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Supporting Information

Condensation of b-diester Titanium enolates with carbonyl substrates: a combined DFT and experimental investigation

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Supporting Information

Content

Table S1. Comparison of the calculated geometrical parameters of the [$TiCl_4\{(OCOCH_3)_2CH_2\}$] complex with the experimental geometrical parameters of the [$TiCl_4\{(OCOCH_2CH_3)_2CH_2\}$].

	Calculated	Experimental
Ti-Cl_1	2.212	2.239
Ti-Cl_2	2.289	2.273
Ti-Cl_3	2.326	2.304
Ti-Cl_4	2.213	2.225
Ti-O	2.231	2.136
C=O	1.219	1.229
C-Ca	1.510	1.498
Cl_1-Ti-O	90.9	91.0
Cl_3-Ti-O	81.8	85.1
Cl_1-Ti-Cl_4	102.2	97.7
Cl_2-Ti-Cl_3	158.6	165.5
O-Ti-O	76.2	79.6
C-Ca-C	113.4	113.2

Table S2. Proton exchange enthalpy and free energy values (kcal mol^{-1}) for the metal-complexed and the free dimethyl malonate (DMM) in the gas phase and dichloromethane solution.

	? H(gas)	? G(gas)	? H(sol)	? G(sol)	? ? G_{solv}
Complexed DMM	64.2	64.5	-15.7	-15.4	-79.9
Free DMM	114.8	115.2	19.3	19.7	-95.5

Table S3. Calculated geometries of the ate 2 and the neutral 2’ titanium enolate.

Parameter	Ate	Neutral
Ti-Cl_1	2.291	2.213
Ti-Cl_2	2.290	2.236
Ti-Cl_3	2.354	2.222
Ti-Cl_4	2.357	-
Ti-O^{ave}	2.055	1.987
C=O^{ave}	1.261	1.278
C-Ca^{ave}	1.397	1.398
Cl_1-Ti-O	90.1	88.5
Cl_3-Ti-O	86.0	86.6
Cl_1-Ti-Cl_4	98.8	-
Cl_2-Ti-Cl_3	169.7	96.7
O-Ti-O	81.1	80.5
C-Ca-C	119.2	118.9

Table S4. Calculated ^{13}C NMR chemical shift for diethyl malonate (DEM) in the gas phase at the B3LYP/LACV3P** level of theory (reference TMS).

Entry	Species	Chemical shift (ppm)		
		Cα	C=O	O*C*H$_3$
1	DEM (ketone)	44.12	173.20	54.79
2	[TiCl$_4${(O=COCH$_3$)$_2$CH$_2$}]	38.53	177.82	59.64
3	Ate titanium enolate	74.10	179.07	53.78
4	Neutral titanium enolate	72.40	182.06	56.93

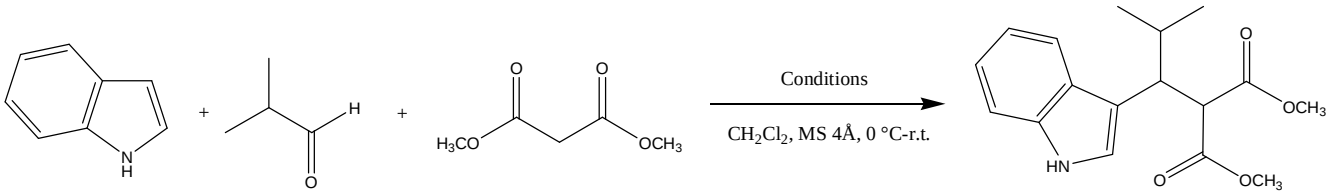
Table S5. ^{1}H and ^{13}C-NMR chemical shift of the titanium enolate of diethyl malonate (DEM) in CD_2Cl_2 before and after the addition of $AgSbF_6$.

Entry	Species	δ (ppm)						
		H-α	OC*H*$_2$CH$_3$	OCH$_2$C*H*$_3$	C-α	CO	O*C*H$_2$CH$_3$	OCH$_2$*C*H$_3$
1	Tetrachlorotitanium enolate of DEM	4.21 (br)	4.15 (4H)	1.29 (6H)	75.6	174.2	62.9	14.4
2	+ $AgSbF_6$ (1.7 eq)	4.00 (br)	4.54 (br, 4H)	1.36 (6H)	67.7	174.5 174.7	38.1	13.5

Table S6. Calculated activation enthalpies and free energies in gas phase and dichloromethane solution for the elimination reaction (step IV). Values are in kcal mol^{-1}.

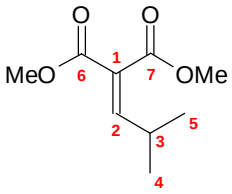
Step	R	? $H^{\dagger}$(g)	? $G^{\dagger}$(g)	? $H^{\dagger}$(sol)	? $G^{\dagger}$(sol)	? ? $G^{\dagger}_{solv}$
IV.a – i)	H	19.6	23.1	10.2	13.6	-9.4
	Ph	20.6	23.5	14.0	16.9	-6.6
	*i*Pr	19.9	25.8	11.0	16.9	-8.9
IV.a – ii)	H	22.0	21.1	11.2	10.3	-10.8
	Ph	21.5	21.3	14.5	14.2	-7.0
	*i*Pr	21.9	21.1	11.8	10.9	-10.2
IV.b	H	54.6	58.1	36.1	39.7	-18.4
	Ph	52.5	55.3	39.5	42.3	-13.0
	*i*Pr	53.1	54.3	39.9	41.1	-13.2

Table S7. Trimolecular condensation in the presence and in the absence of $AgSbF_6$.



Entry	Conditions	Yield (%)
1	$TiCl_4$ (1.0 eq), Et_3N (1.0 eq), $AgSbF_6$ (1.5 eq)	Traces
2	$TiCl_4$ (1.0 eq), Et_3N (1.0 eq)	81

Table S8. ^{1}H-NMR spectra of isobutylidene malonate **Kz** in CD_2Cl_2.



Kz

Entry		δ(H2) [ppm]	δ(H3) [ppm]	δ(H4), δ(H5) [ppm]	δ(OCH_3) [ppm]
1	**Kz**	6.78 (d, $J_{2\text{-}3}$=10.8 Hz)	2.65 (dsp, $J_{2\text{-}3}$=10.8Hz, $J_{3\text{-}4}$=$J_{3\text{-}5}$=6.6 Hz)	1.05 (d, $J_{3\text{-}4}$=$J_{3\text{-}5}$=6.6 Hz)	3.78 (3H) and 3.73 (3H)
2	**Kz** in the reaction mixture	7.81 (br)	2.82 (br)	1.04 and 1.07 (d, $J_{3\text{-}4}$=$J_{3\text{-}5}$=6.6 Hz)	3.73 (br) and 3.72 (br)
3	**Kz** + $TiCl_4$ (1.0 equiv)	7.98 (d, $J_{2\text{-}3}$=10.8 Hz)	3.45 (dsp,[a] $J_{2\text{-}3}$=10.8Hz, $J_{3\text{-}4}$=$J_{3\text{-}5}$=6.6 Hz)	1.20 (d, $J_{3\text{-}4}$=$J_{3\text{-}5}$=6.6 Hz)	4.22 (3H) and 4.17 (3H)

[a] dsp = double septet

Table S9. ^{13}C-NMR spectra of isobutylidene malonate **Kz** in CD_2Cl_2.

Entry		δ(C1) [ppm]	δ(C2) [ppm]	δ(C6), δ(C7) [ppm]	δ(OCH_3) [ppm]	δ(C3) [ppm]	δ(C4), δ(C5) [ppm]
1	**Kz**	126.1	156.1	164.8, 166.3	52.5, 52.6	29.8	22.1
2	**Kz** in the reaction mixture	116.1	156.6	166.9, 167.3	52.8, 52.9	29.9	22.0
3	**Kz** + $TiCl_4$ (1.0 equiv)	116.9	178.0	170.4, 170.8	57.2, 57.3	31.9	21.6

Table S10. Experimental UV/Vis absorption bands and calculated electronic transitions for the free Knoevenagel adduct (**Ky**), its complex with $TiCl_4$ (**$TiCl_4$-Ky**) and the complex in the reaction mixture (**5**).

Entry		Experimental [nm]	Theoretical [nm]	Transitions
1	**Ky**	281 (ε=12320)	283.58 (f=0.4213)	H → L ($\pi \rightarrow \pi^*$)
2			276.80 (f=0.0780)	H-2 → L (n(O)→ π^*)
3			253.05 (f=0.0836)	H-3 → L (n(O)→ π^*)
4		220 (ε=6745)	215.28 (f=0.0443)	H-3(2) → L+2 ($\pi \rightarrow \pi^*$)
5	**$TiCl_4$-Ky**		363.33 (f=0.0304)	H-1(2) → L (d→ π^*)
6			344.63 (f=0.0381)	H-2 → L+1 (d→ d^*)
7		350 (broad)	338.10 (f=0.0975)	H-1 → L+3 (d→ d^*)
8			330.09 (f=0.1274)	H-2 → L+3 (d→ π^*)
9		281 (ε=12945)	289.32 (f=0.0808)	H-4 → L+3 (n(Cl)→ π^*)
10	**5**	n.d.	424.33 (f=0.0278)	H-1 → L (n(Cl)→ π^*)
11		350 (broad)	370.78 (f=0.0122)	H-3 → L (n(Cl,O)→ π^*)
12		332 (broad)	329.28 (f=0.2125)	H-4 → L (d→ π^*)
13		290 (ε=2485)	278.02 (f=0.0247)	H-1 → L+2 (n(Cl)→ π^*)
14		245 (ε=11460)	245.72 (f=0.0078)	H-3 → L+2 (n(Cl,O)→ π^*)

Table S11. IR spectra of benzylidene malonate Ky (KBr disc).

Entry		ν C=O [cm^{-1}]	ν Ti=O [cm^{-1}]
1	**Ky**	1734	/ [a]
2	**Ky** + $TiCl_4$	1671	/ [a]
3	**Ky** in the reaction mixture	1737	1083, 1065
4	**Ky** in the reaction mixture after treatment with water	1734	1082, 1064

[a] / = not observed.

Table S12. IR spectra of isopropylidene malonate Kz (KBr disc).

Entry	Species	ν C=O (cm^{-1})	ν Ti=O (cm^{-1})
1	**Kz**	1733	/ [a]
2	**Kz** + $TiCl_4$	1677	/ [a]
3	**Kz** in the reaction mixture	1737	1031, 1013

[a] / = not observed.

Figure S1. Job's diagram for the complex DEM-$TiCl_4$ at a total concentration of DEM + $TiCl_4$ of 0.82 M.

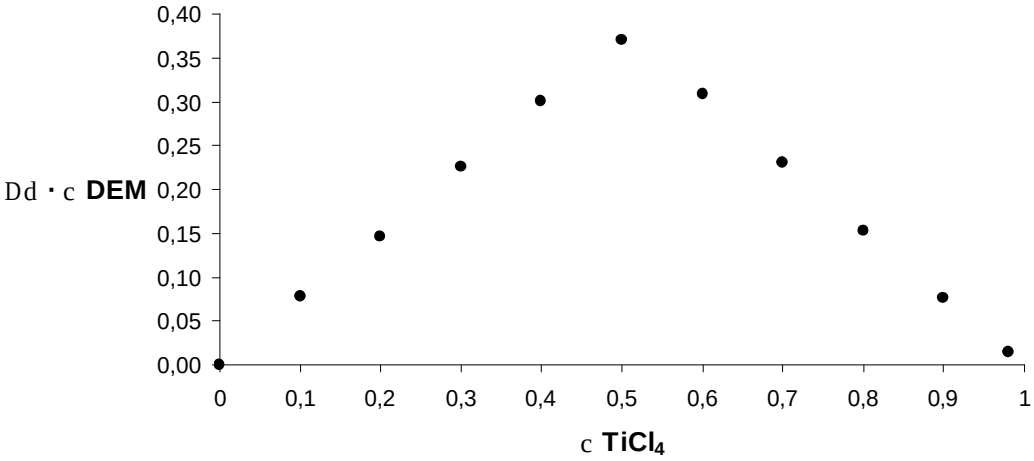


Figure S2. Direct nucleophilic attack of ate enolate complex to the formaldehyde simulated through linear transit calculations.

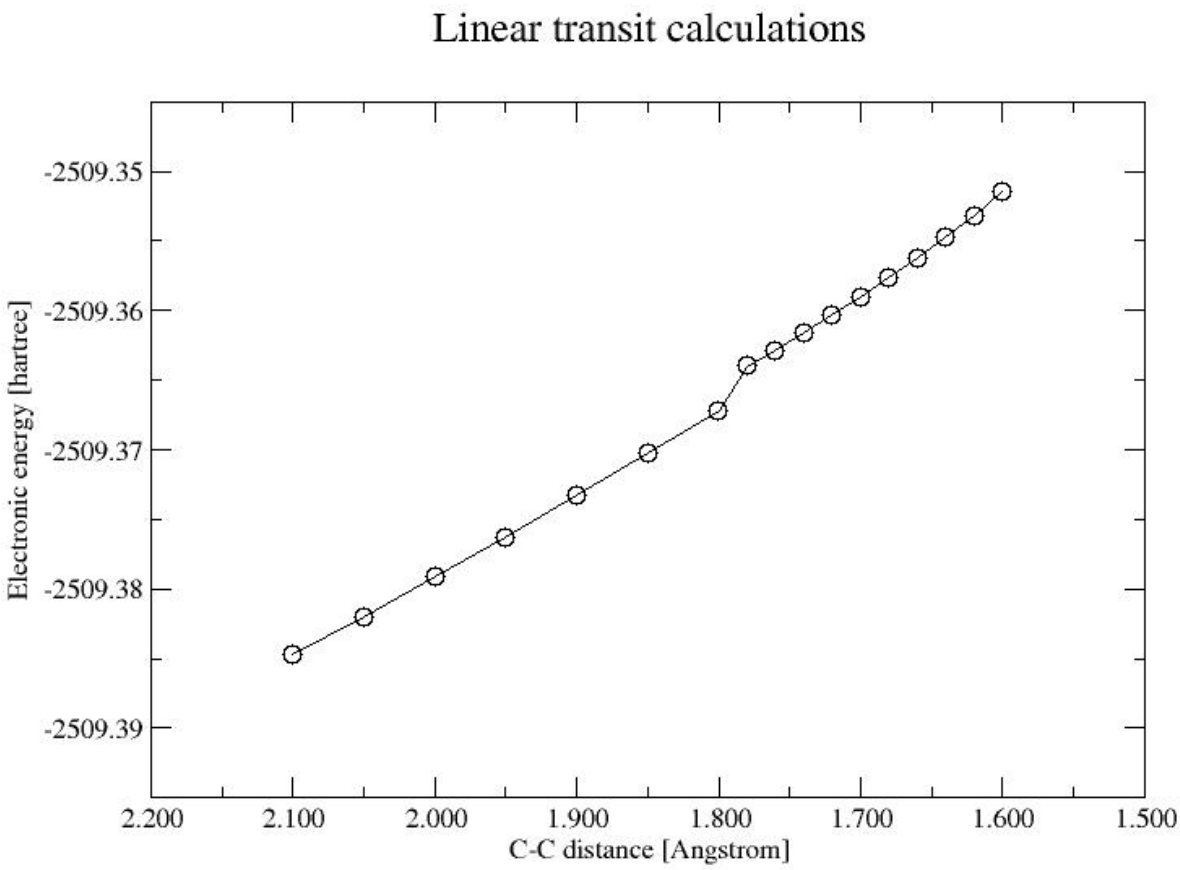
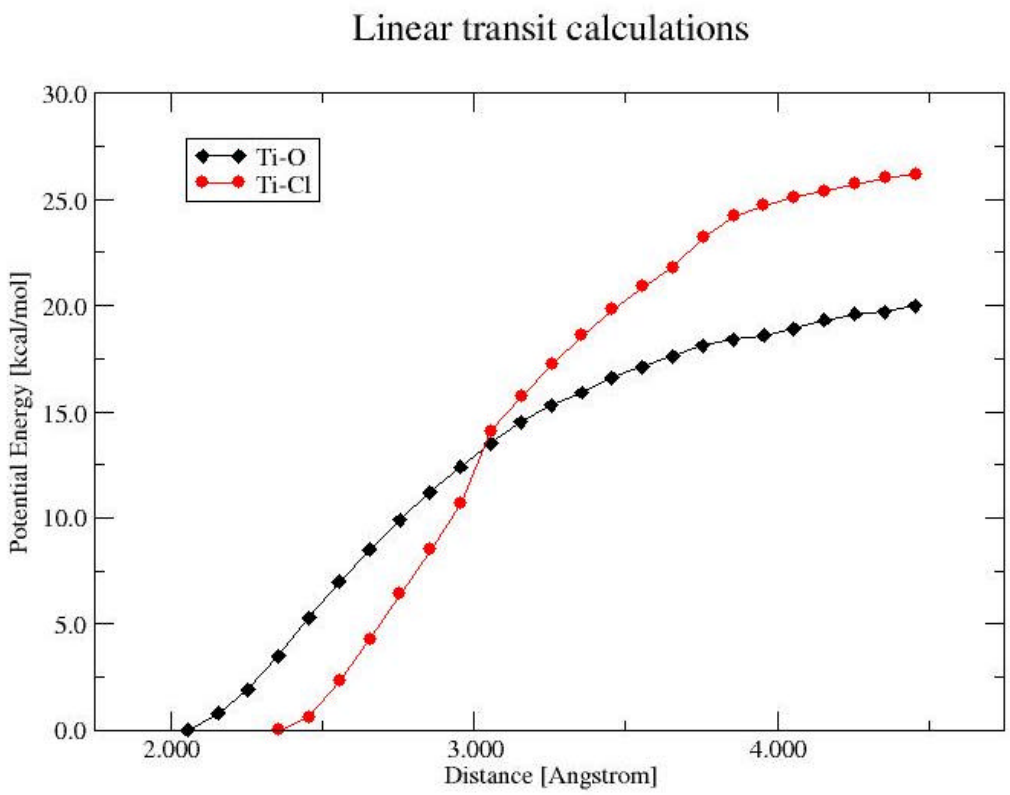


Figure S3. Linear transit calculations simulating the dissociation of Ti-Cl and Ti-O_{ester} bonds of 2 in the gas phase.



Data S1. Calculated geometries: Cartesian coordinates.

Mol: **1**

O	4.27370	0.29220	0.77120
C	3.06640	0.31330	1.29260
O	2.83570	0.77260	2.39840
Ti	1.00560	0.97990	3.65680
Cl	2.24670	1.19640	5.47650
C	2.03680	-0.32410	0.39080
H	2.35600	-0.29390	-0.64860
C	0.65450	0.26170	0.55070
O	0.20250	0.70800	1.59180
H	1.96530	-1.37640	0.69690
O	-0.04470	0.20930	-0.56220
Cl	-1.04620	1.11130	4.47360
Cl	1.16840	3.14560	2.93550
Cl	1.08860	-1.34260	3.57060
C	5.34830	0.82340	1.59960
H	6.24610	0.70210	1.00110
H	5.15590	1.87240	1.81950
H	5.40980	0.25600	2.52710
C	-1.41800	0.69060	-0.49120
H	-1.81240	0.55290	-1.49350
H	-1.97430	0.10370	0.23820
H	-1.42310	1.74070	-0.20300

Mol: **2**

C	4.38300	0.07090	0.99280
O	3.01870	0.30870	1.37600
C	2.83240	0.81590	2.61250
C	1.50560	1.04420	2.98460
C	1.23440	1.56730	4.25110
O	-0.06860	1.76540	4.54040
C	-0.34860	2.30050	5.84420
O	3.85520	1.03850	3.31530
Ti	4.13280	1.75770	5.22010
Cl	3.81920	-0.46840	5.92800
Cl	6.39750	1.50460	4.99000
O	2.08290	1.86630	5.13430
Cl	4.08880	2.58200	7.35700
Cl	4.12990	3.89870	4.24200
H	0.70130	0.81940	2.30340
H	4.32700	-0.33520	-0.01640
H	4.95610	0.99910	1.00290
H	4.85730	-0.64160	1.66900
H	-1.43380	2.38350	5.88920
H	0.01940	1.63310	6.62470
H	0.11800	3.27850	5.97040

Mol: **2’**

C	0.64789	2.61541	1.27158
C	0.99558	2.29662	-0.02849

O	0.13261	2.17872	-1.03013
C	-1.26619	2.38195	-0.78700
C	1.66487	2.70822	2.24626
O	1.26771	3.02573	3.47112
C	2.28669	3.13388	4.49266
O	2.89172	2.51470	2.02634
Ti	3.96798	1.98838	0.35516
Cl	4.57167	0.13329	1.39986
O	2.21299	2.07815	-0.41265
Cl	4.83055	1.52095	-1.65431
Cl	5.24858	3.75234	0.78510
H	-1.74811	2.22478	-1.74844
H	-1.45488	3.40052	-0.43966
H	-1.64210	1.65733	-0.06083
H	1.74755	3.41070	5.39471
H	2.79462	2.17848	4.62236
H	3.01239	3.90078	4.22311
H	-0.36894	2.80080	1.57267

Mol: **3**

C	0.51691	2.24347	-2.28614
C	1.47933	1.59970	-1.52915
O	1.42734	0.26505	-1.31156
C	0.27435	-0.46691	-1.66375
C	0.48887	3.65700	-2.54377
O	-0.46173	3.93625	-3.50717
C	-0.56650	5.29316	-3.90376
O	1.13474	4.55410	-2.05057
Ti	3.84257	2.19818	0.41692
Cl	4.56740	0.06375	0.19687
O	2.50368	2.15760	-1.00484
Cl	5.33472	3.12495	-1.07510
Cl	5.15387	2.74741	2.24593
H	0.43637	-1.48120	-1.26439
H	0.15363	-0.52586	-2.75266
H	-0.60963	-0.03625	-1.21244
H	-1.48117	5.37250	-4.46956
H	-0.58700	5.94954	-3.04719
H	0.28564	5.57526	-4.52996
H	-0.24479	1.67289	-2.76651
C	1.92119	4.64060	0.53360
O	3.08928	4.29586	0.59177
H	1.12493	3.88690	0.51451
C	2.03754	1.66655	1.89602
C	1.50244	6.08537	0.61138
H	0.68700	6.16819	-0.10843
C	2.62459	7.04206	0.24064
H	3.48038	6.92135	0.90148
H	2.97724	6.83372	-0.77494
H	2.27464	8.06441	0.28485
C	0.94005	6.32814	2.02691
H	1.74126	6.23553	2.76406

H	0.51968	7.33235	2.08783
H	0.15995	5.60620	2.27673

Mol: **3'**

Ti	3.86691	2.34422	0.18264
Cl	3.77102	0.41344	1.29068
Cl	4.71360	1.62379	-1.79447
Cl	5.80944	3.14412	1.04966
C	0.53847	3.02254	0.99211
C	1.57373	3.51571	1.78011
O	1.37215	4.20777	2.90469
C	0.03609	4.45229	3.35843
C	0.84764	2.32360	-0.18752
O	-0.19437	1.89390	-0.89664
C	0.08724	1.14229	-2.09722
O	2.01186	2.08303	-0.61864
O	2.81430	3.36647	1.50929
H	0.14558	5.01702	4.28168
H	-0.48594	3.51444	3.56222
H	-0.52338	5.04355	2.62825
H	-0.89003	0.87717	-2.49442
H	0.64191	1.75446	-2.80771
H	0.66653	0.24905	-1.85954
H	-0.49856	3.15705	1.24500
C	4.44717	5.25080	-1.04523
O	3.66976	4.32575	-0.88485
H	5.45603	5.18635	-0.60328
C	4.11933	6.48306	-1.83037
H	3.07256	6.40959	-2.13405
C	4.32877	7.72589	-0.94543
H	5.36497	7.79526	-0.59901
H	4.10790	8.62779	-1.51978
H	3.67614	7.71146	-0.06869
C	5.02248	6.51497	-3.08056
H	6.08103	6.54165	-2.80423
H	4.85651	5.64213	-3.71561
H	4.80524	7.41116	-3.66457

Mol: **4**

C	0.71980	2.91427	-0.97759
C	1.38444	1.54389	-1.13365
O	0.69775	0.57284	-1.77668
C	-0.64693	0.74920	-2.22672
C	0.74023	3.62622	-2.32187
O	-0.38325	4.38330	-2.47073
C	-0.44149	5.15560	-3.68057
O	1.58451	3.53510	-3.17080
Ti	4.06715	2.47142	0.54300
Cl	5.16456	0.41448	0.65468
O	2.48155	1.25230	-0.73048
Cl	5.08123	2.93399	-1.49844
Cl	5.44774	3.73491	1.82079

H	-0.88699	-0.16638	-2.76439
H	-0.74969	1.59758	-2.90644
H	-1.33706	0.86066	-1.38575
H	-1.40179	5.66683	-3.65453
H	0.37517	5.87899	-3.71190
H	-0.37113	4.50728	-4.55581
H	-0.33126	2.77221	-0.71812
C	1.33974	3.71025	0.23697
O	2.71722	3.70605	0.21675
H	1.00490	3.13314	1.11205
C	2.68885	1.70034	2.38290
C	0.80658	5.15891	0.39483
H	-0.24558	5.16632	0.08432
C	1.58754	6.16920	-0.45789
H	2.63049	6.19525	-0.13875
H	1.58712	5.92287	-1.52104
H	1.15736	7.16978	-0.34439
C	0.88154	5.55459	1.87790
H	1.90985	5.47372	2.23825
H	0.54371	6.58582	2.02369
H	0.26133	4.90114	2.49804

Mol: **4’**

Ti	4.23545	2.11125	0.07065
Cl	3.32998	0.12305	0.73149
Cl	4.95253	1.46964	-1.94767
Cl	6.09267	2.03862	1.29053
C	1.91976	4.45179	0.39563
C	2.22096	3.81699	1.74449
O	1.68369	4.27945	2.86530
C	0.70409	5.33590	2.87931
C	1.43743	3.36777	-0.54194
O	0.24580	3.59914	-1.06604
C	-0.25040	2.59387	-1.99561
O	2.10375	2.38096	-0.79755
O	2.99951	2.88404	1.82052
H	0.42971	5.44380	3.92538
H	-0.17756	5.06115	2.29762
H	1.13170	6.27252	2.51707
H	-1.23030	2.95190	-2.29754
H	0.42228	2.51711	-2.84871
H	-0.31648	1.62983	-1.49325
H	1.18505	5.24684	0.45270
C	3.30328	4.99593	-0.16346
O	4.18943	3.93837	-0.25205
H	3.67438	5.72178	0.57822
C	3.16697	5.72383	-1.52113
H	2.78407	4.99404	-2.24521
C	2.20181	6.91533	-1.45274
H	2.49803	7.61915	-0.66693
H	2.21588	7.46246	-2.39816
H	1.16618	6.61402	-1.27361

C	4.55858	6.16546	-1.99450
H	4.98559	6.90767	-1.31164
H	5.24029	5.31687	-2.04467
H	4.49368	6.62132	-2.98572

Mol: TS III.a

C	0.55520	2.84350	-1.21730
C	1.37800	1.67090	-1.12530
O	0.82970	0.46270	-0.88460
C	-0.58450	0.28140	-0.87940
C	0.77660	3.82980	-2.27220
O	-0.39440	4.55170	-2.45830
C	-0.31220	5.58510	-3.44040
O	1.76770	4.06090	-2.91970
Ti	4.05650	2.29440	0.24760
Cl	5.22950	0.33420	0.09690
O	2.61910	1.67800	-1.17830
Cl	5.19610	3.30010	-1.46300
Cl	5.28210	3.31970	1.88160
H	-0.73550	-0.79550	-0.83960
H	-1.04460	0.68520	-1.78540
H	-1.04060	0.73900	0.00390
H	-1.32560	5.96800	-3.55250
H	0.35590	6.38620	-3.11630
H	0.05600	5.19590	-4.39090
H	-0.48880	2.73260	-0.96460
C	1.45490	3.89840	0.47960
O	2.70300	3.81190	0.29550
H	0.99150	3.18390	1.16730
Cl	2.59620	1.27100	1.89810
C	0.83020	5.26660	0.38760
H	0.20600	5.33880	-0.50340
C	1.97200	6.26870	0.24390
H	2.63040	6.21600	1.14710
H	2.57080	6.02350	-0.66890
H	1.55210	7.30140	0.14820
C	0.01770	5.61560	1.63130
H	0.67000	5.53750	2.53700
H	-0.37190	6.66060	1.54120
H	-0.84080	4.90450	1.72760

Mol: TS III.b

TI	4.15790	2.14800	0.19080
Cl	3.66810	0.08840	0.93910
Cl	5.05270	1.56450	-1.77600
Cl	5.99750	2.54860	1.38110
C	1.39720	4.10790	0.46800
C	1.98210	3.68370	1.71980
O	1.58510	4.18780	2.88750
C	0.40620	5.00380	2.98660
C	1.36350	3.11930	-0.58250
O	0.37830	3.26580	-1.46170

C	0.35450	2.32470	-2.56560
O	2.21300	2.22730	-0.72180
O	2.94290	2.90100	1.76890
H	0.27070	5.17460	4.05160
H	-0.46490	4.48430	2.58300
H	0.54660	5.96210	2.48130
H	-0.49330	2.62850	-3.17350
H	1.28470	2.38050	-3.12990
H	0.21980	1.31180	-2.18740
H	0.56850	4.80060	0.47570
C	3.20640	5.06490	-0.15320
O	3.97890	4.07940	-0.38580
H	3.32180	5.57980	0.80930
C	2.77960	5.93580	-1.30600
H	1.71270	5.83250	-1.50590
C	3.13270	7.40140	-1.06980
H	4.22910	7.49280	-0.86610
H	2.87110	7.99920	-1.97880
H	2.55670	7.78700	-0.19140
C	3.53300	5.45140	-2.54150
H	4.63430	5.54510	-2.36720
H	3.27630	4.38040	-2.73880
H	3.24080	6.07370	-3.42430

Mol: **5**

C	2.46957	2.45283	-2.89322
C	2.76965	1.44035	-1.84298
O	2.33314	0.21294	-2.15185
C	2.54976	-0.79260	-1.13545
C	2.12344	2.02578	-4.28097
O	2.94701	1.05272	-4.72857
C	2.66569	0.56033	-6.04438
O	1.24914	2.50538	-4.96705
Ti	3.89114	2.87045	1.16105
Cl	6.01373	2.18114	0.41785
O	3.30721	1.67886	-0.78155
Cl	4.57151	3.56635	3.26625
H	2.07455	-1.69187	-1.52230
H	2.10339	-0.47811	-0.19229
H	3.61939	-0.95056	-0.99090
H	3.39939	-0.22285	-6.22476
H	1.65274	0.15591	-6.09491
H	2.76410	1.35612	-6.78556
C	2.50287	3.74840	-2.52699
O	3.42143	4.25388	0.42287
H	2.78640	3.95567	-1.49276
Cl	2.01193	1.63689	1.91381
C	2.20887	4.96280	-3.35409
H	2.10556	4.69313	-4.40690
C	3.35514	5.97881	-3.18912
H	3.48841	6.24585	-2.13749
H	4.30252	5.57035	-3.55042

H	3.13739	6.88943	-3.75615
C	0.86675	5.56479	-2.88580
H	0.89777	5.80348	-1.81913
H	0.65732	6.48608	-3.43844
H	0.04756	4.86438	-3.06091

Mol: **5’**

Ti	3.45004	1.28292	0.88376
Cl	2.33806	-0.37216	-0.25674
Cl	3.04538	0.65886	3.05855
C	2.25239	4.73332	0.01989
C	2.85201	4.41287	1.34535
O	2.86463	5.41671	2.20200
C	3.40039	5.12623	3.52535
C	2.47787	3.69984	-1.02326
O	2.29032	4.10458	-2.26729
C	2.51286	3.10406	-3.30526
O	2.83675	2.55496	-0.78250
O	3.30359	3.31608	1.65069
H	3.27411	6.04912	4.08374
H	4.45179	4.85493	3.44255
H	2.84605	4.30487	3.97668
H	2.27251	3.61218	-4.23461
H	3.55382	2.78497	-3.28617
H	1.86492	2.24548	-3.13723
C	1.54345	5.87454	-0.13237
O	5.03666	1.18916	0.57797
H	1.50246	6.50738	0.75103
C	0.79338	6.41539	-1.30772
H	0.62630	5.62804	-2.04046
C	-0.56425	6.97379	-0.84400
H	-0.43436	7.78903	-0.12563
H	-1.11709	7.36602	-1.70078
H	-1.17750	6.20033	-0.37504
C	1.65323	7.51383	-1.97649
H	1.88639	8.31956	-1.27462
H	2.59002	7.10229	-2.35590
H	1.10203	7.94643	-2.81498

Mol: **TS1**

C	0.89390	2.83350	0.94530
O	1.19140	2.64370	2.34840
C	1.69560	1.44800	2.67000
C	2.07910	1.20890	4.06180
C	1.80660	2.26330	5.05440
O	2.27480	1.87610	6.30470
C	2.04690	2.81500	7.35630
O	1.74350	0.57890	1.78650
Ti	3.27910	-0.92720	1.41250
Cl	5.00530	-2.38410	1.04730
Cl	1.98750	-2.65250	2.61290
O	3.76310	-0.27170	3.03280

C	3.42340	0.38730	4.21400
Cl	1.92550	-1.43110	-0.45550
Cl	4.34190	0.81830	0.17670
O	1.15940	3.28310	4.95220
N	-0.08550	-0.36360	4.90300
C	0.43140	-1.60120	5.57180
C	1.18470	-1.35790	6.87550
C	-0.87040	0.52130	5.80980
C	-2.15160	-0.08590	6.38390
C	-0.83100	-0.76520	3.66110
C	-1.54740	0.37380	2.94230
H	0.58360	3.87390	0.86870
H	0.09450	2.16360	0.62640
H	1.78010	2.63480	0.34350
H	2.54170	2.40090	8.23470
H	2.46810	3.79170	7.10830
H	0.97810	2.94260	7.54930
H	0.95230	0.33100	4.49490
H	3.28230	-0.37950	4.98730
C	4.66150	1.23850	4.63040
H	-0.08960	-1.22470	3.00720
H	-1.55090	-1.54620	3.93150
H	1.08340	-2.07760	4.83820
H	-0.41260	-2.27940	5.74380
H	-0.20170	0.81620	6.61780
H	-1.09640	1.43030	5.25260
H	0.52560	-1.06780	7.69900
H	1.68090	-2.28820	7.16260
H	1.94900	-0.58790	6.76350
H	-2.85820	-0.37400	5.60250
H	-1.95130	-0.96500	7.00090
H	-2.64420	0.65750	7.01670
H	-2.44860	0.70600	3.46510
H	-0.90480	1.24130	2.79310
H	-1.84610	0.01390	1.95540
C	5.87260	0.31220	4.81460
C	4.96780	2.35480	3.62430
H	4.43190	1.68490	5.59980
H	5.84970	2.91950	3.94490
H	5.16470	1.94200	2.63260
H	4.13920	3.06300	3.53400
H	6.74000	0.88300	5.16350
H	5.66590	-0.46990	5.55340
H	6.13190	-0.17730	3.87420

Mol: **I**

C	0.95020	2.68900	0.66860
O	1.32280	2.71890	2.04940
C	2.14200	1.71240	2.45130
O	2.55240	0.95040	1.51970
Ti	3.45150	-0.87350	1.57920
Cl	1.33650	-1.81910	2.34340

C	2.43690	1.59820	3.81370
C	3.41560	0.51780	4.29410
O	3.81670	-0.35910	3.27100
C	1.72480	2.37960	4.78570
O	0.94240	3.30910	4.65780
O	2.01180	1.93580	6.09630
C	1.32040	2.63100	7.11580
Cl	2.61770	-1.12830	-0.70930
Cl	5.46180	0.14760	0.65500
Cl	4.52670	-2.99420	1.68070
H	0.23680	3.50800	0.55430
H	0.49250	1.73570	0.39940
H	1.81510	2.84240	0.01910
H	1.65470	2.19120	8.05870
H	1.54540	3.70310	7.10230
H	0.23500	2.51970	7.01850
H	2.90160	-0.09230	5.04990
C	4.70260	1.08200	4.96910
H	4.35560	1.70390	5.79950
C	5.53260	1.94530	4.01260
H	5.86110	1.36530	3.14720
H	4.94540	2.78960	3.64160
H	6.41760	2.34420	4.52580
C	5.53860	-0.06970	5.54440
H	5.86170	-0.74010	4.74500
H	6.42710	0.31200	6.06330
H	4.95560	-0.65960	6.26100

Mol: **TS2**

C	0.31011	1.98570	0.76288
O	0.54509	2.06702	2.18498
C	1.31767	1.08409	2.66644
O	1.62277	0.13641	1.94622
Ti	3.75308	-0.72572	1.56294
O	4.00586	-0.25683	3.16559
Cl	5.86765	-1.63030	1.05207
Cl	2.73132	-2.87398	2.30792
Cl	2.65390	-1.20262	-0.72391
Cl	4.21473	1.53206	0.67827
C	1.78829	1.20283	4.05322
C	2.36776	0.02596	4.51505
C	1.79684	2.50820	4.71084
O	1.22397	3.52166	4.36955
O	2.54072	2.51742	5.88234
C	2.58757	3.77432	6.54494
H	-0.21105	2.91059	0.51326
H	-0.30330	1.11466	0.52423
H	1.25613	1.90004	0.22768
H	3.20568	3.61797	7.43055
H	3.03204	4.54253	5.90675
H	1.58808	4.11099	6.83673
H	2.05544	-0.86747	3.98657

C	2.99842	-0.26842	5.85328
C	3.83676	-1.55318	5.80349
H	3.63660	0.56661	6.13845
C	1.87788	-0.39665	6.91121
H	4.26801	-1.75530	6.79255
H	3.22878	-2.41157	5.50340
H	4.63083	-1.45343	5.06519
H	2.31359	-0.63977	7.88750
H	1.31219	0.53140	7.00757
H	1.18489	-1.20205	6.64534

Mol: **TS'**

C	1.69663	3.06396	3.99919
O	1.31764	3.75964	2.77289
C	2.09567	3.52656	1.72610
O	3.07468	2.80317	1.80138
Ti	4.30238	2.22551	0.00672
O	4.11265	3.88332	-0.42559
Cl	3.23677	-0.13001	1.00881
Cl	5.06806	1.31813	-1.89054
Cl	6.12677	2.26670	1.31539
O	2.21850	2.17804	-0.76678
C	1.44961	3.10608	-0.58910
O	0.33503	3.21644	-1.30022
C	0.13452	2.18667	-2.31342
C	1.68846	4.20962	0.43503
C	2.83103	5.06252	-0.04537
C	3.63283	5.99032	0.86643
C	4.72250	6.70219	0.04998
C	2.83434	7.01768	1.71355
N	-1.09682	5.35975	0.74253
C	-1.73321	4.08920	1.16260
C	-3.22364	4.08976	1.58770
C	-0.92662	6.39525	1.78578
C	-2.09271	7.32091	2.14854
C	-1.44032	5.86496	-0.60909
C	-2.91860	6.03399	-0.97952
H	0.91230	3.30375	4.71175
H	2.66409	3.42810	4.34221
H	1.75749	1.99372	3.80810
H	-0.81203	2.43678	-2.78476
H	0.95307	2.21376	-3.03107
H	0.09985	1.20717	-1.83938
H	0.38385	4.89306	0.58191
H	2.66722	5.45243	-1.04776
H	-0.57380	5.87525	2.67990
H	-0.09570	7.00964	1.43082
H	-0.98215	5.17723	-1.32239
H	-0.92400	6.82345	-0.71786
H	-1.58758	3.39825	0.33125
H	-1.12002	3.71344	1.98336
H	-2.43663	7.90457	1.29278

H	-2.94339	6.78827	2.57365
H	-1.74251	8.03100	2.90326
H	-3.44524	5.07826	-0.98977
H	-3.45393	6.71152	-0.31367
H	-2.97639	6.44684	-1.99068
H	-3.82177	3.46121	0.92491
H	-3.33765	3.69960	2.60110
H	-3.66719	5.08237	1.56921
H	4.14146	5.31797	1.56144
H	2.98882	8.02668	1.32061
H	1.75712	6.87465	1.77673
H	3.21558	7.02154	2.73709
H	5.35655	7.29560	0.71312
H	5.34898	5.98168	-0.47411
H	4.27528	7.38371	-0.68195