Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

A DFT study on the NHC catalysed Michael addition of enols to α,β-unsaturated acyl-azoliums. A base catalysed C-C bond-formation step.

Supporting Information

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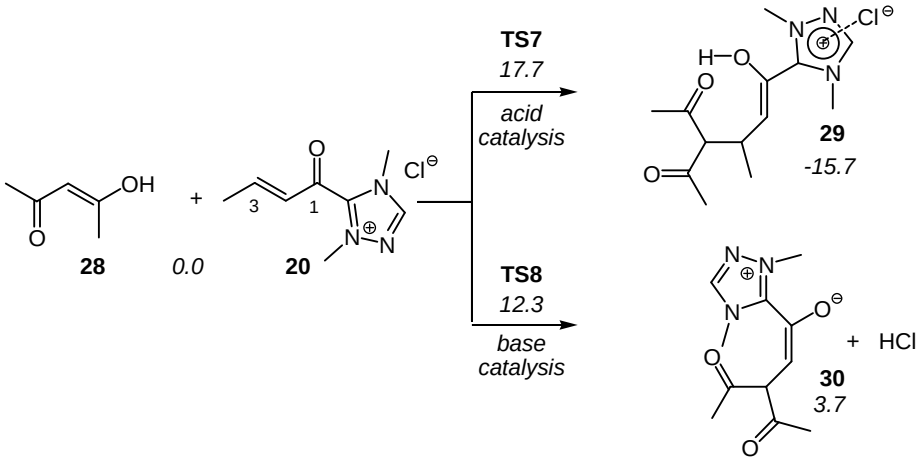
*1. Study of the acid and base catalysed conjugated additions of the enol of acetyl acetone **2** to acyl-azolium intermediate **20**.*

In order to assert the base catalyst role of chloride anion in these NHC catalysed annulation reactions of α,β-unsaturated acyl-azolium intermediates, the C-C bond-formation step in the reactions involving acetyl acetone **2** was analysed (see Scheme 2 in the manuscript). Two paths were studied for this step (see Scheme S1): i) *path a* corresponds to the acid catalysed conjugated addition of enol **28**; and ii) *path b* corresponds to the base catalysed conjugated addition of enol **28** to acyl-azolium intermediate **20**. Relative energies, in gas phase and in toluene (single point energies from gas phase geometries), are given in Table S1.



Scheme S1. Relative energies in toluene, in kcal/mol, are given in italic.

Table S1. Total (E, in au) and relative[a] (ΔE, in kcal/mol) energies, in gas phase and in toluene, of the stationary points involved in the conjugated nucleophilic attack of enol **28** on acyl-azolium intermediate **20**.

	Gas phase		*Toluene*	
	MPWB1K/6-31G**		MPWB1K/6-311G**	
	E	ΔE	E	ΔE
20	-1011.497310		-1011.654325	
28	-345.636681		-345.718144	
TS7	-1357.107398	16.7	-1357.344334	17.7
29	-1357.157224	-14.6	-1357.397437	-15.7
TS8	-1357.115950	11.3	-1357.352849	12.3
30	-1357.134124	-0.1	-1357.366523	3.7

(a) Relative to **20** plus **28**.

Along *path a*, the enol hydrogen of **28** forms a hydrogen bond (HB) with the carbonyl oxygen of acyl-azolium **20**, thus activating electrophilically this α,β-

unsaturated acyl-azolium intermediate. The activation energy associated with the conjugated addition of enol **28** to **20**, *via* **TS7**, is 17.7 kcal/mol; the C-C bond-formation step being exothermic by -15.7 kcal/mol. This activation energy is similar to that found in the conjugated addition of enol **21** to acyl-azolium **20**.

Along *path b*, the enol hydrogen of **28** forms a HB with the chloride anion, thus activating nucleophilically enol **28**. The activation energy associated with the conjugated addition of enol **28** to **20**, *via* **TS8**, is 12.3 kcal/mol; the C-C bond-formation step being endothermic by 3.7 kcal/mol. Although this activation energy is 6.1 kcal/mol higher than that associated with the conjugated addition of enol **21** to **20**, *via* **TS2**, **TS8** remains 5.4 kcal/mol below **TS7**, showing that the base catalysed reaction is yet again favoured over the acid catalysed one.

The geometries of the transition states (TSs) involved in the acid and base catalysed conjugated additions of enol **28** to acyl-azolium **20** are given in Figure S1. At **TS7**, associated with the acid catalysed nucleophilic attack of enol **28** on the conjugated C3 carbon of acyl-azolium intermediate **20**, the length of the C3-C6 forming bond is 2.042 Å. At this TS, the length of the O8-H9 bond is 1.023 Å, while the distance between the acidic H9 hydrogen and the carbonyl O4 oxygen is 1.479 Å; this short H9-O4 distance points to a strong HB.

At **TS8**, associated with the base catalysed nucleophilic attack of enol **28** on the conjugated C3 carbon of acyl-azolium **20**, the length of the C3-C6 forming bond is 2.070 Å. At this TS, the length of the O8-H9 bond is 1.041 Å, while the distance between the acidic H9 hydrogen and chloride anion is 1.793 Å; this short H9-Cl^- distance points to a strong HB. These geometrical parameters are similar to those found at **TS2**.

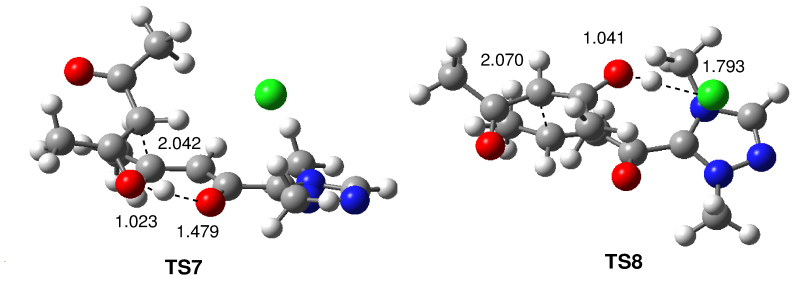


Figure S1. Gas phase geometries of the TSs involved in the acid and base catalysed conjugated additions of enol **28** to acyl-azolium **20**.

*2. ELF bonding analysis along the conjugated nucleophilic approach of enol **21** to acyl-azolium **20**.*

In order to understand the C-C bond formation process along the conjugated nucleophilic approach of enol **21** to acyl-azolium **20**, a topological ELF analysis along the IRC of the corresponding reaction path was carried out, finding ten phases associated to relevant electron density changes. Each of these phases represent a bonding change along the reaction path. The most relevant ELF valence basins and their corresponding N populations of selected points along the reaction path are given in Table S2. For the sake of simplicity, only the monosynaptic V(A) and the disynaptic V(A,B) basins involved in the forming and breaking bond processes will be discussed.

In *Phase I*, d(C3-C6) ≥ 2.729 Å, the presence of two disynaptic basins at acyl-azolium **20**, namely V(C2,C3) and V'(C2,C3), with a population of 1.71 and 1.63e, together with the presence of two disynaptic basins at enol **21**, V(C6,C7) and V'(C6,C7), with a population of 1.79 and 1.71e, which account for the C2=C3 and C6=C7 double bonds, are the most remarkable feature of the reagents. In enol **21**, the disynaptic basin V(O8,H9), which integrates 1.98e, suggest the presence of a O-H σ bond. In *Phase II*, 2.729 > d(C3-C6) ≥ 2.483 Å, the disynaptic basins V(C2,C3) and V'(C2,C3) of acyl-azolium **20** merge into a new disynaptic basin, namely V(C2,C3), with a population of 3.25e. In *Phase III*, 2.483 > d(C3-C6) ≥ 2.188 Å, the disynaptic basins V(C6,C7) and V'(C6,C7) of enol **21** merge into the disynaptic basin V(C6,C7), which integrates 3.30e. It is in *Phase IV*, 2.188 > d(C3-C6) ≥ 2.153 Å, where the electron density experiences the first significant change towards the C-C bond formation. Thus, a monosynaptic basin located at C6, V(C6), integrating 0.40e, appears at enol **21**. Additionally, a monosynaptic basin, V(C2), integrating 0.30e, appears at the C2 carbon of acyl-azolium **20**. Note that the appearance of this V(C2) monosynaptic basin, which has been observed in other ELF analyses of polar reactions,[2] remains until *Phase VII*. The second most relevant change along the IRC appears in *Phase V*, 2.153 > d(C3-C6) ≥ 2.109 Å, with the creation of a new monosynaptic basin at C3, V(C3), integrating 0.17e, while the monosynaptic basin V(C6) increases its electronic integration to 0.45e. Note that monosynaptic basins V(C3) and V(C6) are responsible for the formation of the new C3-C6 single bond in the next phase. Note that **TS2** is located in *Phase V*.

Table S2. Valence basin populations N calculated from the ELF along the ten phases associated with the nucleophilic approach of enol **21** to acyl-azolium **20**. d(A-B) stands for the distance between A and B atoms (in angstroms).

Phase	*I*	*II*	*III*	*IV*	*V* **TS2**	*VI*	*VII*	*VIII*	*IX*	*X*
d(C3-C6)	2.729	2.483	2.188	2.153	2.109	2.004	1.865	1.748	1.727	1.587
d(O9-H9)	1.022	1.034	1.059	1.064	1.071	1.091	1.138	1.301	1.372	1.744
d(Cl-H9)	1.940	1.884	1.821	1.814	1.801	1.770	1.705	1.523	1.452	1.330
V(C1,C2)	2.38	2.50	2.74	2.77	2.83	2.93	3.07	3.52	3.55	3.65
V(C2,C3)	1.71	3.25	3.15	2.83	2.59	2.44	2.28	2.17	2.13	2.07
V'(C2,C3)	1.63									
V(C1,O4)	2.23	2.17	2.05	2.05	2.03	1.99	1.90	1.84	1.80	1.70
V(C6,C7)	1.79	1.75	3.30	2.90	2.79	2.66	2.53	2.32	2.28	2.14
V'(C6,C7)	1.71	1.66								
V(C7,O8)	1.60	1.65	1.78	1.79	1.82	1.86	2.00	2.10	2.13	2.55
V(C2)				0.30	0.34	0.34	0.33			
V(C3)					0.17					
V(C6)				0.40	0.45					
V(C3,C6)						0.91	1.21	1.45	1.52	1.73
V(O8,H9)	1.98	1.91	1.89	1.86	2.00	2.04				
V(H9)							0.47	0.47		
V(H9,Cl10)									1.38	1.67

Indeed, it is in *Phase VI*, 2.109 > d(C3-C6) ≥ 2.004 Å, where the formation of the C3-C6 single bond is initiated with the creation of the new disynaptic basin V(C3,C6), which integrates 0.91e. This disynaptic basin comes from the merging of monosynaptic basins V(C3) and V(C6), which have disappeared at the beginning of this phase. Immediately after the formation of the C3-C6 single bond, in *Phase VII*, 2.004 > d(C3-C6) ≥ 1.865 Å, the H9 hydrogen transfer process from the O8 oxygen to the chloride anion starts, d(O8-H9) = 1.139 Å. From *Phase I* to *Phase VI*, the population of the V(O8,H9) disynaptic basin varied from 1.98 to 2.04e. It is in *Phase VII* where this disynaptic basin disappears and a monosynaptic basin, namely V(H9), with a population of 0.47e, appears at H9. In *Phase VIII*, 1.865 > d(C3-C6) ≥ 1.748 Å, the monosynaptic basin V(C2) disappears. In *Phase IX*, 1.748 > d(C3-C6) ≥ 1.727 Å, the monosynaptic basin V(H9) disappears to be replaced by the new V(H9,Cl10) disynaptic basin with 1.38e, indicating that the H9-Cl10 single bond-formation takes place. Finally, in *Phase X*, 1.727 > d(C3-C6) ≥ 1.587 Å, only the increase of the population of the disynaptic basins V(C3,C6) and V(H9,Cl10) is observed. At the end of this phase, both C3-C6 and H9-Cl10 single bonds have been completely formed.

References

1 (a) L. R. Domingo, P. Pérez, M. J. Aurell, J. A. Sáez, *Curr. Org. Chem.* **2012**, *16*, 2343. (b) L. R. Domingo, P. Pérez, J. A. Sáez, J. A. *Tetrahedron* **2013**, *69*, 107.

Table S3. Total energies, in au, in gas phase and in toluene, of the stationary points involved in the NHC catalysed reaction of but-2-ynal **14** with methyl 2-oxopropanoate **15**.

	gas phase	*Toluene*
	MPWB1K/6-31G**	MPWB1K/6-311G**
14	-229.857474	-229.914130
16	-320.675618	-320.748352
TS1	-550.531521	-550.657468
18	-550.540139	-550.669794
19	-550.569188	-550.691981
20 + Cl^-	-1011.497310	-1011.653525
21	-381.521652	-381.618008
TS2	-1393.008824	-1393.261688
22 + HCl	-1393.041095	-1393.286170
25	-1393.032273	-1393.281082
TS5	-1392.996133	-1393.247012
26	-1393.067661	-1393.318864
TS6	-1392.992752	-1393.245868
27	-1393.059059	-1393.310506
22	-932.175889	-932.393784
23	-932.166953	-932.383115
TS3	-932.165192	-932.381357
24	-932.177733	-932.393204
TS4	-932.165656	-932.377950
17 + **16**	-932.188624	-932.402207

Table S4. MPWB1K/6-31+G** total (E, in au) and relative[a] (ΔE, in kcal/mol) energies, in gas phase and in toluene, of the stationary points involved in the acid and base catalysed conjugated nucleophilic addition of enol **21** to acyl-azolium intermediate **20**.

	Gas phase		*Toluene*	
	E	ΔE	E	ΔE
20	-1011.513617		-1011.526236	
21	-381.5360255		-381.539232	
TS2	-1393.036332	8.35	-1393.052791	7.96
TS6	-1393.021112	17.90	-1393.037886	17.31
22	-1393.067792	-11.39	-1393.077097	-7.30
27	-1393.08665	-23.22	-1393.101423	-22.56

(a) Relative to **20** plus **21**.

Table S5. MPWB1K/6-31G** total and relative[a] enthalpies (H and ΔH), entropies (S and ΔS) free Energies (G and ΔG), computed at 40 °C and 1 atm in toluene, of the stationary points involved in the C-C bond-formation step.

	H au	Δ H kcal/mol	S cal/mol K	Δ S cal/mol K	G au	Δ G kcal/mol
20	-1011.431761		119.2		-1011.491196	
21	-381.505901		83.6		-381.547592	
TS2	-1392.927955	6.1	151.2	-51.6	-1393.003353	22.2
TS5	-1392.914069	14.8	155.3	-47.4	-1392.991542	29.6
TS6	-1392.911274	16.6	152.5	-50.3	-1392.987328	32.3
22	-1392.952390	-9.2	155.2	-47.5	-1393.029800	5.6
25	-1392.945231	-4.7	154.7	-48.1	-1393.022372	10.3
26	-1392.980528	-26.9	150.7	-52.1	-1393.055688	-10.6
27	-1392.971392	-21.2	149.0	-53.8	-1393.045695	-4.3

(a) Relative to **20** plus **21**.

MPWB1K/6-31G** computed total energies, unique imaginary frequency, and cartesian coordinates of the stationary points involved NHC catalysed Michael addition of enols to α,β-unsaturated acyl-azoliums.

14

E(RmPW+HF-B95) = -229.857473723 a.u.

C	-0.10749100	0.20648200	0.00920600
C	-1.53321500	0.39375700	-0.00199500
O	-2.32861300	-0.50662800	-0.00162800
C	1.08607000	0.05833400	0.00178700
C	2.51961200	-0.13093600	-0.00432700
H	-1.85999000	1.44292800	-0.01240200
H	2.87184800	-0.36474200	0.99744000
H	2.79467500	-0.95575600	-0.65630400
H	3.03251300	0.76477400	-0.34373600

16

E(RmPW+HF-B95) = -320.675618364 a.u.

C	0.00197900	-0.99196100	-0.00036800
N	1.02525400	-0.12906300	-0.00015400
N	-1.04226300	-0.11569900	-0.00043700
N	0.70171400	1.19035100	0.00018900
C	2.41344900	-0.48864400	0.00020900
C	-0.58440100	1.16345400	-0.00006800
C	-2.42251200	-0.51632300	0.00035800
H	-1.21118500	2.03557400	-0.00048300
H	-2.44025400	-1.59818600	0.00284700
H	-2.93480000	-0.15172600	-0.88566200
H	-2.93491300	-0.14750800	0.88453700
H	2.90564400	-0.09188300	-0.88227300
H	2.46700100	-1.56909100	-0.00189700
H	2.90448000	-0.09545400	0.88495800

17 + 16

E(RmPW+HF-B95) = -932.188623840 a.u.

C	1.72440200	1.62210300	0.40076500
C	2.64884600	0.79908100	-0.43680400
C	3.03802900	-0.51429900	0.22368000
C	3.85956200	-1.38539900	-0.70505100
C	1.76466200	-1.16916500	0.64180300
C	-0.61232500	0.53406600	-1.55300100
N	-1.63864600	1.21811400	-1.03978300
N	-1.20114100	-0.68074800	-1.74336000
N	-2.80011100	0.53394000	-0.89876600
C	-1.57237800	2.56416500	-0.54304100
C	-2.49692800	-0.63716400	-1.34091600
C	-0.50541200	-1.86056400	-2.17975500

C	0.74187600	-0.41705400	1.01925900
C	-0.57438700	-1.00138200	1.35070400
O	-1.42378900	-0.10498600	1.81164200
C	-2.68420100	-0.61497000	2.20945100
H	3.63234600	-0.30462000	1.11771300
O	1.71521800	2.81149900	0.45668000
H	-2.35996500	3.16350600	-0.98730200
H	-0.60039000	2.96338600	-0.79864500
H	-1.67622100	2.55780300	0.53747700
H	-3.17534800	-1.46829800	-1.38763000
H	0.45585000	-1.54863000	-2.56809400
H	-1.06042900	-2.36519800	-2.96502200
H	-0.35976400	-2.53970700	-1.34351300
H	3.30200700	-1.61195000	-1.61166500
H	4.12373800	-2.32558800	-0.22766000
H	4.77941300	-0.88436400	-0.99423800
H	1.62588600	-2.23776700	0.60607200
O	0.81344000	0.93564200	1.13962900
O	-0.82861000	-2.17108800	1.21404800
H	-3.29753300	0.24842300	2.42711600
H	-3.12621100	-1.20244000	1.41384600
H	-2.56916500	-1.23762600	3.09159800
H	2.08206000	0.59010100	-1.34668300
H	3.50247000	1.41879000	-0.68856600

18

E(RmPW+HF-B95) = -550.540139137 a.u.

C	-1.74096700	-0.28544000	0.27486100
C	-0.52580400	-0.68085800	1.06913200
O	-0.33363900	-1.94221600	1.28693000
C	-2.75225100	-0.03912700	-0.32920600
C	0.63448900	-0.01504400	0.28029000
C	-3.97575200	0.23465900	-1.05866200
N	0.93615500	1.26969600	0.20683800
N	1.59362400	-0.63777100	-0.40575100
N	2.05986300	1.50161200	-0.49696000
C	0.18754500	2.35396700	0.78911400
C	2.43740000	0.32278700	-0.86057900
C	1.67633200	-2.07055900	-0.64563000
H	-0.56771900	-0.02248400	1.97749700
H	3.30890700	0.11429900	-1.45026100
H	0.90738800	-2.50418900	0.00063100
H	2.66962100	-2.41437300	-0.38007100
H	1.48092700	-2.26623700	-1.69429100
H	-3.77188700	0.74156000	-1.99929500
H	-4.50063100	-0.68980300	-1.28782400
H	-4.64905400	0.86298600	-0.48016500
H	0.40104200	2.43212900	1.85051300
H	-0.86981100	2.16432700	0.63889900
H	0.48688400	3.26244200	0.28411600

19

E(RmPW+HF-B95) = -550.569188368 a.u.

C	-1.79465000	-0.46807500	-0.00757000
C	-0.44964500	-0.87334100	0.03109000
C	-2.97639100	-0.21639000	-0.02554300
C	0.62624200	-0.03889200	0.01867500
C	-4.39080500	0.09445700	-0.06843400
N	0.66902700	1.32760900	0.00479300
N	1.96047900	-0.39398400	-0.00378300
N	1.94315400	1.80751300	-0.01594500
C	-0.42733900	2.24277200	0.07055100
C	2.67818000	0.76394900	-0.02332000
C	2.52693500	-1.71331400	-0.07785100
H	3.75139300	0.77650900	-0.04464900
H	2.31409300	-2.28545700	0.81820200
H	3.60120600	-1.60333900	-0.18407200
H	2.13227500	-2.25414700	-0.92936200
H	-4.95513400	-0.75420600	-0.44964000
H	-4.79208300	0.34382500	0.91286500
H	-4.58832700	0.93536300	-0.73097800
H	-1.03323500	2.05995500	0.95354900
H	-1.06359200	2.16163800	-0.80612500
H	0.00260400	3.23516700	0.11887700
O	-0.19158900	-2.24190400	0.01792700
H	-0.60026600	-2.61504900	0.79686800

20

E(RmPW+HF-B95) = -1011.49730951 a.u.

C	-4.37121200	0.25493600	-0.15663600
C	-3.05896300	-0.32746000	-0.51716900
C	-1.88612000	0.07695300	-0.03997100
C	-0.67290000	-0.61895500	-0.46997100
O	-0.67254800	-1.68334900	-1.04375500
C	0.66738100	0.03921200	-0.32274600
N	1.81621000	-0.63682400	-0.48417700
C	2.79312300	0.29568600	-0.56166600
N	2.32170000	1.49275500	-0.55549500
N	0.98662400	1.32129100	-0.46412700
C	1.99617500	-2.05387400	-0.25641500
C	0.15956800	2.46761800	-0.19817600
H	-4.27175300	1.07619900	0.54593300
H	-5.00890300	-0.50511000	0.29236200
H	-4.89297500	0.61231400	-1.04320900
H	-3.05147300	-1.15754600	-1.21213900
H	-1.79802500	0.86222400	0.69128400
H	3.83479600	0.05065200	-0.63467200
H	1.57420700	-2.62219000	-1.07310700
H	1.49313600	-2.29881400	0.67478800
H	3.05878500	-2.24254100	-0.16301000
H	0.73797700	3.34027100	-0.46918200
H	-0.74710800	2.42382600	-0.78925500
H	-0.07882200	2.48343800	0.86297200
Cl	0.28802900	-0.27065800	2.13708100

21

E(RmPW+HF-B95) = -381.521651979 a.u.

C	0.22511500	-0.26788800	0.00000100
C	-1.18055800	0.19839800	-0.00000400
C	-1.53088100	1.47629400	0.00001000
O	1.13235900	0.68730000	-0.00001700
O	-2.05133200	-0.81789100	-0.00000700
C	2.47615100	0.23508200	0.00000400
H	3.08757100	1.12723300	-0.00001800
H	2.67283800	-0.36404200	0.88291200
H	2.67284900	-0.36408800	-0.88287200
O	0.48120000	-1.44745600	0.00001100
H	-0.77452700	2.23925900	0.00001900
H	-2.56938500	1.75961500	0.00001600
H	-1.52612600	-1.62492000	-0.00001100

22

E(RmPW+HF-B95) = -932.175889409 a.u.

C	-1.34771700	1.62138900	-1.06185400
C	0.10564200	1.42792000	-0.82264900
C	0.51506400	0.14922800	-0.62646300
C	1.93462600	-0.06525900	-0.25779600
N	2.69946800	-1.06380300	-0.66711700
N	2.67951300	0.60431300	0.63602700
N	3.91091300	-1.05370500	-0.08857900
C	2.34480600	-2.09032100	-1.61796500
C	3.87443800	-0.03458800	0.69977200
C	2.24553400	1.70262600	1.47644300
C	-1.67056100	2.90118500	-1.80570500
C	-2.11991400	1.59455300	0.28342200
C	-1.70642300	0.45318800	1.15312300
O	-0.89245500	0.57349100	2.03208700
C	-2.30737400	-0.92541900	0.91228900
O	-3.10075400	-0.92527400	-0.15442200
C	-3.56360800	-2.20387500	-0.53391600
H	-1.70015100	0.75850600	-1.62804000
H	0.77709700	2.26924400	-0.74111300
O	-0.18857500	-0.90236000	-0.68597600
H	2.79332400	-1.86766100	-2.58016200
H	1.26146800	-2.09918600	-1.67306800
H	2.72394100	-3.03333100	-1.24504500
H	4.67681400	0.27198800	1.34245000
H	2.40722300	2.65047400	0.97514600
H	2.82208500	1.67291000	2.39356100
H	1.18857600	1.57454100	1.69106600
H	-1.31771400	3.77197700	-1.25404300
H	-2.74231100	3.01540600	-1.95292500
H	-1.19259300	2.90955800	-2.78193300
H	-3.18750900	1.54751200	0.07843500
H	-1.89779400	2.50406800	0.83786700
O	-2.12187900	-1.86857100	1.62012000
H	-4.20151000	-2.05250900	-1.39536600
H	-2.71944900	-2.83589300	-0.79180300
H	-4.11853000	-2.66729200	0.27597700

22 + HCl

E(RmPW+HF-B95) = -1393.04109485 a.u.

C	1.84972100	2.02345100	0.45223800
C	0.36590200	1.98541800	0.39325500
C	-0.19571600	0.79276200	0.70563500
C	-1.65520300	0.62060200	0.53967400
N	-2.44602600	-0.10796700	1.30665000
N	-2.42999000	1.03972200	-0.47158400
N	-3.69768700	-0.17694300	0.83168100
C	-2.08160000	-0.84444800	2.49213400
C	-3.66224100	0.52077000	-0.25104800
C	-1.99592200	1.71919900	-1.67428900
C	2.41598200	3.42423900	0.55854600
C	2.46805800	1.31062000	-0.78447200
C	1.75988900	0.04675400	-1.13088400
O	0.87676900	0.00671000	-1.95084100
C	2.10512500	-1.24889500	-0.42170600
O	3.11995500	-1.12161600	0.40934700
C	3.38236800	-2.26572700	1.20063400
H	2.15290000	1.42773900	1.31417800
H	-0.20998500	2.84375100	0.08459300
O	0.43634800	-0.25080700	1.06972900
H	-2.53338600	-0.37940900	3.36130700
H	-1.00015200	-0.84476800	2.54586800
H	-2.45023000	-1.85631800	2.37748100
H	-4.49455100	0.67138100	-0.91056200
H	-2.04033300	2.79464400	-1.54132900
H	-2.65205200	1.42212400	-2.48344700
H	-0.97808100	1.41152600	-1.88985200
H	-0.22446700	-2.08151800	-1.09999100
H	2.10233400	4.03574500	-0.28650600
H	3.50352700	3.41252400	0.57264100
H	2.07251400	3.91048900	1.46799100
H	3.52120200	1.12038000	-0.59132800
H	2.36903900	1.96042400	-1.65103600
O	1.54885700	-2.29163900	-0.65340500
H	4.21835300	-2.00583100	1.83656300
H	2.50645900	-2.50345200	1.79537000
H	3.62817600	-3.11538800	0.57196000
Cl	-1.52170300	-2.16219900	-1.21282800

23

E(RmPW+HF-B95) = -932.166953443 a.u.

C	1.22554600	-1.49842800	-0.25524700
C	2.39753300	-0.73162500	0.29403400
C	2.69567300	0.63651800	-0.35749800
C	4.01828100	1.16405900	0.16045900
C	1.57571400	1.59125600	-0.15545500
C	-0.15455900	-1.37598500	0.32831500
N	-1.21330800	-1.95308600	-0.22013600
N	-0.59621300	-0.84918800	1.48420400
N	-2.32552000	-1.76739500	0.50608500
C	-1.31369600	-2.49227600	-1.55814300
C	-1.93120800	-1.10473200	1.53275300
C	0.12792600	-0.17191400	2.54233200

C	0.38401800	1.22471000	-0.66947600
C	-0.80189000	2.09180900	-0.39515500
O	-1.94621100	1.47620600	-0.70446400
C	-3.10391500	2.24721800	-0.47207500
H	2.77670800	0.42602000	-1.42649400
O	1.38340000	-2.42134300	-1.02313500
H	-0.80182500	-3.44229700	-1.62076700
H	-0.85315500	-1.77737500	-2.22955300
H	-2.37089200	-2.59869800	-1.76011500
H	-2.55982100	-0.78722400	2.34165700
H	0.80935600	-0.85748600	3.03460700
H	-0.60267200	0.17437600	3.26325700
H	0.66017900	0.67804400	2.13724200
H	3.96969300	1.35521900	1.23201600
H	4.27234700	2.10073000	-0.32848500
H	4.82839900	0.46038300	-0.01710300
H	1.69822700	2.52347000	0.37220100
O	0.21440500	0.11384400	-1.30114300
O	-0.77112700	3.19729600	0.08022700
H	-3.94453600	1.61461100	-0.72841000
H	-3.16145100	2.55807500	0.56748400
H	-3.09991400	3.14014800	-1.09024200
H	2.32292600	-0.59891800	1.37010200
H	3.24144000	-1.39307300	0.11058700

24

E(RmPW+HF-B95) = -932.177733395 a.u.

C	0.67810200	0.71590300	-0.42532300
C	0.43648300	1.77637200	0.65765500
C	-0.77946000	2.57334600	0.21883300
C	-1.13931900	3.67377200	1.19789300
C	-1.90230100	1.61709100	0.01066900
C	1.78696700	-0.27190600	0.02025500
N	3.00457500	-0.28625300	-0.48533600
N	1.76454400	-1.26911600	0.91598700
N	3.77065300	-1.25140800	0.04962600
C	3.56131000	0.56945000	-1.51745200
C	2.99348200	-1.83726600	0.89617200
C	0.64616700	-1.71104400	1.72842100
C	-1.67950100	0.32216400	-0.20561700
C	-2.82291300	-0.60747100	-0.32228700
O	-2.43627000	-1.88512500	-0.34427100
C	-3.49967300	-2.80754100	-0.46239500
H	-0.51994700	3.01210400	-0.74727800
O	0.88106300	1.15867100	-1.58805000
H	3.66789900	1.57821200	-1.13800700
H	2.87380800	0.58738000	-2.35033100
H	4.52724700	0.14945900	-1.76370700
H	3.27347900	-2.67227300	1.50894800
H	0.23270000	-0.86804400	2.26735600
H	1.02313100	-2.44401900	2.43220700
H	-0.12457900	-2.12968300	1.09407300
H	-1.37837700	3.26298600	2.17735300
H	-2.00585300	4.23397800	0.85359400
H	-0.31506400	4.37336700	1.31776300
H	-2.92768000	1.95023100	0.03312200

O	-0.47568600	-0.25524800	-0.29328600
O	-3.97787800	-0.27780700	-0.36309000
H	-3.04397700	-3.78901200	-0.49969400
H	-4.17213500	-2.73104100	0.38698300
H	-4.06903600	-2.61892800	-1.36700000
H	0.25913400	1.33560600	1.64255700
H	1.31495200	2.41595100	0.71876800

25

E(RmPW+HF-B95) = -1393.03227329 a.u.

C	0.56782100	2.63785400	0.56676500
C	0.43905900	1.77611500	-0.42784200
C	0.13244200	0.32733700	-0.19781700
O	-0.81527100	-0.11856100	-1.16402400
O	-0.35304800	0.06449800	1.04452900
C	1.31858400	-0.59249800	-0.48246500
C	-2.07309500	0.38028900	-0.99311200
N	1.25728900	-1.91519600	-0.32933400
N	2.50988000	-0.33866400	-0.99609700
C	-2.48677600	1.48311000	-1.59351000
C	-2.97710500	-0.47307200	-0.18097200
O	-4.10684900	0.14734900	0.12966600
C	-5.02827100	-0.63345100	0.86848000
C	2.46032000	-2.39631300	-0.70512700
C	0.22656000	-2.67290500	0.35359500
N	3.23868400	-1.45820800	-1.12159600
C	3.21231000	0.92062100	-1.10645300
C	0.87319100	4.08016500	0.40265300
H	0.46143600	2.26636600	1.57619600
H	0.54389700	2.08245700	-1.46058100
H	0.43076100	0.02182300	1.66120000
H	-1.82240400	2.05028100	-2.22272100
H	-3.50045300	1.81848500	-1.46328600
O	-2.74166700	-1.60889000	0.12691300
H	-5.88138300	0.00654500	1.05065400
H	-5.32325900	-1.51128500	0.30230200
H	-4.58419400	-0.95396400	1.80509800
H	2.71894200	-3.43615700	-0.66590900
H	-0.75097200	-2.30982000	0.06583500
H	0.34595700	-3.71345100	0.07621000
H	0.37141800	-2.54290000	1.42126800
H	3.26419000	1.35669100	-0.11312200
H	4.20124800	0.67385200	-1.46706000
H	2.71667800	1.58528800	-1.80052900
H	0.96095900	4.36436800	-0.64233100
H	0.09855500	4.69212500	0.86125100
H	1.80459600	4.32801700	0.90897000
Cl	2.29691100	-0.09958300	2.18317100

26

E(RmPW+HF-B95) = -1393.06766076 a.u.

C	-1.62368900	1.97417200	0.37687500
C	-0.21781900	1.72159300	-0.05339400

C	0.38003700	0.56596600	0.23205600
O	-1.67779400	0.01215700	-2.27656800
O	-0.23326300	-0.42362300	0.87522000
C	1.70821400	0.25050300	-0.30524400
C	-2.27957700	0.18660600	-1.25270100
N	1.98119000	-0.76583500	-1.12515900
N	2.82773500	0.93512700	-0.17745200
C	-2.61306200	1.54736200	-0.73022700
C	-2.62171100	-1.04919700	-0.41918700
O	-3.27238500	-0.73133700	0.68624900
C	-3.49281800	-1.81532100	1.57511900
C	3.30192300	-0.67840200	-1.39714600
C	1.09489500	-1.87458200	-1.41938900
N	3.83922700	0.35330300	-0.83952600
C	3.12265600	1.93253900	0.82149300
C	-1.85651700	3.42688600	0.74667300
H	-1.81374800	1.34004600	1.24093500
H	0.28928800	2.44183000	-0.67907900
H	0.47705700	-0.94343900	1.36873800
H	-2.54571900	2.23389700	-1.57061700
H	-3.62160400	1.56727300	-0.32375100
O	-2.32067200	-2.15610400	-0.75052000
H	-4.04667400	-1.41035200	2.41115700
H	-4.05727400	-2.59896300	1.08100200
H	-2.53912400	-2.21503400	1.90473500
H	3.82410600	-1.37920000	-2.01853000
H	0.10434300	-1.50580200	-1.65856300
H	1.49855500	-2.41274700	-2.26758300
H	1.05966100	-2.51165400	-0.54077700
H	2.21952300	2.48264300	1.04571200
H	3.47234100	1.41487300	1.71000300
H	3.88512600	2.59152100	0.42814800
H	-1.65579800	4.08217700	-0.09927000
H	-2.88586600	3.58878700	1.05633500
H	-1.20844800	3.72564700	1.56604700
Cl	2.21323000	-1.46395100	1.94210000

27

E(RmPW+HF-B95) = -1393.05905879 a.u.

C	0.79435300	2.54776400	0.10880300
C	-0.42110300	1.74749500	-0.20296000
C	-1.19282400	1.15135200	0.70166700
C	-2.04048000	0.03781200	0.30165300
N	-2.11074700	-1.11822800	0.93687000
N	-2.84981300	-0.07395900	-0.75562700
N	-2.90724300	-1.98537800	0.30058400
C	-1.23484400	-1.59571400	1.98568800
C	-3.33220800	-1.33889100	-0.72847800
C	-2.97163200	0.84469400	-1.86055700
C	0.91925300	3.77806200	-0.77138400
C	1.95765000	1.58057100	-0.13143400
C	1.90817800	0.41465600	0.80602500
O	1.38631300	0.46811600	1.89344100
C	2.53838500	-0.91355500	0.39959600
O	3.27208900	-0.79218200	-0.68641500
C	3.61291700	-2.02360300	-1.30506100

H	0.79228900	2.84660600	1.15580700
H	-0.49997900	1.40188600	-1.22258000
O	-1.15195500	1.33589200	2.04013000
H	-0.22246300	-1.64679100	1.59101300
H	-1.58556400	-2.58383000	2.24823100
H	-1.28210000	-0.92824900	2.83405600
H	-3.99587200	-1.73397000	-1.47190100
H	-2.17633300	0.62764900	-2.56969400
H	-2.88211300	1.85915600	-1.49193400
H	-3.94227600	0.70770200	-2.32167700
H	-0.22078900	1.32726300	2.30030300
H	0.89945300	3.50196800	-1.82361400
H	1.85593100	4.29589500	-0.58046600
H	0.10558600	4.47441300	-0.58866500
H	2.91856200	2.08197800	0.00964800
H	1.93890600	1.19518300	-1.14813200
O	2.37846700	-1.91048700	1.03782900
H	4.25814500	-1.77241800	-2.13638000
H	4.12336600	-2.67249500	-0.60136500
H	2.69555100	-2.48989700	-1.65312400
Cl	0.11700800	-1.08492100	-1.52962100

28

E(RmPW+HF-B95) = -345.636680767 a.u.

C	-0.00690100	-0.73464700	-0.00027100
C	1.18468700	-0.08213900	0.00003400
O	1.26914200	1.22497300	0.00036900
H	0.33597500	1.55961900	0.00012100
H	-0.02604700	-1.81041000	-0.00056900
C	2.50110800	-0.76321800	-0.00002300
H	2.39371900	-1.84113100	0.00025900
H	3.06842000	-0.45605800	-0.87516500
H	3.06872900	-0.45552700	0.87472000
C	-1.23388000	0.00906300	-0.00017600
O	-1.24758100	1.24212000	-0.00038300
C	-2.52610300	-0.74665300	0.00025700
H	-2.58432000	-1.39271100	-0.87286400
H	-2.58749400	-1.38537100	0.87859600
H	-3.35492800	-0.04960000	-0.00391100

29

E(RmPW+HF-B95) = -1357.15722394 a.u.

C	-1.58213300	1.08437400	-0.72780700
C	-0.12707900	1.07181200	-0.42494400
C	0.80607700	0.44232300	-1.13167900
C	2.13745400	0.25905000	-0.57247500
N	2.81593400	-0.87340800	-0.60383800
N	2.92414100	1.13962000	0.05357100
N	3.98924100	-0.76881300	0.03146600
C	2.32092100	-2.17649800	-0.98252600
C	4.02575600	0.45313300	0.43638200
C	2.56076600	2.45622200	0.51815500
C	-2.15970300	2.48262300	-0.58536900

C	-2.23428000	0.09978600	0.25237600
C	-1.71280200	-1.31135200	0.03665300
O	-1.28441700	-1.65460500	-1.04310000
H	-1.77962700	0.71004200	-1.73028500
H	0.15712700	1.42950800	0.55335300
O	0.62382000	-0.22177500	-2.29205000
H	1.42172200	-2.37714600	-0.40863200
H	3.09535100	-2.88312800	-0.71972100
H	2.10866000	-2.20322300	-2.04219300
H	4.82788600	0.88986100	0.99756800
H	2.03130700	2.34024200	1.46100400
H	1.92730800	2.93273700	-0.21981500
H	3.46576400	3.03597000	0.65342500
H	-0.20926800	-0.70854300	-2.20380600
H	-2.02007000	2.86131300	0.42587000
H	-3.22170600	2.48734200	-0.81541000
H	-1.67018000	3.16914800	-1.27025600
H	-2.00332400	0.38006100	1.28054000
Cl	1.08386800	-0.26831800	2.23365400
C	-1.72277600	-2.22404000	1.20715000
H	-2.63741300	-2.13189500	1.78709600
H	-1.57606100	-3.24906200	0.88861900
H	-0.88915300	-1.90238600	1.84297300
C	-3.74589400	0.07618100	0.03635300
O	-4.18831800	-0.03381000	-1.07540800
C	-4.61706900	0.23687900	1.24094100
H	-4.34026000	-0.46520900	2.02360100
H	-4.46565100	1.23431900	1.65228100
H	-5.65748500	0.10822000	0.96848200

30

E(RmPW+HF-B95) = -1357.13412384 a.u.

C	-1.76958000	-1.35207200	0.02183500
C	-0.34288100	-1.40936200	-0.37854000
C	0.55918700	-0.80126000	0.43716900
C	1.98200300	-0.80230900	0.00089200
N	3.02935300	-0.96251700	0.78973600
N	2.48930700	-0.52316300	-1.20849600
N	4.19131400	-0.80883900	0.13610500
C	3.01237800	-1.24955900	2.20451400
C	3.83847400	-0.53565400	-1.07305800
C	1.75107900	-0.09374400	-2.37739000
C	-2.57485600	-2.50842500	-0.54104900
C	-2.42831700	0.00389000	-0.41179400
C	-1.60103900	1.15844900	0.09348400
O	-0.79291500	1.63826100	-0.68264400
H	-1.82419900	-1.36014400	1.11168600
H	-0.04990300	-1.89571300	-1.29680200
O	0.33937900	-0.20162900	1.52380500
H	3.21091900	-2.30354200	2.36680500
H	2.02986700	-0.96724700	2.56714100
H	3.78586500	-0.65297500	2.67082300
H	4.51719300	-0.32592800	-1.87665600
H	1.60175200	-0.92503200	-3.05828200
H	2.31154900	0.69462400	-2.86555500
H	0.79102300	0.28768100	-2.04668900

H	0.65961200	2.36108600	-0.22014200
H	-2.59697800	-2.47567500	-1.63042600
H	-3.59999500	-2.50420700	-0.17746500
H	-2.12348300	-3.45215200	-0.24802500
H	-2.38485400	0.06202200	-1.49782900
Cl	1.90745800	2.74557100	-0.06526400
C	-1.79977100	1.68131200	1.47121800
H	-2.72907300	2.24941100	1.50585400
H	-1.88665600	0.85918000	2.17083700
H	-0.96377100	2.31398500	1.74077800
C	-3.86288200	0.03572800	0.06218200
O	-4.13831500	-0.08952700	1.22823300
C	-4.91599900	0.19640000	-0.99126800
H	-4.76473700	1.12790800	-1.53389200
H	-4.83261300	-0.60879100	-1.71988200
H	-5.90010600	0.18522900	-0.53852800

TS1

E(RmPW+HF-B95) = -550.531521399 a.u.
1 imaginary frequency: -216.8589 cm^{-1}

C	1.89187400	0.45639300	0.25232800
C	0.80164500	1.08748000	1.01706800
O	0.56062400	2.29381500	0.89263700
C	2.83476100	-0.01321700	-0.32771600
C	-0.67383000	0.01297300	0.24014700
C	3.97240200	-0.56325000	-1.03862200
N	-0.95675200	-1.28053700	0.28120300
N	-1.74196200	0.53710800	-0.38176600
N	-2.14532800	-1.60875200	-0.27564000
C	-0.13403000	-2.30990200	0.85594700
C	-2.60269900	-0.47241800	-0.67585700
C	-1.91255100	1.94005400	-0.70292600
H	0.67996700	0.59349700	1.99639500
H	-3.54032100	-0.33446000	-1.17978300
H	-1.07102300	2.47230200	-0.27051500
H	-2.84346000	2.30092900	-0.27844300
H	-1.92897400	2.06979200	-1.78010200
H	3.65536700	-1.26647400	-1.80545000
H	4.53994800	0.22594600	-1.52570100
H	4.64355700	-1.08694500	-0.36199100
H	-0.56928100	-2.66691600	1.78366500
H	0.84739500	-1.88844000	1.03640900
H	-0.05530500	-3.13316600	0.15562000

TS2

E(RmPW+HF-B95) = -1393.00882435 a.u.
1 imaginary frequency: -374.1817 cm^{-1}

C	1.56402600	2.18269900	0.71110300
C	0.20411700	1.98996000	0.54318600
C	-0.26853600	0.69154200	0.80095700
C	-1.71059400	0.37488600	0.61113100
N	-2.36206800	-0.53157400	1.31082500
N	-2.61003000	0.93039500	-0.20800800

N	-3.64286000	-0.61959800	0.93806400
C	-1.81321000	-1.55936400	2.16618300
C	-3.76481900	0.25988400	0.00429000
C	-2.33116400	1.74991200	-1.36942500
C	2.16853000	3.54598900	0.63805900
C	2.54579600	1.27886000	-0.92798200
C	1.83317500	0.11872500	-1.08427700
O	0.70600900	0.15744500	-1.70956600
C	2.28387300	-1.17831900	-0.50277400
O	3.24659100	-1.00131400	0.39710600
C	3.69632800	-2.19812900	1.00254100
H	2.04929000	1.46497600	1.35781000
H	-0.42946500	2.76275900	0.14193400
O	0.44917100	-0.23094000	1.19320500
H	-2.65128600	-2.00572100	2.68367600
H	-1.10248200	-1.12841400	2.85662700
H	-1.31375500	-2.28077200	1.52738600
H	-4.66514000	0.44626300	-0.54710400
H	-2.35030400	2.80361400	-1.11328800
H	-3.08773600	1.53602600	-2.11318600
H	-1.36553700	1.45852400	-1.76705100
H	0.09712500	-0.67007300	-1.65353900
H	1.71072500	4.14669500	-0.14303500
H	3.23916900	3.50971500	0.46507900
H	2.00807200	4.05569000	1.58732700
H	3.54202600	1.22127400	-0.52552900
H	2.31394900	2.09018900	-1.59856700
O	1.86053400	-2.23986600	-0.84919900
H	4.46856300	-1.90814100	1.70312100
H	2.87575600	-2.68612600	1.51855200
H	4.09337600	-2.87812600	0.25543900
Cl	-1.51007200	-1.61267000	-1.57247800

TS3

E(RmPW+HF-B95) = -932.165192110 a.u.
1 imaginary frequency: -69.5566 cm^{-1}

C	0.95733900	-1.26923700	-0.81486000
C	2.35162500	-0.85211400	-0.37162700
C	2.72533500	0.63536400	-0.43422400
C	3.98320600	0.90404600	0.36520200
C	1.58132700	1.50194200	-0.03853000
C	-0.17242700	-1.26502600	0.22727000
N	-1.40423700	-1.59206300	-0.11724100
N	-0.23141100	-1.02316000	1.54741800
N	-2.25500200	-1.55588700	0.91608000
C	-1.90714400	-1.82367900	-1.45524400
C	-1.52424000	-1.21329300	1.91857700
C	0.82313900	-0.63659700	2.46141900
C	0.41279800	1.23823500	-0.63879900
C	-0.79859000	1.99982000	-0.23380900
O	-1.92026200	1.38807500	-0.61840200
C	-3.10816600	2.05534100	-0.24691600
H	2.92597600	0.84067800	-1.48868100
O	0.82830100	-2.18720100	-1.62167900
H	-1.55038700	-2.77732700	-1.81765900
H	-1.52782700	-1.02881100	-2.08551500

H	-2.98582300	-1.79716800	-1.37787700
H	-1.87483500	-1.08887600	2.92466800
H	1.49290100	-1.46912000	2.64460200
H	0.35679600	-0.34229600	3.39383600
H	1.36325800	0.20889600	2.05171800
H	3.81768600	0.71432300	1.42649500
H	4.30014900	1.93874200	0.26138200
H	4.80232700	0.26646500	0.04099100
H	1.67529600	2.31881700	0.65959500
O	0.28889300	0.24832800	-1.48898400
O	-0.79845700	3.02108000	0.40182300
H	-3.16309800	2.17194900	0.83139800
H	-3.14969400	3.04117200	-0.69968800
H	-3.92382200	1.43937400	-0.60360600
H	2.53969300	-1.23170700	0.63310300
H	3.00294000	-1.41841000	-1.03137700

TS4

E(RmPW+HF-B95) = -932.165655942 a.u.
1 imaginary frequency: -183.0531 cm^{-1}

C	0.42190600	1.04093200	-0.68489600
C	0.14465100	2.05299000	0.39621100
C	-1.25634100	2.61196100	0.18552300
C	-1.65305900	3.57753400	1.28592400
C	-2.18539800	1.45068400	0.09656300
C	1.91970600	-0.08124500	0.18560100
N	3.16250100	-0.13960700	-0.27007200
N	1.83819200	-1.18692500	0.95456400
N	3.87175900	-1.20667900	0.16219700
C	3.78671000	0.81140600	-1.15300700
C	3.03013000	-1.83420700	0.90872300
C	0.65006400	-1.63571800	1.64058500
C	-1.74763700	0.24318400	-0.25007100
C	-2.68788700	-0.89886100	-0.26860800
O	-2.08056400	-2.05843100	-0.50408000
C	-2.95150000	-3.17228600	-0.55057200
H	-1.26932800	3.14558700	-0.76820800
O	0.82355700	1.34835400	-1.78383800
H	4.51816600	1.39881000	-0.60726100
H	3.00497500	1.44100200	-1.55967700
H	4.28307000	0.27268600	-1.95139800
H	3.23892100	-2.74916100	1.42982600
H	0.17430200	-0.78896300	2.12227400
H	0.93293700	-2.36087900	2.39547200
H	-0.04873500	-2.07184200	0.93510200
H	-1.63970900	3.08349500	2.25547900
H	-2.65577400	3.96509700	1.12247000
H	-0.96898400	4.42153200	1.32723100
H	-3.23437600	1.55036800	0.32510500
O	-0.48361000	-0.06397500	-0.60228000
O	-3.86960500	-0.80312000	-0.07520800
H	-2.32745100	-4.03091900	-0.76156200
H	-3.46691300	-3.29477700	0.39708100
H	-3.69348100	-3.04026800	-1.33140100
H	0.19612000	1.58270900	1.37712600
H	0.90279600	2.82713000	0.33690200

TS5

E(RmPW+HF-B95) = -1392.99613347 a.u.
1 imaginary frequency: -412.9769 cm^{-1}

C	-1.16806500	2.33639300	0.63516800
C	-0.00151700	1.90873100	0.08423400
C	0.31664800	0.53943800	0.16497500
O	-0.69188000	0.07163600	-1.46990200
O	-0.27503100	-0.21470200	1.05276400
C	1.60678800	0.05175500	-0.36721800
C	-1.90380600	0.21382500	-1.09074100
N	1.84169600	-1.14451300	-0.90398500
N	2.73592100	0.73087900	-0.46609200
C	-2.54647200	1.41627800	-1.12737000
C	-2.55421800	-0.97564400	-0.44938300
O	-3.66266600	-0.66911200	0.21657600
C	-4.31093200	-1.77101200	0.82368500
C	3.13818800	-1.13791600	-1.27158100
C	0.99115400	-2.31834000	-0.83128000
N	3.70467400	-0.00360400	-1.02777100
C	3.08293700	1.99935000	0.12948600
C	-1.63616300	3.74655100	0.57453500
H	-1.63451600	1.68426600	1.35897700
H	0.52270200	2.51716900	-0.63655000
H	0.44715500	-0.73345300	1.57037700
H	-2.13172000	2.20606300	-1.73014900
H	-3.56149600	1.51281300	-0.78035200
O	-2.14212200	-2.09828800	-0.55502200
H	-5.17015900	-1.36511700	1.34155800
H	-4.62363400	-2.48995300	0.07292300
H	-3.64183600	-2.26437000	1.52113300
H	3.62731700	-1.98195300	-1.71646900
H	-0.03517000	-2.03319500	-1.02063000
H	1.33489200	-3.02182000	-1.57975600
H	1.09980500	-2.73196500	0.16732500
H	2.51426700	2.12286200	1.04247400
H	4.13898400	1.95203700	0.35730700
H	2.88913800	2.81577900	-0.55753200
H	-1.19856500	4.28248200	-0.26290200
H	-2.71741800	3.80656100	0.49964800
H	-1.35164300	4.26303200	1.49103800
Cl	2.09424600	-1.19960600	2.23789000

TS6

E(RmPW+HF-B95) = -1392.99275202 a.u.
1 imaginary frequency: -469.5186 cm^{-1}

C	-1.01510000	1.23085200	-0.81708100
C	0.37257700	1.24749900	-0.59124400
C	1.03581900	0.03232800	-0.68808300
C	2.48805200	-0.08012500	-0.40602400
N	3.12632000	-1.23472600	-0.28187300
N	3.44490500	0.85986500	-0.42645200
N	4.44672200	-1.05922300	-0.13161200

C	2.55861900	-2.53177100	0.01646400
C	4.61607600	0.21307800	-0.21851400
C	3.27401200	2.29044400	-0.38247200
C	-1.79740400	2.50467500	-0.77956900
C	-1.69978300	0.20732800	0.72461400
C	-2.45101100	-0.72573500	0.03959100
O	-1.93779900	-1.63245900	-0.71903200
C	-3.94433900	-0.69326200	-0.01799700
O	-4.43360800	0.42853700	0.49792000
C	-5.84901600	0.50473700	0.50234000
H	-1.32031600	0.53256300	-1.58666800
H	0.80714300	2.05375400	-0.03042200
O	0.49432400	-1.06038600	-0.98765300
H	1.87994800	-2.40292000	0.85441100
H	3.39202600	-3.16462000	0.28911600
H	2.02844100	-2.91876500	-0.84146900
H	5.56178900	0.71419900	-0.15027800
H	2.84888300	2.55392400	0.58249100
H	2.62088900	2.60943300	-1.18543900
H	4.24781200	2.74973800	-0.50029300
H	-0.93769700	-1.48034500	-0.79122900
H	-1.49767900	3.12351200	0.06145700
H	-2.86300200	2.31180800	-0.70492700
H	-1.61598500	3.06674000	-1.69449000
H	-2.24243000	0.91007300	1.33474000
H	-0.73239000	-0.09605500	1.11532000
O	-4.61036900	-1.57802800	-0.46751500
H	-6.09437100	1.46477200	0.93592400
H	-6.23497700	0.42867500	-0.50908300
H	-6.26605200	-0.30184100	1.09646600
Cl	1.62711500	0.20131500	2.16011800

TS7

E(RmPW+HF-B95) = -1357.10739762 a.u.
1 imaginary frequency: -460.7911 cm^{-1}

C	1.39675900	-0.34050400	-1.45673100
C	0.05133400	-0.64866600	-1.19309500
C	-0.75891500	0.39482200	-0.77788400
C	-2.18301100	0.18674800	-0.41409100
N	-2.95184000	1.13145700	0.10949500
N	-3.00893000	-0.83243100	-0.69801200
N	-4.21989100	0.71885600	0.25123200
C	-2.53955600	2.33140700	0.80589300
C	-4.22950400	-0.47056700	-0.23766100
C	-2.64659000	-2.17238300	-1.08803000
C	2.32096100	-1.38484900	-1.98693300
C	2.13629600	0.17550300	0.37476400
C	2.71565100	1.40786100	0.04319800
O	1.95705300	2.38843600	-0.29839800
H	1.54871000	0.64755600	-1.87228800
H	-0.22916600	-1.67092000	-1.02164000
O	-0.38243600	1.58926900	-0.65803900
H	-1.77698800	2.04334800	1.52305400
H	-3.42394800	2.69771000	1.30907200
H	-2.14842300	3.05967200	0.11083200
H	-5.09143800	-1.10633400	-0.29294900

H	-2.04966900	-2.60139700	-0.28660900
H	-2.09263100	-2.15566100	-2.01858900
H	-3.55859300	-2.74139700	-1.21984800
H	0.98405200	2.08449400	-0.38607000
H	2.18035700	-2.33622500	-1.48069200
H	3.36247400	-1.09801000	-1.88298000
H	2.11000000	-1.53105300	-3.04530500
H	1.15210500	0.23842900	0.83062300
Cl	-1.10863700	-0.80210200	1.87670900
C	4.16310800	1.68551700	-0.06253600
H	4.56164900	1.16882800	-0.93433100
H	4.31461600	2.75278400	-0.17255800
H	4.70285100	1.28057100	0.78544500
C	2.96309200	-0.95557500	0.82714600
O	4.14775500	-1.03379800	0.57227200
C	2.23054100	-2.02995800	1.55948000
H	1.80139700	-1.63725800	2.47879000
H	1.36649300	-2.35370800	0.97996100
H	2.89765200	-2.85826400	1.76521900

TS8

E(RmPW+HF-B95) = -1357.11594971 a.u.
1 imaginary frequency: -368.0113 cm^{-1}

C	-1.75161300	-1.44721100	0.55608200
C	-0.41170100	-1.63535700	0.22129000
C	0.48779400	-0.70525100	0.75294200
C	1.92128900	-0.73713200	0.34038200
N	2.91537800	-0.30713000	1.09066600
N	2.47455100	-1.12133800	-0.81584200
N	4.08880700	-0.37569100	0.45476400
C	2.84211200	0.40434300	2.34757000
C	3.79669100	-0.85782700	-0.70445600
C	1.79304600	-1.45266000	-2.04946300
C	-2.75272800	-2.51857700	0.26443400
C	-2.51513800	0.11610600	-0.56549600
C	-1.48320400	1.06350000	-0.49714000
O	-0.52055600	0.85743500	-1.32006500
H	-1.91892000	-0.87355600	1.45900400
H	-0.10726600	-2.38936200	-0.48531400
O	0.18722100	0.19709300	1.53760500
H	3.83862300	0.38908100	2.76746100
H	2.12475500	-0.07227800	2.99944500
H	2.51856000	1.41691300	2.13137300
H	4.50227600	-1.02817500	-1.49350600
H	1.59624800	-2.51787100	-2.10546600
H	2.43057500	-1.15159100	-2.87092500
H	0.86758700	-0.89105000	-2.09297900
H	0.32709600	1.44453800	-1.17991100
H	-2.68715100	-2.86666800	-0.76358600
H	-3.76913200	-2.19624200	0.46405700
H	-2.54910500	-3.36894400	0.91328800
H	-2.53223800	-0.41813700	-1.50518500
Cl	1.97498900	2.11383500	-0.95305500
C	-1.45102400	2.24572200	0.39796500
H	-2.09915000	3.01524800	-0.02190900
H	-1.83011000	1.98346600	1.37574200

H	-0.43814400	2.62650500	0.46486700
C	-3.81476700	0.35559800	0.07779800
O	-3.91083600	0.81111200	1.19561200
C	-5.03444700	-0.01028500	-0.72082300
H	-5.18933000	0.73964700	-1.49526000
H	-4.91274400	-0.96578200	-1.22512000
H	-5.90288800	-0.03277900	-0.07298700