Aluminium porphyrins catalyses the hydrogenation of CO_2 with H_2

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1. General Procedures

All chemicals, gases and solvents were purchased from commercial suppliers; Lach-ner, Sigma-Aldrich, Acros Organics, Abcr, Thermo scientific, BLD pharm and Linde gas. Solvents for synthetic reactions were purified and dried on PureSolv MD 5 automated solvent drying system from Inert®. Unless otherwise indicated, all other solvents were stored over 3Å molecular sieves (20%w/v) and degassed by freeze-thaw method with liquid nitrogen or by sparging with dry N_2 gas before use. Diethylaluminum chloride, porphyrin ligands and 2,4,6-collidine were purchased from Sigma-Aldrich, BLD pharm and Acros organics respectively. All reagents and gases (hydrogen and carbon dioxide) were used as received without further purification. All reactions were conducted under an inert atmosphere of N_2 using standard Schlenk techniques and Glove Box. Column chromatography was performed on silica gel (60µm), which was dried at 180°C overnight prior to use.

NMR spactra were recorded at ambient temperature using a Bruker AVANCE III spectrometer (^{1}H at 400 MHz) or on Varian VNMRS 300 (^{1}H at 300 MHz) in deuterated chloroform ($CDCl_3$) or dimethyl sulfoxide (DMSO-d6) with tetramethyl silane (TMS) as internal standard. Chemical shifts are given in δ-scale (^{1}H NMR spectra were referenced to residual peak of $CDCl_3$ at δ 7.26, ^{13}C NMR spectra at δ 77.0, coupling constants *J* are given in Hz and splitting patterns are designed as s (singlet), d (doublet), t (triplet), and q (quartet).

Elemental analysis was performed on elemental analyzer with thermal conductivity detector (Flash Smart, Thermo Fisher Scientific, Bremen, Germany). For determination of total carbon, nitrogen and hydrogen tin capsules (Elemental Microanalysis, 8 × 5 mm) were used. For oxygen determination the samples were weighted in silver capsules and analyzed by pyrolysis in the presence of Nickel Coated Carbon at 1060 °C. The oxygen present in the sample, combined with the carbon, forms carbon monoxide, which was detected by TCD detector.

All the products of catalytic tests were identified by ^{1}H NMR data in comparison with literature, by GC coupled to mass spectroscopy on a Shimadzu QP-2010 GC-MS with a Supelcowax 10 column and where necessary by comparison with genuine samples of the desired compounds.

2. Catalytic tests

2.1 Effect of water and solvent

NOTE: Catalytic tests were performed in wet (~0.3 wt% of H_2O) or pre-dried sulfolane (stored over 3Å molecular sieves 20%w/v @ 50°C for 72h prior to use) and it was found that water did not affect the reaction (Table S1).

Table S1: Effect of water and air on catalytic tests.

Entry	Pre-dried solvent	Turnover number (TON)
1	YES	36
2	NO	33

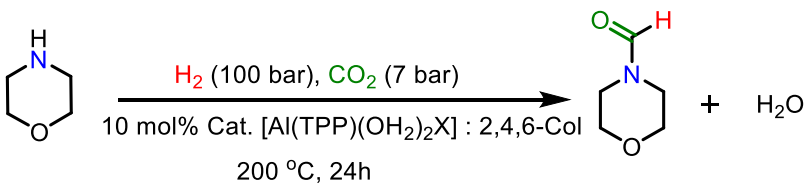
Reaction conditions: morpholine (10 mmol), sulfolane (4 mL), $[Al(TPP)(OH_2)_2]Cl$ and 2,4,6-collidine (1 mol%), CO_2 (7 bar), H_2 (100 bar), 200 °C, 24 h. TON was calculated based on $[Al(TPP)(OH_2)_2]Cl$ in the reaction.

However, the reaction demonstrated sensitivity to the quality of the sulfolane solvent. For reproducibility purposes the reaction was run in sulfolane suplied by Thermofisher as for example sulfolane from Merc (Sigma-Aldrich) was found to be contaminated by sulfolene, which inhibited the desired reaction presumably by its preferential hydrogenation. The reaction was also found to be sensitive to oxygen, which caused irreproducibility issues unless the reaction was setup in the glovebox.

2.2 Reaction Procedure:

Reaction setup was carried out in N_2 filled glovebox to avoid contamination with oxygen. In a 30 mL steel autoclave, $[Al(TPP)(OH_2)_2]Cl$ (67.8 mg, 0.1 mmol), 2,4,6,-collidine (14 µL, 0.1 mmol), and morpholine (88 µL, 1 mmol) were dissolved in sulfolane (4 mL). The autoclave was then sealed, carried out of the glovebox and pressurized with CO_2 (7 bar) following H_2 (100 bar). The temperature and stirring rate were set using the Specview program on Parr 5000 series multi reactor system. Time is taken to start at zero when the heater is turned on. One hour before the specified reaction time, the heating was turned off, and the reaction was allowed to cool down under pressure for the remaining one hour of the test. For example, for a reaction time of 24 hours, the heating was turned off after 23 hours and the reaction was depressurized upon complete cooling of the reaction. Dibromomethane (69.5 µL, 1 mmol) were added to the reactor as internal standard, stirred and a little sample was taken for ^1H NMR analysis in $CDCl_3$. The conversion of morpholine and the yield of N-formylmorpholine were quantified by their respective N-formate signal in ^1H NMR and structures confirmed by GC-MS on Shimadzu QP-2010 GC-MS with a Supelcowax 10 column.

2.3 General test result(s)



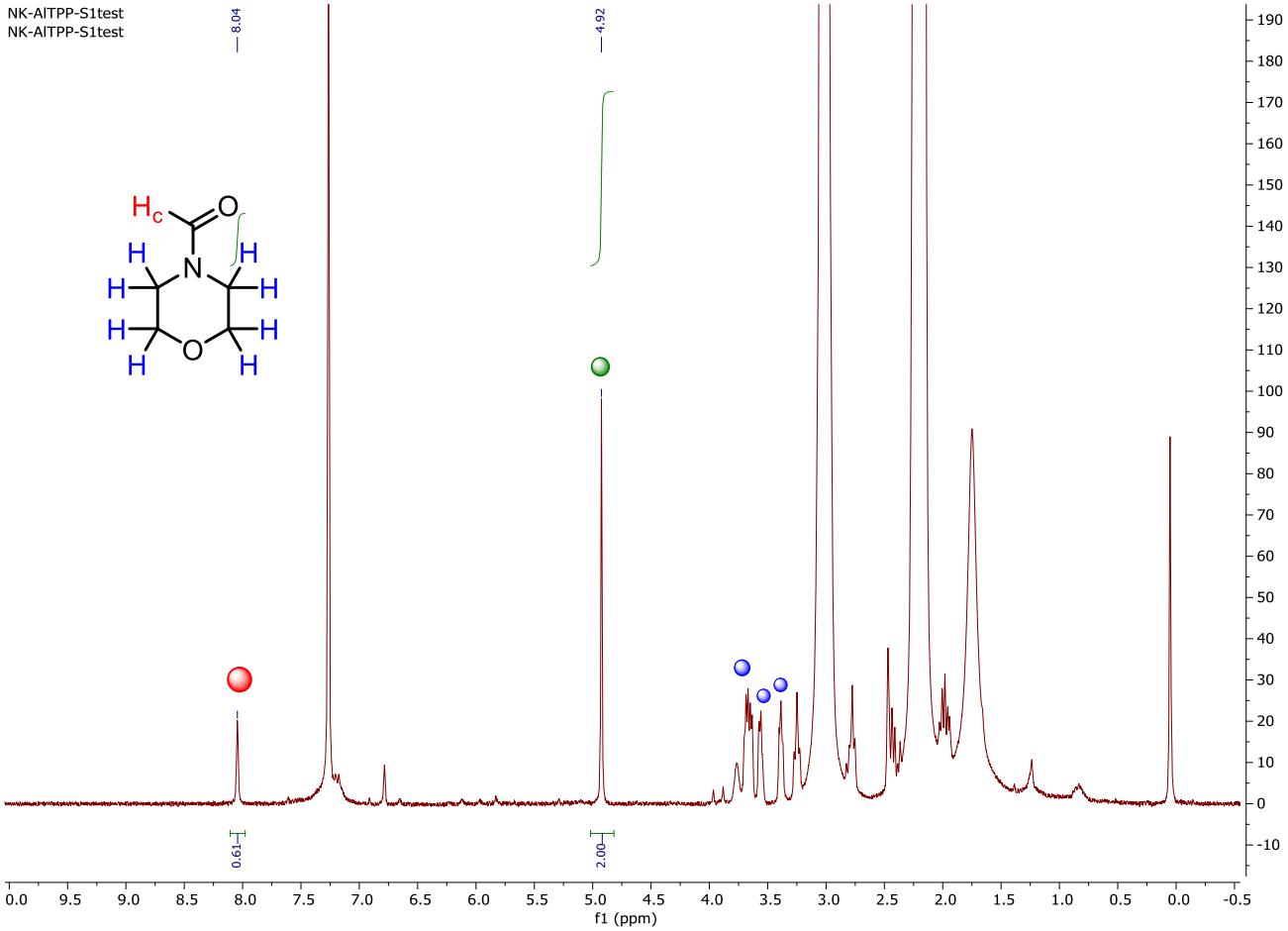


Figure S1: ^{1}H NMR spectrum of the N-formylation of morpholine, the signals corresponding to N-formylmorpholine are indicated with colored spheres. To quantify the reaction, the signal of Hc was utilized, and dibromomethane (69.5 µL, 1 mmol, green sphere) was used as internal standard.

2.4 GC-MS chromatogram and spectrum

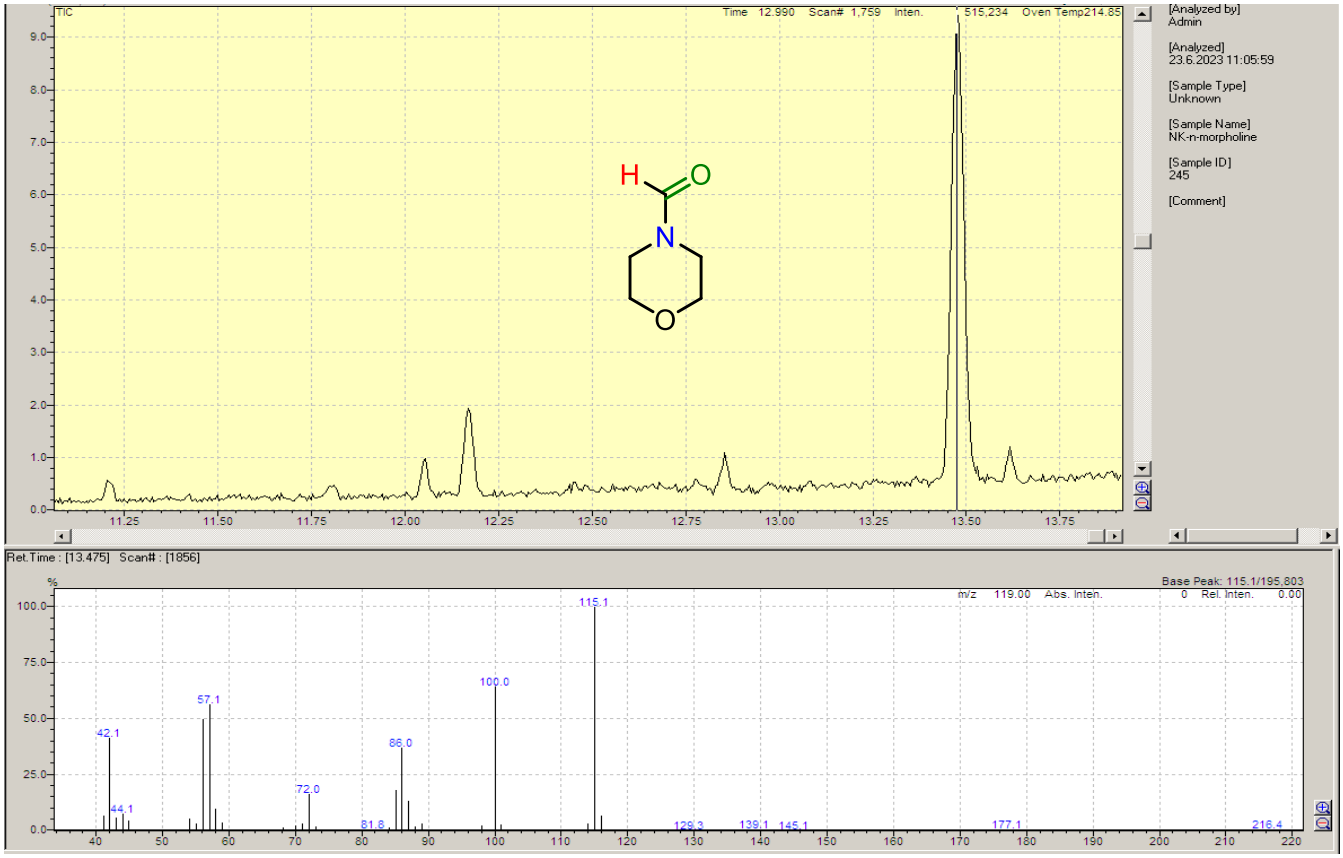


Figure S2: Example GC-MS measurement of N-formylmorpholine

2.5 Effect of reaction solvent

Previously FLPs systems have used aromatic or ethereal solvents such as 1,4-dioxane, THF, diethyl ether and toluene but in the N-formylation reaction aliphatic amines react with CO_2 to form carbamic salts / carbamic acids that are poorly soluble in aromatic and ethereal solvents, which results in mass transfer problems in these solvents. After that we investigated dipolar aprotic solvents with high boiling points. Dimethyl sulfoxide (DMSO), dimethylformamide (DMF) and N-methyl-2-pyrrolidone (NMP) decomposed and in the case of DMF and NMP contributed to the N-formylation of morpholine by formate transfer, which was confirmed by reactions without CO_2 and observation of N-formylmorpholine. Only sulfolane solubilized all reactants in the presence of CO_2 and demonstrated sufficient stability and hence was used throughout this work.

2.6. Control experiments

Table S2: Control experiments for the N-formylation of morpholine[a]

Entry		Temperature °C	Yield[b](%)
1	Without H_2	200	N.D.
2	Without CO_2	200	N.D.
3	Without $[Al(TPP)(OH_2)_2]Cl$	200	4

[a] Standard condition: Solvent (4 mL), H2 (100 bar), CO2 (7bar), 200 °C, 24 h.[b] yield was determined by NMR integration relative to Dibromomethane standard added to reaction mixture after completion.

2.7. Effect of H_2 pressure

Table S3: H_2 pressure effect on N-formylation of morpholine with 7 bar CO_2

Catalyst (LA)	Temperature (C)	CO_2 Pressure (bar)	H_2 Pressure (bar)	Yield % (run 1)	Yield % (run 2)	Yield % (run 3)	Average Yield %
$[Al(TPP)(OH_2)_2]Cl$	200	7	**20**	4	4	5	**4**
$[Al(TPP)(OH_2)_2]Cl$	200	7	**40**	6	4	6	**5**
$[Al(TPP)(OH_2)_2]Cl$	200	7	**60**	10	8	8	**9**
$[Al(TPP)(OH_2)_2]Cl$	200	7	**80**	19	18	15	**17**
$[Al(TPP)(OH_2)_2]Cl$	200	7	**100**	62	60	61	**61**

2.8 Effect of CO_2 pressure

Table S4: CO_2 pressure effect on N-formylation of morpholine with 100 bar H_2

Catalyst (LA)	Temperature (C)	CO_2 Pressure (bar)	H_2 Pressure (bar)	Yield % (run 1)	Yield % (run 2)	Yield % (run 3)	Average Yield %
$[Al(TPP)(OH_2)_2]Cl$	200	**2**	100	46	43	48	**46**
$[Al(TPP)(OH_2)_2]Cl$	200	**4**	100	59	60	57	**59**
$[Al(TPP)(OH_2)_2]Cl$	200	**7**	100	62	60	61	**61**
$[Al(TPP)(OH_2)_2]Cl$	200	**8**	100	58	59	58	**58**
$[Al(TPP)(OH_2)_2]Cl$	200	**10**	100	55	58	57	**56**

2.9 Effect of temperature

Table S5: Temperature effect on N-formylation of morpholine with 100 bar H_2 and 7 bar CO_2

Catalyst (LA)	Temperature (C)	CO_2 Pressure (bar)	H_2 Pressure (bar)	Yield % (run 1)	Yield % (run 2)	Yield % (run 3)	Average Yield %
$[Al(TPP)(OH_2)_2]Cl$	140	**7**	100	0	0	0	**0**
$[Al(TPP)(OH_2)_2]Cl$	160	**7**	100	4	2	3	**3**
$[Al(TPP)(OH_2)_2]Cl$	180	**7**	100	31	32	30	**31**
$[Al(TPP)(OH_2)_2]Cl$	200	**7**	100	62	60	61	**61**

3.0 Synthesis of Catalysts

3.1 Diaqua(*meso*-tetraphenylporphyrin)aluminium chloride [Al(TPP)(OH_2)$_2$]Cl [1]1a

Tetraphenyl porphyrin (H_2TPP) (3 g, 4.87 mmol) was dissolved in dry dichloromethane (250 mL) under nitrogen atmosphere, degassed and stirred for 10 minutes. Then 1.5 equiv. of $AlEt_2Cl$ (1M in Hexane) (7.3 mL, 7.305 mmol) was added dropwise under constant stirring at room temperature and the reaction mixture was kept stirring for 2h. The solvent was evaporated in air using rotary evaporator and collected purple coloured solid was purified by column chromatography (silica 60µm preheated at 180^{o}C for 24h before use, dichloromethane-methanol vol/vol = 10: 1), the obtained product was then dried at 60°C under reduced pressure to remove residual solvents yield 90%. **NOTE:** Literature reports the use of neutral alumina as the stationary phase, however, partial decomposition of the complex was observed in neutral alumina (partially prevented by prolonged activation at 180°C) and hence the stationary phase was exchanged in favour of silica.

^{1}H NMR (400 MHz, DMSO-d6) δ 9.00 (s, 8H), 8.21 (dd, J = 7.5, 1.9 Hz, 8H), 7.91 – 7.84 (m, 12H), 3.33 (s, 4H). ^{13}C NMR (101 MHz, DMSO-d6) δ 147, 141, 134, 132, 128, 127, 120. MS (MALDI-TOF) calculated for M = [Al(TPP)(H_2O)$_2$]$^+$ $C_{44}H_{32}AlN_4O_2$ m/z = 675.2335, found 657.2239 ([M-H_2O]$^+$) and 671.2395 ([M-2H_2O + CH_3OH)]. Elemental analysis; measured N 7.53% (± 0.17), C 74.73% (± 0.99), H 4.15% (± 0.24)

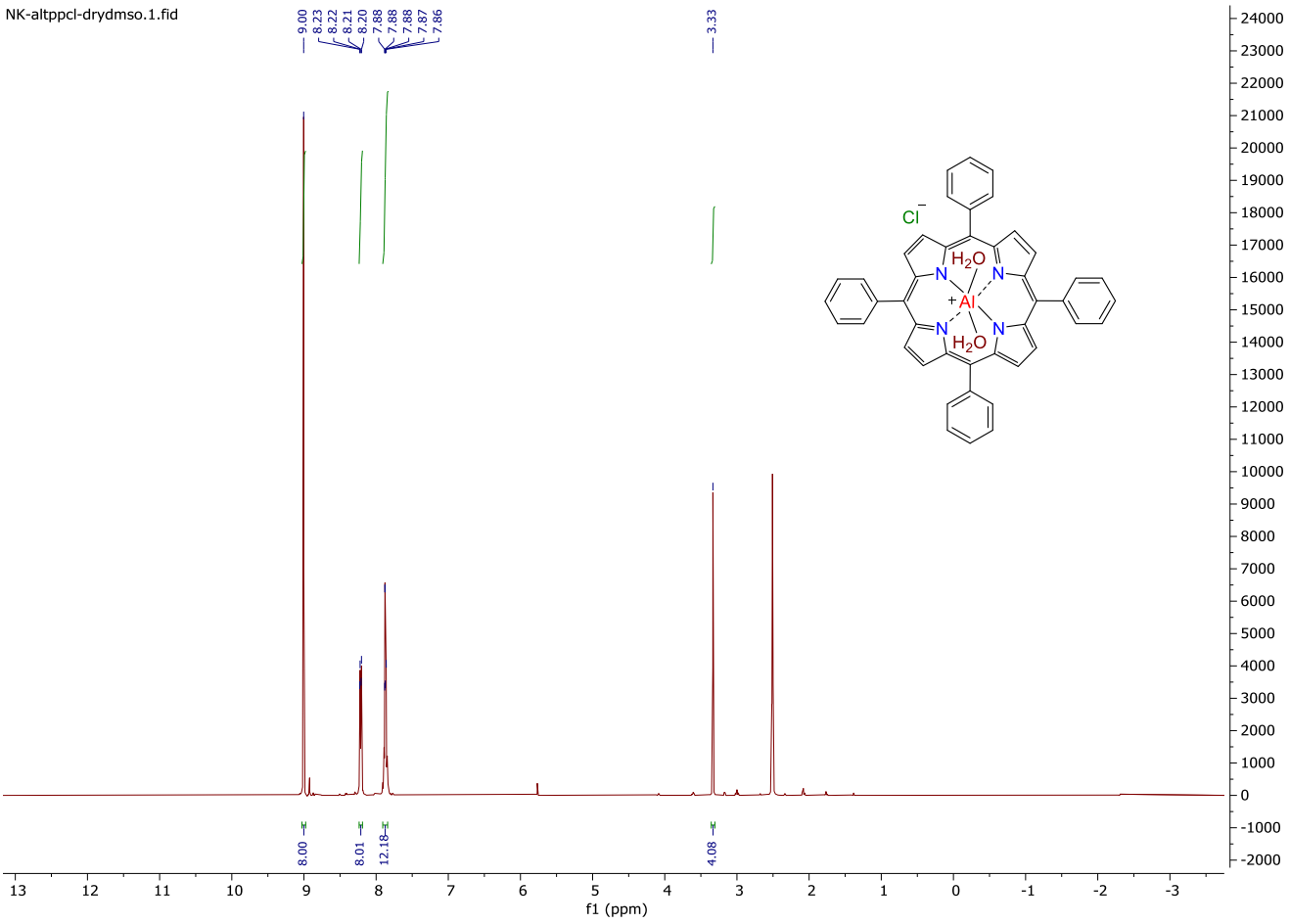


Figure S3 ^{1}H NMR spectrum of [Al(TPP)(OH_2)$_2$]Cl in dry DMSO-d6

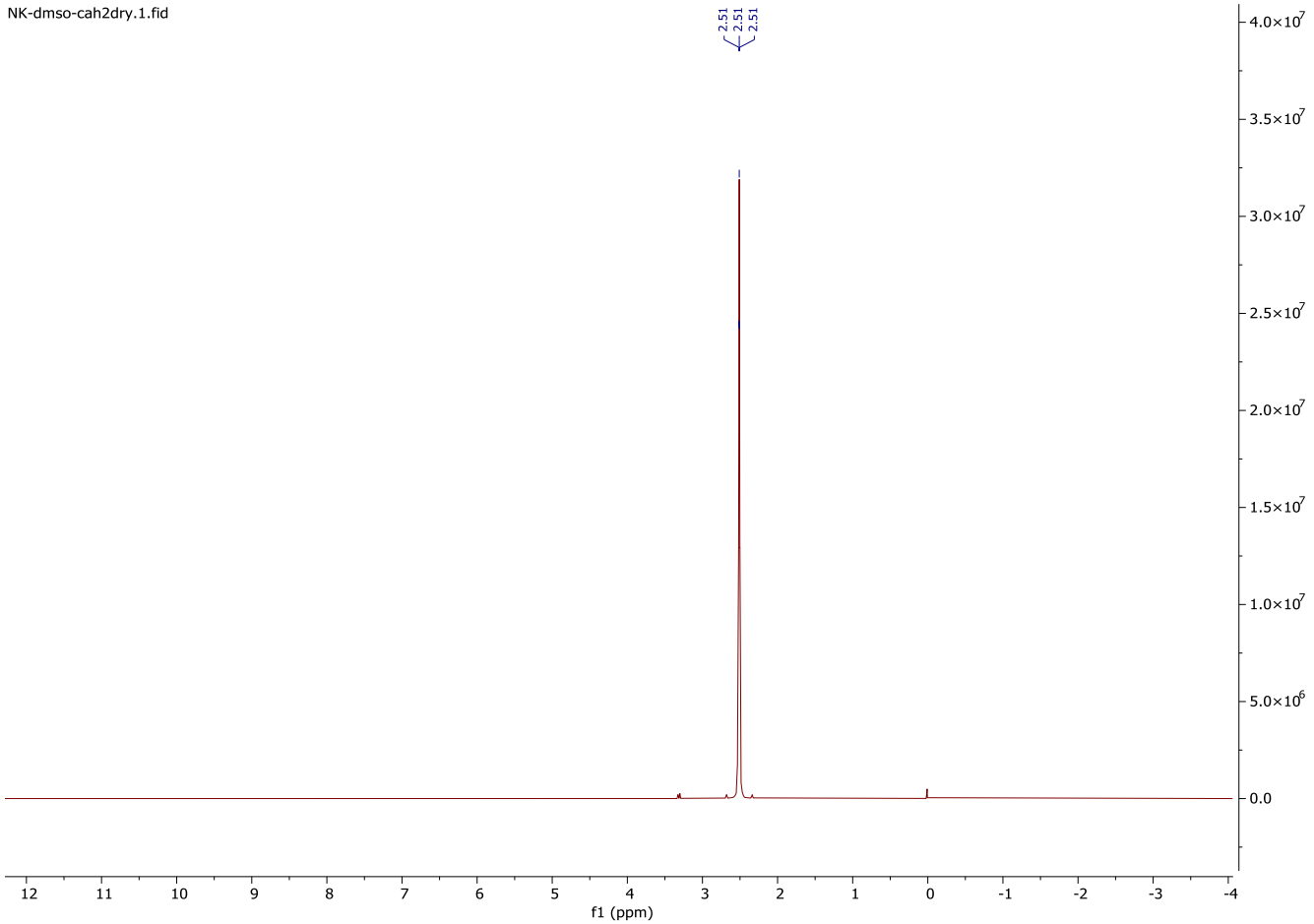


Figure S4 ^{1}H NMR spectrum of dry DMSO-d6

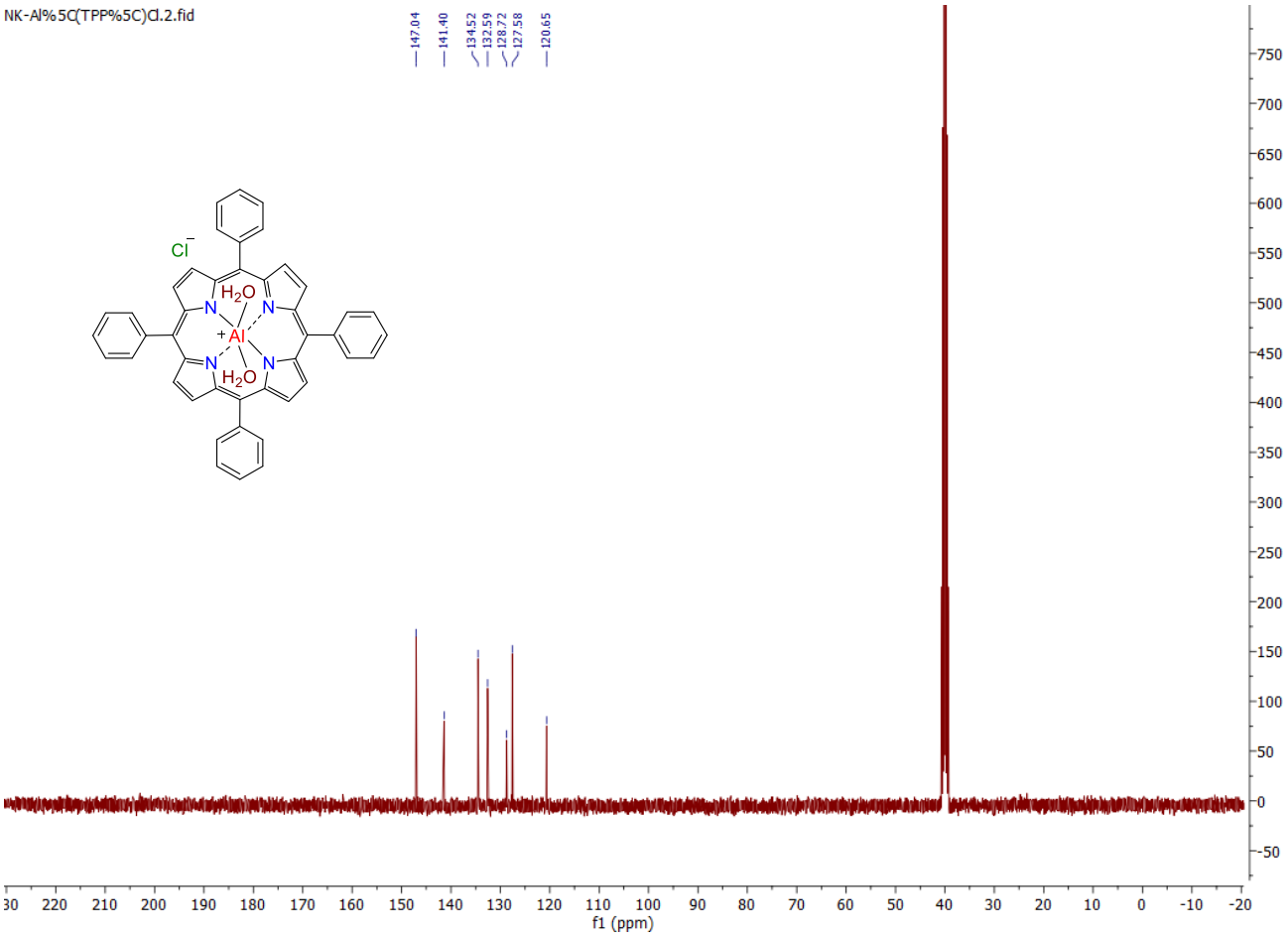


Figure S5 ^{13}C NMR spectrum of [Al(TPP)$(OH_2)_2$]Cl in dry DMSO-d6

Mass Spectrum SmartFormula Report

Analysis Info

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Comment			

Acquisition Parameter

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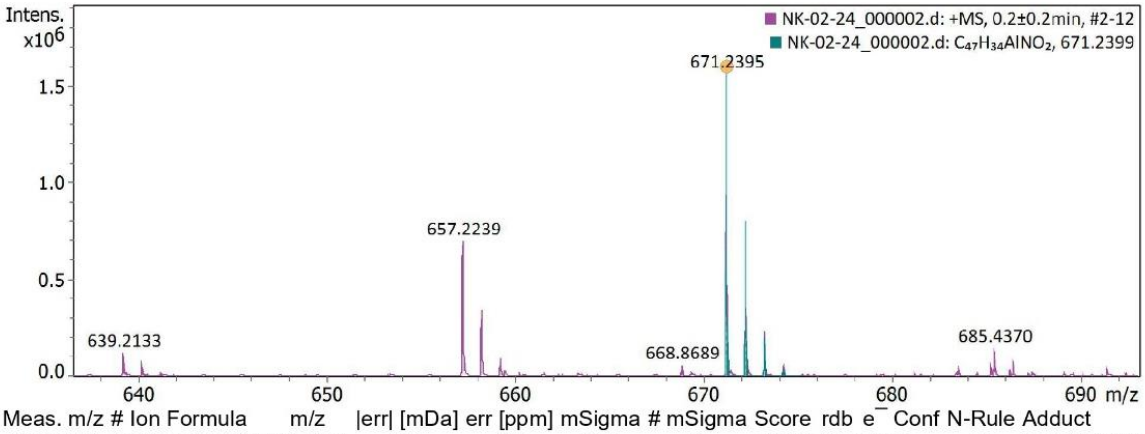

Meas. m/z	#	Ion Formula	m/z	|err| [mDa]	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule	Adduct
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NK-02-24_000002.d

Bruker Compass DataAnalysis 5.3 printed: 05-Jan-22 11:23:19 by: demo Page 1 of 1

Figure S6 Mass spectrum of $[Al(TPP)(OH_2)_2]Cl$

3.2 Diaqua(*meso*-tetraphenylporphyrin)aluminium Triflate [Al(TPP)$(OH_2)_2$]OTf 1b

A 100 mL Schlenk flask was loaded with [Al(TPP)$(OH_2)_2$]Cl **1a** (100 mg, 0.148 mmol) and AgOTf (47.5 mg, 0.185 mmol) and dissolved in dry DCM under inert atmosphere. Reaction mixture was stirred for 48 h at room temperature covered in an aluminium foil to prevent light from reaching the reaction. The supernatant was then filtered and solvent was removed in vacuo and purple solid **1b** was collected (80% yield).^{1}H NMR (300 MHz, ACN-d3) δ = 9.00 (s, 8H, pyrrole), 8.28 – 8.16 (m, 8H, *o*-Ph), 7.94 – 7.79 (m, 12H, m,p-Ph). ^{19}F NMR (282 MHz, DMSO-d6) δ -77.74. ^{13}C NMR (101 MHz, DMSO-d6) δ = 147.0, 141.4, 134.5, 132.6, 128.7, 127.6, 120.7.

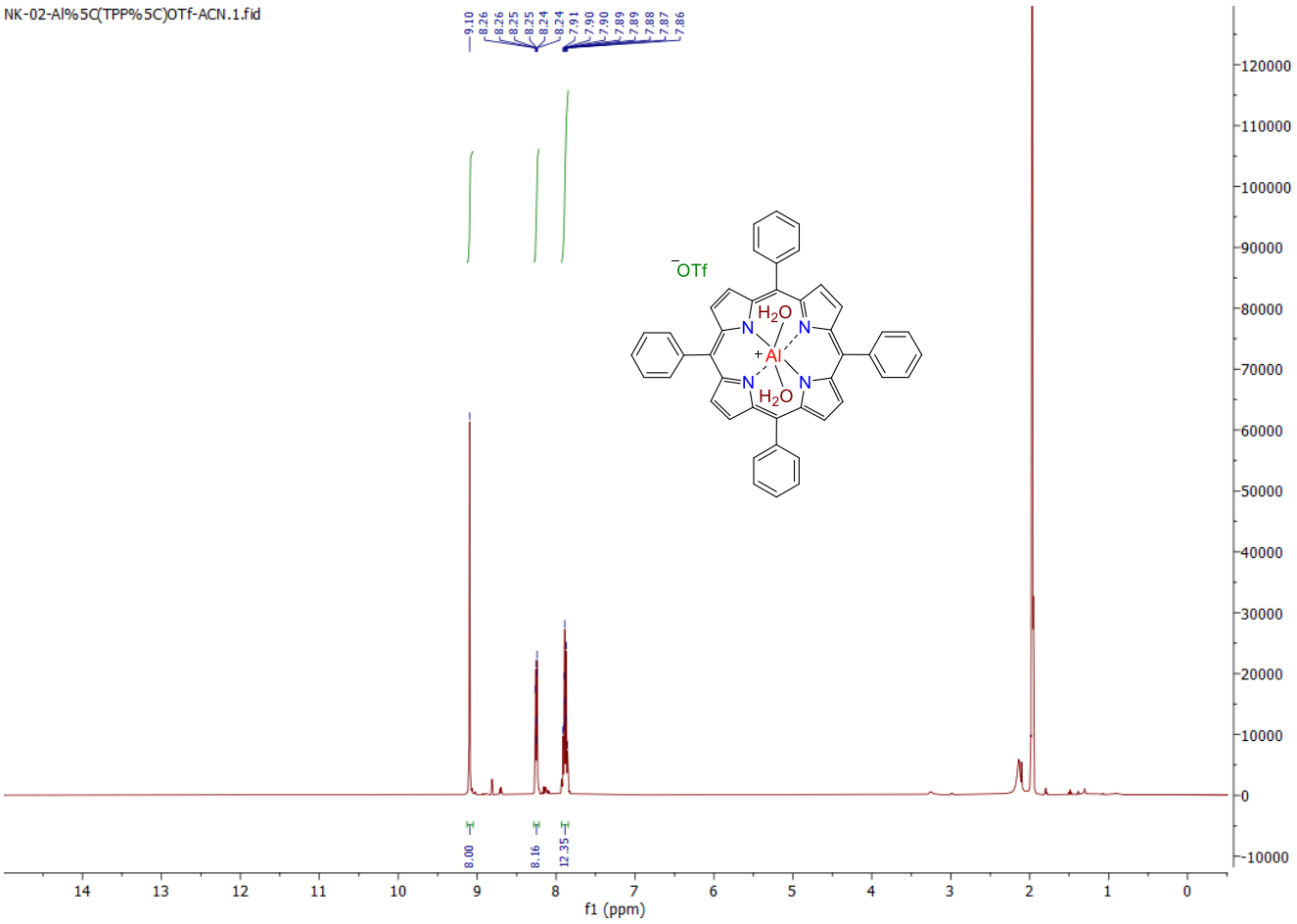


Figure S7 ^{1}H NMR Spectrum of [Al(TPP)$(OH_2)_2$]OTf in ACN-d3

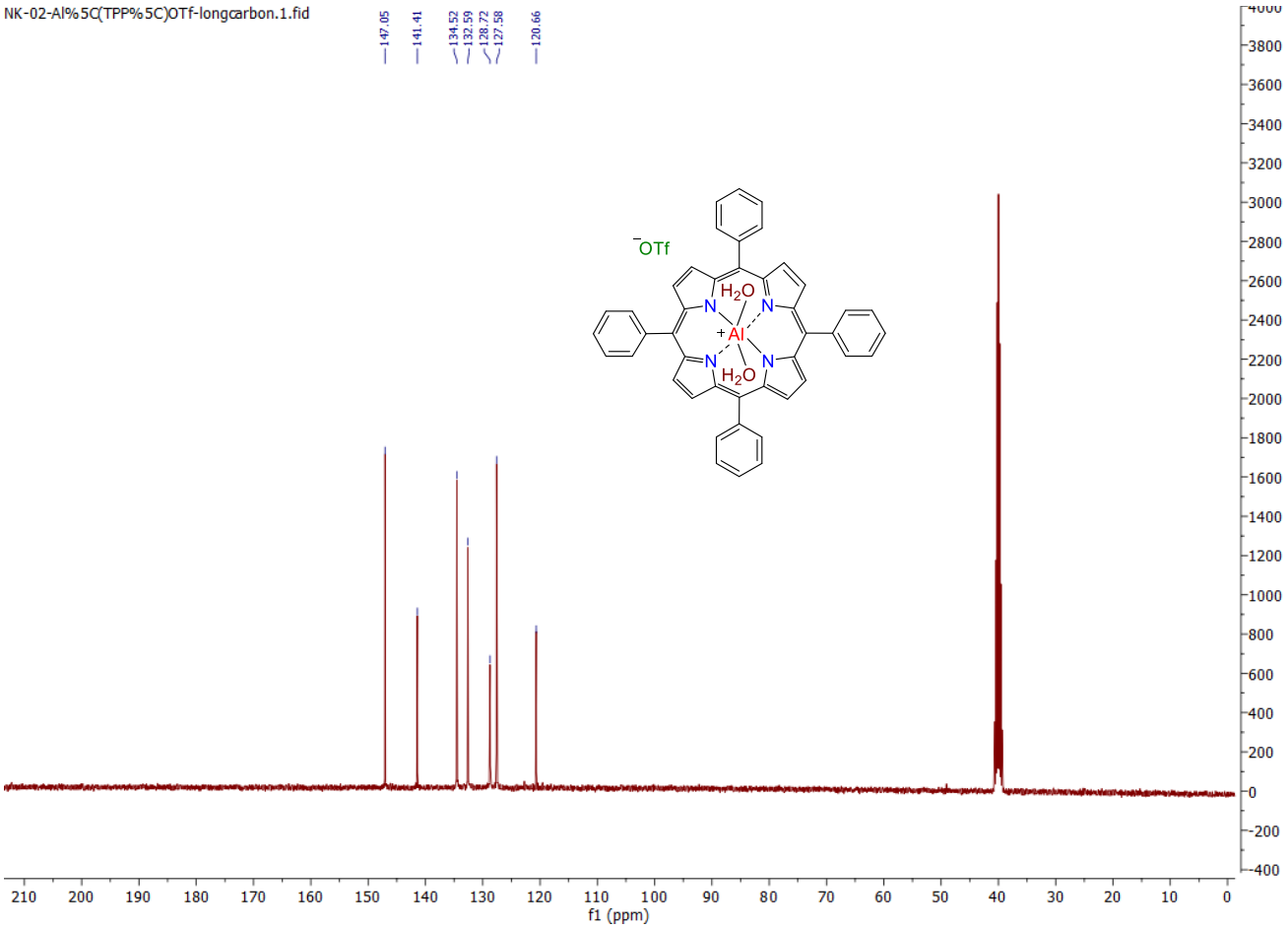


Figure S8 ^{13}C NMR Spectrum of [Al(TPP)$(OH_2)_2$]OTf – DMSO-d6

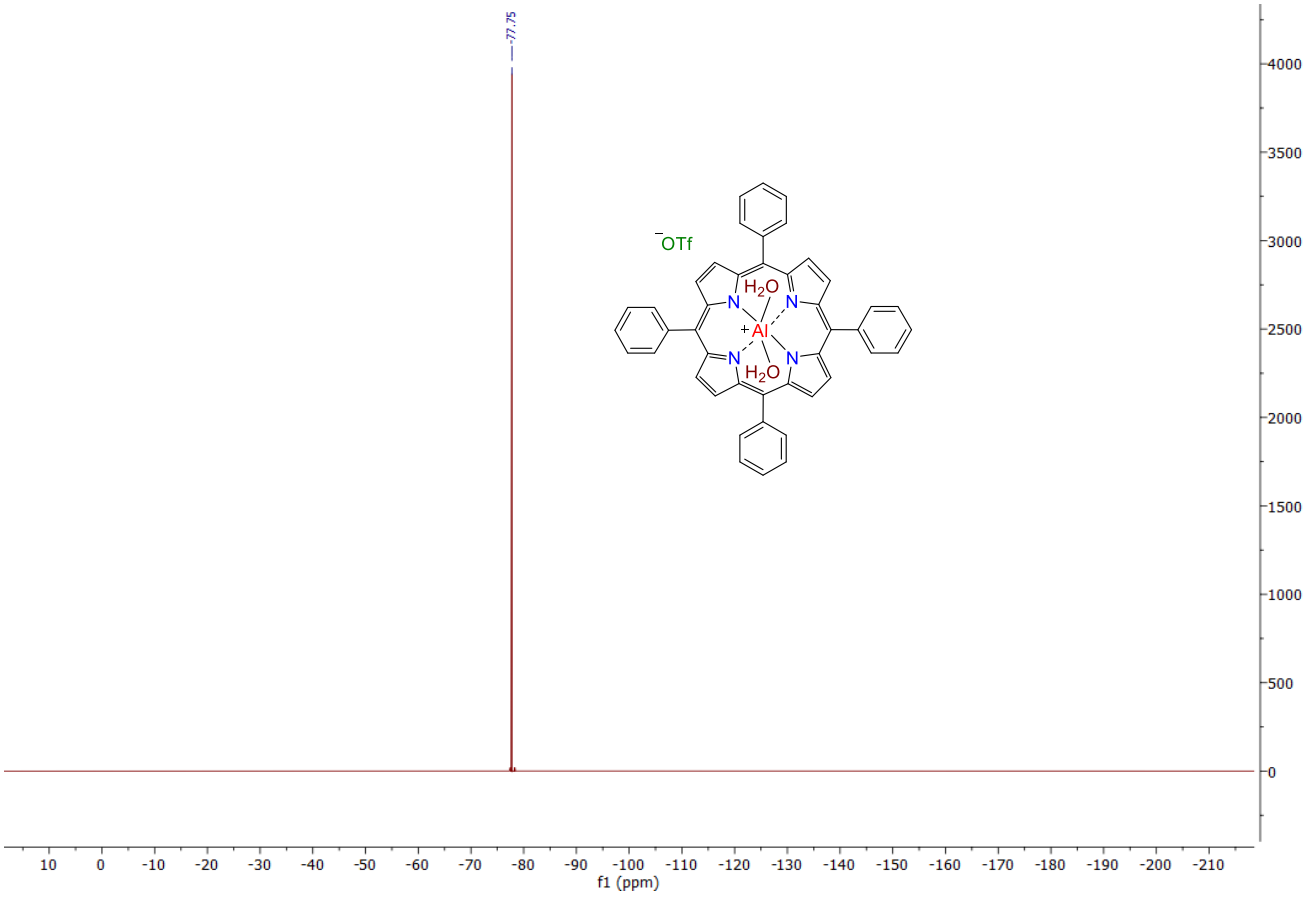


Figure S9 ^{19}F NMR spectrum of [Al(TPP)$(OH_2)_2$]OTf in DMSO-d6

3.3 Diaqua(*meso*-tetraphenylporphyrin)aluminium Perchlorate[Al(TPP)$(OH_2)_2$]ClO_4 1c

A 100 mL Schlenk flask was loaded with [Al(TPP)$(OH_2)_2$]Cl **1a** (200 mg, 0.296 mmol) and $AgClO_4$ (77 mg, 0.37 mmol) and dissolved in dry DCM under inert atmosphere. Reaction mixture was covered in aluminum foil and stirred for 48 h at room temperature. The supernatant was then filtered, solvent removed in vacuo and purple solid **1d** was collected (80% yield). ^{1}H NMR (400 MHz, DMSO) δ 9.00 (s, 8H), 8.23 – 8.18 (m, 8H), 7.88 – 7.83 (m, 12H). ^{13}C NMR (101 MHz, DMSO) δ = 147.0, 141.4, 134.5, 132.6, 128.7, 127.6, 120.7.

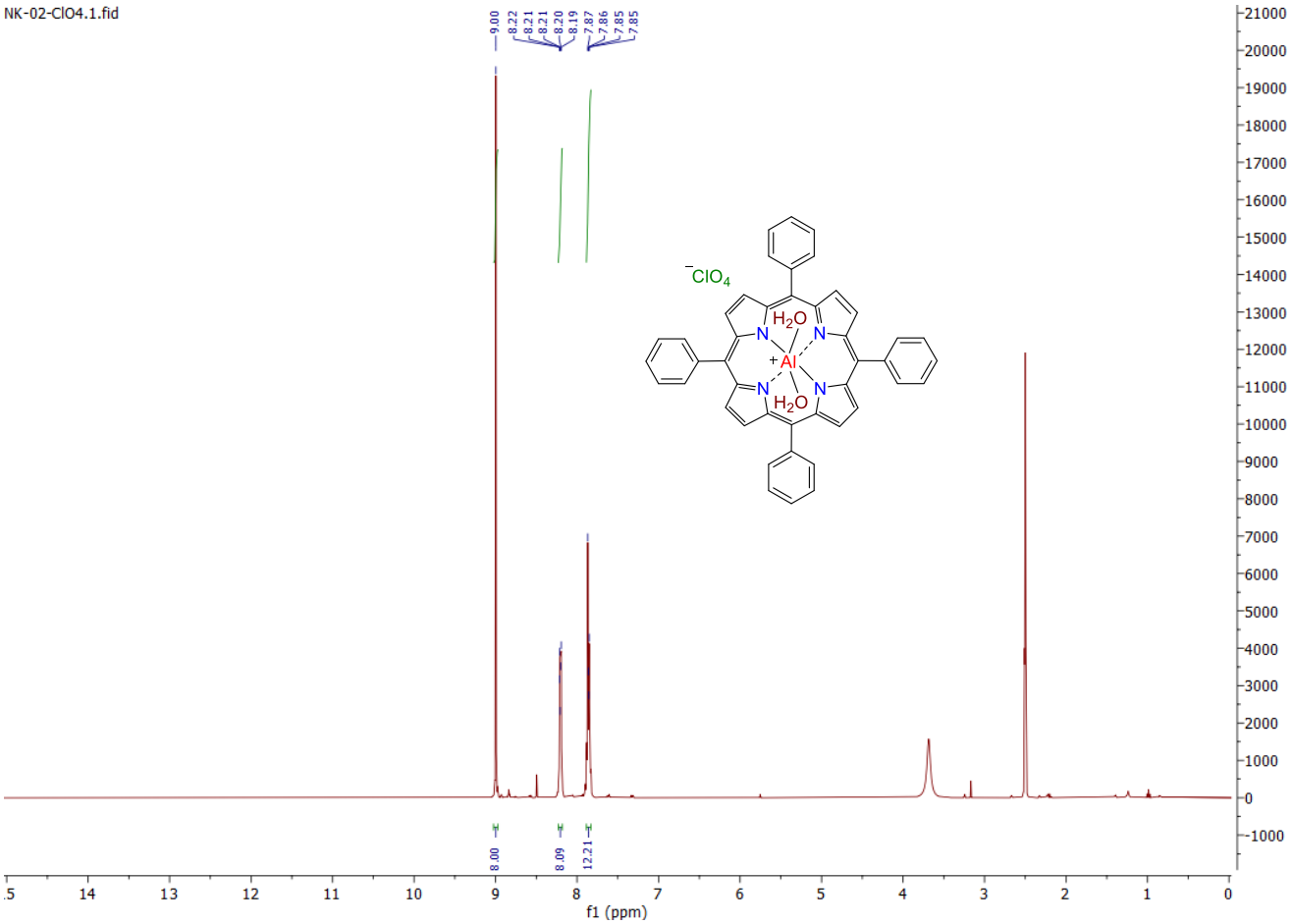


Figure S10 ^{1}H NMR spectrum of [Al(TPP)$(OH_2)_2$]ClO_4

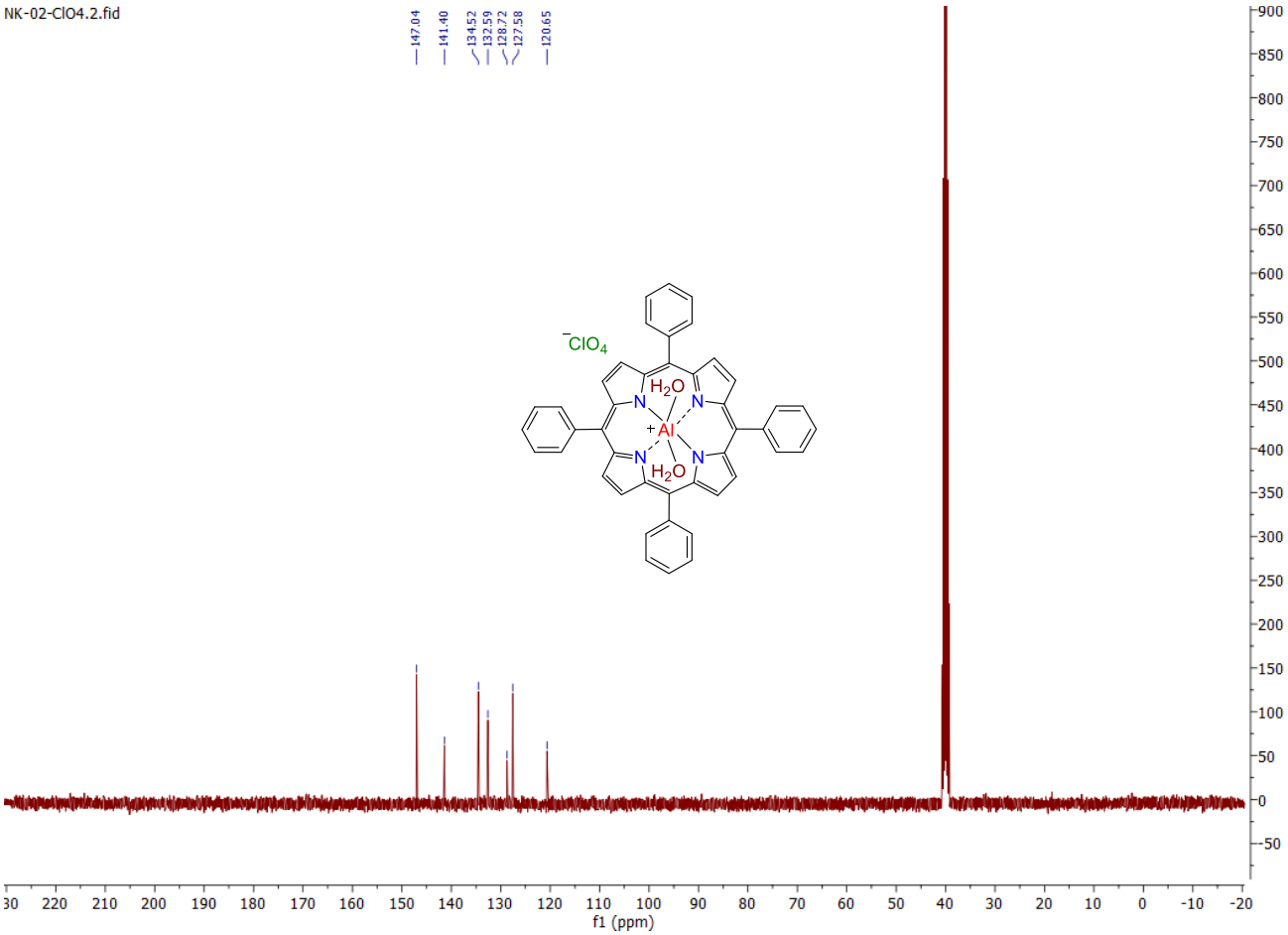


Figure S11 ^{13}C NMR Spectrum of $[Al(TPP)(OH_2)_2]ClO_4$

3.4 Diaqua(meso-Tetra(4-tert-butylphenyl)porphyrin aluminum) Chloride [Al(tBuTPP)(OH_2)]Cl 1d

A 25 mL Schlenk flask was loaded with meso-Tetra(4-tert-butylphenyl) Porphin (200 mg, 0.238 mmol) in dry dichloromethane (250 mL) under nitrogen atmosphere, degassed and stirred for 10 minutes. Then 1.6 equiv. of $AlEt_2Cl$ (1M in Hexane) (0.4 mL, 0.38 mmol) was added dropwise under constant stirring at room temperature and the reaction mixture was kept stirring for 2h. The solvent was evaporated in air using rotary evaporator and collected purple coloured solid was purified by column chromatography (silica 60µm, dichloromethane-methanol vol/vol = 10: 1), the obtained product was then dried at 90°C under reduced pressure to remove residual solvents yield **1d** (86%). ^{1}H NMR (400 MHz, DMSO) δ 9.01 (s, 8H), 8.14 (d, J = 7.7 Hz, 8H), 7.89 (d, J = 7.8 Hz, 8H), 1.60 (s, 36H). ^{13}C NMR (101 MHz, DMSO) δ 150.9, 146.9, 138.5, 134.4, 132.0, 124.4, 120.4, 35.1, 31.9.

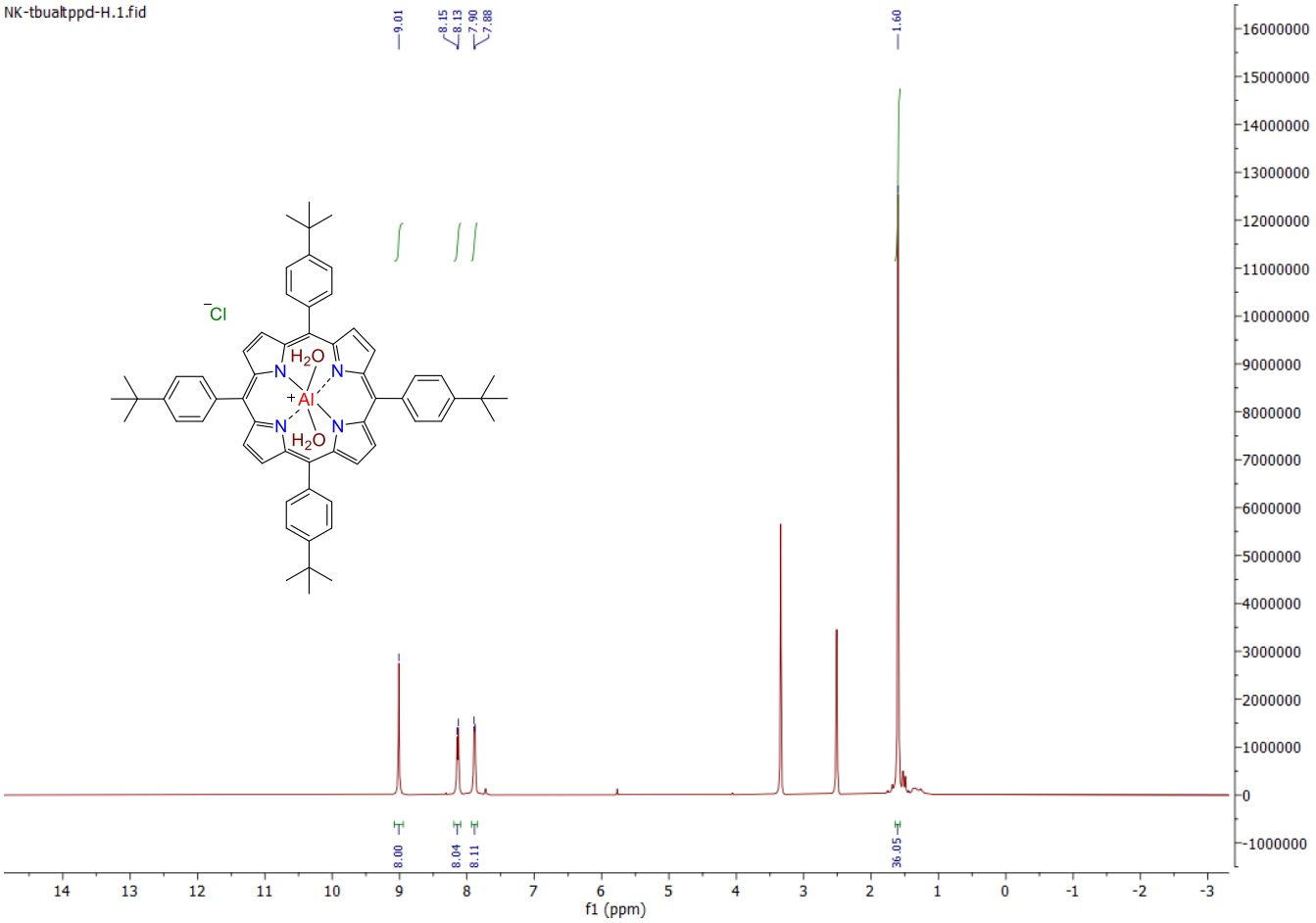


Figure S12 ^{1}H NMR spectrum of [Al(tBuTPP)(OH_2)$_2$]Cl

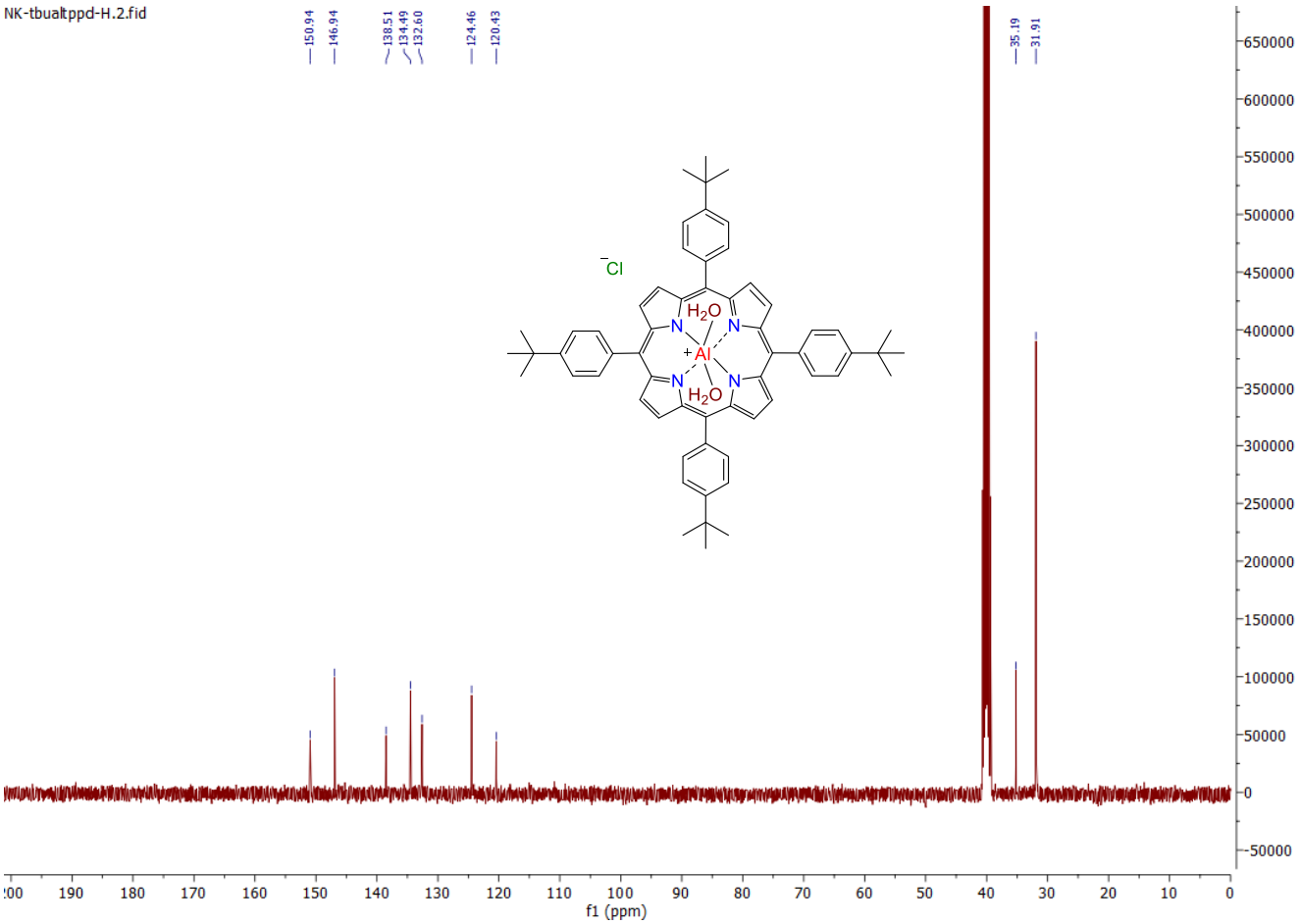
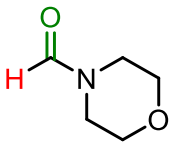


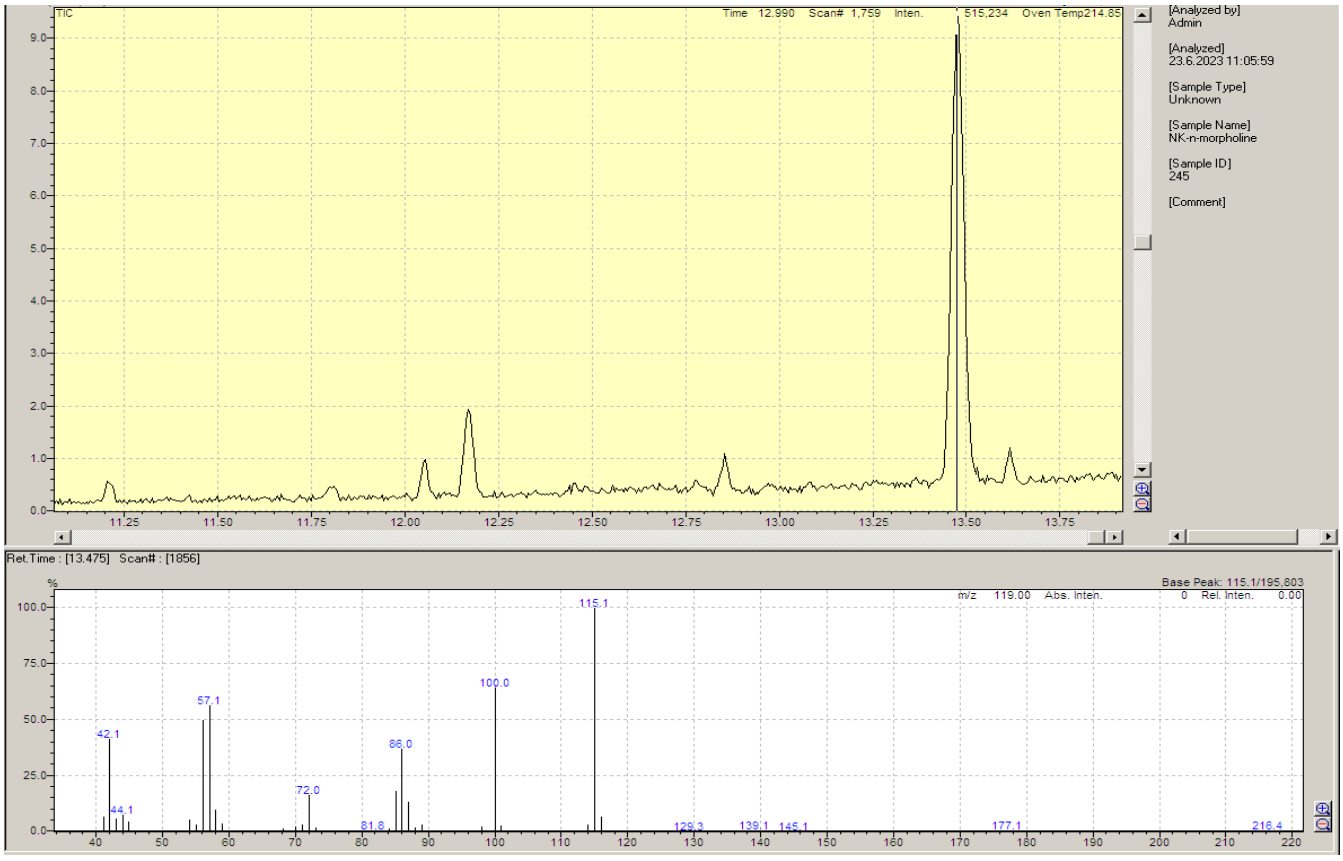
Figure S13 ^{13}C NMR spectrum of [Al(tBuTPP)$(OH_2)_2$]Cl

4.0 Substrate scope

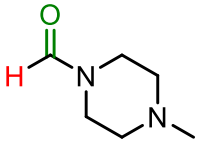
4.1 N-formylmorpholine



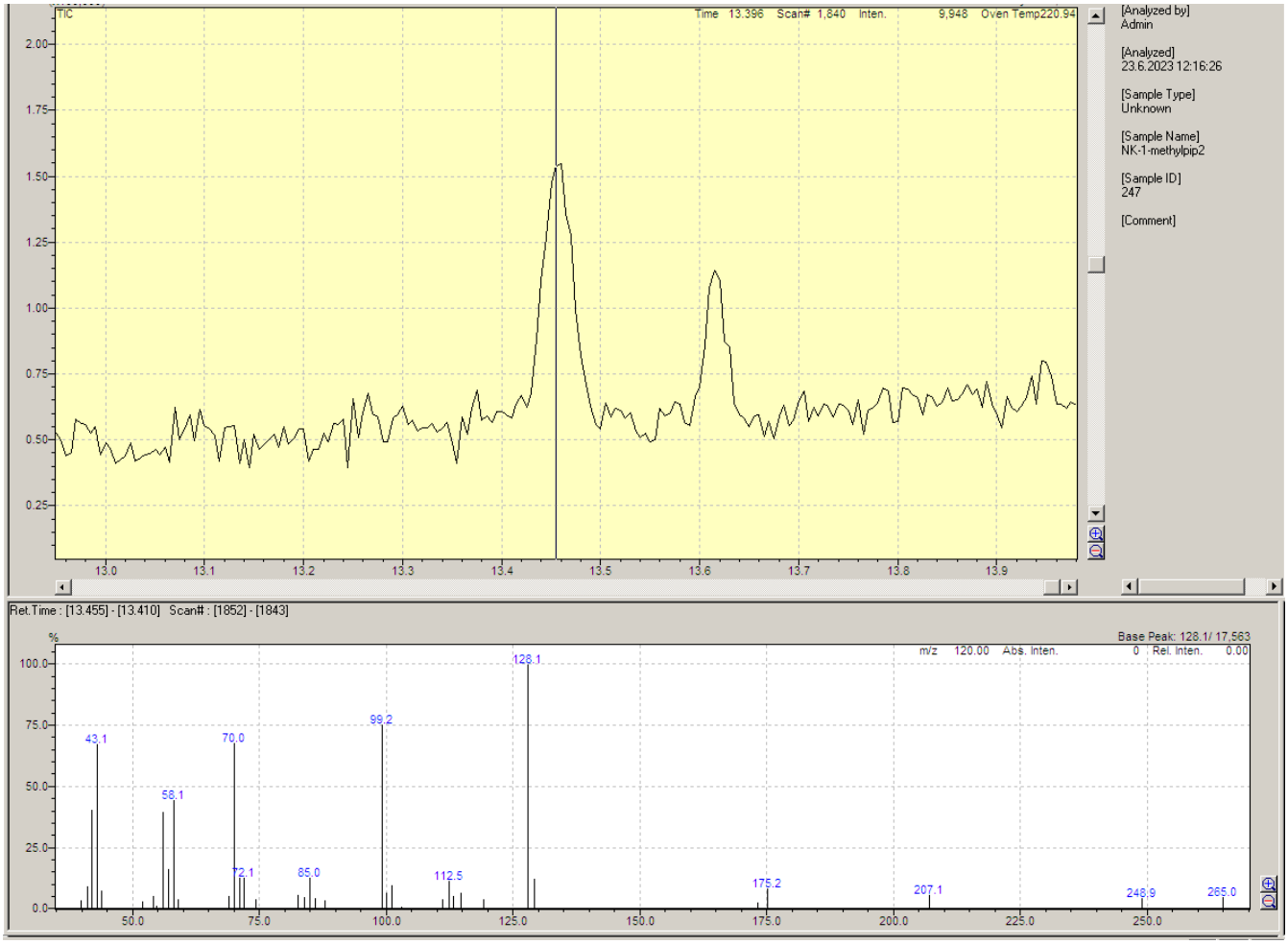
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.00 (s, 1H), 3.61 (dt, *J*=16.6, 4.2, 4H), 3.50 (d, *J*=5.2, 2H), 3.35 (t, *J*=5.0, 2H). GC retention time 13.45. EI-MS (m/z) calculated: 115.1, found 115.1



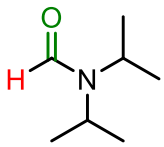
4.2 1-Formyl-4-methylpiperazine



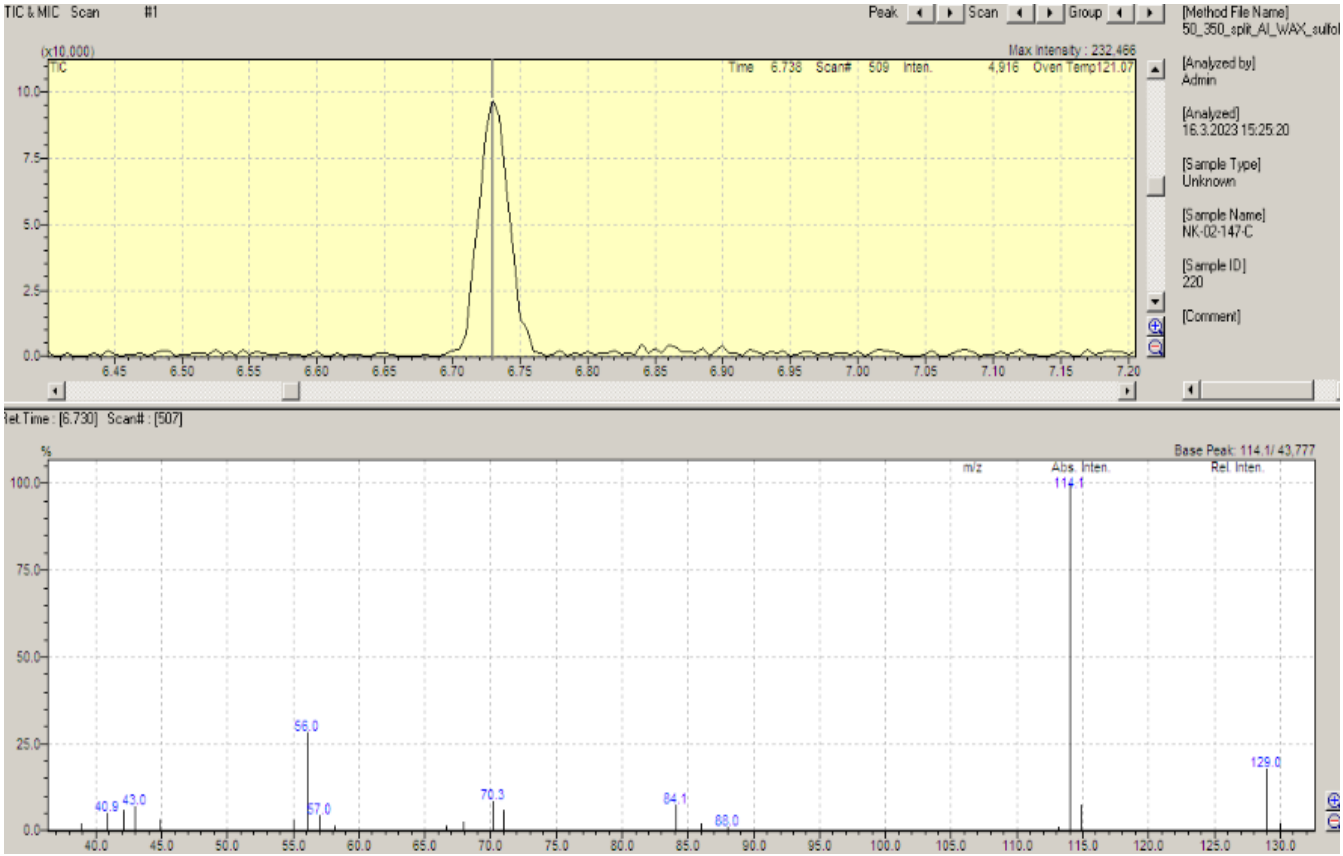
^{1}H NMR (300 MHz, cdcl$_3$) δ 7.98 (s, 1H), 3.66 (d, *J* = 7.1 Hz, 4H), 3.53 (d, *J* = 6.5 Hz, 2H), 3.35 (t, *J* = 5.1 Hz, 2H). GC retention time 13.3 to 13.5 minutes; EI-MS (*m/z*) calculated: 128.1, found 128.1



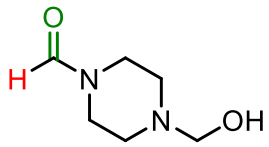
4.3 N,N-diisopropylformamide



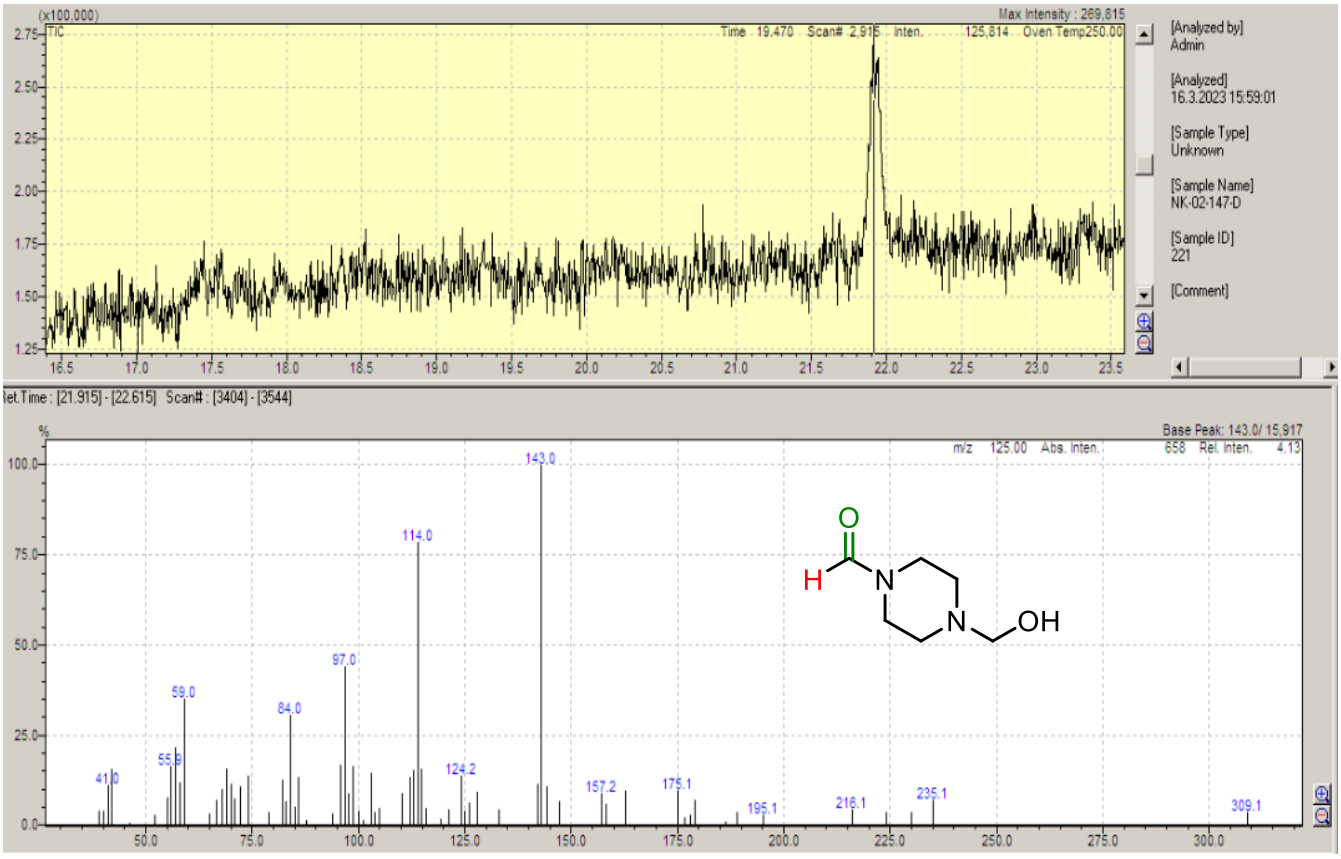
^{1}H NMR (300 MHz, cdcl$_3$) δ 8.04 (s, 1H), all other peaks obscured by starting material and solvent. GC retention time 6.7 to 6.75 minutes; EI-MS (m/z) calculated: 129.1, found 129.0



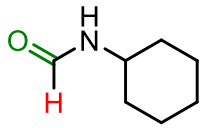
4.4 N-Formyl-4-piperidinemethanol



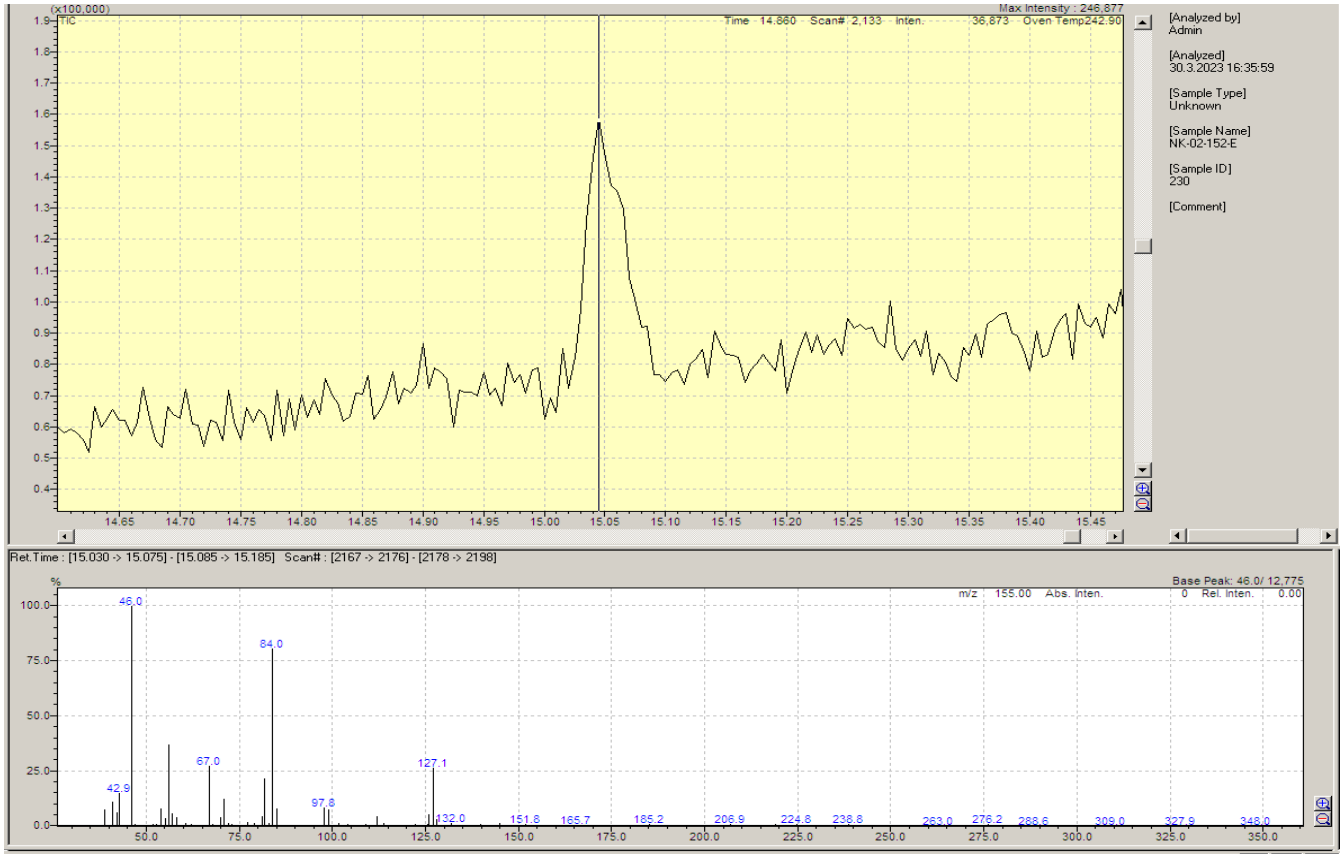
^{1}H NMR (300 MHz, cdcl$_3$) δ 8.05 (s, 1H), 4.42 (d, *J* = 14.1 Hz, 1H), 3.56 (t, *J* = 4.9 Hz, 1H), 3.50 (dd, *J* = 6.0, 2.8 Hz, 1H), 3.43 – 3.34 (m, 2H), 2.70 – 2.53 (m, 1H), 2.00 (q, *J* = 7.1 Hz, 2H), all other peaks obscured by starting material. GC retention time 21.7 to 21.9 minutes; EI-MS (m/z) calculated: 143.2, found 143.0



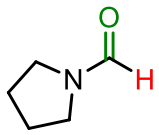
4.5 N-Cyclohexyl formamide



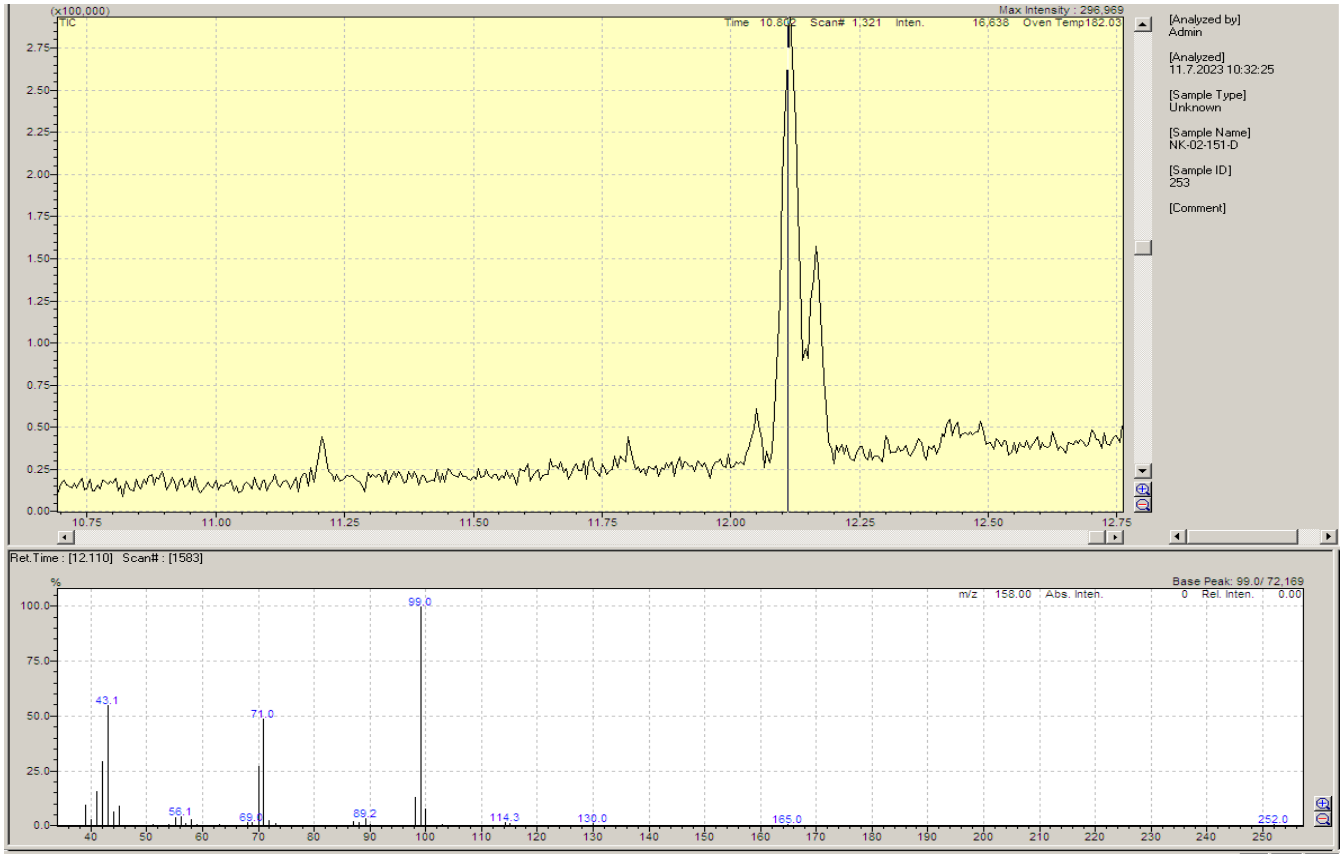
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 3.89 (d, *J* = 11.0 Hz, 1H). all other peaks obscured by reaction solvent. GC retention time 15.0 to 15.1 minutes; EI-MS (m/z) calculated: 127.1, found 127.1



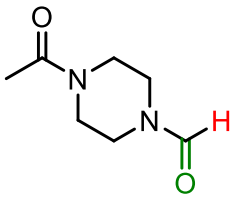
4.6 Pyrrolidine-1-carbaldehyde



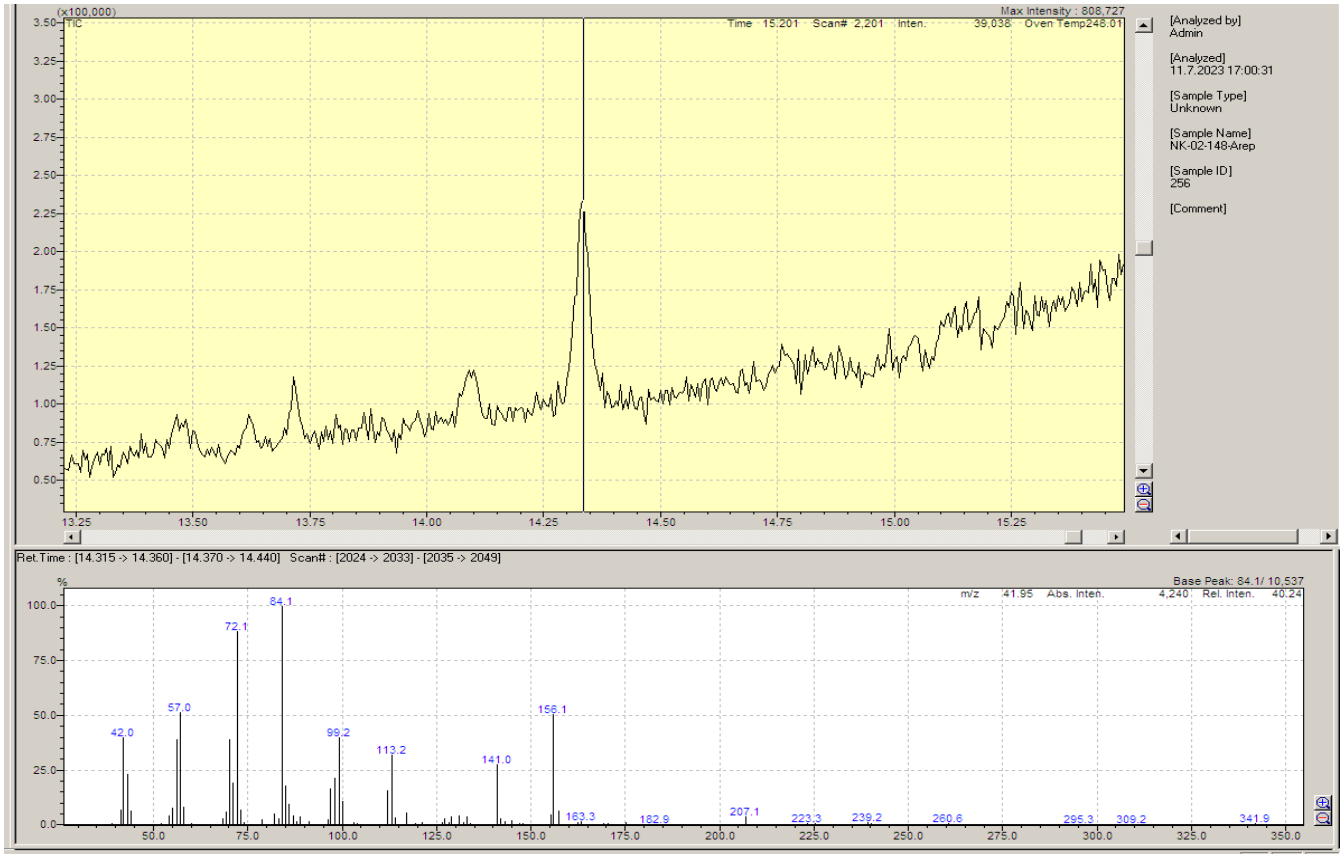
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 3.52 – 3.47 (m, 2H), 3.41 (t, *J* = 6.7 Hz, 2H), 1.95 – 1.88 (m, 4H).
GC retention time 12.05 to 12.15 minutes; EI-MS (m/z) calculated: 99.0, found 99.0



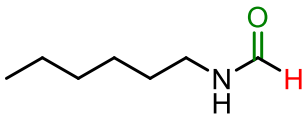
4.7 4-acetylpiperazine-1-carbaldehyde



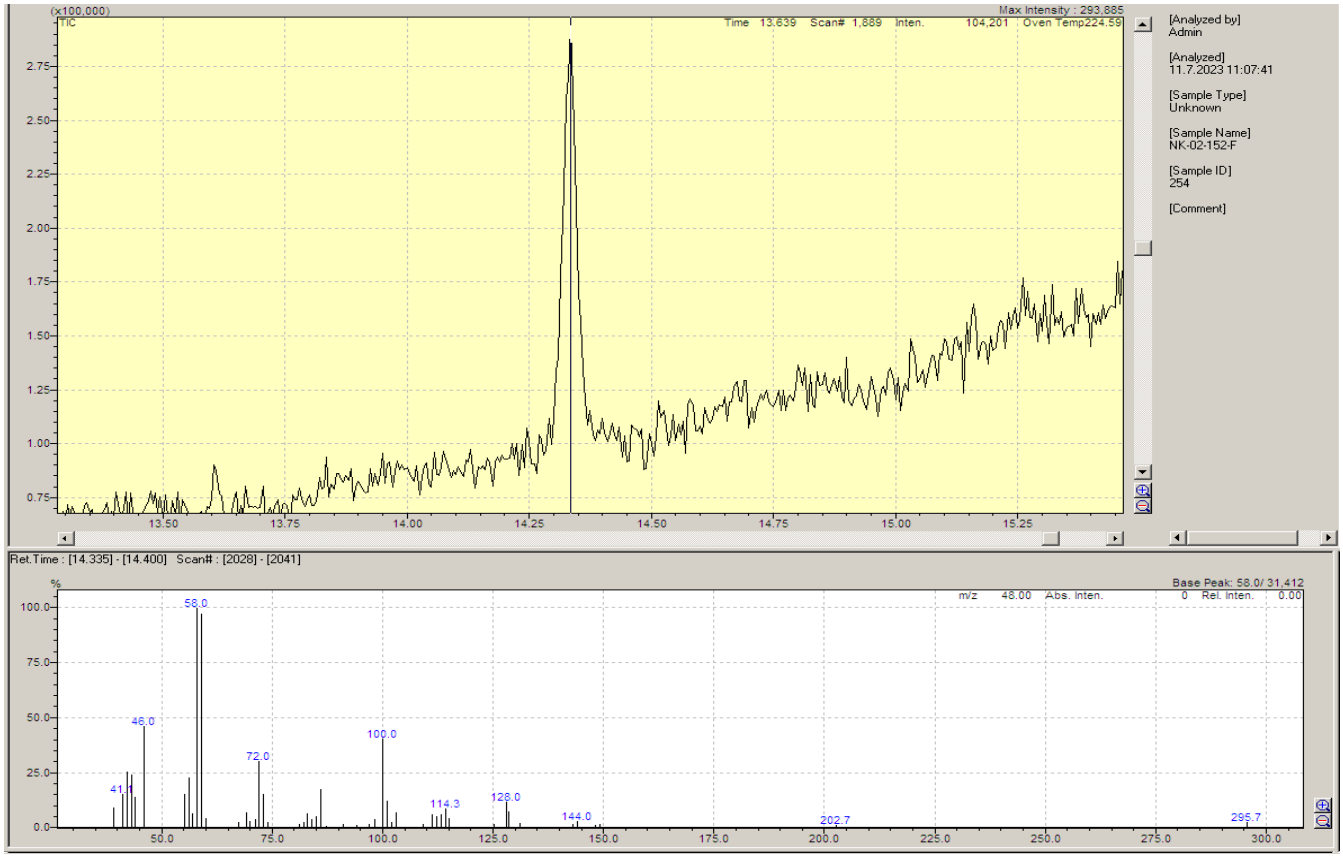
^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.98 (s, 1H), all other peaks obscured by the starting material and reaction solvents. C retention time 14.3 to- 14.4 minutes; EI-MS (m/z) calculated: 156.1, found 156.1



4.8 N-hexylformamide



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 3.29 (q, *J* = 6.7 Hz, 2H), 1.52 (q, *J* = 6.9 Hz, 2H). all other peaks obscured by the reaction solvent and starting material. GC retention time 14.3 to 14.4 minutes; EI-MS (m/z) calculated: 129.1, found 128.0



5.0 Alternative reaction mechanism

The alternative reaction mechanism (Figure S13) also involves activation of H_2 with [Al(TPP)$(OH_2)_2$]Cl : morpholine] or [Al(TPP)$(OH_2)_2$]Cl: collidine leading to the formation of [baseH]Cl and [Al(TPP)(H)] (Figure S14, **I**).[2] The reaction mechanism differs in the CO_2 reduction and N-formylation steps, where CO_2 inserts into the Al-H bond of **I** forming [baseH]Cl and [Al(TPP)(OCHO)] (Figure S14, **II**) and a nucleophilic attack of morpholine on the formate group of **II** leads to the formation of the desired N-formylated product, [baseH]Cl and [Al(TPP)(OH)] (Figure S14, **III**). Nevertheless, [Al(TPP)(OH)] and morpholinium chloride, when used as the reaction catalyst, resulted in 0% of N-formylmorpholine demonstrating that [Al(TPP)(OH)] is not an active catalyst for the reaction. Pre-mixing of [Al(TPP)(OH)] with morpholinium chloride in DCM, evaporation of the solvent under reduced pressure and use of the resulting mixture as the reaction's catalyst improved the N-formylmoprholine yield to 38%, which indicates that elimination of the axial hydroxide instead of the chloride to yield catalytically active species is possible. Nevertheless, activation of [Al(TPP)(OH)] required protonation with excess acid (morpolinium chloride) and reduced pressure for elimination of water, which indicates that such mechanism is unlikely to be the working mechanism of the reaction. Instead, it is the likely reaction pathway towards catalyst deactivation.

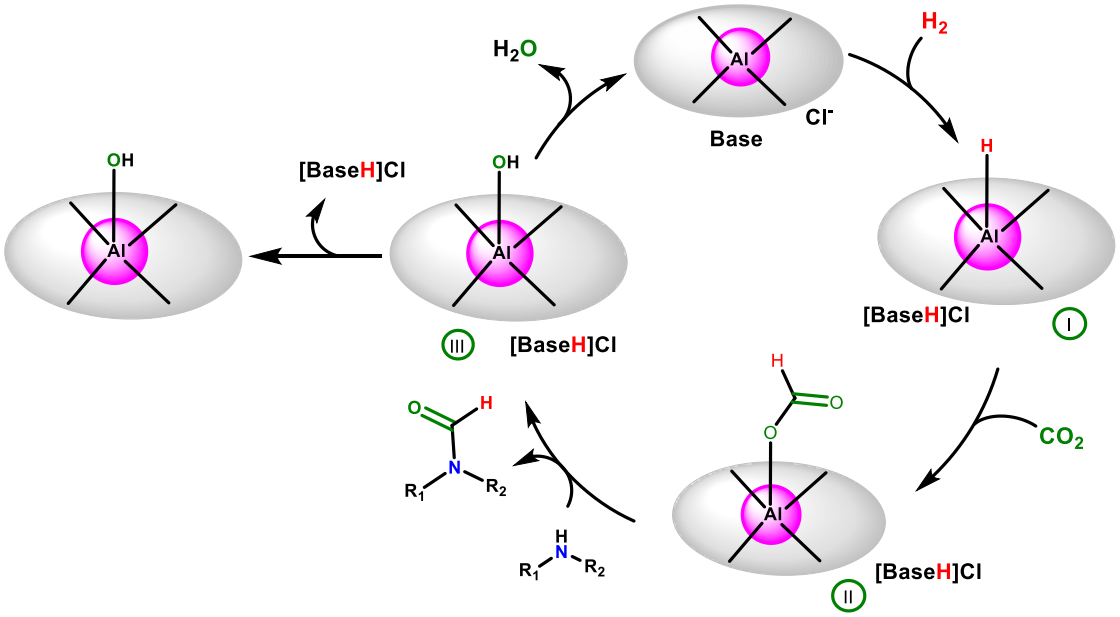


Figure S14 Main group like hydride reaction mechanism for N-formylation of morpholine with CO_2 and H_2 using [Al(TPP)OH] and 2,4,6-collidine as FLP

5.1 Synthesis of hydroxo(*meso*-tetraphenylporphyrin)aluminium [Al(TPP)(OH)][3]

To a solution of tetraphenylporphyrin (1 g, 1.62 mmol) in 100 mL of dry toluene was added 5.5 equiv. of trimethylaluminium (4.5 mL, 2.0 M in Hexane) under N_2 atmosphere. The resulting solution was stirred at room temperature for 4 hr, then 10 mL of water were added and the reaction was stirred overnight. Solvent was evaporated and the purple solid dissolved in DCM. The solution was filtered and evaporated to yield the desired product (0.62 g, 58%). ^{1}H NMR (300 MHz, dmso) δ 8.79 (s, 8H), 8.17 (d, *J* = 23.0 Hz, 8H), 7.82 (m, 12H)). ESI-MS – for M = $C_{44}H_{29}AlN_4O$- calculated m/z: 657.2 measured 657.3 ($M+H^+$), 639.2 ($M-OH^-$) and 671.2 ($M-OH^-$+MeOH).

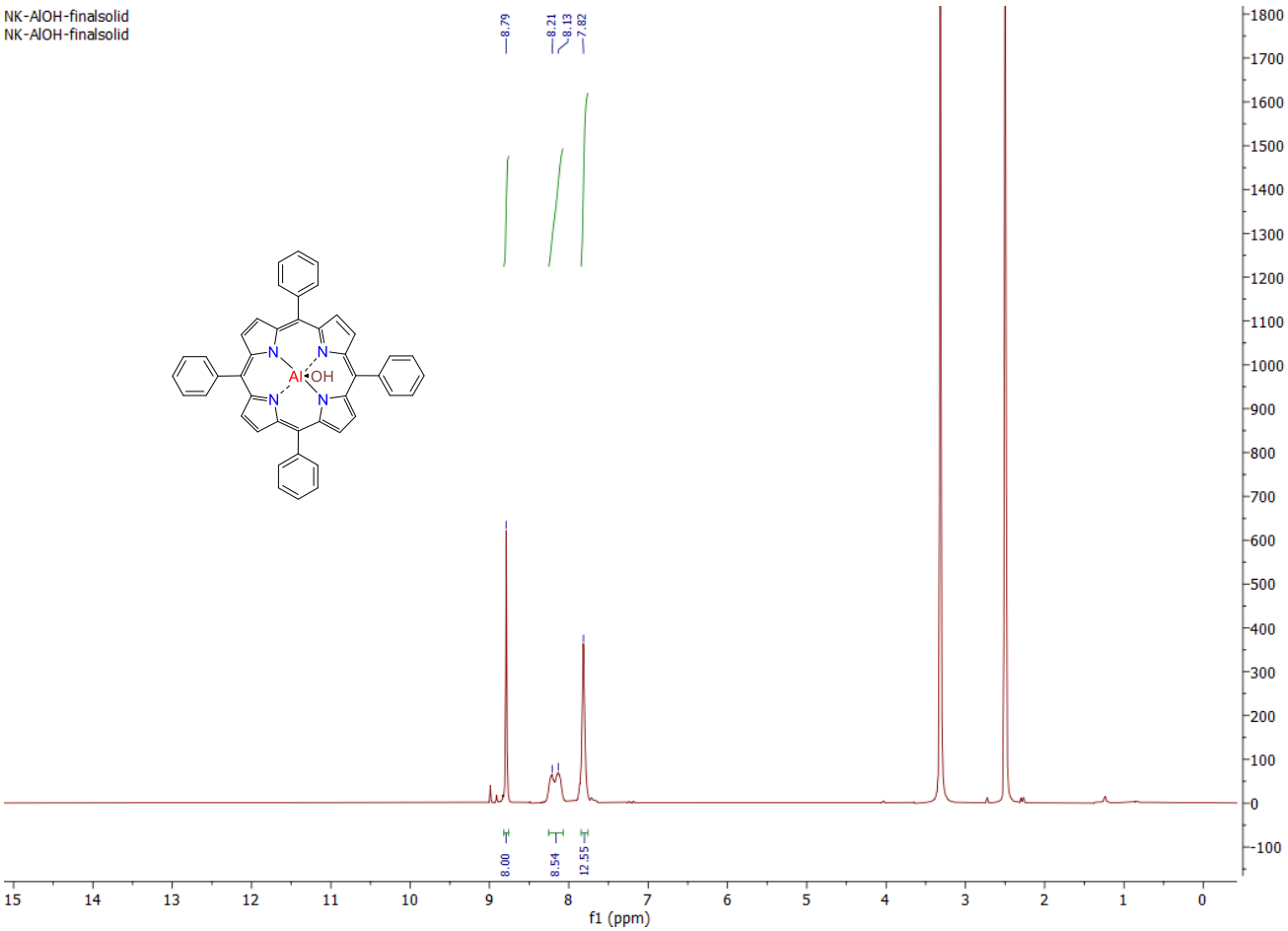


Figure S15 ^{1}H NMR Spectrum of Al(TPP)OH

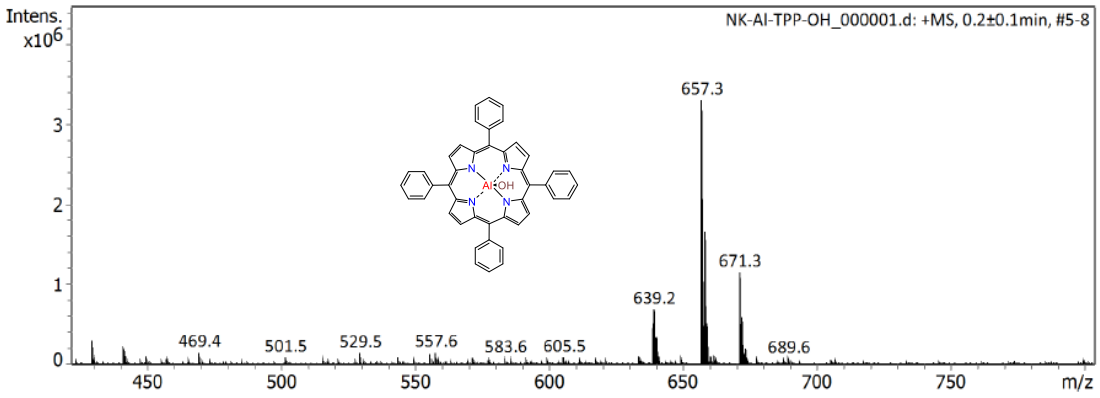
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\HRMS\NK-Al-TPP-OH_000001.d	Acquisition Date	01-Jun-23 16:01:25
Method	bg_low_1.m	Operator	Demo User
Sample Name	NK-Al-TPP-OH	Instrument	compact 8255754.20121
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Not active	Set Capillary	3000 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	2.9 l/min
Scan End	1200 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	0 °C



5.2 Attempts to catalyse the reaction by [Al(TPP)(OH)] with morpholinium chloride

In Glove box, to the autoclave, [Al(TPP)(OH)] (65.6 mg, 0.1 mmol), 2,4,6-collidine (14 µL, 0.1 mmol), morpholinium chloride (13 mg, 0.1 mmol) and morpholine (79.2 µL, 0.9 mmol) were dissolved in sulfolane (4 mL). The autoclave was sealed and purged with 7 bar of CO_2 then topped up with 100 bar of H_2. The temperature and stirring rate were set using Specview program connected to the Parr 5000 series multi reactor system. After 24 h the heating was turned off, the reactor was allowed to cool to room temperature, and the autoclave depressurized. Dibromoethane (69.5 µL, 1 mmol) was added, stirred and an aliquot was taken for ^{1}H NMR in $CDCl_3$. The conversion was quantified by comparing the internal standard of the formate peak.

5.3 Attempts to catalyse the reaction in the presence of molecular sieves

A catalytic test was conducted following the standard reaction procedure. Furthermore, a small amount of activated molecular sieves (heated at 300°C overnight) were introduced into the process. The yield of N-formyl morpholine was decrease to 30%, presumably due to the reaction being inhibited in the presence of the molecular sieves.

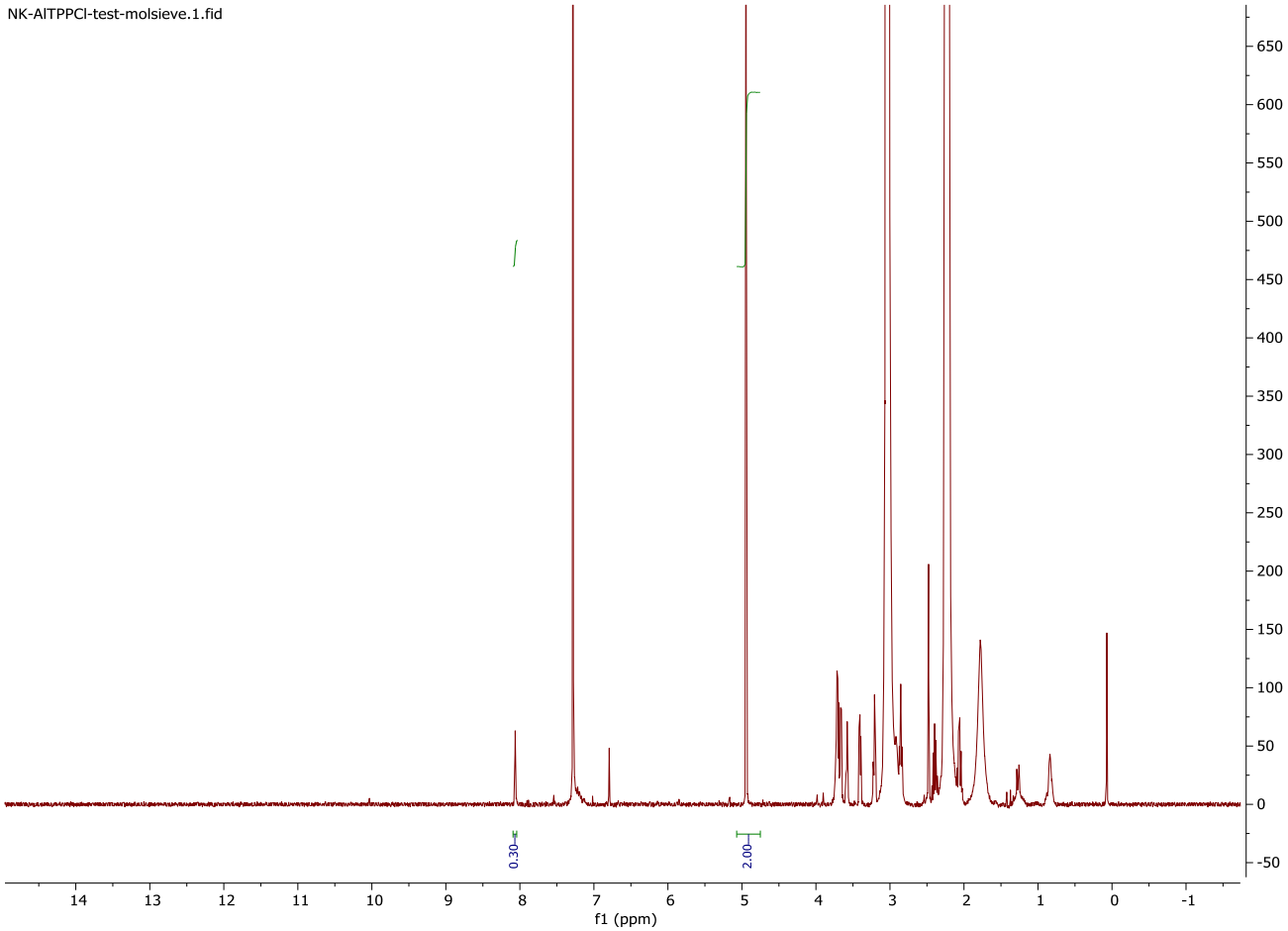


Figure S16 ^{1}H NMR spectrum of the N-formylation of morpholine catalytic test in presence of molecular sieves

5.4 N-formylation of morpholine with CO_2 and D_2

To gain insight into the reaction mechanism, we conducted the N-formylation of morpholine using deuterium gas (D_2) at (50 bar) instead of H_2. As a result, the product N-formyl morpholine was obtained in 33% yield confirmed by GS-MS and NMR data. This result indicates that H_2 (or D_2) acts as a reductant in the reaction.

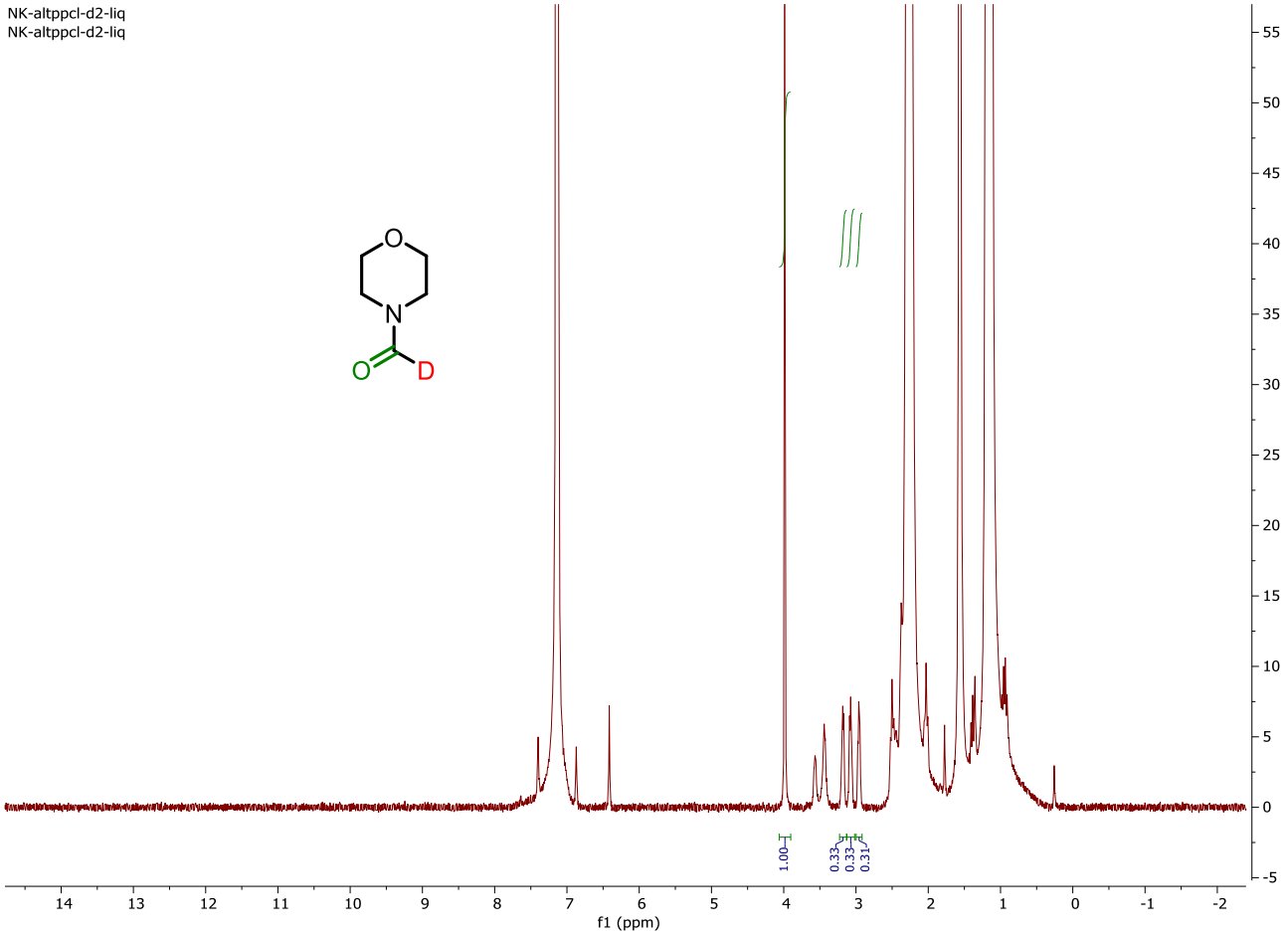


Figure S17 ^{1}H NMR spectrum of the N-formylation of morpholine catalytic test with D_2 instead of H_2

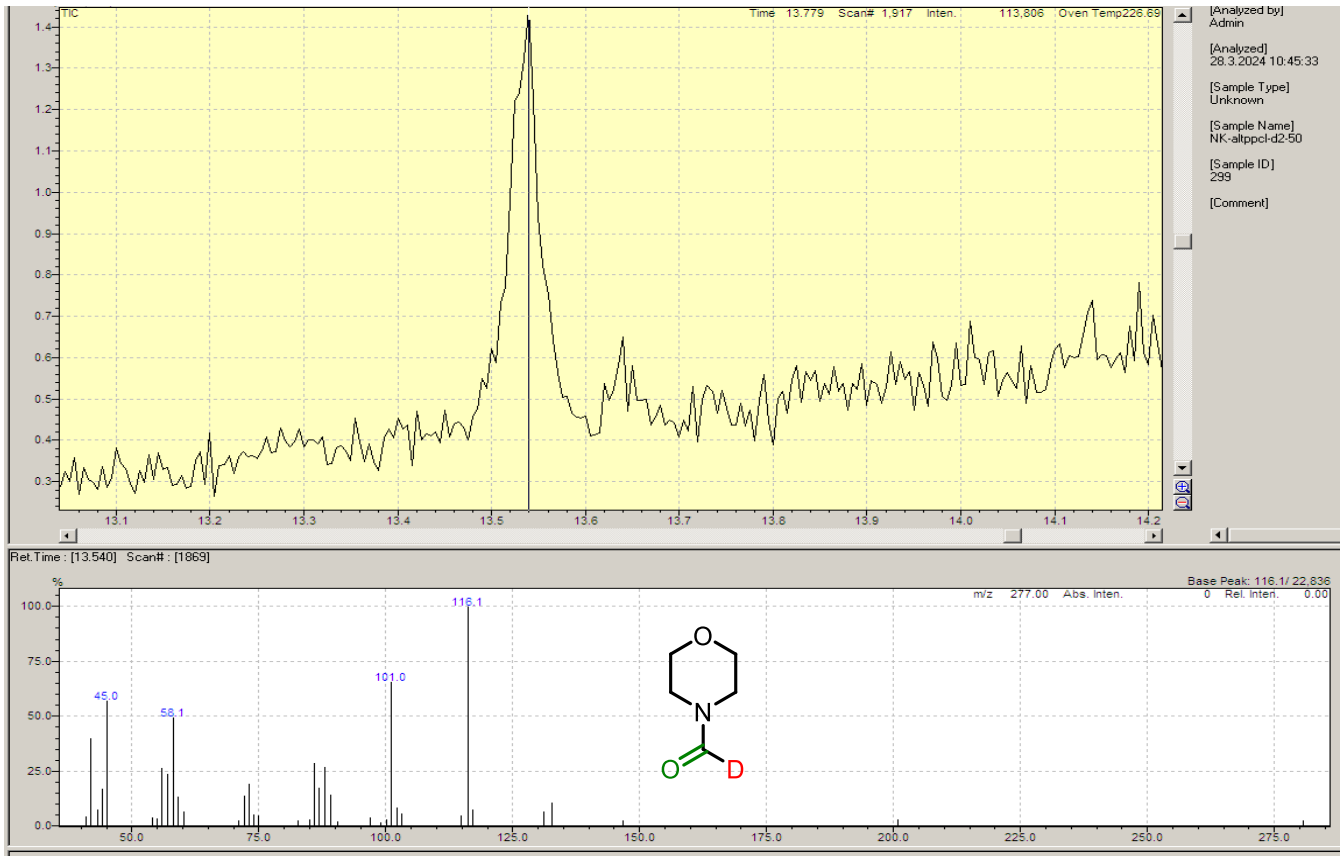


Figure S18 GC-MS spectrum of the N-formylation of morpholine catalytic test with D_2 instead of H_2. Note the weight increase of the sample by +1 compared to the use of H_2. GC retention time remained the same confirming identity of the sample.

5.5 Decomposition of Formic acid with $[Al(TPP)(OH_2)_2]Cl$

We performed a formic acid decomposition experiment in a low-pressure J. Young tap NMR tube to investigate the catalytic N-formylation of amine reaction mechanism. To prepare a reaction mixture solution, 0.2 mL deuterated toluene and 0.3 mL sulfolane were mixed with $[Al(TPP)(OH_2)Cl]$ (7 mg, 0.01 mmol), 2,4,6-collidine (4 μL, 0.01 mmol), and formic acid (76 μL, 2 mmol). After placing the solution in an NMR tube, the ^1H NMR was obtained before heating, revealing the formic acid proton peak at 10.29 ppm. A new H2 peak was seen at 4.45 ppm when the solution was heated to 190°C for 24 hours, causing the formic acid proton peak to disappear.

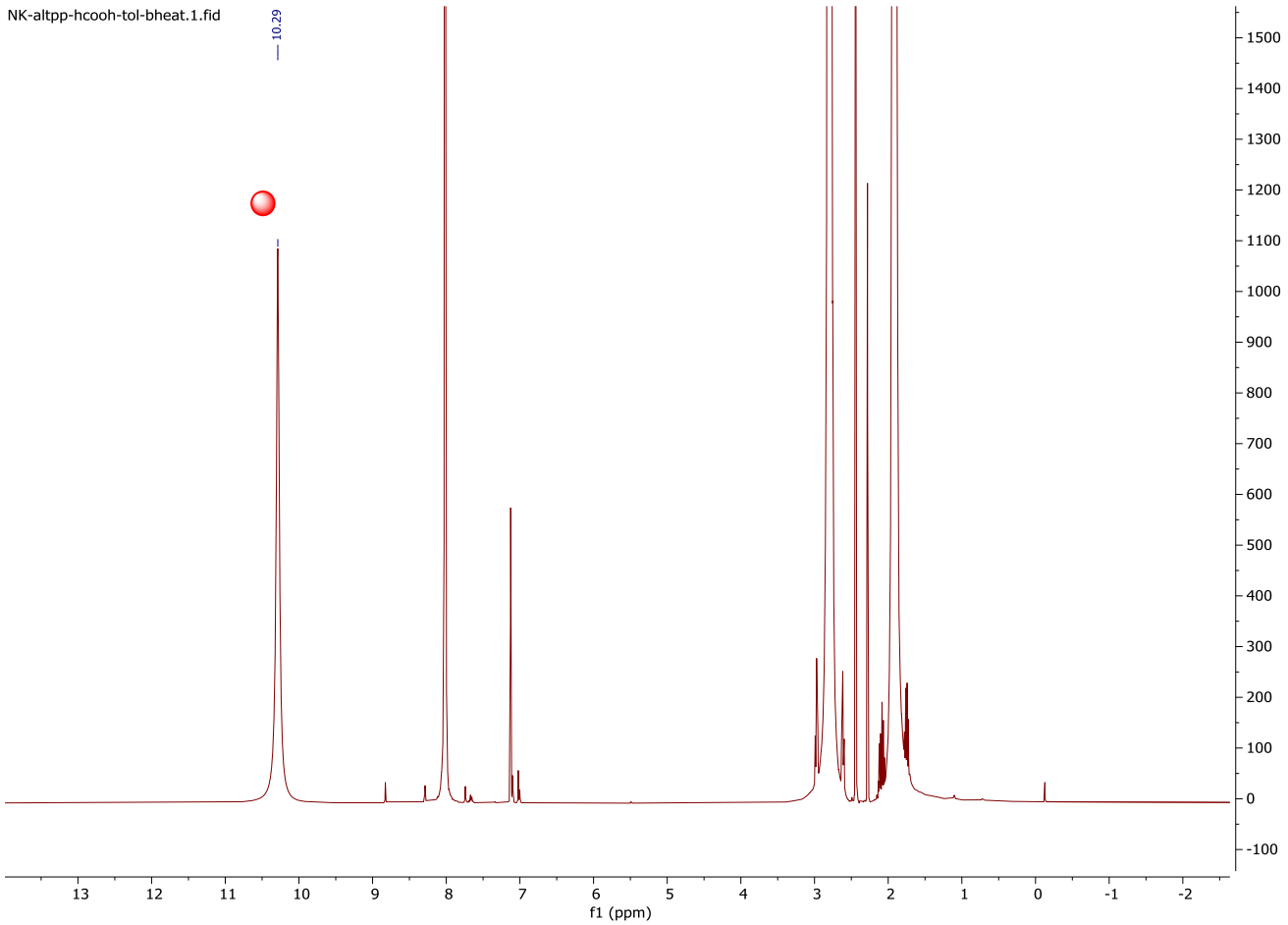


Figure S19 ^{1}H NMR spectrum of formic acid before heating in deuterated toluene-d8 (red ball denotes the proton peak of formic acid)

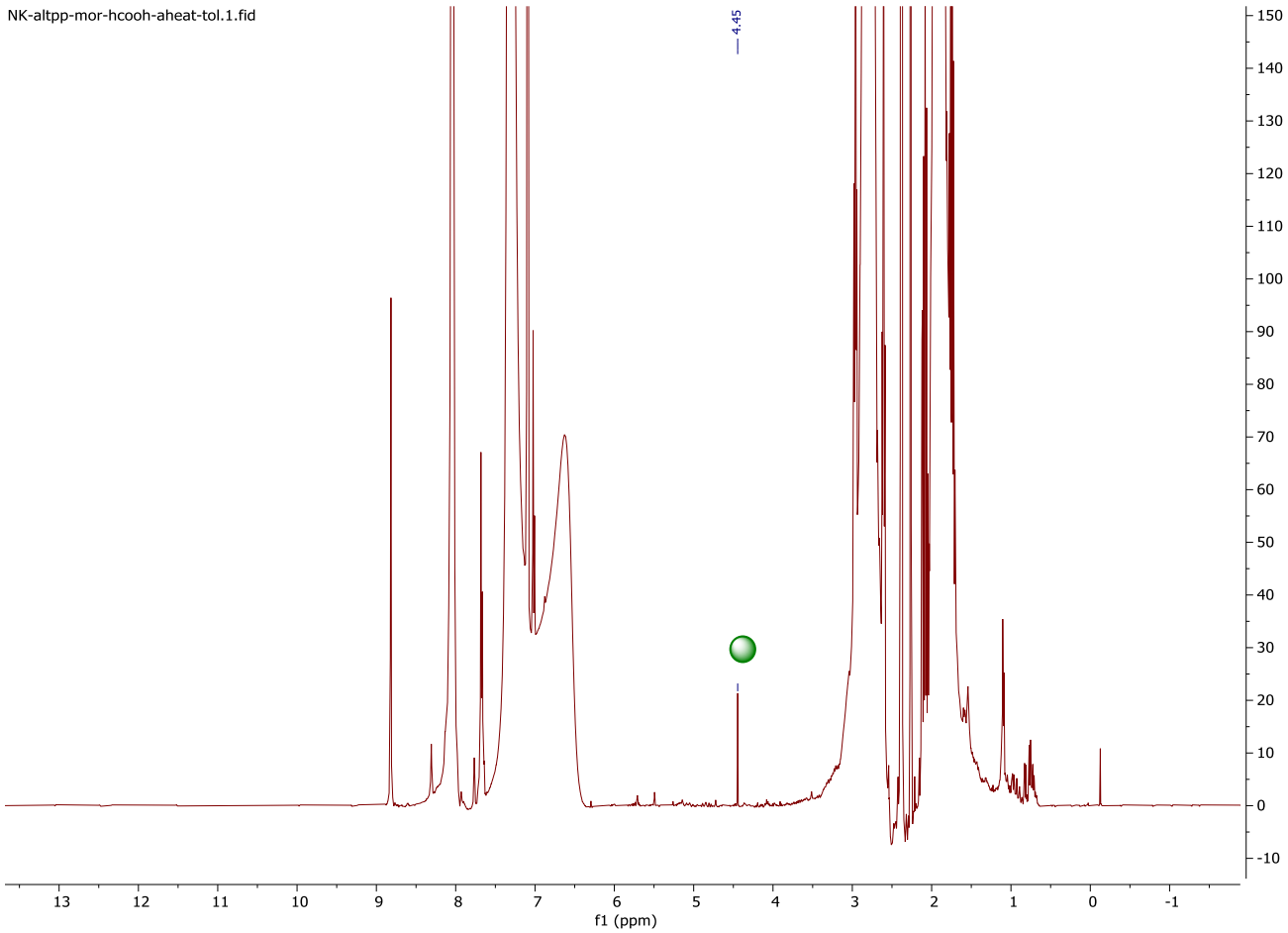


Figure S20 ^{1}H NMR spectrum of formic acid decomposition after heating at 190^{o}C in deuterated toluene-d8 (green ball denotes the H_2 peak)

5.6 Attempt to measure pKa value of [Al(TPP)$(OH_2)_2$]Cl complex

A 4 mM solution of Al(TPP)$(OH_2)_2$ (5.4 mg) was prepared in a 1:1 ACN:H_2O solvent mixture to measure the initial pH, which was found to be 4.17. Gradually, HCl was added to this solution, and the pH was monitored, reaching a final value of 1.4. Similarly, the pH was measured in a basic medium, and the pH was 12.13, at which point the aluminum porphyrin complex began to decompose, leading to precipitation. The stability of the complex in both acidic and basic conditions was tracked using NMR spectroscopy. In the acidic medium, Al(TPP)$(OH_2)_2$ remained stable, whereas in the basic medium, no peaks corresponding to the complex were observed in the ^{1}H NMR spectrum, indicating decomposition.

5.7 Investigation of Al-H participation in the Hydrogenation of CO_2

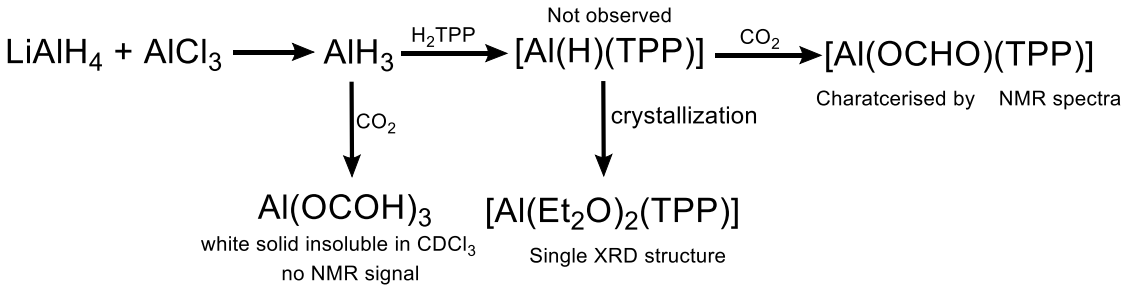


Figure S21 Investigation of participation of [Al(H)(TPP)] in the CO_2 reduction mechanism

Attempted synthesis of hydride(meso-tetraphenylporphyrin)aluminium [Al(H)(TPP)]

Tetraphenyl porphyrin (H_2TPP) (200mg, 0.32 mmol) was dissolved in dry dichloromethane (15 mL) under a nitrogen atmosphere, degassed and stirred for 10 minutes. At -10 ^oC under an inert atmosphere the solution was mixed with an equimolar solution of AlH_3 prepared in dry diethyl ether (10 mL) following a reported procedure. Upon mixing H_2 gas was released from the solution, ^1H NMR signals of the porphyrin ligand shifted downfield and –NH signals of metal free porphyrin disappeared indicative of aluminium complexation. However, signals corresponding to Al-H were not detected.

During crystallization the solution of the complex changed color from dark red to green and purple crystal suitable for an sXRD corresponding to [Al(TPP)].2Et_2O radical was obtained (Figure S22). For details of the analysis and crystallographic details, refer to section 7.0.

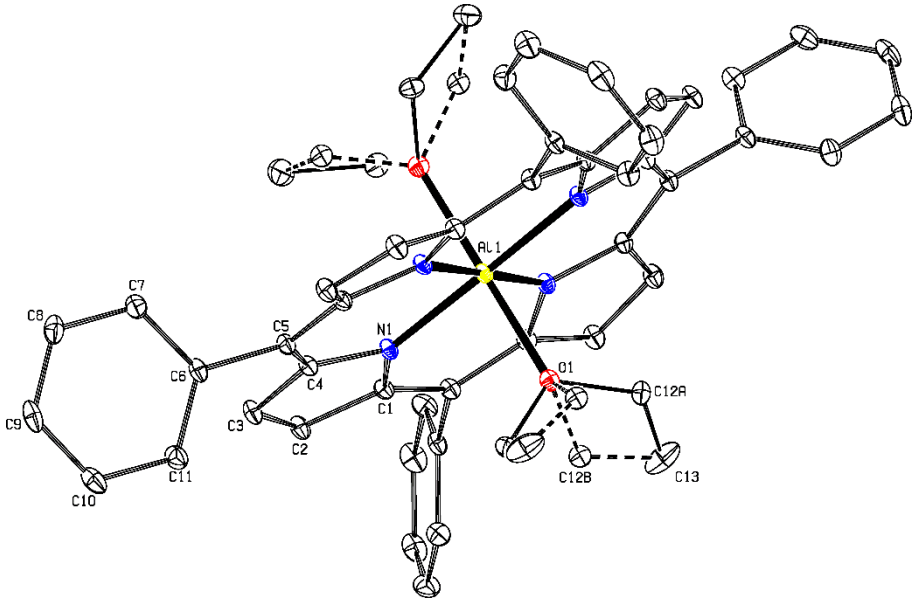


Figure S22: View of the complex [Al(TPP)(Et_2O)$_2$] in its crystal structure with the corresponding atom numbering scheme. Only the symmetrically independent part of the molecule is labelled. All hydrogen atoms were omitted for the sake of clarity. Thermal displacement elipsoids were plotted at the 30 % probability level. Applied colours: C – black, Cl – green, N – blue, O – red, Al – yellow

Upon bubbling CO_2 through a fresh solution of the presumed [Al(H)(TPP)] a new formate signal appears in ^1H NMR spectra corresponding to the 2-electron reduction of CO_2 to formate (Figure S23).

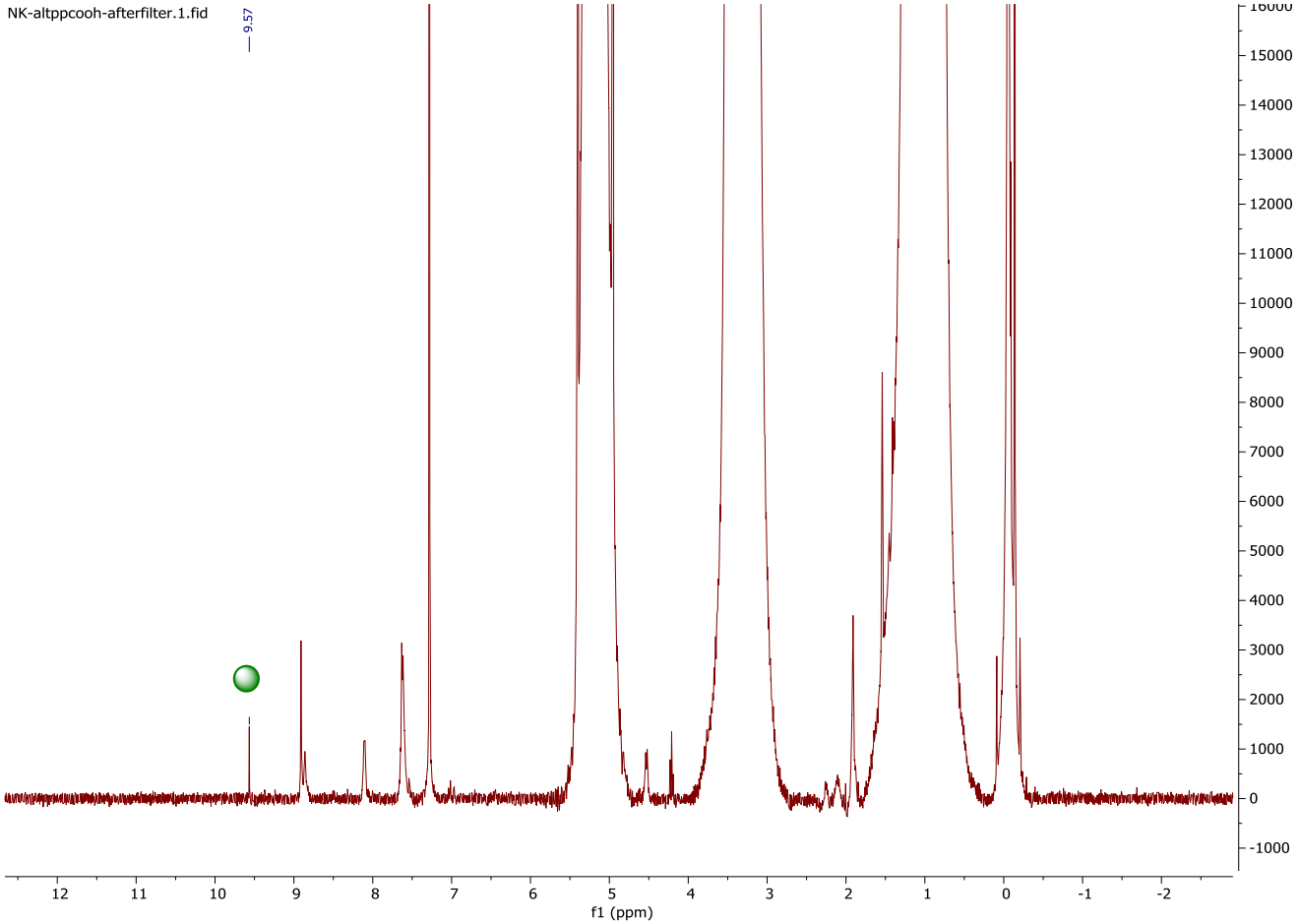


Figure S23 ^{1}H NMR spectrum of Al(TPP)(OCHO) in $CDCl_3$ after bubbling CO_2 (green dot represent formate peak)

We also performed control experiments to rule out CO_2 reduction by residual AlH_3. Freshly prepared AlH_3 readily reacts with CO_2 at room temperature, but the resulting compound is white (instead of purple) and is completely insoluble in $CDCl_3$, without any ^{1}H NMR signal due to its insolubility. These results indicate that the formate originates from [Al(OCHO)(TPP)].

6.0 Computational details

Density functional theory (DFT) calculations were carried out using the Gaussian 16[4] suite of programs. M06-2X[5] functional was employed, and geometry optimizations and transition state calculations were performed with the 6-31+G* basis set. Then, all the geometries were reoptimized at the M06-2X/6-311++G** level of theory to obtain more precise energy values. The solvent effect was included with the self-consistent reaction field (SCRF) approach, using the IEFPCM model[6–8] with DMSO parameters (dielectric constant, ε = 46.7), expected to exhibit similar behaviour to sulfolane (ε = 44.0). Hessian matrix analysis was conducted to confirm structures as minima in cases where no imaginary frequencies were obtained, and as transition states when only one imaginary frequency was found. For all transition states, intrinsic reaction coordinates (IRC) calculations were performed at the M06-2X/6-31+G* level of theory to establish their connection to both reactants and products, thereby confirming their nature. Molecular structures were analyzed and plotted using CylView20 visualization software.[11]

The values of energy shown in this study correspond to enthalpies and were calculated from electronic energies corrected with the thermal correction to Enthalpy at 473K and 100atm. The reaction energy profile is shown relative to a reference energy, E0, which is the sum of the energies of all the initial compounds without considering any interaction between them. The energy values correspond to all the reacting species interacting before the reaction step occurs. In the case of TS3, the energy of the Al(TPP)Cl (or [Al(TPP)(OH_2)]Cl) complex was separately added as a non-interacting component within the transition state to facilitate convergence for the proton transfer, considering the system´s large number of degrees of freedom at that particular stage.

6.1 Carbamate analysis

As carbamates are known to be formed in the presence of amines and CO_2, calculations were made to study their stability and competition with the proposed FLPs (Rx, where x = a for morpholine and x = b for 2,4,6-collidine) (Figure S24).

When morpholine acts as a base in the FLP, two carbamate species can be formed: a zwitterion of the carbamate can interact with the Lewis acid (RBa) or it can be deprotonated with another molecule of morpholine and an anionic FLP is formed (RCa). It can be observed that species Ra and RCa show a similar stability (similar enthalpy values). Then, an equilibrium between them can be stablished, where RBa is an intermediate.

However, when 2,4,6-collidine acts as a base in the FLP, only the zwitterionic form can be generated (RBb), as there is no proton in the base that can be removed. In this case, Rb and RBb present a similar stability and they are close to RBa. This indicates that all this species can be interchanging between each other, in high temperature and high CO2 pressure conditions.

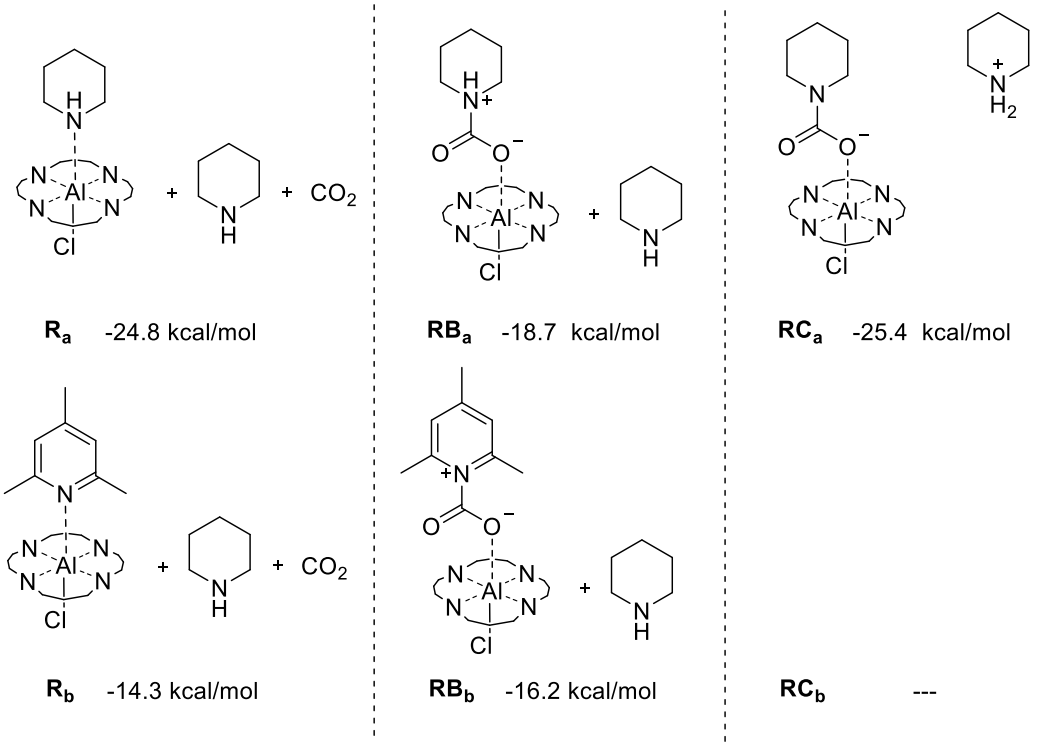


Figure S24 Stability comparison between **Rx** with their corresponding carbamate species (**RBx** and **RCx**).

6.2 I1 analysis

After reaching TS1, two alternative structures corresponding to Al-H could be formed. One of them is I1, in which the chloride remains attached to the Al atom, in an octahedral complex. In the second one (I1B), the protonated base removes the chloride anion from the aluminium complex generating the ammonium cation and a pentacoordinate square pyramidal Al complex.

Both possibilities when chloride is the axial ligand were optimized using both bases (Bx), morpholine (Ba) and 2,4,6-collidine (Bb), and it was found that I1x is more stable than I1Bx by 10.7 and 13.6 kcal/mol, respectively (Figure S25). Also, I1Bx is less stable than TS1x in both cases, indicating that separation of Cl atom from the complex implies another transition state, thus, an even more energetical pathway. Accordingly, I1x was the Al-hydride intermediate considered in the reaction mechanism (MS, Figure 3).

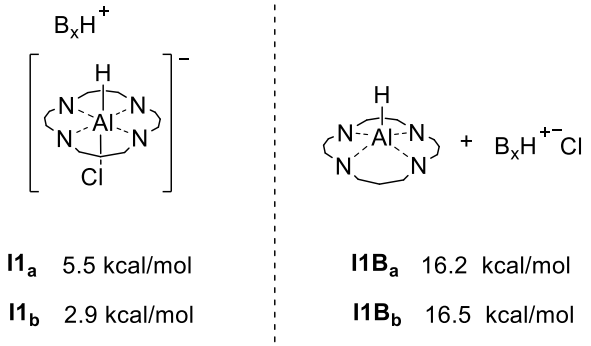


Figure S25 Representation of possible intermediates **I1$_a$** and **I1B$_a$**, after H_2 splitting.

6.3 Deuterium analysis

Due to the experimental results that showed that the reaction proceeds faster when D_2 is used instead of H_2, DFT calculations were performed for the TDI and TDTS species when [[Al(TPP)(OH_2)]Cl : 2,4,6-collidine] is used (Table S6). Surprisingly, although species formed in the presence of D_2 are more energetic, the energetic span for the catalytic cycle slightly decreases, which could favor the catalytic cycle with deuterium.

	H_2 (kcal/mol)	**D_2 (kcal/mol)**
R	-21.2	-19.5
TS2	-3.7	-2.7
δE span	17.5	16.7

Table S6 Relative enthalpies values (kcal/mol) for the TDI and TDTS when [[Al(TPP)(OH_2)]Cl : 2,4,6-collidine] is used as catalyst, and the corresponding enthalpic energy span for the catalytic cycle.

6.4 [[Al(TPP)(OH_2)]Cl : morpholine] complex

Although the 2,4,6-collidine pathway was proven to be more favorable than the one with morpholine, the complex [[Al(TPP)(OH_2)]Cl : morpholine] (R'$_a$) can be formed during the reaction and, thus, it should be considered as an initial compound for the R'$_b$ path, as well as Ra was considered for Rb path. In this way, DFT calculations for R'$_a$ showed a relative enthalpy value of -33.1 kcal/mol and the $\Delta H^{\ddagger}$ from R'$_a$ to TS2'$_b$ is 29.4 kcal/mol.

6.5 Optimized geometries in cartesian coordinates

Al(TPP)Cl
78
scf done: -2615.140921

C	-0.130274	-2.995740	-0.291236
C	-1.061644	-4.090383	-0.275972
N	-0.786660	-1.797057	-0.110286
C	-2.116505	-2.133544	0.027521
C	-2.291755	-3.556843	-0.065059
C	1.248070	-3.164746	-0.406237
H	-0.796189	-5.130764	-0.401351
C	3.185781	1.259411	0.122761
C	2.143958	-2.104659	-0.293208
H	-3.241443	-4.068984	0.003127
N	1.810002	-0.781063	-0.093131
C	3.571864	-2.263944	-0.341020
C	3.014267	-0.119189	0.009948

C	4.111634	-1.037105	-0.128777
C	2.125773	2.155447	0.007274
N	0.793434	1.817987	-0.113186
C	0.133428	3.017615	-0.279938
C	2.296692	3.580459	-0.073721
C	1.066247	4.111536	-0.285382
C	-3.177696	-1.239198	0.156857
C	-3.011394	0.138730	0.038767
N	-1.808017	0.794427	-0.123323
C	-2.140773	2.124212	-0.264267
C	-4.103469	1.073088	0.020669
C	-3.565619	2.300911	-0.190688
C	-1.245689	3.186298	-0.375964
H	4.085374	-3.198047	-0.520315
H	5.156355	-0.760008	-0.102957
H	3.242880	4.097401	0.001411
H	0.802507	5.150487	-0.424180
H	-5.144796	0.813187	0.148420
H	-4.076074	3.250794	-0.267180
C	1.782031	-4.542447	-0.621184
C	1.582804	-5.191475	-1.844691
C	2.075634	-6.479846	-2.048550
C	2.769083	-7.132955	-1.029237
C	2.968434	-6.492747	0.194369
C	2.478083	-5.203420	0.397054
H	1.042510	-4.680999	-2.638139
H	2.629174	-4.704816	1.351336
H	3.503876	-6.997009	0.993345
H	3.151712	-8.136852	-1.187331
Al	0.001269	0.010503	0.247614
H	1.918032	-6.972006	-3.003672
C	4.573593	1.786519	0.284141
C	5.221313	2.438942	-0.770867
C	5.249624	1.610023	1.496214
C	6.523466	2.911792	-0.614179
H	4.703317	2.568271	-1.718066
C	6.551086	2.085529	1.654026
H	4.750090	1.100049	2.316235
C	7.190202	2.737387	0.599159
H	7.017408	3.413350	-1.441130
H	7.064542	1.945945	2.600695
H	8.204269	3.106199	0.721087
C	-1.796589	4.562845	-0.553854
C	-1.730728	5.496992	0.486022
C	-2.399483	4.928142	-1.762473
C	-2.257109	6.777087	0.318914
H	-1.270114	5.214306	1.429481
C	-2.923574	6.209393	-1.930807
H	-2.453888	4.204594	-2.572121
C	-2.853592	7.136116	-0.890371
H	-2.203212	7.492182	1.134425
H	-3.385957	6.482494	-2.874743
H	-3.263110	8.133374	-1.020670
C	-4.550377	-1.792698	0.352675
C	-5.499428	-1.734957	-0.674043
C	-4.895364	-2.392826	1.568686
C	-6.774700	-2.266126	-0.486372
H	-5.232398	-1.277753	-1.623714
C	-6.171819	-2.921441	1.757520
H	-4.159447	-2.441052	2.367548
C	-7.113768	-2.859167	0.730331
H	-7.501654	-2.218742	-1.291751
H	-6.429274	-3.381387	2.707012
H	-8.107334	-3.272259	0.876563
Cl	-0.023251	0.024314	2.467546

Al(TPP)OH$_2$Cl

81

scf done: -2691.581075

C	3.206483	2.581053	-0.366444
C	1.818809	2.284615	-0.140184
N	1.578506	0.937522	-0.304910
C	2.803985	0.386935	-0.616782
C	3.809090	1.410415	-0.697158
C	0.857278	3.266265	0.097646
C	1.324681	4.663309	0.338392
C	1.163415	5.658159	-0.632330
C	1.624507	6.952689	-0.397189
C	2.250952	7.264395	0.810104
C	2.418527	6.275937	1.780158
C	1.960061	4.980444	1.544099
Al	-0.133269	0.017222	0.072914
N	-1.076644	1.753223	-0.141162
C	-2.427307	1.987726	-0.308134
C	-2.700672	3.396797	-0.260868
C	-1.520626	4.021047	-0.010831
C	-0.509122	3.002108	0.022275
C	-3.410663	1.009014	-0.431770
C	-4.830497	1.422081	-0.635000
C	-5.468605	1.152620	-1.850757
C	-6.797911	1.524849	-2.047531
C	-7.502973	2.165460	-1.028418
C	-6.874159	2.432184	0.188301
C	-5.544263	2.062657	0.384156
C	3.073688	-0.972143	-0.749847
C	4.462529	-1.411663	-1.074040
C	5.491050	-1.260428	-0.137028
C	6.784187	-1.686574	-0.436368
C	7.061199	-2.266084	-1.675214
C	6.039743	-2.420748	-2.612745
C	4.745299	-1.997695	-2.312504
N	0.780264	-1.713148	-0.220490
C	0.234208	-2.958448	0.013335
C	1.237405	-3.978614	-0.110097
C	2.393409	-3.353974	-0.454732
C	2.107881	-1.947627	-0.510480
C	-1.118138	-3.228857	0.218168
C	-2.102073	-2.251502	0.077842
N	-1.875677	-0.906222	-0.143970
C	-3.128136	-0.350256	-0.303412
C	-4.144445	-1.358473	-0.188683
C	-3.511029	-2.529332	0.079813
C	-1.521498	-4.638750	0.496606
C	-2.192585	-5.396861	-0.469489
C	-2.548291	-6.718689	-0.205882
C	-2.236858	-7.294910	1.026227
C	-1.565554	-6.545389	1.992474
C	-1.207066	-5.224038	1.727980
H	-3.676326	3.843839	-0.389034
H	-1.339914	5.079644	0.110394
H	-5.207054	-1.176928	-0.270134
H	-3.951616	-3.500300	0.256502
H	1.062507	-5.037117	0.023556
H	3.361513	-3.795909	-0.645091
H	3.643587	3.568549	-0.314248
H	4.843238	1.243842	-0.963744
H	-4.917938	0.652315	-2.643460
H	-5.055804	2.263577	1.334501
H	-7.419053	2.925547	0.987631
H	-8.538666	2.454050	-1.180744
H	-7.281371	1.314040	-2.996777
H	-2.427480	-4.949542	-1.432210
H	-0.681822	-4.638936	2.478791
H	-3.065423	-7.298578	-0.964570
H	-1.319484	-6.988149	2.953014
H	-2.514160	-8.324545	1.231458
H	5.269769	-0.814146	0.829703
H	3.947682	-2.118387	-3.041402
H	7.574069	-1.568043	0.299420
H	6.248926	-2.870677	-3.578748
H	8.068823	-2.597214	-1.908240
H	0.683949	5.412181	-1.576675
H	2.092752	4.206760	2.296624
H	1.497767	7.715985	-1.159178
H	2.907090	6.511442	2.720954
H	2.609832	8.272907	0.992582
O	-0.034097	-0.005872	1.951902
H	0.920493	0.003163	2.348032
H	-0.565850	0.645737	2.440666
Cl	2.650929	0.000177	3.028042

H$_2$

2

scf done: -1.168553

H	1.110354	0.421687	0.005783
H	0.373104	0.421687	0.005783

CO$_2$

3

scf done: -188.577538

O	1.812007	1.305221	0.000000
C	0.649230	1.305221	0.000000
O	-0.513546	1.305221	0.000000

H$_2$O

3

scf done: -76.428776

O	1.341378	0.864005	0.000000
H	2.308434	0.902559	0.000000
H	1.054914	1.788457	0.000000

Morpholine

15

scf done: -287.758039

C	0.496263	-1.087224	0.046532
C	1.016758	0.341833	0.034209
C	-0.920016	1.097982	1.120983
C	-1.482097	-0.314841	1.157154
H	2.105071	0.364638	0.125552
H	0.870677	-1.592198	0.954103
H	0.873473	-1.625410	-0.828295
H	-1.233068	1.668290	1.998491
H	-1.268948	1.613332	0.212872
H	-1.191902	-0.786469	2.112248
H	-2.574599	-0.279305	1.107666
H	0.723509	0.835810	-0.904903
O	0.501462	1.078677	1.135453
N	-0.965869	-1.050477	0.002430
H	-1.335436	-1.998062	0.002967

2,4,6-collidine

20

scf done: -366.171997

C	-2.230312	-1.212022	0.030886
C	-0.836504	-1.199345	-0.054390
C	-0.155058	0.018384	-0.076369
C	-0.921249	1.182566	-0.004473
C	-2.312391	1.092560	0.079017
N	-2.953317	-0.084827	0.095835
H	-0.288721	-2.137020	-0.101802
H	-0.441731	2.158026	-0.011355
C	-3.173110	2.325530	0.160207
H	-3.747713	2.325595	1.091992
H	-2.571849	3.236702	0.121026
H	-3.889380	2.342187	-0.667233
C	1.344209	0.074159	-0.198893
H	1.636108	0.102904	-1.254738
H	1.747289	0.969716	0.281250
H	1.810512	-0.806689	0.250228
C	-3.001126	-2.505416	0.057195
H	-2.334951	-3.369625	0.005617
H	-3.594043	-2.574453	0.974716
H	-3.696511	-2.548707	-0.787121

R$_a$

95

scf done: -2904.109961

C	-0.359522	1.155595	2.638938
N	0.242361	0.042810	1.855168
C	0.099425	-1.225547	2.620599
C	-1.347722	-1.459194	3.020493
O	-1.840795	-0.374848	3.792226
C	-1.788585	0.827467	3.039053
C	-2.448606	-1.677902	-0.372640
N	-1.078347	-1.628267	-0.300087
C	-0.650322	-2.931479	-0.374632
C	-1.778886	-3.819424	-0.499700
C	-2.892730	-3.043187	-0.494148
Al	0.059017	0.021637	-0.310717
Cl	0.146000	0.050794	-2.654031
C	0.678451	-3.365957	-0.342710
C	0.943333	-4.834784	-0.386198
C	1.553065	-5.413552	-1.504880
C	1.802905	-6.784755	-1.542717
C	1.448044	-7.590880	-0.460606
C	0.841739	-7.020573	0.659319
C	0.590154	-5.649754	0.695611
C	-3.316771	-0.582916	-0.343294
C	-4.786203	-0.850308	-0.348465
C	-5.401855	-1.401161	0.781184
C	-6.773474	-1.651399	0.786864
C	-7.542458	-1.355426	-0.339152
C	-6.934983	-0.807155	-1.469267
C	-5.563644	-0.554294	-1.473264
N	-1.581946	1.173570	-0.297536
C	-1.635573	2.545975	-0.295586
C	-3.006332	2.989828	-0.255193
C	-3.781327	1.874939	-0.261614
C	-2.886710	0.746333	-0.307887
C	-0.539098	3.413869	-0.322620
C	0.790791	2.981263	-0.299192
N	1.213914	1.679347	-0.195737
C	2.586419	1.728120	-0.181688
C	3.035532	3.093890	-0.297266
C	1.923870	3.868738	-0.373939
C	3.452115	0.629648	-0.099347
C	3.021294	-0.702421	-0.115347
N	1.719516	-1.130029	-0.219059
C	1.773765	-2.500952	-0.249189
C	3.138741	-2.948251	-0.130168
C	3.910368	-1.835388	-0.040561
C	-0.802336	4.883085	-0.360365
C	-1.367095	5.476462	-1.495036
C	-1.611811	6.848763	-1.526712
C	-1.297759	7.641460	-0.422272
C	-0.736565	7.056705	0.713514
C	-0.488646	5.685094	0.743099
C	4.918170	0.905492	-0.023959
C	5.769368	0.527769	-1.069681
C	7.131538	0.819940	-1.014736
C	7.659742	1.493109	0.087331
C	6.820452	1.866960	1.136961
C	5.458368	1.574032	1.081645
H	4.983240	-1.778317	0.071021
H	3.454319	-3.981929	-0.104156
H	4.068930	3.408352	-0.335803
H	1.866438	4.942671	-0.484084
H	-3.324245	4.022499	-0.219611
H	-4.860192	1.812251	-0.231483
H	-1.716166	-4.894510	-0.594303
H	-3.924195	-3.355121	-0.581805
H	5.356451	0.014679	-1.934704
H	4.804438	1.866153	1.899650
H	7.224968	2.384886	2.001557
H	8.720443	1.721865	0.129323
H	7.778182	0.525678	-1.836082
H	-1.609379	4.857879	-2.355726
H	-0.053772	5.226855	1.628414
H	-2.046149	7.298020	-2.414951
H	-0.492439	7.667348	1.577782
H	-1.489439	8.710071	-0.446580
H	-4.800384	-1.628699	1.658656
H	-5.088207	-0.128855	-2.353665
H	-7.240483	-2.075749	1.670745
H	-7.527711	-0.577001	-2.349686
H	-8.610569	-1.551320	-0.336002
H	1.827014	-4.784358	-2.348198
H	0.121285	-5.202256	1.569248
H	2.273176	-7.222607	-2.418259
H	0.566058	-7.641769	1.506415
H	1.643236	-8.658738	-0.489671
H	-1.980591	-1.595800	2.132478
H	-1.417854	-2.353064	3.644143
H	0.711177	-1.166045	3.530046
H	0.465912	-2.054573	2.010576
H	-2.432166	0.731513	2.153788
H	-2.183663	1.621012	3.676843
H	0.233268	1.313888	3.549177
H	1.246573	0.237914	1.836827
H	7.057680	-1.668601	1.636987
H	6.939405	-0.989882	1.366565

TS1$_a$

95

scf done: -2904.057486

C	-1.683379	1.206712	3.580156
N	-0.821957	0.016305	3.429611
C	-1.558090	-1.243278	3.660438
C	-2.777446	-1.277465	2.751157
O	-3.601648	-0.141226	2.964837
C	-2.890265	1.050890	2.668447
C	-2.581231	-0.808246	-0.879216
N	-1.298559	-1.181063	-0.564406
C	-1.323713	-2.543709	-0.413461
C	-2.653297	-3.044601	-0.658538
C	-3.428163	-1.971141	-0.964555
Al	0.311206	0.010354	-0.492818
Cl	0.565143	0.007167	-2.811455
C	-0.224275	-3.362164	-0.125129
C	-0.476818	-4.818993	0.082458
C	-0.019431	-5.766124	-0.841494
C	-0.269438	-7.123764	-0.645832
C	-0.979322	-7.550539	0.477017
C	-1.441351	-6.613199	1.401238
C	-1.193124	-5.255608	1.203242
C	-3.040347	0.505826	-1.015191
C	-4.494759	0.728261	-1.268045
C	-5.428006	0.456925	-0.259847
C	-6.786255	0.682567	-0.478732
C	-7.224011	1.180842	-1.706888
C	-6.298423	1.455613	-2.713862
C	-4.938947	1.232329	-2.494445
N	-0.890302	1.616223	-0.532341
C	-0.543101	2.915994	-0.264038
C	-1.708341	3.763821	-0.332070
C	-2.751147	2.970316	-0.689963
C	-2.235038	1.628718	-0.800902
C	0.754265	3.382592	-0.024169
C	1.889841	2.565032	-0.076256
N	1.898769	1.202284	-0.215130
C	3.218697	0.831998	-0.271195
C	4.062726	2.000547	-0.212727
C	3.240667	3.071440	-0.066245
C	3.695546	-0.482593	-0.301253
C	2.860297	-1.604896	-0.230262
N	1.490842	-1.595452	-0.265540
C	1.094379	-2.895688	-0.082182
C	2.247015	-3.742149	0.107216
C	3.341452	-2.946537	-0.009100
C	0.956270	4.838440	0.238300
C	0.714852	5.790535	-0.759241
C	0.919711	7.146382	-0.507270
C	1.367218	7.566111	0.745987
C	1.611730	6.623651	1.745191
C	1.409328	5.267652	1.491413
C	5.169762	-0.713249	-0.339989
C	5.753164	-1.323264	-1.456978
C	7.127445	-1.554304	-1.500790
C	7.934010	-1.182124	-0.424983
C	7.359966	-0.578318	0.694383
C	5.986119	-0.345066	0.736171
H	0.146548	0.007544	1.333220
H	4.382007	-3.227377	0.077656
H	2.215182	-4.804863	0.302679
H	5.142116	1.994280	-0.271356
H	3.512517	4.114921	0.014110
H	-1.718671	4.826604	-0.134482
H	-3.785244	3.251637	-0.835172
H	-2.942277	-4.085810	-0.620642
H	-4.478791	-1.958312	-1.219662
H	5.123603	-1.612493	-2.294914
H	5.537983	0.118001	1.611901
H	7.980737	-0.291511	1.538140
H	9.004258	-1.363245	-0.457651
H	7.567087	-2.024241	-2.375652
H	0.373460	5.462787	-1.738108
H	1.599921	4.531986	2.269115
H	0.732754	7.873989	-1.291559
H	1.959657	6.942857	2.723242
H	1.526280	8.622295	0.942091
H	-5.079846	0.077070	0.699574
H	-4.215264	1.447265	-3.276863
H	-7.501911	0.472247	0.310791
H	-6.633319	1.843756	-3.671294
H	-8.282133	1.356054	-1.877380
H	0.527425	-5.433253	-1.720255
H	-1.554199	-4.524736	1.922888
H	0.087747	-7.847111	-1.372918
H	-1.994751	-6.937453	2.277646
H	-1.173260	-8.608053	0.629798
H	-2.460233	-1.306900	1.698466
H	-3.383488	-2.160590	2.963482
H	-1.864544	-1.309820	4.711079
H	-0.888793	-2.078037	3.430113
H	-2.561192	1.029687	1.619175
H	-3.583044	1.883809	2.804882
H	-1.103394	2.089396	3.293035
H	-2.002268	1.310275	4.624074
H	-0.277012	0.008693	2.202275
H	-0.027594	0.076859	4.067995

I1$_a$

98

scf done: -3092.646857

C	2.288094	-3.361241	-0.702957
C	1.036001	-2.667068	-0.510574
N	1.219295	-1.321463	-0.684593
C	2.541757	-1.143538	-0.995652
C	3.210703	-2.421727	-1.041065
C	-0.192453	-3.299078	-0.267056
C	-0.210314	-4.773460	-0.031520
C	0.109209	-5.678329	-1.050388
C	0.069664	-7.051946	-0.813888
C	-0.291021	-7.536242	0.444188
C	-0.615750	-6.640950	1.463718
C	-0.577742	-5.267350	1.225954
Al	-0.176992	0.105506	-0.478381
N	-1.615885	-1.289465	-0.433676
C	-2.962865	-1.092297	-0.595705
C	-3.645900	-2.364060	-0.593889
C	-2.699776	-3.319603	-0.390595
C	-1.428435	-2.639238	-0.319144
C	-3.598182	0.153103	-0.667789
C	-5.080538	0.193829	-0.835313
C	-5.641738	0.715897	-2.006504
C	-7.026116	0.770421	-2.165044
C	-7.865094	0.306992	-1.151238
C	-7.313600	-0.210266	0.021666
C	-5.929377	-0.266262	0.178640
C	3.190830	0.089905	-1.131017
C	4.656355	0.095087	-1.419552
C	5.569760	-0.284750	-0.428621
C	6.939549	-0.262910	-0.687849
C	7.409132	0.139650	-1.939116
C	6.504009	0.523530	-2.928769
C	5.133330	0.503185	-2.669128
N	1.249362	1.510763	-0.592235

C	1.105103	2.833165	-0.267299
C	2.385495	3.498103	-0.339473
C	3.287482	2.569675	-0.755049
C	2.571189	1.323596	-0.889997
C	-0.108102	3.472774	0.026242
C	-1.360480	2.850762	-0.084812
N	-1.576286	1.528146	-0.356024
C	-2.927233	1.371401	-0.494117
C	-3.589917	2.642330	-0.314271
C	-2.621228	3.555297	-0.039961
C	-0.083942	4.921451	0.387690
C	0.282664	5.892142	-0.552151
C	0.287614	7.243396	-0.208919
C	-0.074452	7.640152	1.078980
C	-0.444196	6.679646	2.020798
C	-0.450399	5.328468	1.675988
Cl	-0.383740	0.172405	-2.908219
N	1.056663	-0.277247	3.399256
C	1.990460	0.873784	3.583442
C	3.134379	0.731295	2.592753
O	3.797432	-0.510143	2.762865
C	2.915828	-1.589125	2.498250
C	1.753085	-1.595907	3.475694
H	-0.042215	0.067083	1.250331
H	-4.658154	2.801244	-0.371850
H	-2.737174	4.613113	0.153137
H	-4.709943	-2.501669	-0.727964
H	-2.836286	-4.391006	-0.333141
H	2.432826	-4.428429	-0.608081
H	4.256026	-2.570491	-1.274767
H	2.563274	4.539548	-0.109820
H	4.348342	2.698683	-0.922537
H	-4.986269	1.076616	-2.795525
H	-5.497450	-0.659936	1.095570
H	-7.961034	-0.566916	0.817473
H	-8.943312	0.350421	-1.273473
H	-7.448171	1.174050	-3.080756
H	0.379970	-5.301330	-2.033658
H	-0.833269	-4.566003	2.016806
H	0.315885	-7.743381	-1.614404
H	-0.899391	-7.010683	2.444787
H	-0.321994	-8.606160	0.627730
H	5.198750	-0.586080	0.549818
H	4.425697	0.803240	-3.438153
H	7.639925	-0.556778	0.088645
H	6.863389	0.838766	-3.903971
H	8.476124	0.156169	-2.140769
H	0.556166	5.583764	-1.558272
H	-0.738743	4.578719	2.408955
H	0.570438	7.985924	-0.949347
H	-0.727650	6.980874	3.025028
H	-0.070466	8.692686	1.346336
H	2.750721	0.811536	1.564797
H	3.869500	1.520759	2.758159
H	2.352012	0.854297	4.614274
H	1.426035	1.792409	3.405922
H	2.536820	-1.513661	1.470381
H	3.489030	-2.512432	2.597611
H	1.027213	-2.371655	3.221048
H	2.098899	-1.732891	4.503031
H	0.569349	-0.167477	2.428712
H	0.317583	-0.236643	4.106294
C	-2.211241	-0.994003	2.554373
O	-2.942643	-0.116060	2.346168
O	-1.490988	-1.875298	2.807402

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scf done: -3092.635426

C	2.537554	-3.106173	-0.753310
C	1.237583	-2.548689	-0.467030
N	1.268374	-1.188184	-0.628387
C	2.541809	-0.871758	-1.032085
C	3.330554	-2.073874	-1.147381
C	0.094964	-3.311694	-0.187138
C	0.251085	-4.774680	0.071276
C	0.579741	-5.664925	-0.957122
C	0.704062	-7.029239	-0.696957
C	0.499458	-7.517635	0.594140
C	0.167113	-6.636630	1.623589
C	0.042109	-5.272229	1.362595
Al	-0.285518	0.067300	-0.501689
N	-1.544930	-1.480708	-0.392476
C	-2.909003	-1.439821	-0.521120
C	-3.445721	-2.778578	-0.455927
C	-2.395579	-3.614621	-0.241055
C	-1.206448	-2.796216	-0.228411
C	-3.680686	-0.276122	-0.617423
C	-5.160843	-0.404067	-0.761159
C	-5.790779	0.011662	-1.939726
C	-7.175210	-0.087757	-2.075277
C	-7.945366	-0.600264	-1.031041
C	-7.325393	-1.011865	0.149494
C	-5.941146	-0.914039	0.283356
C	3.043993	0.424734	-1.194577
C	4.473996	0.600207	-1.584046
C	5.503360	0.236949	-0.706508
C	6.836945	0.424585	-1.067755
C	7.155578	0.977001	-2.309027
C	6.135092	1.344946	-3.186384
C	4.801173	1.160124	-2.824031
N	0.977775	1.611303	-0.560697
C	0.693680	2.907849	-0.219697
C	1.890379	3.709852	-0.305980
C	2.878815	2.893645	-0.760841
C	2.303190	1.578105	-0.899842
C	-0.582121	3.407980	0.076282
C	-1.756518	2.653934	-0.055746
N	-1.822894	1.321047	-0.353541
C	-3.148192	1.012797	-0.476117
C	-3.949133	2.198009	-0.278147
C	-3.088170	3.210396	0.005952
C	-0.717584	4.844542	0.460912
C	-0.468090	5.864446	-0.464899
C	-0.611545	7.202186	-0.099345
C	-1.006255	7.535474	1.196900
C	-1.259954	6.525006	2.124682
C	-1.118084	5.187196	1.757636
Cl	-0.463585	0.077406	-2.889662
N	1.538075	-0.112274	3.278041
C	2.433404	1.075902	3.444417
C	3.581624	0.960155	2.457004
O	4.287812	-0.254157	2.640878
C	3.447821	-1.369244	2.393675
C	2.287620	-1.406096	3.370869
H	-0.215740	0.065470	1.312107
H	-5.029007	2.234635	-0.325567
H	-3.321275	4.244894	0.218580
H	-4.490658	-3.037549	-0.556530
H	-2.410143	-4.691143	-0.137123
H	2.796297	-4.153905	-0.687746
H	4.364309	-2.114059	-1.462039
H	1.957182	4.761522	-0.064092
H	3.914203	3.142714	-0.950891
H	-5.189055	0.411503	-2.752327
H	-5.457455	-1.225101	1.206379
H	-7.919561	-1.405522	0.969020
H	-9.023640	-0.676384	-1.135365
H	-7.650871	0.234820	-2.996825
H	0.729691	-5.284905	-1.964824
H	-0.219403	-4.581811	2.161260
H	0.956280	-7.710596	-1.504227
H	0.004374	-7.010138	2.630371
H	0.595646	-8.580354	0.795971
H	5.255938	-0.182417	0.267491
H	4.003959	1.447230	-3.505375
H	7.626528	0.142765	-0.377226
H	6.376218	1.775845	-4.153677
H	8.194480	1.121963	-2.590048
H	-0.169057	5.604390	-1.477386
H	-1.316662	4.398376	2.479252
H	-0.418525	7.983343	-0.828766
H	-1.568228	6.776815	3.135169
H	-1.117693	8.577506	1.481585
H	3.197880	1.016839	1.427234
H	4.287174	1.777669	2.613462
H	2.793085	1.069353	4.475474
H	1.837449	1.972923	3.264578
H	3.068122	-1.327468	1.363677
H	4.054769	-2.268784	2.507498
H	1.587194	-2.209969	3.137180
H	2.639539	-1.501662	4.400217
H	1.017399	-0.050782	2.365975
H	0.805581	-0.102162	3.994370
C	-1.474350	-0.683063	2.407614
O	-2.402447	0.022924	2.251389
O	-0.841319	-1.574441	2.869868

I2$_a$

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scf done: -3092.695524

C	2.017105	-3.574996	-0.466339
C	0.840283	-2.751641	-0.427222
N	1.167254	-1.435730	-0.697169
C	2.528577	-1.437992	-0.930891
C	3.051752	-2.771638	-0.829384
C	-0.450103	-3.231774	-0.205340
C	-0.651255	-4.664173	0.156006
C	-0.349589	-5.693954	-0.741852
C	-0.555592	-7.024680	-0.380507
C	-1.064602	-7.337498	0.880484
C	-1.373411	-6.314742	1.777847
C	-1.170986	-4.983754	1.416321
Al	-0.042239	0.137345	-0.981193
N	-1.577513	-1.068433	-0.581088
C	-2.900083	-0.729435	-0.791169
C	-3.730507	-1.901094	-0.739757
C	-2.918819	-2.944512	-0.427572
C	-1.579584	-2.426229	-0.359437
C	-3.387139	0.572649	-0.900129
C	-4.833922	0.805823	-1.180036
C	-5.212290	1.398689	-2.389850
C	-6.557662	1.640723	-2.664828
C	-7.534216	1.298364	-1.729226
C	-7.160617	0.714833	-0.517916
C	-5.816202	0.468291	-0.241656
C	3.321216	-0.303073	-1.094882
C	4.775186	-0.457649	-1.397156
C	5.669844	-0.895213	-0.414536
C	7.028453	-1.013894	-0.702672
C	7.503874	-0.694815	-1.975386
C	6.617105	-0.253295	-2.957260
C	5.257793	-0.132320	-2.668634
N	1.521412	1.302048	-0.575405
C	1.545574	2.616786	-0.156572
C	2.894887	3.111764	-0.140306
C	3.688659	2.111125	-0.604073
C	2.834723	0.979225	-0.837668
C	0.426969	3.388910	0.153000
C	-0.873465	2.922644	-0.039989
N	-1.216203	1.649684	-0.440206
C	-2.580433	1.680126	-0.629803
C	-3.096420	2.993152	-0.356215
C	-2.042828	3.754478	0.041378
C	0.615247	4.782569	0.651176
C	1.091250	5.791996	-0.192454
C	1.250458	7.091702	0.286340
C	0.936612	7.392948	1.612122
C	0.460453	6.390750	2.457744
C	0.298536	5.091411	1.978709
Cl	-0.127965	0.245098	-3.180334
N	0.431910	-0.917212	2.406207
C	0.717898	0.479613	2.790902
C	2.216600	0.750118	2.819207
O	2.876825	-0.165836	3.679976
C	2.676728	-1.506353	3.257545
C	1.195286	-1.857160	3.251744
H	-2.326179	0.381204	1.949996
H	-4.138016	3.274795	-0.427979
H	-2.043457	4.792334	0.344783
H	-4.800054	-1.911753	-0.895164
H	-3.188880	-3.981873	-0.286929
H	2.040965	-4.634979	-0.256340
H	4.087142	-3.044776	-0.977951
H	3.188364	4.100900	0.182396
H	4.762765	2.111031	-0.729554
H	-4.448379	1.666313	-3.115915
H	-5.515211	0.029922	0.707121
H	-7.916800	0.454731	0.217082
H	-8.582075	1.488731	-1.941680
H	-6.841215	2.096805	-3.608713
H	0.036978	-5.449370	-1.728126
H	-1.417379	-4.181397	2.108622
H	-0.322428	-7.816310	-1.086341
H	-1.773136	-6.551639	2.759364
H	-1.223714	-8.374374	1.161070
H	5.298435	-1.133574	0.579602
H	4.564265	0.214139	-3.430779
H	7.715112	-1.351538	0.067858
H	6.981699	-0.001370	-3.948637
H	8.562316	-0.787466	-2.199599
H	1.329178	5.556913	-1.226940
H	-0.072440	4.307535	2.635085
H	1.616819	7.868911	-0.377700
H	0.214848	6.618788	3.490646
H	1.061255	8.405405	1.984301
H	2.635910	0.659904	1.802985
H	2.426365	1.754022	3.197150
H	0.287062	0.646252	3.785057
H	0.217777	1.156725	2.087609
H	3.095045	-1.640035	2.244347
H	3.229426	-2.143632	3.951262
H	1.040253	-2.872888	2.872594
H	0.789993	-1.799807	4.268249
H	0.740595	-1.058200	1.441496
H	-1.088274	-1.270024	2.536849
C	-2.863805	-0.490990	2.367120
O	-4.072200	-0.492004	2.494904
O	-2.096330	-1.499646	2.707128

TS3$_a$

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scf done: -765.303345

C	1.282274	0.532540	-1.856207
C	2.795256	0.697088	-1.801598
C	2.984528	-0.915926	-0.110988
C	1.481582	-1.151416	-0.100533
H	3.193354	0.949209	-2.786629
H	1.014802	-0.205640	-2.621014
H	0.798092	1.481955	-2.101850
H	3.524241	-1.833065	0.133641
H	3.246592	-0.140228	0.625247
H	1.226191	-1.978217	-0.773507
H	1.128381	-1.390468	0.907843
H	3.060751	1.498968	-1.095012
O	3.419977	-0.512944	-1.401313
N	0.766175	0.056628	-0.560216
H	0.863444	0.776911	0.181106
H	-0.522328	-0.194824	-0.506899
C	0.056671	0.910736	2.708960
H	0.262375	1.126925	3.780720
O	-0.869448	0.092851	2.477236
O	0.778163	1.511191	1.873659
C	-2.592638	0.680683	-0.766067
C	-2.716361	0.439685	-2.262802
C	-2.401995	-1.866558	-1.994695
C	-2.267856	-1.721352	-0.487015
H	-3.403779	1.159290	-2.710814
H	-3.584045	0.662847	-0.298129
H	-2.125739	1.650555	-0.569060
H	-2.861782	-2.823450	-2.247704
H	-1.410056	-1.814961	-2.471346
H	-3.246384	-1.853504	-0.009770
H	-1.576609	-2.468334	-0.087154
H	-1.732384	0.544300	-2.747235
O	-3.239274	-0.852287	-2.527351
N	-1.745375	-0.375866	-0.178710
H	-1.646805	-0.236957	0.844009

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scf done: -3380.479130

C	0.816885	1.678735	2.299760
C	2.047061	1.535369	3.038887
N	0.375814	0.449833	1.876315
C	1.297428	-0.462752	2.327175
C	2.360777	0.214535	3.028945
C	0.209983	2.907368	2.019394
H	2.599539	2.346234	3.492611
C	-3.518946	1.952176	-0.958846
C	-0.910181	3.045204	1.190659
H	3.223608	-0.266146	3.468011
N	-1.626244	2.023554	0.622611
C	-1.396784	4.316484	0.714915
C	-2.550751	2.617547	-0.200106
C	-2.398009	4.050582	-0.163540
C	-3.718339	0.567563	-0.916121
N	-2.960676	-0.334039	-0.213973
C	-3.551759	-1.556865	-0.401606
C	-4.811077	-0.106376	-1.571320
C	-4.715094	-1.421038	-1.242288
C	1.210229	-1.853355	2.191724
C	0.107810	-2.512813	1.632609
N	-0.975627	-1.917108	1.039835
C	-1.846277	-2.932401	0.728669
C	-0.082139	-3.941539	1.691819
C	-1.300547	-4.198835	1.150358
C	-3.070255	-2.784981	0.068191
H	-0.996751	5.280210	0.998470
H	-2.984390	4.754176	-0.737914
H	-5.557967	0.374421	-2.187869
H	-5.359425	-2.233671	-1.548126
H	0.617739	-4.644183	2.122560
H	-1.793690	-5.155225	1.046021
C	0.824864	4.152015	2.569958
C	2.063417	4.606855	2.103018
C	2.623504	5.778027	2.611423
C	1.950653	6.506830	3.592980
C	0.714695	6.060919	4.061731
C	0.154074	4.890656	3.551143
H	2.583522	4.041595	1.333029
H	-0.809393	4.541984	3.914847
H	0.185605	6.623019	4.825662
H	2.386990	7.418881	3.989246
Al	-1.338632	0.059829	0.888736
H	3.583582	6.122190	2.238208
C	-4.416605	2.759529	-1.837775
C	-4.294408	2.669054	-3.229044
C	-5.390715	3.603045	-1.292420
C	-5.129496	3.412517	-4.062007
H	-3.537780	2.014082	-3.655189
C	-6.228053	4.344720	-2.125051
H	-5.494073	3.671147	-0.212191
C	-6.098542	4.251654	-3.511185
H	-5.022317	3.336237	-5.140052
H	-6.982984	4.993072	-1.690132
H	-6.750498	4.829820	-4.159220
C	-3.887494	-4.004849	-0.202307
C	-5.117899	-4.182653	0.440620
C	-3.446059	-4.976253	-1.108190
C	-5.891632	-5.314324	0.186015
H	-5.464562	-3.430404	1.144986
C	-4.220578	-6.106644	-1.365384
H	-2.494567	-4.838607	-1.616558
C	-5.444771	-6.278359	-0.718018
H	-6.842644	-5.442111	0.694633
H	-3.868869	-6.850990	-2.073711
H	-6.047959	-7.158929	-0.918053
C	2.323638	-2.694955	2.723220
C	3.131553	-3.422563	1.841912
C	2.565563	-2.784476	4.098765
C	4.170060	-4.217488	2.325548
H	2.941733	-3.361333	0.772901
C	3.602068	-3.581149	4.583523
H	1.933028	-2.231767	4.789069
C	4.407947	-4.297565	3.697898
H	4.792066	-4.773275	1.629904
H	3.777062	-3.644609	5.653460
H	5.215659	-4.917300	4.075747
Cl	-2.571521	0.048116	2.878175
C	4.936849	0.161388	-3.907713
C	4.007399	-1.040656	-3.840780
C	5.140420	-1.932428	-1.992003
C	6.124354	-0.775378	-1.960839
H	3.007337	-0.752032	-4.172482
H	4.542989	0.992006	-3.315876
H	5.089285	0.492573	-4.936291
H	4.965756	-2.299771	-0.979649
H	5.537224	-2.757499	-2.602730
H	5.761626	0.024915	-1.310531
H	7.120092	-1.086746	-1.639210
H	4.380315	-1.847674	-4.489314
O	3.886532	-1.514264	-2.508410
N	6.259118	-0.195624	-3.326698
H	6.753884	-0.865100	-3.926511
H	6.935239	0.656925	-3.261928
C	9.106162	0.970224	-2.987684
H	10.058459	1.516982	-2.831318
O	9.148813	-0.269472	-3.098666
O	8.059673	1.692313	-3.034957
C	0.489163	1.246465	-1.327659
C	1.514911	1.002542	-2.424221
C	0.437469	-0.967382	-3.082270
C	-0.629421	-0.788968	-2.013016
H	1.880398	1.951024	-2.824978
H	-0.330206	1.867772	-1.704970
H	0.952776	1.759056	-0.479366
H	0.020052	-1.458813	-3.963867
H	1.266538	-1.580483	-2.691474
H	-1.478753	-0.226728	-2.415837
H	-0.989907	-1.761317	-1.664087
H	2.367048	0.431174	-2.020500
O	0.942473	0.289350	-3.510993
N	-0.097079	-0.031865	-0.852392
H	0.679973	-0.586952	-0.474447

R$_b$

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scf done: -2982.5103431

C	-3.870040	1.054557	-0.585359
C	-2.462092	1.341253	-0.591656
N	-1.728929	0.177071	-0.527524
C	-2.664201	-0.833323	-0.491290
C	-3.994818	-0.290074	-0.506237
C	-1.949844	2.632333	-0.650783
C	-2.893306	3.782804	-0.771009
C	-3.719279	4.142111	0.295847
C	-4.585986	5.224841	0.183515
C	-4.635956	5.958319	-0.998744
C	-3.815197	5.605892	-2.066679
C	-2.946523	4.524661	-1.952960
Al	0.253882	0.001534	-0.725310
N	0.417382	1.976547	-0.446340
C	1.567944	2.712031	-0.272009
C	1.272915	4.118630	-0.266000
C	-0.061909	4.239280	-0.456581
C	-0.588682	2.906370	-0.556909
C	2.849971	2.198673	-0.114468

C	3.987581	3.146906	0.066308
C	4.646042	3.225173	1.295388
C	5.709814	4.105534	1.468112
C	6.126859	4.912280	0.412752
C	5.475983	4.836795	-0.815793
C	4.410031	3.959082	-0.988122
C	-2.400366	-2.198715	-0.454779
C	-3.549973	-3.150499	-0.461790
C	-4.381554	-3.239565	-1.581452
C	-5.457038	-4.121867	-1.594294
C	-5.715623	-4.924981	-0.486650
C	-4.889993	-4.846145	0.631177
C	-3.812015	-3.966149	0.641869
N	0.056326	-1.972448	-0.440868
C	1.071732	-2.902493	-0.448486
C	0.537822	-4.235369	-0.433181
C	-0.810984	-4.116743	-0.421636
C	-1.105748	-2.709835	-0.427122
C	2.434057	-2.629520	-0.411595
C	2.940351	-1.337632	-0.307240
N	2.196820	-0.178298	-0.263686
C	3.122252	0.834154	-0.140771
C	4.455402	0.301796	-0.112546
C	4.343177	-1.043463	-0.225046
C	3.389664	-3.775353	-0.421520
C	4.092788	-4.113679	0.736840
C	4.976228	-5.188735	0.733935
C	5.165296	-5.933436	-0.427420
C	4.467105	-5.600777	-1.585074
C	3.581363	-4.527134	-1.581992
Cl	0.414425	-0.018756	-2.951192
H	1.999524	4.901592	-0.118379
H	-0.652453	5.140942	-0.493057
H	5.354376	0.892161	-0.033372
H	5.131475	-1.778591	-0.255695
H	1.128637	-5.137494	-0.423150
H	-1.547448	-4.903992	-0.416245
H	-4.652869	1.794632	-0.628297
H	-4.901432	-0.871622	-0.457281
H	4.318134	2.595521	2.115619
H	3.903331	3.896119	-1.945063
H	5.799036	5.459109	-1.641886
H	6.956050	5.596708	0.546942
H	6.211178	4.161977	2.427034
H	3.940340	-3.532322	1.640516
H	3.035897	-4.265597	-2.482241
H	5.514059	-5.445922	1.638747
H	4.611888	-6.175811	-2.491965
H	5.853722	-6.770142	-0.429859
H	-4.178529	-2.615914	-2.445230
H	-3.167303	-3.911909	1.511945
H	-6.091046	-4.183007	-2.470842
H	-5.083788	-5.468662	1.496582
H	-6.554418	-5.610738	-0.495926
H	-3.680272	3.569591	1.216164
H	-2.305768	4.249200	-2.783594
H	-5.219632	5.495563	1.019705
H	-3.851213	6.171561	-2.990145
H	-5.311322	6.800929	-1.087193
H	3.446484	-0.161079	3.236847
H	3.590252	-0.191818	2.508904
C	-0.436063	-0.940240	2.656206
C	-1.772326	-1.317549	2.739682
C	-2.770665	-0.345516	2.756389
C	-2.364253	0.984319	2.719228
C	-1.005537	1.293977	2.649589
N	-0.060093	0.346977	2.592305
H	-2.028647	-2.370536	2.782894
H	-3.099420	1.781448	2.747943
C	-0.536164	2.722128	2.696495
H	-1.282903	3.404562	2.287182
H	-0.348837	3.010454	3.735293
H	0.397313	2.833718	2.144587
C	-4.222362	-0.728949	2.836418
H	-4.865466	0.102995	2.547434
H	-4.433322	-1.577998	2.181697
H	-4.479595	-1.025410	3.857068
C	0.660629	-1.969099	2.680451
H	1.018722	-2.103662	3.705662
H	0.307308	-2.933767	2.310387
H	1.502678	-1.635180	2.074325

TS1$_b$

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scf done: -2982.474780

C	3.556321	-2.966497	0.124647
C	2.214673	-2.516714	-0.154952
N	2.164751	-1.147087	-0.147427
C	3.439591	-0.721388	0.116639
C	4.316654	-1.853293	0.288200
C	1.136544	-3.375496	-0.394578
C	1.399187	-4.845028	-0.419415
C	2.176172	-5.413088	-1.435650
C	2.420488	-6.785700	-1.455744
C	1.893022	-7.605251	-0.457264
C	1.118662	-7.046672	0.560280
C	0.871983	-5.674588	0.577498
Al	0.546669	0.006290	-0.463234
N	-0.620462	-1.640351	-0.535093
C	-1.969306	-1.689528	-0.779799
C	-2.379097	-3.047606	-1.034654
C	-1.266957	-3.820600	-0.927377
C	-0.175641	-2.937901	-0.605127
C	-2.841385	-0.591534	-0.819892
N	-4.291160	-0.847546	-1.070375
C	-4.908340	-0.344639	-2.223890
C	-6.259150	-0.584251	-2.470271
C	-7.014942	-1.331711	-1.566299
C	-6.408693	-1.844923	-0.419713
C	-5.056589	-1.607139	-0.177121
C	3.868761	0.610106	0.173211
C	5.314595	0.869297	0.449861
C	5.838540	0.660492	1.730430
C	7.187541	0.900025	1.990336
C	8.027464	1.349352	0.970877
C	7.512587	1.558273	-0.308970
C	6.163212	1.319729	-0.567563
N	1.676343	1.659544	-0.260428
C	1.264713	2.961394	-0.378944
C	2.391131	3.853842	-0.243448
C	3.480163	3.078013	-0.012004
C	3.028225	1.707575	-0.031020
C	-0.052194	3.392685	-0.567229
C	-1.148074	2.527538	-0.645346
N	-1.105110	1.156432	-0.611501
C	-2.409422	0.734333	-0.712092
C	-3.296144	1.872302	-0.745011
C	-2.514934	2.981363	-0.716176
C	-0.316796	4.861444	-0.628162
C	-0.731485	5.461669	-1.822260
C	-0.990975	6.830932	-1.872859
C	-0.840700	7.614650	-0.728387
C	-0.428866	7.023629	0.466650
C	-0.168311	5.654705	0.515781
Cl	0.851757	-0.030448	-2.784349
H	0.423888	0.025964	1.341392
H	-4.375497	1.820051	-0.774999
H	-2.827082	4.016688	-0.719366
H	-3.383558	-3.360548	-1.282475
H	-1.183805	-4.889642	-1.065639
H	3.866141	-4.000289	0.188397
H	5.374966	-1.793923	0.501401
H	2.342375	4.931825	-0.309502
H	4.500242	3.394351	0.156102
H	-4.320403	0.230845	-2.934553
H	-4.585575	-2.012022	0.713947
H	-6.986910	-2.430489	0.289410
H	-8.068013	-1.516286	-1.756576
H	-6.719481	-0.189820	-3.371359
H	2.584565	-4.773811	-2.214577
H	0.270916	-5.236971	1.371473
H	3.021217	-7.214299	-2.252552
H	0.707415	-7.678149	1.342346
H	2.084524	-8.674101	-0.472078
H	5.182611	0.311392	2.524261
H	5.761205	1.479459	-1.565128
H	7.581123	0.736678	2.989312
H	8.161040	1.905438	-1.108051
H	9.078154	1.535486	1.172663
H	-0.848375	4.849781	-2.713364
H	0.149467	5.192118	1.447629
H	-1.309355	7.284766	-2.806793
H	-0.312434	7.626901	1.362239
H	-1.043650	8.680778	-0.767332
C	-2.181978	-1.200493	2.650631
C	-3.538637	-1.231308	2.954574
C	-4.265447	-0.041994	3.040511
C	-3.571794	1.161935	2.887777
C	-2.206515	1.148630	2.630048
N	-1.559540	-0.022095	2.485752
H	-4.027369	-2.190748	3.105243
H	-4.087822	2.114132	2.976141
C	-1.382136	2.402227	2.568529
H	-0.453792	2.240206	2.015089
H	-1.941173	3.216479	2.100467
H	-1.119921	2.710620	3.586912
C	-5.751431	-0.059942	3.260127
H	-6.059350	-0.946970	3.819067
H	-6.086489	0.833605	3.792165
H	-6.260972	-0.083384	2.288934
C	-1.363610	-2.453993	2.520138
H	-1.800169	-3.118638	1.767101
H	-0.334832	-2.226945	2.232489
H	-1.352415	-2.990016	3.474525
H	-0.416951	-0.003656	1.881568

I1$_b$

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scf done: -3171.065133

C	3.580028	-2.811119	-0.138114
C	2.209968	-2.404607	-0.329395
N	2.125519	-1.040035	-0.356914
C	3.402887	-0.572704	-0.215954
C	4.320953	-1.676736	-0.081369
C	1.143464	-3.294780	-0.484393
C	1.431774	-4.758199	-0.440806
C	2.189990	-5.371780	-1.440812
C	2.446603	-6.738633	-1.392542
C	1.950254	-7.506431	-0.342237
C	1.193477	-6.902482	0.658372
C	0.933921	-5.536335	0.607602
Al	0.441474	0.061947	-0.479567
N	-0.666636	-1.621723	-0.665068
C	-2.003089	-1.710633	-0.946275
C	-2.364440	-3.083412	-1.198850
C	-1.238364	-3.821575	-1.036453
C	-0.181668	-2.901553	-0.700827
C	-2.906906	-0.639579	-0.997817
C	-4.339263	-0.930907	-1.299469
C	-4.936669	-0.395390	-2.445800
C	-6.270713	-0.656835	-2.740108
C	-7.030448	-1.457962	-1.891735
C	-6.444367	-2.003920	-0.753290
C	-5.108289	-1.745201	-0.462979
C	3.790824	0.771371	-0.206548
C	5.244835	1.080227	-0.060816
C	5.886339	0.890175	1.165218
C	7.240896	1.178421	1.303897
C	7.967461	1.659486	0.217802
C	7.334073	1.852030	-1.007008
C	5.979203	1.564314	-1.145382
N	1.537142	1.751405	-0.405584
C	1.068936	3.034989	-0.423553
C	2.170246	3.965977	-0.342585
C	3.301965	3.226462	-0.263124
C	2.898889	1.840621	-0.303287
C	-0.271161	3.422950	-0.518411
C	-1.337146	2.527146	-0.641630
N	-1.246323	1.161752	-0.683784
C	-2.526800	0.697041	-0.837985
C	-3.455011	1.802677	-0.831248
C	-2.719238	2.933698	-0.712813
C	-0.585152	4.881543	-0.467022
C	-1.067753	5.548882	-1.595229
C	-1.363754	6.907456	-1.538589
C	-1.182442	7.613429	-0.352115
C	-0.702120	6.955693	0.777053
C	-0.404182	5.597425	0.719249
Cl	0.683028	0.072016	-2.903077
H	0.324477	0.045241	1.226262
H	-4.527834	1.714985	-0.896266
H	-3.071502	3.952094	-0.664588
H	-3.346672	-3.428644	-1.479204
H	-1.120207	-4.887227	-1.154814
H	3.922400	-3.830949	-0.062657
H	5.389048	-1.585607	0.038622
H	2.076802	5.040500	-0.349377
H	4.319646	3.574717	-0.182090
H	-4.345418	0.223366	-3.111837
H	-4.653670	-2.178763	0.419551
H	-7.026212	-2.631861	-0.088583
H	-8.070515	-1.659439	-2.119016
H	-6.715119	-0.237168	-3.634869
H	2.572083	-4.773520	-2.260878
H	0.345172	-5.062553	1.386375
H	3.031420	-7.203886	-2.177260
H	0.806198	-7.494054	1.479539
H	2.151350	-8.570474	-0.304420
H	5.315258	0.520060	2.009875
H	5.484181	1.711572	-2.099250
H	7.727542	1.029846	2.260706
H	7.894504	2.224035	-1.856619
H	9.022140	1.883501	0.325458
H	-1.206350	4.998244	-2.519391
H	-0.029646	5.083479	1.598501
H	-1.733168	7.414669	-2.422077
H	-0.560609	7.498743	1.704072
H	-1.413544	8.671122	-0.308047
C	-2.423865	-1.282547	2.474694
C	-3.782118	-1.326818	2.731521
C	-4.520989	-0.146636	2.831213
C	-3.842474	1.070710	2.747766
C	-2.476340	1.092507	2.533582
N	-1.830545	-0.078730	2.368844
H	-4.264612	-2.291729	2.835022
H	-4.372269	2.009129	2.856136
C	-1.650920	2.339833	2.540726
H	-0.711008	2.192783	2.007535
H	-2.200110	3.167044	2.091911
H	-1.421774	2.600938	3.577541
C	-6.009684	-0.193603	2.997094
H	-6.307715	-1.035074	3.622924
H	-6.391888	0.731965	3.425704
H	-6.469895	-0.330760	2.013108
C	-1.568442	-2.502533	2.337273
H	-2.016466	-3.197068	1.623984
H	-0.563888	-2.244732	2.003185
H	-1.501833	-3.005105	3.305092
H	-0.825913	-0.042378	1.996772
C	2.256735	-0.737851	2.771536
O	2.679561	0.336136	2.838036
O	1.860612	-1.823775	2.749392

TS2$_b$

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scf done: -3171.055951

C	-3.203903	3.261187	-0.099919
C	-1.910865	2.682260	-0.377175
N	-1.997622	1.316570	-0.385806
C	-3.307052	1.015995	-0.126166
C	-4.070528	2.227541	0.052347
C	-0.749858	3.431850	-0.596767
C	-0.867274	4.919776	-0.626057
C	-1.581067	5.558432	-1.646934
C	-1.689035	6.948306	-1.672365
C	-1.087087	7.715631	-0.674501
C	-0.375084	7.087089	0.347760
C	-0.264714	5.697530	0.370058
Al	-0.486784	0.006149	-0.611941
N	0.836358	1.535926	-0.693758
C	2.185674	1.451654	-0.930049
C	2.725089	2.761610	-1.198929
C	1.690647	3.638213	-1.112398
C	0.517177	2.868023	-0.787318
C	2.947768	0.274732	-0.961332
C	4.417967	0.391811	-1.195444
C	4.997609	-0.156416	-2.347493
C	6.367909	-0.043679	-2.576674
C	7.180624	0.620089	-1.656923
C	6.612846	1.177443	-0.511248
C	5.241563	1.066063	-0.285601
C	-3.860095	-0.268439	-0.059137
C	-5.319138	-0.386985	0.241907
C	-5.792783	-0.136564	1.534574
C	-7.152576	-0.246876	1.823023
C	-8.053005	-0.608172	0.820137
C	-7.587911	-0.858759	-0.471177
C	-6.227560	-0.749046	-0.758463
N	-1.781394	-1.528560	-0.474260
C	-1.487932	-2.863895	-0.534275
C	-2.691086	-3.646506	-0.373779
C	-3.706409	-2.766572	-0.183768
C	-3.129108	-1.445001	-0.249814
C	-0.214925	-3.420063	-0.694463
C	0.959740	-2.667247	-0.788625
N	1.051944	-1.298246	-0.757774
C	2.390161	-1.005602	-0.860270
C	3.161241	-2.224936	-0.901085
C	2.274524	-3.252510	-0.870675
C	-0.092951	-4.909475	-0.720662
C	0.189088	-5.579809	-1.915568
C	0.310689	-6.969149	-1.934533
C	0.153274	-7.701552	-0.757522
C	-0.126844	-7.039528	0.438446
C	-0.249205	-5.650573	0.456150
Cl	-0.714282	0.065923	-2.966675
H	-0.405430	-0.037994	1.178727
H	4.240087	-2.279617	-0.941666
H	2.483232	-4.313622	-0.880560
H	3.756529	2.973642	-1.443227
H	1.710446	4.707969	-1.268133
H	-3.410080	4.320090	-0.028455
H	-5.130227	2.270322	0.263016
H	-2.738247	-4.726526	-0.395576
H	-4.752186	-2.981127	-0.012220
H	4.365901	-0.666385	-3.070516
H	4.800639	1.508600	0.603392
H	7.235617	1.700553	0.208834
H	8.248430	0.706356	-1.834497
H	6.799288	-0.471072	-3.477047
H	-2.047347	4.959858	-2.425699
H	0.286740	5.206339	1.168586
H	-2.241758	7.431089	-2.472936
H	0.093236	7.677632	1.129718
H	-1.172472	8.798072	-0.693356
H	-5.088366	0.143445	2.314712
H	-5.863603	-0.942113	-1.764695
H	-7.507516	-0.052278	2.830839
H	-8.283649	-1.138324	-1.256901
H	-9.112173	-0.694031	1.043996
H	0.311130	-5.007270	-2.831824
H	-0.466071	-5.131810	1.387374
H	0.527130	-7.478429	-2.869077
H	-0.248635	-7.603308	1.358732
H	0.248330	-8.783266	-0.772023
C	2.459513	1.177573	2.554130
C	3.778363	1.167419	2.979449
C	4.460224	-0.042608	3.144547
C	3.760747	-1.236453	2.934716
C	2.431656	-1.208909	2.546307
N	1.851525	-0.006894	2.340006
H	4.277455	2.114452	3.163556
H	4.243468	-2.196625	3.087739
C	1.570114	-2.425807	2.415069
H	0.671698	-2.219389	1.827995
H	2.126578	-3.243417	1.951986
H	1.257151	-2.746581	3.414928
C	5.914014	-0.057864	3.514067
H	6.182566	0.821357	4.103632
H	6.172811	-0.960821	4.071108
H	6.516182	-0.044657	2.597337
C	1.668563	2.429244	2.331414
H	2.114272	3.010653	1.517419
H	0.628761	2.207371	2.078370
H	1.693018	3.042264	3.236966
H	0.884863	0.001764	1.925314
C	-1.625436	-0.053921	2.504808
O	-1.827137	-1.212165	2.613418
O	-1.713189	1.100326	2.743233

I2$_b$

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scf done: -3171.113019

C	-3.895969	1.801826	-0.307278
C	-2.461781	1.838770	-0.398507
N	-1.944311	0.564065	-0.497802
C	-3.048608	-0.264241	-0.512044
C	-4.260842	0.500599	-0.405650
C	-1.737371	3.026197	-0.446815
C	-2.474047	4.323281	-0.372890
C	-3.254209	4.759815	-1.449002
C	-3.937978	5.972814	-1.377618
C	-3.850056	6.759057	-0.228327
C	-3.074153	6.329202	0.848568
C	-2.387550	5.117855	0.775501
Al	-0.049489	0.046455	-0.913653
N	0.483886	1.957744	-0.578156
C	1.758886	2.482144	-0.657693
C	1.714709	3.917678	-0.714389
C	0.406747	4.272952	-0.648276
C	-0.349899	3.055330	-0.557817
C	2.942892	1.750036	-0.674737
C	4.244457	2.477210	-0.748372
C	5.055644	2.350746	-1.882214
C	6.276336	3.019842	-1.956106
C	6.701427	3.819955	-0.895064
C	5.898792	3.951261	0.238331
C	4.676190	3.284946	0.309835
C	-3.028746	-1.652998	-0.611541
C	-4.317607	-2.400413	-0.726140
C	-5.233820	-2.443262	0.331648
C	-6.422147	-3.162046	0.200330
C	-6.709150	-3.840233	-0.984402
C	-5.801726	-3.796683	-2.043258
C	-4.612022	-3.082080	-1.913477
N	-0.564035	-1.864208	-0.565303
C	0.267824	-2.964966	-0.512556
C	-0.497576	-4.180189	-0.506209
C	-1.805133	-3.820877	-0.556079
C	-1.841558	-2.384783	-0.597435
C	1.659320	-2.937433	-0.482441
C	2.385806	-1.749222	-0.502769
N	1.863638	-0.475096	-0.592920
C	2.963567	0.358174	-0.602664
C	4.177317	-0.400961	-0.490916
C	3.818643	-1.707474	-0.421169
C	2.407283	-4.229438	-0.441168
C	3.156538	-4.642509	-1.548978

C	3.860844	-5.845125	-1.516959
C	3.825823	-6.646970	-0.375617
C	3.080926	-6.242558	0.732187
C	2.374588	-5.040906	0.697966
Cl	-0.105467	0.056016	-3.130567
H	-3.041178	-1.436326	2.297351
H	5.170848	0.022541	-0.442819
H	4.458585	-2.571341	-0.307387
H	2.578214	4.561916	-0.800317
H	-0.018420	5.266652	-0.665006
H	-4.531649	2.668690	-0.194386
H	-5.257640	0.084176	-0.389453
H	-0.079780	-5.176163	-0.465346
H	-2.675047	-4.462317	-0.551847
H	4.723321	1.727407	-2.708637
H	4.050401	3.393006	1.192211
H	6.223145	4.571361	1.068664
H	7.653216	4.339589	-0.951606
H	6.894007	2.916555	-2.843262
H	-3.320463	4.146036	-2.343973
H	-1.782514	4.781813	1.614509
H	-4.537860	6.303351	-2.220360
H	-3.003123	6.935397	1.746761
H	-4.384001	7.702957	-0.172223
H	-5.024551	-1.905738	1.254373
H	-3.903700	-3.047942	-2.737787
H	-7.124674	-3.191128	1.028242
H	-6.018715	-4.317629	-2.971123
H	-7.635626	-4.398161	-1.083065
H	3.182532	-4.017609	-2.438249
H	1.792177	-4.730572	1.561614
H	4.435634	-6.155524	-2.384450
H	3.048978	-6.860453	1.624574
H	4.375516	-7.583094	-0.350200
C	0.819593	1.070715	2.593801
C	2.201785	0.967168	2.635290
C	2.815736	-0.284772	2.717665
C	1.998734	-1.422002	2.735337
C	0.619295	-1.294201	2.695409
N	0.080710	-0.057910	2.612080
H	2.796897	1.875007	2.627016
H	2.438152	-2.413058	2.801096
C	-0.335555	-2.444527	2.790950
H	-1.004725	-2.470981	1.924911
H	0.206175	-3.389831	2.844798
H	-0.951826	-2.346134	3.691240
C	4.307232	-0.397456	2.848923
H	4.583272	-0.321211	3.907110
H	4.668577	-1.356042	2.470204
H	4.810056	0.411142	2.311208
C	0.086183	2.376287	2.598352
H	0.669596	3.141893	2.079623
H	-0.893959	2.274857	2.125774
H	-0.069021	2.703074	3.632759
H	-1.009998	0.055977	2.654031
C	-3.372194	-0.455274	2.708756
O	-4.579653	-0.313268	2.948411
O	-2.452133	0.405509	2.884290

TS3$_b$ and TS3'$_b$

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scf done: -843.710108

C	-1.654965	0.844327	-0.410336
C	-3.042050	0.814010	-0.349124
C	-3.698954	-0.298898	0.181810
C	-2.916890	-1.361775	0.638706
C	-1.531180	-1.291839	0.568580
N	-0.939404	-0.203456	0.042408
H	-3.607316	1.663626	-0.719646
H	-3.381892	-2.249285	1.056658
C	-0.639251	-2.380827	1.080474
H	-0.103164	-2.012518	1.961219
H	-1.225036	-3.258676	1.357862
H	0.093850	-2.672884	0.322858
C	-5.197432	-0.337357	0.281857
H	-5.661163	0.219913	-0.535586
H	-5.568473	-1.364699	0.269909
H	-5.516276	0.124010	1.223212
C	-0.897867	2.007792	-0.979337
H	-1.576133	2.838552	-1.181334
H	-0.131820	2.342022	-0.271423
H	-0.416688	1.723216	-1.920867
C	2.311721	0.557442	-1.020696
C	3.777370	0.895353	-0.781775
C	3.866643	-0.527312	1.071545
C	2.408318	-0.923908	0.895026
H	4.286140	1.101890	-1.726049
H	2.229455	-0.270739	-1.734226
H	1.796732	1.426571	-1.437513
H	4.446923	-1.356078	1.483425
H	3.940722	0.332268	1.757160
H	2.345515	-1.826169	0.275490
H	1.942809	-1.112616	1.864706
H	3.854027	1.784831	-0.135974
O	4.459723	-0.189685	-0.174115
N	1.646082	0.150340	0.230310
H	1.568970	0.953289	0.881932
H	0.276199	-0.110169	0.085733
C	0.014301	1.444464	2.729835
H	-0.834291	1.923967	3.271749
O	0.179896	0.217674	2.911450
O	0.697799	2.207613	1.992683

I3$_b$

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scf done: -3458.886072

C	3.724423	-2.722418	-0.161765
C	2.400346	-2.325807	-0.553191
N	2.282833	-0.953807	-0.553338
C	3.526384	-0.489350	-0.187591
C	4.417179	-1.585691	0.079318
C	1.405497	-3.234206	-0.893518
C	1.733288	-4.690962	-0.918944
C	1.912287	-5.401543	0.268937
C	2.205790	-6.761614	0.239322
C	2.323465	-7.423084	-0.980000
C	2.146457	-6.720073	-2.168650
C	1.851505	-5.360281	-2.138598
Al	0.720358	0.113754	-1.205089
N	-0.375760	-1.558326	-1.199784
C	-1.725331	-1.678794	-1.442093
C	-2.087199	-3.060197	-1.609217
C	-0.954520	-3.783889	-1.449122
C	0.102551	-2.847105	-1.188700
C	-2.640592	-0.633342	-1.511109
C	-4.076373	-0.956225	-1.758292
C	-4.815190	-1.661701	-0.805009
C	-6.154980	-1.961041	-1.033062
C	-6.766199	-1.567083	-2.220306
C	-6.033616	-0.869933	-3.177836
C	-4.696233	-0.563599	-2.947467
C	3.912531	0.844064	-0.098917
C	5.323518	1.156770	0.272099
C	6.370951	0.817776	-0.588509
C	7.688139	1.102670	-0.243291
C	7.973837	1.727708	0.967691
C	6.936088	2.072160	1.829094
C	5.618346	1.790861	1.481443
N	1.704934	1.777692	-0.681923
C	1.253015	3.071160	-0.816446
C	2.315549	4.006994	-0.576653
C	3.420104	3.278993	-0.287568
C	3.033995	1.895355	-0.345211
C	-0.060135	3.457256	-1.055406
C	-1.102834	2.544991	-1.186666
N	-0.983570	1.172173	-1.190556
C	-2.266251	0.701868	-1.374165
C	-3.197688	1.792760	-1.446401
C	-2.475142	2.934456	-1.346301
C	-0.374436	4.915676	-1.105957
C	-1.013647	5.532264	-0.028392
C	-1.299622	6.893515	-0.067064
C	-0.948624	7.648747	-1.183133
C	-0.310592	7.038910	-2.259717
C	-0.023401	5.677363	-2.221325
Cl	1.172458	0.171917	-3.390120
H	-3.082402	-3.418731	-1.816835
H	-0.834988	-4.855047	-1.486992
H	-4.264953	1.689439	-1.561866
H	-2.830073	3.952440	-1.369899
H	2.213485	5.079964	-0.615752
H	4.410468	3.635902	-0.054929
H	4.064983	-3.742246	-0.078833
H	5.438271	-1.486533	0.411140
H	-4.336642	-1.975198	0.117951
H	-4.124411	-0.022648	-3.693662
H	-6.502433	-0.565016	-4.105935
H	-7.808823	-1.801633	-2.399330
H	-6.718507	-2.495386	-0.277205
H	-1.283333	4.940058	0.840332
H	0.473469	5.199362	-3.058582
H	-1.793698	7.363844	0.774824
H	-0.037030	7.621766	-3.131233
H	-1.171483	8.708656	-1.213388
H	6.147770	0.332893	-1.532638
H	4.810569	2.067682	2.149674
H	8.490487	0.838450	-0.921876
H	7.150528	2.559857	2.772597
H	8.999946	1.947807	1.237143
H	1.819432	-4.884873	1.217730
H	1.712665	-4.810637	-3.063300
H	2.339438	-7.303556	1.168015
H	2.238807	-7.229239	-3.120662
H	2.551815	-8.481973	-1.003836
C	0.980022	0.657375	2.356999
C	2.233613	0.255671	2.809469
C	2.526802	-1.098862	2.938002
C	1.511764	-1.999379	2.629081
C	0.273627	-1.531002	2.190194
N	0.020420	-0.222964	2.030067
H	2.980010	1.003672	3.053145
H	1.678499	-3.066061	2.732277
C	-0.859885	-2.483919	1.930922
H	-0.495204	-3.491074	1.720044
H	-1.517080	-2.533967	2.803680
H	-1.469085	-2.143874	1.093501
C	3.875610	-1.557690	3.418395
H	4.079744	-2.579789	3.097188
H	4.663815	-0.905257	3.035634
H	3.917734	-1.527112	4.510791
C	0.642041	2.120496	2.262857
H	0.194024	2.461130	3.201594
H	1.536305	2.719248	2.076135
H	-0.075742	2.295717	1.463346
C	-2.793431	1.520061	2.081892
C	-3.630860	0.277051	1.855037
C	-5.360198	1.295340	3.268556
C	-4.441189	2.495947	3.424939
H	-4.251950	0.391585	0.963337
H	-3.011899	-0.615183	1.754994
H	-2.128022	1.378777	2.943428
H	-2.177559	1.712057	1.205136
H	-6.026217	1.431658	2.414911
H	-5.955888	1.131544	4.165916
H	-5.032994	3.404097	3.531182
H	-3.815487	2.377434	4.320026
O	-3.619085	2.657265	2.283149
N	-4.560041	0.071396	2.999661
H	-4.020902	-0.181751	3.830026
H	-5.240180	-0.800661	2.770305
C	-5.372801	-2.931582	2.332218
H	-5.929992	-3.874905	2.171426
O	-4.138675	-2.965603	2.371620
O	-6.097237	-1.891728	2.453155

R'$_a$

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scf done: -2980.557595

C	-0.115004	1.125518	2.769161
N	0.488487	0.039974	1.945249
C	0.448790	-1.242864	2.703156
C	-0.954570	-1.538576	3.204920
O	-1.436735	-0.476743	4.013210
C	-1.495700	0.726326	3.262686
C	-2.320880	-1.725277	-0.080629
N	-0.950482	-1.644018	-0.137474
C	-0.504425	-2.936233	-0.285235
C	-1.620583	-3.846655	-0.322428
C	-2.744620	-3.097233	-0.185575
Al	0.147251	0.031041	-0.147854
C	0.831058	-3.338519	-0.384513
C	1.127845	-4.797401	-0.495954
C	1.669869	-5.321075	-1.674998
C	1.953078	-6.682402	-1.778045
C	1.700762	-7.532988	-0.701328
C	1.163832	-7.017259	0.478853
C	0.878077	-5.656532	0.580415
C	-3.205807	-0.650446	0.021435
C	-4.665322	-0.948540	0.118580
C	-5.202651	-1.467112	1.301321
C	-6.565605	-1.748873	1.391045
C	-7.400085	-1.517708	0.296971
C	-6.868028	-1.002980	-0.886236
C	-5.505982	-0.717771	-0.975849
N	-1.509259	1.138150	-0.112941
C	-1.595547	2.510102	-0.167450
C	-2.970192	2.925143	-0.061408
C	-3.716561	1.795149	0.043658
C	-2.802934	0.685500	-0.011757
C	-0.523208	3.401868	-0.271442
C	0.816904	3.002418	-0.269252
N	1.270562	1.711021	-0.155761
C	2.641657	1.791564	-0.158974
C	3.058423	3.166023	-0.284795
C	1.928577	3.913854	-0.366533
C	3.531904	0.710603	-0.111933
C	3.128034	-0.627933	-0.179496
N	1.829050	-1.077570	-0.277527
C	1.910685	-2.449733	-0.344702
C	3.285906	-2.869047	-0.285053
C	4.037404	-1.743917	-0.167784
C	-0.828212	4.860362	-0.364823
C	-1.445325	5.381402	-1.507769
C	-1.732404	6.742895	-1.596322
C	-1.408923	7.596324	-0.540981
C	-0.796458	7.083290	0.602983
C	-0.506461	5.722394	0.689764
C	4.989965	1.019171	-0.021523
C	5.860447	0.697484	-1.069985
C	7.213825	1.023135	-0.990626
C	7.713096	1.674036	0.138049
C	6.853737	1.993747	1.189415
C	5.500646	1.668026	1.109640
H	5.111198	-1.670312	-0.076539
H	3.623142	-3.895988	-0.304771
H	4.084389	3.502596	-0.335027
H	1.846128	4.984443	-0.491500
H	-3.309852	3.951462	-0.056817
H	-4.789245	1.711542	0.148634
H	-1.544796	-4.917180	-0.452142
H	-3.773238	-3.430239	-0.179783
H	5.470123	0.202367	-1.955724
H	4.830393	1.917417	1.928659
H	7.235709	2.494715	2.073986
H	8.767054	1.928238	0.198694
H	7.876358	0.772443	-1.813741
H	-1.695796	4.714693	-2.329399
H	-0.032734	5.319920	1.582152
H	-2.207616	7.136094	-2.490166
H	-0.545545	7.741489	1.429556
H	-1.633796	8.656510	-0.609332
H	-4.549023	-1.644572	2.152753
H	-5.078367	-0.322588	-1.894871
H	-6.974432	-2.147562	2.314841
H	-7.513452	-0.824839	-1.741435
H	-8.461183	-1.738406	0.365999
H	1.864662	-4.657175	-2.513648
H	0.464474	-5.251664	1.501328
H	2.369444	-7.077691	-2.699867
H	0.969106	-7.673175	1.322199
H	1.922279	-8.593084	-0.781137
H	-1.644138	-1.705162	2.365933
H	-0.938504	-2.434257	3.829420
H	1.123878	-1.165395	3.564239
H	0.803018	-2.049100	2.055387
H	-2.192106	0.599698	2.422344
H	-1.885249	1.499694	3.927783
H	-0.168384	2.038080	2.169062
H	0.530822	1.314253	3.635567
H	1.481459	0.279243	1.874042
H	7.121415	-1.550919	1.582001
H	7.031407	-0.873299	1.298182
O	0.084328	0.099803	-2.108681
H	-0.823653	0.066151	-2.550411
H	0.648890	-0.545473	-2.566045
Cl	-2.523645	0.020032	-3.541015

R'$_b$

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scf done: -3058.950561

C	3.787173	-1.084419	-0.197216
C	2.385515	-1.348581	-0.366576
N	1.657938	-0.180366	-0.298134
C	2.596981	0.816382	-0.138886
C	3.916538	0.256546	-0.042077
C	1.874370	-2.631623	-0.551608
C	2.840858	-3.758896	-0.710706
C	3.027643	-4.695056	0.311946
C	3.942240	-5.735971	0.157003
C	4.677575	-5.850829	-1.023161
C	4.497593	-4.919392	-2.046201
C	3.585364	-3.876592	-1.889547
Al	-0.300386	0.003889	-0.541290
N	-0.496893	-1.975467	-0.399821
C	-1.658506	-2.711059	-0.307501
C	-1.376433	-4.116026	-0.414742
C	-0.036491	-4.235329	-0.597137
C	0.508963	-2.906587	-0.549216
C	-2.937377	-2.188088	-0.135441
C	-4.085428	-3.127672	0.031690
C	-4.708595	-3.250854	1.278262
C	-5.783392	-4.123389	1.445503
C	-6.245917	-4.877735	0.366828
C	-5.630487	-4.756470	-0.879565
C	-4.554481	-3.885630	-1.046499
C	2.343633	2.185733	-0.119560
C	3.493943	3.129121	-0.002550
C	4.440596	3.216233	-1.030624
C	5.515166	4.098109	-0.929098
C	5.656916	4.901923	0.202692
C	4.716070	4.823982	1.229605
C	3.639085	3.944459	1.125765
N	-0.105109	1.974421	-0.350406
C	-1.112278	2.909333	-0.463601
C	-0.571225	4.239833	-0.447381
C	0.773459	4.115276	-0.310142
C	1.057805	2.707813	-0.245510
C	-2.478655	2.640220	-0.490715
C	-2.996903	1.353175	-0.362807
N	-2.261199	0.187706	-0.275362
C	-3.196720	-0.818742	-0.146533
C	-4.526235	-0.274937	-0.144510
C	-4.403213	1.068213	-0.296118
C	-3.426655	3.790168	-0.582953
C	-4.161749	4.189377	0.538841
C	-5.038752	5.270033	0.458141
C	-5.188999	5.960289	-0.745339
C	-4.458042	5.567328	-1.866719
C	-3.578910	4.487751	-1.785483
H	-2.115935	-4.902539	-0.359370
H	0.542720	-5.139067	-0.724738
H	-5.432155	-0.859170	-0.062046
H	-5.188343	1.808461	-0.359207
H	-1.155646	5.146633	-0.516959
H	1.514765	4.900179	-0.259925
H	4.561194	-1.839051	-0.180281
H	4.820082	0.824621	0.128950
H	-4.345222	-2.661034	2.116728
H	-4.076215	-3.786793	-2.017952
H	-5.988683	-5.338130	-1.723803
H	-7.083443	-5.556629	0.496595
H	-6.257820	-4.213694	2.418176
H	-4.039411	3.651052	1.476307
H	-3.007465	4.180146	-2.657738
H	-5.602422	5.573377	1.335405
H	-4.571295	6.100235	-2.806129
H	-5.872550	6.801697	-0.808469
H	4.325923	2.591781	-1.913499
H	2.902478	3.892156	1.923517
H	6.239840	4.158489	-1.735637
H	4.818481	5.447467	2.112818
H	6.494921	5.587903	0.282462
H	2.458719	-4.602707	1.234108
H	3.445190	-3.146367	-2.683173
H	4.081429	-6.454558	0.959204
H	5.067384	-5.002900	-2.966891
H	5.389355	-6.661951	-1.144153
H	-3.782134	0.464341	3.248521
H	-3.802344	0.380973	2.513265
C	0.232108	0.927819	2.758420
C	1.590900	1.117522	3.001139
C	2.446890	0.017536	3.082915
C	1.875041	-1.247266	2.953602
C	0.499571	-1.368381	2.738464
N	-0.299944	-0.298282	2.602840
H	1.981173	2.125594	3.116603
H	2.491388	-2.141436	3.023468
C	-0.160062	-2.721138	2.718769
H	0.427004	-3.451538	2.154539
H	-0.258337	-3.098322	3.743559
H	-1.160095	-2.651217	2.285306
C	3.918268	0.200386	3.340510
H	4.492988	-0.655165	2.976102
H	4.290383	1.105866	2.850314
H	4.105053	0.302886	4.415693
C	-0.720499	2.093265	2.720889
H	-1.079917	2.311566	3.733793
H	-0.236874	2.995396	2.331893
H	-1.589265	1.855358	2.102246
O	-0.311467	0.043180	-2.440337
H	0.603929	0.141371	-2.897929
H	-0.770676	-0.690945	-2.883951
Cl	2.262912	0.297094	-3.779037

TS1'$_b$

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scf done: -3058.921507

C	3.817587	-2.465605	0.438989
C	2.429865	-2.180821	0.179269
N	2.245912	-0.827801	0.019582
C	3.487417	-0.259478	0.165889
C	4.475563	-1.278084	0.410640
C	1.440912	-3.160553	0.071760
C	1.833221	-4.591506	0.231314
C	2.661087	-5.213497	-0.710588
C	3.017213	-6.553176	-0.561208
C	2.550960	-7.284385	0.532070

C	1.724060	-6.671484	1.474060
C	1.365067	-5.332753	1.322396
Al	0.517023	0.129592	-0.276623
N	-0.460319	-1.630828	-0.325934
C	-1.775702	-1.841561	-0.667948
C	-2.031042	-3.250619	-0.816465
C	-0.868988	-3.893347	-0.529465
C	0.104643	-2.878521	-0.228455
C	-2.747211	-0.847879	-0.844295
C	-4.137650	-1.256870	-1.202536
C	-4.694593	-0.844565	-2.420802
C	-5.992474	-1.213094	-2.770007
C	-6.754756	-1.998152	-1.904113
C	-6.207866	-2.418676	-0.691771
C	-4.907564	-2.053346	-0.346589
C	3.780582	1.106828	0.108614
C	5.205987	1.532147	0.256248
C	5.841837	1.467026	1.500977
C	7.169686	1.870093	1.638017
C	7.875466	2.342043	0.530762
C	7.247859	2.409679	-0.713428
C	5.919510	2.007348	-0.849508
N	1.460009	1.899295	-0.189924
C	0.901941	3.150682	-0.280331
C	1.929038	4.160894	-0.211691
C	3.111135	3.510198	-0.070350
C	2.812616	2.099637	-0.057905
C	-0.456842	3.435397	-0.436286
C	-1.441599	2.449900	-0.557764
N	-1.230733	1.090088	-0.562739
C	-2.473507	0.519253	-0.735475
C	-3.483724	1.542624	-0.794826
C	-2.846017	2.736222	-0.681521
C	-0.883605	4.865838	-0.455777
C	-1.397714	5.442660	-1.622872
C	-1.797143	6.778379	-1.635015
C	-1.689217	7.551939	-0.478758
C	-1.178237	6.984666	0.688934
C	-0.776221	5.649521	0.699470
H	0.372508	0.214379	1.524678
H	-4.545889	1.362224	-0.885711
H	-3.282624	3.725250	-0.666942
H	-2.974478	-3.685659	-1.114251
H	-0.673447	-4.956563	-0.546212
H	4.228413	-3.450100	0.613204
H	5.532357	-1.098213	0.550074
H	1.757021	5.226547	-0.270585
H	4.100702	3.936021	0.020625
H	-4.100998	-0.236384	-3.098805
H	-4.482969	-2.383473	0.596818
H	-6.792839	-3.029715	-0.010341
H	-7.767387	-2.282630	-2.174011
H	-6.406887	-0.888322	-3.719814
H	3.015246	-4.642723	-1.565653
H	0.721057	-4.853268	2.056174
H	3.656465	-7.026150	-1.300925
H	1.358339	-7.234328	2.327832
H	2.829725	-8.327470	0.648624
H	5.289752	1.101927	2.363637
H	5.429410	2.058389	-1.818717
H	7.651219	1.817099	2.610048
H	7.791596	2.774635	-1.579814
H	8.909617	2.655904	0.637196
H	-1.478977	4.840095	-2.524240
H	-0.377040	5.207331	1.609542
H	-2.190157	7.214733	-2.548563
H	-1.092415	7.580260	1.593000
H	-2.001139	8.592073	-0.488020
C	-2.204945	-1.176447	2.711161
C	-3.585371	-1.318019	2.823411
C	-4.410223	-0.194402	2.771240
C	-3.799494	1.061649	2.689666
C	-2.416129	1.156787	2.621058
N	-1.658478	0.043356	2.593563
H	-4.009314	-2.312726	2.935663
H	-4.398497	1.968413	2.679334
C	-1.691940	2.471974	2.649330
H	-0.717238	2.400094	2.159092
H	-2.279459	3.257204	2.167178
H	-1.521156	2.765019	3.691573
C	-5.907035	-0.323978	2.776822
H	-6.220575	-1.312209	3.121539
H	-6.367586	0.438630	3.410664
H	-6.288645	-0.184559	1.758086
C	-1.278473	-2.357962	2.753407
H	-1.612891	-3.136268	2.060486
H	-0.257070	-2.068628	2.496142
H	-1.273178	-2.785331	3.761836
H	-0.447196	0.140103	2.019023
O	0.798506	0.069272	-2.210229
Cl	1.355123	-2.467842	-3.636494
H	0.076565	0.473021	-2.721502
H	0.991061	-0.826554	-2.639980

I1'$_b$

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scf done: -3247.513269

C	3.792943	-2.620985	-0.321347
C	2.399682	-2.280824	-0.455774
N	2.241675	-0.921605	-0.408089
C	3.497221	-0.394911	-0.262740
C	4.473804	-1.452947	-0.210012
C	1.376612	-3.221697	-0.605722
C	1.750577	-4.665483	-0.654578
C	2.479659	-5.180779	-1.728828
C	2.820585	-6.529420	-1.766875
C	2.439068	-7.376223	-0.729531
C	1.713092	-6.869814	0.345321
C	1.368994	-5.522007	0.381173
Al	0.489774	0.076086	-0.351028
N	-0.531456	-1.649410	-0.595535
C	-1.879110	-1.806334	-0.785134
C	-2.179833	-3.186424	-1.069382
C	-1.005302	-3.863199	-1.019796
C	0.020561	-2.898125	-0.720660
C	-2.841244	-0.788066	-0.733433
C	-4.268561	-1.143065	-0.983568
C	-4.926751	-0.602174	-2.094044
C	-6.256828	-0.919172	-2.349881
C	-6.948240	-1.779772	-1.500796
C	-6.298172	-2.331789	-0.400521
C	-4.965873	-2.018776	-0.147353
C	3.815130	0.966247	-0.194231
C	5.253012	1.344596	-0.053154
C	5.922029	1.134145	1.154619
C	7.262638	1.484110	1.287359
C	7.947326	2.047564	0.213917
C	7.286218	2.260633	-0.992719
C	5.945481	1.911233	-1.125347
N	1.508147	1.824813	-0.343505
C	0.970307	3.084004	-0.338316
C	2.020660	4.070164	-0.261799
C	3.191927	3.392180	-0.195137
C	2.866733	1.988390	-0.250180
C	-0.391554	3.398404	-0.384729
C	-1.414652	2.447846	-0.442504
N	-1.257858	1.087671	-0.482149
C	-2.521132	0.560989	-0.560445
C	-3.500930	1.617420	-0.490575
C	-2.816853	2.784636	-0.427871
C	-0.782280	4.839135	-0.350288
C	-1.330265	5.451200	-1.479903
C	-1.700991	6.792089	-1.445053
C	-1.529672	7.534148	-0.279310
C	-0.985843	6.930418	0.851332
C	-0.613385	5.589843	0.815563
H	0.474097	0.006546	1.335762
H	-4.569783	1.475011	-0.487992
H	-3.214690	3.785238	-0.363929
H	-3.159392	-3.577137	-1.293708
H	-0.837346	-4.914536	-1.192868
H	4.190980	-3.623240	-0.313701
H	5.538037	-1.311015	-0.106077
H	1.870591	5.138166	-0.257294
H	4.189483	3.795132	-0.117920
H	-4.375522	0.055491	-2.758680
H	-4.459722	-2.457734	0.704075
H	-6.826567	-3.006763	0.262762
H	-7.985372	-2.023366	-1.698759
H	-6.752383	-0.496576	-3.216110
H	2.773151	-4.520752	-2.537930
H	0.804874	-5.123916	1.218329
H	3.381670	-6.918655	-2.608226
H	1.415793	-7.523068	1.157173
H	2.705798	-8.426011	-0.758900
H	5.383826	0.699975	1.990153
H	5.429530	2.073988	-2.065516
H	7.770816	1.319103	2.230147
H	7.814056	2.696492	-1.832763
H	8.991106	2.319541	0.317072
H	-1.462862	4.870520	-2.386708
H	-0.190420	5.117207	1.695993
H	-2.121608	7.257006	-2.328895
H	-0.853005	7.501761	1.762468
H	-1.818837	8.578038	-0.252008
C	-2.163971	-1.507772	2.665406
C	-3.501194	-1.640150	2.991038
C	-4.301912	-0.509547	3.163956
C	-3.704082	0.749021	3.073817
C	-2.355741	0.860384	2.788323
N	-1.650726	-0.266669	2.565956
H	-3.920263	-2.634682	3.089991
H	-4.283570	1.650412	3.230648
C	-1.610516	2.156850	2.769758
H	-0.693487	2.076750	2.184780
H	-2.235169	2.950866	2.361686
H	-1.342399	2.422478	3.795884
C	-5.773205	-0.651359	3.409673
H	-5.985056	-1.527330	4.022975
H	-6.184441	0.236384	3.888424
H	-6.279413	-0.787146	2.448389
C	-1.247373	-2.668815	2.439919
H	-1.694198	-3.365898	1.728357
H	-0.279981	-2.341930	2.059562
H	-1.095993	-3.197200	3.384051
H	-0.671335	-0.163245	2.169013
C	2.559118	-0.944264	3.119376
O	2.942695	0.134533	3.280188
O	2.197536	-2.035682	2.999604
O	0.584119	0.144661	-2.351708
H	-0.249437	0.346115	-2.860406
H	1.266924	0.728978	-2.702611
Cl	-1.819781	0.779272	-4.051108

TS2'$_b$

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scf done: -3247.504276

C	5.225428	-8.506179	6.537902
C	6.580476	-8.090377	6.272292
N	6.840781	-6.898603	6.898213
C	5.685333	-6.552467	7.548837
C	4.670894	-7.553019	7.330128
C	7.474582	-8.810151	5.472911
C	7.034037	-10.132557	4.938514
C	6.804476	-11.209437	5.802706
C	6.392365	-12.443321	5.300950
C	6.201110	-12.612703	3.929287
C	6.425456	-11.543568	3.061160
C	6.841427	-10.311473	3.563370
Al	8.496875	-5.777422	6.709219
N	9.289366	-7.127363	5.442150
C	10.542334	-7.108522	4.876778
C	10.809427	-8.363143	4.221958
C	9.702800	-9.135499	4.382454
C	8.754381	-8.356107	5.134059
C	11.465185	-6.056862	4.952383
C	12.783835	-6.221120	4.272795
C	13.956279	-6.280309	5.038668
C	15.195607	-6.445251	4.422286
C	15.280206	-6.554248	3.033458
C	14.117308	-6.507592	2.264485
C	12.877484	-6.346326	2.881915
C	5.497916	-5.416591	8.345127
C	4.156074	-5.210645	8.968909
C	3.067934	-4.820629	8.180385
C	1.812355	-4.627087	8.755191
C	1.632639	-4.823346	10.124927
C	2.713071	-5.213201	10.916918
C	3.968801	-5.405485	10.341532
N	7.756669	-4.471716	8.052519
C	8.368348	-3.334932	8.517061
C	7.483754	-2.621075	9.404617
C	6.316567	-3.314048	9.435545
C	6.495171	-4.469085	8.591790
C	9.639838	-2.880317	8.155801
C	10.458332	-3.513661	7.215805
N	10.174083	-4.675333	6.540511
C	11.256864	-4.912372	5.728695
C	12.209211	-3.836623	5.844685
C	11.722841	-2.979787	6.778548
C	10.141266	-1.615360	8.774305
C	11.137189	-1.655087	9.755561
C	11.612425	-0.474653	10.326547
C	11.097428	0.756322	9.919092
C	10.105630	0.803004	8.938596
C	9.630168	-0.377653	8.368899
H	7.665523	-4.871695	5.437388
H	13.129496	-3.756411	5.283328
H	12.163308	-2.057699	7.132475
H	11.733541	-8.621684	3.724433
H	9.542965	-10.148088	4.038994
H	4.765410	-9.407952	6.158455
H	3.670186	-7.523770	7.738577
H	7.728468	-1.702209	9.919247
H	5.412403	-3.073510	9.977447
H	13.881690	-6.209941	6.121997
H	11.971551	-6.320859	2.282395
H	14.172547	-6.597879	1.183374
H	16.246292	-6.680373	2.553782
H	16.095580	-6.493472	5.028384
H	6.956283	-11.077250	6.871149
H	7.012571	-9.476166	2.888135
H	6.222649	-13.272175	5.981838
H	6.274977	-11.667066	1.992725
H	5.878513	-13.573249	3.538688
H	3.211441	-4.667276	7.113128
H	4.811175	-5.711956	10.956943
H	0.975975	-4.321892	8.133276
H	2.579347	-5.370045	11.983233
H	0.654927	-4.673268	10.573065
H	11.537865	-2.616045	10.069714
H	8.859177	-0.344696	7.602224
H	12.384326	-0.517689	11.089327
H	9.702714	1.758213	8.614896
H	11.467713	1.675539	10.363199
C	9.097964	-5.182478	2.324321
C	9.989177	-4.938069	1.292046
C	10.776278	-3.781744	1.294563
C	10.599617	-2.854470	2.328471
C	9.679187	-3.095388	3.333883
N	8.993056	-4.259037	3.301762
H	10.079148	-5.668401	0.493171
H	11.169934	-1.931193	2.348623
C	9.337594	-2.121095	4.417114
H	8.870218	-2.618899	5.270832
H	10.230827	-1.590349	4.752166
H	8.627223	-1.386067	4.022652
C	11.806352	-3.554165	0.228390
H	11.525800	-4.045174	-0.705796
H	11.959871	-2.488345	0.046498
H	12.762283	-3.978991	0.558519
C	8.240926	-6.406733	2.414056
H	8.873641	-7.295387	2.510419
H	7.562591	-6.361666	3.270144
H	7.652015	-6.509224	1.498126
H	8.385306	-4.482543	4.117819
C	6.055825	-4.268873	5.193026
O	6.105686	-3.213350	5.725275
O	5.560816	-5.147742	4.572080
O	9.320210	-6.790893	8.193962
H	10.322257	-6.731326	8.286468
H	8.953528	-6.549438	9.061613
Cl	12.277941	-6.725584	8.652730

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scf done: -3247.557300

C	-3.964411	1.673731	-0.242873
C	-2.538753	1.761893	-0.391210
N	-1.975604	0.502390	-0.457553
C	-3.048765	-0.367759	-0.406133
C	-4.282293	0.356037	-0.273358
C	-1.863636	2.972819	-0.519553
C	-2.650968	4.241304	-0.484709
C	-3.474350	4.597425	-1.558014
C	-4.205935	5.783876	-1.520947
C	-4.123438	6.622423	-0.408930
C	-3.305400	6.271743	0.665559
C	-2.570701	5.087495	0.626715
Al	-0.063055	0.061771	-0.808551
N	0.396184	1.987673	-0.625723
C	1.652079	2.558147	-0.680198
C	1.553982	3.986008	-0.796669
C	0.231621	4.292471	-0.783178
C	-0.480404	3.052452	-0.656089
C	2.862025	1.874520	-0.623297
C	4.132677	2.654345	-0.662242
C	4.982346	2.550847	-1.770044
C	6.173390	3.274246	-1.812265
C	6.527857	4.104431	-0.747965
C	5.683476	4.214236	0.357184
C	4.490017	3.494357	0.398231
C	-2.983695	-1.755783	-0.513329
C	-4.251062	-2.545706	-0.570035
C	-5.102225	-2.644494	0.536328
C	-6.274096	-3.396764	0.459032
C	-6.609211	-4.055885	-0.723541
C	-5.767709	-3.958077	-1.832014
C	-4.595400	-3.208060	-1.754850
N	-0.515107	-1.871856	-0.611559
C	0.361757	-2.940288	-0.615860
C	-0.355869	-4.182918	-0.627752
C	-1.677894	-3.875081	-0.608489
C	-1.773122	-2.442453	-0.597418
C	1.751157	-2.857243	-0.588535
C	2.431894	-1.643419	-0.541594
N	1.863597	-0.386315	-0.578423
C	2.931868	0.486304	-0.546669
C	4.170502	-0.231628	-0.444085
C	3.861046	-1.552469	-0.441909
C	2.549521	-4.119536	-0.608578
C	3.282954	-4.465629	-1.748940
C	4.033347	-5.640243	-1.775764
C	4.060922	-6.478760	-0.660959
C	3.333686	-6.139010	0.479983
C	2.580645	-4.965805	0.504787
H	-2.926664	-1.377330	2.571850
H	5.146920	0.225827	-0.367911
H	4.531181	-2.397365	-0.365108
H	2.394979	4.659377	-0.882722
H	-0.230342	5.267370	-0.850557
H	-4.629411	2.520048	-0.143628
H	-5.261588	-0.095835	-0.205340
H	0.101620	-5.162153	-0.636465
H	-2.520583	-4.551533	-0.587025
H	4.691973	1.909231	-2.598821
H	3.828625	3.585697	1.256462
H	5.952287	4.859318	1.188378
H	7.456942	4.665692	-0.780835
H	6.823681	3.190743	-2.678084
H	-3.536399	3.942874	-2.423891
H	-1.932448	4.812134	1.463298
H	-4.838885	6.052665	-2.361431
H	-3.238853	6.918981	1.534991
H	-4.694388	7.545641	-0.379772
H	-4.857206	-2.125757	1.459397
H	-3.939746	-3.130995	-2.618782
H	-6.924252	-3.466924	1.326090
H	-6.023067	-4.464063	-2.758334
H	-7.522038	-4.641150	-0.781791
H	3.260809	-3.810674	-2.616482
H	2.013434	-4.703796	1.394382
H	4.595365	-5.899684	-2.667993
H	3.352082	-6.785485	1.352283
H	4.646471	-7.392989	-0.681287
C	0.856661	1.063429	2.510830
C	2.239906	0.970704	2.645157
C	2.852689	-0.278299	2.737644
C	2.026874	-1.404304	2.699004
C	0.648398	-1.254609	2.575266
N	0.082794	-0.037229	2.455502
H	2.835395	1.878980	2.684463
H	2.454884	-2.400629	2.776424
C	-0.280017	-2.435053	2.639764
H	-1.039158	-2.384585	1.854113
H	0.264928	-3.375874	2.534451
H	-0.793961	-2.449453	3.608213
C	4.339485	-0.400761	2.925027
H	4.584683	-0.354856	3.992380
H	4.710739	-1.350775	2.532452
H	4.865997	0.417222	2.424702
C	0.163410	2.398474	2.492903
H	0.784491	3.158035	2.007534
H	-0.794493	2.337220	1.971241
H	-0.032995	2.726759	3.520373
H	-1.536139	0.275729	2.599950
C	-3.353090	-0.388527	2.812551
O	-4.530027	-0.243322	3.067471
O	-2.487291	0.600490	2.799830
O	-0.131453	0.088308	-2.696505
H	-0.371051	-0.749675	-3.129417
H	0.702463	0.452776	-3.183318
Cl	2.201659	1.096215	-4.087217

I3'$_b$

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scf done: -3535.325995

C	2.473214	0.554691	-2.240675
C	1.048392	0.712521	-2.166080
N	0.674389	1.189614	-0.924324
C	1.858775	1.341494	-0.229776
C	2.973365	0.928210	-1.036426
C	0.193976	0.420175	-3.224462
C	0.781873	-0.007483	-4.530290
C	1.295335	-1.298124	-4.691560
C	1.832740	-1.696461	-5.914949
C	1.860806	-0.806174	-6.988715
C	1.349787	0.482830	-6.834413
C	0.811685	0.880211	-5.610739
Al	-1.166556	1.670656	-0.333913
N	-1.900785	0.830757	-1.984765
C	-3.224752	0.653703	-2.323335
C	-3.344117	0.207821	-3.684739
C	-2.083666	0.100051	-4.174646
C	-1.193057	0.480094	-3.113358
C	-4.318165	0.876598	-1.491830
C	-5.687470	0.634515	-2.033043
C	-6.116231	-0.662113	-2.338406

C	-7.396875	-0.878416	-2.846618
C	-8.255307	0.200057	-3.062356
C	-7.829220	1.496334	-2.768325
C	-6.551631	1.713706	-2.254460
C	1.994551	1.843965	1.062376
C	3.365423	1.990569	1.634689
C	4.267261	2.907166	1.080377
C	5.548416	3.048625	1.610739
C	5.944235	2.273607	2.701340
C	5.050970	1.360657	3.262083
C	3.768403	1.222398	2.733122
N	-0.424676	2.149856	1.455939
C	-1.132918	2.655192	2.526449
C	-0.242515	3.065484	3.576220
C	1.017498	2.804233	3.146058
C	0.899311	2.230420	1.832720
C	-2.518369	2.698219	2.644138
C	-3.376799	2.213982	1.659374
N	-3.000981	1.712340	0.428793
C	-4.184623	1.369611	-0.195219
C	-5.302171	1.630725	0.667124
C	-4.803376	2.169349	1.809582
C	-3.109303	3.224859	3.911046
C	-3.610940	2.339044	4.870619
C	-4.155347	2.823539	6.059182
C	-4.202696	4.197794	6.297047
C	-3.703537	5.085180	5.343374
C	-3.157953	4.600614	4.154576
H	-4.277379	0.005667	-4.190734
H	-1.771782	-0.219849	-5.159147
H	-6.335351	1.428158	0.421489
H	-5.344285	2.500584	2.684934
H	-0.554298	3.489518	4.520620
H	1.949792	2.983716	3.662377
H	3.011058	0.192351	-3.105575
H	4.004644	0.923930	-0.712638
H	-5.444215	-1.503536	-2.177912
H	-6.205269	2.720842	-2.034178
H	-8.490838	2.340116	-2.941309
H	-9.252215	0.031728	-3.459067
H	-7.720909	-1.892004	-3.064580
H	-3.570689	1.268215	4.681901
H	-2.768142	5.289567	3.409377
H	-4.540813	2.127849	6.798608
H	-3.739027	6.155628	5.522771
H	-4.627005	4.575490	7.222532
H	3.957864	3.513940	0.232966
H	3.072072	0.515970	3.177646
H	6.235937	3.766171	1.172878
H	5.350489	0.754747	4.112011
H	6.942822	2.382598	3.113672
H	1.271629	-1.991269	-3.854488
H	0.411231	1.883634	-5.488688
H	2.226573	-2.702065	-6.028628
H	1.369183	1.180675	-7.666256
H	2.278869	-1.115908	-7.941828
C	-0.318274	-1.128391	1.609212
C	1.049651	-1.388629	1.540362
C	1.599374	-1.936879	0.381934
C	0.718573	-2.243900	-0.654406
C	-0.644463	-1.972643	-0.516584
N	-1.150199	-1.386338	0.583402
H	1.683784	-1.154158	2.391609
H	1.088139	-2.700354	-1.569381
C	-1.624273	-2.395664	-1.576008
H	-1.139076	-2.518927	-2.549036
H	-2.084246	-3.352415	-1.302515
H	-2.435230	-1.670551	-1.673296
C	3.074521	-2.214653	0.279560
H	3.393005	-2.279651	-0.764252
H	3.653315	-1.426884	0.772974
H	3.318321	-3.163663	0.770641
C	-0.926002	-0.592979	2.878357
H	-1.231292	-1.423741	3.526419
H	-0.210411	0.022451	3.433285
H	-1.812574	0.005292	2.661336
C	-4.168617	-1.516175	1.941525
C	-4.815386	-1.964540	0.644664
C	-6.375093	-3.303715	2.002063
C	-5.653287	-2.780710	3.234334
H	-5.614851	-1.276689	0.351832
H	-4.089463	-2.049127	-0.167723
H	-3.329597	-2.179309	2.200825
H	-3.778190	-0.503491	1.826688
H	-7.214769	-2.654865	1.739913
H	-6.738102	-4.322499	2.149593
H	-6.354628	-2.691759	4.065484
H	-4.847768	-3.472015	3.526042
O	-5.116412	-1.491078	2.997613
N	-5.449423	-3.300098	0.834553
H	-4.718124	-4.008112	0.958742
H	-5.990203	-3.579024	-0.076043
C	-5.823473	-4.086240	-2.227154
H	-6.156765	-4.451634	-3.220577
O	-4.617598	-3.825738	-2.065396
O	-6.739127	-3.965733	-1.351895
O	-1.186953	3.449847	-0.985526
H	-0.418911	3.737174	-1.508558
H	-2.034715	3.742792	-1.490059
Cl	-3.593851	4.290570	-2.378023

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scf done: -3092.683891

C	3.497622	1.035895	-2.443621
C	2.075888	1.123357	-2.671600
N	1.462230	1.732601	-1.607144
C	2.457701	2.013631	-0.705611
C	3.731045	1.568015	-1.216079
C	1.432342	0.595669	-3.796321
C	2.265954	-0.022562	-4.871697
C	2.950774	-1.223951	-4.656576
C	3.719934	-1.793764	-5.670398
C	3.814003	-1.167048	-6.913235
C	3.134496	0.030688	-7.137157
C	2.364171	0.597882	-6.122790
Al	-0.505094	2.154297	-1.407781
N	-0.876606	1.172088	-3.123846
C	-2.105323	0.913039	-3.675032
C	-1.957554	0.125624	-4.874094
C	-0.626354	-0.064214	-5.057616
C	0.043446	0.595656	-3.963357
C	-3.337937	1.341946	-3.175753
C	-4.575823	0.968144	-3.921493
C	-5.492556	0.076198	-3.352226
C	-6.652488	-0.280884	-4.038604
C	-6.910245	0.253471	-5.301605
C	-6.002880	1.145251	-5.874736
C	-4.841696	1.499389	-5.188746
C	2.293648	2.640255	0.533823
C	3.502857	2.841294	1.388917
C	4.473083	3.786296	1.037010
C	5.597794	3.977352	1.838779
C	5.764893	3.223546	3.001005
C	4.802039	2.279173	3.358392
C	3.676687	2.090195	2.556666
N	-0.140778	3.019458	0.367771
C	-1.046323	3.667023	1.167397
C	-0.393438	4.174214	2.349957
C	0.916208	3.831481	2.252104
C	1.067059	3.113816	1.009716
C	-2.415464	3.808153	0.915375
C	-3.060846	3.243984	-0.188930
N	-2.471928	2.475448	-1.160689
C	-3.479496	2.106181	-2.013322
C	-4.734171	2.666880	-1.574300
C	-4.472653	3.380958	-0.450198
C	-3.235800	4.581968	1.894508
C	-4.183200	3.933752	2.695589
C	-4.946940	4.654526	3.612712
C	-4.772996	6.033360	3.737477
C	-3.831197	6.687157	2.942439
C	-3.066111	5.964933	2.027254
Cl	-0.245729	4.197111	-2.538951
N	-0.107944	-1.773741	-0.126866
C	-0.627056	-3.165953	-0.279509
C	0.399134	-4.150848	0.260366
O	1.641196	-4.004260	-0.402524
C	2.176176	-2.711531	-0.197166
C	1.252479	-1.641356	-0.754371
H	-2.772288	-0.237945	-5.484598
H	-0.132928	-0.612967	-5.847864
H	-5.681638	2.541886	-2.079993
H	-5.164436	3.954654	0.150692
H	-0.883370	4.715253	3.147496
H	1.716162	4.045996	2.947201
H	4.214944	0.611254	-3.131898
H	4.676077	1.660185	-0.698966
H	-5.288120	-0.339372	-2.368052
H	-4.136222	2.197508	-5.632788
H	-6.199170	1.568252	-6.855616
H	-7.814149	-0.022959	-5.836327
H	-7.353510	-0.976923	-3.587263
H	-4.315852	2.858714	2.598871
H	-2.333445	6.473837	1.405617
H	-5.676189	4.138519	4.230350
H	-3.692196	7.760533	3.032264
H	-5.368294	6.595434	4.450922
H	4.340025	4.375178	0.132701
H	2.925228	1.354666	2.833907
H	6.341814	4.716330	1.556080
H	4.926178	1.688090	4.261056
H	6.640813	3.371924	3.625560
H	2.879324	-1.716746	-3.690076
H	1.834909	1.531634	-6.296249
H	4.242765	-2.728200	-5.488907
H	3.204245	0.525648	-8.101318
H	4.413405	-1.609994	-7.703021
H	0.533972	-4.015723	1.343647
H	0.051557	-5.168354	0.077119
H	-0.799294	-3.319845	-1.345826
H	-1.576428	-3.235116	0.252704
H	2.350596	-2.542061	0.876250
H	3.134649	-2.666276	-0.717281
H	1.618793	-0.634263	-0.544206
H	1.105287	-1.764024	-1.832395
H	-0.016139	-1.546207	0.871948
H	-3.932741	0.321059	0.918815
H	-3.497939	0.540587	0.359688
C	-1.058210	-0.679735	-0.726956
O	-0.616132	0.448267	-0.409900
O	-1.992782	-1.092673	-1.365327

RC_a

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scf done: -3092.246514

C	3.393311	0.963915	-2.566755
C	1.958706	1.002255	-2.732219
N	1.379671	1.660102	-1.681270
C	2.401398	2.004734	-0.838661
C	3.666638	1.577790	-1.386951
C	1.280605	0.417641	-3.809376
C	2.085598	-0.320851	-4.827796
C	2.758700	-1.499775	-4.484522
C	3.510062	-2.191190	-5.433744
C	3.600116	-1.709889	-6.740291
C	2.935667	-0.534275	-7.091375
C	2.182907	0.154674	-6.141052
Al	-0.595967	2.010609	-1.398258
N	-0.989879	1.159781	-3.182395
C	-2.226127	0.975582	-3.738413
C	-2.124135	0.148964	-4.917934
C	-0.810930	-0.156603	-5.069252
C	-0.106654	0.488139	-3.985395
C	-3.435184	1.487589	-3.253825
C	-4.677708	1.219540	-4.037186
C	-5.677762	0.391182	-3.513395
C	-6.838388	0.133107	-4.241616
C	-7.014224	0.703340	-5.503012
C	-6.023556	1.531189	-6.032263
C	-4.862037	1.785983	-5.303919
C	2.265224	2.622337	0.408747
C	3.500712	2.839961	1.221922
C	4.401235	3.859422	0.895864
C	5.552394	4.056789	1.658453
C	5.814884	3.235017	2.755105
C	4.921900	2.215049	3.085767
C	3.771222	2.019190	2.322552
N	-0.183922	2.927853	0.349897
C	-1.076849	3.520382	1.201773
C	-0.397997	3.987985	2.388200
C	0.916919	3.691689	2.228982
C	1.043027	3.033100	0.950035
C	-2.449222	3.680287	0.975147
C	-3.107689	3.212539	-0.167304
N	-2.542965	2.489333	-1.183181
C	-3.552634	2.220562	-2.067427
C	-4.786596	2.815907	-1.609515
C	-4.510086	3.432685	-0.432879
C	-3.257277	4.395674	2.007694
C	-4.219361	3.707990	2.757170
C	-4.975958	4.373283	3.721153
C	-4.780978	5.736574	3.945539
C	-3.825681	6.430420	3.201914
C	-3.068258	5.763195	2.239943
Cl	-0.280931	4.156103	-2.534348
N	0.180746	-1.657387	-0.472434
C	0.307913	-2.985497	-1.049905
C	1.011639	-3.907112	-0.064379
O	2.260911	-3.371304	0.346607
C	2.082660	-2.108721	0.973224
C	1.436391	-1.111763	0.024436
H	-2.955907	-0.165429	-5.533011
H	-0.353357	-0.769838	-5.833136
H	-5.731062	2.773608	-2.134248
H	-5.183437	3.994635	0.199516
H	-0.873456	4.479647	3.225539
H	1.735209	3.900079	2.904653
H	4.090633	0.520335	-3.263829
H	4.630696	1.729071	-0.920809
H	-5.536749	-0.055114	-2.531613
H	-4.090904	2.433133	-5.714734
H	-6.154746	1.981097	-7.012093
H	-7.918300	0.503379	-6.070548
H	-7.603548	-0.515152	-3.824492
H	-4.369249	2.645182	2.582287
H	-2.326259	6.304196	1.657652
H	-5.716289	3.825917	4.297358
H	-3.670763	7.492491	3.368246
H	-5.370583	6.255598	4.695476
H	4.194029	4.499875	0.041882
H	3.073840	1.224151	2.577446
H	6.242471	4.853517	1.396305
H	5.120842	1.570432	3.937035
H	6.710906	3.388726	3.349182
H	2.689665	-1.874367	-3.465764
H	1.668024	1.072592	-6.414023
H	4.023060	-3.106254	-5.152385
H	3.004584	-0.150680	-8.105140
H	4.185478	-2.247454	-7.480399
H	0.373700	-4.060273	0.819813
H	1.220638	-4.875136	-0.525372
H	0.887371	-2.938600	-1.987237
H	-0.686763	-3.368009	-1.281177
H	1.458240	-2.233266	1.871579
H	3.075166	-1.762909	1.272854
H	1.240246	-0.168234	0.536193
H	2.126349	-0.914795	-0.813236
H	-4.178466	0.275170	0.669816
H	-3.554875	0.499871	0.337063
C	-0.860759	-0.835402	-0.884398
O	-0.779507	0.394025	-0.467975
O	-1.796725	-1.307422	-1.542731

Morpholinium

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scf done: -288.207357

C	0.538454	-1.087659	0.023708
C	1.017155	0.355270	0.034649
C	-0.913762	1.107768	1.115481
C	-1.513998	-0.286953	1.179015
H	2.104597	0.371407	0.114976
H	0.861666	-1.617922	0.920851
H	0.870227	-1.623690	-0.865704
H	-1.241227	1.680388	1.983869
H	-1.246038	1.628291	0.205347
H	-1.222764	-0.801287	2.096497
H	-2.600273	-0.270855	1.088753
H	0.726313	0.867199	-0.894423
O	0.499595	1.049919	1.153681
N	-0.965511	-1.098359	0.037851
H	-1.324603	-0.731227	-0.851957
H	-1.308256	-2.062468	0.098800

RB_b

103

scf done: -3171.093364

C	-0.041348	0.009850	0.097021
C	-0.008140	0.061274	1.492057
C	1.198873	0.056865	2.172778
N	2.345775	0.011926	1.453034
C	2.377995	-0.014939	0.096077
C	1.176190	-0.028569	-0.589938
C	3.668244	-0.026295	2.208866
O	3.902584	-1.056683	2.798620
C	1.291090	0.106846	3.668307
C	3.709867	-0.014341	-0.592080
C	-1.340659	0.021072	-0.651825
O	4.277550	1.061819	2.065470
Al	6.039464	1.611806	2.704564
Cl	8.141190	2.397799	3.437829
N	5.147191	3.326157	3.257708
C	4.474641	3.563334	4.427368
C	4.021028	4.933224	4.470112
C	4.420939	5.514893	3.310159
C	5.107696	4.497855	2.550280
C	4.264552	2.639561	5.458122
C	4.818828	1.354038	5.470864
N	5.629858	0.819413	4.503129
C	6.003220	-0.416108	4.957315
C	5.399162	-0.677296	6.240979
C	4.648643	0.411513	6.550486
C	5.557461	4.679114	1.237678
C	6.088093	3.651428	0.450363
N	6.342998	2.368834	0.862902
C	6.856105	1.712608	-0.226443
C	6.887558	2.595870	-1.367784
C	6.437024	3.803594	-0.941523
C	6.793885	-1.343395	4.268866
C	7.191971	-1.181259	2.938404
N	6.855204	-0.131472	2.121626
C	7.396035	-0.416618	0.895850
C	8.112807	-1.667986	0.945815
C	8.000886	-2.132549	2.216046
C	7.345396	0.401649	-0.239717
C	7.897139	-0.145484	-1.514440
C	7.267461	-1.225131	-2.145591
C	7.780413	-1.751806	-3.330336
C	8.933026	-1.206709	-3.896370
C	9.570079	-0.133952	-3.271702
C	9.055101	0.393046	-2.088293
C	3.430798	3.065700	6.621595
C	2.061061	3.305887	6.458958
C	1.278437	3.707697	7.540635
C	1.857819	3.877817	8.798192
C	3.222789	3.644364	8.968572
C	4.003883	3.239949	7.886914
C	7.169124	-2.602991	4.974743
C	6.668674	-3.836314	4.538966
C	7.008067	-5.013157	5.204551
C	7.854221	-4.970849	6.313404
C	8.355944	-3.746333	6.755259
C	8.013196	-2.569191	6.090997
C	5.407938	6.036432	0.630684
C	6.229663	7.088715	1.049707
C	6.088791	8.360429	0.495016
C	5.123099	8.593524	-0.484316
C	4.298492	7.549925	-0.905885
C	4.440228	6.278791	-0.350867
H	5.516306	-1.588915	6.809158
H	4.035255	0.570527	7.425581
H	8.422358	-3.035141	2.634336
H	8.645567	-2.111730	0.116990
H	7.223950	2.323981	-2.357634
H	6.340152	4.716295	-1.511484
H	3.474486	5.381719	5.287241
H	4.255550	6.530884	2.981217
H	6.004712	-3.865549	3.678702
H	8.404683	-1.614954	6.433227
H	9.015894	-3.706293	7.616164
H	8.119973	-5.887108	6.831066
H	6.609433	-5.961786	4.858780
H	6.371409	-1.652546	-1.702654
H	9.556471	1.222688	-1.597200
H	7.279545	-2.586966	-3.809799
H	10.471411	0.290669	-3.702439
H	9.334108	-1.617040	-4.817660
H	6.981844	6.905250	1.812310
H	3.794622	5.466565	-0.674404
H	6.734269	9.167359	0.827409
H	3.542274	7.724954	-1.664721
H	5.012735	9.583222	-0.916009
H	1.609774	3.175962	5.478719
H	5.068023	3.063136	8.018143
H	0.217086	3.886856	7.400261
H	3.681685	3.779917	9.942877
H	1.249607	4.192142	9.640386
H	5.276725	-2.992361	0.739139
H	5.092531	-2.542427	1.300097
H	-0.927456	0.103394	2.065399
H	1.197098	-0.065280	-1.673759
H	3.579728	-0.284008	-1.639886
H	4.164540	0.979679	-0.527537
H	4.403090	-0.721397	-0.125182
H	0.324361	0.390790	4.082623
H	1.578289	-0.870606	4.064100
H	2.043166	0.833740	3.993854
H	-1.498140	1.008486	-1.097263
H	-1.322908	-0.708472	-1.464573
H	-2.180967	-0.196425	0.008383

R_b-D_2

103

scf done: -3058.951583

C	3.591788	-1.652275	-0.259232
C	2.166013	-1.709822	-0.418852
N	1.614663	-0.453243	-0.307736
C	2.684816	0.392907	-0.120984
C	3.910905	-0.351924	-0.059963
C	1.474833	-2.900148	-0.621043
C	2.267075	-4.151099	-0.812974
C	2.353004	-5.108288	0.199673
C	3.104229	-6.264574	0.012451
C	3.775332	-6.473944	-1.189269
C	3.695105	-5.522329	-2.202156
C	2.946433	-4.364456	-2.013914
Al	-0.296466	0.015619	-0.534451

N	-0.774691	-1.912116	-0.442320
C	-2.027518	-2.474821	-0.335059
C	-1.947417	-3.904133	-0.443954
C	-0.642693	-4.211695	-0.642068
C	0.086213	-2.975877	-0.603278
C	-3.216070	-1.778628	-0.147135
C	-4.484966	-2.544460	0.021899
C	-5.126980	-2.558405	1.261850
C	-6.314818	-3.263659	1.430095
C	-6.871976	-3.957510	0.359561
C	-6.237666	-3.944617	-0.879879
C	-5.048590	-3.241882	-1.048322
C	2.628546	1.779681	-0.052466
C	3.903298	2.544144	0.065318
C	4.822080	2.520818	-0.987893
C	6.013956	3.232081	-0.896188
C	6.300730	3.971518	0.248571
C	5.388121	4.002681	1.298950
C	4.193040	3.295196	1.206406
N	0.179603	1.926854	-0.304119
C	-0.680786	2.998421	-0.406898
C	0.045019	4.234472	-0.342961
C	1.352572	3.914752	-0.186075
C	1.432603	2.481579	-0.161267
C	-2.069155	2.930323	-0.458502
C	-2.768183	1.731980	-0.350331
N	-2.208718	0.474111	-0.262114
C	-3.277778	-0.387860	-0.146869
C	-4.514822	0.339939	-0.154619
C	-4.200189	1.649971	-0.298642
C	-2.837740	4.205662	-0.552384
C	-3.543659	4.686046	0.552663
C	-4.249587	5.882106	0.469253
C	-4.256309	6.606964	-0.719588
C	-3.553181	6.133434	-1.823772
C	-2.844976	4.938203	-1.740483
H	-2.787340	-4.576923	-0.377412
H	-0.200271	-5.186053	-0.774778
H	-5.493515	-0.107862	-0.086467
H	-4.869861	2.492090	-0.368249
H	-0.400616	5.215079	-0.395315
H	2.194902	4.582154	-0.099984
H	4.249086	-2.507075	-0.279749
H	4.885007	0.074725	0.117595
H	-4.689544	-2.016374	2.093577
H	-4.555543	-3.226370	-2.014241
H	-6.669537	-4.478945	-1.717638
H	-7.797526	-4.505369	0.489989
H	-6.803256	-3.271603	2.397180
H	-3.532006	4.120079	1.478510
H	-2.295562	4.567285	-2.598807
H	-4.791303	6.248521	1.333064
H	-3.556046	6.693131	-2.751455
H	-4.806583	7.537965	-0.784655
H	4.584467	1.948779	-1.878895
H	3.479550	3.329097	2.022125
H	6.717234	3.211505	-1.720231
H	5.604518	4.577931	2.191209
H	7.230140	4.523750	0.320279
H	1.834874	-4.943316	1.138189
H	2.884051	-3.619727	-2.800044
H	3.167215	-6.999403	0.806120
H	4.214995	-5.679871	-3.139577
H	4.359583	-7.374633	-1.334963
H	-3.674684	0.820085	3.242619
H	-3.714515	0.775304	2.502405
C	0.300945	0.790861	2.776066
C	1.668751	0.854784	3.016043
C	2.423945	-0.315583	3.067080
C	1.744066	-1.520408	2.918458
C	0.364471	-1.515207	2.710700
N	-0.337271	-0.378624	2.599770
H	2.144533	1.820170	3.147619
H	2.278103	-2.464149	2.964459
C	-0.410367	-2.803286	2.665288
H	0.134633	-3.583313	2.132227
H	-0.584658	-3.158189	3.685280
H	-1.378636	-2.647720	2.190982
C	3.907647	-0.263790	3.303897
H	4.392918	-1.179070	2.963933
H	4.351903	0.585742	2.779853
H	4.114425	-0.141601	4.370726
C	-0.540395	2.037827	2.755713
H	-0.893930	2.258084	3.767506
H	0.031428	2.897591	2.399985
H	-1.414858	1.893719	2.121495
O	-0.292169	0.105661	-2.423197
H	0.579633	0.390418	-2.874478
H	-0.678003	-0.616155	-2.934242
Cl	2.220742	0.888193	-3.644363

$TS2_b$-D_2

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scf done: -3247.505129

C	5.199789	-8.511449	6.564434
C	6.546493	-8.097562	6.266301
N	6.830917	-6.919300	6.905330
C	5.696101	-6.580135	7.594185
C	4.674799	-7.573962	7.390725
C	7.411369	-8.806510	5.429468
C	6.948577	-10.114052	4.880828
C	6.706234	-11.196582	5.730200
C	6.276777	-12.415256	5.214073
C	6.080756	-12.563432	3.843565
C	6.318801	-11.488934	2.990519
C	6.752640	-10.271802	3.506326
Al	8.475487	-5.794107	6.668161
N	9.245750	-7.147447	5.393082
C	10.504664	-7.155956	4.844306
C	10.753301	-8.415831	4.195300
C	9.627140	-9.158989	4.332673
C	8.689206	-8.363250	5.077608
C	11.438503	-6.115344	4.912351
C	12.770410	-6.306444	4.268166
C	13.923596	-6.305057	5.061332
C	15.176506	-6.487247	4.485277
C	15.295694	-6.672864	3.110179
C	14.153128	-6.688320	2.315113
C	12.899107	-6.511320	2.891971
C	5.529767	-5.449835	8.399069
C	4.213238	-5.257454	9.077080
C	3.095811	-4.865641	8.336858
C	1.866239	-4.682301	8.962351
C	1.742863	-4.890102	10.333674
C	2.853153	-5.281124	11.077089
C	4.083199	-5.463766	10.451661
N	7.752587	-4.467653	7.995265
C	8.360493	-3.315813	8.421443
C	7.500296	-2.609578	9.337457
C	6.354333	-3.326166	9.430598
C	6.518444	-4.485802	8.592269
C	9.612338	-2.849123	8.015536
C	10.418934	-3.499438	7.080216
N	10.139086	-4.685404	6.448319
C	11.223240	-4.947957	5.647446
C	12.164530	-3.860088	5.716266
C	11.672665	-2.969728	6.610684
C	10.108914	-1.562733	8.588529
C	11.176466	-1.557176	9.488826
C	11.646119	-0.358018	10.016328
C	11.054461	0.846995	9.646617
C	9.991062	0.848869	8.747788
C	9.520310	-0.350518	8.221477
H	7.600176	-4.924334	5.392515
H	13.078746	-3.793968	5.148379
H	12.104381	-2.031269	6.921286
H	11.676849	-8.697057	3.715536
H	9.449622	-10.164603	3.985853
H	4.724115	-9.400278	6.181569
H	3.689066	-7.548632	7.827837
H	7.747576	-1.683174	9.831059
H	5.473426	-3.100453	10.010642
H	13.821388	-6.175733	6.134237
H	12.011047	-6.536345	2.271995
H	14.235459	-6.838473	1.244921
H	16.272381	-6.811426	2.661869
H	16.060338	-6.488851	5.112352
H	6.862566	-11.080854	6.797217
H	6.936020	-9.432429	2.843831
H	6.097927	-13.249167	5.882446
H	6.164584	-11.596812	1.923420
H	5.744386	-13.511986	3.442143
H	3.196893	-4.702453	7.268898
H	4.949136	-5.770102	11.028566
H	1.006173	-4.375215	8.379115
H	2.762553	-5.446602	12.144147
H	0.785578	-4.747702	10.820882
H	11.636131	-2.497673	9.773854
H	8.692811	-0.351731	7.519576
H	12.472889	-0.365743	10.716757
H	9.528593	1.783737	8.453930
H	11.420688	1.780619	10.056844
C	9.209671	-5.105441	2.359512
C	10.220243	-4.832504	1.457527
C	10.981712	-3.667934	1.579128
C	10.649920	-2.753341	2.581636
C	9.609849	-3.020317	3.451043
N	8.960089	-4.195563	3.321642
H	10.424115	-5.546233	0.668214
H	11.195754	-1.824036	2.686866
C	9.112295	-2.067370	4.489729
H	8.563667	-2.587372	5.276939
H	9.941899	-1.513535	4.927711
H	8.433702	-1.354135	4.013937
C	12.147126	-3.425915	0.669842
H	11.960246	-3.832089	-0.324202
H	12.378675	-2.364382	0.593493
H	13.023623	-3.937764	1.080658
C	8.364863	-6.339143	2.324109
H	9.000264	-7.227110	2.338961
H	7.679771	-6.376608	3.172115
H	7.785076	-6.352702	1.398862
H	8.282376	-4.450842	4.064787
C	5.973565	-4.498074	5.113250
O	5.880844	-3.470539	5.680943
O	5.590795	-5.389554	4.442808
O	9.339527	-6.776915	8.134652
H	10.328810	-6.682557	8.270626
H	8.924879	-6.706552	9.002815
Cl	12.266765	-6.572225	8.641595

7.0 X-ray diffraction analysis

The crystallization experiments with $[Al(TPP)(OH_2)_2]Cl$ yielded two kinds of solvates of this cationic complex with different solvating molecules based on the crystallization conditions. The crystals of $[Al(TPP)(OH_2)_2]Cl{\cdot}CH_2Cl_2{\cdot}2Et_2O$ separated from the solution of $[Al(TPP)(OH_2)_2]Cl$ (cca 4 mg) in dichloromethane (3 mL) after vapours of diethylether were allowed to diffuse into it whereas the crystals of $[Al(TPP)(OH_2)_2]Cl{\cdot}C_8H_{11}N{\cdot}2CH_2Cl_2$ (where $C_8H_{11}N$ stands for 2,4,6-collidine) were acquired by the diffusion of vapours of hexane into the solution of $[Al(TPP)(OH_2)_2]Cl$ (cca 4 mg) and 2,4,6-collidine (4 µL) in dichloromethane (3 ml).

The crystallization of a reduced aluminium TPP complex (cca 10 mg) obtained from the reaction between AlH_3 and H_2TPP from a green dichloromethane-diethylether (1:1) solution (cca 4 ml) mixed with heptane (cca 2 ml) afforded purple crystals of $[Al(TPP)(Et_2O)_2]$ that developed in a green mother liquor.

Selected crystals were attached to goniometer heads of a Bruker D8 VENTURE Kappa Duo diffractometer with a PHOTONIII detector, an Incoatec IμS microfocus sealed tube source and a Cryostream Cooler (Oxford Cryostreams). The diffraction data ($\pm h$, $\pm k$, $\pm l$, $2\theta \leq 55°$) were collected at 120(2) K using monochromated MoK_α radiation (λ = 0.71073 Å) and reduced using the software of the diffractometer (SAINT[12]). The data were corrected for absorption using methods incorporated in the diffractometer software (SADABS[13]).

Direct methods (SHEXT-2018[14]) were implemented in the elucidation of the crystal structures. The structures were refined by weighted full-matrix least-squares against F^2 method (SHELXL-2019[15]). All non-hydrogen atoms were refined with anisotropic displacement parameters. A corresponding difference electron density maximum was identified for each hydrogen atom and these were then refined isotropically. All the C-H hydrogen atoms were further refined as riding atoms with U_{iso}(H) = 1.2 U_{eq}(pivot carbon atom) in the case of CH and CH_2 groups or with U_{iso}(H) = 1.5 U_{eq}(pivot carbon atom) in the case of CH_3 groups. The hydrogen atoms of water molecules were held in the positions of their corresponding difference electron density maxima using the rigid-body model with U_{iso}(H) = 1.5 U_{eq}(pivot oxygen atom). The symmetrically independent ethyl group of coordinated diethylether moiety in the structure of $[Al(TPP)(Et_2O)_2]$ was modelled disordered over two positions. The positions were refined as equivalent with relative occupancy ratio of 7:3.

Selected structure solution parameters are listed in Table S7 (structures of $[Al(TPP)(OH_2)_2]Cl{\cdot}CH_2Cl_2{\cdot}2Et_2O$ and $[Al(TPP)(OH_2)_2]Cl{\cdot}C_8H_{11}N{\cdot}2CH_2Cl_2$) and Table S8 (structure of $[Al(TPP)(Et_2O)_2]$). All geometric parameters and graphics were calculated and plotted using PLATON[16] software. Displacement ellipsoid ORTEP[17] plots are contained in the Figure S26 (structures of

[Al(TPP)$(OH_2)_2$]Cl·CH_2Cl_2·2Et_2O and [Al(TPP)$(OH_2)_2$]Cl·$C_8H_{11}N$·2CH_2Cl_2) and Figure S27 (structure of [Al(TPP)$(Et_2O)_2$]). The respective selected bond parameters of the [Al(TPP)$(OH_2)_2$]$^+$ cation in the structures of [Al(TPP)$(OH_2)_2$]Cl·CH_2Cl_2·2Et_2O and [Al(TPP)$(OH_2)_2$]Cl·$C_8H_{11}N$·2CH_2Cl_2 are listed in Table S9 and Table S10, respectively. The selected bond parameters of the [Al(TPP)$(Et_2O)_2$] complex are listed in Table S11. The provided values are rounded with respect to their estimated standard deviations that are given with one decimal place. The associated crystallographic information files can be accessed in Cambridge Crystallographic Data Centre at https://www.ccdc.cam.ac.uk/structures/ under submission codes CCDC-2357273, CCDC-2357274 and CCDC-2386191, respectively.

Table S7: Basic crystallographic data and structure refinement details for the crystals of $[Al(TPP)(OH_2)_2]Cl{\cdot}CH_2Cl_2{\cdot}2Et_2O$ and $[Al(TPP)(OH_2)_2]Cl{\cdot}C_8H_{11}N{\cdot}2CH_2Cl_2$.

Structure code	$[Al(TPP)(OH_2)_2]Cl{\cdot}CH_2Cl_2{\cdot}2Et_2O$	$[Al(TPP)(OH_2)_2]Cl{\cdot}C_8H_{11}N{\cdot}2CH_2Cl_2$
Empirical formula	$C_{53}H_{54}AlCl_3N_4O_4$	$C_{54}H_{47}AlCl_5N_5O_2$
Formula weight [g·mol^{-1}]	944.33	1002.19
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
a [Å]	12.8578(4)	13.4603(5)
b [Å]	25.901(2)	14.4286(5)
c [Å]	15.8434(6)	14.8360(5)
α [°]		65.646(1)
β [°]	113.448(1)	68.390(1)
γ [°]		83.657(1)
V [Å^3]	4840.6(4)	2437.5(2)
Z	4	2
F(000)	1984	1040
Calculated density [g·cm^3]	1.296	1.365
μ(Mo Kα) [mm^{-1}]	0.257	0.364
crystal size [mm]	0.124 x 0.346 x 0.350	0.060 x 0.092 x 0.355
θ range [°]	1.897–29.154	2.006–27.461
Collected diffractions	145016	92637
Independent diffractions	13044	11148
Observed[a] diffractions	11525	10178
R_{int}[b] [%]	4.38	3.76
Number of parameters	590	607
R, wR[c] (observed) [%]	4.89, 11.41	4.24, 10.15
R, wR[c] (all data) [%]	5.63, 11.82	4.64, 10.39
Goodness of fit[d]	1.086	1.051
$\Delta\rho_{max}$ and $\Delta\rho_{min}$ (e·Å^{-3})	−0.791, 1.098	−0.630, 0.691
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$; where $P = (F_o^2 + 2F_c^2)/3$.	
	a = 0.0449	a = 0.0382
	b = 4.0219	b = 2.4623
CCDC submission code	2357273	2357274

[a] $I > 2\sigma(I)$

[b] $R_{int} = \Sigma|F_o^2 - F_{o,mean}^2|/\Sigma F_o^2$

[c] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR(F^2) = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma w(F_o^2)^2]^{½}$

[d] $S = [\Sigma(w(F_o^2 - F_c^2)^2)/(N_{diffrns} - N_{par})]^{½}$

Table S8: Basic crystallographic data and structure refinement details for the crystals of [Al(TPP)(Et_2O)$_2$].

Structure code	[Al(TPP)(Et_2O)$_2$]
Empirical formula	$C_{52}H_{48}AlN_4O_2$
Formula weight [g·mol^{-1}]	787.92
Crystal system	tetragonal
Space group	$P4_2/n$
a [Å]	14.4907(3)
b [Å]	
c [Å]	9.9423(3)
α [°]	
β [°]	
γ [°]	
V [Å^3]	2087.7(1)
Z	2
F(000)	834
Calculated density [g·cm^3]	1.253
μ(Mo Kα) [mm^{-1}]	0.096
crystal size [mm]	0.150 x 0.182 x 0.283
θ range [°]	2.484–27.482
Collected diffractions	35401
Independent diffractions	2390
Observed[a] diffractions	2275
R_{int}[b] [%]	3.22
Number of parameters	140
R, wR[c] (observed) [%]	3.90, 9.67
R, wR[c] (all data) [%]	4.06, 9.78
Goodness of fit[d]	1.115
$\Delta\rho_{max}$ and $\Delta\rho_{min}$ (e·Å^{-3})	−0.390, 0.308
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$; where $P = (F_o^2 + 2F_c^2)/3$.
	a = 0.0374
	b = 1.1782
CCDC submission code	2386191

[a] $I > 2\sigma(I)$

[b] $R_{int} = \Sigma|F_o^2 - F_{o,mean}^2|/\Sigma F_o^2$

[c] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR(F^2) = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma w(F_o^2)^2]^{½}$

[d] $S = [\Sigma(w(F_o^2 - F_c^2)^2)/(N_{diffrns} - N_{par})]^{½}$

Table S9: List of selected bond lengths and angles in $[Al(TPP)(OH_2)_2]Cl \cdot CH_2Cl_2 \cdot 2Et_2O$.

bond	value [Å]	angle	value [°]	torsion	value [°]
Al1-O1	1.927(1)	O1-Al1-O2	177.94(5)	C4-N1-C1-C20	179.3(1)
Al1-O2	1.916(1)	O1-Al1-N1	90.26(5)	Al1-N1-C1-C20	-1.2(2)
Al1-N1	2.012(1)	O1-Al1-N2	91.18(5)	C4-N1-C1-C2	-0.7(2)
Al1-N2	1.998(1)	O1-Al1-N3	88.20(5)	Al1-N1-C1-C2	178.9(1)
Al1-N3	2.014(1)	O1-Al1-N4	89.76(5)	C1-N1-C4-C5	177.9(1)
Al1-N4	1.993(1)	O2-Al1-N1	90.54(5)	Al1-N1-C4-C5	-1.6(2)
N1-C1	1.377(2)	O2-Al1-N2	90.73(5)	C1-N1-C4-C3	0.3(2)
N1-C4	1.375(2)	O2-Al1-N3	91.01(5)	Al1-N1-C4-C3	-179.3(1)
N2-C6	1.376(2)	O2-Al1-N4	88.34(5)	C9-N2-C6-C5	-178.7(1)
N2-C9	1.377(2)	N1-Al1-N2	89.33(5)	Al1-N2-C6-C5	0.7(2)
N3-C11	1.375(2)	N1-Al1-N3	178.42(5)	C9-N2-C6-C7	1.4(2)
N3-C14	1.377(2)	N1-Al1-N4	90.41(5)	Al1-N2-C6-C7	-179.1(1)
N4-C16	1.376(2)	N2-Al1-N3	90.32(5)	C6-N2-C9-C10	-177.5(1)
N4-C19	1.378(2)	N2-Al1-N4	179.03(6)	Al1-N2-C9-C10	3.0(2)
C1-C2	1.439(2)	C1-N1-Al1	126.80(9)	C6-N2-C9-C8	-0.7(2)
C2-C3	1.352(2)	C4-N1-Al1	127.72(9)	Al1-N2-C9-C8	179.9(1)
C3-C4	1.437(2)	C6-N2-Al1	127.87(9)	C14-N3-C11-C10	-179.3(1)
C4-C5	1.394(2)	C9-N2-Al1	126.70(9)	Al1-N3-C11-C10	1.7(2)
C5-C6	1.394(2)	C11-N3-Al1	127.05(9)	C14-N3-C11-C12	0.4(2)
C6-C7	1.436(2)	C14-N3-Al1	127.22(9)	Al1-N3-C11-C12	-178.6(1)
C7-C8	1.353(2)	C16-N4-Al1	127.35(9)	C11-N3-C14-C15	177.4(1)
C8-C9	1.436(2)	C19-N4-Al1	127.11(9)	Al1-N3-C14-C15	-3.7(2)
C9-C10	1.395(2)	N1-C1-C2	110.3(1)	C11-N3-C14-C13	-1.3(2)
C10-C11	1.396(2)	N1-C1-C20	125.6(1)	Al1-N3-C14-C13	177.7(1)
C11-C12	1.439(2)	N1-C4-C3	110.4(1)	C19-N4-C16-C15	179.0(1)
C12-C13	1.352(2)	N1-C4-C5	125.4(1)	Al1-N4-C16-C15	0.0(2)
C13-C14	1.441(2)	N2-C6-C5	125.7(1)	C19-N4-C16-C17	-1.4(2)
C14-C15	1.395(2)	N2-C6-C7	110.3(1)	Al1-N4-C16-C17	179.6(1)
C15-C16	1.396(2)	N2-C9-C8	110.4(1)	C16-N4-C19-C20	-176.2(1)
C16-C17	1.435(2)	N2-C9-C10	126.1(1)	Al1-N4-C19-C20	2.8(2)
C17-C18	1.348(2)	N3-C11-C10	125.3(1)	C16-N4-C19-C18	1.4(2)
C18-C19	1.437(2)	N3-C11-C12	110.3(1)	Al1-N4-C19-C18	-179.6(1)
C19-C20	1.396(2)	N3-C14-C13	110.0(1)		
C1-C20	1.397(2)	N3-C14-C15	125.2(1)		
C5-C27	1.494(2)	N4-C16-C15	125.8(1)		
C10-C33	1.493(2)	N4-C16-C17	110.2(1)		
C15-C39	1.491(2)	N4-C19-C18	110.1(1)		
C20-C21	1.490(2)	N4-C19-C20	125.8(1)		

Table S10: List of selected bond lengths and angles in $[Al(TPP)(OH_2)_2]Cl \cdot C_8H_{11}N \cdot 2CH_2Cl_2$.

bond	value [Å]	angle	value [°]	torsion	value [°]
Al1-O1	1.962(1)	O1-Al1-O2	179.29(5)	C4-N1-C1-C20	-176.8(2)
Al1-O2	1.883(1)	O1-Al1-N1	89.94(5)	Al1-N1-C1-C20	-1.5(2)
Al1-N1	1.995(1)	O1-Al1-N2	88.35(5)	C4-N1-C1-C2	0.8(2)
Al1-N2	2.004(1)	O1-Al1-N3	89.26(5)	Al1-N1-C1-C2	176.1(1)
Al1-N3	1.990(1)	O1-Al1-N4	88.33(5)	C1-N1-C4-C5	-176.1(1)
Al1-N4	2.003(1)	O2-Al1-N1	90.75(5)	Al1-N1-C4-C5	8.6(2)
N1-C1	1.378(2)	O2-Al1-N2	91.82(5)	C1-N1-C4-C3	0.9(2)
N1-C4	1.380(2)	O2-Al1-N3	90.05(5)	Al1-N1-C4-C3	-174.4(1)
N2-C6	1.376(2)	O2-Al1-N4	91.49(5)	C9-N2-C6-C5	178.8(1)
N2-C9	1.378(2)	N1-Al1-N2	89.68(5)	Al1-N2-C6-C5	-1.2(2)
N3-C11	1.379(2)	N1-Al1-N3	179.20(6)	C9-N2-C6-C7	1.4(2)
N3-C14	1.376(2)	N1-Al1-N4	90.62(5)	Al1-N2-C6-C7	-178.7(1)
N4-C16	1.380(2)	N2-Al1-N3	90.30(5)	C6-N2-C9-C10	175.5(2)
N4-C19	1.377(2)	N2-Al1-N4	176.66(5)	Al1-N2-C9-C10	-4.4(2)
C1-C2	1.439(2)	C1-N1-Al1	127.1(1)	C6-N2-C9-C8	-2.2(2)
C2-C3	1.353(2)	C4-N1-Al1	127.2(1)	Al1-N2-C9-C8	177.9(1)
C3-C4	1.437(2)	C6-N2-Al1	127.2(1)	C14-N3-C11-C10	-174.6(2)
C4-C5	1.392(2)	C9-N2-Al1	127.0(1)	Al1-N3-C11-C10	1.4(2)
C5-C6	1.398(2)	C11-N3-Al1	127.1(1)	C14-N3-C11-C12	1.3(2)
C6-C7	1.438(2)	C14-N3-Al1	127.0(1)	Al1-N3-C11-C12	177.3(1)
C7-C8	1.355(2)	C16-N4-Al1	127.1(1)	C11-N3-C14-C15	-178.3(1)
C8-C9	1.437(2)	C19-N4-Al1	126.6(1)	Al1-N3-C14-C15	5.6(2)
C9-C10	1.396(2)	N1-C1-C2	110.2(1)	C11-N3-C14-C13	-0.9(2)
C10-C11	1.399(2)	N1-C1-C20	125.6(1)	Al1-N3-C14-C13	-176.9(1)
C11-C12	1.437(2)	N1-C4-C3	110.1(1)	C19-N4-C16-C15	-179.3(1)
C12-C13	1.352(2)	N1-C4-C5	125.5(1)	Al1-N4-C16-C15	-8.5(2)
C13-C14	1.437(2)	N2-C6-C5	125.5(1)	C19-N4-C16-C17	0.6(2)
C14-C15	1.400(2)	N2-C6-C7	110.1(1)	Al1-N4-C16-C17	171.3(1)
C15-C16	1.399(2)	N2-C9-C8	110.0(1)	C16-N4-C19-C20	170.6(1)
C16-C17	1.440(2)	N2-C9-C10	125.4(1)	Al1-N4-C19-C20	-0.2(2)
C17-C18	1.352(2)	N3-C11-C10	125.7(1)	C16-N4-C19-C18	-2.1(2)
C18-C19	1.434(2)	N3-C11-C12	110.0(1)	Al1-N4-C19-C18	-172.8(1)
C19-C20	1.400(2)	N3-C14-C13	110.0(1)		
C1-C20	1.396(2)	N3-C14-C15	125.9(1)		
C5-C27	1.496(2)	N4-C16-C15	125.0(1)		
C10-C33	1.496(2)	N4-C16-C17	110.0(1)		
C15-C39	1.490(2)	N4-C19-C18	110.3(1)		
C20-C21	1.497(2)	N4-C19-C20	125.8(1)		

Table S11: List of selected bond lengths and angles in [Al(TPP)(Et_2O)$_2$].

bond	value [Å]	angle	value [°]	torsion	value [°]
Al1-O1	2.038(1)	O1-Al1-N1	89.66(3)	C4-N1-C1-C5	179.5(2)
Al1-N1	1.989(1)	C1-N1-Al1	127.4(1)	Al1-N1-C1-C5	5.8(2)
N1-C1	1.388(2)	C4-N1-Al1	127.2(1)	C4-N1-C1-C2	2.0(1)
N1-C4	1.390(2)	N1-C1-C2	110.3(1)	Al1-N1-C1-C2	-171.7(1)
C1-C2	1.426(2)	N1-C4-C3	110.3(1)	C1-N1-C4-C5	174.2(1)
C2-C3	1.361(2)	N1-C4-C5	125.2(1)	Al1-N1-C4-C5	-12.1(2)
C3-C4	1.427(2)	C1-C2-C3	107.2(1)	C1-N1-C4-C3	-2.8(2)
C4-C5	1.396(2)	C2-C3-C4	107.1(1)	Al1-N1-C4-C3	170.9(1)
C5-C6	1.493(2)	C3-C4-C5	124.5(1)	N1-C4-C5-C1	1.8(2)
C6-C7	1.391(2)	C4-C5-C1	123.5(1)	N1-C1-C5-C4	-7.5(2)
C7-C8	1.389(2)				
C8-C9	1.482(2)				
C9-C10	1.383(2)				
C10-C11	1.391(2)				
C11-C6	1.393(2)				

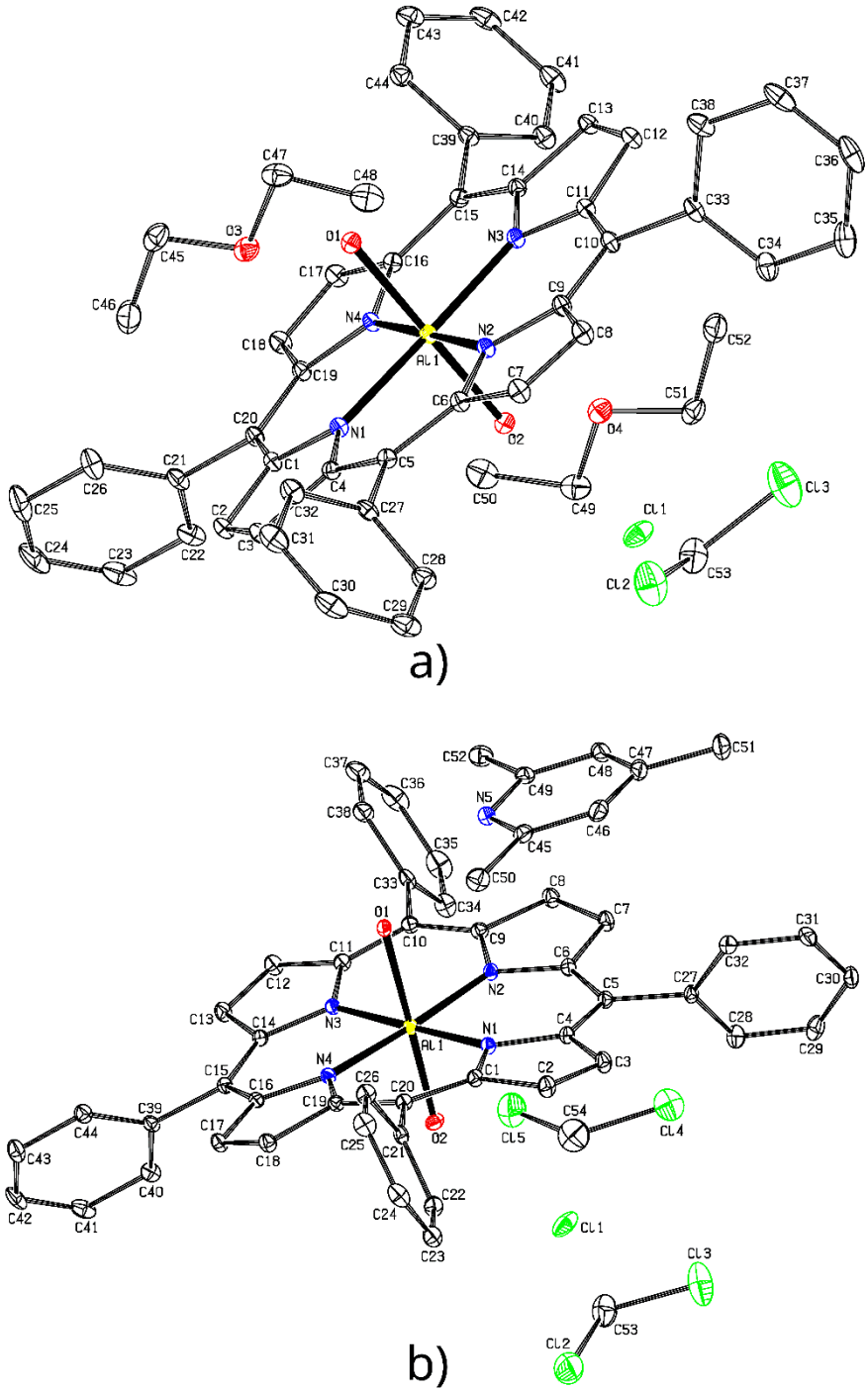

Figure S26: View of the asymmetric units in the crystal structures of $[Al(TPP)(OH_2)_2]Cl{\cdot}CH_2Cl_2{\cdot}2Et_2O$ (a) and $[Al(TPP)(OH_2)_2]Cl{\cdot}C_8H_{11}N{\cdot}2CH_2Cl_2$ (b) with the corresponding atom numbering schemes. All hydrogen atoms were omitted for the sake of clarity. Thermal displacement elipsoids were plotted at the 30 % probability level. Applied colours: C – black, Cl – green, N – blue, O – red, Al – yellow.

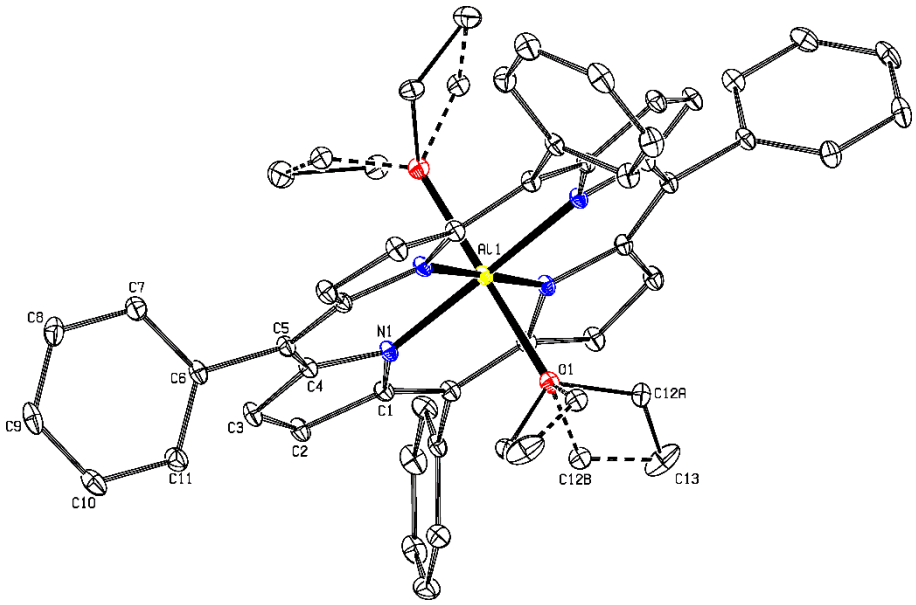

Figure S27: View of the complex [Al(TPP)(Et_2O)$_2$] in its crystal structure with the corresponding atom numbering scheme. Only the symmetrically independent part of the molecule is labelled. All hydrogen atoms were omitted for the sake of clarity. Thermal displacement elipsoids were plotted at the 30 % probability level. Applied colours: C – black, Cl – green, N – blue, O – red, Al – yellow.

The solvate $[Al(TPP)(OH_2)_2]Cl{\cdot}CH_2Cl_2{\cdot}2Et_2O$ crystallized in monoclinic system with space group $P2_1/n$ and four formula units in the unit cell (Figure S28). The solvate $[Al(TPP)(OH_2)_2]Cl{\cdot}C_8H_{11}N{\cdot}2CH_2Cl_2$ crystallized in triclinic system with space group $P{-}1$ and two formula units in the unit cell (Figure S29). The coordination surroundings of the aluminum central atom of the $[Al(TPP)(OH_2)_2]^+$ cation is a tetragonal bipyramid with the axial Al-O bonds relatively shorter than the equatorial Al-N bonds in both structures. The difference between Al-O and Al-N bond lengths falls in the range of 0.07–0.10 Å and 0.03–0.12 Å for $[Al(TPP)(OH_2)_2]Cl{\cdot}CH_2Cl_2{\cdot}2Et_2O$ and $[Al(TPP)(OH_2)_2]Cl{\cdot}C_8H_{11}N{\cdot}2CH_2Cl_2$, respectively. The porphyrin core adopts a ruffled conformation in both cases with the ruffle being relatively more pronounced in the case of the 2,4,6-collidine solvate. The corresponding ruffling torsion angle[18] (C1-N1-N3-C14 and C6-N2-N4-C19, respectively) values are 7.6(2)°, −6.1(2)° for the former structure and −16.6(2)°, 11.6(2)° for the latter. The phenyl groups of the thetraphenylporphyrin ligand are in both structures tilted out of the plane of the porphyrin core resulting in a synclinal or an anticlinal conformation at the pivotal C-C bond (C5-C27, C10-C33, C15-C39 and C20-C21). The corresponding torsion angles are listed in Table S12.

The complex $[Al(TPP)(Et_2O)_2]$ crystallized in tetragonal system with space group $P4_2/n$ with two formula units in the unit cell (Figure S30). The central aluminum atom Al1 and the oxygen atom O1 of the coordinated diethylether molecule occupy Wyckoff positions 2b with site symmetry −4 and 4f with site symmetry 2, respectively. Thus, only one fourth of the molecule is symmetrically independent. The aluminum central atom in the complex $[Al(TPP)(Et_2O)_2]$ has a similar tetragonal bipyramidal coordination environment to the cation $[Al(TPP)(OH_2)_2]^+$ with the difference between Al1-O1 and Al1-N1 bond lengths equal to 0.05 Å. The ruffling torsion angles C1-N1-N1-C4 are equal to 12.6(1)° or −12.6(1)° thanks to symmetry. The ruffle of the porphyrin core in the $[Al(TPP)(Et_2O)_2]$ complex is slightly more pronounced than in an analogous complex with tetrahydrofurane (THF), $[Al(TPP)(THF)_2]$ that has been described in the literature with ruffling torsion angle values of 4.2(3)° and −6.0(3)°.[19]

Table S12: Selected torsion angles related to the conformation of phenyl groups of $[Al(TPP)(OH_2)_2]^+$ cation in the structures of $[Al(TPP)(OH_2)_2]Cl{\cdot}CH_2Cl_2{\cdot}2Et_2O$ and $[Al(TPP)(OH_2)_2]Cl{\cdot}C_8H_{11}N{\cdot}2CH_2Cl_2$.

torsion angle	value [°]	
	$[Al(TPP)(OH_2)_2]Cl{\cdot}CH_2Cl_2{\cdot}2Et_2O$	$[Al(TPP)(OH_2)_2]Cl{\cdot}C_8H_{11}N{\cdot}2CH_2Cl_2$
C4-C5-C27-C28	110.7(2)	111.1(2)
C9-C10-C33-C34	70.3(2)	68.2(2)
C14-C15-C39-C40	66.3(2)	58.5(2)
C19-C20-C21-C22	68.3(2)	105.0(2)

The crystal structures of both solvates are dominated by columnar stacks of $[Al(TPP)(OH_2)_2]^+$ cations. Each void between neighbouring cations within one such stack in the structure of $[Al(TPP)(OH_2)_2]Cl{\cdot}CH_2Cl_2{\cdot}2Et_2O$ is occupied by the chloride anion and the solvating molecules of dichloromethane and diethylether (Figure S31a). In the case of the other solvate with 2,4,6-collidine, $[Al(TPP)(OH_2)_2]Cl{\cdot}C_8H_{11}N{\cdot}2CH_2Cl_2$, the voids between nearest complex cations in single stack accommodate either a pair of inversion related chloride anions and four dichloromethane molecules or a pair of collidine molecules (Figure S31b). The formation of such stacks is supported by a set of four hydrogen bonds donated by the water molecules coordinating central atom of aluminium in the $[Al(TPP)(OH_2)_2]^+$ cation in both structures. In the case of the crystal structure of the solvate $[Al(TPP)(OH_2)_2]Cl{\cdot}CH_2Cl_2{\cdot}2Et_2O$, two of the hydrogen bonds are accepted by the chloride anion and the other two by the oxygen atom of each solvating diethylether molecule (Table S13). Two of the four hydrogen bonds observed in the crystal structure of the solvate $[Al(TPP)(OH_2)_2]Cl{\cdot}C_8H_{11}N{\cdot}2CH_2Cl_2$ are also accepted by the chloride anion, but the other two are accepted by the nitrogen atom of the solvating collidine molecule (Table S14). These hydrogen bonds are assembled into infinite chains that propagate along the stack in the [1 0 1] direction in the case of the former structure and along the *c* axis in the case of the latter.

Table S13: Hydrogen bond parameters in the crystal structure of $[Al(TPP)(OH_2)_2]Cl{\cdot}CH_2Cl_2{\cdot}2Et_2O$.

D-H···A	symmetry operation	distance H···A [Å]	distance D···A [Å]	angle DHA [°]
O1-H1A···O3	*x*, *y*, *z*	1.91	2.699(2)	164
O1-H1B···Cl1	1/2+*x*, 3/2−*y*, 1/2+*z*	2.18	3.013(1)	176
O2-H2A···O4	*x*, *y*, *z*	1.85	2.725(2)	173
O2-H2B···Cl1	*x*, *y*, *z*	2.16	2.960(1)	172

Table S14: Hydrogen bond parameters in the crystal structure of $[Al(TPP)(OH_2)_2]Cl{\cdot}C_8H_{11}N{\cdot}2CH_2Cl_2$.

D-H···A	symmetry operation	distance H···A [Å]	distance D···A [Å]	angle DHA [°]
O1-H1A···N5	*x*, *y*, *z*	2.00	2.826(2)	171
O1-H1B···N5	1−*x*, 1−*y*, 2−*z*	2.10	2.888(2)	174
O2-H2A···Cl1	*x*, *y*, *z*	2.03	2.936(1)	174
O2-H2B···Cl1	1−*x*, 1−*y*, 1−*z*	2.11	2.984(1)	175

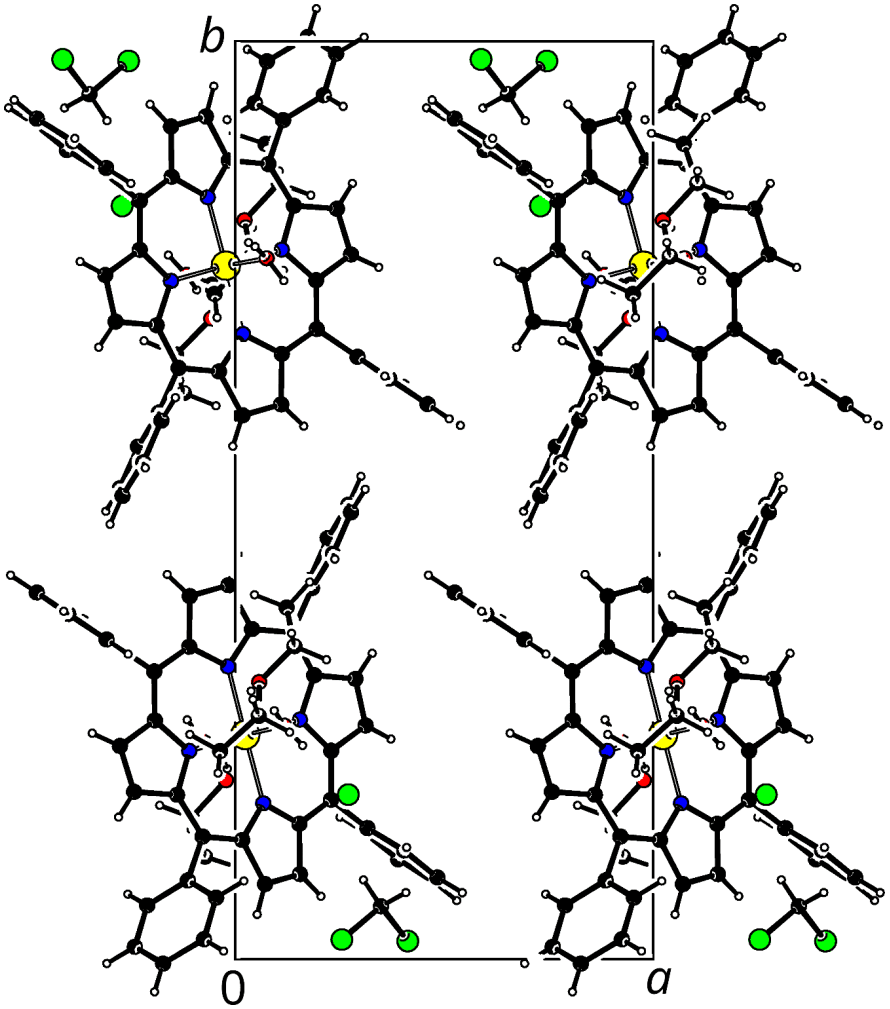

Figure S28: Crystal packing of $[Al(TPP)(OH_2)_2]Cl \cdot CH_2Cl_2 \cdot 2Et_2O$ viewed along the axis *c*. The unit cell is outlined by a solid line. Applied colors: C – black, H – black contour, Cl – green, N – blue, O – red, Al – yellow.

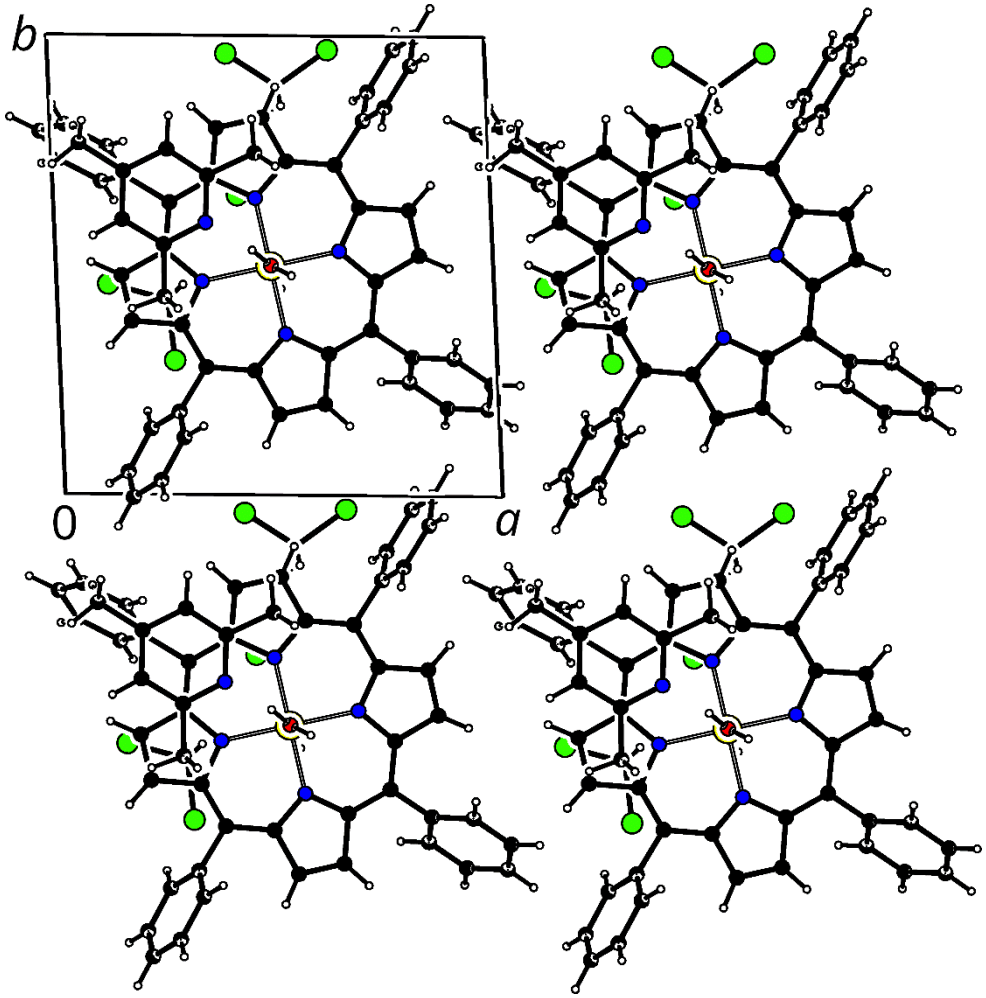

Figure S29: Crystal packing of $[Al(TPP)(OH_2)_2]Cl{\cdot}C_8H_{11}N{\cdot}2CH_2Cl_2$ viewed along the axis *c*. The unit cell is outlined by a solid line. Applied colors: C – black, H – black contour, Cl – green, N – blue, O – red, Al – yellow.

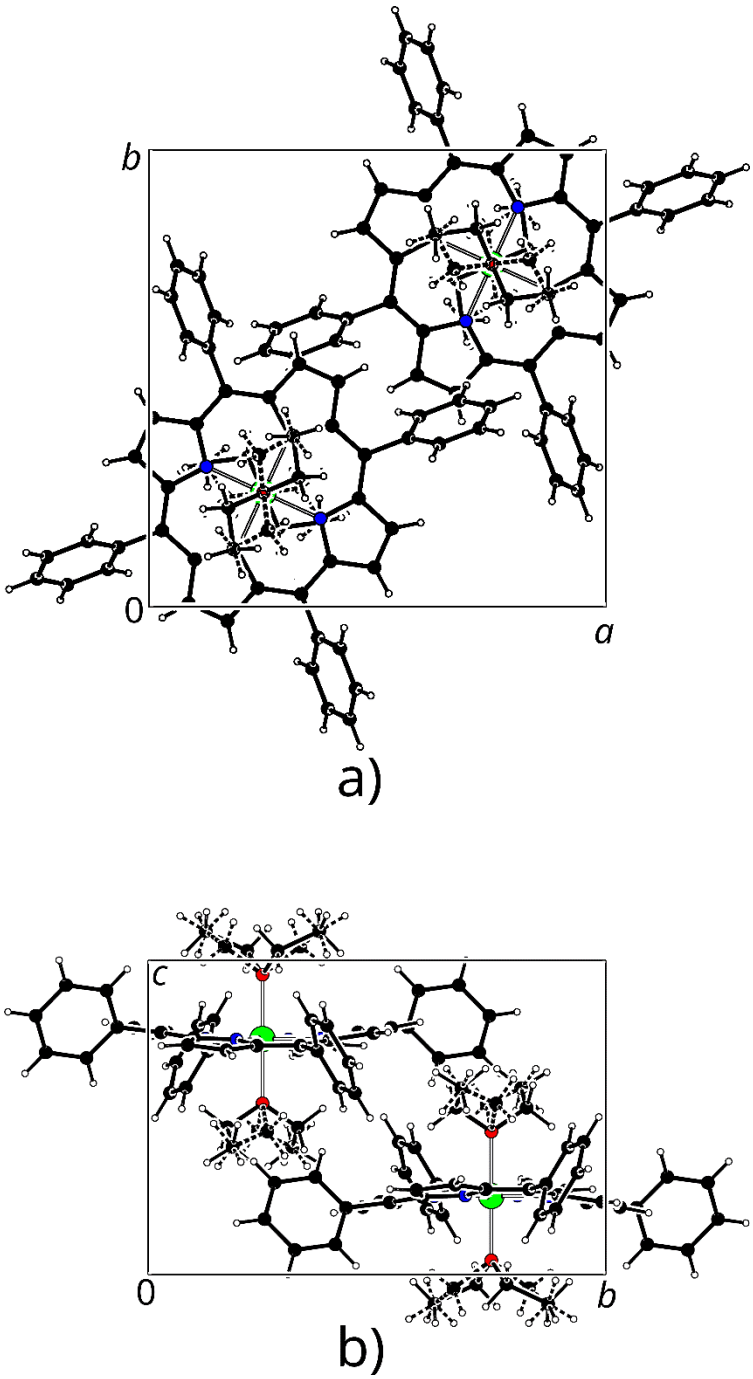

Figure S30: Crystal packing of [Al(TPP)(Et_2O)$_2$] viewed along the axis *c* (a) or along the axis *a* (b). The unit cell is outlined by a solid line. Applied colors: C – black, H – black contour, Al – green, N – blue, O – red.

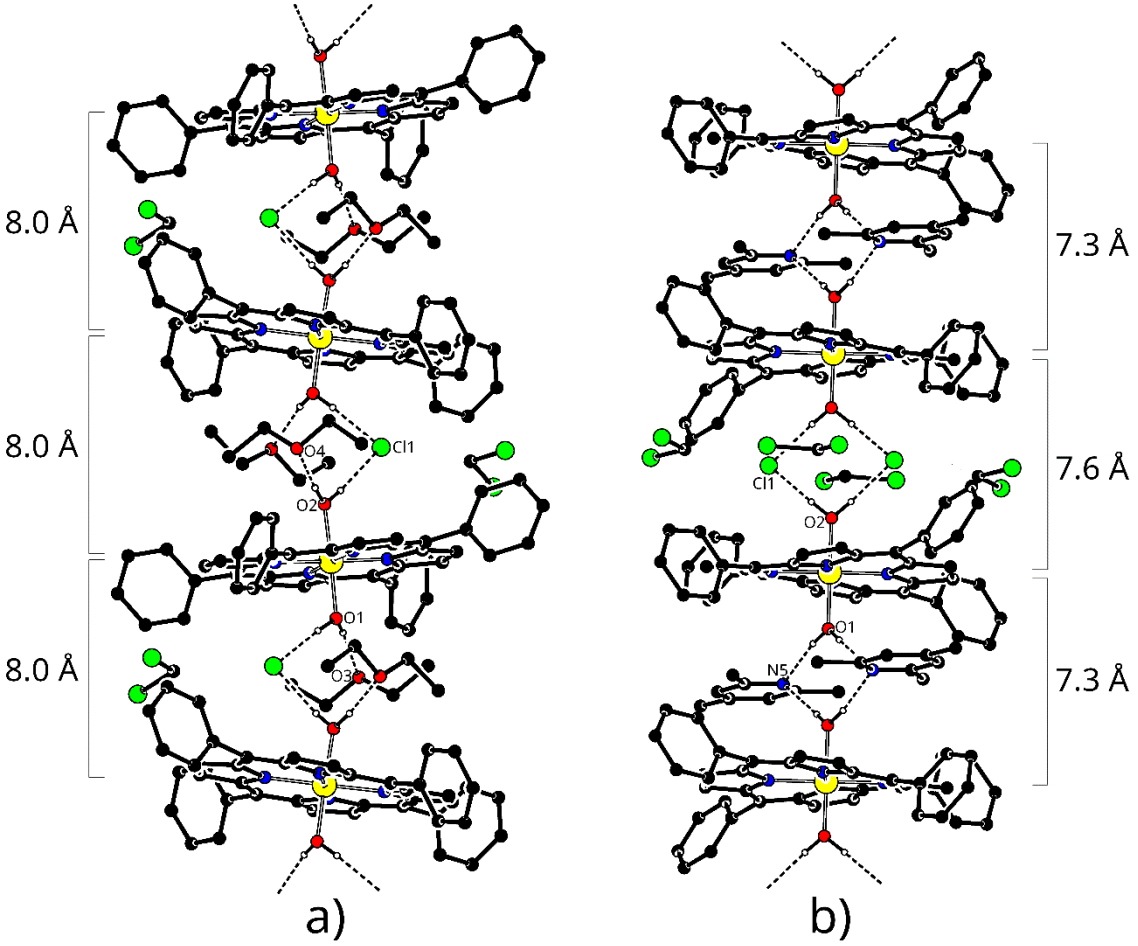

Figure S31: View of sections of chains of hydrogen bonds in the crystal structures of $[Al(TPP)(OH_2)_2]Cl{\cdot}CH_2Cl_2{\cdot}2Et_2O$ (a) and $[Al(TPP)(OH_2)_2]Cl{\cdot}C_8H_{11}N{\cdot}2CH_2Cl_2$ (b) with denoted approximate distances between central atoms of neighbouring complexes within one chain. All C-H hydrogen atoms were omitted for the sake of clarity. Hydrogen bonds are indicated by dashed lines. Applied colours: C – black, H – black contour, Cl – green, N – blue, O – red, Al – yellow.

8.0 References

[1] Y. Qin, H. Guo, X. Sheng, X. Wang, F. Wang, *Green Chem.* **2015**, *17*, 2853–2858.

[2] D. W. Stephan, G. Erker, *Angew. Chemie - Int. Ed.* **2010**, *49*, 46–76.

[3] G. J. E. Davidson, L. H. Tong, P. R. Raithby, J. K. M. Sanders, *Chem. Commun.* **2006**, 3087–3089.

[4] D. J. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratch, **2016**, Gaussian, Inc., Wallingford CT.

[5] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215–241.

[6] M. Cossi, V. Barone, R. Cammi, J. Tomasi, *Chem. Phys. Lett.* **1996**, *255*, 327–335.

[7] V. Barone, M. Cossi, J. Tomasi, *J. Chem. Phys.* **1997**, *107*, 3210–3221.

[8] E. Cancès, B. Mennucci, J. Tomasi, *J. Chem. Phys.* **1997**, *107*, 3032–3041.

[9] P. Ros, G. C. A. Schuit, *Theor. Chim. Acta* **1966**, *4*, 1–12.

[10] T. Lu, F. Chen, *J. Comput. Chem.* **2012**, *33*, 580–592.

[11] C. Y. Legault, **2020**, Cylview20, Université de Sherbrooke. (http://www.cylview.org)

[12] Bruker, *SAINT*, Bruker AXS Inc., Madison, Wisconsin, USA, 2019.

[13] Bruker, *SADABS*, Bruker AXS Inc., Madison, Wisconsin, USA, 2005.

[14] G. M. Sheldrick, Using phases to determine the space group. *Acta Crystallogr., Sect. A: Found. Adv.* **2018**, *74*, 353–353.

[15] G. M. Sheldrick, Crystal structure refinement with SHELXL. *Acta Crystallogr., Sect. C: Struct. Chem.* **2015**, *71*, 3–8.

[16] A. L. Spek, *checkCIF* validation ALERTS: what they mean and how to respond. *Acta Crystallogr., Sect. E: Crystallogr. Commun.* **2020**, *76*, 1–11.

[17] L. J. Farrugia, WinGX and ORTEP for Windows: an update. *J. Appl. Crystallogr.* **2012**, *45*, 849–854.

[18] T. Vangberg, A. Ghosh, A First-Principles Quantum Chemical Analysis of the Factors Controlling Ruffling Deformations of Porphyrins: Insights from the Molecular Structures and Potential Energy Surfaces of Silicon, Phosphorus, Germanium, and Arsenic Porphyrins and of a Peroxidase Compound I Model. *J. Am. Chem. Soc.* **1999**, *121*, 12154–12160.

[19] J. A. Cissell, T. P. Vaid, A. L. Rheingold, Aluminum Tetraphenylporphyrin and Aluminum Phtalocyanine Neutral Radicals. *Inorg. Chem.* **2006**, *45*, 2367–2369.