_3Ac-VI	+9.3	-48.3	-75.3
VII + F_3Ac-VIII	+516.7	+458.8	-1.3

[a] Calculated with reference to the best conformer of each species. [b] Using gas phase (U)M06-2X/def2-TZVP geometries.

Table S16. Energy values for the species shown in Scheme S07.

System	E_{tot} ((U)M06-2X/ def2-TZVP)	H_{298} ((U)M06-2X/ def2-TZVP)	$G_{298,qh}$ ((U)M06-2X/ def2-TZVP)	E_{tot} (SMD(AcCN)/ (U)M06-2X/ def2-TZVP)[a]

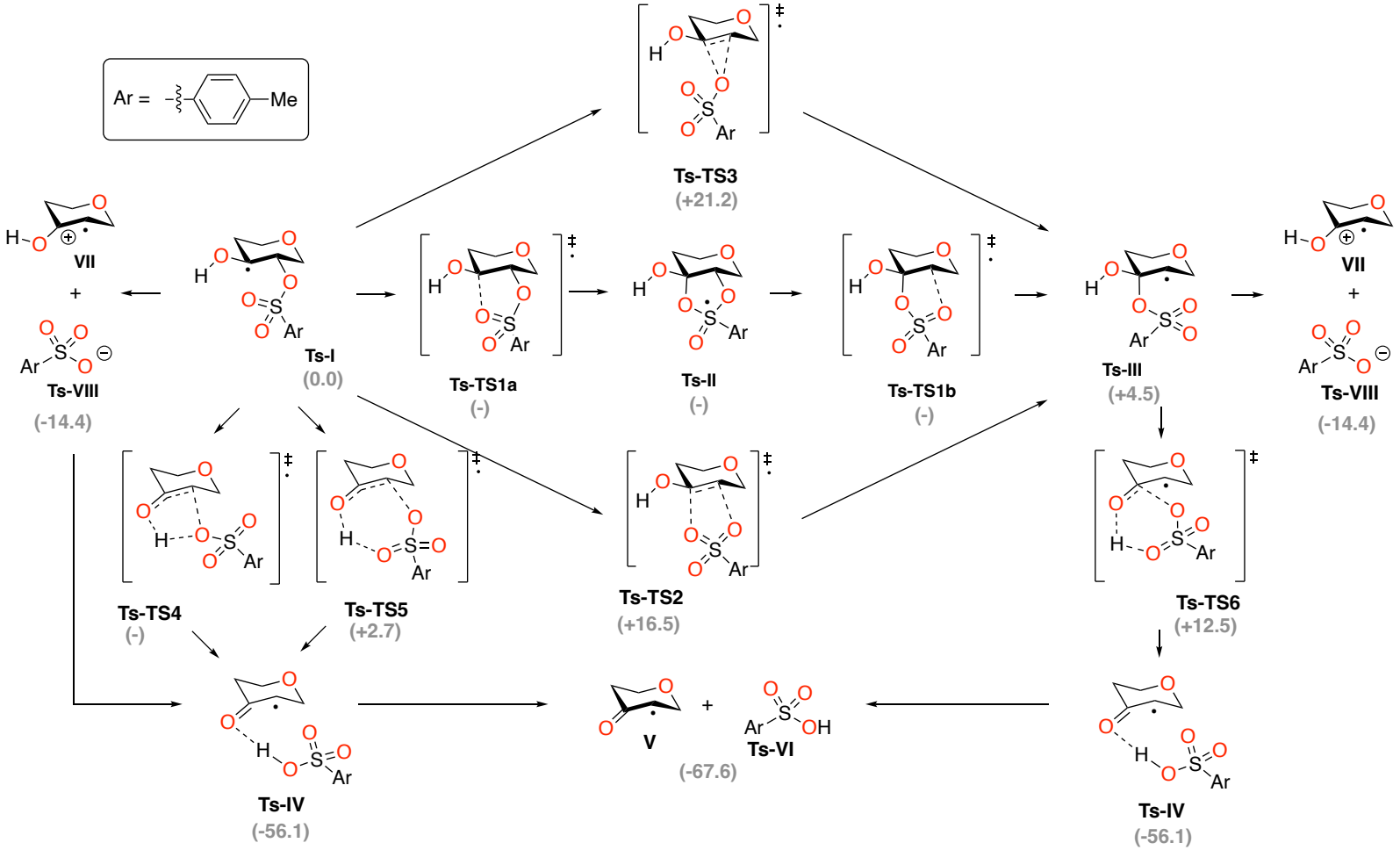
F_3Ac-I				
cf3o_024f	-871.9754764	-871.8066551	-871.8603783	-871.9866529
cf3o_005	-871.9737848	-871.8050774	-871.858999	-871.9863961
cf3o_002	-871.9705136	-871.8018975	-871.8561909	-871.9862664
cf3o_006	-871.9698767	-871.8012146	-871.8551244	-871.9832658
cf3o_003	-871.9692225	-871.8006447	-871.8548174	-871.9844424
F_3Ac-TS1a				
cf3o_014	-871.936265	-871.769774 (imag=-842 cm^{-1})	-871.82138	-871.9535418
cf3o_025	-871.938213	-871.771791 (imag=-780 cm^{-1})	-871.823067	-871.9519496
F_3Ac-II				
cf3o_015r	-871.9712265	-871.8018324	-871.852589	-871.9840268
cf3o_012	-871.9722843	-871.8029234	-871.8535979	-871.9843843
cf3o_008	-871.9707019	-871.8014352	-871.8524888	-871.9852363
cf3o_026r	-871.970777	-871.8014442	-871.8522907	-871.9848634
cf3o_013	-871.9707018	-871.8014345	-871.852489	-871.9852298
cf3o_027	-871.9663774	-871.7972922	-871.8488439	-871.9827735
F_3Ac-TS1b				
cf3o_015	-871.933739	-871.767841 (imag=-950 cm^{-1})	-871.818883	-871.9468529
cf3o_026	-871.932497	-871.766688 (imag=-965 cm^{-1})	-871.817776	-871.9467982
F_3Ac-III				

cf3o_016	-871.9758084	-871.8086579	-871.8622656	-871.9876934
cf3o_021f	-871.9741279	-871.8070165	-871.8603714	-871.9859001
cf3o_004	-871.9708503	-871.803983	-871.8578137	-871.9859393
cf3o_023r	-871.9673148	-871.8003222	-871.854447	-871.9812529
cf3o_011r	-871.9666438	-871.799835	-871.8541202	-871.9802929
cf3o_028f	-871.9644219	-871.797591	-871.8517858	-871.9797664
F_3Ac-TS2				
cf3o_010	-871.951503	-871.785469 (imag=-201 cm^{-1})	-871.839631	-871.9744422
cf3o_028	-871.946562	-871.780736 (imag=-219 cm^{-1})	-871.834971	-871.9708178
F_3Ac-TS3				
cf3o_029	-871.948998	-871.782836 (imag=-99 cm^{-1})	-871.837195	-871.9744456
cf3o_023	-871.948748	-871.783077 (imag=-86 cm^{-1})	-871.837839	-871.9727427
cf3o_011	-871.946156	-871.780013 (imag=-70 cm^{-1})	-871.834729	-871.9721898
F_3Ac-TS4				
cf3o_022	-871.955057	-871.788748 (imag=-127 cm^{-1})	-871.842629	-871.9755341
F_3Ac-TS5				
cf3o_024	-871.968618	-871.802049 (imag=-153 cm^{-1})	-871.855571	-871.9829721

F_3Ac-TS6				
cf3o_021	-871.961688	-871.797078 (imag=-263 cm^{-1})	-871.850493	-871.9783358
F_3Ac-IV				
cf3o_021r	-871.9889742	-871.8228224	-871.8793383	-872.0038835
cf3o_022f	-871.9890951	-871.8230136	-871.8801027	-872.0048235
F_3Ac-V				
cf3o_007	-345.1158220	-344.9975398	-345.0354352	-345.1303555
F_3Ac-VI				
cf3o_009	-526.851572	-526.805578	-526.8433206	-526.8589014
F_3Ac-VII				
cf3o_019	-345.4496196	-345.3188634	-345.3569734	-345.5527916
F_3Ac-VIII				
cf3o_018	-526.3238902	-526.2910025	-526.3286389	-526.4075287

[a] Using gas phase (U)M06-2X/def2-TZVP geometries.

4.6 Tosyl



Scheme S08. Tosyl group migration and elimination pathways for model substrate **Ts-I**. Gibbs free energy differences ($\Delta G_{298,qh,sol}$) relative to radical **Ts-I** ((U)M06-2X/def2-TZVP//SMD(acetonitrile) results in kJ/mol) are given in brackets.

Table S17. Reaction energies for the species shown in Scheme S08 (in kJ/mol).[a]

System	ΔH_{298}[b] (M06-2X/ def2-TZVP)	$\Delta G_{298,qh}$[b] (M06-2X/ def2-TZVP)	$\Delta G_{298,qh,sol}$[b] (M06-2X/ def2-TZVP)	$\Delta G_{298,qh,sol}$[c] (M06-2X/ def2-TZVP)
Ts-I	0.0	0.0	0.0	0.0
Ts-TS1a	-	-	-	-
Ts-II	-	-	-	-
Ts-TS1b	-	-	-	-
Ts-III	-0.4	+1.2	+4.5	+3.1
Ts-TS2	+48.4	+49.0	+16.5	-
Ts-TS3	+54.0	+54.2	+21.2	-
Ts-TS4	-	-	-	-
Ts-TS5	+8.5	+8.9	**+2.7**	+5.5
Ts-TS6	+15.0	+16.7	+12.5	-
Ts-IV	-39.3	-46.1	-56.1	-61.6
V + Ts-VI	+20.9	-39.5	-64.5	-57.0
VII + Ts-VIII	+496.2	+436.4	-14.4	-4.0

[a] Calculated with reference to the best conformer of each species.
[b] Using gas phase (U)M06-2X/def2-TZVP geometries.
[c] Using solution phase SMD(AcCN)/(U)M06-2X/def2-TZVP geometries.

Table S18. Energy values for the species shown in Scheme S08.

System	E_{tot}	H_{298}	$G_{298,qh}$	E_{tot}

	((U)M06-2X/ def2-TZVP)	((U)M06-2X/ def2-TZVP)	((U)M06-2X/ def2-TZVP)	(SMD(AcCN)/ (U)M06-2X/ def2-TZVP)[a]
Ts-I				
acoc_034r	**-1240.5352481**	-1240.2605480	-1240.323089	**-1240.5600523**
acoc_025fo	-1240.5351436	-1240.2605516	-1240.3232717	-1240.5585967
acoc_003r	-1240.5339315	-1240.2590468	-1240.3211663	-1240.5576437
acoc_002	-1240.5331516	-1240.2583994	-1240.3210744	-1240.5559220
acoc_001	-1240.5331266	-1240.2583542	-1240.3213057	-1240.5558915
acoc_011	-1240.5308510	-1240.2565312	-1240.3185414	-1240.5541248
acoc_020	-1240.5279146	-1240.2530400	-1240.3157632	-1240.5503152
acoc_027fo	-1240.5255547	-1240.2510769	-1240.3134502	-1240.5514554
acoc_022re	-1240.5222934	-1240.2479421	-1240.3115957	-1240.5463931
Ts-III				
acoc_021re	-1240.5338039	-1240.2607124	-1240.3223993	-1240.5576006
acoc_023fo	-1240.5330710	-1240.2600041	-1240.3228110	-1240.5551594
acoc_013	-1240.5330702	-1240.2600046	-1240.3225041	-1240.5551609
acoc_006fo	-1240.5330702	-	-	-
acoc_014f	-1240.5274505	-1240.2545329	-1240.3164226	-1240.5543606
acoc_022fo	-1240.5257373	-1240.2529527	-1240.3160464	-1240.5514617
acoc_026re	-1240.5233328	-1240.2504399	-1240.3129462	-1240.5474182
acoc_027re	-1240.5205693	-1240.2476380	-1240.3100134	-1240.5470817
Ts-TS2				
acoc_022	-1240.5144494	-1240.2421058 (imag=-45.8 cm^{-1})	-1240.3045958	-1240.5514798
Ts-TS3				
acoc_006	-1240.5138515	-1240.2416967 (imag=-46.2 cm^{-1})	-1240.3047152	-1240.5495724

acoc_026	-1240.5123341	-1240.2399700 (imag=-54.2 cm^{-1})	-1240.3026325	-1240.5494994
acoc_027	-1240.5085114	-1240.2362491 (imag=-31.1 cm^{-1})	-1240.2981093	-1240.5502042
Ts-TS4				
Ts-TS5				
acoc_025	-1240.5298253	-1240.2573282 (imag=-217.2 cm^{-1})	-1240.3198989	-1240.55678292
acoc_017	-1240.5268295	-1240.2547985 (imag=-221.7 cm^{-1})	-1240.3154635	-1240.55186437
acoc_003	-1240.5263289	-1240.2532819 (imag=-217.9 cm^{-1})	-1240.3157663	-1240.55254363
acoc_005	-1240.5263290	-	-	-
Ts-TS6				
acoc_023	-1240.5264638	-1240.2548314 (imag=-238.7 cm^{-1})	-1240.3169205	-1240.55139180
acoc_021	-1240.5250330	-1240.2534681 (imag=-238.3 cm^{-1})	-1240.3148276	-1240.55333296
acoc_014	-1240.5105320	-1240.2381849 (imag=-96.4 cm^{-1})	-1240.3006414	-1240.55159222
Ts-IV				
acoc_017re	-1240.5476360	-1240.2755302	-1240.3404013	-1240.5728096
acoc_019	-1240.5469262	-1240.2753786	-1240.3408385	-1240.5705354
acoc_009r	-1240.5468806	-1240.2747918	-1240.3386940	-1240.5774564
acoc_021fo	-1240.5462133	-1240.2740335	-1240.3380161	-1240.5720761
acoc_025re	-1240.5459560	-1240.2743978	-1240.3398376	-1240.5728249
acoc_014r	-1240.5442376	-1240.2725172	-1240.3372786	-1240.5723262

V				
aco_007	-345.1158220	-344.9975398	-345.0354352	-345.1303555
Ts-VI				
acoc_004	-895.4067935	-895.2550492	-895.3028841	-895.42640624
VII				
aco_019	-345.4496196	-345.3188634	-345.3569734	-345.5527916
aco_020	-345.4473655	-345.3167618	-345.3549276	-345.5519952
Ts-VIII				
acoc_018	-894.8920480	-894.7527043	-894.8000807	-894.98518355

[a] Using gas phase (U)M06-2X/def2-TZVP geometries.

The influence of solvation was assessed for tosyl group migration and elimination pathways through reoptimization of intermediates and transition states at the SMD(AcCN)/(U)M06-2X/def2-TZVP level of theory. These results show minimal deviation to those calculated with the gas phase geometries.

Table S19. Energy values for the species shown in Scheme S08.

System	E_{tot} (SMD(AcCN)/ M06-2X/ def2-TZVP)[a]	H_{298} (SMD(AcCN)/ M06-2X/ def2-TZVP)[a]	$G_{298,qh}$ (SMD(AcCN)/ M06-2X/ def2-TZVP)[a]
Ts-I			
acocsol_034r	**-1240.56074420**	**-1240.286866**	**-1240.346148**
acocsol_001	-1240.55896252	-1240.285272	-1240.345063
acocsol_017	-1240.55817853	-1240.284066	-1240.343187
acocsol_012r	-1240.55817852	-1240.284067	-1240.343188
acocsol_019	-1240.55627242	-1240.282272	-1240.341776

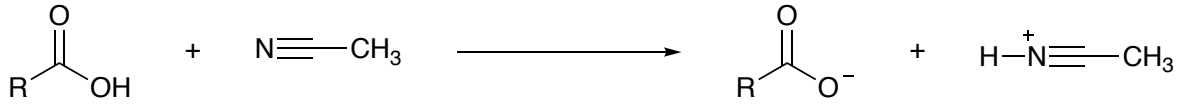
acocsol_018	-1240.55626904	-1240.282293	-1240.342708
acocsol_010f	-1240.55626449	-1240.282265	-1240.341896
acocsol_020	-1240.55487658	-1240.281557	-1240.340964
acocsol_021	-1240.55152069	-1240.277924	-1240.338204
acocsol_022	-1240.55264485	-1240.278721	-1240.338167
acocsol_023	-1240.55262799	-1240.278730	-1240.338438
Ts-TS5			
acocsol_034	**-1240.55758248**	**-1240.285218** (imag=-293 cm^{-1})	**-1240.344068**
acocsol_035	-1240.55758243	-	-
acocsol_024	-1240.55692210	-1240.284675 (imag=-284 cm^{-1})	-1240.343864
acocsol_012	-1240.55290323	-1240.280390 (imag=-271 cm^{-1})	-1240.339776
acocsol_011	-1240.55290324	-1240.280392 (imag=-270 cm^{-1})	-1240.339786
acocsol_010	-1240.55203131	-1240.279605 (imag=-242 cm^{-1})	-1240.339011
Ts-IV			
acocsol_034f	**-1240.58038213**	**-1240.309560**	**-1240.369608**
acocsol_007	-1240.57967219	-1240.308923	-1240.369131
acocsol_024r	-1240.57639881	-1240.305984	-1240.368473
acocsol_005	-1240.57639634	-1240.305971	-1240.368466
acocsol_033	-1240.57635796	-1240.306941	-1240.367568
acocsol_014f	-1240.57631397	-1240.305967	-1240.368826
acocsol_032	-1240.57612064	-1240.305610	-1240.368187
acocsol_013r	-1240.57612054	-1240.306556	-1240.366685
acocsol_015r	-1240.57612057	-1240.305614	-1240.368240

V			
aco_007sol	-345.1305303	-345.0124047	-345.0472302
Ts-VI			
acocsol_009	**-895.427339880**	-895.276134	**-895.320630**
acocsol_016	-895.427301315	**-895.277122**	-895.320010
VII			
aco_019sol	**-345.5531468**	**-345.4224408**	**-345.4574849**
aco_020sol	-345.5523892	-345.4216836	-345.4567290
Ts-VIII			
acocsol_008	-894.985926190	-894.846514	-894.890176

[a] Using solution phase SMD(AcCN)/M06-2X/def2-TZVP geometries.

5.0 Calculated Relative pK_a Data

Relative pK_a values in acetonitrile were calculated ((U)M06-2X/def2-TZVP//SMD(acetonitrile) level of theory) for acid leaving groups according to the proton exchange with acetonitrile solvent as depicted:



$$pK_{a(calc)} = \frac{\Delta G}{2.303 * RT} \qquad \text{(Eq. S01)}$$

Calculated pK_a values were adjusted by benchmarking against experimental pK_a data in acetonitrile for acids where it was available (acetic acid, benzoic acid, toluenesulfonic acid).[10] The equation resulting from the linear relationship between calculated and experimental data for these acids (Equation S01) was then used to adjust the calculated values to obtain relative pK_a data.

Table S20. Experimental and calculated ((U)M06-2X/def2-TZVP//SMD(acetonitrile) level of theory) pK_a data for leaving groups in acetonitrile.

Acid	**Experimental pK_a (acetonitrile)**	**Calculated pK_a (unadjusted)**	**Calculcated pK_a (adjusted)**
AcOH	23.5	34.3	23.8
PivOH	–	34.5	24.0
BzOH	21.5	31.2	21.2
Cl_3CCO_2H	–	21.1	12.6
F_3CCO_2H	–	20.7	12.2
TsOH	8.5	16.5	8.6

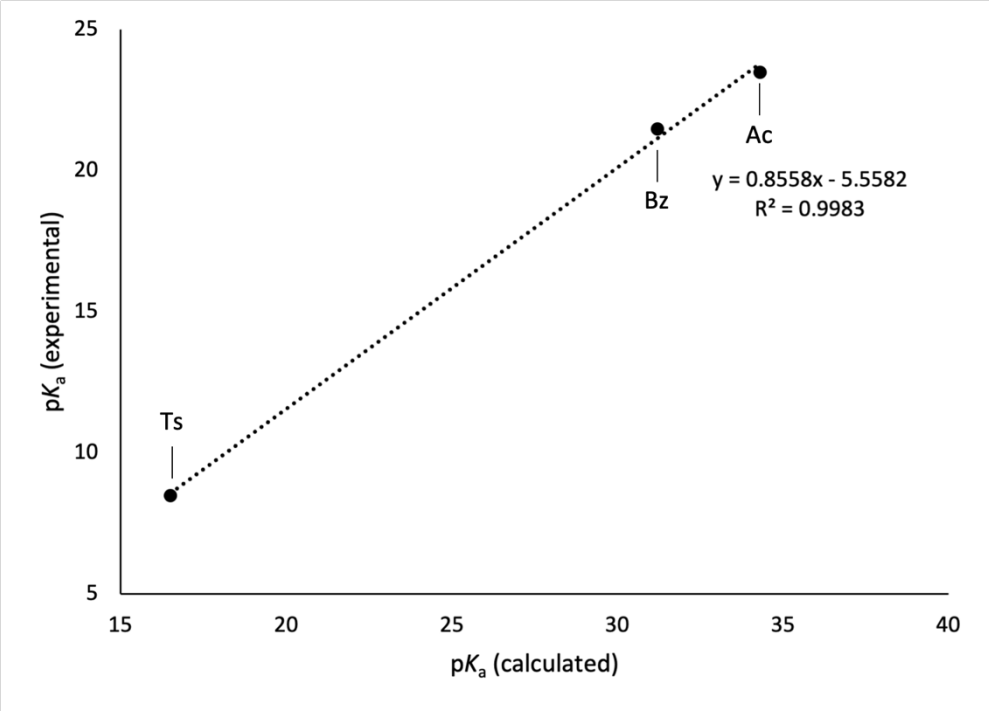


Figure S04. Calculated vs experimental pK_a for acetic acid, benzoic acid, and toluenesulfonic acid.

$$pK_{a(calc,adjusted)} = 0.8558 * \left(pK_{a(calc)}\right) - 5.5582 \qquad \text{(Eq. S02)}$$

A linear relationship between the free energy of activation of **TS5** and the calculated pK_a of the leaving group in acetonitrile was observed (Figure S05a.)

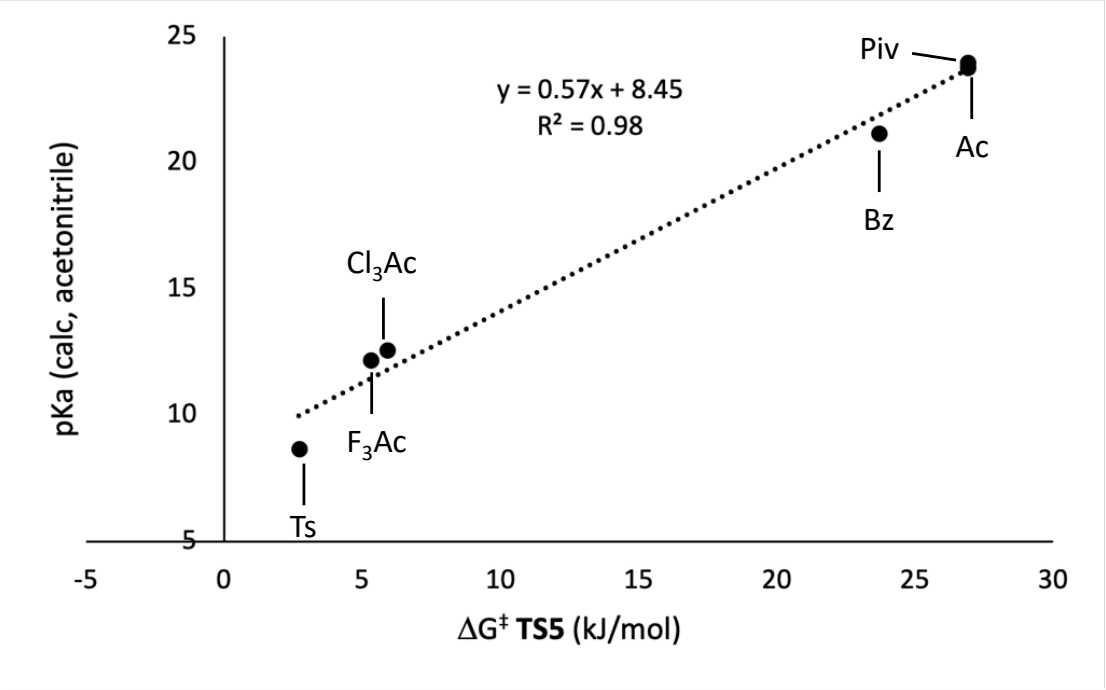


Figure S05a. Free energy of activation ($\Delta G^{\ddagger}$, kJ/mol) for **TS5** vs the calculated pK_a of the leaving group in acetonitrile for leaving groups acetyl, pivaloyl, benzoyl, trichloroacetyl, trifluoroacetyl, and tosyl.

A similarly good correlation is observed between the free energy of activation of **TS5** and the reaction energy for heterolytic dissociation ΔG(**VII** + **VIII**), again in full support of the charge-separating character in the elimination transition state **TS5**.

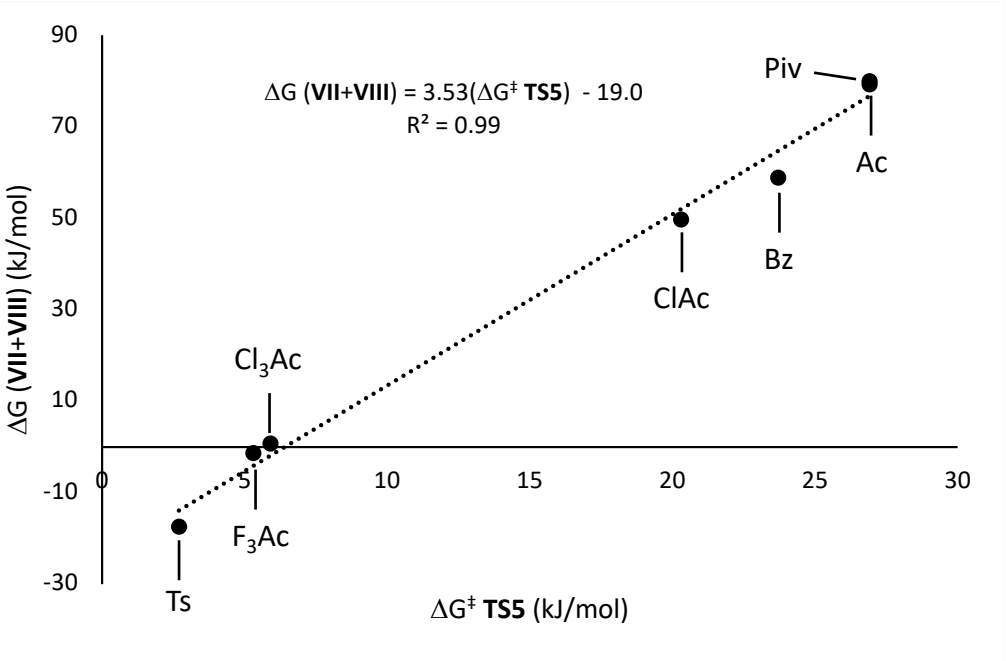


Figure S05b. Free energy of activation (ΔG‡, kJ/mol) for **TS5** vs the reaction energy for heterolytic dissociation ΔG(**VII** + **VIII**) in acetonitrile for leaving groups acetyl, pivaloyl, benzoyl, trichloroacetyl, trifluoroacetyl, and tosyl.

6.0 Experimental Results

6.1 General Information

Materials

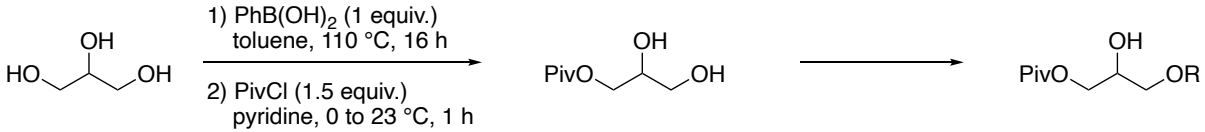
Stainless steel needles and syringes were used to transfer air and moisture sensitive liquids. Schlenk flasks and 4 Å molecular sieves were stored at 140 °C for at least 24 hours before use. Acetonitrile was HPLC grade and purified using a solvent purification system equipped with columns of activated alumina under nitrogen (Innovative Technology, Inc.). Other solvents and reagents were used without further purification. Flash column chromatography was performed using neutral silica gel (60 Å, 230 – 400 mesh, Silicycle). Thin-layer chromatography (TLC) was performed using aluminum backed silica gel plates (details), and compounds were visualized by UV irradiation at 254 nm and by staining with $KMnO_4$ solution.

Instrumentation

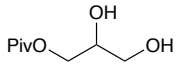
Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C) spectra were recorded on a 500 MHz Agilent DD2 Spectrometer or a 400 MHz Bruker Spectrometer. Chemical shifts for protons are recorded in parts per million (ppm) relative to tetramethylsilane and are referenced to residual protium in the solvent ($CDCl_3$: δ 7.26). Chemical shifts for carbons are recorded in parts per million (ppm) relative to tetramethylsilane and are referenced to residual carbon in the solvent ($CDCl_3$: δ 77.16). Data are represented in the following order: chemical shift (δ, ppm); multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br s, broad singlet); coupling constant (J, Hz); number of protons; assignment. Proton assignments were made based on coupling constants and 2D NMR spectra. High-resolution mass spectra (HRMS) were obtained on a JEOL AccuTOF JMS- T1000LC mass spectrometer equipped with a DART (direct analysis in real time) ion source. Infrared (IR) spectra were obtained on a Perkin-Elmer Spectrum 100 instrument equipped with a singlebounce diamond/ZnSe ATR accessory as neat samples. Spectral features are tabulated as follows: wavenumber (cm^{-1}); intensity (s-strong, m- medium, w-weak).

6.2 Preparation of Substrates

General Preparation of Substrates



(S1) – 1-O-(trimethylacetyl)glycerol



Prepared according to adapted literature procedures.[11]

Glycerol (1 equiv.) and phenylboronic acid (1 equiv.) in a round bottom flask equipped with a magnetic stir bar were dissolved in toluene (5 mL/mmol). The reaction flask was sealed and stirred at 110 °C for 16 hours. After 16 hours, the reaction mixture was cooled to room temperature then solvent was removed under reduced pressure, azeotroped three times with toluene, followed by drying under high vacuum to dryness. Boronic ester intermediate was dissolved in pyridine (2 mL/mmol) and cooled to 0 °C. Trimethylacetyl chloride (1.2 equiv.) was added and the reaction was warmed to room temperature and stirred for 1 hour. Reaction was dilute with toluene and filtered through Celite, then concentrated under reduced pressure. Crude reaction residue was dissolved in ethyl acetate (40 mL/mmol), poured into a separatory funnel containing 1M sorbitiol:1M Na_2CO_3 (40 mL/mmol) and shaken for 5 minutes. Aqueous layer was extracted with ethyl acetate (3 x 40 mL/mmol), combined organic layers dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Crude residue was purified by flash column chromatography on silica (75% ethyl acetate in hexanes) to yield (**S1**) as a clear, colourless oil (77%).

Spectral data were in agreement with those previously reported.[12]

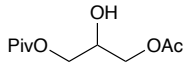
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.14 (dt, *J* = 5.4, 0.9 Hz, 2H), 3.94–3.87 (m, 1H), 3.72 – 3.63 (m, 1H), 3.61–3.53 (m, 1H), 1.20 (s, 9H).

General Procedure A

Adapted according to literature procedures.[13]

To a solution of 1-O-(trimethylacetyl)glycerol (1 equiv.) and 2-aminoethyl diphenylborinate (10 mol%) in acetonitrile (5 mL/mmol) was added the acid chloride (1.2 equiv.) followed by DIPEA (1.2 equiv.). The reaction was stirred at room temperature for 4 hours (or until reaction was indicated complete by TLC) then dilute with ethyl acetate. Reaction mixture was extracted with water, then aqueous layer was extracted twice more with ethyl acetate. Combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Crude residue was purified by flash column chromatography on silica.

(1a) – 1-*O*-acetyl-3-*O*-pivaloylglycerol



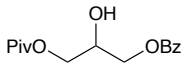
Prepared according to General Procedure A with acetyl chloride to yield (**1a**) as a clear oil (89%).
Purified by flash column chromatography on silica (20% to 30% ethyl acetate in hexanes).

Spectral data were in agreement with those previously reported.[14]

R*f* = 0.36 (30% ethyl acetate in hexanes)

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 4.26–4.06 (m, 5H), 2.10 (s, 3H), 1.22 (s, 9H).

(1b) – 1-*O*-benzoyl-3-*O*-pivaloylglycerol



Prepared according to General Procedure A with benzoyl chloride to yield (**1b**) as a light yellow oil (59%).
Purified by flash column chromatography on silica (20% to 30% ethyl acetate in hexanes).

R*f* = 0.30 (30% ethyl acetate in hexanes)

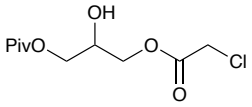
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.06–8.02 (m, 2H, Ar-H), 7.59–7.53 (m, 1H, Ar-H), 7.46–7.44 (m, 2H, Ar-H), 4.46 – 4.36 (m, 2H, H-1), 4.28 – 4.21 (m, 3H, H-2, H-3), 1.22 (s, 9H, -C(CH_3)$_3$).

^{13}C NMR (126 MHz $CDCl_3$): δ (ppm) = 178.8, 166.7, 133.4, 129.8, 129.7, 128.6, 68.6, 65.8, 65.3, 39.0, 27.3.

IR (neat, cm^{-1}): 3472 (w), 2968 (w), 1716 (s), 1602 (w), 1481 (m), 1453 (m), 1268 (s), 1156 (s), 1109 (s), 1070 (s), 1027 (m), 710 (s).

HRMS (DART^{+}, m/z): calculated for $C_{15}H_{21}O_5$ $[M+H]^+$: 281.13835; found: 281. 13928.

(1c) – 1-*O*-chloroacetyl-3-*O*-pivaloylglycerol



Prepared according to General Procedure A with chloroacetyl chloride to yield (**1c**) as a clear oil (69%).
Purified by flash column chromatography on silica (20% to 30% ethyl acetate in hexanes).

R*f* = 0.35 (30% ethyl acetate in hexanes)

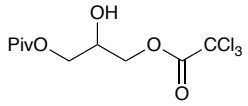
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 4.31 – 4.09 (m, 7H),

^{13}C NMR (126 MHz $CDCl_3$): δ (ppm) = 178.9, 167.4, 68.3, 66.7, 65.0, 40.8, 39.0, 27.2.

IR (neat, cm^{-1}): 3461 (w), 2969 (w), 1727 (s), 1482 (m), 1396 (m), 1284 (m), 1152 (s), 1038 (m), 940 (w), 781 (m).

HRMS ($DART^+$, m/z): calculated for $C_{10}H_{18}O_5Cl$ $[M+H]^+$: 253.08373; found: 253.08424.

(1d) – 1-*O*-trichloroacetyl-3-*O*-pivaloylglycerol



Prepared according to General Procedure A with trichloroacetyl chloride to yield (**1d**) as a colourless oil (48%).
Purified by flash column chromatography on silica (20% to 30% ethyl acetate in hexanes). Material was isolated as a 3:1 mixture of (#) and 2-trichloroacetoxy-1-pivaloyloxypropan-3-ol due to trichloroacetoxy migration.

R*f* = 0.45 (30% ethyl acetate in hexanes)

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 4.47–4.37 (m, 2H, H-1), 4.25–4.19 (m, 3H, H2, H3), 1.22 (s, 9H, -$C(CH_3)_3$).

^{13}C NMR (126 MHz $CDCl_3$): δ (ppm) = 178.9, 162.0, 77.7, 69.2, 68.0, 64.8, 39.1, 27.3.

IR (neat, cm^{-1}): 3459 (w), 2972 (w), 1768 (s), 1719 (m), 1481 (m), 1368 (w), 1236 (s), 1155 (s), 1003 (m), 826 (s), 679 (s).

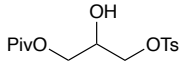
HRMS ($DART^+$, m/z): calculated for $C_{10}H_{16}O_5Cl_3$ $[M+H]^+$: 321.00578; found: 321.00636.

NMR peaks for the acyl migrated product: 2-trichloroacetoxy-1-pivaloyloxypropan-3-ol:

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 5.28 – 5.24 (m, 1H), 4.55 – 4.53 (m, 1H), 4.31 (dd, *J* = 12.4, 6.5 Hz, 1H), 3.86 (d, *J* = 5.2 Hz, 2H), 3.81 – 3.77 (m, 1H), 1.20 (s, 9H).

^{13}C NMR (126 MHz $CDCl_3$): δ (ppm) = 178.5, 161.6, 66.7, 61.8, 60.9, 40.1, 39.0, 27.2.

(1e) – 1-*O*-tosyl-3-*O*-pivaloylglycerol



Prepared according to General Procedure A with tosyl chloride (1.5 equiv.) and DIPEA (1.5 equiv.) to yield (**1e**) as a white solid (34%). Purified by flash column chromatography on silica (20% to 30% ethyl acetate in hexanes).

R*f* = 0.15 (30% ethyl acetate in hexanes)

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.82–7.78 (m, 2H, Ar-H), 7.38–7.34 (m, 2H, Ar-H), 4.13 (dd, *J* = 4.8, 1.7 Hz, 2H, H-1), 4.11–4.01 (m, 3H, H-2, H-3), 2.53 (d, *J* = 4.5 Hz, 1H, -OH), 2.45 (s, 3H, $-CH_3$), 1.17 (s, 9H, $-C(CH_3)_3$).

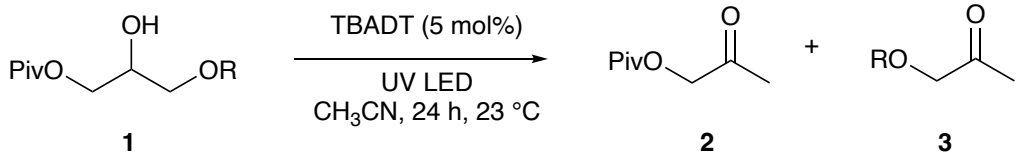
^{13}C NMR (126 MHz $CDCl_3$): δ (ppm) = 178.8, 145.4, 132.6, 130.1, 128.2, 70.2, 68.2, 64.5, 39.0, 27.2, 21.8.

IR (neat, cm^{-1}): 3497 (w), 2976 (w), 1717 (s), 1596 (m), 1458 (m), 1354 (s), 1290 (m), 1175 (s), 1162 (s), 1096 (m), 983 (s), 928 (s), 833 (s), 812 (s), 664 (s).

HRMS (DART^{+}, m/z): calculated for $C_{15}H_{23}O_6S$ $[M+H]^+$: 331.12194; found: 331.12099.

6.3 Intramolecular Competition Experiments

General Procedure B

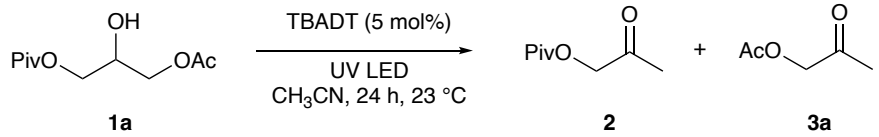


1 **2** **3**

Substrate (**1**) (1 equiv.), tetrabutylammonium decatungstate (5 mol%) and a small magnetic stir bar were added to a 1 dram vial. A rubber septum was used to seal the vial, which was then evacuated and backfilled with argon three times on a Schlenk line. Dry, degassed acetonitrile (0.125 M) was added to the vial under a balloon of argon. The rubber septum was removed and quickly replaced with the vial cap which was sealed with Teflon tape and parafilm. The vial was placed 5 inches from a UV LED Kessil lamp and stirred at 1050 rpm for 24 hours at 25 °C. After 24 hours the crude reaction was concentrated under reduced pressure and analyzed by ^{1}H NMR spectroscopy.

Competition experiment with 1-*O*-acetyl-3-*O*-pivaloylglycerol (1a)

1-*O*-acetyl-3-*O*-pivaloylglycerol (**1a**) was subjected to General Procedure B. ^{1}H NMR spectra analysis of the crude reaction mixture reveals the formation of products (**2**) and (**3a**) in a 1.1:1 ratio. ^{1}H NMR spectra for (**2**)[15] and (**3a**)[16] are consistent with literature reports.



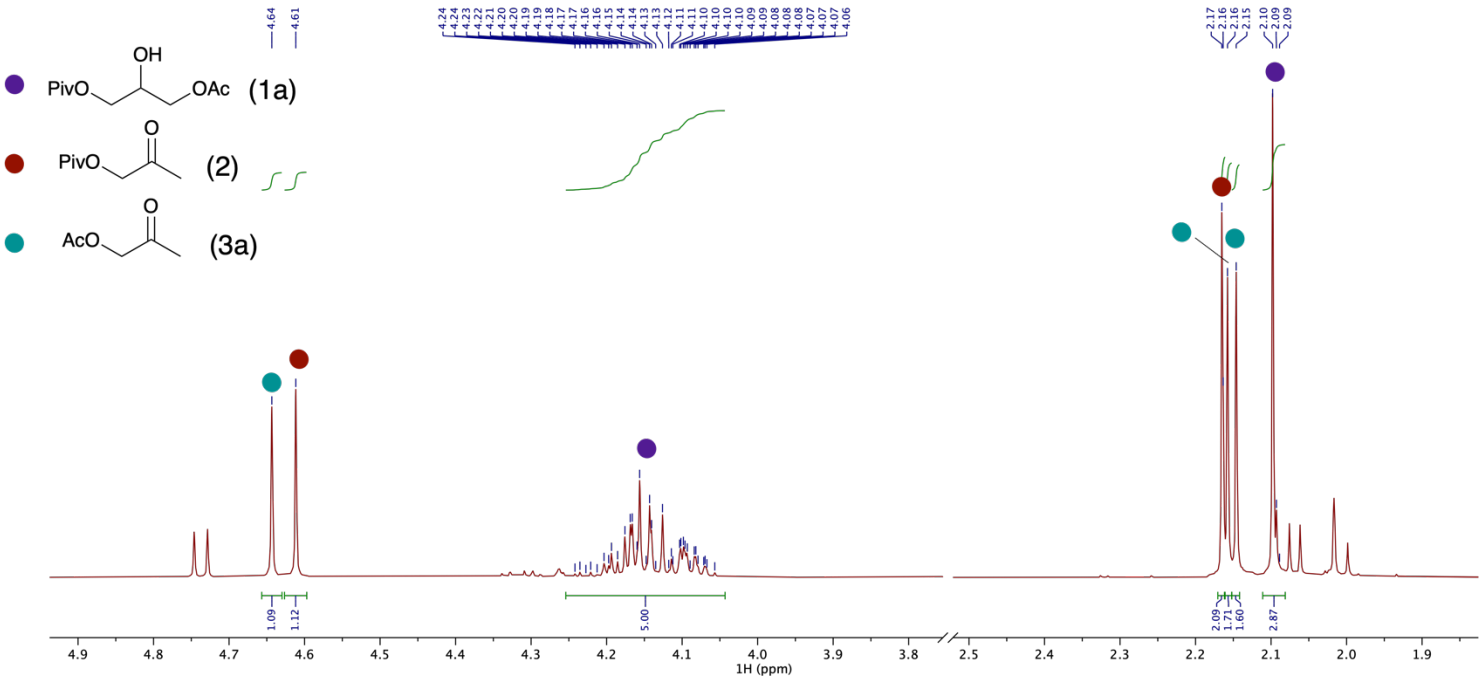


Figure S06. ^{1}H NMR spectra (prior to purification) of intramolecular competition experiment of 1-*O*-acetyl-3-*O*-pivaloylglycerol (**1a**) to form products (**2**) and (**3a**).

Competition experiment with 1-*O*-benzoyloxy-3-*O*-pivaloylglycerol (1b)

1-*O*-benzoyl-3-*O*-pivaloylglycerol (**1b**) was subjected to General Procedure B. ^{1}H NMR spectra analysis of the crude reaction mixture reveals the formation of products (**2**) and (**3b**) in a 1.7:1 ratio. ^{1}H NMR spectra for (**2**)[15] and (**3b**)[17] are consistent with literature reports.

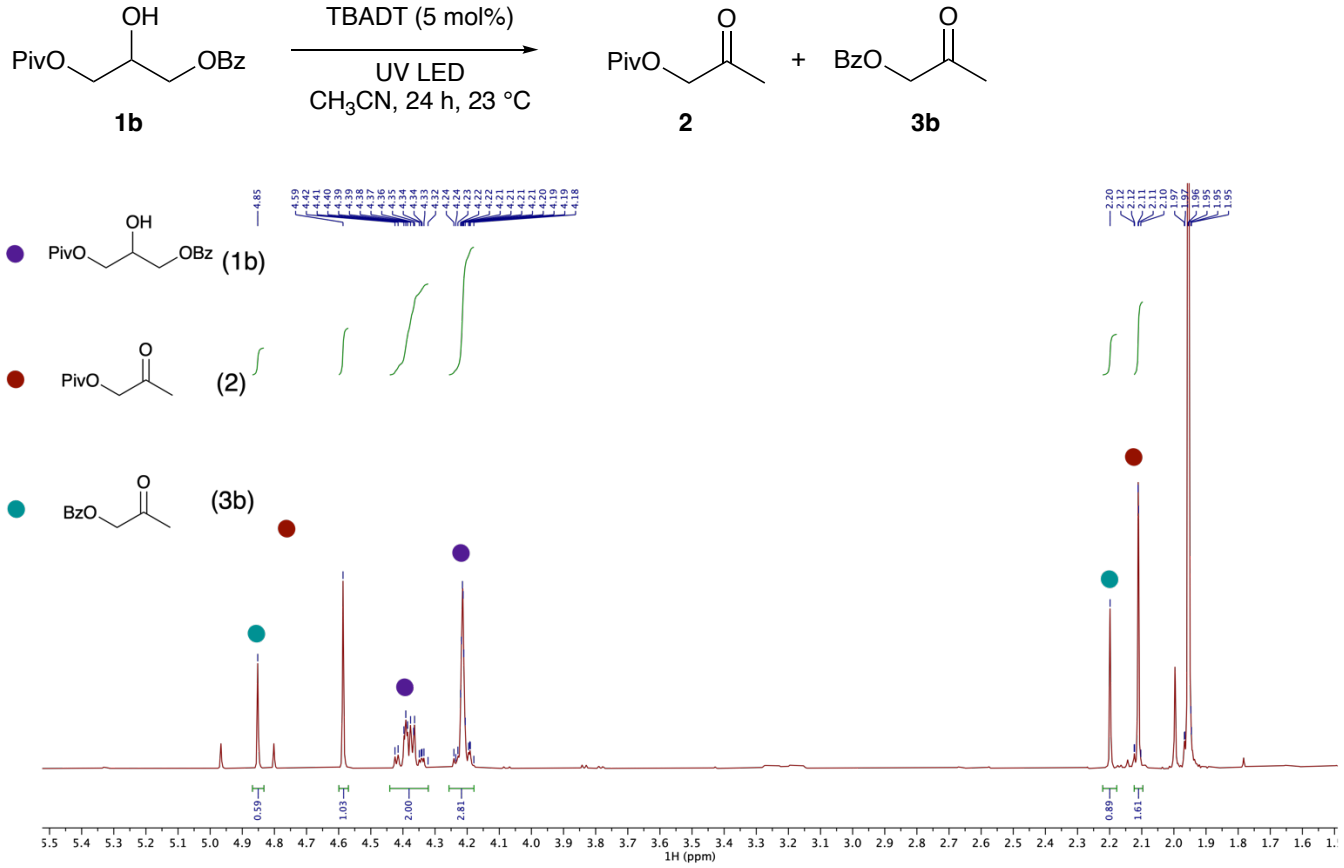


Figure S07. ^{1}H NMR spectra (prior to purification) of intramolecular competition experiment of 1-*O*-benzoyl-3-*O*-pivaloylglycerol (**1b**) to form products (**2**) and (**3b**).

Competition experiment with 1-*O*-chloroacetyl-3-*O*-pivaloylglycerol (1c)

1-*O*-chloroacteyl-3-*O*-pivaloylglycerol (**1c**) was subjected to General Procedure B. ^{1}H NMR spectra analysis of the crude reaction mixture reveals the formation of products (**2**) and (**3c**) in a 5.4:1 ratio. ^{1}H NMR spectra for (**2**)[15] is consistent with literature reports.

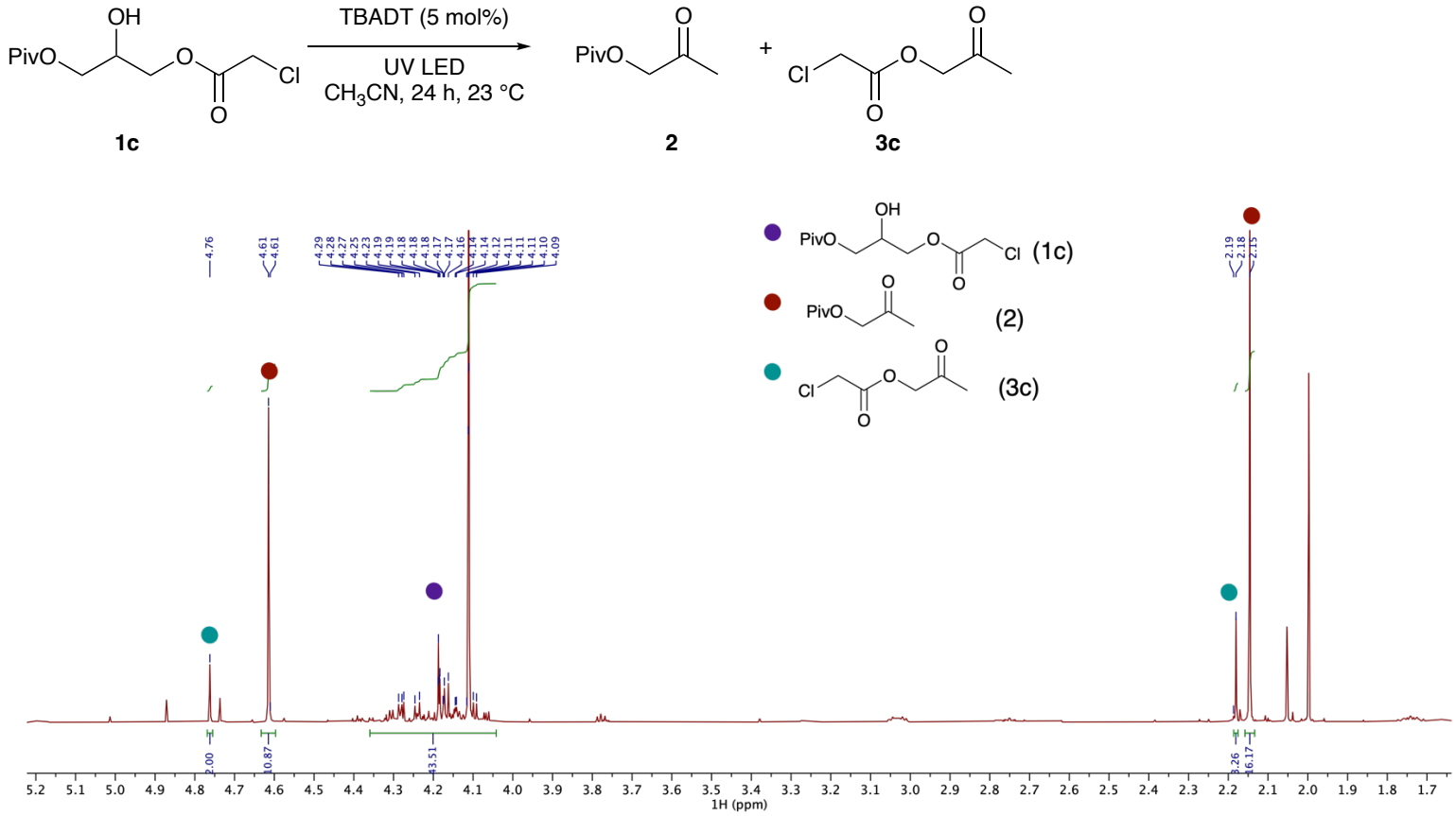


Figure S08. ^{1}H NMR spectra (prior to purification) of intramolecular competition experiment of 1-*O*-chloroacetyl-3-*O*-pivaloylglycerol (**1c**) to form products (**2**) and (**3c**).

Competition experiment with 1-*O*-trichloroacetyl-3-*O*-pivaloylglycerol (1d)

1-*O*-trichloroacteyl-3-*O*-pivaloylglycerol (**1d**) was subjected to General Procedure B. ^{1}H NMR spectra analysis of the crude reaction mixture reveals the formation of product (**2**). Product (**3d**) was not observed. ^{1}H NMR spectra for (**2**)[15] is consistent with literature reports.

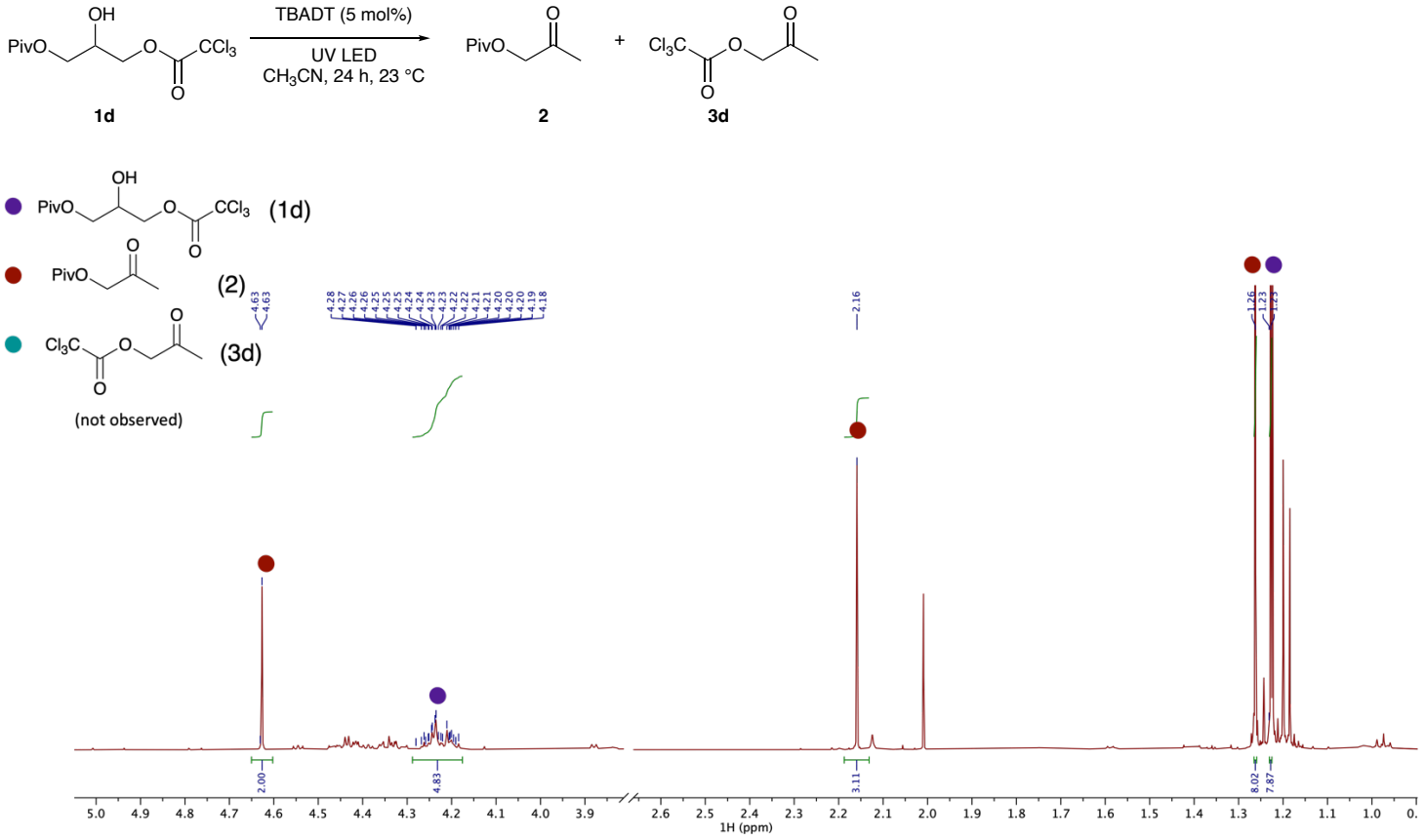


Figure S09. ^{1}H NMR spectra (prior to purification) of intramolecular competition experiment of 1-*O*-trichloroacetyl-3-*O*-pivaloylglycerol (**1d**) to form products (**2**) and (**3d**).

Competition experiment with 1-*O*-tosyl-3-*O*-pivaloylglycerol (1e)

1-*O*-tosyl-3-*O*-pivaloylglycerol (**1e**) was subjected to General Procedure B. ^{1}H NMR spectra analysis of the crude reaction mixture reveals the formation of product (**2**). Product (**3e**) was not observed. ^{1}H NMR spectra for (**2**)[15] and (**3e**)[18] (not observed) are consistent with literature reports.

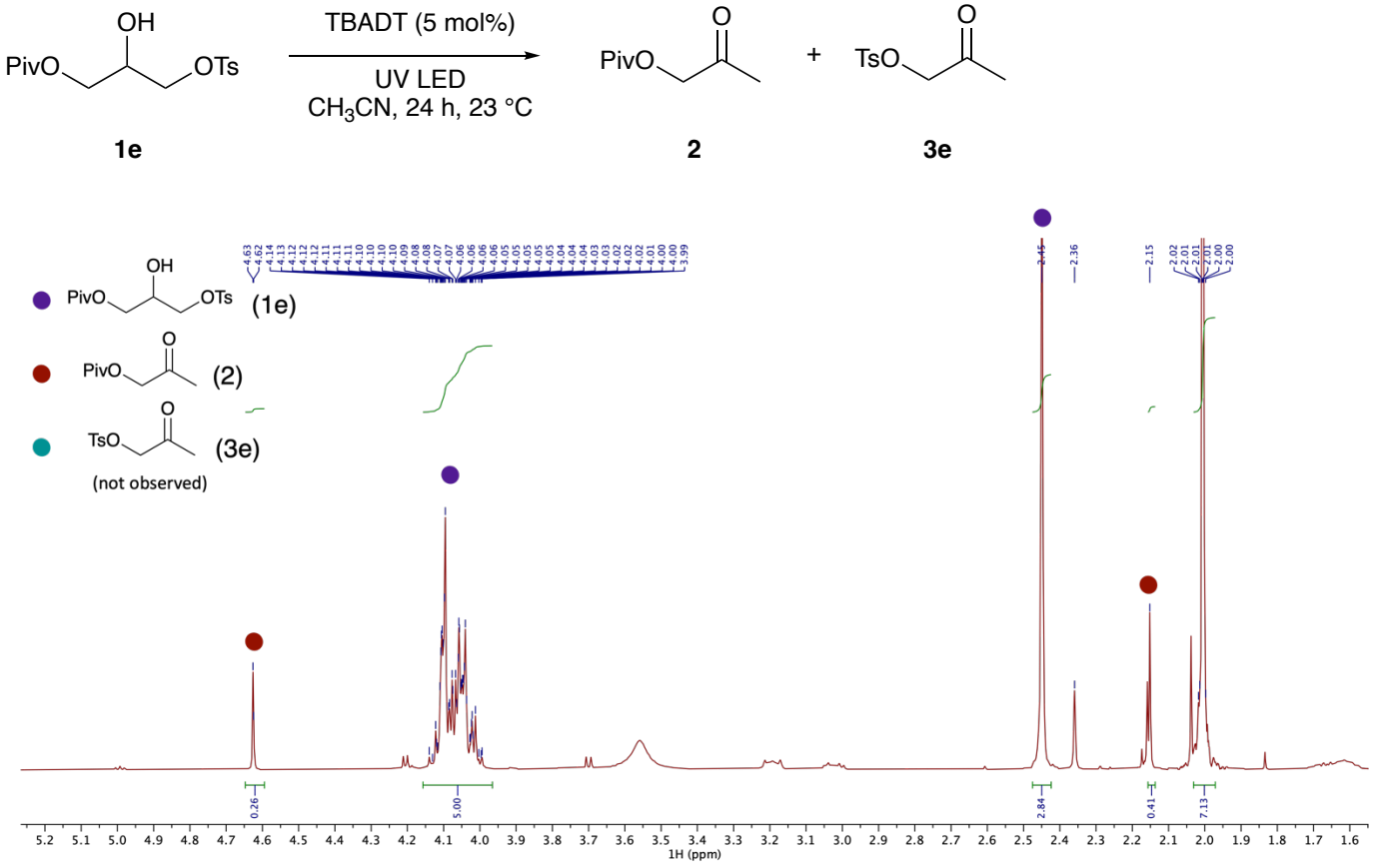
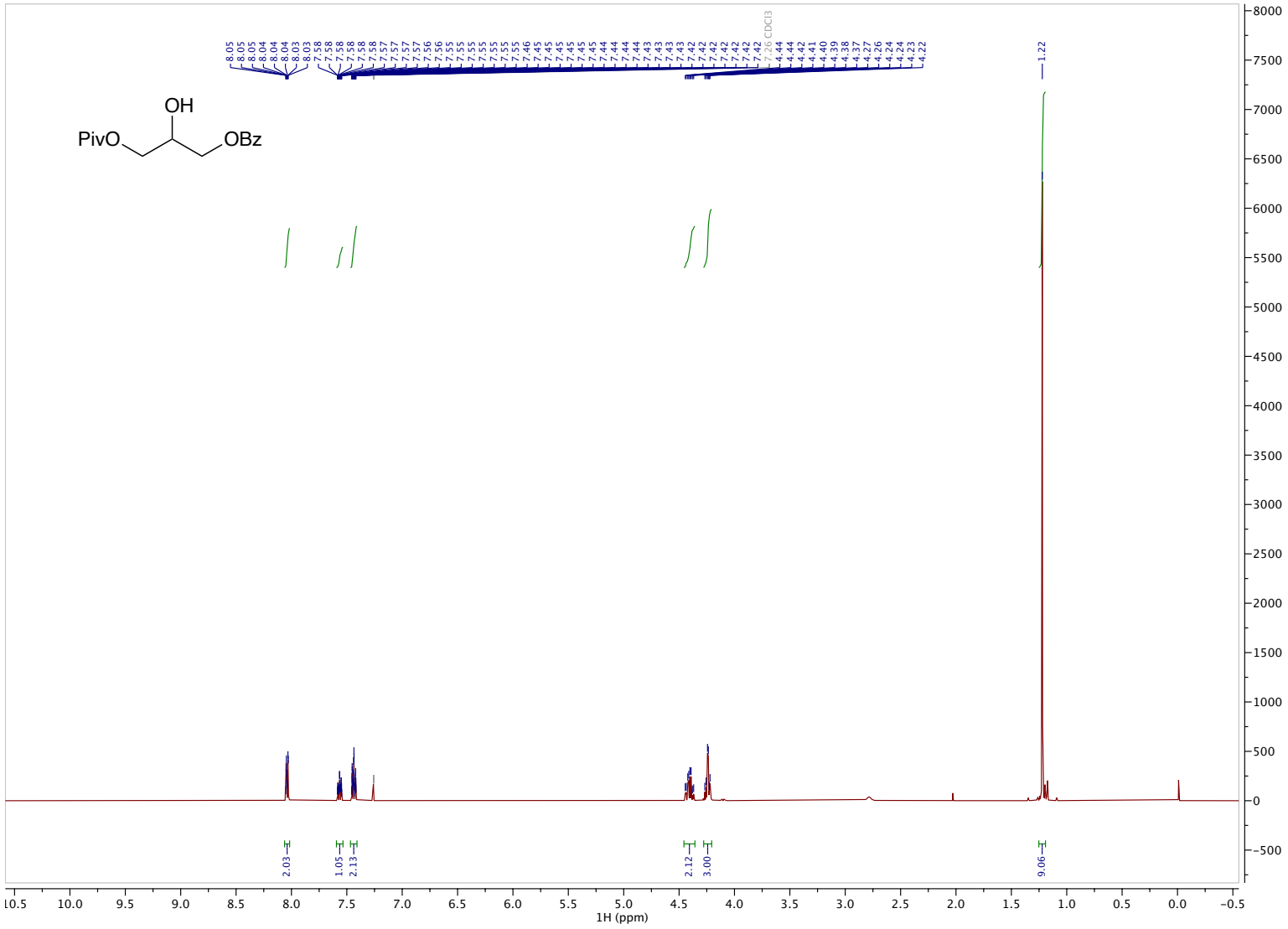


Figure S10. ^{1}H NMR spectra (prior to purification) of intramolecular competition experiment of 1-*O*-tosyl-3-*O*-pivaloylglycerol (**1e**) to form products (**2**) and (**3e**).

6.4 NMR Spectra

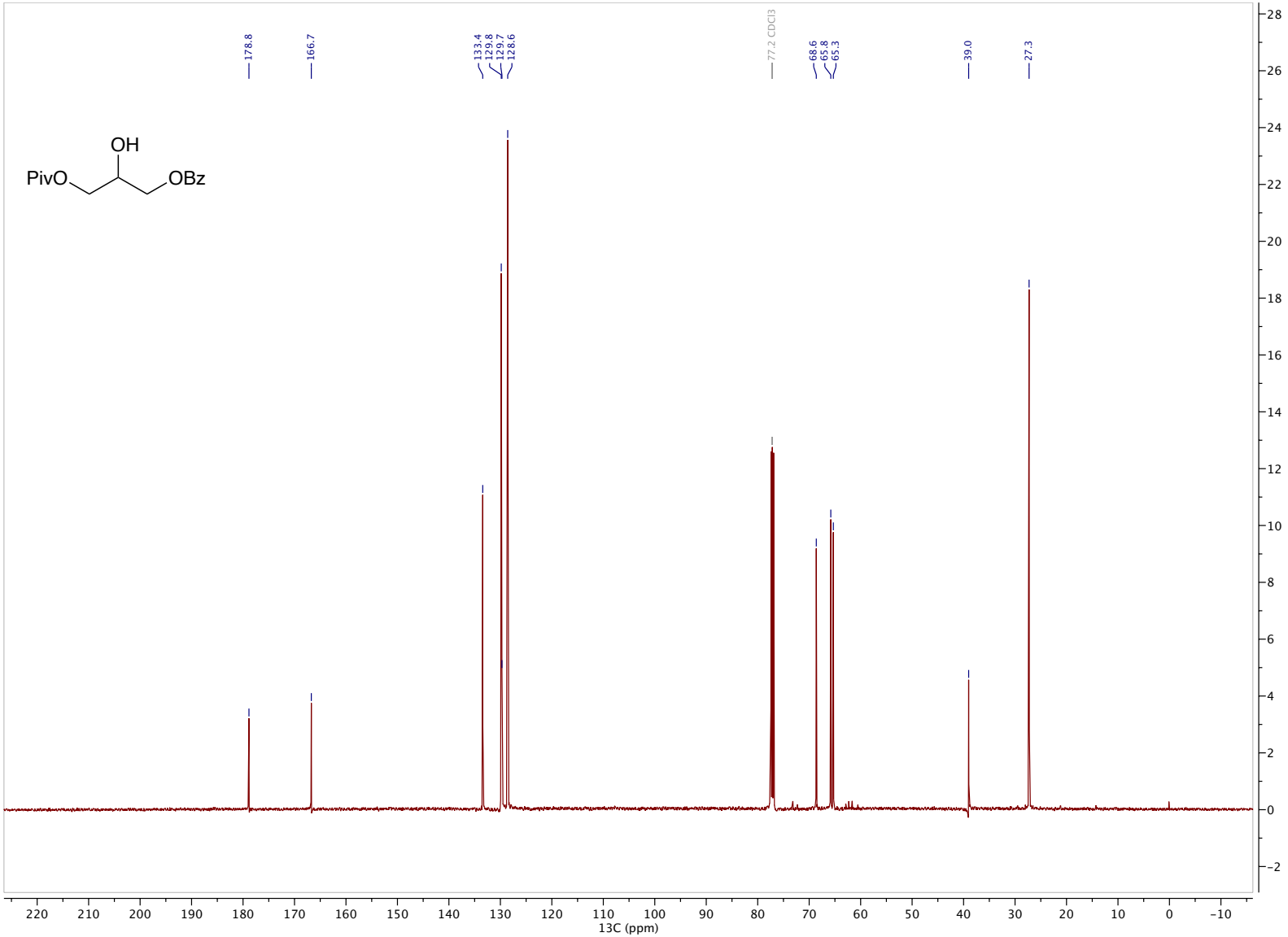
(1b) – 1-*O*-benzoyl-3-*O*-pivaloylglycerol

^{1}H NMR (500 MHz, $CDCl_3$)

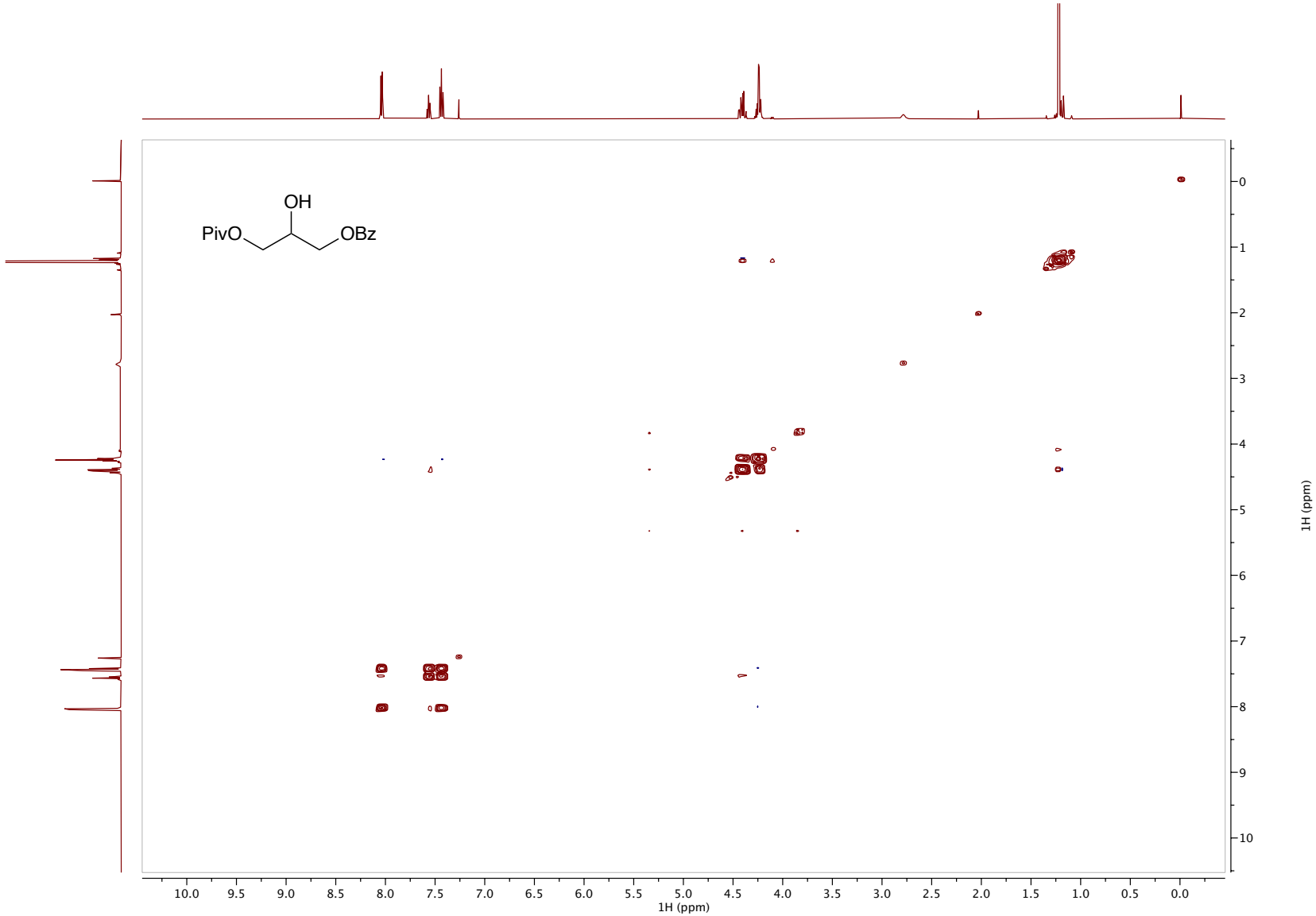


(1b) – 1-*O*-benzoyl-3-*O*-pivaloylglycerol

^{13}C NMR (126 MHz, $CDCl_3$)

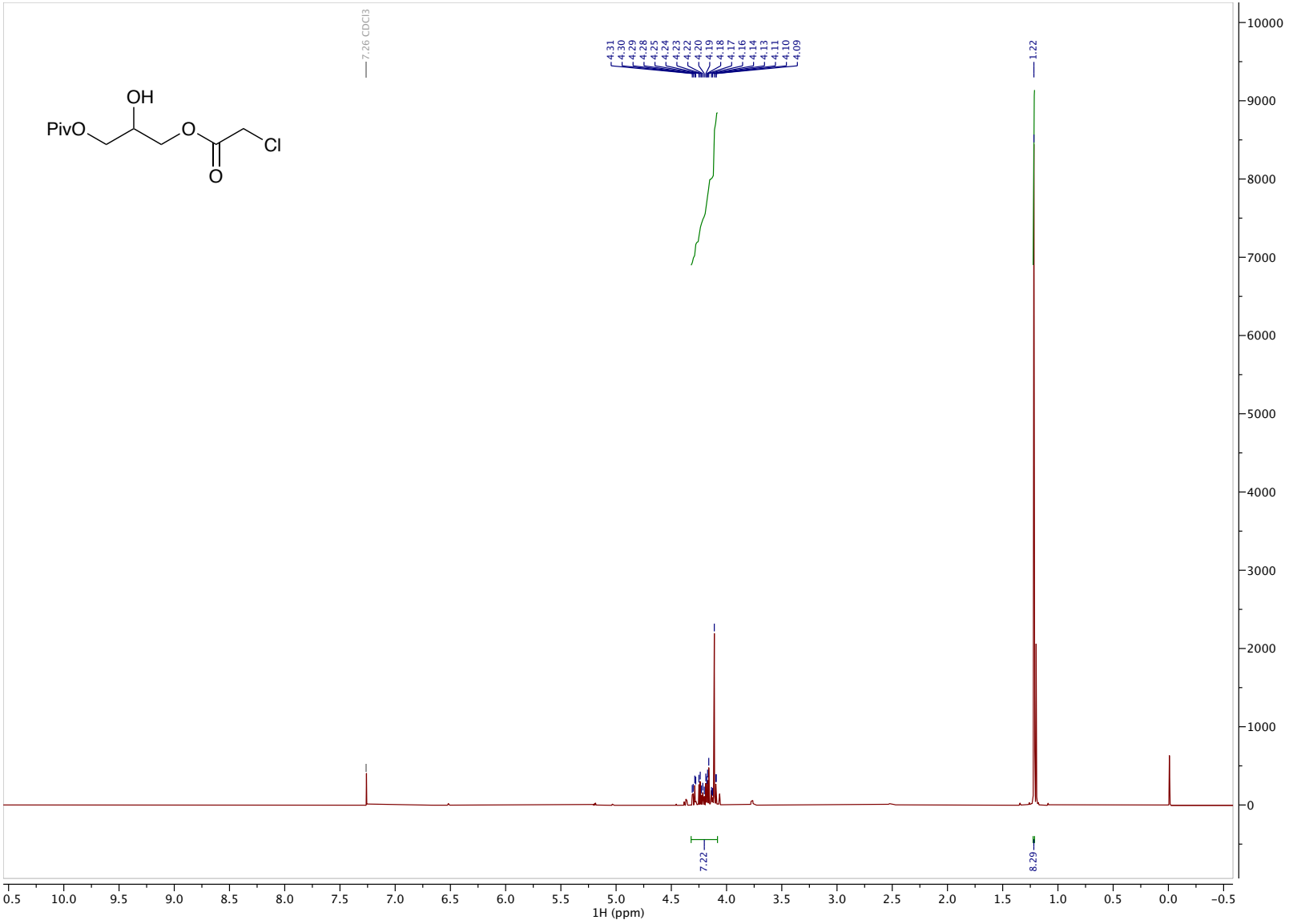


(1b) – 1-*O*-benzoyl-3-*O*-pivaloylglycerol
COSY NMR (500 MHz, $CDCl_3$)



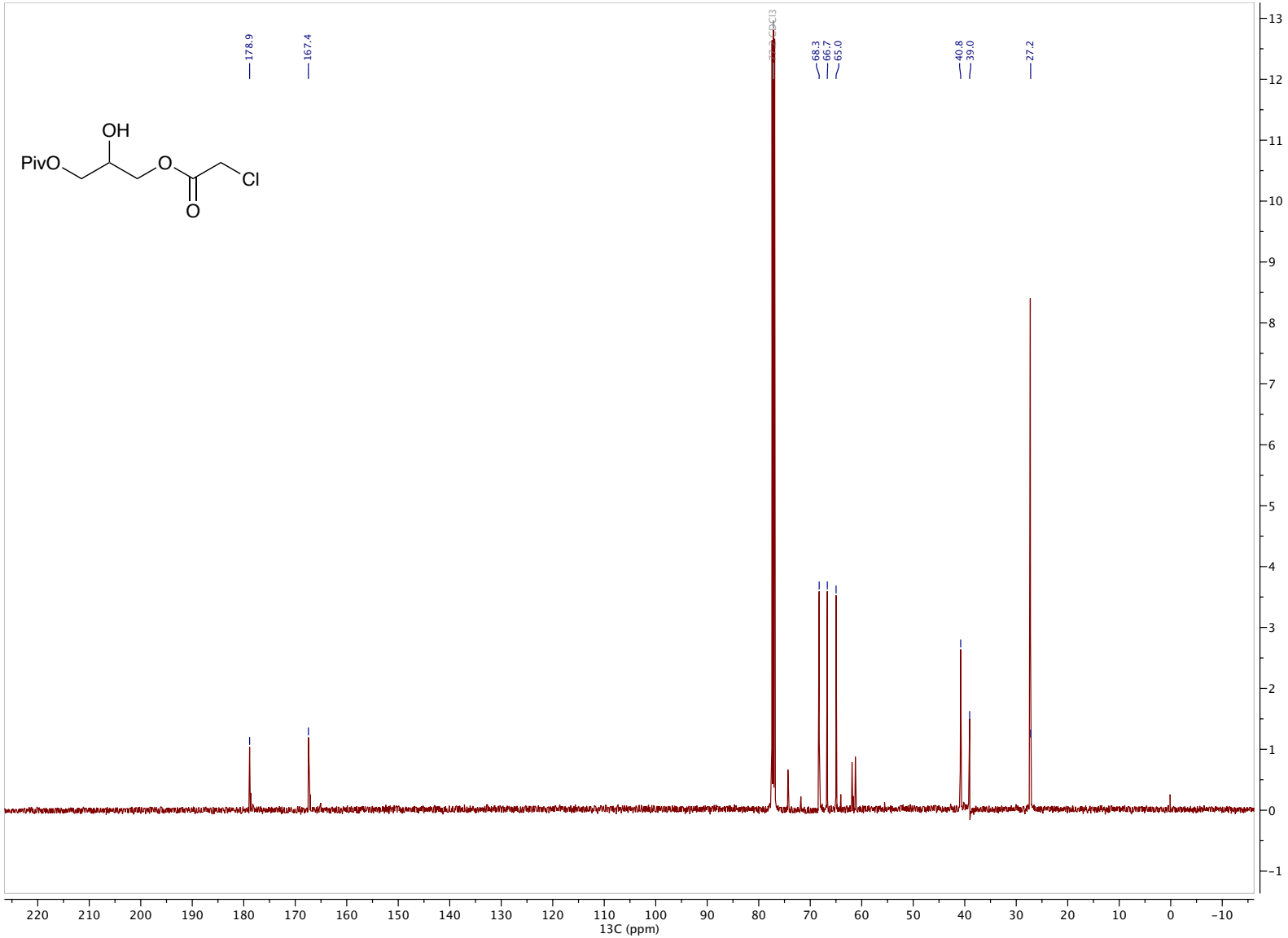
(1c) – 1-*O*-chloroacetyl-3-*O*-pivaloylglycerol

^{1}H NMR (500 MHz, $CDCl_3$)

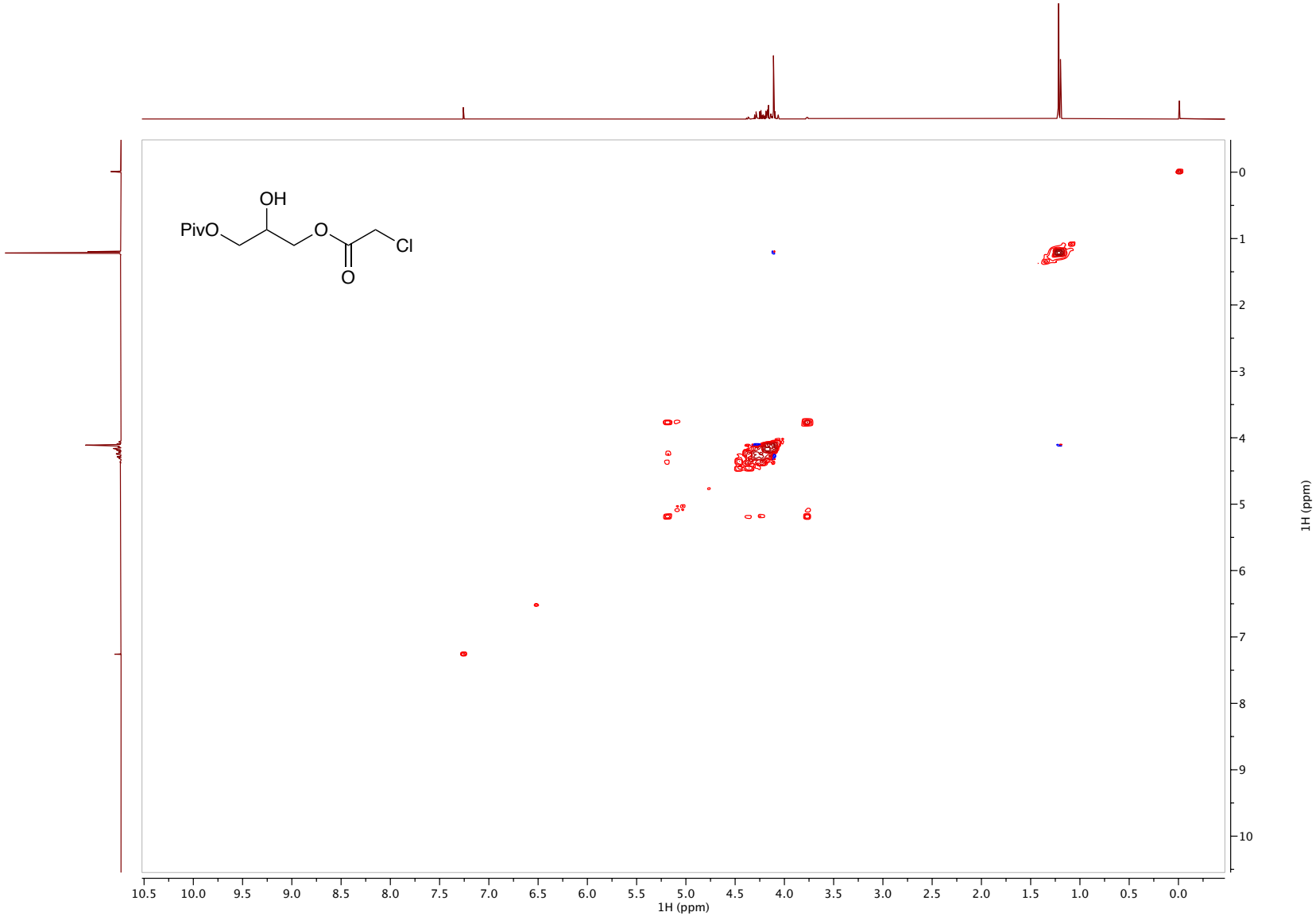


(1c) – 1-*O*-chloroacetyl-3-*O*-pivaloylglycerol

^{13}C NMR (126 MHz, $CDCl_3$)

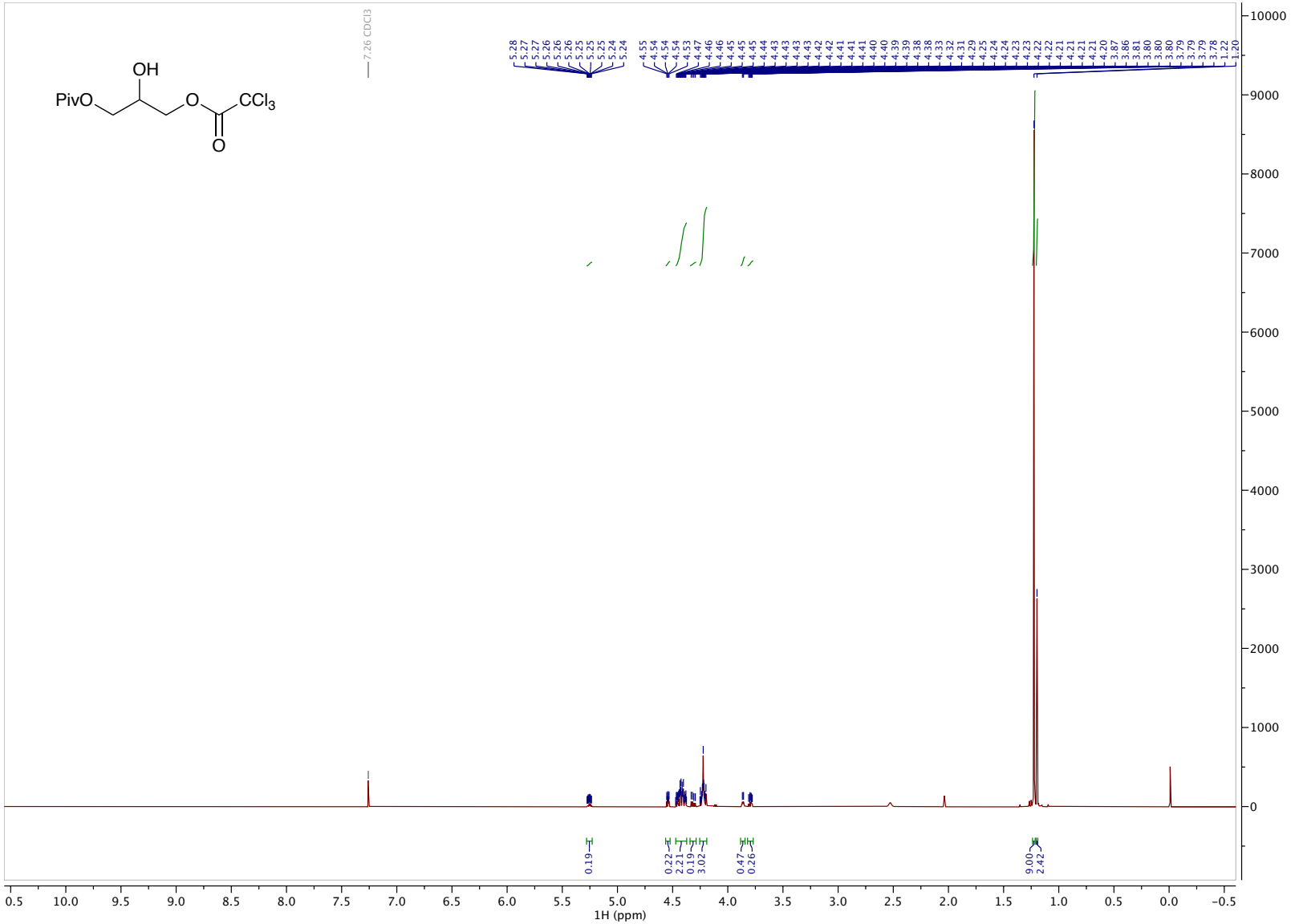


(1c) – 1-*O*-chloroacetyl-3-*O*-pivaloylglycerol
COSY NMR (500 MHz, $CDCl_3$)



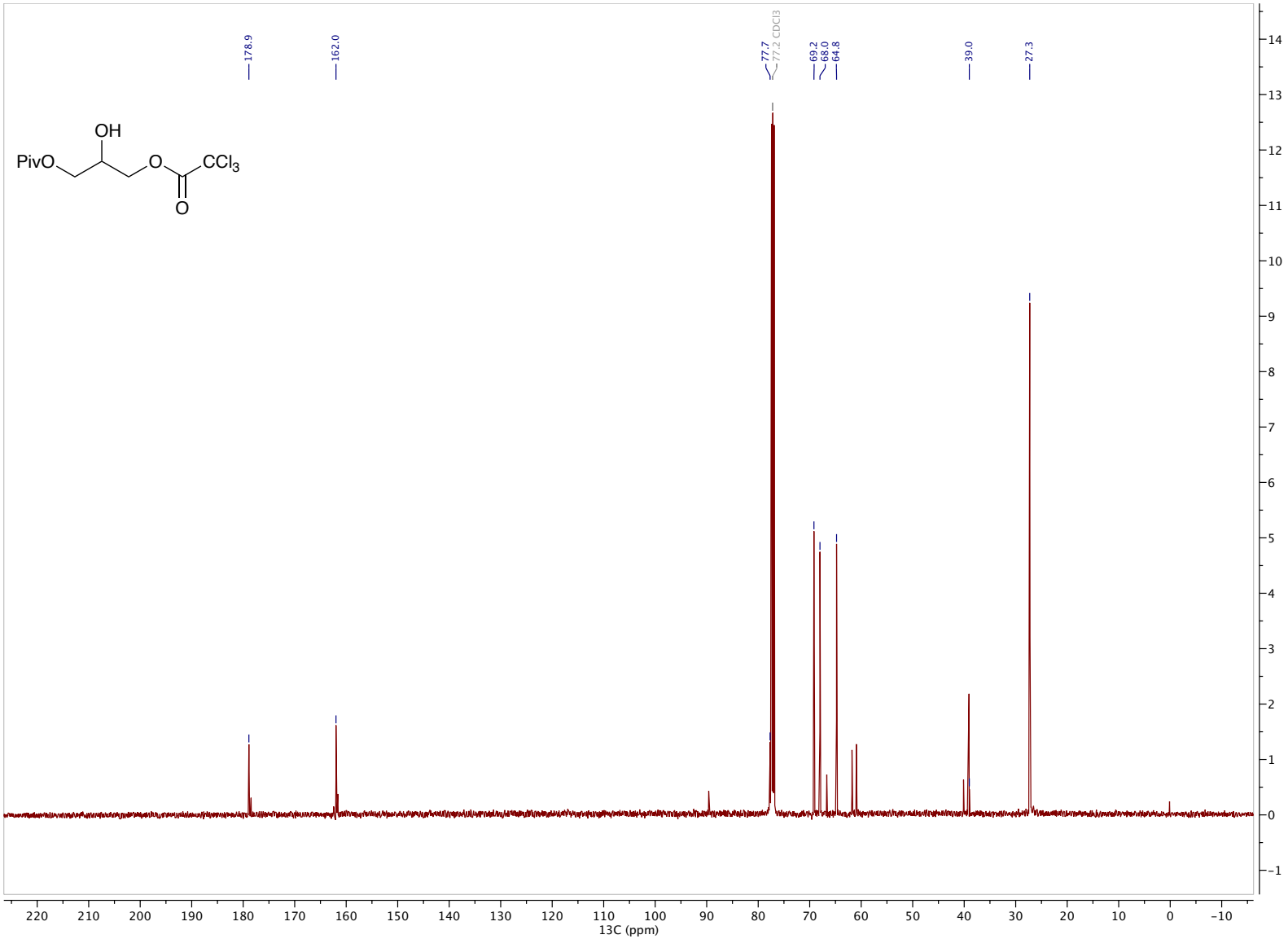
(1d) – 1-*O*-trichloroacetyl-3-*O*-pivaloylglycerol

^{1}H NMR (500 MHz, $CDCl_3$)



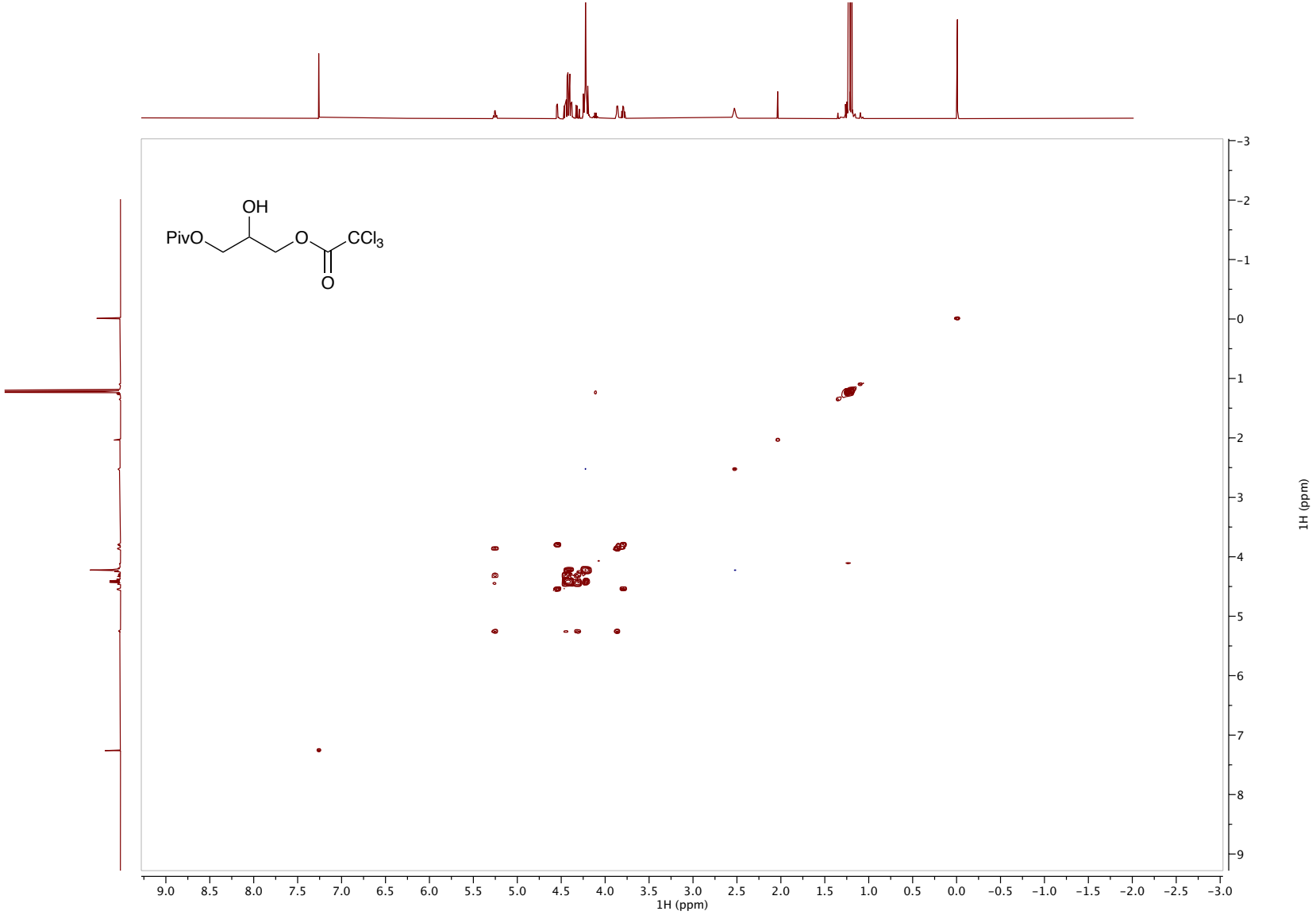
(1d) – 1-*O*-trichloroacetyl-3-*O*-pivaloylglycerol

^{13}C NMR (126 MHz, $CDCl_3$)



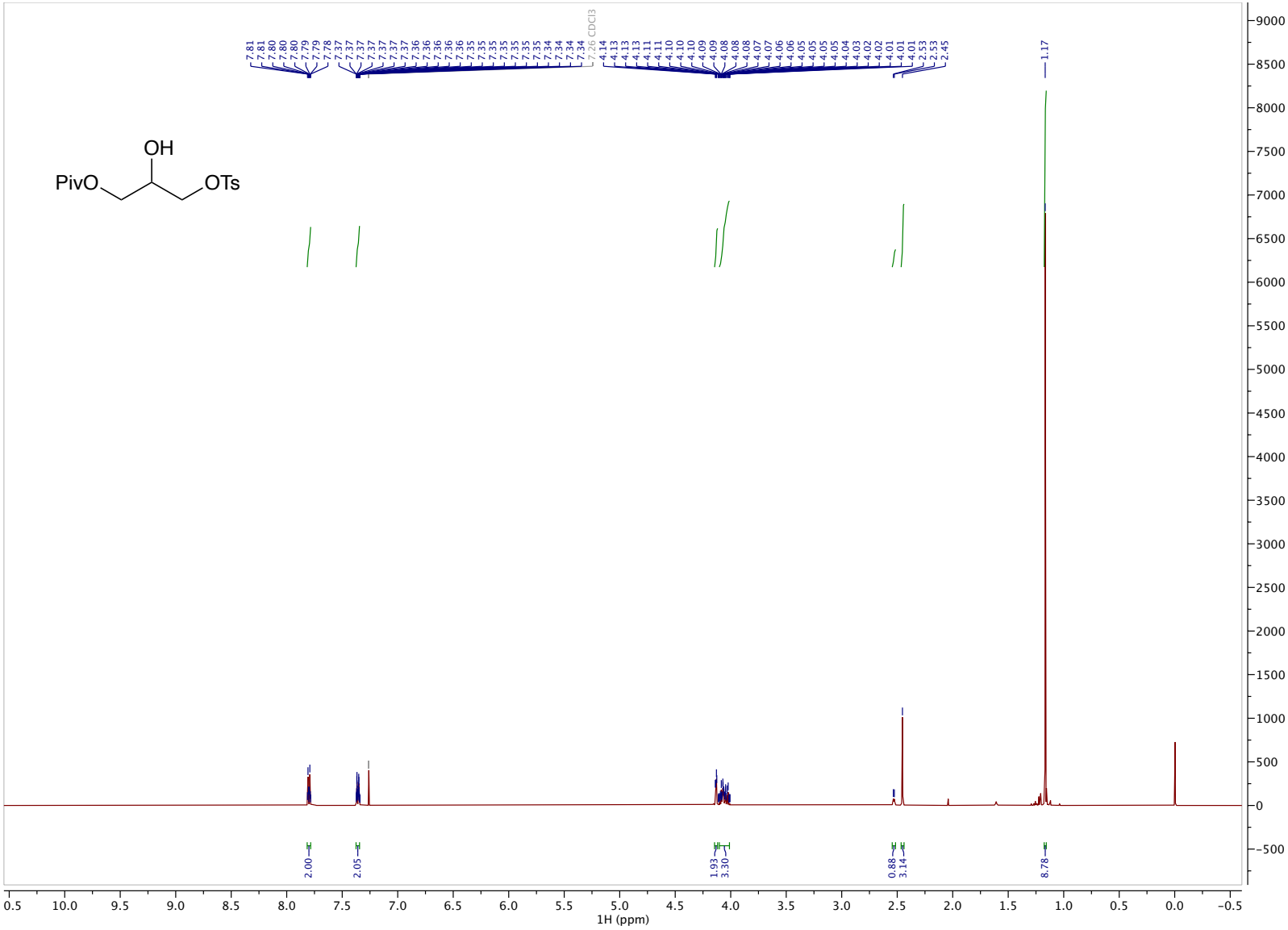
(1d) – 1-*O*-trichloroacetyl-3-*O*-pivaloylglycerol

COSY NMR (500 MHz, $CDCl_3$)



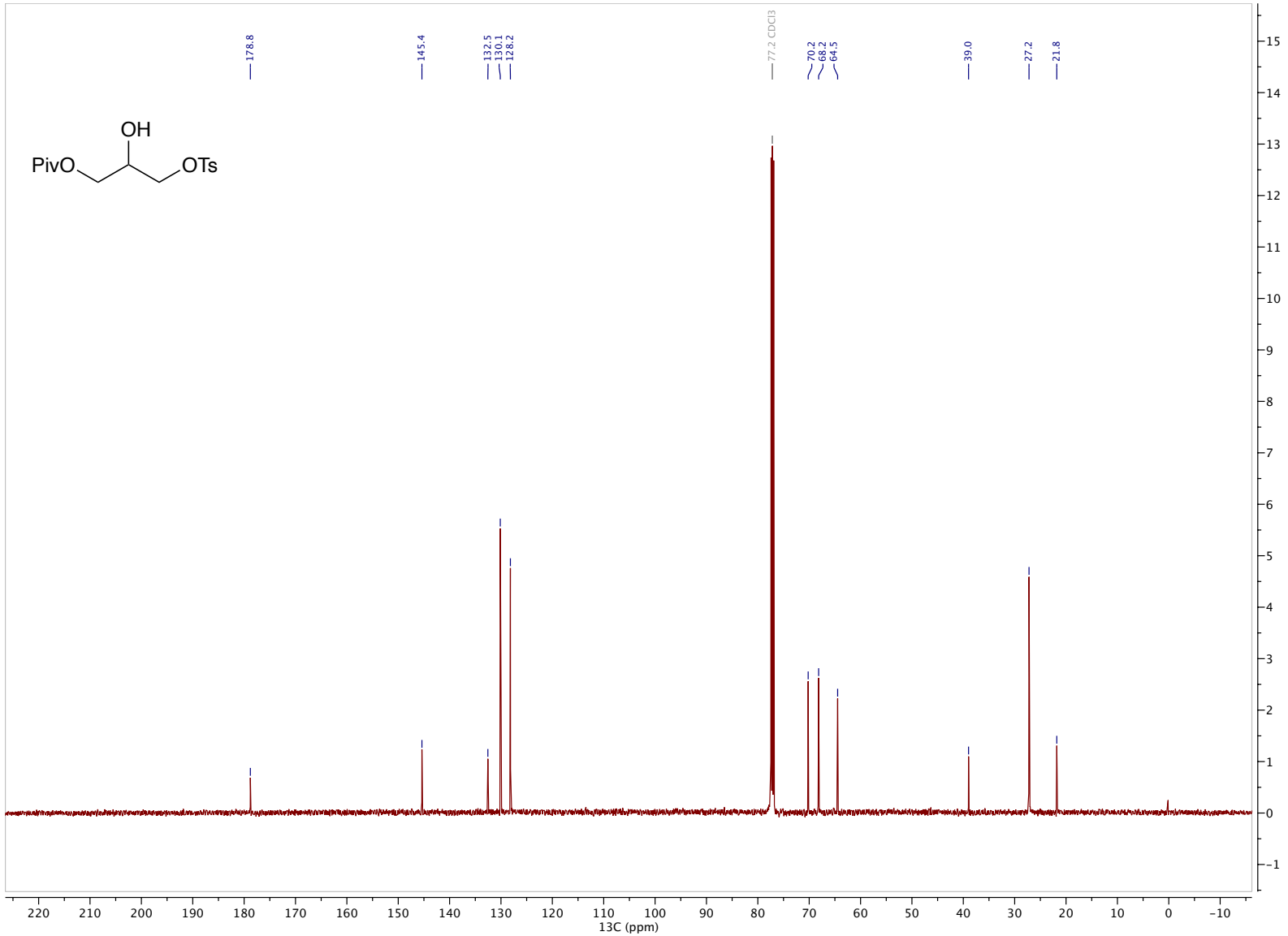
(1e) – 1-*O*-tosyl-3-*O*-pivaloylglycerol

^{1}H NMR (500 MHz, $CDCl_3$)

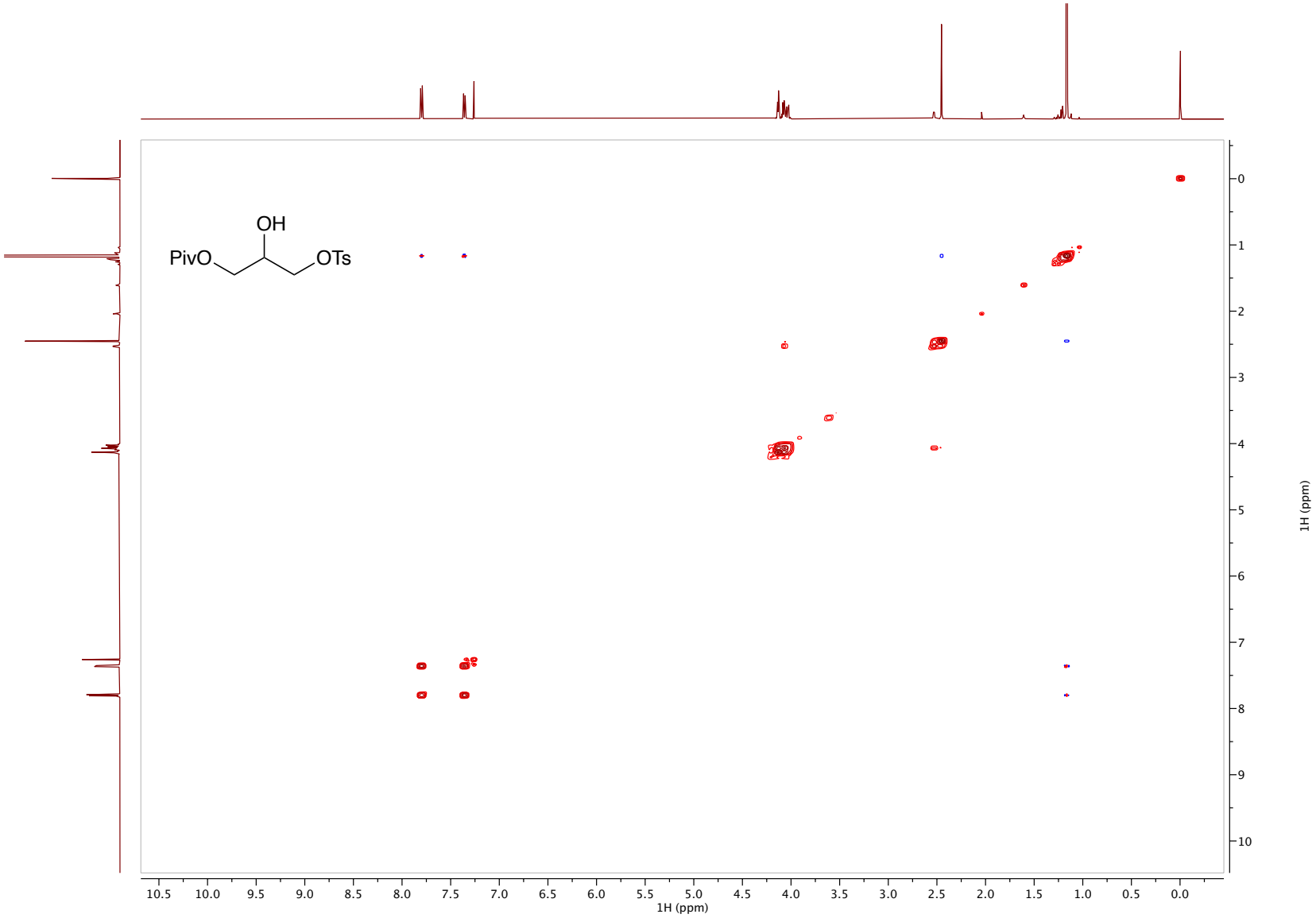


(1e) – 1-*O*-tosyl-3-*O*-pivaloylglycerol

^{13}C NMR (126 MHz, $CDCl_3$)



(1e) – 1-*O*-tosyl-3-*O*-pivaloylglycerol
COSY NMR (500 MHz, $CDCl_3$)



7.0 Calculated Structures

Cartesian coordinates for intermediates and transitions states identified. Optimized at (U)M062X/def2TZVP level, best conformer only.

7.1 Acetyl

Ac-I

O	-2.36600	-1.20861	-0.49703
C	-1.02764	-1.51208	-0.21932
C	-0.10821	-0.30100	-0.39589
C	-0.69773	0.92346	0.21677
C	-2.18248	1.07139	0.26452
C	-2.87483	-0.26948	0.43123
O	1.12947	-0.73386	0.23958
C	2.26052	-0.09414	-0.04043
C	3.45340	-0.79535	0.53711
O	-0.05477	2.10430	0.05622
O	2.31434	0.92651	-0.68455
H	-2.73248	-0.65291	1.44981
H	-2.52299	1.53836	-0.66973
H	0.84865	1.94313	-0.26663
H	-0.72108	-2.31055	-0.89311
H	-0.91882	-1.86506	0.81427
H	3.56412	-1.76764	0.05723
H	4.34176	-0.19399	0.37435
H	3.29535	-0.96781	1.60072
H	-3.94268	-0.18593	0.23762
H	-2.45806	1.75278	1.07369
H	0.12374	-0.13384	-1.45604

Ac-TS1a

O	0.84974	0.29931	1.10658

C	1.69878	-0.41963	0.50159
O	1.18592	-1.13294	-0.53432
C	-0.12305	-0.59885	-0.87348
C	-0.18525	0.79795	-0.35849
C	-1.44323	1.35360	0.21888
C	-2.29425	0.24605	0.82647
O	-2.41890	-0.83061	-0.07775
C	-1.18893	-1.49520	-0.23494
O	0.59720	1.63511	-1.09495
C	3.16638	-0.15883	0.44153
H	-1.84076	-0.10373	1.76055
H	-2.00619	1.84817	-0.58086
H	0.59669	2.51177	-0.69430
H	-1.36806	-2.36924	-0.85820
H	-0.80749	-1.82748	0.73720
H	3.48748	0.33027	1.35773
H	3.71452	-1.09200	0.31758
H	3.39893	0.48428	-0.41524
H	-3.30068	0.60479	1.03479
H	-1.20338	2.10659	0.97732
H	-0.16550	-0.61088	-1.96230

Ac-II

O	-0.79711	0.57011	-0.85166
C	0.21243	0.91605	0.09377
C	0.08012	-0.26174	1.06629
O	-1.32111	-0.52693	1.04093
C	-1.82741	0.02859	-0.11964
C	1.55960	1.03801	-0.57839
C	2.11450	-0.32130	-0.96778
O	2.13319	-1.18929	0.14889

C	0.82809	-1.49948	0.56634
O	-0.07965	2.14050	0.69274
C	-2.82547	-0.76782	-0.87369
H	1.51385	-0.76648	-1.77064
H	2.23272	1.51749	0.13314
H	-0.97651	2.10367	1.04956
H	0.90193	-2.24312	1.35821
H	0.25317	-1.93138	-0.26388
H	-3.62412	-1.08281	-0.20506
H	-3.24762	-0.16710	-1.67688
H	-2.36232	-1.66177	-1.31005
H	3.14297	-0.23183	-1.31305
H	1.45379	1.69294	-1.44427
H	0.37845	0.02137	2.07433

Ac-TS1b

O	-0.80311	0.55467	-0.89220
C	0.29870	0.97284	-0.02249
C	0.20676	0.08672	1.19010
O	-1.58850	0.04799	1.09704
C	-1.74671	-0.06820	-0.15798
C	1.57951	0.76980	-0.80619
C	1.88404	-0.71454	-0.94515
O	1.95461	-1.34304	0.31810
C	0.70562	-1.31404	0.98774
O	0.15582	2.31872	0.27516
C	-2.56358	-1.10866	-0.84334
H	1.11458	-1.20036	-1.55996
H	2.38526	1.26612	-0.26461
H	-0.63989	2.42570	0.81114

H	0.84355	-1.82392	1.93833
H	-0.03165	-1.88042	0.39666
H	-3.14121	-1.65322	-0.10059
H	-3.24978	-0.64771	-1.55559
H	-1.92895	-1.80194	-1.40426
H	2.85141	-0.86490	-1.42162
H	1.47122	1.24543	-1.78219
H	0.38884	0.56495	2.14179

Ac-III

C	1.61166	-0.79608	1.29376
C	0.66968	0.35565	1.21544
C	0.18342	0.76662	-0.13408
O	-0.37228	2.02910	-0.17852
C	1.31174	0.69060	-1.14713
C	2.08547	-0.61047	-0.99264
O	2.62253	-0.73023	0.30762
O	-0.79946	-0.22898	-0.61245
H	1.43457	-1.46745	-1.20971
H	1.97366	1.53640	-0.95894
C	-1.96698	-0.29783	0.03085
H	-1.07988	2.05925	0.48081
O	-2.26202	0.40769	0.96391
C	-2.86187	-1.35025	-0.55624
H	2.11377	-0.82362	2.25997
H	1.06003	-1.74659	1.17894
H	-3.78606	-1.39670	0.01075
H	-3.06976	-1.10511	-1.59748
H	-2.35443	-2.31415	-0.53898
H	2.92974	-0.63748	-1.67969
H	0.88998	0.78710	-2.14810

H	0.17947	0.73821	2.09820

Ac-TS2

C	-1.35424	-1.40635	-0.74118
C	-0.60395	-0.19451	-1.20794
C	-0.58220	0.95539	-0.42331
O	-0.13898	2.07278	-0.99975
C	-1.41583	1.05018	0.81385
C	-1.73370	-0.35124	1.31566
O	-2.29380	-1.11585	0.27070
O	1.47191	-0.93203	-0.84623
H	-0.81835	-0.82159	1.69167
H	-2.34497	1.56689	0.55280
C	1.85917	-0.26366	0.13212
H	0.00570	2.74917	-0.32641
O	1.17061	0.58766	0.75082
C	3.28801	-0.47065	0.61369
H	-1.91617	-1.83580	-1.57082
H	-0.63239	-2.15581	-0.39470
H	3.32416	-0.42235	1.69947
H	3.67909	-1.41611	0.24972
H	3.89413	0.34441	0.21653
H	-2.47249	-0.31911	2.11420
H	-0.88726	1.62983	1.57173
H	-0.25301	-0.13494	-2.22594

Ac-TS3

C	1.37553	-1.07261	1.16249
C	0.84289	0.32014	1.22374
C	0.82577	1.11927	0.09768

O	0.59417	2.42480	0.11992
C	1.35042	0.61761	-1.20221
C	1.49925	-0.89945	-1.16654
O	2.16895	-1.28619	0.01958
O	-1.30556	0.74452	0.06605
H	0.51721	-1.37643	-1.21479
H	2.31871	1.09720	-1.37404
C	-1.95885	-0.37074	-0.02837
H	0.08686	2.66156	0.90753
O	-1.48095	-1.49040	0.02330
C	-3.45289	-0.15226	-0.21736
H	2.01726	-1.24860	2.02881
H	0.53708	-1.77864	1.19867
H	-3.86232	0.31785	0.67655
H	-3.62780	0.52056	-1.05548
H	-3.93689	-1.10976	-0.38885
H	2.11310	-1.24225	-1.99700
H	0.67101	0.94312	-1.99097
H	0.46012	0.70174	2.16223

Ac-TS4

C	-1.32118	-1.11031	-1.11990
C	-0.60811	0.19856	-1.22502
C	-0.63471	1.06846	-0.13915
O	0.12934	2.12843	-0.10357
C	-1.58292	0.87655	0.98875
C	-2.03590	-0.58186	1.05080
O	-2.41273	-1.03968	-0.23275
O	1.74938	0.21083	-0.99610
H	-1.22313	-1.19295	1.44954
H	-2.44261	1.53380	0.82231

C	1.91007	-0.32776	0.14820
H	0.90462	1.92626	-0.67354
O	1.01107	-0.52644	0.97393
C	3.33763	-0.73854	0.47947
H	-1.72029	-1.40601	-2.08937
H	-0.59736	-1.87057	-0.79371
H	3.38897	-1.16181	1.47816
H	3.67311	-1.46677	-0.25837
H	3.98962	0.13061	0.40136
H	-2.91568	-0.67935	1.68354
H	-1.08887	1.18179	1.91070
H	-0.17409	0.50920	-2.16159

Ac-TS5

O	-2.57875	-1.06099	-0.26766
C	-1.29765	-1.39505	-0.75101
C	-0.36303	-0.21547	-0.81117
C	-0.73379	0.99049	-0.20227
C	-1.98810	1.09956	0.59845
C	-2.51446	-0.29485	0.91469
O	1.12829	-0.85666	0.31278
C	2.19668	-0.19178	0.11381
C	3.47489	-0.83215	0.59955
O	0.04811	2.03034	-0.24632
O	2.25713	0.90812	-0.46853
H	-1.86268	-0.78763	1.64720
H	-2.73247	1.65843	0.02341
H	1.00627	1.68657	-0.46911
H	-1.44285	-1.80359	-1.75075
H	-0.83889	-2.17001	-0.12578
H	3.90846	-1.38659	-0.23439

H	4.17973	-0.06196	0.90208
H	3.27644	-1.52604	1.41176
H	-3.52352	-0.25089	1.32025
H	-1.77934	1.66907	1.50593
H	0.32344	-0.15834	-1.64500

Ac-TS6

C	-2.31216	-0.43532	-1.06086
C	-1.31589	0.66397	-1.15620
C	-0.40865	0.90229	-0.07269
O	0.37798	1.92686	-0.15390
C	-0.79787	0.35352	1.27275
C	-1.62400	-0.91609	1.12654
O	-2.72044	-0.69277	0.26007
O	2.32196	0.72570	0.59647
H	-0.99867	-1.72808	0.74173
H	-1.40594	1.13103	1.74673
C	2.03270	-0.30893	-0.05677
H	1.28325	1.61005	0.33680
O	0.87174	-0.57809	-0.48654
C	3.13417	-1.28822	-0.37079
H	-3.20925	-0.19576	-1.63330
H	-1.86768	-1.34210	-1.50695
H	3.84668	-1.31332	0.45061
H	2.72924	-2.27633	-0.57151
H	3.65537	-0.93299	-1.26122
H	-2.04505	-1.21505	2.08452
H	0.09233	0.20320	1.88253
H	-1.14009	1.17826	-2.09054

Ac-IV

C	-2.70094	-0.24099	-1.01562
C	-1.75119	0.89772	-0.92097
C	-0.83866	1.04006	0.17258
O	-0.00734	1.95037	0.18807
C	-0.93829	0.02201	1.28194
C	-1.59250	-1.25576	0.77729
O	-2.84409	-0.95305	0.18442
O	2.50426	0.90448	0.39859
H	-0.93593	-1.74801	0.05106
H	-1.55080	0.45671	2.07743
C	2.40727	-0.28047	-0.19630
H	1.62006	1.34032	0.42369
O	1.36316	-0.75661	-0.57253
C	3.74352	-0.95052	-0.33897
H	-3.69520	0.11095	-1.30335
H	-2.35499	-0.91059	-1.82247
H	4.22055	-1.02530	0.63764
H	3.61641	-1.93465	-0.77804
H	4.38556	-0.33600	-0.96990
H	-1.79624	-1.94564	1.59385
H	0.05832	-0.16226	1.68165
H	-1.67091	1.60070	-1.73972

V

C	-1.16357	-1.18390	0.03550
C	0.32207	-1.23784	0.06893
C	1.13944	-0.06134	-0.02161
O	2.36224	-0.12685	0.00045
C	0.41000	1.26207	-0.14443
C	-1.03345	1.13435	0.31925

O	-1.67015	0.06671	-0.35569
H	-1.07579	0.96484	1.40395
H	0.43139	1.56121	-1.19538
H	-1.55855	-1.92242	-0.66716
H	-1.55264	-1.45764	1.03195
H	-1.60650	2.03173	0.09337
H	0.95819	2.01255	0.42567
H	0.82020	-2.18916	0.20362

Ac-VI

C	0.00000	0.15473	0.00000
O	0.18833	1.33761	0.00000
O	-1.23826	-0.37849	0.00000
H	-1.86478	0.35940	0.00000
C	1.05840	-0.90692	0.00000
H	0.93783	-1.53912	0.87918
H	0.93783	-1.53912	-0.87918
H	2.03812	-0.44103	0.00000

VII

C	-1.21093	-1.17363	0.02761
C	0.26069	-1.24480	0.08727
C	1.02771	-0.06751	-0.01590
O	2.31202	-0.21492	-0.00672
C	0.37255	1.25854	-0.12354
C	-1.09172	1.14586	0.31492
O	-1.69727	0.07086	-0.36650
H	-1.15809	1.00392	1.39971
H	0.41745	1.56216	-1.17749
H	2.80281	0.62286	-0.07285

H	-1.58864	-1.92835	-0.67121
H	-1.59393	-1.47242	1.02314
H	-1.63823	2.04540	0.04632
H	0.92499	2.00032	0.45947
H	0.76588	-2.19208	0.23647

Ac-VIII

C	0.00000	0.21141	0.00000
O	1.10288	0.79312	0.00000
O	-1.14823	0.70058	0.00000
C	0.04425	-1.34416	0.00000
H	-0.48581	-1.71839	0.87899
H	-0.48581	-1.71839	-0.87899
H	1.06891	-1.71635	0.00000

7.2 Pivaloyl

Piv-I

O	-3.11856	-1.36595	-0.48174
C	-1.73599	-1.49939	-0.30410
C	-0.99591	-0.17271	-0.48903
C	-1.69165	0.93953	0.21865
C	-3.17669	0.89196	0.36326
C	-3.67911	-0.53280	0.51543
O	0.32996	-0.45826	0.03838
C	1.34915	0.32669	-0.29988
C	2.68625	-0.23094	0.16144
O	-1.21281	2.19824	0.07725
O	1.21284	1.36453	-0.90573
H	-3.42032	-0.92851	1.50605

H	-3.63567	1.34221	-0.52760
H	-0.32492	2.16597	-0.31958
H	-1.37650	-2.22787	-1.02931
H	-1.51125	-1.86903	0.70487
C	2.91181	-1.58514	-0.52217
C	3.79096	0.74700	-0.22318
C	2.64309	-0.41590	1.68311
H	-4.75951	-0.58274	0.39277
H	-3.48274	1.50337	1.21618
H	-0.86887	0.06131	-1.55437
H	3.82321	0.89824	-1.30177
H	4.75351	0.35148	0.10418
H	3.63533	1.71840	0.24557
H	2.91789	-1.48024	-1.60866
H	2.13829	-2.29998	-0.24400
H	3.87985	-1.98418	-0.21527
H	1.87018	-1.12652	1.97215
H	2.44978	0.53201	2.18818
H	3.60885	-0.79221	2.02408

Piv-TS1a

O	0.09181	0.33611	0.97463
C	0.91450	-0.35188	0.30119
O	0.35137	-1.03899	-0.72635
C	-1.00707	-0.56439	-0.93391
C	-1.09830	0.81346	-0.37520
C	-2.31928	1.27567	0.34787
C	-3.04467	0.10342	0.99477
O	-3.20141	-0.94894	0.06706
C	-1.95988	-1.53822	-0.23153

O	-0.46132	1.71669	-1.17043
C	2.40089	-0.09465	0.19329
H	-2.48220	-0.25007	1.86604
H	-2.98658	1.76313	-0.37186
H	-0.48800	2.58716	-0.75723
H	-2.15237	-2.40000	-0.86774
H	-1.46949	-1.88095	0.68680
C	2.90838	0.42478	1.53587
C	3.10915	-1.40221	-0.16868
C	2.66139	0.94934	-0.90380
H	-4.04285	0.39760	1.31427
H	-2.04393	2.01563	1.10727
H	-1.14509	-0.55141	-2.01471
H	2.23233	0.62887	-1.85363
H	3.73753	1.08734	-1.03433
H	2.21988	1.90914	-0.63504
H	3.97708	0.63671	1.46915
H	2.74971	-0.31385	2.32330
H	2.38801	1.33907	1.82065
H	2.76249	-1.78115	-1.12980
H	2.92364	-2.16631	0.58834
H	4.18558	-1.23186	-0.22991

Piv-II

C	-1.83736	-1.56251	-0.31182
C	-1.01357	-0.48322	-1.02246
C	-1.00219	0.83354	-0.24998
O	-0.62079	1.83955	-1.14468
C	-2.29096	1.17077	0.47526
C	-2.90653	-0.06563	1.10906

O	-3.07853	-1.07468	0.13500
O	0.36008	-0.84425	-1.00039
H	-2.27086	-0.43698	1.92236
H	-2.98534	1.58059	-0.25935
C	0.86652	-0.39382	0.19378
H	-0.46704	2.64867	-0.64333
O	0.03670	0.59880	0.69107
C	2.34859	-0.14315	0.23367
H	-2.03556	-2.39003	-0.99059
H	-1.24624	-1.93785	0.53372
C	2.75419	0.16280	1.67524
C	3.06695	-1.39929	-0.25875
C	2.69090	1.04784	-0.67273
H	-3.89370	0.15594	1.51123
H	-2.08491	1.93767	1.22626
H	-1.32078	-0.33236	-2.05475
H	2.80831	-2.25924	0.36162
H	4.14687	-1.24924	-0.20914
H	2.79609	-1.62596	-1.28990
H	2.20858	1.95702	-0.31154
H	2.35524	0.86497	-1.69401
H	3.77061	1.21109	-0.68143
H	2.52336	-0.68057	2.32831
H	2.22885	1.04148	2.05060
H	3.82753	0.35534	1.72427

Piv-TS1b

O	-0.02657	0.78748	-0.71757
C	1.29571	0.95830	-0.11122
C	1.22590	0.25369	1.21546

O	-0.50772	0.68734	1.41455
C	-0.92732	0.50619	0.23941
C	2.29395	0.33173	-1.06350
C	2.16557	-1.18460	-1.03616
O	2.33565	-1.68992	0.27115
C	1.31350	-1.23866	1.14675
O	1.56299	2.31341	0.00264
C	-2.19577	-0.19954	-0.17147
H	1.18442	-1.48515	-1.42752
H	3.29320	0.62768	-0.74326
H	0.96541	2.68500	0.66322
H	1.52515	-1.66633	2.12407
H	0.34653	-1.64070	0.79753
C	-2.86306	-0.78399	1.07011
C	-3.12004	0.84515	-0.82034
C	-1.90421	-1.30480	-1.19440
H	2.93692	-1.64591	-1.65087
H	2.11802	0.72547	-2.06602
H	1.68826	0.76109	2.04940
H	-3.80123	-1.26292	0.78599
H	-3.07505	-0.00677	1.80400
H	-2.22312	-1.52902	1.54510
H	-1.38133	-0.90497	-2.06290
H	-2.84477	-1.74581	-1.53015
H	-1.29616	-2.09907	-0.75831
H	-2.64503	1.29217	-1.69454
H	-3.36173	1.63949	-0.11281
H	-4.04959	0.36833	-1.13691

Piv-III

C	2.19755	-0.79468	1.38868
C	1.63484	0.56410	1.15049
C	1.16452	0.88075	-0.23001
O	0.97296	2.22532	-0.47418
C	2.13907	0.32759	-1.25508
C	2.52349	-1.10417	-0.91046
O	3.10407	-1.18134	0.37396
O	-0.08594	0.13996	-0.48588
H	1.64118	-1.75599	-0.96168
H	3.02562	0.96211	-1.23665
C	-1.16498	0.48322	0.22224
H	0.35244	2.55446	0.19134
O	-1.17459	1.39493	1.01395
C	-2.35795	-0.41166	-0.07986
H	2.74227	-0.83372	2.33087
H	1.38230	-1.53900	1.44280
C	-3.55754	0.07049	0.72757
C	-2.66421	-0.34984	-1.58064
C	-1.98951	-1.84624	0.31897
H	3.26881	-1.47945	-1.60992
H	1.68011	0.38950	-2.24252
H	1.37584	1.21860	1.96905
H	-3.53089	-0.97702	-1.79605
H	-1.82075	-0.70669	-2.16999
H	-2.89706	0.67024	-1.89080
H	-4.41554	-0.57081	0.52028
H	-3.81759	1.09636	0.46747
H	-3.34833	0.04095	1.79652
H	-2.84232	-2.50224	0.13672
H	-1.73770	-1.90519	1.37989
H	-1.14203	-2.21039	-0.26155

Piv-TS2

C	-2.12622	-1.40236	-0.84721
C	-1.60039	-0.05277	-1.23655
C	-1.60414	0.98835	-0.31378
O	-1.38104	2.21606	-0.78391
C	-2.25816	0.82174	1.02034
C	-2.32804	-0.65912	1.36519
O	-2.93674	-1.36631	0.30713
O	0.57774	-0.54235	-1.23526
H	-1.31744	-1.03914	1.55403
H	-3.27100	1.23130	0.95104
C	1.01465	0.02832	-0.21795
H	-1.21803	2.81989	-0.04870
O	0.32594	0.72028	0.57453
C	2.51046	-0.14489	0.13956
H	-2.74723	-1.80300	-1.64874
H	-1.27827	-2.08293	-0.70170
C	2.56375	-0.98294	1.42074
C	3.25714	-0.85354	-0.98401
C	3.11705	1.23501	0.39528
H	-2.94188	-0.82363	2.24876
H	-1.70168	1.37656	1.77683
H	-1.40564	0.17258	-2.27307
H	2.03564	-0.48104	2.23138
H	3.60348	-1.13342	1.71927
H	2.11151	-1.96461	1.26340
H	3.06408	1.85698	-0.50048
H	4.16817	1.12844	0.67206
H	2.59029	1.74473	1.20067
H	3.20097	-0.28359	-1.91154

H	2.83535	-1.83969	-1.17413
H	4.30793	-0.96783	-0.70869

Piv-TS3

C	-1.84048	-1.39799	-0.90528
C	-1.60449	0.05287	-1.17351
C	-2.00720	0.99313	-0.27288
O	-1.93073	2.28118	-0.59680
C	-2.51203	0.61749	1.07765
C	-2.31085	-0.87736	1.32080
O	-2.70831	-1.61119	0.18591
O	0.23879	0.44339	0.22250
H	-1.25759	-1.06812	1.54873
H	-3.57164	0.88333	1.14594
C	1.19565	-0.03667	-0.49910
H	-2.07606	2.83478	0.17928
O	1.09250	-0.50160	-1.62097
C	2.56149	-0.00795	0.23909
H	-2.31203	-1.85896	-1.77470
H	-0.87420	-1.89214	-0.74773
C	2.84981	1.41246	0.72662
C	2.46373	-0.96168	1.43315
C	3.65439	-0.47207	-0.71608
H	-2.92674	-1.21774	2.15098
H	-1.96375	1.19856	1.82629
H	-1.17126	0.35607	-2.11491
H	2.21945	-1.97408	1.10401
H	1.69767	-0.62984	2.13423
H	3.42193	-0.99846	1.95613
H	2.88556	2.11245	-0.11034

H	3.81800	1.43847	1.23161
H	2.08292	1.74895	1.42321
H	3.71640	0.18228	-1.58537
H	3.45616	-1.48080	-1.07563
H	4.61697	-0.46227	-0.19952

Piv-TS4

C	2.13840	-1.03722	1.22558
C	1.60706	0.35899	1.19403
C	1.65664	1.07105	0.00029
O	1.03342	2.21311	-0.13264
C	2.48199	0.61090	-1.14665
C	2.73872	-0.89167	-1.03813
O	3.15422	-1.23185	0.26974
O	-0.74031	0.66536	1.11482
H	1.82575	-1.43101	-1.30028
H	3.42887	1.16003	-1.12280
C	-1.05942	0.02081	0.06373
H	0.28683	2.19352	0.50649
O	-0.25651	-0.39860	-0.77872
C	-2.57264	-0.23780	-0.12360
H	2.57459	-1.25724	2.19925
H	1.29995	-1.72783	1.05535
C	-2.83618	-0.91222	-1.46401
C	-3.02599	-1.14458	1.02425
C	-3.31080	1.09995	-0.04748
H	3.54598	-1.18790	-1.70480
H	1.96115	0.86222	-2.07010
H	1.28930	0.84130	2.10416
H	-2.30930	-1.86334	-1.53314
H	-2.49828	-0.28593	-2.28976

H	-3.90711	-1.09430	-1.57927
H	-3.13652	1.58173	0.91380
H	-4.38378	0.93753	-0.17096
H	-2.97905	1.77477	-0.83985
H	-2.83508	-0.67099	1.98673
H	-2.50039	-2.10155	0.99593
H	-4.09618	-1.34439	0.93544

Piv-TS5

O	-3.35749	-1.25441	-0.24014
C	-2.08963	-1.38453	-0.84195
C	-1.31939	-0.09091	-0.88170
C	-1.78311	1.01073	-0.15153
C	-2.96945	0.90026	0.74696
C	-3.29061	-0.56903	0.99054
O	0.33483	-0.60630	0.06507
C	1.29149	0.20060	-0.16246
C	2.70695	-0.26908	0.19260
O	-1.14266	2.14388	-0.17093
O	1.15734	1.33463	-0.66687
H	-2.52422	-1.02205	1.63220
H	-3.82295	1.39596	0.27483
H	-0.17319	1.94417	-0.49726
H	-2.26553	-1.74252	-1.85600
H	-1.48650	-2.13197	-0.31301
C	3.51062	-0.30205	-1.11240
C	3.31672	0.76173	1.14677
C	2.69546	-1.64930	0.83986
H	-4.26001	-0.68425	1.47178
H	-2.75760	1.42832	1.67849
H	-0.71957	0.11297	-1.75833

H	3.31982	1.75124	0.69199
H	4.34389	0.47750	1.38315
H	2.75462	0.81085	2.08147
H	3.51927	0.68028	-1.58299
H	3.08714	-1.02242	-1.81537
H	4.53873	-0.60105	-0.89921
H	2.26518	-2.39519	0.17188
H	2.11206	-1.64810	1.76063
H	3.71847	-1.94663	1.07854

Piv-TS6

C	-2.95868	-0.85868	-1.03697
C	-2.22496	0.41993	-1.22972
C	-1.44807	0.96713	-0.15720
O	-0.89910	2.12566	-0.33398
C	-1.77439	0.48844	1.23104
C	-2.29066	-0.94286	1.20748
O	-3.36462	-1.06378	0.29380
O	1.21197	1.46595	0.61237
H	-1.48256	-1.62862	0.93246
H	-2.56279	1.15372	1.59817
C	1.19386	0.32713	0.07516
H	0.02578	2.06932	0.21574
O	0.14393	-0.22642	-0.36494
C	2.52163	-0.41711	-0.06960
H	-3.85741	-0.88616	-1.65457
H	-2.30471	-1.68418	-1.36838
C	3.24545	-0.38552	1.27850
C	2.30087	-1.85576	-0.52330
C	3.34420	0.34717	-1.11475

H	-2.68255	-1.22794	2.18192
H	-0.90508	0.60726	1.87699
H	-2.11986	0.86021	-2.21134
H	1.79391	-1.89163	-1.48688
H	1.69340	-2.40673	0.19596
H	3.26450	-2.36011	-0.61707
H	2.83773	0.35380	-2.08187
H	4.31438	-0.13716	-1.24136
H	3.50470	1.37741	-0.79815
H	4.21971	-0.86822	1.18088
H	2.67703	-0.92129	2.04161
H	3.39093	0.63991	1.61409

Piv-IV

C	-3.58941	-0.52509	-1.03143
C	-2.80624	0.73682	-0.98960
C	-1.94779	1.06530	0.10758
O	-1.24909	2.08075	0.08154
C	-1.93411	0.10806	1.27388
C	-2.39449	-1.27433	0.83512
O	-3.66151	-1.18195	0.20582
O	1.36492	1.40084	0.45611
H	-1.65951	-1.71090	0.14939
H	-2.62009	0.49816	2.03166
C	1.46356	0.18292	-0.07088
H	0.43049	1.71254	0.41043
O	0.50889	-0.44291	-0.46837
C	2.89839	-0.32190	-0.10959
H	-4.61557	-0.32968	-1.35405
H	-3.13749	-1.18501	-1.79257
C	3.46156	-0.31555	1.31632

C	2.92085	-1.73370	-0.68254
C	3.71936	0.62465	-0.99402
H	-2.52079	-1.93888	1.68754
H	-0.93175	0.08619	1.70036
H	-2.80368	1.39669	-1.84726
H	4.48703	-0.68888	1.30076
H	2.87564	-0.96289	1.97183
H	3.46221	0.69071	1.73283
H	3.32371	0.65062	-2.01098
H	4.75115	0.27163	-1.03955
H	3.71370	1.63741	-0.59326
H	2.50715	-1.75332	-1.69045
H	2.33257	-2.41524	-0.06802
H	3.94955	-2.09607	-0.71852

Piv-VI

C	-0.93522	0.19021	0.00006
O	-1.50405	1.24603	0.00010
O	-1.60938	-0.97877	0.00003
H	-2.55201	-0.75994	-0.00005
C	0.56985	-0.01215	0.00003
C	0.95759	-0.80569	1.25392
C	0.95782	-0.80196	-1.25616
C	1.25046	1.35151	0.00206
H	0.96764	1.93110	-0.87633
H	2.33324	1.21718	-0.00004
H	0.97064	1.92694	0.88417
H	0.66948	-0.26417	-2.16106
H	0.48313	-1.78227	-1.26793
H	2.04032	-0.93901	-1.27336

H	0.48618	-1.78764	1.26059
H	0.66532	-0.27268	2.16038
H	2.04052	-0.93910	1.27309

Piv-VIII

C	-1.05639	0.02971	0.00053
O	-1.60007	1.15030	0.00054
O	-1.58786	-1.09952	0.00029
C	0.52053	0.01077	0.00018
C	0.98814	-0.74712	1.24249
C	0.98650	-0.74026	-1.24704
C	1.09631	1.42079	0.00342
H	0.67409	-0.21246	-2.15235
H	0.53843	-1.73409	-1.26264
H	2.07936	-0.83446	-1.26622
H	0.53997	-1.74096	1.25319
H	0.67709	-0.22442	2.15122
H	2.08102	-0.84148	1.25961
H	0.75233	1.97569	-0.87020
H	2.19329	1.39270	0.00045
H	0.75731	1.96990	0.88270

7.3 Benzoyl

Bz-I

O	-2.3791890	-1.1910630	-0.4815990
C	-1.0519830	-1.5169220	-0.1779890
C	-0.1040060	-0.3308520	-0.3712240

C	-0.6727270	0.9195390	0.2078530
C	-2.1542530	1.1023830	0.2277290
C	-2.8796780	-0.2179820	0.4159780
O	1.1163160	-0.7756560	0.2874260
C	2.2633080	-0.1756580	-0.0078310
O	0.0011250	2.0806930	0.0343540
O	2.3392770	0.8307170	-0.6776570
H	-2.7608930	-0.5795210	1.4455240
H	-2.4697210	1.5537690	-0.7228850
H	0.9056530	1.8905470	-0.2699230
H	-0.7539870	-2.3381590	-0.8278780
H	-0.9657920	-1.8461900	0.8658140
H	-3.9423910	-0.1153140	0.2041680
H	-2.4263700	1.8093300	1.0158390
H	0.1434350	-0.1935120	-1.4320200
C	3.4491070	-0.8622030	0.5694040
C	4.7012540	-0.2988520	0.3427270
C	3.3295880	-2.0313690	1.3148390
C	5.8334980	-0.9056850	0.8598380
H	4.7660850	0.6107920	-0.2390710
C	4.4655460	-2.6342390	1.8316290
H	2.3518680	-2.4590870	1.4862430
C	5.7152680	-2.0728710	1.6040960
H	6.8080660	-0.4699990	0.6844120
H	4.3768210	-3.5428380	2.4121650
H	6.6004580	-2.5465740	2.0087070

Bz-TS1a

O	0.9262620	0.3422170	1.0145690
C	1.7553380	-0.2302530	0.2602360
O	1.2143090	-0.8970760	-0.7884140

C	-0.1506080	-0.4562210	-0.9801840
C	-0.2812780	0.9045690	-0.3882580
C	-1.5051960	1.3338530	0.3405070
C	-2.2184250	0.1303630	0.9446770
O	-2.3453500	-0.8970480	-0.0152410
C	-1.0927670	-1.4637460	-0.3124430
O	0.4202240	1.8221170	-1.0865150
H	-1.6597310	-0.2376230	1.8119190
H	-2.1745390	1.8379430	-0.3667230
H	0.4062830	2.6711440	-0.6290910
H	-1.2667880	-2.3108080	-0.9730630
H	-0.6076810	-1.8222070	0.6021100
H	-3.2253320	0.3983900	1.2591100
H	-1.2407950	2.0534450	1.1228420
H	-0.2876820	-0.4147100	-2.0613180
C	3.1879570	-0.0839980	0.2986110
C	3.7775800	0.6539450	1.3367460
C	4.0104320	-0.7009090	-0.6559550
C	5.1508370	0.7876740	1.3997310
H	3.1378070	1.1116580	2.0795570
C	5.3843610	-0.5637660	-0.5770610
H	3.5577970	-1.2756770	-1.4520320
C	5.9633820	0.1799700	0.4458590
H	5.5967400	1.3647750	2.1997730
H	6.0120330	-1.0388090	-1.3202220
H	7.0389740	0.2816460	0.5030790

Bz-II

O	-0.47599	-0.91895	-0.05488
C	0.39774	0.06365	0.29615
O	-0.23594	1.09479	0.90283

C	-1.63573	0.87522	0.73861
C	-1.70631	-0.64579	0.61721
C	-2.86266	-1.18100	-0.20289
C	-3.12595	-0.31527	-1.42444
O	-3.29918	1.03176	-1.03463
C	-2.10025	1.57455	-0.54242
O	-1.67098	-1.17228	1.90648
H	-2.29701	-0.39305	-2.13839
H	-3.74490	-1.17549	0.43829
H	-1.56039	-2.12852	1.84803
H	-2.27034	2.63257	-0.35263
H	-1.30075	1.47924	-1.28961
H	-4.04446	-0.62014	-1.92266
H	-2.64657	-2.21341	-0.48869
H	-2.15213	1.22671	1.62830
C	1.76336	0.01590	0.05315
C	2.35653	-1.12565	-0.54747
C	2.59909	1.11011	0.40028
C	3.71272	-1.15566	-0.78290
H	1.73116	-1.96607	-0.81616
C	3.95200	1.05023	0.15333
H	2.15898	1.98396	0.86087
C	4.52690	-0.07566	-0.43873
H	4.15084	-2.03309	-1.24198
H	4.57685	1.89188	0.42472
H	5.59086	-0.11102	-0.62770

Bz-TS1b

O	-0.57358	-0.32390	-1.04832
C	-1.94848	-0.53683	-0.58757

C	-1.85500	-0.74453	0.89713
O	-0.22149	-1.62121	0.68977
C	0.29070	-0.84291	-0.15990
C	-2.71898	0.71855	-0.94769
C	-2.27094	1.87694	-0.06710
O	-2.42427	1.56504	1.30207
C	-1.58260	0.49262	1.69525
O	-2.48900	-1.61837	-1.25981
H	-1.22258	2.12671	-0.27705
H	-3.77917	0.51793	-0.79124
H	-2.01733	-2.41371	-0.98205
H	-1.75646	0.32572	2.75547
H	-0.53000	0.79178	1.55761
H	-2.88096	2.75900	-0.25464
H	-2.55689	0.93631	-2.00453
H	-2.46740	-1.52717	1.31976
C	1.63928	-0.32572	-0.12548
C	2.09055	0.57398	-1.10034
C	2.51974	-0.76077	0.87457
C	3.39315	1.03826	-1.05917
H	1.41191	0.89817	-1.87749
C	3.81571	-0.28291	0.90845
H	2.16553	-1.46803	1.61272
C	4.25959	0.61640	-0.05699
H	3.73699	1.73497	-1.81265
H	4.48920	-0.61485	1.68790
H	5.27744	0.98225	-0.03033

Bz-III

O	-0.42636	-0.07985	-0.50308
C	-1.80175	-0.62357	-0.51627

C	-2.26696	-0.78696	0.89204
O	0.35104	-1.99712	0.35811
C	0.53789	-0.86555	-0.02583
C	-2.61482	0.44916	-1.21877
C	-2.76260	1.67714	-0.33199
O	-3.38567	1.34886	0.89106
C	-2.61003	0.44592	1.65503
O	-1.83956	-1.77893	-1.26818
H	-1.77995	2.12910	-0.14164
H	-3.59776	0.02602	-1.42774
H	-1.31613	-2.44654	-0.80231
H	-3.19032	0.20538	2.54474
H	-1.68793	0.95621	1.98642
H	-3.39571	2.42168	-0.81202
H	-2.12776	0.69481	-2.16314
H	-2.14194	-1.73743	1.38863
C	1.87364	-0.20705	-0.01339
C	2.05097	1.10253	-0.44945
C	2.95794	-0.94229	0.45543
C	3.31381	1.67332	-0.41443
H	1.20207	1.66364	-0.81455
C	4.21787	-0.36832	0.48880
H	2.79258	-1.95827	0.78826
C	4.39562	0.93931	0.05397
H	3.45505	2.69108	-0.75329
H	5.06218	-0.93859	0.85281
H	5.38060	1.38747	0.07973

Bz-TS2

C	-2.68023	1.61119	-0.34015
C	-2.20774	0.82861	0.84759

C	-2.19402	-0.56445	0.80131
O	-2.00334	-1.20318	1.95141
C	-2.78526	-1.29500	-0.36024
C	-2.81274	-0.37583	-1.57368
O	-3.44770	0.83826	-1.23628
O	-0.00750	1.22630	0.65151
H	-1.78886	-0.19508	-1.91834
H	-3.80765	-1.57891	-0.09037
C	0.46129	0.13976	0.25654
H	-1.84039	-2.13985	1.78312
O	-0.21157	-0.89512	0.01415
H	-3.31860	2.43195	-0.01259
H	-1.80650	2.03967	-0.84616
H	-3.38997	-0.81935	-2.38261
H	-2.20665	-2.19738	-0.56127
H	-2.05608	1.31833	1.79622
C	1.95587	0.05775	0.04295
C	2.75367	1.16593	0.30492
C	2.53338	-1.12086	-0.41535
C	4.12471	1.09422	0.11016
H	2.28307	2.07231	0.66086
C	3.90463	-1.19095	-0.61078
H	1.89511	-1.97103	-0.61383
C	4.70090	-0.08371	-0.34798
H	4.74553	1.95681	0.31525
H	4.35380	-2.10867	-0.96803
H	5.77134	-0.13883	-0.50028

Bz-TS3

C	-2.52060	1.48521	-0.59682
C	-2.24425	0.81626	0.70897

C	-2.52343	-0.51102	0.87629
O	-2.42218	-1.04550	2.08676
C	-2.91747	-1.37632	-0.26980
C	-2.76015	-0.61596	-1.58594
O	-3.29345	0.68231	-1.46075
O	-0.27292	-0.33375	0.19192
H	-1.70042	-0.56983	-1.85268
H	-3.95434	-1.69732	-0.12817
C	0.59728	0.60786	0.34377
H	-2.47295	-2.00769	2.04022
O	0.36372	1.76686	0.64897
H	-3.09067	2.39973	-0.42477
H	-1.56618	1.76691	-1.05704
H	-3.31224	-1.11075	-2.38249
H	-2.27941	-2.26584	-0.26711
H	-1.88229	1.40085	1.54151
C	2.02400	0.16402	0.08815
C	2.33621	-1.15029	-0.24095
C	3.03610	1.11173	0.19046
C	3.65562	-1.51457	-0.46697
H	1.54004	-1.87816	-0.31610
C	4.35432	0.74653	-0.03562
H	2.76606	2.12674	0.44922
C	4.66532	-0.56677	-0.36470
H	3.89760	-2.53820	-0.72264
H	5.14097	1.48568	0.04495
H	5.69478	-0.85160	-0.54113

Bz-TS4

C	-2.60585	-0.06109	1.64447
C	-2.20508	-1.05576	0.60363

C	-2.28948	-0.69471	-0.73924
O	-1.75871	-1.43920	-1.67171
C	-3.03845	0.51153	-1.17571
C	-3.16323	1.49943	-0.01564
O	-3.57959	0.83362	1.15991
O	0.08795	-1.36967	0.26786
H	-2.19982	1.98826	0.14445
H	-4.03120	0.19030	-1.50752
C	0.50578	-0.19851	-0.01456
H	-1.03332	-1.94559	-1.24500
O	-0.21721	0.76018	-0.31329
H	-3.03997	-0.56515	2.50690
H	-1.70377	0.47568	1.97060
H	-3.92437	2.24559	-0.23393
H	-2.51714	0.95281	-2.02464
H	-1.97123	-2.07094	0.88073
C	2.00387	0.00026	0.02105
C	2.53834	1.23436	-0.33241
C	2.84765	-1.03614	0.40461
C	3.91055	1.43076	-0.30323
H	1.86171	2.02551	-0.62613
C	4.22032	-0.83839	0.43520
H	2.41264	-1.98801	0.67724
C	4.75243	0.39450	0.08085
H	4.32560	2.39168	-0.57898
H	4.87641	-1.64524	0.73552
H	5.82387	0.54822	0.10441

Bz-TS5

O	3.76902	-1.40365	0.38603
C	2.52958	-1.29133	1.04680

C	1.88192	0.05697	0.86223
C	2.41016	0.94843	-0.08257
C	3.52404	0.54850	-0.99054
C	3.69602	-0.96480	-0.95235
O	0.15397	-0.45490	0.10599
C	-0.71443	0.47198	0.22693
O	1.88540	2.12906	-0.25374
O	-0.45329	1.66137	0.49101
H	2.85683	-1.45366	-1.46324
H	4.44606	1.03824	-0.66308
H	0.92868	2.10075	0.14236
H	2.72710	-1.46484	2.10417
H	1.83368	-2.06210	0.69572
H	4.62244	-1.26682	-1.43718
H	3.30376	0.90547	-1.99838
H	1.36575	0.48646	1.71038
C	-2.14665	0.06871	0.04149
C	-3.13947	1.04009	0.11498
C	-2.48563	-1.25784	-0.20349
C	-4.46826	0.68423	-0.05469
H	-2.85149	2.06497	0.30568
C	-3.81535	-1.61119	-0.37323
H	-1.70070	-1.99961	-0.25925
C	-4.80638	-0.64080	-0.29875
H	-5.24144	1.43918	0.00288
H	-4.08030	-2.64298	-0.56371
H	-5.84445	-0.91783	-0.43147

Bz-TS6

C	2.79976	-0.67625	1.55571
C	2.26991	0.61613	1.04319

C	2.11515	0.81566	-0.36268
O	1.75143	1.96471	-0.84670
C	2.84165	-0.10878	-1.28445
C	3.03979	-1.46970	-0.63175
O	3.64566	-1.32396	0.63783
O	-0.41363	1.86525	0.28805
H	2.07486	-1.97798	-0.53338
H	3.81107	0.34985	-1.50038
C	-0.59649	0.66624	-0.02269
H	0.89375	2.21889	-0.31160
O	0.33148	-0.13997	-0.35146
H	3.37731	-0.51801	2.46748
H	1.94541	-1.32524	1.81269
H	3.70825	-2.08919	-1.22619
H	2.27964	-0.17788	-2.21471
H	1.84507	1.34249	1.72269
C	-1.99424	0.12390	-0.01139
C	-3.05172	0.97209	0.29931
C	-2.23661	-1.21324	-0.30707
C	-4.34863	0.48279	0.31435
H	-2.83794	2.00811	0.52484
C	-3.53435	-1.70069	-0.29150
H	-1.40146	-1.85683	-0.54814
C	-4.59008	-0.85300	0.01913
H	-5.17248	1.14193	0.55506
H	-3.72456	-2.74090	-0.52167
H	-5.60323	-1.23431	0.03059

Bz-IV

C	-3.71141	-1.63282	-0.10773
C	-2.57617	-0.67669	-0.06330

C	-2.78358	0.73634	-0.03407
O	-1.84173	1.53507	-0.02008
C	-4.21144	1.23041	-0.01757
C	-5.16099	0.12440	0.41970
O	-4.95463	-1.03094	-0.36714
O	0.84951	1.28051	-0.04739
H	-5.00878	-0.11518	1.48090
H	-4.46544	1.55344	-1.03057
C	1.31995	0.04613	0.01880
H	-0.14009	1.27290	-0.03750
O	0.61646	-0.93716	0.07932
H	-3.54603	-2.37887	-0.88930
H	-3.74351	-2.18297	0.84878
H	-6.20043	0.41616	0.28261
H	-4.26878	2.10374	0.63272
H	-1.55643	-1.04297	-0.01740
C	2.80983	-0.02303	0.01170
C	3.41254	-1.27490	0.07635
C	3.59047	1.12634	-0.05769
C	4.79385	-1.37815	0.07156
H	2.78135	-2.15196	0.12939
C	4.97314	1.01964	-0.06226
H	3.10864	2.09282	-0.10749
C	5.57416	-0.23044	0.00223
H	5.26417	-2.35139	0.12160
H	5.58277	1.91202	-0.11614
H	6.65372	-0.31106	-0.00159

Bz-VI

C	1.69762	0.12277	-0.00001
O	2.31972	1.14981	-0.00005

O	2.30151	-1.08061	0.00005
H	3.25434	-0.91308	0.00004
C	0.21423	0.03017	0.00000
C	-0.51124	1.21739	0.00002
C	-0.44392	-1.19568	-0.00002
C	-1.89538	1.17855	0.00002
H	0.02743	2.15567	0.00003
C	-1.83004	-1.22970	-0.00002
H	0.13055	-2.11141	-0.00004
C	-2.55421	-0.04503	0.00000
H	-2.46235	2.09999	0.00004
H	-2.34588	-2.18074	-0.00004
H	-3.63628	-0.07483	0.00000

Bz-VIII

C	-0.00005	1.82632	0.00000
O	1.12699	2.35385	0.00000
O	-1.12714	2.35374	0.00000
C	0.00000	0.27564	0.00000
C	-1.19653	-0.43366	0.00000
C	1.19656	-0.43359	0.00000
C	-1.20089	-1.82310	0.00000
H	-2.11327	0.14308	0.00000
C	1.20100	-1.82303	0.00000
H	2.11327	0.14320	0.00000
C	0.00008	-2.52363	0.00000
H	-2.14068	-2.36456	0.00000
H	2.14082	-2.36443	0.00000
H	0.00010	-3.60778	0.00000

7.4 Chloromethyl

ClAc-I

O	-3.17533	-1.19967	-0.44681
C	-1.82725	-1.50886	-0.23555
C	-0.91572	-0.29501	-0.43573
C	-1.47879	0.92606	0.20327
C	-2.95848	1.06945	0.33774
C	-3.63943	-0.27532	0.51941
O	0.34707	-0.73279	0.16034
C	1.46266	-0.08857	-0.15266
C	2.64836	-0.84356	0.41056
O	-0.85042	2.11009	0.01501
O	1.52013	0.92992	-0.78666
H	-3.44675	-0.67371	1.52379
H	-3.35041	1.55253	-0.56737
H	0.04344	1.96144	-0.33562
H	-1.55295	-2.29712	-0.93475
H	-1.67155	-1.87746	0.78652
H	2.69628	-1.82022	-0.06709
Cl	4.17202	-0.00244	0.15575
H	2.49288	-0.99116	1.47699
H	-4.71549	-0.19125	0.37982
H	-3.18871	1.73616	1.17289
H	-0.71078	-0.12327	-1.50029

ClAc-TS1a

O	0.19022	-0.03922	1.22560
C	0.94803	-0.78242	0.55709
O	0.43862	-1.25867	-0.59874
C	-0.77184	-0.52725	-0.92925

C	-0.69862	0.80983	-0.27651
C	-1.89185	1.44851	0.34568
C	-2.89958	0.39483	0.78613
O	-3.11452	-0.54029	-0.24990
C	-1.97692	-1.34244	-0.44583
O	0.23062	1.59506	-0.85628
C	2.40948	-0.88908	0.72457
H	-2.53618	-0.11989	1.68220
H	-2.35488	2.10915	-0.39624
H	0.37842	2.39148	-0.33238
H	-2.23616	-2.10180	-1.18094
H	-1.69380	-1.83907	0.48918
H	2.67780	-0.75719	1.76660
H	2.77909	-1.83308	0.33735
Cl	3.32397	0.40752	-0.19370
H	-3.86233	0.85198	1.00668
H	-1.58432	2.06440	1.19717
H	-0.74689	-0.42077	-2.01361

ClAc-II

O	-0.11638	0.87000	-0.84550
C	1.16629	0.82936	-0.22016
C	0.80354	0.26454	1.15349
O	-0.51228	0.78524	1.35992
C	-1.02848	1.09153	0.14219
C	2.10452	-0.02269	-1.05161
C	1.79869	-1.50322	-0.89182
O	1.81383	-1.84806	0.47792
C	0.72565	-1.26567	1.15234
O	1.64488	2.12497	-0.03027
C	-2.42940	0.86225	-0.13629
H	0.82148	-1.74483	-1.32746

H	3.11864	0.17310	-0.70109
H	1.77635	2.53517	-0.89303
H	0.73211	-1.64081	2.17400
H	-0.22029	-1.55720	0.67948
H	-3.05031	1.16685	0.69843
H	-2.73423	1.33880	-1.06104
Cl	-2.82243	-0.94718	-0.38833
H	2.56002	-2.10880	-1.38032
H	2.02978	0.28826	-2.09666
H	1.46247	0.65774	1.92388

ClAc-TS1b

O	0.07872	-0.93583	-0.84646
C	-1.26997	-0.70610	-0.31586
C	-1.11281	-0.35003	1.13040
O	0.42497	-1.38760	1.28247
C	0.93233	-1.17773	0.15765
C	-1.85589	0.42645	-1.14723
C	-1.23942	1.76070	-0.75025
O	-1.42810	1.99758	0.62835
C	-0.70342	1.06526	1.41537
O	-1.99180	-1.88568	-0.41245
C	2.36084	-0.89458	-0.09355
H	-0.16919	1.77096	-0.99154
H	-2.93059	0.45136	-0.96205
H	-2.10013	-2.10622	-1.34468
H	-0.88757	1.31795	2.45679
H	0.37047	1.18878	1.21320
H	2.95131	-1.20295	0.76164
H	2.70058	-1.38375	-1.00176
Cl	2.69989	0.88148	-0.35633

H	-1.72476	2.57967	-1.27882
H	-1.68384	0.21620	-2.20629
H	-1.76451	-0.86875	1.81654

ClAc-III

C	2.11856	-1.08035	1.26211
C	1.42736	0.23955	1.23828
C	1.07854	0.82046	-0.08934
O	0.78950	2.16697	-0.06800
C	2.18861	0.56777	-1.09274
C	2.67678	-0.87073	-1.00278
O	3.14571	-1.16524	0.29543
O	-0.08355	0.07458	-0.64456
H	1.87135	-1.56451	-1.27708
H	3.00489	1.24808	-0.84845
C	-1.24987	0.21898	-0.02096
H	0.10770	2.31671	0.60170
O	-1.43591	0.89683	0.95105
C	-2.30318	-0.59854	-0.74272
H	2.58048	-1.25957	2.23205
H	1.39097	-1.89311	1.08645
Cl	-3.87394	-0.52890	0.04767
H	-2.39863	-0.22008	-1.75850
H	-1.97377	-1.63409	-0.79225
H	3.51433	-1.03286	-1.67915
H	1.81931	0.80339	-2.09130
H	0.99354	0.65930	2.13383

ClAc-TS2

C	-1.67264	-1.62273	-0.70363

C	-1.26058	-0.27571	-1.21235
C	-1.54437	0.86619	-0.46477
O	-1.36593	2.03735	-1.06149
C	-2.37540	0.78310	0.77306
C	-2.33193	-0.63854	1.31760
O	-2.66618	-1.55023	0.29423
O	0.97322	-0.45206	-0.81905
H	-1.33199	-0.84793	1.71227
H	-3.40419	1.04161	0.50127
C	1.14804	0.29295	0.15115
H	-1.44619	2.75228	-0.41728
O	0.27093	0.95269	0.76435
C	2.55637	0.49062	0.72835
H	-2.09176	-2.21311	-1.51866
H	-0.78111	-2.14225	-0.33141
H	2.52945	0.24603	1.78671
Cl	3.81589	-0.48359	-0.04187
H	2.81922	1.53995	0.62015
H	-3.06515	-0.77124	2.11057
H	-2.01106	1.50006	1.50977
H	-0.90062	-0.16159	-2.22243

ClAc-TS3

C	-1.55714	-1.45367	-0.86018
C	-1.34932	0.00036	-1.12723
C	-1.93669	0.94002	-0.32510
O	-1.87364	2.21731	-0.67533
C	-2.62071	0.56506	0.94317
C	-2.38283	-0.91188	1.25534
O	-2.56875	-1.68675	0.09356
O	0.24912	0.51843	0.49651

H	-1.36814	-1.04113	1.64283
H	-3.69067	0.77218	0.84040
C	1.31946	0.11617	-0.09988
H	-2.18223	2.78456	0.04153
O	1.41465	-0.41456	-1.18457
C	2.54036	0.41057	0.79055
H	-1.87075	-1.95114	-1.77950
H	-0.60293	-1.89602	-0.55042
H	2.62685	1.48742	0.91202
H	2.38601	-0.03977	1.76723
Cl	4.05692	-0.20138	0.12250
H	-3.09905	-1.26766	1.99312
H	-2.22551	1.19243	1.74846
H	-0.79128	0.30742	-1.99941

ClAc-TS4

C	1.96634	-0.44282	1.51670
C	1.61201	0.83436	0.82541
C	1.55333	0.85034	-0.56597
O	1.05862	1.87471	-1.20886
C	2.09867	-0.26220	-1.38458
C	2.19424	-1.53638	-0.54499
O	2.78243	-1.25824	0.71051
O	-0.65075	1.43681	0.84061
H	1.19495	-1.95674	-0.41326
H	3.09211	0.03559	-1.73587
C	-1.21579	0.43600	0.29020
H	0.45727	2.33830	-0.58955
O	-0.66372	-0.47192	-0.32104
C	-2.73842	0.46953	0.47243
H	2.52387	-0.23911	2.42994

H	1.03374	-0.95928	1.78484
Cl	-3.59314	-0.87665	-0.29386
H	-2.95435	0.45313	1.53776
H	-3.11903	1.39934	0.05786
H	2.83862	-2.26401	-1.03357
H	1.45389	-0.40042	-2.25212
H	1.52722	1.75224	1.38472

ClAc-TS5

O	-3.37339	-1.04557	-0.18968
C	-2.12071	-1.38078	-0.73944
C	-1.18365	-0.20401	-0.83221
C	-1.52300	0.99467	-0.19041
C	-2.72759	1.09589	0.68207
C	-3.24619	-0.30089	1.00121
O	0.35256	-0.86376	0.20029
C	1.40948	-0.19628	-0.05604
C	2.66671	-0.91007	0.42701
O	-0.75300	2.04515	-0.27263
O	1.46770	0.88968	-0.63593
H	-2.56250	-0.80979	1.69231
H	-3.49804	1.67120	0.15988
H	0.17302	1.73200	-0.56941
H	-2.31647	-1.77510	-1.73616
H	-1.63570	-2.16565	-0.14760
H	2.75502	-1.84987	-0.11336
Cl	4.15138	0.01640	0.19529
H	2.55390	-1.13154	1.48525
H	-4.23350	-0.25763	1.45676
H	-2.46400	1.64747	1.58648
H	-0.54643	-0.13518	-1.70363

ClAc-TS6

C	-3.05552	-0.58298	-1.01861
C	-2.21001	0.63809	-1.07597
C	-1.29937	0.92530	-0.01443
O	-0.65118	2.04724	-0.06154
C	-1.52588	0.23197	1.29761
C	-2.18088	-1.12536	1.08654
O	-3.34596	-0.98986	0.29456
O	1.47663	1.03445	0.57628
H	-1.47547	-1.81112	0.60684
H	-2.20454	0.87965	1.86292
C	1.29386	0.04767	-0.15710
H	0.26748	1.85531	0.40030
O	0.17608	-0.34952	-0.60467
C	2.46268	-0.81685	-0.61284
H	-4.00843	-0.41633	-1.52290
H	-2.53045	-1.38662	-1.56394
Cl	4.01444	-0.36605	0.09979
H	2.25002	-1.85244	-0.36022
H	2.54014	-0.73549	-1.69494
H	-2.50136	-1.55001	2.03563
H	-0.58907	0.16290	1.84915
H	-2.14774	1.23142	-1.97746

ClAc-IV

O	3.21951	-1.45579	0.28404
C	2.09375	-1.31013	1.11180
C	1.50815	0.05402	1.07906
C	1.82419	0.99392	0.04833

C	2.89994	0.59715	-0.93113
C	3.00313	-0.92132	-1.00709
O	-1.38941	1.81857	0.40811
C	-1.72699	0.59948	0.01464
C	-3.23400	0.44717	0.08727
O	1.22350	2.06757	-0.05579
O	-0.96037	-0.25213	-0.34522
H	2.08616	-1.34315	-1.43810
H	3.85180	1.00966	-0.58577
H	-0.41013	1.96368	0.29881
H	2.40272	-1.57595	2.12536
H	1.30075	-2.01911	0.81748
Cl	-3.77615	-1.18892	-0.27691
H	-3.56981	0.72047	1.08483
H	-3.68473	1.13563	-0.62489
H	3.84824	-1.22953	-1.61939
H	2.66791	1.04350	-1.89778
H	0.74676	0.31908	1.80055

ClAc-VI

C	-0.85196	0.41003	0.00000
O	-0.47335	1.53908	0.00000
O	-2.15028	0.05453	0.00000
H	-2.67438	0.86865	0.00000
C	0.00000	-0.84017	0.00000
H	-0.24394	-1.42915	0.88189
H	-0.24394	-1.42915	-0.88189
Cl	1.72135	-0.48109	0.00000

ClAc-VIII

C	1.05309	-0.34876	0.00000
O	0.66056	-1.51722	0.00000
O	2.20247	0.13514	0.00000
C	0.00000	0.80538	0.00000
H	0.14962	1.41916	0.88419
H	0.14962	1.41916	-0.88419
Cl	-1.73659	0.32227	0.00000

7.5 Trichloromethyl

Cl_3Ac-I

C	-2.03343	-1.42575	0.05558
C	-1.55981	-0.06649	-0.46301
C	-2.44997	1.02322	0.01298
O	-2.02769	2.25772	-0.37389
C	-3.91658	0.74987	0.05484
C	-4.17811	-0.66452	0.55750
O	-3.40916	-1.60007	-0.16733
O	-0.23385	0.18772	0.04707
H	-3.93445	-0.73442	1.62517
H	-4.34467	0.85596	-0.95271
C	0.77054	-0.36604	-0.60865
H	-2.68107	2.92069	-0.12778
O	0.69726	-1.05754	-1.57601
C	2.11469	-0.00427	0.07800
H	-1.51069	-2.22579	-0.46498
H	-1.80291	-1.48057	1.12784
Cl	3.45205	-0.65597	-0.84940
Cl	2.25603	1.75481	0.18972
Cl	2.09909	-0.72066	1.69909
H	-5.22145	-0.94112	0.41768

H	-4.42353	1.47484	0.70025
H	-1.49944	-0.07759	-1.55768

Cl_3Ac-TS1a

O	-0.41925	0.32225	0.99718
C	0.35758	-0.33624	0.27746
O	-0.18488	-1.01729	-0.74284
C	-1.55991	-0.57488	-0.93719
C	-1.69053	0.80878	-0.40146
C	-2.88800	1.24670	0.36885
C	-3.57150	0.05736	1.03098
O	-3.72540	-0.99437	0.10198
C	-2.48269	-1.56645	-0.21810
O	-1.05071	1.71008	-1.16916
C	1.83834	-0.07797	0.14414
H	-2.98217	-0.28540	1.88828
H	-3.58540	1.72661	-0.32733
H	-1.07836	2.58386	-0.76099
H	-2.67305	-2.42893	-0.85339
H	-1.97109	-1.90437	0.69023
Cl	2.43163	0.72301	1.59404
Cl	2.68043	-1.62390	-0.08369
Cl	2.19241	0.96309	-1.28658
H	-4.56805	0.32940	1.37306
H	-2.59648	1.98940	1.11850
H	-1.69929	-0.57731	-2.01777

Cl_3Ac-II

C	-2.37664	-1.58418	-0.29371
C	-1.56850	-0.50989	-1.02870

C	-1.54788	0.81745	-0.27427
O	-1.17076	1.80567	-1.17608
C	-2.81594	1.15887	0.48167
C	-3.42376	-0.07413	1.13040
O	-3.60848	-1.08845	0.16321
O	-0.18633	-0.87387	-1.01835
H	-2.78065	-0.44273	1.93881
H	-3.52130	1.57041	-0.24107
C	0.32891	-0.37309	0.12817
H	-0.89929	2.59042	-0.68482
O	-0.48317	0.58123	0.66074
C	1.79488	-0.12042	0.14926
H	-2.58262	-2.42006	-0.95938
H	-1.77336	-1.95009	0.54785
Cl	2.28115	0.29173	1.79877
Cl	2.64216	-1.56713	-0.39846
Cl	2.23406	1.25552	-0.93555
H	-4.40573	0.15105	1.54221
H	-2.59028	1.92823	1.22372
H	-1.87876	-0.37352	-2.06137

Cl_3Ac-TS1b

O	0.43308	0.94817	-0.54613
C	1.80056	1.00234	0.00839
C	1.78445	0.19137	1.26609
O	-0.00383	0.61533	1.58858
C	-0.42676	0.62201	0.41782
C	2.70653	0.41988	-1.06614
C	2.56691	-1.09467	-1.13127
O	2.82649	-1.67030	0.13151
C	1.84588	-1.29713	1.08488

O	2.09272	2.31636	0.32347
C	-1.70092	-0.03924	-0.04983
H	1.56088	-1.36826	-1.47072
H	3.73291	0.68124	-0.80503
H	2.10374	2.83784	-0.48762
H	2.10487	-1.78995	2.01870
H	0.86499	-1.67274	0.75787
Cl	-2.67332	-0.51426	1.33043
Cl	-2.59331	1.11745	-1.06254
Cl	-1.35762	-1.49738	-1.05912
H	3.29467	-1.51609	-1.82270
H	2.45892	0.87683	-2.02778
H	2.24361	0.64844	2.12917

Cl_3Ac-III

C	-2.65689	-0.87555	-1.35261
C	-2.17906	0.52809	-1.19910
C	-1.74140	0.96435	0.15510
O	-1.62601	2.32271	0.32071
C	-2.64948	0.39613	1.22826
C	-2.92389	-1.07826	0.96542
O	-3.51870	-1.26190	-0.30193
O	-0.41942	0.31714	0.44512
H	-1.99281	-1.65595	1.03109
H	-3.58318	0.95800	1.19142
C	0.59839	0.68337	-0.29707
H	-1.08121	2.67465	-0.39666
O	0.60460	1.53270	-1.14075
C	1.85290	-0.16923	0.03747
H	-3.21274	-0.99738	-2.28117
H	-1.79428	-1.56480	-1.38632

Cl	3.22762	0.38713	-0.89427
Cl	2.19937	-0.04348	1.76534
Cl	1.47294	-1.85036	-0.38924
H	-3.62647	-1.47152	1.69791
H	-2.18100	0.54960	2.20079
H	-1.95428	1.14295	-2.05825

Cl_3Ac-TS2

C	-2.50862	-1.38313	-0.95501
C	-2.25576	0.05514	-1.27335
C	-2.35222	1.01560	-0.26232
O	-2.27697	2.27831	-0.62534
C	-2.82219	0.64757	1.10388
C	-2.63868	-0.85025	1.32116
O	-3.22053	-1.55762	0.24680
O	0.07240	-0.10904	-1.45458
H	-1.57168	-1.08090	1.40750
H	-3.88625	0.90110	1.16525
C	0.44261	0.30022	-0.35192
H	-2.21593	2.85188	0.15048
O	-0.21681	0.86716	0.53368
C	1.93700	-0.02656	0.03870
H	-3.10528	-1.83836	-1.74607
H	-1.54002	-1.90016	-0.92097
Cl	1.84681	-1.55946	0.94732
Cl	2.95425	-0.24430	-1.37955
Cl	2.62139	1.23035	1.06937
H	-3.15012	-1.17261	2.22544
H	-2.27365	1.22623	1.84785
H	-2.11627	0.37899	-2.29227

Cl_3Ac-TS3

C	2.22202	-1.34907	1.02731
C	2.19514	0.13058	1.21163
C	2.67380	0.95699	0.22211
O	2.79304	2.24638	0.47542
C	3.00629	0.43584	-1.13153
C	2.58137	-1.02757	-1.25594
O	2.96958	-1.73691	-0.10047
O	0.31933	0.64872	-0.04986
H	1.49767	-1.08265	-1.39458
H	4.08399	0.54269	-1.29220
C	-0.60259	0.22053	0.70972
H	2.98670	2.74260	-0.33010
O	-0.55845	-0.11601	1.87179
C	-1.96198	0.03718	-0.07550
H	2.69234	-1.81317	1.89634
H	1.18986	-1.71966	0.97413
Cl	-2.27244	1.40518	-1.15069
Cl	-1.75410	-1.44681	-1.04386
Cl	-3.31172	-0.16627	1.02674
H	3.07880	-1.49918	-2.10052
H	2.48490	1.04946	-1.87293
H	1.86391	0.54993	2.15053

Cl_3Ac-TS4

C	2.89939	-0.97478	1.23485
C	2.24334	0.36775	1.21236
C	2.16171	1.05775	0.00263
O	1.43314	2.13307	-0.11858
C	2.92111	0.62470	-1.19706

C	3.31637	-0.84699	-1.06856
O	3.85744	-1.10014	0.21277
O	-0.09176	0.35763	1.28079
H	2.43897	-1.47323	-1.24383
H	3.81632	1.25104	-1.27151
C	-0.44089	-0.19047	0.20457
H	0.76882	2.14549	0.59968
O	0.26202	-0.66189	-0.67727
C	-1.99793	-0.15618	-0.04290
H	3.41879	-1.12684	2.18014
H	2.11407	-1.73821	1.14222
Cl	-2.48235	-1.27735	-1.30665
Cl	-2.88454	-0.51465	1.43991
Cl	-2.35125	1.51362	-0.56454
H	4.09437	-1.09335	-1.78761
H	2.30374	0.80229	-2.07761
H	1.94795	0.84504	2.13313

Cl_3Ac-TS5

O	-3.83021	-1.31066	-0.26756
C	-2.56296	-1.35170	-0.87872
C	-1.86985	-0.01085	-0.88803
C	-2.42414	1.04333	-0.14572
C	-3.57074	0.83158	0.78041
C	-3.79241	-0.66225	0.98453
O	-0.23638	-0.44040	0.02941
C	0.66868	0.41092	-0.22088
C	2.10970	-0.10449	0.10335
O	-1.90292	2.24668	-0.17879
O	0.54218	1.52327	-0.71533
H	-2.99065	-1.08381	1.60346

H	-4.46628	1.28913	0.34888
H	-0.97787	2.18270	-0.55097
H	-2.72350	-1.68617	-1.90303
H	-1.91176	-2.07628	-0.37726
Cl	2.51182	-1.27246	-1.17476
Cl	3.27293	1.21004	0.09205
Cl	2.13051	-0.90585	1.67735
H	-4.74629	-0.85319	1.47179
H	-3.36460	1.34363	1.72255
H	-1.30957	0.25434	-1.77584

Cl_3Ac-TS6

C	-3.44292	-0.86813	-1.00788
C	-2.89223	0.50547	-1.13962
C	-2.09101	1.04995	-0.09594
O	-1.70155	2.28474	-0.22266
C	-2.16539	0.40344	1.25475
C	-2.49746	-1.07738	1.12606
O	-3.65254	-1.25077	0.32665
O	0.61127	1.72337	0.57455
H	-1.64839	-1.61532	0.69287
H	-2.97594	0.91554	1.78467
C	0.61162	0.65870	-0.04952
H	-0.82672	2.36362	0.28487
O	-0.35537	0.08738	-0.61148
C	1.94708	-0.15830	-0.07419
H	-4.40106	-0.94972	-1.52313
H	-2.74106	-1.56027	-1.50525
Cl	3.33946	0.87325	0.21414
Cl	1.78449	-1.33371	1.25755
Cl	2.13935	-1.01642	-1.60012

H	-2.72929	-1.50299	2.09990
H	-1.24252	0.57563	1.80879
H	-2.94363	1.04021	-2.07779

Cl_3Ac-IV

O	4.37680	-1.20989	0.18816
C	3.12044	-1.43587	0.77260
C	2.29881	-0.20643	0.90856
C	2.61573	0.99997	0.20898
C	3.89088	1.01323	-0.59403
C	4.28970	-0.40752	-0.97263
O	-0.64321	1.39213	0.53576
C	-0.86295	0.33093	-0.19630
C	-2.34269	-0.12870	-0.08083
O	1.87181	1.98664	0.24127
O	-0.06281	-0.27121	-0.85432
H	3.55858	-0.83597	-1.67034
H	4.67740	1.46117	0.01932
H	0.32261	1.67351	0.46600
H	3.29598	-1.89161	1.74992
H	2.54015	-2.16358	0.17896
Cl	-2.66492	-1.43867	-1.20149
Cl	-2.57477	-0.69680	1.58712
Cl	-3.41920	1.22990	-0.41501
H	5.27033	-0.42974	-1.44343
H	3.74184	1.64739	-1.46763
H	1.39403	-0.24163	1.50162

Cl_3Ac-VI

C	-1.33431	0.02877	0.00000

O	-2.01365	1.00387	0.00000
O	-1.78099	-1.22449	0.00000
H	-2.74880	-1.19341	0.00000
C	0.21289	0.05442	0.00000
Cl	0.78107	-0.78332	1.45220
Cl	0.78107	-0.78332	-1.45220
Cl	0.78107	1.71130	0.00000

Cl_3Ac-VIII

C	-1.49483	-0.04762	0.00000
O	-2.04349	1.04759	0.00000
O	-1.88444	-1.21093	0.00000
C	0.14053	0.02976	0.00000
Cl	0.77548	-0.80346	1.44729
Cl	0.77548	-0.80346	-1.44729
Cl	0.77548	1.69009	0.00000

7.6 Trifluoromethyl

F_3Ac-I

C	-1.44843	-1.39497	0.19117
C	-0.95475	-0.06586	-0.38444
C	-1.85129	1.05062	0.01014
O	-1.41411	2.26006	-0.43380
C	-3.31987	0.78573	0.03353
C	-3.60040	-0.60024	0.60057
O	-2.81857	-1.57376	-0.05791
O	0.36195	0.21052	0.14397
H	-3.38278	-0.61763	1.67593
H	-3.72486	0.84292	-0.98736

C	1.37867	-0.37724	-0.45856
H	-2.06707	2.93955	-0.23618
O	1.34433	-1.13281	-1.37941
C	2.69821	0.05732	0.21829
H	-0.91765	-2.22307	-0.27437
H	-1.24621	-1.39595	1.27040
F	3.72876	-0.52741	-0.36618
F	2.85515	1.37567	0.13769
F	2.69165	-0.28381	1.50629
H	-4.64128	-0.87987	0.44948
H	-3.83676	1.54475	0.62997
H	-0.86512	-0.13498	-1.47508

F_3Ac-TS1a

O	0.13060	0.29570	1.04075
C	0.90378	-0.39640	0.34704
O	0.37062	-1.08490	-0.67424
C	-0.98225	-0.59118	-0.91996
C	-1.06428	0.80723	-0.41703
C	-2.27003	1.32155	0.28941
C	-3.02875	0.18166	0.95742
O	-3.19662	-0.88857	0.05214
C	-1.97044	-1.52319	-0.20941
O	-0.33722	1.65378	-1.17032
C	2.37994	-0.09397	0.19056
H	-2.48517	-0.16151	1.84418
H	-2.91888	1.80876	-0.44746
H	-0.34473	2.53962	-0.78825
H	-2.17783	-2.39269	-0.82966
H	-1.50556	-1.85920	0.72425
F	2.86794	0.41486	1.31732

F	3.06222	-1.20025	-0.10653
F	2.62235	0.79158	-0.78838
H	-4.02374	0.50597	1.25559
H	-1.97606	2.07344	1.02871
H	-1.08738	-0.61244	-2.00400

F_3Ac-II

C	-1.88154	-1.54897	-0.22828
C	-0.98797	-0.55364	-0.97537
C	-0.94097	0.80893	-0.28776
O	-0.46529	1.72856	-1.21470
C	-2.22834	1.24852	0.37900
C	-2.92821	0.08132	1.05644
O	-3.11060	-0.97472	0.13490
O	0.37327	-0.97975	-0.87937
H	-2.34672	-0.27100	1.91696
H	-2.87505	1.65256	-0.40071
C	0.86393	-0.43056	0.25826
H	-0.26102	2.55513	-0.76131
O	0.06042	0.57051	0.71605
C	2.33668	-0.13796	0.23613
H	-2.09217	-2.41044	-0.85894
H	-1.33990	-1.89365	0.66251
F	2.75069	0.23483	1.44666
F	3.02108	-1.21601	-0.13639
F	2.65236	0.85280	-0.61145
H	-3.91836	0.37328	1.40122
H	-2.00437	2.04470	1.09295
H	-1.24335	-0.45776	-2.02751

F_3Ac-TS1b

O	-0.06398	0.88918	-0.69688
C	1.29739	0.93848	-0.11100
C	1.21641	0.25080	1.21495
O	-0.56990	0.74932	1.44919
C	-0.95113	0.65398	0.26758
C	2.19228	0.21725	-1.10805
C	1.97895	-1.28827	-1.03471
O	2.19891	-1.75189	0.27991
C	1.22273	-1.25025	1.17600
O	1.64068	2.26197	0.08564
C	-2.15534	-0.15772	-0.17257
H	0.96315	-1.54609	-1.36014
H	3.22639	0.45141	-0.85177
H	1.69555	2.70259	-0.77036
H	1.44766	-1.66140	2.15691
H	0.23272	-1.61785	0.86751
F	-2.99115	-0.33941	0.83789
F	-2.80187	0.45927	-1.16079
F	-1.80271	-1.37097	-0.63676
H	2.69059	-1.80766	-1.67413
H	1.98279	0.59441	-2.11235
H	1.66935	0.77037	2.04525

F_3Ac-III

C	2.22948	-0.72576	1.41739
C	1.63446	0.60749	1.11637
C	1.16225	0.85988	-0.27194
O	0.94952	2.17961	-0.58428
C	2.10034	0.24195	-1.28974
C	2.49340	-1.16688	-0.86751

O	3.11094	-1.15718	0.40208
O	-0.11999	0.09717	-0.46970
H	1.61248	-1.82119	-0.85242
H	2.98763	0.87418	-1.33296
C	-1.16230	0.50014	0.21500
H	0.39746	2.57629	0.10361
O	-1.23332	1.42703	0.97015
C	-2.37009	-0.42426	-0.06395
H	2.80154	-0.69460	2.34362
H	1.42880	-1.47591	1.54587
F	-3.43781	-0.00308	0.58840
F	-2.64891	-0.45752	-1.36367
F	-2.09058	-1.66590	0.33453
H	3.21956	-1.58379	-1.56290
H	1.61341	0.24795	-2.26521
H	1.35234	1.28714	1.90736

F_3Ac-TS2

C	-2.17467	-1.40472	-0.81560
C	-1.64409	-0.07362	-1.23984
C	-1.64767	0.99486	-0.34096
O	-1.32603	2.17997	-0.81721
C	-2.27264	0.86329	1.00593
C	-2.36273	-0.61108	1.38132
O	-2.98222	-1.32860	0.33506
O	0.64239	-0.60872	-1.21239
H	-1.35847	-0.99902	1.57900
H	-3.27944	1.29080	0.94675
C	1.03080	-0.03844	-0.18900
H	-1.21545	2.81672	-0.09815
O	0.37874	0.61868	0.64236

C	2.55094	-0.14104	0.13970
H	-2.79424	-1.82470	-1.60874
H	-1.32213	-2.07821	-0.65963
F	2.72875	-0.71063	1.33485
F	3.21994	-0.85634	-0.75477
F	3.09913	1.07619	0.18370
H	-2.98131	-0.74610	2.26576
H	-1.68900	1.42388	1.73685
H	-1.37301	0.10752	-2.26772

F_3Ac-TS3

C	-1.84057	-1.41460	-0.85837
C	-1.56878	0.02218	-1.15295
C	-1.99514	0.99857	-0.28413
O	-1.89253	2.26242	-0.65065
C	-2.51585	0.66033	1.06814
C	-2.32585	-0.83012	1.35008
O	-2.72231	-1.58364	0.22616
O	0.26113	0.38477	0.21699
H	-1.27734	-1.02404	1.59250
H	-3.57559	0.93134	1.11324
C	1.19937	-0.09049	-0.49928
H	-2.07063	2.85540	0.09044
O	1.16423	-0.59375	-1.60169
C	2.56905	0.00157	0.24198
H	-2.31299	-1.87835	-1.72639
H	-0.88557	-1.92613	-0.68742
F	2.83180	1.25692	0.61376
F	2.54716	-0.75198	1.34766
F	3.56998	-0.41791	-0.51689
H	-2.95327	-1.14479	2.18102

H	-1.97557	1.26153	1.80612
H	-1.10698	0.29871	-2.08972

F_3Ac-TS4

C	2.09608	-1.07332	1.20255
C	1.58569	0.33196	1.20370
C	1.66943	1.07846	0.02972
O	1.07001	2.23308	-0.08378
C	2.47266	0.62308	-1.13247
C	2.71267	-0.88505	-1.05171
O	3.11803	-1.25043	0.25241
O	-0.72382	0.53173	1.11718
H	1.79729	-1.41210	-1.32903
H	3.42695	1.15977	-1.10931
C	-1.04668	-0.02810	0.03494
H	0.36232	2.27985	0.58838
O	-0.32815	-0.41757	-0.87594
C	-2.58508	-0.21711	-0.11414
H	2.51723	-1.32411	2.17515
H	1.24925	-1.74641	1.00703
F	-2.91116	-0.79626	-1.26173
F	-3.06249	-0.97289	0.87747
F	-3.20633	0.96519	-0.06108
H	3.52050	-1.17511	-1.71975
H	1.94609	0.89956	-2.04576
H	1.28304	0.80030	2.12683

F_3Ac-TS5

O	-3.26610	-1.28276	-0.27803
C	-2.00566	-1.35845	-0.89918

C	-1.26118	-0.04435	-0.88066
C	-1.77228	1.01042	-0.10796
C	-2.91416	0.81641	0.82758
C	-3.19327	-0.67263	0.99167
O	0.36216	-0.56142	0.00256
C	1.28895	0.27946	-0.20410
C	2.68719	-0.26336	0.19448
O	-1.21590	2.19918	-0.12341
O	1.21176	1.40501	-0.67922
H	-2.40453	-1.14345	1.59144
H	-3.79569	1.32215	0.42177
H	-0.29982	2.11893	-0.50912
H	-2.18589	-1.66020	-1.93031
H	-1.38108	-2.12065	-0.42051
F	3.01697	-1.28786	-0.59464
F	3.62202	0.66604	0.07973
F	2.68168	-0.69810	1.45355
H	-4.15026	-0.83952	1.48157
H	-2.67616	1.29215	1.78126
H	-0.70542	0.22488	-1.76996

F_3Ac-TS6

C	-2.3111650	-0.3724560	-1.1138230
C	-1.3154050	0.7306000	-1.1388190
C	-0.4259310	0.9186300	-0.0325290
O	0.3565600	1.9472870	-0.0552770
C	-0.8163920	0.2847050	1.2729200
C	-1.6234620	-0.9853690	1.0413790
O	-2.7180800	-0.7167850	0.1863450
O	2.3125960	0.7686960	0.6647060
H	-0.9867900	-1.7646140	0.6101770

H	-1.4426950	1.0243340	1.7827080
C	2.0113600	-0.2252880	-0.0211670
H	1.2534990	1.6392530	0.4436490
O	0.8914820	-0.5131570	-0.4979360
C	3.1288470	-1.2540540	-0.3262740
H	-3.2077200	-0.0948480	-1.6697760
H	-1.8666420	-1.2457730	-1.6225500
F	4.2919350	-0.8895300	0.1886570
F	2.8001640	-2.4432680	0.1833410
F	3.2776200	-1.3977960	-1.6421380
H	-2.0441100	-1.3491490	1.9764390
H	0.0661310	0.1134440	1.8886680
H	-1.1320730	1.2969680	-2.0412200

F_3Ac-IV

O	3.90789	-1.10893	0.17258
C	2.66319	-1.47621	0.70791
C	1.72698	-0.33518	0.87072
C	1.95080	0.92612	0.23714
C	3.23433	1.09020	-0.53580
C	3.77768	-0.26909	-0.95706
O	-1.37156	1.20307	0.59142
C	-1.58467	0.13495	-0.12996
C	-3.08311	-0.24297	-0.10723
O	1.12726	1.84603	0.30469
O	-0.78241	-0.51838	-0.73560
H	3.11203	-0.73494	-1.69520
H	3.96010	1.58898	0.11225
H	-0.40097	1.47813	0.54273
H	2.85450	-1.95614	1.67058
H	2.17050	-2.22855	0.06773

F	-3.30700	-1.31953	-0.84234
F	-3.47534	-0.49801	1.14164
F	-3.82717	0.75392	-0.58025
H	4.76888	-0.17852	-1.39640
H	3.04313	1.74108	-1.38881
H	0.81664	-0.47865	1.43667

F_3Ac-VI

C	-0.29275	-0.90375	0.00000
O	-1.41425	-1.29532	0.00000
O	0.80814	-1.64751	0.00000
H	0.54664	-2.58050	0.00000
C	0.08636	0.59235	0.00000
F	0.80814	0.88492	1.07914
F	0.80814	0.88492	-1.07914
F	-1.00067	1.34033	0.00000

F_3Ac-VIII

C	-0.21913	-1.03677	0.00000
O	-1.41902	-1.32393	0.00000
O	0.81261	-1.71640	0.00000
C	0.08903	0.50768	0.00000
F	0.81261	0.88061	1.07794
F	0.81261	0.88061	-1.07794
F	-0.99947	1.29402	0.00000

7.7 Tosyl

Ts-I

C	-3.90006	0.83577	-0.28600
C	-3.35396	0.75135	0.99767
C	-2.19611	0.03659	1.23457
C	-1.56799	-0.60189	0.16990
C	-2.08776	-0.53753	-1.11164
C	-3.25463	0.18363	-1.33016
S	-0.07890	-1.48666	0.47887
C	-5.16890	1.60650	-0.51484
O	0.96437	-0.34639	0.74261
C	1.48431	0.41845	-0.43396
C	1.53663	1.87953	-0.01610
O	2.62370	2.16310	0.82107
C	3.85975	1.91294	0.17916
C	4.02355	0.43094	-0.12717
C	2.81320	-0.08910	-0.81900
O	2.92734	-1.32583	-1.34382
O	0.28726	-2.16317	-0.73818
H	4.63596	2.26335	0.85667
H	4.90666	0.26062	-0.74696
H	2.06010	-1.76310	-1.38909
H	1.58774	2.48830	-0.92927
H	0.62865	2.13360	0.52996
H	3.91314	2.49810	-0.74874
H	4.17453	-0.12000	0.81103
H	0.75517	0.29182	-1.23872
H	-1.77899	-0.04016	2.23050
H	-1.59099	-1.05859	-1.91921
H	-3.85169	1.25059	1.82044
H	-3.66994	0.23396	-2.32902
H	-5.07973	2.62327	-0.13021
H	-5.41530	1.65991	-1.57372
H	-6.00352	1.13303	0.00521

O	-0.19486	-2.20661	1.69765

Ts-III

C	-2.90593	1.27303	-0.58127
C	-2.21294	0.24946	0.30085
C	-1.23625	0.91353	1.21000
C	-0.44959	2.07293	0.69629
O	-1.24419	2.95333	-0.07506
C	-1.90345	2.27911	-1.12617
O	-3.15899	-0.50756	0.94632
O	-1.49288	-0.61627	-0.69299
S	-0.52233	-1.75707	-0.21166
O	-0.91429	-2.16441	1.10921
C	1.03484	-0.94392	-0.09980
C	1.61715	-0.72325	1.13580
C	2.82016	-0.03341	1.19994
C	3.44019	0.43646	0.04639
C	2.83355	0.19119	-1.18760
C	1.63856	-0.49947	-1.26987
C	4.74801	1.17240	0.11217
O	-0.47220	-2.69642	-1.27672
H	-1.16849	1.77480	-1.76773
H	-3.64035	1.78603	0.04071
H	-2.70664	-1.19886	1.45229
H	-0.04047	2.65532	1.52084
H	0.39857	1.72224	0.08283
H	-2.40951	3.04168	-1.71574
H	-3.42548	0.74640	-1.38191
H	-1.09689	0.52640	2.20836
H	1.12897	-1.08730	2.02992
H	1.17115	-0.69609	-2.22636

H	3.28330	0.14200	2.16314
H	3.30927	0.54676	-2.09370
H	4.99241	1.45579	1.13439
H	5.55730	0.54561	-0.26747
H	4.71884	2.07460	-0.49932

Ts-TS2

C	-4.50495	0.07186	-0.19176
C	-3.74962	1.13053	0.31450
C	-2.38234	1.01159	0.48894
C	-1.75303	-0.17945	0.15144
C	-2.48061	-1.24443	-0.34936
C	-3.85286	-1.11159	-0.51898
S	0.00392	-0.32176	0.34071
O	0.34864	0.36687	1.57838
C	2.89100	0.69741	0.98486
C	2.74916	1.18565	-0.32492
O	0.57806	0.38416	-0.82499
C	3.40136	-0.67990	1.20540
O	4.09868	-1.18316	0.09343
C	3.34555	-1.08045	-1.10122
C	3.22085	0.39106	-1.49063
O	0.32380	-1.73449	0.33247
O	2.38008	2.42989	-0.45425
C	-5.99372	0.20994	-0.35101
H	2.35198	-1.51824	-0.97264
H	4.20629	0.78517	-1.76631
H	2.14038	2.62314	-1.37241
H	4.08838	-0.68983	2.05358
H	2.53557	-1.31115	1.46155
H	3.89407	-1.62770	-1.86434

H	2.53200	0.52797	-2.32455
H	2.59264	1.32223	1.81237
H	-1.79749	1.82607	0.89639
H	-1.97040	-2.16740	-0.59051
H	-4.24567	2.05722	0.57980
H	-4.42588	-1.94468	-0.90856
H	-6.48844	0.20018	0.62244
H	-6.25015	1.15144	-0.83819
H	-6.40479	-0.60591	-0.94392

Ts-TS3

S	-0.37161	1.79988	-0.11239
O	-0.95904	1.62402	-1.42444
C	-3.00744	-0.45302	0.59601
C	-1.88782	-1.08138	1.12790
O	-1.17503	1.11542	0.94560
C	-3.29571	-0.57325	-0.85477
O	-2.65767	-1.69214	-1.42277
C	-1.26066	-1.64795	-1.21193
C	-0.94747	-1.85434	0.27191
O	-1.74039	-1.08383	2.43011
H	-0.86402	-0.69027	-1.55261
H	-1.06082	-2.90979	0.54407
H	-0.86600	-1.41518	2.67917
H	-4.36823	-0.69309	-1.01547
H	-2.97156	0.36163	-1.34073
H	-0.82323	-2.45090	-1.80183
H	0.07966	-1.55108	0.50164
H	-3.62575	0.14879	1.24618
C	1.14193	0.85860	-0.11693
C	1.79201	0.62737	1.09182

C	1.65025	0.33115	-1.29076
C	2.93759	-0.14894	1.11713
H	1.39116	1.05966	2.00092
C	2.80275	-0.44685	-1.25393
H	1.13920	0.52980	-2.22403
C	3.45984	-0.70101	-0.05530
H	3.44503	-0.32730	2.05843
H	3.19777	-0.85995	-2.17426
C	4.72202	-1.51654	-0.01713
H	5.59522	-0.86660	0.06602
H	4.73240	-2.18834	0.84125
H	4.83517	-2.11211	-0.92194
O	-0.03535	3.13830	0.27929

Ts-TS5

C	4.25125	-0.82467	-0.33639
C	3.28193	-1.44943	0.45173
C	2.05693	-0.85272	0.68013
C	1.79388	0.38753	0.11127
C	2.73517	1.03002	-0.67279
C	3.96168	0.41674	-0.89096
S	0.23074	1.14958	0.38075
O	0.29744	2.51744	-0.03942
C	5.58036	-1.48831	-0.56245
O	-0.70358	0.33272	-0.49139
C	-2.49117	0.60775	-0.01445
C	-3.16503	0.65262	-1.35554
O	-3.53675	-0.61531	-1.82560
C	-4.34320	-1.30332	-0.89453
C	-3.53063	-1.66780	0.34052
C	-2.76220	-0.48980	0.82708

O	-2.23447	-0.58610	2.02641
O	-0.13067	0.93625	1.78062
H	-4.71432	-2.19492	-1.39556
H	-4.16619	-2.04085	1.14646
H	-1.47193	0.05510	2.11404
H	-4.04965	1.30150	-1.26707
H	-2.48763	1.09119	-2.08550
H	-5.20214	-0.67934	-0.61352
H	-2.81610	-2.46186	0.09655
H	-2.32319	1.57141	0.45502
H	1.30924	-1.33150	1.29921
H	2.50594	1.99943	-1.09425
H	3.49807	-2.41507	0.89345
H	4.70544	0.91494	-1.50058
H	5.44869	-2.48870	-0.97730
H	6.19917	-0.91224	-1.24823
H	6.12315	-1.59405	0.37856

Ts-TS6

C	-3.17842	1.07590	-0.44339
C	-2.39077	0.27087	0.53530
C	-1.28069	0.89917	1.17988
C	-0.67776	2.12222	0.58481
O	-1.60413	2.88239	-0.15143
C	-2.28546	2.10847	-1.11972
O	-3.02484	-0.72238	1.10155
O	-1.34128	-0.71369	-0.83531
S	-0.39706	-1.75189	-0.28916
O	-0.79808	-2.11386	1.06709
C	1.13725	-0.87827	-0.13058
C	1.74367	-0.72153	1.10272

C	2.91851	0.01650	1.19728
C	3.49391	0.59580	0.07243
C	2.86782	0.41552	-1.16354
C	1.70031	-0.31730	-1.27195
C	4.77343	1.37844	0.16625
O	-0.20583	-2.81643	-1.22123
H	-1.56883	1.60439	-1.77602
H	-3.97105	1.57685	0.12032
H	-2.35587	-1.35263	1.46640
H	-0.28104	2.76823	1.36884
H	0.17144	1.81633	-0.05166
H	-2.88151	2.80248	-1.70835
H	-3.63718	0.39596	-1.15940
H	-0.80585	0.40366	2.01504
H	1.29888	-1.18004	1.97643
H	1.21809	-0.45679	-2.23152
H	3.39609	0.13793	2.16214
H	3.30763	0.85659	-2.05045
H	5.03439	1.58807	1.20233
H	5.59733	0.82006	-0.28243
H	4.69274	2.32604	-0.36740

Ts-IV

C	-0.99486	-2.32171	0.29278
C	-0.54714	-1.57916	1.38182
C	0.61704	-0.82546	1.30549
C	1.33790	-0.81727	0.12349
C	0.92638	-1.56768	-0.97098
C	-0.23603	-2.31364	-0.87936
S	2.76210	0.22097	-0.02365
O	3.67941	-0.38115	-0.93042

C	-2.27200	-3.11116	0.36256
O	2.17562	1.46790	-0.77016
C	-1.09887	1.20824	-1.09108
C	-2.39405	0.67968	-1.59261
O	-3.49632	1.06724	-0.81418
C	-3.26619	0.86770	0.56642
C	-2.21220	1.84438	1.06972
C	-0.97932	1.81503	0.20026
O	0.08411	2.30043	0.59970
O	3.16237	0.59981	1.29225
H	-2.94325	-0.16666	0.74231
H	-2.60831	2.86311	1.04888
H	1.47740	1.91678	-0.21085
H	-2.57769	1.03362	-2.61015
H	-2.32133	-0.42065	-1.64400
H	-4.21884	1.02208	1.06906
H	-1.91092	1.62972	2.09607
H	-0.21599	1.13485	-1.71331
H	0.96854	-0.24260	2.14700
H	1.52391	-1.56546	-1.87399
H	-1.11301	-1.59530	2.30619
H	-0.56110	-2.90616	-1.72702
H	-2.11536	-4.13848	0.03213
H	-2.66960	-3.13397	1.37609
H	-3.03356	-2.67386	-0.28854

Ts-VI

O	2.34558	-1.30365	0.48457
O	2.28617	0.23071	-1.39995
H	2.41168	-0.62925	-1.82526
C	0.13049	-0.00682	0.07471

C	-0.54991	1.20398	0.03287
C	-0.54891	-1.21355	0.07795
C	-1.93112	1.19318	-0.01855
H	0.00408	2.13317	0.05180
C	-1.93565	-1.20433	0.02915
H	0.00398	-2.14170	0.13487
C	-2.64326	-0.00779	-0.02162
H	-2.47175	2.13155	-0.05097
H	-2.47521	-2.14326	0.03669
C	-4.14506	0.00578	-0.05616
H	-4.54723	-0.99391	-0.21055
H	-4.54545	0.39073	0.88362
H	-4.50979	0.65175	-0.85545
S	1.88851	0.00101	0.12499
O	2.32501	1.16820	0.80606

Ts-VIII

O	2.35137	1.35478	-0.35742
O	2.29577	-0.36891	1.37149
C	0.17196	0.01643	-0.02122
C	-0.52590	-1.18682	-0.01836
C	-0.53077	1.20856	-0.01774
C	-1.91023	-1.18969	-0.00481
H	0.03611	-2.11237	-0.03762
C	-1.92266	1.19985	-0.00468
H	0.02884	2.13506	-0.03414
C	-2.63140	0.00539	0.00352
H	-2.44793	-2.13286	-0.00453
H	-2.46605	2.13926	-0.00394
C	-4.13709	-0.01296	0.01278
H	-4.53218	-0.50623	-0.87842

H	-4.52038	-0.55499	0.88029
H	-4.54134	0.99917	0.04304
S	1.97236	-0.00080	0.00354
O	2.32808	-1.01070	-0.97886

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