Lewis Acid Promoted Dearomatization of Naphthols
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1. General information

A. Experimental

All reactions using oxygen- and/or moisture-sensitive materials were carried out with anhydrous solvents under a nitrogen atmosphere using oven-dried glassware and standard Schlenk techniques. Dry solvents were collected from a dry solvent purification system. Reagents and substrates were purchased from commercial sources and used as received. Et₂Zn (1 M in hexane), EtI (1 M in hexane), Me₂Al (1 M in hexane), Ph₂PH, Zn dust, CuCl, AlCl₃ and other Lewis acids were purchased from Sigma Aldrich; B(C₆F₅)₃ from abcr GmbH; 1-naphthol from Acros Organics; 2-naphthol from Alfa-Aesar; dppf and ZnCl₂ from TCI. 4-ethynaphthalen-1-ol (2) was synthesized according to the literature procedures.[1][2] Reactions were temperature controlled, for which the MW unit adjusted the power used (maximum 250 W, average 20 W). Purification of the products was performed by column chromatography using Merck 60 Å 230-400 mesh silica gel. Components were visualized by UV light and permanganate staining (KMnO₄ 3g, K₂CO₃ 10g, water 300 mL). NMR data was collected on a Varian VXR-400 (1H at 400 MHz; 13C at 101 MHz; 31P at 161.94 MHz) equipped with a 5 mm 2-gradient broadband probe and Bruker 500 MHz AVANCE III HD (1H at 500 MHz and 13C at 126 MHz). Chemical shifts are reported in parts per million (ppm) relative to residual solvent peak (CDCl₃, 1H: 7.26 ppm, 13C: 77.16 ppm; toluene, 1H: 7.26 ppm, 13C: 128.03 ppm; DCM, 1H: 2.08 ppm, 13C: 39.52 ppm). Multiplicity is reported with the usual abbreviations (s: singlet, d: doublet, dd: doublet of doublets, t: triplet, q: quartet, m: multiplet, td: triplet of doublets, dt: doublet of triplets). Exact mass spectra were recorded on a LTQ Orbitrap XL apparatus with ESI ionization. Enantiomeric excess (ee) were determined by chiral HPLC analysis using a Shimadzu LC-10ADVP HPLC equipped with a Shimadzu SPDM10AVP diode array detector.

B. Computational details

Geometries of all the stationary points were fully optimized at the M06[3][4]def2svp[4] computational level using the Gaussian09 program.[8] The minimum or transition state nature of all the presented stationary points was confirmed through the calculation of frequencies, having the minima 0 imaginary frequencies and the transition states 1. Imaginary frequencies as well as absolute energies are reported at the Cartesianes section. Moreover, for each of the stationary points the stability of the wave function was analyzed and confirmed[6,7] The effect of the solvent (DCM) was modeled using the polarizable continuum model (PCM) with the default parameters implemented in the Gaussian09 package.

In the manuscript, as well as in the supporting information, the energies are reported as relative Gibbs free energies with respect to two molecules of 1 and one molecule of Al₂Cl₄ molecules unless it is specified otherwise. Energies are expressed in kcal/mol, they are computed using the standard conditions considered in Gaussian, i.e. 298.25 K and 1 atm.

2. Lewis acid promoted tautomerization of naphthols to ketones: optimization.

Different conditions to tautomerize the 1-naphthol (1) were explored (Table S1). We started with exploring Lewis acids (LAs) containing boron, and we found that only when B(C₆F₅)₃ behaves as LA the complex between 1-naphthol and B(C₆F₅)₃ exists in equilibrium with the ketone form, in agreement with previous reports.[8] (Note: 1H NMR chemical shift of the newly formed -CH₂ group in toluene is 2.61 ppm, while in DCM the chemical shift of the group is 4.16 ppm. This is likely due to anisotropy effect of toluene, which surrounds the complex by π-π interaction).

Moreover, when the LA is changed from a boron to an aluminium species the equilibrium is completely shifted towards Mono 1a (Table S1, entries 7 and 8). Then, we also explored the effect of the concentration of the LA in this equilibrium. We found in the presence of B(C₆F₅)₃ increasing the number of equivalents of the LA in the solution does not promote the tautomerization, however, in the case of AlCl₃ this equilibrium is completely shifted towards 1a with only one equivalent of LA (see Table S2, entries 7 and 8).

Lewis acid effect

![Lewis acid effect](image)

Table S1. Conditions scope.

| Entry | LA       | Solvent | Ratio 1/Mono 1a |
|-------|----------|---------|-----------------|
| 3     | BPr₃     | toluene | 100/0           |
| 4     | BPr₃     | DCM    | 100/0           |
| 5     | BB₃      | DCM    | 100/0           |
| 6     | B(OPr)₃  | DCM    | 100/0           |
**Concentration effect**

| Entry | LA          | Conc, mM | LA equiv | Ratio LA | Ratio Mono 1a/Bis 1a |
|-------|-------------|----------|----------|----------|----------------------|
| 1     | B(6-F)C6B3  | 15       | 1        | 99/1     | -                    |
| 2     | B(6-F)C6B3  | 15       | 2        | 98/2     | -                    |
| 3     | B(6-F)C6B3  | 30       | 1        | 90/10    | -                    |
| 4     | B(6-F)C6B3  | 60       | 1        | 80/20    | -                    |
| 5     | AlCl3       | 60       | 0.1      | 90/10    | -                    |
| 6     | AlCl3       | 60       | 0.5      | 50/50    | -                    |
| 7     | AlCl3       | 30       | 1        | 0/100    | -                    |
| 8     | AlCl3       | 60       | 1        | 0/100    | -                    |
| 9     | AlCl3       | 60       | 2        | 0/100    | 67/33                |
| 10    | AlCl3       | 60       | 3        | 0/100    | 0/100                |
| 11    | AlCl3       | 40       | 3        | 0/100    | 50/50                |
| 12    | AlCl3       | 60+1equiv phenol | 2 | 0/100 | - |

1equiv of AlCl3 at 0 °C is pale yellow precipitate in DCM, 2equiv of AlCl3 at 0 °C is red DCM solution.
3. Mechanistic studies

A. NMR studies of naphthol intermediate formation

A solution of naphthol (60 mM in DCM-d2) was added to solid AlCl₃ (0.5, 1, 2 and 3 equiv), previously added in an NMR tube (under N₂ atmosphere), obtaining a suspension. After 5 min. of ultrasonication, ¹H NMR experiments were performed on the reaction mixture (table S3, figure S1). We have found, in line with the previously presented results, that one equivalent of the LA is enough to shift the equilibrium towards Mono 1a, and when more LA is added the equilibrium is shifted towards a double LA coordination on the naphthone.

![Diagram](image)

Table S3. Studying of formation mono- and bi-aluminium complexes.

| Entry | AlCl₃ equiv | Ratio 1 / Mono 1a / Bis 1a° |
|-------|-------------|-----------------------------|
| 1-naphthol (1) | 2 | 50 / 50 / 0 |
| 2 | 0.5 | 0 / 100 / 0 |
| 3 | 1 | 0 / 67 / 33 |
| 4 | 2 | 0 / 0 / 100 |
| 5 | 3 | 0 / 0 / 100 |

2-naphthol (4)

| Entry | AlCl₃ equiv | Ratio 1 / Mono 1a / Bis 1a° |
|-------|-------------|-----------------------------|
| 2 | 0.5 | 50 / 50 / 0 |
| 3 | 1 | 0 / 100 / 0 |
| 4 | 2 | 0 / 0 / 100 |
| 5 | 3 | 0 / 0 / 100 |

Figure S1A. ¹H NMR study of formation mono- and bi-aluminium complexes with 1-naphthol in DCM-d2.
B. Computational studies

To understand how naphthol 1 and dearomatized naphthone bind AlCl₃ we resorted to molecular modelling. We first explored the relative stability of AlCl₃ as a monomer and as a dimer in solution. We found that the dimerization is a highly exergonic process (-18.14 kcal/mol, see scheme S1-a) and consequently aluminium species participate in the reaction in its dimer form. In an attempt to rationalize the interaction between Al₂Cl₆ and I, we explored the formation of II-a and II. These two species are in equilibrium and species II is energetically the most favorable. In the presence of an excess of the LA the equilibrium will be shifted to II-a, thus explaining enhanced solubility of the species formed in this reaction condition. Next to this, we have explored the possibility of a double coordination of AlCl₃ to II, however the formation of complex II-b is too endergonic to be a competitive species (scheme S1-b).

We moved next to explore dearomatized species V. We have found that species V-a and V-b are almost degenerated and that they are close in energy to species V. These findings, are in line with the solubility characteristics found during the reaction exploration, compounds V-a and V-b must be more soluble in DCM than V thus the increase in the number of equivalents of AlCl₃ will not only shift the equilibrium towards their formation but also increase the solubility of the reaction mixture.

Scheme S1. a) Analysis of the equilibrium of AlCl₃ as a monomer and as a dimer. b) Study of the formation of mono- and bi-aluminum complexes from naphthol. Calculations were performed at the PCM(DCM)/M06/def2svp computational level. The energies reported correspond to relative Gibbs free energies with respect to two units of I and Al₂Cl₆. Energies are computed at normal conditions of temperature and pressure and expressed in kcal/mol.
To understand the overall picture of the process we next explored the dearomatization of naphthol in the absence of Al\(_2\)Cl\(_3\) and in the presence of ½ equivalent (Scheme S2). As expected, we found that 1,3 or 1,5 hydrogen migration towards dearomatization possess very high barriers both in the presence and absence of the LA (see scheme S2A and B). Consequently we wondered whether the dearomatization reaction would be facilitated intermolecularly using additional molecule of naphthol (Scheme S2C). In line with the experimental evidence, we found that the intermolecular dearomatization of two naphthol units, in the absence of any Lewis acid auxiliary, is quite high (34.54 kcal/mol). However, in the presence of 1/2 or 1 equivalent of Al\(_2\)Cl\(_6\) the barriers decrease significantly from 34.54 to 5.59 and 17.94, respectively.

Scheme S2. Top: A and B) Relative energies for the dearomatization of naphthol as a monomer without Lewis acid and in the presence of one molecule of AlCl\(_3\) (from left to right). Bottom: C) Relative energies for the dearomatization of naphthol as an aggregate without Lewis acid, in the presence of ½ and 1 equivalent of Al\(_2\)Cl\(_6\) (from left to right).

Connected to this we have explored all the possible orientations for the aggregated species to evaluate the influence of the conformational disposition in the relative energies. To do so, we chose a set of four initial orientations: with a 0º and 180º degrees of the COCO internal coordinate being, both alcohols present in the same side of the molecule or in opposite (Scheme S3). The energetic analysis of these complexes with respect to free naphthol and ½ of Al\(_2\)Cl\(_6\) lead us to conclude that the interaction of two activated naphthol molecules is the most exergonic, and that the preferred orientation of the two rings is \(\mu_{12}=0\), table S4. Moreover, we observe that the formation of IV is exergonic (-12.15 kcal/mol), in agreement with \(^1\)H-NMR studies.

Scheme S3. Explored orientations for the naphthol dimer, in the absence of AlCl\(_3\), with one and two molecules of the LA. The same orientations were considered for the naphthone derivative.

Table S4. Analysis of the energies of the different dimeric aggregates that can be present in the reaction media (naphthol, naphthone) and their combination, in the presence of none, one or two AlCl\(_3\) molecules. The energies are reported with respect to two units of I and AlCl\(_6\), and they are reported as relative Gibbs free energies. Energies are expressed in kcal/mol.
With this information in hand, we proposed two paths that can account for the intermolecular dearomatization of naphthol towards the naphthone derivative. The energetically most feasible path involves the initial coordination of an AlCl$_3$ molecule to the lone pair of the oxygen atom at the naphthol, and subsequent interaction of this species with a second unit of naphthol. Once III is formed, it can further progress through a hydrogen migration that involves an energy penalty of only 5.59 kcal/mol and yields one unit of an AlCl$_3$ activated tetralone and a naphthol molecule, the latter can subsequently participate in a second loop of this catalytic cycle. Alternatively, it can be proposed that two units of II interact with each other leading to complex III-a in a very exergonic process (-16.73 kcal/mol). However, the evolution of this complex through TS-IIIa-IVa involves a barrier of 17.94 kcal/mol, i.e. more than twice the energy penalty of TS-III-IV, thus even this mechanism is feasible at the working conditions it is not competitive with the one previously described (Scheme S4). Once V is formed it can further interact with another V molecule or another ketone in a very favorable process, this aggregate can then further react with any nucleophile present in the reaction media through a 1,4-addition.

Scheme S4. Left: Mechanistic alternatives explored for the aluminium catalyzed dearomatization of naphthols promoted by AlCl$_3$. Right: Energy profiles for the explored paths and Anisotropy of the induced current density (ACID) analysis of II and V.

An ACID analysis reveals that the aluminium while being responsible for the activation of the naphthol moiety it does not alter the aromaticity and conjugation of II. Analogous conclusions can be extracted from the ACID of intermediate V.

2-naphthol

Analogously, we have also explored the mechanism behind the dearomatization of 2-naphthol (Table S4). We first analyzed the interaction of two 2-naphthol units, both activated and one none activated ones and, finally, among two activated 2-naphthol units. We found that also in this case the latter constitutes the most exergonic process (-21.52 kcal/mol).

Table S4. Analysis of the energies of the different dimeric species that can be present in the reaction media (2-naphthol, 2-naphthone) and their combination, in the presence of none, one or two AlCl$_3$ molecules (from left to right). Energies are expressed in kcal/mol.
Then, we explored the energy barrier for the intermolecular dearomatization of 2-naphthol obtaining that the barrier is even lower than for 1-naphthol, 4.51 kcal/mol (see Scheme S5).

Scheme S5. Relative energies for the dearomatization of 2-naphthol as a dimer in the presence of one molecule of AlCl$_3$. The energies are reported with respect to the uncoordinated 2-naphthol and AlCl$_3$, and they are reported as relative Gibbs free energies. Energies are expressed in kcal/mol.
4. Lewis acid promoted tautomerization of \textit{N}-Methylnaphthalen-1-amine

In order to explore whether the dearomatization protocol can be expanded towards different functionalized naphthalene derivatives, we explored the tautomerization of \textit{N}-Methylnaphthalene (8). For this purpose, \textit{N}-Methylnaphthalen-1-amine 8 (78.5 mg, 0.5 mmol) was dissolved in 5 mL of CH$_2$Cl$_2$ (purple solution) was added to AlCl$_3$ (2.0 equiv, 133 mg, 1 mmol). After 2 minutes of vigorous stirring, HPPh$_2$ (1.1 equiv, 96 μL, 0.55 mmol) dissolved in 1.0 mL of CH$_2$Cl$_2$ was added slowly and the reaction was stirred during 3 days. After this time, the mixture was quenched using a saturated aqueous solution of Na$_2$CO$_3$ and the product was extracted with DCM. Combined organic fractions were dried over MgSO$_4$ and evaporated under reduce pressure. Column chromatography using SiO$_2$ was carried out resulted in 72 mg (43% yield) of the addition product.

Optimization of the reaction conditions (Table S4)

As it can be observed in table S4, the reaction conditions were optimized trying different Lewis acids, temperatures and solvents. When AlBr$_3$ was used as Lewis Acid (table S4, entry 1) the conversion to the non-hydrolysed product was slightly bigger than when AlCl$_3$ was used (table S4, entry 2) but after column chromatography only 13% of the hydrolysed product could be obtained in comparison with the 43% yield obtained with AlCl$_3$. The use of other Lewis acids does not provide the desired product and only starting material was recovered after 3 days of reaction (entries 3-7).

Later on, the use of other chlorinated and non-chlorinated solvents were tried giving unsatisfactory results (entries 8-14). Finally increasing the reaction temperature led to lower conversion (entry 15, change from 45% to 18%).

From presented results, it can be concluded that the optimal reaction conditions to achieve dearomatization of an amine are the same used for 1-naphthol.

Table S4. Optimization of the reaction conditions using \textit{N}-Methylnaphthalen-1-amine as substrate.

| Entry | Lewis Acid | Solvent | T (°C) | Conversion (%) |
|-------|------------|---------|--------|---------------|
| 1     | AlBr$_3$   | DCM     | RT     | 59 (13)       |
| 2     | AlCl$_3$   | DCM     | RT     | 45 (43)       |
| 3     | FeCl$_3$   | DCM     | RT     | 0             |
| 4     | TiCl$_4$   | DCM     | RT     | 0             |
| 5     | CeCl$_3$   | DCM     | RT     | 0             |
| 6     | BF$_3$·$\text{OEt}_2$ + CeCl$_3$ | DCM | RT | 8 (0) |
| 7     | B(C$_6$F$_5$)$_3$ | DCM | RT | 0 |
| 8     | AlCl$_3$   | CHCl$_3$ | RT | 34 (22) |
| 9     | AlCl$_3$   | CCl$_4$ | RT | 0 |
| 10    | AlCl$_3$   | DCE     | RT     | 0             |
| 11    | AlCl$_3$   | PhMe    | RT     | 35 (17)       |
| 12    | AlCl$_3$   | THF     | RT     | 0             |
| 13    | AlCl$_3$   | MeCN    | RT     | 0             |
| 14    | AlCl$_3$   | Neat    | RT     | 0             |
| 15    | AlCl$_3$   | DCM     | 50     | 18            |

a) Reaction carried out using 0.5 mmol of (1-aminomethyl)naphthalene, 2 equiv of the corresponding LA and 1.1 equiv of HPPh$_2$ using 6 mL of solvent under nitrogen atmosphere. b) Isolated yield of the hydrolysed product in parenthesis.
5. Synthesis and characterization of compounds

NMR study of naphthone intermediates:

Procedure: To AlCl₃ (1 or 2 equiv), a solution of naphthol (60 mM in DCM-d2) was added in an NMR-tube under N₂ atmosphere obtaining a suspension. After 5 min of ultrasonication, NMR experiment was performed.

Naphthalen-1(4H)-one·AlCl₃ (Mono 1a).

$^1$H NMR (CD₂Cl₂, 400 MHz): δ 8.48 (dd, J = 8.2, 1.3 Hz, 1H), 8.31 (dt, J = 9.9, 3.3 Hz, 1H), 7.97 (td, J = 7.6, 1.4 Hz, 1H), 7.77 (d, J = 7.9 Hz, 1H), 7.73 (t, J = 7.7 Hz, 1H), 7.56 (dt, J = 9.8, 1.7 Hz, 1H), 4.34 – 4.28 (m, 2H) ppm.

$^{13}$C NMR (CD₂Cl₂, 100 MHz): δ 194.0, 167.8, 150.3, 140.2, 132.0, 131.7, 131.6, 130.1, 38.2 ppm.

Naphthalen-1(4H)-one·B(C₆F₅)₃ (Mono 1a).

$^1$H NMR (CD₂Cl₂, 400 MHz): δ 8.49 (d, J = 8.2 Hz, 1H), 7.98 (dt, J = 10.1, 3.3 Hz, 1H), 7.52 (dd, J = 9.9, 1.5 Hz, 1H); 7.73 – 7.59 (m, 1H); 7.52 (dd, J = 9.9, 1.5 Hz, 1H); 6.46 (t, J = 3.9 Hz, 1H); 4.27 – 4.16 (m, 3H); 2.75 (dt, J = 7.7, 5.9 Hz, 1H); 2.40 (m, 1H); 1.31 (t, J = 7.4 Hz, 3H); 0.75 (t, J = 7.5 Hz, 3H) ppm.

$^{13}$C NMR (CD₂Cl₂, 100 MHz): δ 192.7, 165.5, 148.4, 139.2, 131.9, 131.8, 131.7, 126.6, 37.5 ppm.

4-Ethynaphthalen-1(4H)-one·AlCl₃ (Mono 2a) + 4-ethynaphthalen-1(2H)-one·AlCl₃ (Mono 2b).

$^1$H NMR (CD₂Cl₂, 400 MHz): δ 8.48 (m, 1H); 8.22 (dd, J = 9.9, 3.3 Hz, 1H), 8.14 (t, J = 7.7 Hz, 1H), 7.97 (td, J = 7.7, 1.4 Hz, 1H), 7.85 (d, J = 8.2 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.73 – 7.59 (m, 1H); 7.52 (dd, J = 9.9, 1.5 Hz, 1H); 6.46 (t, J = 3.9 Hz, 1H); 4.27 – 4.16 (m, 3H); 2.75 (dt, J = 7.7, 5.9 Hz, 1H); 2.40 (m, 1H); 1.31 (t, J = 7.4 Hz, 3H); 0.75 (t, J = 7.5 Hz, 3H) ppm.

$^{13}$C NMR (CD₂Cl₂, 100 MHz): δ 172.9, 145.5, 140.5, 133.5, 132.4, 131.6, 131.5, 130.8, 129.8, 128.6, 128.3, 47.8, 44.1, 31.0, 27.5, 15.2, 12.3 ppm.

4-Nitronaphthalen-1(4H)-one·2AlCl₃ (Bis 3a).

$^1$H NMR (CD₂Cl₂, 400 MHz): 9.33 – 8.90 (m, 1H), 8.84 – 8.49 (m, 2H), 8.44 – 8.14 (m, 1H), 8.15 – 7.89 (m, 1H), 7.84 – 7.30 (m, 1H), 1.09 (s, 1H) ppm.
Naphthalen-2(1H)-one∙AlCl₃ (Mono 4a).

$^1$H NMR (CD$_2$Cl$_2$, 400 MHz): $\delta$ 8.60 (d, $J = 9.4$ Hz, 1H), 7.82 – 7.76 (m, 2H), 7.64 – 7.60 (m, 2H), 7.06 (d, $J = 9.4$ Hz, 1H), 4.63 (s, 2H) ppm.

$^{13}$C NMR (CD$_2$Cl$_2$, 100 MHz): $\delta 212.3, 168.4, 140.9, 137.3, 135.5, 131.6, 131.3, 131.2, 126.1, 46.2$ ppm.

Naphthalen-2(1H)-one∙2AlCl₃ (Bis 4a).

$^1$H NMR (CD$_2$Cl$_2$, 400 MHz): $\delta$ 8.88 – 8.64 (m, 1H), 7.95 – 7.79 (m, 2H), 7.72 – 7.62 (m, 2H), 7.17 – 7.09 (m, 1H), 4.67 (s, 2H) ppm.

$^{13}$C NMR (CD$_2$Cl$_2$, 100 MHz): $\delta 212.1, 170.0, 141.4, 137.9, 135.9, 131.8, 131.4, 131.3, 125.9, 46.4$ ppm.

Cu-catalysed addition of organometallics to naphthols:

**Method A:** In an oven dried Schlenk, a DCM solution (3 mL) of naphthol (0.347 mmol) was added, at RT and under nitrogen, to AlCl₃ (0.093 g, 0.694 mmol). To the obtained solution, CuCl (0.0017 g, 0.017 mmol) and dppf (0.0096 g, 0.017 mmol) were added and the mixture was stirred for 5 min. ZnEt$_2$ (1.0 M in hexane, 0.69 mL 0.694 mmol) was added at the same temperature for 30 sec. Then, the reaction was stirred vigorously at RT for 10 min. Finally, the mixture was quenched with NH$_4$Cl (saturated, 10 mL) and extracted with Et$_2$O (3 x 10 mL). The combined organic fractions were dried over MgSO$_4$ and evaporated. The desired product was isolated by column chromatography on silica using EtOAc/pentane (2:98, v/v) as an eluent.

**Method B:** A solution of 1-naphthol (0.347 mmol) in DCM (3 mL) was added, at RT under nitrogen atmosphere, to AlCl₃ (0.093 g, 0.694 mmol). To the obtained solution, CuCl (0.0017 g, 0.017 mmol) and dppf (0.0096 g, 0.017 mmol) were added and the resulting mixture was stirred for 5 min. Me$_3$Al (1.0 M in hexane, 1.38 mL, 1.39 mmol) was added at the same temperature for 30 sec. Subsequently, the reaction was stirred vigorously at RT for 10 min. Then, the mixture was quenched by NH$_4$Cl (saturated, 10 mL) and extracted with Et$_2$O (3 x 10 mL). The combined organic fractions were dried over MgSO$_4$ and evaporated. The desired product was isolated by column chromatography on silica using EtOAc/pentane (2:98, v/v) as an eluent.
3-Ethyl-3,4-dihydronaphthalen-1(2H)-one (5a), colorless oil, 50% yield, synthesized following Method A.

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.01 (dd, $J$ = 7.8, 1.4 Hz, 1H), 7.47 (td, $J$ = 7.5, 1.5 Hz, 1H), 7.30 (t, $J$ = 7.5 Hz, 1H), 7.25 (d, $J$ = 7.5 Hz, 1H), 3.01 (m, 1H), 2.78 (m, 1H), 2.69 (dd, $J$ = 16.2, 10.7 Hz, 1H), 2.31 (dd, $J$ = 16.5, 12.1 Hz, 1H), 2.11 (m, 1H), 1.49 (m, 2H), 0.99 (t, $J$ = 7.4 Hz, 3H) ppm.

$^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 201.3, 146.5, 136.1, 135.1, 131.6, 129.6, 129.2, 47.8, 39.7, 38.5, 31.2, 13.8 ppm.

HRMS (ESI+, m/Z): calc. for 175.1117 [M+H]$^+$, found 175.1118.

trans-3,4-Diethyl-3,4-dihydronaphthalen-1(2H)-one (5b), colorless oil, 24% yield, synthesized following Method A.

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.98 (dd, $J$ = 7.8, 1.4 Hz, 1H), 7.47 (td, $J$ = 7.5, 1.5 Hz, 1H), 7.29 (t, $J$ = 7.6, 1.2 Hz, 1H), 7.22 (d, $J$ = 7.7 Hz, 1H), 2.88 (dd, $J$ = 17.7, 5.2 Hz, 1H), 2.68 (m, 1H), 2.51 (m, 1H), 2.12 (m, 1H), 1.73 (m, 2H), 1.45 – 1.27 (m, 2H), 1.01 (t, $J$ = 7.4 Hz, 3H), 0.90 (t, $J$ = 7.4 Hz, 3H) ppm.

$^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 200.7, 149.3, 136.1, 134.2, 132.4, 129.5, 129.2, 47.6, 41.8, 41.3, 31.9, 29.3, 15.1, 14.5 ppm.

HRMS (ESI+, m/Z): calc. for 203.1430 [M+H]$^+$, found 203.1432.

4-Ethyl-3,4-dihydronaphthalen-2-(1H)-one (5c), colorless oil, 31% yield, synthesized following Method A.

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.23 – 7.18 (m, 3H), 7.13 – 7.09 (m, 1H), 3.58 (s, 2H), 3.02 – 2.95 (m, 1H), 2.69 (dd, $J$ = 16.3, 5.6 Hz, 1H), 2.54 (dd, $J$ = 16.3, 4.3 Hz, 1H), 1.68 – 1.48 (m, 2H), 0.94 (t, $J$ = 5.7 Hz, 3H) ppm.

$^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 213.20, 142.53, 135.40, 131.31, 130.41, 129.41, 129.21, 46.56, 46.44, 43.87, 30.48, 14.53 ppm.

HRMS (ESI+, m/Z): calc. for 175.1117 [M+H]$^+$, found 175.1117.

3-Methyl-3,4-dihydronaphthalen-1(2H)-one (5d), colorless oil, 55% yield, synthesized following Method B.

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 8.01 (d, $J$ = 7.85 Hz, 1H), 7.46 (t, $J$ = 7.85 Hz, 1H), 7.29 (t, $J$ = 7.85 Hz, 1H), 7.23 (d, $J$ = 7.85 Hz, 1H), 3.01 – 2.92 (m, 1H), 2.78 – 2.61 (m, 2H), 2.40 – 2.24 (m, 2H), 1.13 (d, $J$ = 5.74 Hz, 3H) ppm.

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 201.15, 146.44, 136.14, 134.87, 131.48, 129.41, 129.21, 46.56, 46.44, 43.87, 30.48, 14.53 ppm.

HRMS (ESI+, m/Z): calc. for 161.0970 [M+H]$^+$, found 161.0961.
SUPPORTING INFORMATION

Phospha-Michael 1,4-addition to naphthols:

Procedure: To a solution of naphthol (0.347 mmol) in DCM (5 mL), AlCl₃ (0.093 g, 0.694 mmol) was added at RT under nitrogen atmosphere. Then, a solution of Ph₃P·H (0.382 mmol) in DCM (0.5 mL) was added at the same temperature in one portion. The reaction was stirred at RT for 24 h. Then, the mixture was quenched by NH₄Cl (saturated, 10 mL) and extracted with EtOAc (3 x 10 mL). The combined organic fractions were dried over MgSO₄ and evaporated. Then, the desired product was isolated by column chromatography on silica using EtOAc/pentane (2:98, v/v) as an eluent.[13]

![Chemical structure](image)

3-(Diphenylphosphanylidene)-3,4-dihydronaphthalen-1(2H)-one (6a), colorless solid, 85% yield.

1H NMR (CDCl₃, 400 MHz): δ 8.02 (dd, J = 7.8, 1.4 Hz, 1H), 7.53 (m, 4H), 7.45 (td, J = 7.5, 1.5 Hz, 1H), 7.42 – 7.34 (m, 6H), 7.31 (t, J = 7.5 Hz, 1H), 7.16 (d, J = 7.7 Hz, 1H), 3.12 (m, 1H), 2.96 (dd, J = 7.8, 5.7 Hz, 2H), 2.74 (m, 1H), 2.53 (m, 1H) ppm.

13C NMR (CDCl₃, 100 MHz): δ 199.5 (d, J = 12.0 Hz), 146.2 (d, J = 13.4 Hz), 138.0 (d, J = 13.2 Hz), 137.5 (d, J = 12.9 Hz), 136.3 (d, J = 14.3 Hz), 136.1 (d, J = 19.9 Hz), 135.0, 132.0 (d, J = 11.5 Hz), 131.4 (d, J = 7.2 Hz), 131.3, 129.7 (d, J = 20.5 Hz), 44.3 (d, J = 13.7 Hz), 35.6 (d, J = 3.0 Hz), 35.5 (d, J = 8.8 Hz) ppm.

31P NMR (CDCl₃, 161.94 MHz): δ –5.48 ppm.

1H NMR (CDCl₃, 500 MHz) δ 8.05 – 8.03 (m, 1H), 7.55 (m, 4H), 7.47 (td, J = 7.5, 1.2 Hz, 1H), 7.44 – 7.37 (m, 6H), 7.33 (t, J = 7.5 Hz, 1H), 7.17 (d, J = 7.6 Hz, 1H), 3.14 (m, 1H), 2.98 (d, J = 7.9 Hz, 2H), 2.76 (dd, J = 16.9, 3.1 Hz, 1H), 2.55 (dd, J = 16.8, 13.0 Hz, 1H) ppm.

13C NMR (CDCl₃, 126 MHz) δ 199.53, 146.18, 146.18, 138.03, 137.57, 136.35, 136.31, 136.14, 135.01, 132.08, 131.96, 131.39, 131.32, 129.84, 129.64, 44.33, 35.61, 35.55 ppm.

31P NMR (CDCl₃, 202 MHz): δ –8.48 ppm.

HRMS (ESI+, m/z): calc. for 331.1246 [M+H]⁺, found 331.1248.

![Chemical structure](image)

3-(Bis(4-ethoxyphenyl)phosphanylidene)-3,4-dihydronaphthalen-1(2H)-one (6b), colorless oil, 71% yield.

1H NMR (CDCl₃, 400 MHz) δ 7.99 (d, J = 7.8 Hz, 1H), 7.59 – 7.39 (m, 5H), 7.29 (t, J = 7.5 Hz, 1H), 7.14 (d, J = 7.6 Hz, 1H), 6.93 (d, J = 8.4 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 3.81 (s, 3H), 3.80 (s, 3H), 3.22 – 2.87 (m, 3H), 2.74 – 2.63 (m, 1H), 2.60 – 2.46 (m, 1H) ppm.

13C NMR (CDCl₃, 100 MHz) δ 196.9 (d, J = 12.2 Hz), 160.6 (d, J = 7.1 Hz), 143.6 (d, J = 13.5 Hz), 135.0 (d, J = 14.4 Hz), 134.8 (d, J = 14.1 Hz), 133.6, 132.4, 128.6 (d, J = 1.1 Hz), 127.0 (d, J = 22.0 Hz), 126.5 (d, J = 10.7 Hz), 126.1 (d, J = 10.6 Hz), 114.4 (d, J = 8.1 Hz), 55.2, 41.7 (d, J = 14.5 Hz), 33.6 (d, J = 10.3 Hz), 32.9 (d, J = 17.8 Hz) ppm.

31P NMR (CDCl₃, 161.94 MHz) δ –11.39 ppm.

HRMS (ESI+, m/z): calc. for 391.1458 [M+H]⁺, found 391.14576.
3-(Bis(2-methoxyphenyl)phosphaneyl)-3,4-dihydronaphthalen-1(2H)-one (6c), colorless oil, 80% yield.

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 8.00 (dd, $J = 7.8, 0.9$ Hz, 1H), 7.42 (td, $J = 7.5, 1.2$ Hz, 1H), 7.38 – 7.19 (m, 5H), 7.16 (d, $J = 7.7$ Hz, 1H), 7.02 – 6.76 (m, 4H), 3.75 (s, 3H), 3.74 (s, 3H), 3.33 – 3.18 (m, 1H), 3.16 – 2.93 (m, 2H), 2.77 – 2.71 (m, 1H), 2.66 – 2.57 (m, 1H) ppm.

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 197.8 (d, $J = 12.2$ Hz), 162.0 (d, $J = 5.9$ Hz), 161.9 (d, $J = 5.9$ Hz), 144.4 (d, $J = 14.4$ Hz), 134.0 (d, $J = 8.7$ Hz), 133.7 (d, $J = 8.5$ Hz), 133.5, 132.5, 130.7 (d, $J = 9.1$ Hz), 128.7 (d, $J = 1.1$ Hz), 127.0 (d, $J = 34.2$ Hz), 121.0 (d, $J = 3.4$ Hz), 110.8 (d, $J = 1.8$ Hz), 110.7 (d, $J = 1.9$ Hz), 55.7, 55.6, 42.4 (d, $J = 14.1$ Hz), 33.7 (d, $J = 19.5$ Hz), 31.7 (d, $J = 11.9$ Hz) ppm.

$^{31}$P NMR (CDCl$_3$, 161.94 MHz) $\delta$ –28.52 ppm.

HRMS (ESI+, m/Z): calc. for 391.1458 [M+H]$^+$, found 391.14576.

3-(Diisopropylphosphoryl)-3,4-dihydronaphthalen-1(2H)-one (6d), colorless oil, 30% yield.

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 8.01 (dd, $J = 7.7, 0.6$ Hz, 1H), 7.49 (td, $J = 7.6, 1.0$ Hz, 1H), 7.33 (t, $J = 7.5$ Hz, 1H), 7.27 (d, $J = 7.6$ Hz, 1H), 3.31 (m, 1H), 3.16 (m, 1H), 3.00 – 2.67 (m, 3H), 2.39 – 2.11 (m, 2H), 1.38 – 1.08 (m, 12H) ppm.

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 195.9 (d, $J = 13.3$ Hz), 142.9 (d, $J = 13.8$ Hz), 134.2, 131.8 (d, $J = 1.0$ Hz), 128.9 (d, $J = 1.0$ Hz), 127.5, 127.5, 39.0 (d, $J = 3.0$ Hz), 32.2 (d, $J = 58.9$ Hz), 29.9, 29.6 (d, $J = 3.0$ Hz), 25.7 (d, $J = 26.1$ Hz), 25.1 (d, $J = 25.7$ Hz), 16.8 (d, $J = 2.8$ Hz), 16.6 (d, $J = 1.4$ Hz), 16.6 (d, $J = 1.2$ Hz).

$^{31}$P NMR (CDCl$_3$, 161.94 MHz) $\delta$ 51.16 ppm.

HRMS (ESI+, m/Z): calc. for 279.15084 [M+H]$^+$, 279.15084.

trans-3-(Diphenylphosphaneyl)-4-nitro-3,4-dihydronaphthalen-1(2H)-one (6e-trans), colorless oil, 7% yield.

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 8.03 (d, $J = 7.8$ Hz, 1H), 7.53 – 7.41 (m, 5H), 7.40 – 7.29 (m, 7H), 3.23 – 3.18 (m, 1H), 3.15 – 3.01 (m, 1H), 2.65 (q, $J = 7.3$ Hz, 1H), 2.57 – 2.48 (m, 1H), 1.89 – 1.69 (m, 2H), 0.99 (t, $J = 7.4$ Hz, 3H) ppm.

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 196.5 (d, $J = 2.6$ Hz), 146.3 (d, $J = 2.8$ Hz), 136.3 (d, $J = 14.4$ Hz), 135.9 (d, $J = 14.1$ Hz), 133.9, 133.8 (d, $J = 7.1$ Hz), 133.7 (d, $J = 10.1$ Hz), 132.0 (d, $J = 1.7$ Hz), 129.7, 129.4 (d, $J = 0.8$ Hz), 129.3 (d, $J = 0.7$ Hz), 128.8 (d, $J = 2.2$ Hz), 128.7 (d, $J = 2.4$ Hz), 127.3 (d, $J = 8.0$ Hz), 42.3 (d, $J = 14.6$ Hz), 36.0 (d, $J = 15.3$ Hz), 35.3 (d, $J = 11.3$ Hz), 29.8 (d, $J = 6.3$ Hz), 12.6 ppm.

$^{31}$P NMR (CDCl$_3$, 161.94 MHz) $\delta$ –16.08 ppm.

HRMS (ESI+, m/Z): calc. for 359.1559 [M+H]$^+$, found 359.1565.
cis-3-(Diphenylphosphaneyl)-4-nitro-3,4-dihydronaphthalen-1(2H)-one (6e-cis), colorless oil, 43% yield.

\(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 8.04 (dd, \(J = 7.7, 1.0\) Hz, 1H), 7.61 – 7.55 (m, 2H), 7.55 – 7.48 (m, 2H), 7.44 (td, \(J = 7.5, 1.4\) Hz, 1H), 7.41 – 7.30 (m, 7H), 7.08 (d, \(J = 7.5\) Hz, 1H), 3.32 – 3.25 (m, 1H), 2.89 – 2.79 (m, 1H), 2.63 – 2.57 (m, 1H), 2.51 – 2.40 (m, 2H), 1.55 – 1.44 (m, 1H), 0.82 (t, \(J = 7.4\) Hz, 3H) ppm.

\(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 197.4 (d, \(J = 13.1\) Hz), 148.4 (d, \(J = 7.2\) Hz), 135.8 (d, \(J = 13.9\) Hz), 135.4 (d, \(J = 13.2\) Hz), 133.9 (d, \(J = 18.7\) Hz), 133.7 (d, \(J = 17.9\) Hz), 132.9, 131.8, 129.5 (d, \(J = 5.1\) Hz), 129.3 (d, \(J = 1.5\) Hz), 128.9 (d, \(J = 1.9\) Hz), 128.8 (d, \(J = 2.2\) Hz), 128.1, 127.3, 42.4 (d, \(J = 9.8\) Hz), 37.9 (d, \(J = 12.3\) Hz), 37.3 (d, \(J = 17.0\) Hz), 24.4 (d, \(J = 15.6\) Hz), 12.5 (d, \(J = 0.7\) Hz).

\(^{31}\)P NMR (CDCl\(_3\), 161.94 MHz): \(\delta\) –18.48 ppm.

HRMS (ESI+, m/Z): calc. for 359.1559 [M+H]\(^+\), found 359.1563.

trans-3-(Diphenylphosphaneyl)-4-nitro-3,4-dihydronaphthalen-1(2H)-one (6f-trans), colorless oil, 4% yield.

cis-3-(diphenylphosphaneyl)-4-nitro-3,4-dihydronaphthalen-1(2H)-one (6f-cis), colorless oil, 2% yield.

\(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta\) 8.26 – 8.08 (m, 1H); 7.78 – 7.29 (m, 13H); 5.65 (s, 1H); 5.50 (s, 1H); 3.97 (s, 1H); 3.49 (dt, \(J = 13.5, 4.5\) Hz, 1H); 3.16 (m, 1H); 2.64 (dd, \(J = 19.0, 6.5\) Hz, 1H); 2.60 (dd, \(J = 18.4, 5.2\) Hz, 1H) ppm.

\(^{13}\)C NMR (CDCl\(_3\), 126 MHz) \(\delta\) 197.4 (d, \(J = 10.2\) Hz), 196.6; 137.5, 137.5, 137.2, 136.9, 136.8, 136.6, 136.5, 136.3, 136.0, 135.9, 135.3, 135.1, 134.9, 134.0, 133.4, 133.0, 132.9, 132.1, 132.0, 131.9, 131.9, 131.8, 131.7, 130.9, 130.3; 88.6 (d, \(J = 20.5\) Hz); 87.9 (d, \(J = 13.9\) Hz); 39.7 (d, \(J = 19.4\) Hz); 38.7 (d, \(J = 11.1\) Hz); 38.5 (d, \(J = 10.6\) Hz), 38.3 (d, \(J = 6.9\) Hz) ppm.

\(^{31}\)P NMR (CDCl\(_3\), 161.94 MHz): \(\delta\) –17.09, –14.81 ppm.

HRMS (ESI+, m/Z): calc. for 376.3712 [M+H]\(^+\), found 376.3713.

4-(Diphenylphosphaneyl)-3,4-dihydronaphthalen-2(1H)-one (6g), 3% yield.

\(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.66 – 7.57 (m, 4H), 7.46 (dd, \(J = 3.3, 2.0\) Hz, 6H), 7.25 – 7.09 (m, 4H), 4.02 (dt, \(J = 4.7, 2.6\) Hz, 1H), 3.97 (d, \(J = 20.7\) Hz, 1H), 3.54 (d, \(J = 20.3\) Hz, 1H), 2.89 – 2.70 (m, 1H), 2.65 (m, 1H) ppm.

\(^{31}\)P NMR (CDCl\(_3\), 161.94 MHz): \(\delta\) –11.27 ppm.

HRMS (ESI+, m/Z): calc. for 331.1246 [M+H]\(^+\), found 331.1248.
**Cu-catalysed reduction of naphthols by Et$_3$SiH:**

**Procedure:** To a solution of naphthol (0.347 mmol) in DCM (5 mL) AlCl$_3$ (0.093 g, 0.694 mmol) was added at RT under nitrogen atmosphere. To the obtained solution, CuCl (0.0034 g, 0.035 mmol) and dppf (0.0192 g, 0.035 mmol) were added and the mixture was stirred for 5 min. Then, Et$_3$SiH (0.097 g, 0.416 mmol) in DCM (0.5 mL) was added at the same temperature for 30 sec. The reaction was stirred vigorously at RT for 10 min. Finally, the mixture was quenched by NH$_4$Cl (saturated, 10 mL) and extracted with Et$_2$O (3 x 10 mL). The combined organic fractions were dried over MgSO$_4$ and evaporated. The desired product was isolated by column chromatography on silica using EtOAc/pentane (2:98, v/v) as an eluent.

3,4-Dihydronaphthalen-1(2H)-one (7a), colorless oil, 60% yield.

$^1$H NMR (CDCl$_3$, 400 MHz): δ 8.04 (dd, $J = 7.8$, 1.4 Hz, 1H), 7.46 (td, $J = 7.4$, 1.4 Hz, 1H), 7.31 (t, $J = 7.8$ Hz, 1H), 7.25 (d, $J = 7.7$ Hz, 1H), 2.97 (t, $J = 6.1$ Hz, 2H), 2.66 (dd, $J = 7.2$, 5.9 Hz, 2H), 2.14 (m, 2H) ppm.

$^{13}$C NMR (CDCl$_3$, 100 MHz): δ 201.1, 147.2, 136.1, 135.3, 131.4, 129.8, 129.3, 41.8, 32.4, 25.9 ppm.

HRMS (ESI+, m/z): calc. for 147.0804 [M+H]$^+$, found 147.0807.

4-Ethyl-3,4-dihydronaphthalen-1(2H)-one (7b), colorless oil, 18% yield.

$^1$H NMR (CDCl$_3$, 400 MHz): δ 8.03 (dd, $J = 7.8$, 1.4 Hz, 1H), 7.49 (td, $J = 7.5$, 1.5 Hz, 1H), 7.31 (t, $J = 7.8$ Hz, 1H), 7.29 (d, $J = 7.5$, 1H), 2.88 – 2.82 (m, 1H), 2.77 (m, 1H), 2.58 (dt, $J = 17.8$, 5.2 Hz, 1H), 2.24 (m, 1H), 2.07 (m, 1H), 1.85 – 1.65 (m, 2H), 1.03 (t, $J = 7.4$ Hz, 3H) ppm.

$^{13}$C NMR (CDCl$_3$, 100 MHz): δ 201.2, 150.9, 136.0, 134.6, 130.9, 130.0, 129.2, 42.2, 37.7, 30.1, 29.0, 14.8 ppm.

HRMS (ESI+, m/z): calc. for 175.1117 [M+H]$^+$, found 175.1118.

3,4-Dihydronaphthalen-2(1H)-one (7c), colorless oil, 40% yield.

$^1$H NMR (CDCl$_3$, 400 MHz): δ 7.27 – 7.19 (m, 3H), 7.12 (dd, $J = 5.6$, 2.2 Hz, 1H), 3.59 (s, 2H), 3.06 (t, $J = 6.7$ Hz, 2H), 2.55 (t, $J = 6.7$ Hz, 2H) ppm.

$^{13}$C NMR (CDCl$_3$, 100 MHz): δ 213.4, 139.3, 135.9, 130.9, 130.2, 129.6, 129.5, 47.7, 40.8, 31.0 ppm.

HRMS (ESI+, m/z): calc. for 147.0804 [M+H]$^+$, found 147.0804.
6. NMR spectra in numerical order of compounds

$^1$H NMR (CD$_2$Cl$_2$, 400 MHz)

$^{13}$C NMR (CD$_2$Cl$_2$, 100 MHz)
naphthalen-1-(4H)-one* \( \text{B(C_6F_5)_3} \) (Mono 1a)

\(^1\)H NMR (CD_2Cl_2, 400 MHz)

naphthalen-1-(4H)-one* \( \text{B(C_6F_5)_3} \) (Mono 1a)

\(^{13}\)C NMR (CD_2Cl_2, 100 MHz)
$^{13}$C NMR (CD$_2$Cl$_2$, 100 MHz)

**Mono 2a**

**Mono 2b**

**COSY**
SUPPORTING INFORMATION

4-ethyl-naphthalen-1-ol
(2)

$^{13}$C NMR (CDCl$_3$, 100 MHz)

Bis 3a

$^1$H NMR (CD$_2$Cl$_2$, 400 MHz)
$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
$^{13}$C NMR (CDCl$_3$, 100 MHz)

$^{31}$P NMR (CDCl$_3$, 161.94 MHz)
**SUPPORTING INFORMATION**

**Figure 1**: 
1H NMR (CDCl₃, 500 MHz) for compound 6a. 

**Figure 2**: 
1H NMR (CDCl₃, 500 MHz) for compound 6a after 31P decoupling.
SUPPORTING INFORMATION

^{13}\text{C NMR (CDCl}_3, 126 \text{ MHz) \text{ (31P decoupled)}}
**SUPPORTING INFORMATION**

**31P NMR** (CDCl₃, 202 MHz)

**1H NMR** (CDCl₃, 400 MHz)
$^{13}$C NMR (CDCl$_3$, 100 MHz)

$^{31}$P NMR (CDCl$_3$, 161.94 MHz)
$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
**SUPPORTING INFORMATION**

**31P NMR** (CDCl$_3$, 161.94 MHz)

![31P NMR spectrum](image)

**1H NMR** (CDCl$_3$, 400 MHz)

![1H NMR spectrum](image)
Supporting Information

$^{31}$P NMR (CDCl$_3$, 161.94 MHz)

6e-trans

COSY
$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 126 MHz)
$^{31}$P NMR (CDCl$_3$, 161.94 MHz)

$^1$H NMR (CDCl$_3$, 400 MHz)
$^{31}$P NMR (CDCl$_3$, 161.94 MHz)

$^1$H NMR (CDCl$_3$, 400 MHz)
$^{13}$C NMR (CDCl$_3$, 100 MHz)
$^{13}$C NMR (CDCl$_3$, 100 MHz)

$^1$H NMR (CDCl$_3$, 400 MHz)
$^{13}$C NMR (CDCl$_3$, 100 MHz)
7. Cartesian coordinates

I

Zero-point correction= 0.151187
(Hartree/Particle)

Thermal correction to Energy= 0.159146
Thermal correction to Enthalpy= 0.160090

Thermal correction to Gibbs Free Energy= 0.118641
Sum of electronic and zero-point Energies= -3245.409307
Sum of electronic and thermal Energies= -3245.396219
Sum of electronic and thermal Free Energies= -3245.397163

Num. Imaginary Frequencies: 0

Al  -1.945122  1.573267  -0.000011
Cl  -0.620100  1.938777  -0.000008
Cl  0.392426  0.942973  -0.000002
Cl  0.026933  -0.437000  -0.000001
Cl  -1.359183  -0.777619  -0.000001
Cl  -2.321450  0.211237  -0.000007
H   2.053835  2.335290  -0.000001
H   -2.729228  2.339248  -0.000015
H   -0.325645  2.995166  -0.000011
C   1.772230  1.274646  -0.000001
C   1.039770  -1.428034  -0.000007
H  -3.382995  -0.068372  -0.000009
C   2.369085  -1.070185  -0.000010
C   2.738208  0.294716  -0.000007
H   0.744979  -2.462483  -0.000009
H   3.145690  -1.843629  -0.000014
H   3.795172  0.570594  -0.000010
O  -1.655331  -2.095246  -0.000002
H  -2.619941  -2.220506  -0.000002

Al2Cl6

Zero-point correction= 0.010885
(Hartree/Particle)

Thermal correction to Energy= 0.023029
Thermal correction to Enthalpy= 0.023973

Thermal correction to Gibbs Free Energy= -0.031744
Sum of electronic and zero-point Energies= -3245.409307
Sum of electronic and thermal Energies= -3245.396219
Sum of electronic and thermal Free Energies= -3245.397163

Num. Imaginary Frequencies: 0

Al  -1.602240  -0.000095  -0.000059
Cl  -2.620313  -1.822199  0.000157
Cl  -2.618770  1.822982  -0.000153
Cl  0.000038  -0.006621  1.622665
Cl  0.000036  -0.006651  -1.622644
Al  1.602226  -0.000087  0.000149
Cl  2.620174  -1.822326  -0.000189
Cl  2.618845  1.822956  -0.000095

II

Zero-point correction= 0.004808
(Hartree/Particle)

Thermal correction to Energy= 0.010151
Thermal correction to Enthalpy= 0.011095

Thermal correction to Gibbs Free Energy= -0.024577
Sum of electronic and zero-point Energies= -1622.682127
Sum of electronic and thermal Energies= -1622.676784
Sum of electronic and thermal Free Energies= -1622.711512

Num. Imaginary Frequencies: 0

Al  0.000000  0.000000  0.000000
Cl  0.000000  2.079890  0.000000
Cl  1.801237  -1.039945  0.000000
Cl  -1.801237  -1.039945  0.000000

III
SUPPORTING INFORMATION

Zero-point correction = 0.309566
(Hartree/Particle)
Thermal correction to Energy = 0.339362
Thermal correction to Enthalpy = 0.334906
Thermal correction to Gibbs Free Energy = 0.252604
Sum of electronic and zero-point Energies= -2543.288503
Sum of electronic and thermal Energies= -2543.265665
Sum of electronic and thermal Enthalpies= -2543.264721
Sum of electronic and thermal Free Energies= -2543.342376

Num. Imaginary Frequencies: 0

Zero-point correction = 0.305061
(Hartree/Particle)
Thermal correction to Energy = 0.327900
Thermal correction to Enthalpy = 0.328844
Thermal correction to Gibbs Free Energy = 0.251189

C 1.442546 1.203122 -1.518978
C 0.224418 1.963064 -1.307849
C 0.218330 2.953668 -0.292606
C 1.259749 3.070878 0.606308
C 2.391855 2.257036 0.478605
C 2.516825 1.319893 -0.593666
H -0.425000 2.127416 -2.184324
H 4.082075 1.805872 1.276812
O 3.334760 2.420907 1.393350
C 1.422847 -2.341968 0.714381
C 1.235515 -3.357969 -0.257391
O 0.216331 -3.267186 -1.178621
C -0.637044 -2.144030 -1.194262
C -0.468058 -1.137634 -0.267597
C 0.540385 -1.218835 0.734167
C 1.914317 -4.219486 -0.256303
O -1.234535 -0.007016 -0.328665
H 1.232626 3.787661 1.432738
H -0.667315 3.590401 -0.183851
C 3.664234 0.504009 -0.763527
C 3.748782 -0.386986 -1.816896
H 2.689240 -0.479996 -2.740257
C 1.557848 0.295219 -2.590279
H 4.508899 0.556603 -0.064970
H 4.640943 -1.003982 -1.937396
H 2.764691 -1.176991 -3.579849
H 0.726051 2.11423 -3.300499
C 2.465516 -2.402254 1.675212
C 0.701654 -0.225547 1.731251
C 1.722736 -0.316418 2.650051
C 2.619842 -1.409541 2.615556
C 3.146103 -3.262951 1.654965
H -0.002558 0.613984 1.766865
H 1.839305 0.460193 3.415105
C 3.428894 -1.471779 3.352408
H 0.071514 -4.061339 -1.919278
C -1.430556 -2.040407 -1.943031
C -0.551533 1.036704 -0.753889
Al 2.984724 0.157268 0.117354
Cl -3.154769 -0.516243 2.135982
Cl -3.306077 2.261915 -0.131198
Cl -4.155564 -1.013988 -1.229350

IV

Zero-point correction = 0.308763
(Hartree/Particle)
Thermal correction to Energy = 0.332818
Thermal correction to Enthalpy = 0.333762
Thermal correction to Gibbs Free Energy = 0.252239
Sum of electronic and zero-point Energies= -2543.301715
Sum of electronic and thermal Energies= -2543.277660
Sum of electronic and thermal Enthalpies= -2543.276716
Sum of electronic and thermal Free Energies= -2543.358239

Num. Imaginary Frequencies: 0

C 1.586469 3.660353 -1.119895
C 0.609191 4.137641 -0.273818
C -0.186963 3.252256 0.492731
### SUPPORTING INFORMATION

| C  | 0.034445 | 1.841860 | 0.402522 |
|----|----------|----------|----------|
| C  | 1.041896 | 1.401381 | -0.496162 |
| C  | 1.802354 | 2.269832 | -1.237223 |
| H  | -1.370631 | 4.813600 | 1.419104 |
| H  | 2.197426 | 4.351016 | -1.709720 |
| H  | 0.420025 | 5.215639 | -0.190706 |
| C  | -1.205030 | 3.731049 | 1.557277 |
| C  | -0.753015 | 0.966904 | 1.195953 |
| H  | 0.563964 | -0.355134 | -1.380685 |
| C  | -1.731796 | 1.469127 | 2.023317 |
| C  | -1.966276 | 2.861430 | 2.101728 |
| H  | -0.567331 | -0.112222 | 1.164014 |
| C  | -2.327969 | 0.782210 | 2.635557 |
| C  | -2.749698 | 3.244603 | 2.760002 |
| O  | 1.214588 | 0.230986 | -0.660825 |
| H  | 2.564089 | 1.869775 | -1.913923 |
| C  | -3.954819 | 0.405910 | -1.787838 |
| C  | -4.288225 | -0.306127 | -0.534159 |
| C  | -3.257826 | -1.275944 | -0.055931 |
| C  | -2.028712 | -1.410942 | -0.725192 |
| C  | -1.705550 | -0.531916 | 1.854066 |
| C  | -2.768825 | 0.284218 | -2.413988 |
| H  | -4.443624 | -1.944680 | 1.617391 |
| H  | -4.715958 | 1.083300 | -2.194965 |
| H  | -4.490502 | 0.451461 | 0.255230 |
| C  | -3.492266 | -0.254390 | 1.081922 |
| C  | -1.084106 | -2.353101 | -0.286402 |
| C  | -1.239260 | -3.117524 | 0.841980 |
| C  | -2.534855 | -9.256462 | 1.553718 |
| H  | -0.155211 | -2.487763 | -0.852405 |
| C  | -0.581608 | -3.840737 | 1.186742 |
| C  | -2.732834 | -3.550417 | 2.433759 |
| O  | -0.548483 | -0.441296 | -2.306174 |
| H  | -2.525038 | 0.852276 | -3.317808 |
| Al  | 2.572370 | -0.996837 | 0.150372 |
| C  | 2.511481 | -2.791332 | -1.001967 |
| Cl  | 4.372850 | 0.113104 | -0.052296 |
| H  | 1.966579 | -1.257546 | 2.174643 |
| H  | -5.265715 | -0.819519 | -0.651740 |

**V**

Zero-point correction = 0.157279

(Hartree/Particle)

Thermal correction to Energy = 0.172163
Thermal correction to Enthalpy = 0.173107
Thermal correction to Gibbs Free Energy = 0.112051

Sum of electronic and zero-point Energies = -2083.019876
Sum of electronic and thermal Energies = -2083.004992
Sum of electronic and thermal Enthalpies = -2083.004048
Sum of electronic and thermal Free Energies = -2083.065104

Num. Imaginary Frequencies: 0

| C  | -1.635288 | -2.556643 | -0.009857 |
|----|----------|----------|----------|
| C  | -3.002585 | -2.006689 | -0.002695 |
| C  | -3.101187 | -0.515626 | -0.030490 |
| C  | -1.939900 | -0.279844 | -0.011231 |
| O  | -0.631216 | -0.348486 | -0.018979 |
| H  | -0.526443 | -1.785171 | -0.018416 |
| H  | -5.257710 | -0.506349 | 0.011576 |
| H  | -1.531178 | -3.648337 | -0.011089 |
| H  | -3.559436 | -2.428927 | -0.865326 |
| H  | -4.349504 | 0.108219 | 0.043891 |
| C  | -2.041863 | 1.682784 | -0.012303 |
| H  | -3.548296 | -2.426567 | 0.872099 |
| C  | -3.286043 | 2.287577 | -0.005021 |
| C  | -4.441721 | 1.494443 | 0.003895 |

**II-a**

Zero-point correction = 0.163365

(Hartree/Particle)

Thermal correction to Energy = 0.185243
Thermal correction to Enthalpy = 0.186187

Sum of electronic and zero-point Energies = -3705.712454
Sum of electronic and thermal Energies = -3705.690577
Sum of electronic and thermal Enthalpies = -3705.689632
Sum of electronic and thermal Free Energies = -3705.767530

Num. Imaginary Frequencies: 0

**II-b**

Zero-point correction = 0.163736

(Hartree/Particle)

Thermal correction to Energy = 0.185369
Thermal correction to Enthalpy = 0.186313

Sum of electronic and zero-point Energies = -3705.693959
Sum of electronic and thermal Energies = -3705.672326
Sum of electronic and thermal Enthalpies = -3705.671982
Sum of electronic and thermal Free Energies = -3705.748131

Num. Imaginary Frequencies: 0
SUPPORTING INFORMATION

Zero-point correction= 0.163018 (Hartree/Particle)
Thermal correction to Energy= 0.184578
Thermal correction to Enthalpy= 0.185531
Thermal correction to Gibbs Free Energy= 0.109341
Sum of electronic and zero-point Energies= -3705.736420
Sum of electronic and thermal Energies= -3705.719907
Sum of electronic and thermal Free Energies= -3705.790907

0.109341 (Hartree/Particle)

V-b

Zero-point correction= 0.163018 (Hartree/Particle)
Thermal correction to Energy= 0.184578
Thermal correction to Enthalpy= 0.185531
Thermal correction to Gibbs Free Energy= 0.109341
Sum of electronic and zero-point Energies= -3705.736420
Sum of electronic and thermal Energies= -3705.719907
Sum of electronic and thermal Free Energies= -3705.790907

0.109341 (Hartree/Particle)

V-c

Zero-point correction= 0.163199 (Hartree/Particle)
Thermal correction to Energy= 0.185034
Thermal correction to Enthalpy= 0.185978
Thermal correction to Gibbs Free Energy= 0.107459
Sum of electronic and zero-point Energies= -3705.736420
Sum of electronic and thermal Energies= -3705.719907
Sum of electronic and thermal Free Energies= -3705.790907

0.107459 (Hartree/Particle)
**SUPPORTING INFORMATION**

C  -2.360511 -0.312895  0.296899
C   -2.190361 -1.704430  0.611446
H   -6.700335  -0.970380 -1.155176
H   -3.404017  -3.642773  0.646963
H   -4.703599  -2.808816 -1.053318
C   -5.876407  -2.688822  -0.978283
C   -3.783297   1.531543  -0.534566
H  -1.231719  -2.029132  1.031726
H   -4.940289   1.986325 -1.046373
H  -6.031352   1.080938 -1.268061
H  -2.950084   2.217380 -0.353312
H  -5.117549   3.047774 -1.278512
H  -6.982953   1.440633  -1.674659
H  -5.296332  -2.532996  0.554201
O  -1.417469   0.519581   0.478607
Cl  0.296473  0.572248  1.032410
Cl  2.796640  0.427732   2.925916
Cl  2.333140  0.097899  0.176843
Cl  1.282047  -0.078362   0.870687
Cl  0.866210  -0.044488  0.000018
Cl  2.499694  -0.139787  0.157361
Cl  2.798050  2.248458  0.057211
Cl  0.427732  2.925916 -1.198758
C  1.726377  1.301110  -0.74397
C  1.144509  -1.434149  0.963656
H  -0.307199  -0.153743  0.163717
C  2.459200  -1.010362  -0.076176
C  2.749317   0.365684  -0.013829
H  0.891674  -2.499694  0.139787
H  3.276925  -1.738153  0.114193
H  3.787559  0.699535  -0.045591
O  -1.774015  -2.011997  -0.263997
H  -2.796640  -1.130738  -0.437187

**Zero-point correction= 0.144729**
(Hartree/Particle)

Thermal correction to Energy= 0.152508
Thermal correction to Enthalpy= 0.153452
Thermal correction to Gibbs Free Energy= 0.112212

Sum of electronic and zero-point Energies= -460.179370
Sum of electronic and thermal Energies= -460.171591
Sum of electronic and thermal Enthalpies= -460.170646
Sum of electronic and thermal Free Energies= -460.211886

Num. Imaginary Frequencies: 1

Imaginary Frequency: -2100.7582

C  -2.004441  1.492259  0.024169
C  -0.699019  1.868609  -0.092120
C  0.372660  0.905176  -0.026420
C  0.099925  -0.490798   0.068143
C  -1.282047  -0.866210  0.044488
C  -2.333140  0.097899  0.176843
H  1.962542  2.369090  -0.157361
H  -2.798050  2.248458  0.057211
H  -0.427732  2.925916 -1.198758
C  1.726377  1.301110  -0.74397
C  1.144509  -1.434149  0.963656
H  -0.307199  -0.153743  0.163717
C  2.459200  -1.010362  -0.076176
C  2.749317   0.365684  -0.013829
H  0.891674  -2.499694  0.139787
H  3.276925  -1.738153  0.114193
H  3.787559  0.699535  -0.045591
O  -1.774015  -2.011997  -0.263997
H  -2.796640  -1.130738  -0.437187

**Zero-point correction= 0.144729**
(Hartree/Particle)

Thermal correction to Energy= 0.152508
Thermal correction to Enthalpy= 0.153452
Thermal correction to Gibbs Free Energy= 0.112212

Sum of electronic and zero-point Energies= -460.179370
Sum of electronic and thermal Energies= -460.171591
Sum of electronic and thermal Enthalpies= -460.170646
Sum of electronic and thermal Free Energies= -460.211886

Num. Imaginary Frequencies: 1

Imaginary Frequency: -1571.1925
Zero-point correction=  0.150684 
(Hartree/Particle)
Thermal correction to Energy=  0.158763
Thermal correction to Enthalpy=  0.159707
Thermal correction to Gibbs Free Energy=  0.117632

Sum of electronic and zero-point Energies=  460.260967 (Hartree/Particle)
Sum of electronic and thermal Energies=  460.419924 
Sum of electronic and thermal Enthalpies=  460.419924 
Sum of electronic and thermal Free Energies=  460.302098 

Num. Imaginary Frequencies: 0



Zero-point correction=  0.150729 
(Hartree/Particle)
Thermal correction to Energy=  0.165371
Thermal correction to Enthalpy=  0.166315
Thermal correction to Gibbs Free Energy=  0.106213

Sum of electronic and zero-point Energies=  2082.925166 (Hartree/Particle)
Sum of electronic and thermal Energies=  2083.080081 
Sum of electronic and thermal Enthalpies=  2083.080081 
Sum of electronic and thermal Free Energies=  2082.969682 

Num. Imaginary Frequencies: 1
Imaginary Frequency:  -1995.9608



Zero-point correction=  0.142480 
(Hartree/Particle)
Thermal correction to Energy=  0.150539
Thermal correction to Enthalpy=  0.151483
Thermal correction to Gibbs Free Energy=  0.109813

Sum of electronic and zero-point Energies=  -2082.979210 
Sum of electronic and thermal Energies=  -2083.135065 
Sum of electronic and thermal Enthalpies=  -2083.135065 
Sum of electronic and thermal Free Energies=  -2083.004972 

Num. Imaginary Frequencies: 1
Imaginary Frequency:  -2128.6082
| Elements | C | C | Cl | Cl | Cl |
|----------|---|---|----|----|----|
| Atomic Coordinates | H | 0.581762 | H | 5.173612 | 1.713282 | 0.487710 |
| C | 4.210086 | 1.262535 | C | 3.180913 | 2.070307 |
| H | 2.499599 | 1.262535 | C | 0.754776 | 0.564609 |
| C | 2.789083 | 2.278167 | C | 2.292293 | 3.373628 |
| H | 2.492215 | 1.598679 | C | 1.150105 | 2.172414 |
| Cl | 0.397055 | 0.386300 | Al | 2.218045 | 0.189009 |
| H | 0.474886 | -2.228489 | H | 0.474886 | 0.397055 |
| Cl | 2.960150 | -1.077259 | Cl | 2.686166 | -1.077259 |

**Imaginary Frequency:**

| Elements | Cl | Cl | Al | H | O |
|----------|----|----|----|---|---|
| Imaginary Coordinates | H | 0.225238 | H | 0.225238 | H |
| C | 2.651673 | 2.960150 | C | 2.218045 | 0.189009 |
| Cl | 2.960150 | 2.172414 | Al | 2.218045 | 0.189009 |
| H | 0.474886 | -2.228489 | H | 0.474886 | 0.397055 |
| Cl | 2.960150 | -1.077259 | Cl | 2.686166 | -1.077259 |

**Supporting Information:**

- **Sum of electronic and thermal Free Energies:**
  - 2083.065104
- **Num. Imaginary Frequencies:** 0

- **TS-II-V**
  - **Zero-point correction:** 0.149850
  - **(Hartree/Particle)**
  - **Thermal correction to Energy:** 0.164348
  - **Thermal correction to Enthalpy:** 0.165292
  - **Thermal correction to Gibbs Free Energy:** 0.159225
- **Sum of electronic and zero-point Energies:** -2082.813838
- **Sum of electronic and thermal Energies:** -2082.793940
- **Sum of electronic and thermal Enthalpies:** -2082.798396
- **Sum of electronic and thermal Free Energies:**

- **TS-VIII-V**
  - **Zero-point correction:** 0.152164
  - **(Hartree/Particle)**
  - **Thermal correction to Energy:** 0.167611
  - **Thermal correction to Enthalpy:** 0.167656
  - **Thermal correction to Gibbs Free Energy:** 0.108242
- **Sum of electronic and zero-point Energies:** -2082.878760
- **Sum of electronic and thermal Energies:** -2082.864213
- **Sum of electronic and thermal Enthalpies:** -2082.863268
- **Sum of electronic and thermal Free Energies:**

- **III-b**
  - **Zero-point correction:** 0.302919
  - **(Hartree/Particle)**
  - **Thermal correction to Energy:** 0.320925
  - **Thermal correction to Enthalpy:** 0.321869
  - **Thermal correction to Gibbs Free Energy:** 0.256070
- **Sum of electronic and zero-point Energies:** -920.556505
- **Sum of electronic and thermal Energies:** -920.538499
- **Sum of electronic and thermal Enthalpies:** -920.537555
- **Sum of electronic and thermal Free Energies:**

- **Num. Imaginary Frequencies:** 1
- **Imaginary Frequency:** -1753.7446
- **Sum of electronic and thermal Free Energies:**

- **Num. Imaginary Frequencies:** 1
  - **Imaginary Frequency:** -1578.4159
- **C | 0.679065 | -1.868641 | 0.169129**
- **C | 2.299572 | -2.062769 | 0.114747**
- **C | 2.788083 | -0.648899 | 0.075513**
- **C | 1.772049 | 0.159776 | -0.420929**
- **C | 0.564609 | -0.670666 | -0.67872**
- **C | 0.754776 | -2.068274 | -1.19832**
- **C | 4.839535 | -0.746025 | 0.77452**
- **H | 0.102407 | -2.533814 | 0.924407**
- **H | 2.499599 | -2.702078 | 0.995353**
- **C | 4.029381 | -0.116955 | 0.390529**
- **C | 1.937699 | 1.522155 | -0.596134**
- **H | 2.731408 | -2.658841 | -0.72803**
- **C | 3.180913 | 2.070307 | -0.25952**
- **C | 4.210086 | 1.262535 | 0.22523**
- **H | 1.117857 | 2.141499 | -0.976523**
- **H | 3.347594 | 3.146829 | -0.376454**
- **H | 5.173612 | 1.713282 | 0.487710**
- **O | -0.593288 | -0.151289 | -1.03887**
- **H | 0.581762 | -2.749995 | -2.04316**
- **Al | -1.956270 | 0.239616 | 0.03928**
- **Cl | -2.583807 | 1.640990 | -0.804774**
- **Cl | -1.148316 | 1.435813 | 1.620036**
- **Cl | -3.426839 | 1.247409 | -1.141611**
### SUPPORTING INFORMATION

**Zero-point correction** = 0.303711  
(Hartree/Particle)

**Thermal correction to Energy** = 0.321224

**Thermal correction to Enthalpy** = 0.322168

**Thermal correction to Gibbs Free Energy** = 0.258233

**Sum of electronic and zero-point Energies** = -920.558225

**Sum of electronic and thermal Energies** = -920.540712

**Sum of electronic and thermal Enthalpies** = -920.539768

**Sum of electronic and thermal Free Energies** = -920.603703

### Num. Imaginary Frequencies: 0

### Imaginary Frequency: -143.4154

| C   | -1.833928 | -1.311051 | 0.353250 |
| O   | -0.917876 | -2.337277 | 0.698455 |
| C   | 0.123887 | -2.044047 | 1.564393 |
| O   | 0.320900 | -0.757856 | 2.081635 |
| C   | -0.527774 | 0.329455 | 1.755354 |
| C   | -1.656702 | 0.007811 | 0.870800 |
| H   | -1.063510 | -3.349318 | 0.299263 |
| H   | 1.361249 | 1.885428 | 1.442406 |
| O   | -0.319976 | 1.523129 | 2.144831 |
| C   | 2.254300 | 0.721939 | -0.086961 |
| C   | 1.907189 | 2.056189 | 0.446771 |
| C   | 0.861363 | 2.778897 | -0.269756 |
| C   | 0.056000 | 2.172291 | -1.182762 |
| C   | 0.244841 | 0.802259 | -1.482409 |
| C   | 1.386727 | 0.073302 | -1.000281 |
| C   | 2.789511 | 2.657674 | 0.689684 |
| C   | -0.585112 | -0.704681 | -2.325835 |
| C   | -0.827165 | -2.840155 | 1.847970 |
| C   | -2.580725 | 1.017499 | 0.529043 |
Supporting Information

III-a

Zero-point correction= 0.316796
(Hartree/Particle)

Thermal correction to Energy= 0.347806
Thermal correction to Enthalpy= 0.348750
Thermal correction to Gibbs Free Energy= 0.249844

Sum of electronic and zero-point Energies= -4166.024554
Sum of electronic and thermal Energies= -4165.993544
Sum of electronic and thermal Enthalpies= -4165.992600
Sum of electronic and thermal Free Energies= -4166.091506

Num. Imaginary Frequencies: 0

III-b

Num. Imaginary Frequencies: 1

Imaginary Frequency: 1

C  0.860889   -1.977851   1.169939
C  1.113725   -0.955152   2.172187
C  0.055163   -0.090023   2.557208
C  -1.101648    0.002675   1.790336
C  -1.219683   -0.834505   0.693984
C  -0.329850   -1.890786   0.391366
H   1.928088   -1.139930   2.889599
H  -1.838302   -0.183505   -1.074856
H  -2.213289   -0.564100   -0.227263
C  -0.800488   2.330450   -0.963665
H  -1.129066   1.551075   -2.107053
H  -0.296204   0.524546   -2.507112
C   0.867544   0.204634   -1.765556
C   1.192027   0.930656   -0.636118
C   0.395092   2.049695   -0.238703
H  -2.041998   1.786558   -2.689872
O   2.198570   0.544729   0.183674
H  -1.852279   0.782652   1.962628
C   0.212487   0.611033   3.384992
C  -0.556047   -2.804289   -0.667291
C   0.391664   -3.761165   -0.949202
C   1.585752   -3.824905   -0.199085
C   1.820079   -2.949177   0.843296
H  -1.482556   -2.744747   -1.248965
H   0.223754   -4.474034   -1.762800
H   2.339994   -4.577956   -0.450834
H   2.757458   -2.986761   1.410420
C   -1.641925   3.379753   -0.508555
C   0.733407   2.844877   0.882682
C   -1.001400   3.085100   2.309263
H  -1.309367   4.122787   0.599345
H  -2.571307   3.581605   -1.051583
H   1.672542   2.640060   1.409359
H   0.172381   4.477747   2.156985
H  -1.964482   4.927132   0.941822
H  -0.537569   -0.060395   -3.402598
H   1.498747   -0.644965   -2.050631
H   1.676853   -0.139101   1.385398
Al  3.951579   0.212520   -0.168329
Cl  4.760755   2.064758   -0.823910
Cl  4.616182   -0.468831   1.757877
Cl  4.096462   -1.361526   -1.615099
Cl  -4.142642   -0.414267   -0.001577
Cl  -4.491489   -2.192563   1.076000
Cl  -4.417878   1.397622   1.057776
Cl  -4.606168   -0.344833   -2.064545

IV-a

TS-III-a-IV-a
SUPPORTING INFORMATION

Zero-point correction= 0.317577
(Hartree/Particle)

Thermal correction to Energy= 0.347948
Thermal correction to Enthalpy= 0.348893
Thermal correction to Gibbs Free Energy= 0.254137

Sum of electronic and thermal Free Energies= -4166.092604

H C
-2.04079 1.315379 0.568475
C -0.80420 1.698448 1.144518
H -0.68686 2.174690 2.423960
H -5.35191 1.222830 1.495099
C -1.74620 2.663119 4.252249
C -3.97542 2.043740 3.330972
C -4.46655 1.100883 0.859401
C -2.18939 -0.791668 0.740485
H 1.13569 1.287973 0.975959
C -3.43112 0.448568 1.221157
H -4.58272 0.060652 0.418124
H 1.31421 0.641659 1.380213
C -3.22593 0.400452 2.234629
C -5.35503 0.331269 0.815675
O 0.39729 -1.549959 0.380224
C 0.295590 2.459698 2.816824
C 1.673294 1.954445 2.087166
C -2.59176 2.497176 1.222306
C -2.27364 2.699289 -1.450558
C -0.97305 2.341900 -0.633210
C 0.81809 1.757672 0.287072
O -0.398338 1.565479 1.617753
C -4.21042 3.511797 -0.672811
H -1.921443 1.798850 3.142398
H -3.59039 2.781591 1.574596
C -3.21672 3.244168 -1.052285
C -0.66635 2.563736 -1.988918
H 0.135093 0.300790 0.863099
C -1.609946 0.300918 -2.850703
H -2.88921 3.429199 -2.376992
H 0.332997 2.333087 -2.384596
C -1.356068 2.358449 0.930046
C -3.63785 3.847623 -0.085856
O 1.123040 1.340758 -0.167448
O 0.318820 1.698789 0.230124
Al 0.984260 -2.965878 1.235564
C 2.947440 -2.919877 -0.694668
Cl -0.428272 -3.856523 -1.679842
Cl 1.007262 -0.670055 -2.580844
Al 2.867372 1.353324 0.709745
Cl 4.135888 0.870545 0.904479
Cl 3.014840 2.622170 1.639692
Cl 2.665452 -0.291165 2.104929

III-b-00

Zero-point correction= 0.303711
(Hartree/Particle)

Thermal correction to Energy= 0.321224
Thermal correction to Enthalpy= 0.322168
Thermal correction to Gibbs Free Energy= 0.258233

Sum of electronic and zero-point Energies= -920.558225
Sum of electronic and thermal Energies= -920.540712
Sum of electronic and thermal Enthalpies= -920.539768
Sum of electronic and thermal Free Energies= -920.60370308

Num. Imaginary Frequencies: 0

C -2.728958 -0.790926 0.067646
C -1.961507 -2.170631 0.182361
C -0.993064 -2.580634 1.066905
C -0.295874 -1.646148 1.864381
C 0.581250 -0.300209 1.771820
C -1.598679 0.162522 0.883918
C -2.492215 -2.891991 -0.450445
C 0.794632 0.234451 2.989860

III-b-0180

Zero-point correction= 0.302919
(Hartree/Particle)

Thermal correction to Energy= 0.320925
Thermal correction to Enthalpy= 0.321869
Thermal correction to Gibbs Free Energy= 0.256070

Sum of electronic and zero-point Energies= -920.556505
Sum of electronic and thermal Energies= -920.538499
Sum of electronic and thermal Enthalpies= -920.537555
Sum of electronic and thermal Free Energies= -920.603354

Num. Imaginary Frequencies: 0

C -2.278958 -0.790926 0.067646
C -1.961507 -2.170631 0.182361
C -0.993064 -2.580634 1.066905
C -0.295874 -1.646148 1.864381
C 0.581250 -0.300209 1.771820
C -1.598679 0.162522 0.883918
C -2.492215 -2.891991 -0.450445
C 0.794632 0.234451 2.989860
SUPPORTING INFORMATION

O 0.065376 0.641158 2.490749
C 2.885030 -1.968184 -0.302553
C 3.216784 -0.761048 0.269491
C 2.466927 0.403511 -0.037033
C 1.357260 0.313947 -0.934219
C 1.008581 -0.966966 -1.461084
C 1.774256 -2.074897 -1.756017
H 3.649206 1.733698 1.999769
H 3.474817 -2.864656 -0.077883
H 4.071515 -0.675780 0.951798
H 2.802177 1.671668 0.504628
C 0.661060 1.498324 -1.264920
H -0.781553 -0.527743 -2.032865
H 1.022981 2.715076 0.753489
C 2.098264 2.801822 0.159317
H -0.168971 1.456012 -2.001106
H 0.473237 3.619823 -0.103863
H 2.375870 3.774173 0.582489
O -0.055085 -1.124743 -2.288150
H 1.479659 -0.303874 -1.594950
H 0.492129 -1.984067 2.550012
H -0.742575 -3.644196 1.156385
H -1.928433 1.535541 0.776466
H -2.883554 1.960350 -0.119855
C -3.542345 1.025829 -0.951180
C -3.248669 -0.361714 -0.855983
H -1.399539 2.254051 1.411187
C -3.130182 0.305650 1.966499
H -4.265391 1.372003 1.668671
H -3.767047 -1.047315 -1.490278

III-b-0b

Zero-point correction= 0.303730
(Hartree/Particle)
Thermal correction to Energy= 0.32186
Thermal correction to Entropy= 0.22220
Thermal correction to Gibbs Free Energy= 0.257674
Sum of electronic and zero-point Energies= -920.559002
Sum of electronic and thermal Energies= -920.541225
Sum of electronic and thermal Enthalpies= -920.540280
Sum of electronic and thermal Free Energies= -920.602731

Num. Imaginary Frequencies: 0

C -1.943111 1.238814 0.232664
C -1.305368 2.432492 0.658532
C -0.212757 2.914324 -0.024553
C 0.319078 2.207872 -1.124623
C -0.261899 1.035112 -1.545189
C -1.442815 0.541620 -0.909125
H -1.703819 2.963120 1.531940
H 0.283215 -0.593846 -2.415224
O 0.291155 0.366114 -2.593646
C 2.020483 -1.079052 -0.253380
C 1.443747 -2.189594 -0.929077
C 0.322033 -2.801428 -0.416361
C -0.277256 -2.334917 0.703581
C 0.248178 -1.245488 1.436759
C 1.418154 -0.591946 0.944096
H 1.921309 -2.560987 -1.845056
H -1.133265 -1.198932 2.757641
O -0.296146 -0.742513 2.564126
H 1.219716 2.557704 -1.641392
H 0.273963 3.841966 -0.299126
H -2.138040 -0.620483 -1.376142
H -2.355312 -1.068571 -0.719004
H -3.719506 -0.412724 0.443992
H -3.081142 0.717395 0.901870
H -1.793400 -1.114307 -2.282472
H -3.784732 -1.949385 0.107964
H -4.602685 -0.795797 0.968295
H -4.451116 1.246511 1.789586
C 3.179110 -0.424497 -0.742863
C 1.986204 0.523164 1.607081
C 3.115167 1.132673 1.107900
C 3.716491 0.654450 -0.078802
C 3.638647 -0.797281 -1.667146
C 1.508240 0.854105 2.519689
C 3.549178 1.994625 1.627711
H 4.614497 1.146851 -0.470017
H -0.119675 -3.663691 -0.929953
SUPPORTING INFORMATION

**IV-b-00**

Zero-point correction = 0.302646

(Hartree/Particle)

Thermal correction to Energy = 0.320451
Thermal correction to Entropy = 0.321395

Thermal correction to Gibbs Free Energy = 0.256077

Sum of electronic and zero-point Energies = -920.584243
Sum of electronic and thermal Energies = -920.540618

Sum of electronic and thermal Enthalpies= -920.539673
Sum of electronic and thermal Free Energies= -920.596166

Num. Imaginary Frequencies: 0

**IV-b-00b**

Zero-point correction= 0.303417

(Hartree/Particle)

Thermal correction to Energy= 0.320853
Thermal correction to Entropy= 0.321797

Thermal correction to Gibbs Free Energy= 0.259806

Sum of electronic and zero-point Energies= -920.591299
Sum of electronic and thermal Energies= -920.541963
Sum of electronic and thermal Enthalpies= -920.540749
Sum of electronic and thermal Free Energies= -920.604460

**IV-b-0180**

Zero-point correction= 0.302977

(Hartree/Particle)
SUPPORTING INFORMATION

C  -1.981503  1.203425  -0.272192
C  -3.134306  0.907997  0.634368
C  -3.634044  -0.486396  0.588268
C  -3.040838  -1.458917  -0.125518
H  -1.822719  -1.215519  -0.896644
H  -1.371786  0.184957  -1.024368
H  -2.358267  1.147766  1.585125
O  -1.195664  -2.155669  -1.393326
H  4.49802  1.138415  -0.922322
H  3.575969  -0.910401  -0.204971
C  1.300651  0.882752  2.415556
H  0.267775  0.180958  2.993179
H  -0.166809  -1.037225  2.421599
H  0.418138  -1.508997  1.267940
H  1.661118  1.815936  2.867047
H  -0.207724  0.554368  3.907773
H  -0.965601  -1.612793  2.904345
H  0.085974  -2.461897  0.842066
C  -1.489493  2.509042  -0.379921
C  -0.310669  0.488903  -1.890857
C  -0.556134  1.789830  -2.001056
C  -0.431654  2.801176  -1.223997
H  -1.955664  3.306022  0.213385
H  0.138224  -0.319182  -2.477694
H  0.984550  2.022023  -2.679719
H  -0.062535  3.830395  -1.308929
H  -4.520063  -0.718453  1.193482
H  -3.409404  -2.491122  -0.119511
H  -3.395933  2.032020  1.135449
O  1.576527  -2.297987  -1.263659
H  0.587440  -2.318204  -1.264572
H  -3.971247  1.605916  0.421936

IV-b-0b180b

Zero-point correction= 0.302706
(Hartree/Particle)
Thermal correction to Energy= 0.320633
Thermal correction to Enthalpy= 0.321577
Thermal correction to Gibbs Free Energy= 0.256304
Sum of electronic and zero-point Energies= -920.517750
Sum of electronic and thermal Energies= -920.538231
Sum of electronic and thermal Enthalpies= -920.532879
Sum of electronic and thermal Free Energies= -920.598421

Num. Imaginary Frequencies: 0

C  1.834743  1.323749  0.353396
C  0.943980  2.274711  0.911897
C  0.038969  1.891188  1.874394
C  -0.025694  0.552054  2.307121
C  0.822389  -0.399206  1.777569
C  1.789562  -0.038302  0.790043
H  0.993928  3.313707  0.564608
H  1.240488  -2.282035  1.711556
O  0.698053  -1.668450  2.233556
C  -2.319920  -0.586917  -0.038432
C  -2.101814  -1.959746  0.518076
C  -1.011178  -2.734594  -0.129293
C  -0.254444  -2.257688  -1.124714
C  -0.447651  -0.914402  -1.688865
C  -1.522683  -0.088677  -1.081174
H  -1.887426  -1.892519  1.606570
O  0.232483  -0.511091  -2.621225
C  -0.753211  -2.393695  0.364267
H  -0.649659  2.625478  2.098598
C  2.710256  -0.964132  0.232422
C  3.623964  -0.573135  -0.718702

C  3.661950  0.769745  -1.158743
C  2.788467  1.691284  -0.631938
H  2.719105  -2.013367  0.556828
H  4.326504  -1.304473  -1.133459
H  4.391220  1.072688  -1.918611
H  2.814351  2.736576  -0.964661
C  -3.329290  2.256168  0.484076
C  -1.739121  2.056044  -1.574496
H  -2.744563  2.002392  -1.048266
H  -3.546371  1.505675  -0.013993
H  -3.961147  -0.161158  1.297337
H  -1.092349  1.561150  -2.384580
H  -2.912173  3.012782  -1.438207
H  -4.345834  2.127618  0.406148
H  -0.834628  -3.749328  0.259609
H  0.544208  -2.853761  -1.583200
H  -3.044765  -2.544987  0.466894

V-b-00

Zero-point correction= 0.302114
(Hartree/Particle)
Thermal correction to Energy= 0.320211
Thermal correction to Enthalpy= 0.321155
Thermal correction to Gibbs Free Energy= 0.253542
Sum of electronic and zero-point Energies= -920.550900
Sum of electronic and thermal Energies= -920.532803
Sum of electronic and thermal Enthalpies= -920.531859
Sum of electronic and thermal Free Energies= -920.594972

Num. Imaginary Frequencies: 0
|       | Hartree/Particle | Thermal correction to Enthalpy= | Thermal correction to Energy= | Sum of electronic and zero-point Energies= | Sum of electronic and thermal Energies= | Sum of electronic and thermal Enthalpies= | Sum of electronic and thermal Free Energies=   |
|-------|------------------|---------------------------------|-------------------------------|---------------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------------|
| H     | -3.11864         | 1.476650                        | 1.855763                      | -920.548518                                 | -920.531203                            | -920.530259                            | 920.594340                                      |
| H     | -1.874218        | -2.450504                       | 2.041725                      |                                             |                                         |                                         |                                               |
| H     | 2.151043         | -1.170473                       | -1.687492                     | -920.531203                                 |                                         |                                         |                                               |

V-b-0180

Zero-point correction= 0.301745

Thermal correction to Energy= 0.319992
Thermal correction to Enthalpy= 0.320037
Thermal correction to Gibbs Free Energy= 0.255348

Sum of electronic and zero-point Energies= -920.550051
Sum of electronic and thermal Energies= -920.531784
Sum of electronic and thermal Enthalpies= -920.530840
Sum of electronic and thermal Free Energies= 920.598339

Num. Imaginary Frequencies: 0

|       | Hartree/Particle | Thermal correction to Enthalpy= | Thermal correction to Energy= | Sum of electronic and zero-point Energies= | Sum of electronic and thermal Energies= | Sum of electronic and thermal Enthalpies= | Sum of electronic and thermal Free Energies=   |
|-------|------------------|---------------------------------|-------------------------------|---------------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------------|
| C     | 1.542258         | 1.441724                        | 0.065771                      |                                             |                                         |                                         |                                               |
| C     | 2.637890         | 1.200981                        | 1.056672                      |                                             |                                         |                                         |                                               |
| C     | 3.563755         | 0.092288                        | 0.713213                      |                                             |                                         |                                         |                                               |
| C     | 3.367693         | -0.737417                       | -0.324414                     |                                             |                                         |                                         |                                               |
| C     | 2.204117         | -0.618666                       | -1.213049                     |                                             |                                         |                                         |                                               |
| C     | 1.335909         | 0.567793                        | -1.01313                      |                                             |                                         |                                         |                                               |
| H     | 1.275432         | 0.982466                        | 2.046807                      |                                             |                                         |                                         |                                               |
| O     | 1.963943         | -1.461617                       | -2.066838                     |                                             |                                         |                                         |                                               |
| C     | 0.220551         | -2.569337                       | 0.512331                      |                                             |                                         |                                         |                                               |
| C     | -0.879626        | -2.383960                       | -0.464394                     |                                             |                                         |                                         |                                               |
| C     | -1.823286        | -1.261464                       | -0.155055                     |                                             |                                         |                                         |                                               |
| C     | -1.586075        | -0.389282                       | 0.920068                      |                                             |                                         |                                         |                                               |
| C     | -0.409008        | -0.559710                       | 1.798019                      |                                             |                                         |                                         |                                               |
| C     | 0.441500         | -1.736031                       | 1.541936                      |                                             |                                         |                                         |                                               |
| H     | -3.141499        | -1.736295                       | -1.795411                     |                                             |                                         |                                         |                                               |
| H     | 0.896656         | -3.418079                       | 0.341509                      |                                             |                                         |                                         |                                               |
| H     | -0.411961        | -2.220734                       | -1.462103                     |                                             |                                         |                                         |                                               |
| C     | -2.928234        | -1.057703                       | -0.953077                     |                                             |                                         |                                         |                                               |
| C     | -2.474967        | 0.662416                        | 1.180230                      |                                             |                                         |                                         |                                               |
| C     | -3.596365        | 0.850287                        | 0.386545                      |                                             |                                         |                                         |                                               |
| C     | -3.833371        | -0.015911                       | -0.686446                     |                                             |                                         |                                         |                                               |
| H     | -2.253161        | 1.321505                        | 2.027283                      |                                             |                                         |                                         |                                               |
| H     | -4.293321        | 1.669458                        | 0.597728                      |                                             |                                         |                                         |                                               |
| H     | -4.718530        | 0.124289                        | -1.318090                     |                                             |                                         |                                         |                                               |
| O     | -0.132733        | 0.233809                        | 2.690161                      |                                             |                                         |                                         |                                               |
| H     | 1.279188         | -1.883414                       | 2.234853                      |                                             |                                         |                                         |                                               |
| H     | 4.047993         | -1.570212                       | -0.540109                     |                                             |                                         |                                         |                                               |
| H     | 4.430620         | -0.055315                       | 1.371504                      |                                             |                                         |                                         |                                               |
| C     | 0.288681         | 0.802539                        | -1.917079                     |                                             |                                         |                                         |                                               |
| C     | -0.552662        | 1.891031                        | -1.751724                     |                                             |                                         |                                         |                                               |
| H     | -0.355985        | 2.756550                        | -0.66863                      |                                             |                                         |                                         |                                               |
| C     | 0.681043         | 2.532825                        | 0.226751                      |                                             |                                         |                                         |                                               |
| H     | 0.161210         | 0.104815                        | -2.752869                     |                                             |                                         |                                         |                                               |
| H     | -1.373108        | 2.069123                        | -2.456341                     |                                             |                                         |                                         |                                               |
| H     | -1.023446        | 3.614640                        | -0.526778                     |                                             |                                         |                                         |                                               |
| H     | 0.829331         | 3.206453                        | 1.080708                      |                                             |                                         |                                         |                                               |
| H     | -1.442175        | -3.333844                       | -0.581562                     |                                             |                                         |                                         |                                               |
| H     | 3.214642         | 2.133910                        | 1.226192                      |                                             |                                         |                                         |                                               |

V-b-0b180b

Zero-point correction= 0.301302

Thermal correction to Energy= 0.319452
Thermal correction to Enthalpy= 0.320396
Thermal correction to Gibbs Free Energy= 0.253910

Sum of electronic and zero-point Energies= -920.509873
Sum of electronic and thermal Energies= -920.491723
Sum of electronic and thermal Enthalpies= -920.490779
Sum of electronic and thermal Free Energies= 920.557265

Num. Imaginary Frequencies: 0

|       | Hartree/Particle | Thermal correction to Enthalpy= | Thermal correction to Energy= | Sum of electronic and zero-point Energies= | Sum of electronic and thermal Energies= | Sum of electronic and thermal Enthalpies= | Sum of electronic and thermal Free Energies=   |
|-------|------------------|---------------------------------|-------------------------------|---------------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------------|
| C     | -1.437220        | -1.175227                       | -0.863112                     |                                             |                                         |                                         |                                               |
| C     | -2.212441        | -1.793083                       | 0.075543                      |                                             |                                         |                                         |                                               |
| C     | -3.028103        | -1.022483                       | 0.965357                      |                                             |                                         |                                         |                                               |
| C     | -3.063218        | 0.339561                        | 0.932632                      |                                             |                                         |                                         |                                               |
### SUPPORTING INFORMATION

| Element | X | Y | Z |
|---------|---|---|---|
| C       | -2.257885 | 1.092310 | -0.015476 |
| H       | -1.442339 | 0.269734 | -0.949157 |
| O       | -2.214302 | -2.887682 | 0.154138 |
| C       | 0.928903 | 0.079609 | 1.604895 |
| C       | 0.314760 | 1.378234 | 2.030624 |
| C       | 0.622475 | 2.539091 | 1.160860 |
| C       | 1.456578 | 2.471360 | 0.110725 |
| C       | 2.136064 | 1.230508 | -0.282355 |
| C       | 1.813536 | 0.017501 | 0.516072 |
| O       | -0.787970 | 1.268359 | 2.112440 |
| O       | 2.906352 | 1.191965 | -1.230286 |
| H       | -3.688576 | 0.922057 | 1.619207 |
| H       | -3.43187 | -1.558584 | 1.699911 |
| C       | -0.668086 | 0.907321 | -1.882172 |
| C       | 0.195714 | 0.200013 | -2.787049 |
| H       | 0.251113 | -1.148102 | -2.750108 |
| C       | -0.571119 | -1.954887 | -1.812407 |
| H       | -0.719902 | 2.003168 | -1.910954 |
| H       | 0.818673 | 0.768390 | -3.485351 |
| C       | 0.316273 | -1.291406 | -3.430422 |
| C       | 1.026923 | -2.628699 | -1.235926 |
| H       | 0.624910 | -1.099162 | 2.295170 |
| C       | 2.388006 | -1.205413 | 0.145034 |
| C       | 2.083585 | -2.366751 | 0.841087 |
| H       | 1.193106 | -2.310847 | 1.919370 |
| H       | -0.075012 | -1.056476 | 3.140290 |
| H       | 0.976335 | -1.203870 | -0.708002 |
| H       | 2.539899 | -3.321441 | 0.552472 |
| H       | 0.944505 | -3.223858 | 2.473208 |
| H       | 0.136367 | 3.490205 | 1.412476 |
| H       | 1.678344 | 3.348328 | -0.510418 |
| H       | 0.632272 | 1.617121 | 3.069654 |
| C       | -1.195127 | -2.659391 | -2.405740 |
| C       | -2.104517 | 1.053070 | 0.310370 |

### III-00

Zero-point correction= 0.310370

(Hartree/Particle)

Thermal correction to Energy= 0.334400

Thermal correction to Enthalpy= 0.335344

Thermal correction to Gibbs Free Energy= 0.253833

Sum of electronic and zero-point Energies= -2543.29364

Sum of electronic and thermal Energies= -2543.275334

Sum of electronic and thermal Enthalpies= -2543.274390

Sum of electronic and thermal Free Energies= -2543.355901

### III-018

Zero-point correction= 0.309565

(Hartree/Particle)

Thermal correction to Energy= 0.333961

Thermal correction to Enthalpy= 0.334905

Thermal correction to Gibbs Free Energy= 0.252601

Sum of electronic and zero-point Energies= -2543.294318

Sum of electronic and thermal Energies= -2543.269922

Sum of electronic and thermal Enthalpies= -2543.268978

Sum of electronic and thermal Free Energies= -2543.351282

### Num. Imaginary Frequencies: 0

| C       | 1.998570 | 3.567234 | -0.900638 |
|---------|---------|---------|---------|
| C       | 0.941933 | 4.005955 | -0.137652 |
| C       | 0.076704 | 3.087950 | 0.514129 |
| C       | 0.315206 | 1.687163 | 0.380227 |
| C       | 1.388154 | 1.291292 | -0.455531 |
| C       | 2.222742 | 2.181931 | -1.076305 |
| C       | -1.209399 | 4.590996 | 1.401136 |
| C       | 2.663337 | 4.284767 | -1.392898 |
| C       | 0.751997 | 5.079202 | -0.016730 |
| C       | -1.020957 | 3.514739 | 1.305094 |
| C       | -0.515261 | 0.766901 | 1.066113 |
| C       | 0.815099 | -0.532610 | -1.149512 |
| C       | -1.567566 | 1.216086 | 1.829158 |
| C       | -1.829430 | 2.601540 | 1.941655 |
| C       | -0.313535 | -0.308375 | 0.990015 |
| C       | -0.230486 | 0.493834 | 2.355659 |
| C       | -2.674106 | 2.945824 | 2.548707 |
| O       | 1.591296 | -0.081727 | -0.659865 |
| H       | 3.037144 | 1.806233 | -1.704845 |
The document contains a table of quantum chemical data for a molecule, including bond distances, thermal corrections to various energies, and imaginary frequencies. The table also includes the sum of electronic and thermal free energies. There are additional supporting information sections with further details on the energies and frequencies. The document appears to be a scientific report or paper, likely from a chemistry or physics journal, given the context of the data presented.
### Zero-point correction = 0.317248

(Hartree/Particle)

| Energy Component | Value          |
|------------------|---------------|
| Thermal correction to Energy | 0.347947 |
| Thermal correction to Enthalpy | 0.348891 |
| Thermal correction to Gibbs Free Energy | 0.252289 |
| Sum of electronic and zero-point Energies | -4166.026365 |
| Sum of electronic and thermal Energies | -4165.995666 |
| Sum of electronic and thermal Enthalpies | -4165.994722 |

| 4166.091324 |

#### Num. Imaginary Frequencies: 0

| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| C    | 0.602109 | -2.205493 | 1.626873 |
| C    | 0.218215 | -1.762842 | 2.918661 |
| C    | -0.914413 | -1.004703 | 3.095218 |
| C    | -1.695476 | -0.617502 | 1.983640 |
| C    | -1.337362 | -1.054066 | 0.735648 |
| C    | -0.217326 | -1.887928 | 0.501031 |

### Supporting Information

- **Sum of electronic and thermal Energies** = 4166.047603
- **Thermal correction to Gibbs Free Energy** = 0.250855
- **Sum of electronic and zero-point Energies** = -4166.047603
- **Sum of electronic and thermal Energies** = -4166.016642
- **Sum of electronic and thermal Enthalpies** = -4166.015697
- **Sum of electronic and thermal Free Energies** = -4166.113160
SUPPORTING INFORMATION

Zero-point correction= 0.315711
(Hartree/Particle)
Thermal correction to Energy= 0.347035
Thermal correction to Enthalpy= 0.347979
Sum of electronic and thermal Enthalpies= -4166.024015
Sum of electronic and thermal Free Energies= -4166.055340
Sum of electronic and thermal Free Energies= -4166.121860

Num. Imaginary Frequencies: 0

C -0.470955 -1.448521 2.047320
C -0.926327 -2.651458 1.436451
C -0.348673 -3.123583 0.281506
C 0.699132 -2.399681 -0.335496
C 1.124988 -1.231156 0.235024
C 0.602247 -0.715600 1.446881
H 1.689240 0.168561 -0.946883
O 2.091684 -0.458015 -0.434904
C 0.414010 1.027834 -2.665658
C 0.872227 2.206318 -2.113259
C 0.289666 2.735866 -0.931062
C -0.783256 2.032361 -0.302325
H -1.157028 0.790476 -0.869961
H -0.617477 0.294961 -0.227546
H 1.580791 4.473184 -0.819407
H 0.852663 0.641303 -3.591780

H 1.693967 2.756100 -2.586718
C 0.745093 3.944185 -0.364656
C -1.400386 2.576571 0.850144
C -1.739413 -0.312229 0.702108
C -0.947554 3.764613 1.375121
C 0.141796 4.445523 0.783693
H -2.240417 2.050129 1.318325
C -1.431766 4.186705 2.282457
H 0.497301 5.383274 1.224052
O -2.089534 0.073282 -0.168096
H -0.955655 -0.672937 -2.414878
H 1.153946 -2.735478 -1.274025
H -0.706275 -4.050143 -1.78564
C 0.167199 0.477090 2.055591
C 0.484055 0.929411 3.216405
C -0.594045 0.226869 3.803516
H -1.064610 -0.932588 3.230903
H 1.885644 1.038171 1.584777
H 0.848517 1.851446 3.682581
H -1.053985 0.610061 4.720695
H -1.898821 -1.483156 3.651993
Al 3.865576 -0.599436 -2.309243
Cl 4.418261 1.432775 -0.852309
Cl 4.351771 -1.214370 1.608759
Cl 4.459473 -2.019496 -1.872502
Al -3.815316 -0.607250 -0.674369
Cl -4.426429 -1.281126 1.246374
Cl -4.707954 1.155584 -1.424495
Cl -3.472990 -2.143820 -2.096713

IV-a-0bb0

Zero-point correction= 0.315711
(Hartree/Particle)
Thermal correction to Energy= 0.347035
Thermal correction to Enthalpy= 0.347979
Thermal correction to Gibbs Free Energy= 0.249190
Sum of electronic and thermal Enthalpies= -4166.024015
Sum of electronic and thermal Free Energies= -4166.055340
Sum of electronic and thermal Free Energies= -4166.121860

Num. Imaginary Frequencies: 0
SUPPORTING INFORMATION

C -0.559164 -0.736395 1.783643
C 0.362914 -0.978212 2.782339
C 1.226330 -2.098916 2.714140
H 1.784463 -3.854941 1.606738
H -1.253545 0.108839 1.859804
H 0.418432 -0.301267 3.634841
H 1.957786 -2.265932 3.510922
H -0.944517 -0.096126 -2.367027
H -2.276237 -2.026835 -2.321823
H 6.690729 0.046894 0.854208
O 1.513115 1.013098 0.543600
H 0.976043 0.438022 1.160883
Al 0.611936 2.329662 -0.402543
Cl 2.097840 3.720877 -0.956874
Cl -0.207637 1.278202 -2.160991
Cl -0.948930 2.876798 0.864511
Al -0.088153 0.029392 0.070601
Cl -4.550861 1.766561 -1.054303
Cl -5.028600 -1.764813 -0.556078
Cl -4.039965 0.283580 2.175968

IV-a-0b180b

Zero-point correction = 0.316485
(Hartree/Particle)
Thermal correction to Energy = 0.347657
Thermal correction to Enthalpy = 0.348602
Thermal correction to Gibbs Free Energy = 0.251231
Sum of electronic and zero-point Energies= -1466.042897
Sum of electronic and thermal Energies= -1466.011724
Sum of electronic and thermal Enthalpies= -1466.010780
Sum of electronic and thermal Free Energies= -1466.108151

Zero-point correction= 0.316341
(Hartree/Particle)
Thermal correction to Energy= 0.347424
Thermal correction to Enthalpy= 0.348368
Thermal correction to Gibbs Free Energy= 0.251258
Sum of electronic and zero-point Energies= -1466.058619
Sum of electronic and thermal Energies= -1466.027536
Sum of electronic and thermal Enthalpies= -1466.026592
Sum of electronic and thermal Free Energies= -1466.123702

V-a-00

Zero-point correction= 0.316341
(Hartree/Particle)
Thermal correction to Energy= 0.347424
Thermal correction to Enthalpy= 0.348368
Thermal correction to Gibbs Free Energy= 0.251258
Sum of electronic and zero-point Energies= -1466.058619
Sum of electronic and thermal Energies= -1466.027536
Sum of electronic and thermal Enthalpies= -1466.026592
Sum of electronic and thermal Free Energies= -1466.123702

Num. Imaginary Frequencies: 0

C -0.381595 -1.416281 -1.202365
C -0.623552 -0.498305 -2.257480
C 0.405854 0.212361 -2.827660
C 1.735590 0.008677 -2.394263
C 1.937424 -0.882881 -1.382393
C 0.950822 -1.603651 -0.718509
H -1.657676 -0.359130 -2.598140
H 3.674427 -1.961338 -1.395929
O 3.517808 -1.133965 -1.070781
O 0.354385 1.607015 1.524409
O 0.392842 0.740313 2.735375
O -0.802348 -0.086357 2.969661
C -1.871872 -0.092553 2.144241
C -1.896625 0.741453 0.972725
C -0.770032 1.603988 0.671870
H 1.282405 0.072881 2.867453
O -2.891930 0.741818 0.190401
H 2.574931 0.533779 -2.861429
H 0.208816 0.927492 -3.633313
C 1.182473 -2.491169 0.362546
C 0.132996 -3.181481 0.927331
C -1.182248 -3.024679 0.433072
C -0.372160 -2.160823 -0.762581
H 2.199021 -2.617268 0.751178
H 0.320369 -3.863875 1.763884
H -2.007361 -3.586694 0.885001
H -2.449590 -2.040565 -1.002026
C 1.433570 2.437615 1.212613
C -0.302214 2.434612 -0.464494
H 0.123580 3.257022 -0.762581
C 1.392548 2.535374 0.087895
H 2.315000 2.438823 1.865488
H -1.686448 2.412124 -1.109922

H 0.248561 3.905230 -1.634954
H 2.249350 3.896020 -0.142162
H -0.805300 -0.728108 3.859333
Al 4.537067 -0.092235 0.012071
Cl 6.290573 -1.230196 -0.340505
Cl -4.490671 1.844856 -0.840121
Cl 3.795002 -0.212296 2.000351
H 0.595106 1.351146 3.641779
Al -4.535080 0.065369 -0.182205
Cl -4.468045 -0.275791 -2.294028
Cl -5.924661 1.569469 0.397849
Cl -4.801447 -1.773459 0.884644

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SUPPORTING INFORMATION

### V-a-0180

| Element | X (Å) | Y (Å) | Z (Å) |
|---------|-------|-------|-------|
| Cl      | 2.086844 | 3.678192 | 1.087762 |
| H       | -1.205043 | -3.548341 | 2.672346 |
| H       | -0.277932 | -3.372767 | -2.261680 |
| Al      | 3.639376 | -0.240042 | -0.93875 |
| Cl      | 4.590107 | -2.152784 | 0.035821 |
| Cl      | 3.198861 | 0.293025 | -2.117987 |
| Cl      | 4.656570 | 1.284971 | 0.985221 |

Zero-point correction= 0.316156

(Hartree/Particle)

Thermal correction to Energy= 0.347217

Thermal correction to Enthalpy= 0.348161

Thermal correction to Gibbs Free Energy= -0.250620

Sum of electronic and thermal Energies= -416.052397

Sum of electronic and thermal Enthalpies= -416.052364

Sum of electronic and thermal Free Energies= -416.128134

Num. Imaginary Frequencies: 0

C 0.333563 1.866963 -2.290814
C 1.207033 0.780315 -2.813746
H 0.768061 -0.592264 -2.519213
C -0.322464 -0.876877 -1.770515
C -1.136321 0.179381 -1.235236
C -0.798631 1.564049 -1.505550
C 1.362751 0.881895 -3.907997
O -2.150396 -0.072995 -0.515217
C -0.788119 -0.592059 2.519188
C -1.207003 0.780556 2.813683
C -0.333577 1.866963 2.290733
C 0.798723 1.564127 1.505483
C 1.136323 0.179430 1.235205
C 0.322396 -0.876761 1.770150
H -1.501983 3.445936 3.175163
H -1.385689 -1.413458 2.904303
H -2.241230 0.884162 2.407232
C -0.626728 3.206301 2.560941
C 1.611496 2.597501 1.000055
C 1.301708 3.916881 1.272870
C 0.180854 4.218777 2.059291
H 2.456076 2.338412 0.393482
C 1.930802 4.723055 0.880876
H -0.061120 5.264088 2.281677
C 2.194363 -0.073033 0.515190
H 0.597088 -1.910706 1.531534
H -0.597222 -1.910798 -1.531512
C 1.385569 1.413712 -2.904319
C -1.611334 2.597494 -1.000141
C -1.301465 3.916840 -1.272991
C -0.180597 4.218665 -2.059428
C 0.626918 3.206105 -2.561058
H -2.484927 2.335468 -0.393745
H -1.930525 4.723065 -0.881014
H 0.061441 5.263936 -2.281843
C 1.502183 3.449129 -3.175293
Al -3.264551 -1.459537 -0.102123
Cl -2.087001 -3.166954 0.425173
Cl -4.351932 -0.701042 1.574680
Cl -4.424428 -1.768906 -1.857925
H -1.362725 0.892713 3.907930
H 2.241273 0.883868 2.407311
Al 3.264465 -1.459659 -0.102191
Cl 2.086844 -3.167063 -0.424997
Cl 4.351880 -0.701332 -1.574673
Cl 4.424328 -1.768963 1.858006

V-a-0b0b

Zero-point correction= 0.316459

(Hartree/Particle)

Thermal correction to Energy= 0.347503

Thermal correction to Enthalpy= 0.348447

Thermal correction to Gibbs Free Energy= 0.250965

Sum of electronic and zero-point Energies= -416.061366

Sum of electronic and thermal Energies= -416.030322

Sum of electronic and thermal Enthalpies= -416.029378

Sum of electronic and thermal Free Energies= -416.126860

Num. Imaginary Frequencies: 0

V-a-0b180
SUPPORTING INFORMATION

Zero-point correction= 0.315439
(Hartree/Particle)
Thermal correction to Energy= 0.346730
Thermal correction to Entropy= 0.347675
Thermal correction to Gibbs Free Energy= 0.248036
Sum of electronic and zero-point Energies= -4166.060189
Sum of electronic and thermal Energies= -4166.28897
Sum of electronic and thermal Enthalpies= -4166.279753
Sum of electronic and thermal Free Energies= -4166.127591

Num. Imaginary Frequencies: 0

XII-b-00

Zero-point correction= 0.303571
(Hartree/Particle)
Thermal correction to Energy= 0.321368
Thermal correction to Entropy= 0.322313
Thermal correction to Gibbs Free Energy= 0.254924
Sum of electronic and zero-point Energies= -920.557702
Sum of electronic and thermal Energies= -920.539890
Sum of electronic and thermal Enthalpies= -920.538736
Sum of electronic and thermal Free Energies= 920.606349

Num. Imaginary Frequencies: 0
**SUPPORTING INFORMATION**

### Sum of electronic and thermal Free Energies

| Element | X Coord | Y Coord | Z Coord | ΔZ Energy | ΔY Energy | ΔX Energy |
|---------|---------|---------|---------|-----------|-----------|-----------|
| C       | 1.781521 | -1.218653 | 0.689416 |           |           |           |
| C       | 0.803011 | -1.606233 | 1.638181 |           |           |           |
| C       | -0.442850 | -2.032110 | 1.299357 |           |           |           |
| C       | -0.772429 | -2.086145 | -1.395141 |           |           |           |
| C       | 0.164718 | -1.733136 | -1.086778 |           |           |           |
| C       | 1.452426 | -1.289776 | -0.699228 |           |           |           |
| H       | 1.049204 | -1.557339 | 2.706056 |           |           |           |
| H       | -2.834788 | 0.606691 | -1.248816 |           |           |           |
| H       | -1.749695 | 1.360440 | -2.618402 |           |           |           |
| H       | -0.791929 | 1.795499 | -0.672176 |           |           |           |
| H       | -0.997221 | 1.465864 | 0.701619  |           |           |           |
| C       | -2.127131 | 0.693652 | 0.671185  |           |           |           |
| C       | -3.009297 | 0.248265 | 0.109912  |           |           |           |
| H       | 0.515941 | 2.773503 | -2.099449 |           |           |           |
| C       | -3.555540 | 0.249531 | -1.995963 |           |           |           |
| H       | -1.603686 | 1.624277 | -2.679824 |           |           |           |
| H       | 0.364524 | -2.527490 | -1.040369 |           |           |           |
| C       | -0.036309 | 1.856446 | 1.656799  |           |           |           |
| C       | 1.078487 | 2.593402 | 1.269443  |           |           |           |
| C       | 1.284844 | 2.916299 | -0.092712 |           |           |           |
| H       | -0.195259 | 1.624731 | 2.711273  |           |           |           |
| H       | 1.816542 | 2.905996 | 2.017666  |           |           |           |
| H       | 2.179090 | 3.476507 | -0.389515 |           |           |           |
| H       | -1.391932 | -2.325493 | 1.978027  |           |           |           |
| H       | 2.427122 | -0.885834 | -1.850947 |           |           |           |
| C       | 3.662662 | -0.433171 | -1.247119 |           |           |           |
| C       | 3.987884 | -0.366215 | 0.128849  |           |           |           |
| C       | 3.064532 | -0.753318 | 1.073336  |           |           |           |
| H       | 2.173001 | -0.938914 | -2.716604 |           |           |           |
| H       | 4.402570 | -0.123158 | 1.994550  |           |           |           |
| H       | 4.975885 | -0.007570 | 0.437881  |           |           |           |
| H       | 3.305063 | -0.703195 | 2.143389  |           |           |           |
| O       | -4.006811 | -0.593988 | 0.496682  |           |           |           |
| H       | -6.419351 | -0.750491 | -0.243319 |           |           |           |
| O       | -1.999036 | -2.487656 | -0.550820 |           |           |           |
| H       | -2.655799 | -2.348023 | 0.157322  |           |           |           |
| H       | -0.108094 | -1.771198 | -2.148877 |           |           |           |
| H       | -2.279427 | 0.404237 | 2.114438  |           |           |           |

**XII-b-0b0b**

Zero-point correction= 0.302811

(Hartree/Particle)

Thermal correction to Energy= 0.320873

Thermal correction to Enthalpy= 0.321817

Thermal correction to Gibbs Free Energy= 0.255001

Sum of electronic and zero-point Energies= 920.558081

Sum of electronic and thermal Energies= 920.540018

Sum of electronic and thermal Enthalpies= 920.539074

Sum of electronic and thermal Free Energies= -920.605890

**XII-b-0b180b**

Zero-point correction= 0.303114

(Hartree/Particle)

Thermal correction to Energy= 0.320982

Thermal correction to Enthalpy= 0.321926

Thermal correction to Gibbs Free Energy= 0.256423

Sum of electronic and zero-point Energies= 920.556898

Sum of electronic and thermal Energies= 920.539030

Sum of electronic and thermal Enthalpies= 920.538086

Sum of electronic and thermal Free Energies= 920.603589

**Nut. Imaginary Frequencies:**

| C       | 1.270082 | -0.969813 | 1.000986 |
| C       | 0.058166 | -0.945069 | 1.736817 |
| C       | -1.018104 | -1.707784 | 1.356987 |
| C       | -0.938677 | -2.531278 | 0.206050 |
| C       | 0.233235 | -2.596615 | -0.518392 |
| C       | 1.355695 | -1.819388 | -0.143489 |
| H       | 0.014721 | -0.292537 | 2.616602 |
| H       | -1.222508 | 0.916811 | -0.979055 |
| O       | 0.000767 | 0.924291 | -1.701147 |
| H       | 1.029579 | 1.759035 | -1.349330 |
| H       | 0.889463 | 2.632207 | -0.240529 |
| O       | -0.288276 | 2.660864 | 0.476493 |
| H       | -1.366308 | 1.807261 | 0.127650 |
| C       | 0.115385 | 0.236328 | -2.548848 |
| H       | -1.957633 | -1.670129 | 1.924417 |
| C       | 2.567333 | -1.837770 | -0.884669 |
| C       | 3.631813 | -1.046409 | -0.517964 |
| C       | 3.541926 | -0.197375 | 0.611396 |
| C       | 2.383720 | -0.164871 | 1.353374 |
| C       | 2.636522 | -2.493976 | -1.761893 |
| C       | 4.558491 | -1.071569 | -1.03700 |
| C       | 4.395122 | 0.431935 | 0.889706 |
| C       | 2.289556 | 0.493343 | 2.228362 |
| C       | -2.289050 | 0.045416 | -1.310185 |
SUPPORTING INFORMATION

Zeropoint correction = 0.302694 (Hartree/Particle)

Thermal correction to Energy = 0.320636
Thermal correction to Enthalpy = 0.321580
Thermal correction to Gibbs Free Energy = 0.255226

Sum of electronic and zero-point Energies = -920.557622
Sum of electronic and thermal Energies = -920.539680
Sum of electronic and thermal Enthalpies = -920.538736
Sum of electronic and thermal Free Energies = -920.605091

Num. Imaginary Frequencies: 0

C 0.620762 1.560212 1.033582
C 1.337060 0.614305 1.870072
C 2.424503 -0.071500 1.449049
C 2.905016 0.076032 0.079199
C 2.458364 1.310574 -0.660024
C 1.148390 1.897002 -0.228723
H 0.930247 0.424879 2.873014
C 0.740124 -1.540651 -1.444201
C -0.399670 -0.852645 -1.784835
C -1.549278 -0.881432 -0.955564
H -1.507097 -1.666118 0.238901
C -0.323201 -2.369085 0.568489
H 0.792122 -2.293379 -0.240443
C -2.742884 0.443810 -2.188317
C 1.625913 -1.152627 -2.090840
C -0.430681 -2.604308 -2.711209
C -2.725508 -0.153317 -2.671033
C -2.653826 -1.684940 1.077280
C -3.778711 -0.961974 0.752018
C -3.819129 -0.187787 -0.432743
C -2.623131 -2.285875 1.995157
C -4.653286 -0.985832 0.543945
C -4.722664 0.380706 -0.681111
C 2.895636 -0.845283 2.066111
C 0.447045 2.783873 -1.044220
C -0.767627 3.325301 -0.624754
C -1.296582 2.967758 0.623686
C -0.600655 2.111603 1.448666
C 0.855741 3.045699 -2.029596
C -1.311042 4.014483 -1.281273
C -2.252616 3.409593 0.950383
H -1.003804 1.834118 2.430777
O 1.924412 -2.930509 0.130521
H 2.704702 -2.446889 -0.221085
O 3.641470 -0.751253 -0.449028
H 2.489198 1.119132 -1.747153
H -0.269026 -2.948973 1.497595
H 3.262933 2.060488 -0.478325

XIII-b-00b

Zero-point correction = 0.301991 (Hartree/Particle)

Thermal correction to Energy = 0.320240
Thermal correction to Enthalpy = 0.321184
Thermal correction to Gibbs Free Energy = 0.252792

Sum of electronic and zero-point Energies = -920.552457
Sum of electronic and thermal Energies = -920.534208
### SUPPORTING INFORMATION

| Sum of electronic and thermal Enthalpies= | 920.53264 | C | -0.985110 | -2.268087 | 0.808145 |
| --- | --- | --- | --- | --- | --- |
| Sum of electronic and thermal Free Energies= | 920.601655 | - | C | -0.734829 | -1.388732 | 1.949186 |
| Num. Imaginary Frequencies: 0 | C | 0.632101 | -0.746837 | 2.039933 |
| H | -0.324218 | -0.039249 | -1.055317 |
| C | 1.563663 | -0.860581 | 0.851271 |
| C | -2.263197 | -0.102078 | -2.57994 |
| C | -2.390902 | -0.607229 | -2.77226 |
| C | -3.319182 | -0.502102 | -1.07369 |
| C | -3.039205 | 0.317338 | -0.138821 |
| H | -0.501709 | 0.017201 | -3.044584 |
| H | -2.627220 | -1.262518 | -3.126108 |
| H | -4.254148 | -1.077966 | -1.232818 |
| C | -3.730868 | 0.393687 | 0.705073 |
| C | 2.032493 | -1.789798 | -1.339108 |
| C | 2.744246 | -0.161376 | 0.801704 |
| C | 3.585109 | -0.267971 | -0.302546 |
| H | 2.158947 | 2.857137 | 1.74038 |
| C | 1.491114 | -1.398265 | 2.364584 |
| C | -2.671468 | 0.129417 | 1.024884 |
| C | -3.711155 | 0.034546 | -0.128279 |
| C | -3.671957 | -0.919145 | -0.009061 |
| C | -2.598801 | -1.772322 | -1.031403 |
| C | -2.686041 | 0.879103 | 1.826995 |
| H | -4.568667 | 0.722124 | 0.210533 |
| H | -4.504037 | -0.982944 | -1.620107 |
| C | -2.567491 | -2.571938 | -1.836078 |
| C | 3.162594 | 0.811551 | 0.327402 |
| C | 1.518209 | -0.086265 | -1.172795 |
| C | 2.744183 | -0.707767 | -1.492909 |
| C | 3.572479 | -0.256186 | -0.462783 |
| H | 3.799862 | 1.176199 | 1.143201 |
| C | 0.865477 | -0.449703 | 2.533866 |
| C | 3.055345 | -1.555658 | -2.133344 |
| H | 4.593647 | -0.739759 | -0.275802 |
| H | -0.045433 | 3.945530 | 1.462038 |
| H | -0.476575 | 0.091910 | 2.621194 |
| C | 1.758369 | -3.231957 | 0.450411 |
| H | 2.465874 | -2.984102 | 1.069699 |
| C | -1.763032 | 3.253371 | -0.363909 |
| H | -0.325116 | -3.285790 | -1.055535 |
| H | -1.035823 | 0.889231 | -1.247553 |
| C | -0.220720 | 2.110799 | -2.215351 |

**XIV-b-00**

| Zero-point correction= | 0.301269 |
| --- | --- |
| (Hartree/Particle) | |
| Thermal correction to Energy= | 0.319570 |
| Thermal correction to Enthalpy= | 0.320514 |
| Thermal correction to Gibbs Free Energy= | 0.253196 |
| Sum of electronic and zero-point Energies= | -920.550641 |
| Sum of electronic and thermal Energies= | -920.532339 |
| Sum of electronic and thermal Enthalpies= | -920.531935 |
| Sum of electronic and thermal Free Energies= | -920.598713 |

**Num. Imaginary Frequencies: 0**

| C | -0.654181 | -1.440596 | 1.791129 |
| C | 0.201115 | -2.017563 | 0.917772 |
| C | 1.417066 | -1.374411 | 0.453783 |
| C | 1.788828 | -0.120815 | 0.993858 |
| C | 0.948966 | 0.506955 | 2.060473 |
| C | -0.411411 | -0.098839 | 2.322232 |
| H | 1.869238 | -2.931017 | -0.964577 |
| H | -1.590426 | -1.929322 | 2.086773 |
| H | -0.035299 | -3.006574 | 0.499943 |
| C | 2.203694 | -1.962981 | -0.548274 |
| C | 2.943727 | 0.497134 | 0.523364 |
| C | 3.718575 | -0.092752 | -0.473558 |
| C | 3.347456 | -1.326467 | -1.014832 |
| C | 3.231318 | 1.471737 | 0.939926 |
| C | 4.619883 | 0.415453 | -0.835050 |
| C | 3.955271 | -1.790228 | -1.799652 |
| C | -1.516146 | -1.449741 | -1.868192 |
| C | -0.615744 | -0.485111 | -2.160668 |
| C | -0.578348 | 0.799377 | -1.480355 |
| C | -1.567140 | 1.012466 | -0.525458 |
| C | -2.678759 | 0.132653 | -0.261334 |
| C | -2.530902 | -1.261372 | -0.828148 |
| H | 1.209517 | 1.471726 | -2.491974 |
SUPPORTING INFORMATION

Zero-point correction = 0.301732

(Hartree/Particle)

Thermal correction to Energy = 0.319757

Thermal correction to Enthalpy = 0.320701

Thermal correction to Gibbs Free Energy = -0.256484

Sum of electronic and zero-point Energies = -920.549386

Sum of electronic and thermal Energies = -920.531361

Sum of electronic and thermal Enthalpies = -920.530417

Sum of electronic and thermal Free Energies = -920.596434

Num. Imaginary Frequencies: 0

C -1.725374 -1.170872 0.457947
C -0.574854 -1.884405 0.983936
C 0.350524 -1.311722 1.785677
C 0.253871 0.093818 2.184165
C -1.002578 0.839288 1.792673
C -1.941800 0.167315 0.838995
H -0.449490 -2.931847 0.674955
C 3.163258 -0.998921 -0.125563
C 3.025352 0.331493 0.065760
C 1.913542 1.099962 -0.468899
C 0.969625 0.463085 -1.298645
C 1.172031 -0.968035 -1.690532
C 2.177818 -1.765636 -0.891750
C 2.486174 2.933262 0.517016
C 3.978135 -1.568733 0.336146
C 3.751173 0.871818 0.688487
C 1.747930 2.452210 -0.136511
C -0.128146 1.188600 -1.761732
C -0.287385 2.531638 -1.423963
C 0.654150 3.167963 0.611318
C -0.875652 0.686720 -2.439064
H -1.159180 3.085207 -1.792168
H 0.530068 4.223710 -0.345562
H 1.226261 -1.865775 2.144423
C -3.038861 0.851665 0.314495
C -3.905439 0.231031 -0.582827
C -3.687181 -1.094549 -0.967815
C -2.603949 -1.790121 -0.445484
H -3.206400 1.896257 0.608550
H -4.759102 0.786135 -0.988263
H -4.367195 -1.583402 -1.674173
H -2.419650 -2.832404 -0.736138
O 2.181539 -2.984647 -0.925330
O 1.134025 0.650241 2.820332
H -0.683328 1.831967 1.405232
H 0.217242 -1.527767 -1.724156
H -1.532029 0.675200 2.742703
H 1.550489 -1.000255 -2.737557

XIV-b-0b0b

Zero-point correction = 0.301683

(Hartree/Particle)

Thermal correction to Energy = 0.319838

Thermal correction to Enthalpy = 0.320782

Thermal correction to Gibbs Free Energy = 0.254281

Sum of electronic and zero-point Energies = -920.547984

Sum of electronic and thermal Energies = -920.529820

Sum of electronic and thermal Enthalpies = -920.528885

Sum of electronic and thermal Free Energies = -920.595386

Num. Imaginary Frequencies: 0

C -0.579708 1.642838 -0.474981
C -1.548749 1.184087 -1.521166
C -2.776716 0.439145 -1.047879
C -3.143729 0.610414 0.359167
C -2.296367 1.185025 1.241003
C -0.978773 1.678161 0.875955
C 0.978757 -1.678115 0.876048
C 2.296345 -1.184962 1.241094
C 3.143723 -0.610397 0.359243
C 2.776735 -0.439198 -1.047817
C 1.548773 -1.184157 -1.521088
C 0.579716 -1.642860 -0.474896
H 2.581146 -1.260137 2.259632
H -4.105662 0.19602 0.670199
C -0.082641 2.159022 1.851343
C 1.181680 2.589805 1.499491
C 1.580528 2.541385 0.162482
C 0.702522 2.074391 -0.815226
C -0.417476 2.183131 2.899246
C 1.869792 2.959638 2.267755
H 2.589170 2.860506 -0.125221
H 1.022473 2.043180 -1.865088
H 0.092610 -2.158930 1.851445
C -0.702508 -2.074432 -0.815141
C -1.580530 -2.541380 0.162574
C -1.181705 -2.589733 1.499592
H 0.417427 -2.182987 2.899354
H -1.022441 -2.043273 -1.865010
H -2.589167 -2.860516 -1.125131
H -1.869829 -2.959529 2.267863
H 4.109352 -0.194572 0.670271
H -2.581186 1.260253 2.299532
O -3.442088 -0.230165 -1.820292
O 3.442122 0.230071 -1.820522
H -1.058229 0.593068 -2.138038
H 1.058265 -0.593172 -2.317992
H 1.948380 -2.079027 -2.050183
H -1.948353 2.078932 -2.050305

XIV-b-0b180b

Zero-point correction = 0.301620

(Hartree/Particle)

Thermal correction to Energy = 0.319756

Thermal correction to Enthalpy = 0.320700

Thermal correction to Gibbs Free Energy = 0.254172

Sum of electronic and zero-point Energies = -920.549576
### SUPPORTING INFORMATION

| Sum of electronic and thermal Energies= | -920.531441 | H | 2.066361 | -3.522023 | -0.581215 |
| Sum of electronic and thermal Enthalpies= | -920.530496 | C | 4.658348 | -3.112498 | 0.101679 |
| Sum of electronic and thermal Free Energies= | -920.597024 | C | 5.365751 | -0.403944 | 0.278341 |

#### Num. Imaginary Frequencies: 0

| C | 1.008218 | -1.457148 | 0.943747 |
| C | -0.298154 | -2.060996 | 1.151782 |
| C | -1.138813 | -2.370239 | 0.140536 |
| C | -0.778213 | -2.104119 | -1.254033 |
| C | 0.674216 | -1.782755 | -1.524857 |
| C | 1.483305 | -2.175889 | -0.370732 |
| H | -0.614112 | -2.221423 | 2.192030 |
| C | -1.640170 | 1.048897 | -0.464945 |
| C | -1.064935 | 1.197778 | -1.789733 |
| C | 0.153597 | 1.739561 | -2.010633 |
| C | 0.987855 | 2.232651 | -0.913377 |
| C | 0.438118 | 2.105582 | 0.489868 |
| C | -0.914616 | 1.483550 | 0.659937 |
| H | -1.660901 | 0.831330 | -2.637051 |
| H | -2.146530 | -2.761143 | 0.324326 |
| C | 2.710737 | -0.644463 | -0.569192 |
| C | 3.467075 | -0.199034 | 0.514086 |
| C | 3.002566 | -0.386689 | 1.817642 |
| C | 1.778997 | -1.014880 | 2.028396 |
| H | 3.072441 | -0.485831 | -1.593443 |
| C | 4.423033 | 0.306934 | 0.338867 |
| H | 3.596128 | -0.038467 | 2.670150 |
| C | 1.396963 | -1.159117 | 3.047159 |
| C | -2.908557 | 0.465774 | -0.294822 |
| C | -1.469091 | 1.319130 | 1.928635 |
| C | 3.376702 | 0.743561 | 2.089484 |
| C | -3.453418 | 0.316770 | 0.971492 |
| C | -3.454193 | 0.116589 | -1.180385 |
| H | -0.998624 | 1.651862 | 2.807058 |
| H | -3.149323 | 0.626926 | 3.094842 |
| H | -4.442597 | -0.137512 | 1.099425 |
| H | 0.569051 | 1.836530 | -3.020772 |
| H | 0.732567 | -1.108419 | -2.399756 |
| O | -1.588239 | -2.172227 | -2.163329 |
| O | 2.084311 | 2.732238 | -1.105680 |
| H | 1.194509 | 1.541934 | 1.078425 |
| H | 0.454611 | 3.121960 | 0.534633 |
| H | 1.115806 | -2.743951 | -1.874127 |

#### XII-00

**Zero-point correction=** 0.310119  
**Thermal correction to Energy=** 0.334411  
**Thermal correction to Enthalpy=** 0.335386  
**Thermal correction to Gibbs Free Energy=** 0.251716  

| Sum of electronic and zero-point Energies= | -2543.296839 |
| Sum of electronic and thermal Energies= | -2543.272546 |
| Sum of electronic and thermal Enthalpies= | -2543.271602 |
| Sum of electronic and thermal Free Energies= | -2543.355241 |

#### Num. Imaginary Frequencies: 0

| C | 1.400215 | -1.492538 | -0.752988 |
| C | 2.342412 | -2.463238 | -0.510421 |
| C | 3.671448 | -2.124836 | -0.195901 |
| C | 4.033445 | -0.745764 | -0.068494 |
| C | 3.054957 | 0.245683 | -0.335559 |
| C | 1.779523 | -0.136556 | 0.859158 |
| C | 4.373697 | -4.169532 | 0.030482 |
| H | 0.372053 | -1.760289 | -1.019640 |

#### XII-0180

**Zero-point correction=** 0.301680  
**Thermal correction to Energy=** 0.334633  
**Thermal correction to Enthalpy=** 0.335577  
**Thermal correction to Gibbs Free Energy=** 0.253687  

| Sum of electronic and zero-point Energies= | -2543.296839 |
| Sum of electronic and thermal Energies= | -2543.272546 |
| Sum of electronic and thermal Enthalpies= | -2543.271602 |
| Sum of electronic and thermal Free Energies= | -2543.355241 |

#### Num. Imaginary Frequencies: 0

| C | 3.116805 | -2.022816 | -0.421013 |
| C | 1.707240 | -2.091567 | -0.573199 |
| C | 0.898487 | -1.055152 | -0.171748 |
| C | 1.495717 | 0.080564 | 0.413670 |
| C | 2.849972 | 0.202874 | 0.576816 |
| C | 3.698605 | -0.853027 | 0.158382 |
| H | 1.267462 | -2.986548 | -1.029044 |
| C | -1.863915 | -1.970935 | 2.091968 |
| C | -2.687971 | -2.725664 | 1.291746 |
| C | -3.469725 | -2.126661 | 0.270303 |
| C | -3.403438 | -0.710395 | 0.094722 |
| C | -2.564031 | 0.054356 | 0.942489 |
| C | -1.805310 | -0.572466 | 1.901287 |
| C | -4.358635 | -3.975678 | -0.435407 |
| H | -1.245073 | -2.441322 | 2.866032 |
| H | -2.741656 | -3.812203 | 1.430023 |
| C | -4.312665 | -2.888663 | -0.579392 |
| H | -4.179188 | -0.109001 | -0.930196 |
SUPPORTING INFORMATION

Zero-point correction= 0.309683

(Hartree/Particle)

Thermal correction to Energy= 0.339318

Thermal correction to Enthalpy= 0.34862

Thermal correction to Gibbs Free Energy= 0.253645

Sum of electronic and zero-point Energies= -2543.296926

Sum of electronic and thermal Energies= -2543.296724

Sum of electronic and thermal Enthalpies= -2543.296717

Sum of electronic and thermal Free Energies= -2543.352964

Num. Imaginary Frequencies: 0

C  2.218955  -1.175376  0.235885
C  0.838680  -0.856669  0.328642
C  0.077745  -0.877218  -0.808068
C  0.592332  -1.228118  -2.071496
C  1.926632  -1.539684  -2.175105
C  2.774969  -1.507867  -1.036914
C  0.172624  2.325154  -0.128874
C  1.534178  2.125134  -1.370648
C  2.504438  2.067463  -0.401629
C  2.195299  2.216605  0.866283
C  0.848136  2.451543  1.328747
C  -0.180668  2.507235  0.346892
H  1.801743  1.988330  2.425931
H  -0.073238  -1.239152  -0.931584
C  4.165890  -1.769574  -1.130233
C  4.971667  -1.690744  -0.177599
C  4.419455  -1.356441  1.241845
C  0.371095  -1.111398  1.367661
C  4.587986  -2.027836  -2.109266
H  6.046115  -1.888387  -0.102843
H  5.071292  -1.298937  2.121059
H  2.637363  -0.844020  2.339148
H  -0.846430  2.290550  -2.000308
C  -1.536268  2.682969  0.692117
C  -2.520533  2.647949  -2.669993
C  -2.182621  2.438222  -1.629264
H  -0.593845  2.140053  -3.053914
H  -1.795994  2.820040  1.748696

H  -3.571946  2.761889  0.018923
H  -2.979616  2.397932  -2.384193
H  3.553682  1.884636  -0.671580
H  2.355588  -1.809070  -3.147551
Al  -2.612614  -1.201267  0.422302
Cl  -2.304290  -3.292225  0.272562
Cl  -2.224455  -0.40946  2.357178
Cl  -4.356764  -0.428702  -0.509846
O  -1.281198  -0.507058  -0.730745
H  -1.473471  0.328552  -1.240653
O  3.090287  2.120059  1.937683
H  3.946542  1.852653  1.560365
H  0.400586  -0.575180  1.291600
H  0.595531  2.563280  2.389386

XII-0b180b

Zero-point correction= 0.310174

(Hartree/Particle)

Thermal correction to Energy= 0.334723

Thermal correction to Enthalpy= 0.335217

Thermal correction to Gibbs Free Energy= 0.254679

Sum of electronic and zero-point Energies= -2543.29667

Sum of electronic and thermal Energies= -2543.275217

Sum of electronic and thermal Enthalpies= -2543.271573

Sum of electronic and thermal Free Energies= -2543.352111

Num. Imaginary Frequencies: 0

C  -2.874532  -1.356999  -0.956939
C  -2.076409  -1.300967  -2.129357
C  -0.730873  -1.029655  -2.057478
C  -0.156406  -0.800786  -0.792953
C  -0.871199  -0.861740  0.372022
C  -2.259420  -1.142461  0.315975
C  -2.551572  -1.477314  -3.101560
C  0.419408  2.507691  0.622857
C  -0.506120  2.441088  1.700692
C  -1.849519  2.278984  1.465721
C  -2.339428  2.184291  0.137592
C  -1.468193  2.278499  -0.928215
C  -0.079684  2.420742  -0.707966
C  -0.130078  2.505351  2.729243
C  -0.101878  -0.981795  -2.153038
C  -3.068017  -1.176843  1.483329
C  -4.412894  -1.184054  1.398404
C  -5.022346  -1.640765  0.140189
C  -4.268884  -1.612043  -1.010100
H  -2.580822  -1.007138  2.455310
H  -5.023137  -1.444538  2.308349
H  -6.099190  -1.836643  -0.087080
H  -4.735233  -1.781541  -1.988363
C  1.817442  2.612101  0.843943
C  0.857826  2.411819  -1.780850
C  2.214445  2.498672  -1.536319
C  2.701678  2.606166  -0.210204
C  2.184003  2.673732  1.875881
C  0.480592  2.337297  -2.809345
C  2.922051  2.40830  -2.373549
C  3.783031  2.665397  -0.031176
C  -2.558334  2.211043  2.301703
Al  2.572604  -1.297541  0.285136
Cl  2.314693  -0.605615  2.282393
Cl  2.157693  -3.359075  0.026283
Cl  -4.305261  -0.551646  -0.692007
O  -0.386885  0.660631  1.355674
O  4.125026  -0.472582  -0.744331
H  1.406592  0.390305  -1.206503
### SUPPORTING INFORMATION

**Zero-point correction=** 0.308781  
(Hartree/Particle)  
Thermal correction to Energy= 0.33396  
Thermal correction to Enthalpy= 0.334340  
Thermal correction to Gibbs Free Energy= 0.251586  

**Sum of electronic and zero-point Energies=** -2543.303191  
Sum of electronic and thermal Energies= -2543.278576  
Sum of electronic and thermal Enthalpies= -2543.277632  
Sum of electronic and thermal Free Energies= -2543.360386

**Num. Imaginary Frequencies: 0**

| Element | X     | Y     | Z     |
|---------|-------|-------|-------|
| O       | -3.650023 | 1.993070 | -0.114673 |
| H       | -4.135118 | 1.833352 | 0.713267 |
| H       | -1.859641 | 2.191379 | -1.949064 |

**Thermal correction to Gibbs Free Energy=** 0.252206  

| Element | X     | Y     | Z     |
|---------|-------|-------|-------|
| C       | 4.710805 | 0.122955 |       |
| C       | 5.770475 |       |       |
| C       | 4.640709 |       |       |
| C       | 4.460709 |       |       |
| C       | 0.858723 |       |       |
| C       | 3.317267 |       |       |
| C       | 2.029208 |       |       |
| C       | 0.871712 |       |       |
| C       | 3.090255 |       |       |
| C       | 0.578966 | 1.336415 |       |
| C       | 0.237564 | 0.755532 | 1.744481 |
| C       | 1.216135 | 1.508077 | 1.004214 |
| C       | 0.818759 | 2.171084 | -0.176056 |
| C       | -0.604311 | 2.909077 | -0.624242 |
| C       | -1.485291 | 1.145150 | 0.100197 |
| H       | 2.846347 | 1.046108 | 2.350727 |
| H       | -1.750880 | -0.208479 | 1.918576 |
| H       | 0.566146 | 0.283886 | 2.680270 |
| C       | 2.554018 | 1.574213 | 1.434544 |
| C       | 1.766933 | 2.893977 | -0.898209 |
| C       | 0.290255 | 2.951789 | 0.464399 |
| C       | 3.487905 | 2.291803 | 0.703338 |
| H       | 1.464307 | 3.413188 | -1.815773 |
| C       | 3.825173 | 3.518670 | -1.046916 |
| C       | 4.530913 | 2.337479 | 1.034583 |
| C       | 0.871712 | -1.980192 | 0.085955 |
| H       | 2.029208 | -2.257993 | 0.729725 |
| C       | 3.317267 | -1.728136 | 0.317613 |
| C       | 3.408947 | -0.988521 | 0.877891 |
| C       | 2.185954 | -0.798129 | -1.726301 |
| C       | 0.871712 | -1.207162 | 0.080416 |
| C       | 4.377170 | -2.494451 | 2.035762 |
| H       | -0.100060 | -2.343105 | 0.444004 |
| C       | 2.011430 | -2.881926 | 1.634048 |
| C       | 4.460953 | -1.916162 | 1.108918 |
| C       | 4.640709 | -0.456922 | -1.256433 |
| C       | 5.770475 | -0.642800 | -0.461171 |
| C       | 5.681810 | -1.373145 | 0.226022 |
| C       | 4.710805 | 0.122955 | -2.185881 |
| H       | 6.729990 | -0.212154 | -0.769534 |
| H       | 6.569721 | -1.520122 | 1.351010 |
| H       | 2.148837 | 0.216400 | -2.167569 |
| H       | -0.680065 | 1.875912 | -1.704937 |
| O       | -2.287203 | 0.925782 | -0.390759 |
| O       | -0.177097 | -0.630720 | -1.532657 |
| H       | -1.085371 | 3.099687 | -0.509415 |
| H       | 2.246411 | -1.485498 | 2.600082 |
| Al      | -3.973614 | -0.260628 | -0.031231 |
| Cl      | -3.056135 | -2.190167 | 0.041127 |
| Cl      | -4.758010 | 0.316818 | 1.871436 |
| Cl      | -5.355282 | -0.026700 | -1.630632 |

**XIV-00b**

**Zero-point correction=** 0.308331  
(Hartree/Particle)  
Thermal correction to Energy= 0.333119  
Thermal correction to Enthalpy= 0.334063  
Thermal correction to Gibbs Free Energy= 0.250298
SUPPORTING INFORMATION

| Sum of electronic and zero-point Energies= | -2543.305358 |
| Sum of electronic and thermal Energies= | -2543.280571 |
| Sum of electronic and thermal Enthalpies= | -2543.279626 |
| Sum of electronic and thermal Free Energies= | 2543.363392 |

Num. Imaginary Frequencies: 0

C: -1.901692, 1.403401, 0.866264
C: -2.765160, 0.457568, 1.643998
C: -4.174183, 0.219100, 1.147637
C: -4.649374, -1.060750, 0.047149
C: -3.841554, -1.959154, -0.558907
C: -2.448522, -2.152455, -0.194547
C: -1.655652, 1.234334, -1.323621
C: -1.096513, -0.205705, -2.163069
C: 0.195508, -0.224507, -2.071007
C: 1.057674, 0.320505, -1.084557
C: 0.581130, 1.414691, -0.195900
C: -0.841313, 1.842871, -0.346369
H: -1.756366, 0.241450, -2.916485
H: -5.634356, -0.517318, -0.262498
H: -1.642565, -0.666495, -0.892498
H: -1.923153, -1.130659, -1.410651
H: 0.304711, -0.231240, -0.557714
H: 0.241987, -2.475719, -0.482382
H: -0.555026, -1.574658, -1.188790
H: -2.086307, 3.648394, -1.710230
H: 0.317892, -3.946029, -1.107093
H: 1.236266, -2.586352, -0.575917
H: -0.117637, -0.866674, -0.829249
H: -2.999664, 1.630436, -1.464820
H: -1.384359, 2.832915, 0.471016
H: -2.716836, 3.214454, 0.324943
H: -3.527554, 2.614797, -0.644209
H: -3.619038, 1.149095, -2.231326
H: -0.750556, 3.308179, 1.232523
H: -3.191535, 3.989265, 0.134093
H: -4.575430, 2.914950, -0.743699
H: 0.591611, -1.011727, -2.719435
H: -4.231627, -2.572344, -1.383068
O: -4.879145, 0.628680, 1.686339
O: 2.240066, -0.115211, -0.971259
O: -2.278137, 0.533757, 1.751042
O: 0.797498, 1.111641, 0.852490
O: 1.271553, 2.273565, 0.357170
O: -2.866411, -0.821691, 2.688737
Al: 3.648135, 0.130945, 0.167370
Cl: 5.175745, -1.170260, -0.524571
Cl: 2.868572, -0.405216, 2.091647
Cl: 4.140011, 2.205790, 0.042024

XIV-0b180b

Zero-point correlation= 0.308653
(Hartree/Particle)

Thermal correction to Energy= 0.333425
Thermal correction to Enthalpy= 0.334369
Thermal correction to Gibbs Free Energy= 0.251083

Sum of electronic and zero-point Energies= -2543.305352
Sum of electronic and thermal Energies= -2543.280571
Sum of electronic and thermal Enthalpies= -2543.279626
Sum of electronic and thermal Free Energies= 2543.363392

Num. Imaginary Frequencies: 0

C: -1.655294, 2.388308, 0.293056
C: -0.403197, 2.607751, 0.962115
C: 0.763891, 1.981633, 0.623193
C: 0.781555, 1.067809, -0.466160
SUPPORTING INFORMATION

Zero-point correction= 0.316081
(Hartree/Particle)

Thermal correction to Energy= 0.347242
Thermal correction to Enthalpy= 0.348186
Thermal correction to Gibbs Free Energy= 0.249469

Sum of electronic and zero-point Energies= -4165.995125
Sum of electronic and thermal Energies= -4165.994181
Sum of electronic and thermal Enthalpies= -4165.092898

Num. Imaginary Frequencies: 0

C 2.572454 -1.853046 1.326946
C 1.758476 -1.503034 2.434612
C 0.402661 -1.324109 2.293547
H 0.168277 -1.479729 1.015894
C 0.565449 -1.827019 -0.086255
H 0.961917 -2.030077 0.048612
H 2.226224 -1.379716 3.418652
H 1.011625 1.076078 -2.218778
C 2.376025 1.037314 -2.386442
C 3.255965 1.250925 -1.294835
C 2.060142 1.497757 0.000252
H 1.298699 1.519971 0.162250
C 0.499833 1.317830 -0.930518
H 5.081983 1.038955 -2.447327
C 0.326357 0.924750 -3.060609
H 2.799899 0.848745 -3.379912
C 4.666055 1.226490 -1.449876
H 3.565236 1.701201 0.956532
C 4.947721 1.672184 0.912385
H 5.493847 1.434112 -0.371503
H 3.155751 1.882938 2.088450

H 5.617836 1.834727 1.764149
H 6.581628 1.415866 -0.502437
H -0.230112 -1.066128 3.149701
C 2.772560 -2.374911 -1.062693
C 4.129496 -2.539516 -0.911992
C 4.736653 -2.363882 0.354419
C 3.974578 -2.028416 1.448896
H 2.296891 -2.506009 -2.042562
H 4.748091 -2.806817 -1.776220
H 5.819480 -2.496113 0.458849
H 4.438460 -1.889062 2.433204
Al -2.816651 -2.002984 -0.309421
Cl -2.357391 -1.014350 -2.177682
Cl -2.407515 -4.066881 -0.344559
Cl -4.607111 -1.320046 0.563323
O -0.899795 1.344298 -0.767643
H -1.370226 0.709507 -1.380319
O -1.550904 -1.243212 0.878378
H -1.185308 -0.491329 1.463347
H 0.102644 -1.924978 -1.075970
H 0.868463 1.674391 1.159602
Al -1.973844 2.501647 0.282006
Cl -0.999695 4.366381 0.272425
Cl -3.826668 2.308092 -0.705783
Cl -1.939130 1.519651 2.209138

XII-a-080b

Zero-point correction=                           0.316765
(Hartree/Particle)

Thermal correction to Energy=                    0.347326
Thermal correction to Enthalpy=                  0.348270
Thermal correction to Free Energy=               0.252098

Sum of electronic and zero-point Energies=       -4165.034481
Sum of electronic and thermal Energies=          -4166.003919
Sum of electronic and thermal Enthalpies=        -4166.002975
Sum of electronic and thermal Free Energies=     -4166.099148

Num. Imaginary Frequencies: 0

C 1.720174 2.028803 -1.275563
C 1.290632 0.714622 -0.954772
C 2.224286 -0.204323 -0.558510
C -3.600582 0.079647 -0.473908
C -4.028235 1.349200 -0.777385
C -3.108195 2.353190 -1.178120
C -1.144003 0.892161 2.581691
C -0.175821 1.837407 2.156292
C 1.033265 1.436366 1.639361
C 1.307025 0.058333 1.553575
C 0.437581 -0.895554 2.013107
C -0.822189 -0.497435 2.524563
H -0.415910 2.905483 2.215693
H -4.297477 -0.707320 -0.165564
C -3.527469 3.673609 -1.482872
C -2.613504 4.630862 -1.857134
C -1.238108 4.310147 1.942962
C -0.799921 0.307603 -2.312177
H -4.584880 3.915785 -1.411783
H -2.948029 5.648229 -2.089010
H -0.519365 5.082633 -2.238449
H 0.265436 2.781970 -1.721222
C -2.429630 1.282697 3.034770
C -1.809391 -1.450399 2.911537
C -3.054410 -1.036035 3.321717
H -3.368763 0.341093 3.388577
H -2.666678 3.256201 3.080460
H -1.547857 -2.518983 2.889377
**SUPPORTING INFORMATION**

**XII-a-00b**

Zero-point correction= 0.317370

(Hartree/Particle)

Thermal correction to Energy= 0.347882

Thermal correction to Enthalpy= 0.348827

Thermal correction to Gibbs Free Energy= 0.253057

Sum of electronic and zero-point Energies= -4166.031686

Sum of electronic and thermal Energies= -4166.001174

Sum of electronic and thermal Enthalpies= -4166.002229

Sum of electronic and thermal Free Energies= -4166.095999

Num. Imaginary Frequencies: 0

**C**
-1.082793 -2.262865 -0.887468
-0.450649 -1.853432 -2.090186
-0.774292 -1.231182 -2.066927
-1.394262 -1.003224 -0.823162
-0.846453 -1.401570 0.356501
-0.419759 -2.038869 0.356429
-0.963031 -2.028047 -3.043428
-1.082282 -2.262834 0.887403
-0.450708 1.853383 2.090127
-0.774240 1.231143 2.066882
-1.394241 1.003221 0.823162
-0.846448 1.401567 -0.356541
-0.419769 2.038856 -0.356483
-0.963117 2.027972 0.304360
-1.268216 -0.900544 -2.987466
-1.086787 -2.382921 1.563520
-2.352598 -2.930002 1.533272
-2.998606 -2.179221 -1.535946
-2.375791 -2.848659 -0.885221
-0.576793 -2.204447 2.518823
-2.860283 -3.187147 2.469859
-4.005359 -3.606663 0.287901
-2.877436 -3.015770 1.845498
2.375824 2.848630 0.885137
1.086780 2.382915 -1.535946
2.352582 2.929993 -1.533534
2.999915 3.173283 -0.296040
2.877487 3.015732 1.845406
0.576773 2.204449 2.518876
2.860243 3.187146 2.469952
4.005365 3.606665 -0.280812
-1.268146 0.900492 -2.987426
3.422172 -0.644352 0.143320
3.834215 -0.113739 2.166071
4.506692 -2.716246 -1.175207

**Cl**
5.505505 0.691090 -0.890412
1.343752 -1.177787 1.317493
2.612265 -0.297177 -0.816525
2.544213 0.562691 -1.305319
-2.612241 0.297166 0.816505
-2.544160 -0.562692 1.305309
-1.343767 1.177799 -1.317527
-4.221728 0.644367 -0.143265
-5.505496 -0.691084 0.890488
-4.506679 2.716257 0.172620
-3.834319 0.113798 -2.166044

**Zero-point correction= 0.316326**

(Hartree/Particle)

Thermal correction to Energy= 0.347232

Thermal correction to Enthalpy= 0.348176

Thermal correction to Gibbs Free Energy= 0.250649

Sum of electronic and zero-point Energies= -4166.047409

Sum of electronic and thermal Energies= -4166.016503

Sum of electronic and thermal Enthalpies= -4166.015559

Sum of electronic and thermal Free Energies= -4166.113085

Num. Imaginary Frequencies: 0
SUPPORTING INFORMATION

Al  -1.017005  2.738053  -0.207794
Cl  -1.000270  4.854180  -0.191951
Cl  -1.896344  1.821052  1.508402
Cl  -1.966339  1.917807  -1.981202

XIII-a-0180

Zero-point correction= 0.315924
(Hartree/Particle)
Thermal correction to Energy= 0.347176
Thermal correction to Enthalpy= 0.348120
Thermal correction to Gibbs Free Energy= -

Sum of electronic and thermal Enthalpies= 4166.010715
Sum of electronic and thermal Energies= -4166.010715
Sum of electronic and thermal Free Energies= -

Zero-point correction= 0.316586
(Hartree/Particle)
Thermal correction to Energy= 0.347433
Thermal correction to Enthalpy= 0.348377
Thermal correction to Gibbs Free Energy= -

Sum of electronic and zero-point Energies= -4166.014518
Sum of electronic and thermal Energies= -4166.014518
Sum of electronic and thermal Enthalpies= -
Sum of electronic and thermal Free Energies= -4166.109756

Num. Imaginary Frequencies: 0

C  -0.048320  2.560791  -1.329613
C  0.561622  1.279553  -1.557260
C -1.091012  0.091962  -1.460841
H  -1.483132  0.078543  -1.105720
H  -2.214107  1.358411  -0.906366
C  -1.421723  2.618129  -1.015491
H  1.629459  1.255963  -1.817787
C  1.524064  -1.183194  1.339265
C  0.189888  -1.190583  1.670252
C  -0.941665  0.008594  2.008493
H  0.221266  1.246917  1.971662
C  1.589714  1.242634  1.599621
C  2.201438  0.051024  1.313306
H  -2.397984  -0.944623  2.421666
H  2.061395  -2.112454  1.119149
H  -0.368933  -2.134500  1.683457
C  -1.858879  0.011215  2.385213
C  -0.463003  2.446390  2.293503
C  -1.792808  2.417950  2.648236
C  -2.496582  1.191555  2.696299
H  0.086305  3.395792  2.256548
H  -2.312518  3.351029  2.894020
C  -3.556265  1.180439  2.974261
C  -0.394202  2.385213  1.150175
C  -2.018398  3.858994  -0.795329
C  -1.263173  5.025813  -0.872246
C  0.103094  4.972471  -1.171404
C  0.705998  3.746178  -1.407456
H  -3.086679  3.907337  -0.550561
C  -1.743727  5.994028  -0.693254
C  0.689491  5.895441  -1.231998
H  1.773275  3.683940  -1.649320
O  3.565684  0.031772  0.976112
H  4.048279  0.817263  1.311048
O  -2.083882  -1.023618  -0.961725
H  -2.719136  1.300399  0.884496
H  2.144826  2.188490  1.556447
H  -3.066120  1.366196  -1.620327
Al  4.543010  -1.033005  -0.297131
Cl  6.310369  0.133125  -0.319788
Cl  4.706421  -2.959358  0.559884
Cl  3.331932  -0.948460  2.038283
Al  -3.626249  -1.860698  -0.486101
Cl  -3.010590  -3.305470  0.968396
Cl  -4.962199  -0.413411  0.353811
Cl  -4.373985  -2.725346  -2.281053

XIII-a-0b180b
Zero-point correction= 0.150986
(Hartree/Particle)

Thermal correction to Energy= 0.159001
Thermal correction to Enthalpy= 0.157300
Thermal correction to Gibbs Free Energy= -0.002938

Sum of electronic and zero-point Energies= -4166.011257
Sum of electronic and thermal Energies= -4166.010967
Sum of electronic and thermal Enthalpies= -4166.011049
Sum of electronic and thermal Free Energies= -4166.010449

C -0.030174 0.412664 1.981591
C 0.251494 -0.977189 1.897770
C 1.534250 -1.426521 1.691517
C 2.566875 0.477170 1.572535
C 2.352521 0.873425 1.616309
C 1.034172 1.352437 1.822838
H -0.574938 -1.691373 2.000789
H -0.676229 2.470372 -1.411037
H -1.915036 3.135808 -1.121205
H -3.069773 2.483831 -0.787978
H -3.083307 1.067028 -0.709661
H -1.877183 2.287887 -1.094565
H -0.636727 1.059741 -1.397779
H -1.918091 4.233274 -1.156739
H 1.768919 -2.493842 1.618896
H 0.750560 2.739478 1.908734
H -0.529742 3.177411 2.156536
H -1.583686 2.247546 2.320997
H -1.341804 0.896016 2.230196
H 1.573399 3.453813 1.781857
H -0.737656 4.251122 2.229248
H -2.599332 2.609377 2.519744
H -2.157499 0.169950 2.347785
O 0.490838 3.206070 -1.689653
O 0.563600 0.410348 -1.678397
O 1.579223 0.149113 -1.581758
O 1.680052 2.548383 -1.958980
O 0.442419 4.301716 -1.688835
H 0.608498 -0.686320 -1.672517
H 2.643451 0.623947 -2.189287
H 2.593982 3.113997 -2.172224
H -3.392080 3.021286 -0.547961
H 3.190488 1.571909 1.508691
O 3.889306 -0.943261 1.382490
O 4.231695 -1.472235 2.133319
O -4.130722 0.464609 -0.333638
O -1.692887 -0.477568 -0.309430
H -2.182532 -0.322502 -1.976606
Al 4.814396 -1.027638 -2.776683
Cl 5.167891 0.598933 -0.810059
Cl 3.435629 -0.020000 -1.542852
Cl 6.510075 -2.143312 0.324260
Al -4.690684 -1.266763 -0.154949
Cl -6.710010 -1.146556 0.486189
Cl -4.420720 -2.134320 -2.088969
Cl -3.389498 -2.149574 1.305648

2-naphthol

Zero-point correction= 0.150986
(Hartree/Particle)

Thermal correction to Energy= 0.159001
Thermal correction to Enthalpy= 0.159945
Thermal correction to Gibbs Free Energy= -0.118350

Sum of electronic and zero-point Energies= -460.296943
Sum of electronic and thermal Energies= -460.296162
Sum of electronic and thermal Enthalpies= -460.296084
Sum of electronic and thermal Free Energies= -460.302278

WILEY-VCH
H 2.224197 1.463683 -0.831070
H -0.968636 0.952388 2.471220
O -2.204583 -0.784108 1.149699
O -0.200963 0.800753 -0.447428
H -0.717515 -0.497711 3.430313
H 1.894749 0.903718 -2.404026
Al -3.425717 -1.380869 -0.129611
Cl -2.744469 -0.489593 -1.942034
Cl -3.189020 -3.503010 -0.133483
Cl -5.305778 -0.705422 0.567132
Al -0.729927 2.591499 -0.562012
Cl -0.816537 2.914691 -2.655171
Cl -2.559834 2.581861 0.514110
Cl 0.841111 3.639206 0.424764

XIV-a-0b0b

Cl 0.841111 3.639206 -0.523364
Cl 1.385758 2.507165 1.359679

SUPPORTING INFORMATION

Zero-point correction= 0.315586
(Hartree/Particle)
Thermal correction to Energy= 0.346756
Thermal correction to Enthalpy= 0.347700
Thermal correction to Gibbs Free Energy= 0.249947
Sum of electronic and thermal Free Energies= -4166.060267
Sum of electronic and thermal Enthalpies= -4166.028513
Sum of electronic and thermal Free Energies= -4166.126266

Num. Imaginary Frequencies: 0

Thermal correction to Gibbs Free Energy= 0.249947
Sum of electronic and thermal Enthalpies= -4166.060267
Sum of electronic and thermal Free Energies= -4166.028513
Sum of electronic and thermal Free Energies= -4166.126266

Num. Imaginary Frequencies: 0
SUPPORTING INFORMATION

XIV-a-0b180b

Zero-point correction= 0.315439
(Hartree/Particle)
Thermal correction to Energy= 0.346730
Thermal correction to Enthalpy= 0.347757
Thermal correction to Gibbs Free Energy= 0.248036
Sum of electronic and zero-point Energies= -4166.060189
Sum of electronic and thermal Energies= -4166.028897
Sum of electronic and thermal Enthalpies= -4166.027953
Sum of electronic and thermal Free Energies= -4166.127591

TS-XII-XIV

Zero-point correction= 0.305336
(Hartree/Particle)
Thermal correction to Energy= 0.328889
Thermal correction to Enthalpy= 0.329833
Thermal correction to Gibbs Free Energy= 0.250591
Sum of electronic and zero-point Energies= -2543.290183
Sum of electronic and thermal Energies= -2543.266630
Sum of electronic and thermal Enthalpies= -2543.265680
Sum of electronic and thermal Free Energies= -2543.344928

Imaginary Frequencies:
Num. Imaginary Frequencies: 0

Imaginary Frequencies: 0

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8. References

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