Supporting Information

5,15-*Meso*-diacylated calix[4]pyrroles: Structural diversities and enhanced binding towards dihydrogenphosphate ion

Sanjeev P. Mahanta, B. Sathish Kumar and Pradeepta K. Panda*

School of Chemistry, University of Hyderabad, Hyderabad, India, hyd-500046
Email: pkpsc@uohyd.ernet.in; pradeepta.panda@gmail.com

Instrumentation and reagents:

NMR spectra were recorded on a Bruker Avance-400 MHz and 500 MHz FT NMR spectrometer using tetramethylsilane (TMS, $\delta = 0$) as an internal standard at room temperature. Mass spectral determinations were carried out by Shimadzu-LCMS-2010 mass spectrometer and elemental analysis were obtained through Thermo Finnigan Flash EA 1112 analyzer. Melting points were determined by open capillary tubes on a BIO-TECH, India apparatus. IR spectra were recorded on a JASCO-FT-IR model 5300 and NICOLET 5700 FT-IR spectrometer. DSC data were collected in Pyris Diamond DSC, Perkin Elmer Calorimeter. Crystallographic data for *cis*-**6** (DCM solvate) was collected on Oxford Gemini A Ultra diffractometer with dual source. Mo-K_α (λ = 0.71073 Å) radiation was used to collect the X-ray reflections of the crystal. Data reduction was performed using CrysAlis^{Pro} 171.33.55 software.[S1] Structures were solved and refined using Olex2-1.0 with anisotropic displacement parameters for non-H atoms. Hydrogen atoms on N were located from the Fourier map in all of the crystal structures. All C–H atoms were fixed geometrically. Empirical absorption correction was done using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. A check of the final CIF file using PLATON[S2] did not show any missed symmetry.

Crystallographic data for 4, *cis*-**6** (water solvate), *trans*-**6** (both 1,2- and 1,3- alternate conformation) were collected on BRUKER SMART-APEX CCD diffractometer. Mo-K α (λ = 0.71073 Å) radiation was used to collect X-ray reflections on the single crystal. Data reduction was performed using Bruker SAINT[S3] software. Intensities for absorption were corrected using SADABS[S4] and refined using SHELXL-97[S5] with anisotropic displacement parameters for non-H atoms. Hydrogen atoms on O and N were experimentally located in difference electron density maps. All C–H atoms were fixed geometrically using HFIX command in SHELX-TL. A check of the final CIF file using PLATON[S2] did not show any missed symmetry.

Crystallographic data (excluding the structure factor) for structures **4**, *cis*-**6** (water and DCM solvate)**,** *trans*-**6** (the two polymorphs) in this paper have been deposited in the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 804419-22 and 804966. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

X-ray powder diffraction of all samples were recorded on Bruker D8 Advance diffractometer using Cu-Kα X-radiation (λ = 1.54056 Å) at 40 kV and 30 mA. Diffraction patterns were

collected over a 2θ range of 5-50° at a scan rate of 1° min^{-1}. Powder Cell 2.4 was used for Rietveld refinement.[S6]

Microcalorimetric titrations were performed using an isothermal titration calorimeter (ITC) purchased from Microcal Inc., MA. The Origin software provided by Microcal Inc. was used to calculate the binding constant (K_a) and the enthalpy change (ΔH). The solvent acetonitrile was purchased from Sigma-Aldrich® and used as such.

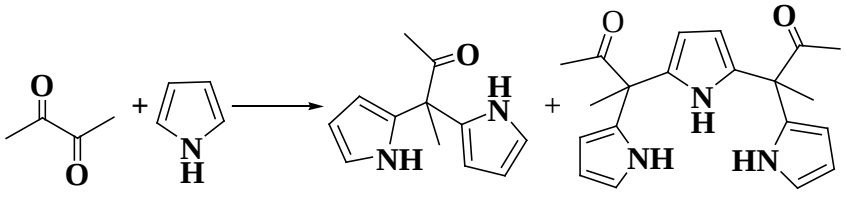
^{1}H NMR spectroscopy based titration studies were carried out in a 400 MHz NMR spectrometer. The receptor solutions were titrated by adding known quantities of concentrated solution of the anions in question. The data were fitted to a 1:1 binding profile in MATLAB 7.0 package according to the method of Wilcox[S7] using the changes in the pyrrolic NH resonances in the ^{1}H NMR spectra.

All tetrabutylammonium salts for NMR and ITC titration were purchased from Sigma-Aldrich® and were directly used in the titration experiment.

All quantum mechanical DFT calculations were performed with the Gaussian 03 program package[S8]. The restricted Becke three-parameter hybrid (B3)[S9] functional was used along with Lee-Yang-Parr (LYP)[S10] correction. The 6-31+G (d,p) basis set is employed in all calculations reported below.

[S1] Oxford Diffraction (**2008**). CrysAlis CCD and CrysAlis RED. Versions 1.171.33.55. Oxford Diffraction Ltd, Yarnton, Oxfordshire, England.
[S2] (a) Spek, A. L.; *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, **2002**; (b) Spek, A. L.; *J. Appl. Cryst.* **2003**, *36*, 7-13.
[S3] SAINT, version 6.45 /8/6/03, Bruker AXS, **2003**.
[S4] Sheldrick, G. M.; *SADABS*, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Germany, **1997**.
[S5] Sheldrick, G. M.; *SHELXS-97* and *SHELXL-97*, Programs for the Solution and Refinement of Crystal Structures, University of Göttingen, Germany, **1997**.
[S6] Powder Cell, Program for structure visualization, powder pattern calculation and profile fitting, www.ccp14.ac.uk.
[S7] Wilcox, C. S. in Frontiers in Supramolecular Organic Chemistry and Photochemistry; Schneider, H. J., Dürr, H., Eds.; VCH: Weinheim, **1991**.
[S8] Frisch, M.J. et. al., *Gaussian 03, Revision B.05*, Gaussian, Inc., Pittsburgh PA. **2003**.
[S9] Becke, A. D. *J. Chem. Phys.* **1993**, 98, 5648-5652.
[S10] Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B.* **1988**, 37, 785-789.

A. Method for the synthesis of compound 4:



4 **5**

Method A:

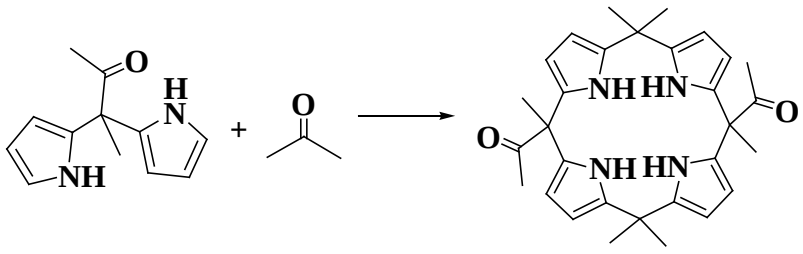
Pyrrole (5 mL, 72 mmol, 10 eq), 2,3-Butanedione (0.6 mL ,7.2 mmol, 1eq) and TFA (0.1 mL, 1.44 mmol, 0.2 eq) was stirred for 5 min under N_2 atmosphere. The reaction mixture was quenched by adding Et_3N. The excess pyrrole was removed by heating the mixture at ~70-80 ^{o}C under reduced pressure. The product was purified by distillation under reduced pressure (temperature ~ 150 ^{o}C). The desired product **4** obtained as white oil 550 mg (40%) which crystallizes upon storing in freezer. The residue upon purification by column chromatography using silica gel in EtOAc: Hexanes (80:20) yielded a little amount of the tripyrromethane **5**.

Method B:
To a solution of 2,3-butanedione (1 mL, 11.3 mmol, 1 eq) in boiling water (8 mL), conc. HCl (0.04 mL) were added, followed by drop wise addition of pyrrole (1.6 mL, 22.6 mmol, 2 eq). After refluxing for 45 min, the suspension was left to cool and then neutralized with 10% aqueous $NaHCO_3$. The compound was extracted with ethyl acetate, dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by distillation under reduced pressure (temperature ~ 150^{o} C) to yield **4** as white oil (1.56 g, 67%) which converts to white crystalline solid in freezer.

Meso acylated dipyrromethane **4**: mp- 72-74 ^{o} C; FT-IR Data (KBr) - 3362, 1705 cm^{-1}; ^{1}H NMR (in $CDCl_3$, 400MHz): δ in ppm 8.45 (br, s, 2H, NH), 6.74 (s, 2H, pyrrole CH), 6.18 (s, 2H, pyrrole CH), 6.06 (s , 2H, pyrrole CH), 2.13 (s, 3H, CH_3), 1.85 (s, 3H, CH_3); ^{13}C NMR (in $CDCl_3$, 400MHz): δ in ppm 210.04, 132.34, 118.07, 108.35, 106.82, 52.75, 26.60, 25.10; LCMS m/z calcd. for $C_{12}H_{14}N_2O$ (M+H) 203, found 203; Elemental analysis for $C_{12}H_{14}N_2O$ calcd. (found); C 71.26 (71.42), H 6.98 (6.93), N 13.85 (13.96); Crystal structure also obtained.

Meso diacylated tripyrromethane **5**: FT-IR Data (KBr) - 3736.7, 3392.1, 1704 cm^{-1}; ^{1}H NMR spectrum (in $CDCl_3$, 400MHz): δ in ppm 8.49-8.69 (br m, 3H, NH), 6.74 (s, 2H, pyrrole CH), 6.16 (m, 2H, pyrrole CH), 5.95-6.01 (m , 4H, pyrrole CH), 2.10 (s, 3H, CH_3), 1.81 (s, 3H, CH_3); ^{13}C NMR spectrum (in $CDCl_3$, 400MHz): δ in ppm 209.67, 132.81, 132.08, 118.05, 108.46, 106.83, 106.76, 52.66, 26.53, 25.00; LCMS m/z calcd. for $C_{12}H_{14}N_2O$ (M-H) 336, found 336; Elemental analysis was not obtained as the compound is not very stable.

B. Method for the synthesis of compound 6:



6

Meso-acylated dipyrromethane **4** (2 g, 9.9 mmol) was dissolved in a mixture of dry acetone (70 mL) and dry dichloromethane (400 mL) at room temperature under nitrogen atmosphere and

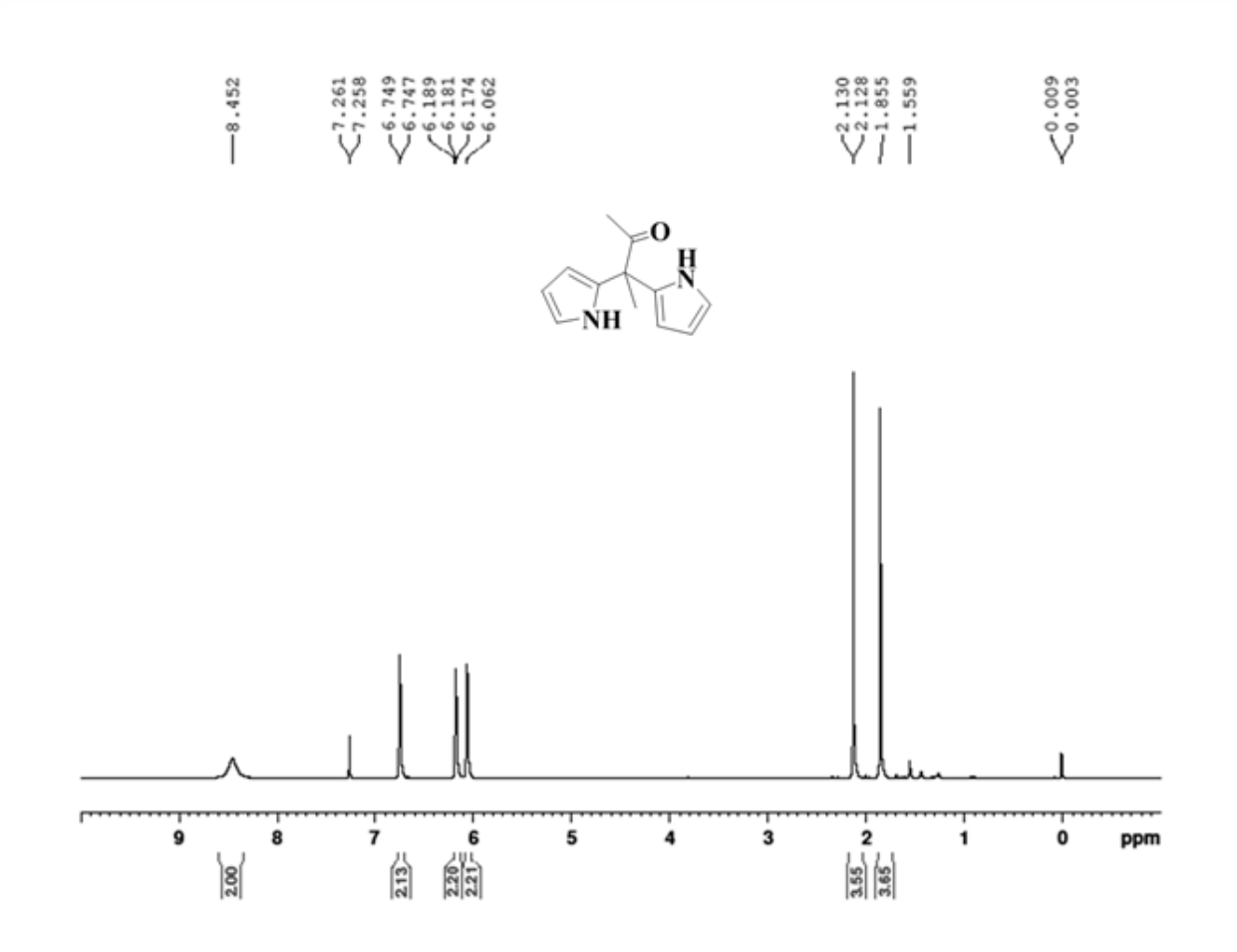
then $BF_3.OEt_2$ (0.122 mL, 0.9 mmol) was added. The reaction mixture was stirred at room temperature for 30 min. The reaction was quenched with 1M sodium hydroxide. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (20 ml × 3), and the combined organic layer was dried over anhydrous sodium sulfate. The solutions were evaporated under reduced pressure, and the residue was purified by column chromatography over silica gel (eluent: 20% EtOAc + 80% Hexanes) to afford the required *meso*-diacylated calixpyrrole **6** with *trans* (263 mg, 11%) and *cis* (350 mg, 14%) isomers as white solid.

Trans-**6** isomer: mp- 226-228^o C; FT-IR Data (KBr) - 1684 cm^{-1}; ^1H NMR (in $CDCl_3$, 400MHz): δ in ppm 7.41(br, s, 4H, NH), 5.92-5.97 (m, 8H, pyrrole CH), 2.17 (d, 6H, CH_3), 1.76 (d, 6H, CH_3), 1.54(s, 12H, CH_3); ^1H NMR (in CD_3CN, 400MHz): δ in ppm 8.38(br, s, 4H, NH), 5.83-5.89 (m, 8H, pyrrole CH), 2.01 (s, 6H, CH_3), 1.71 (s, 6H, CH_3), 1.53 (s, 12H, CH_3); ^{13}C NMR (in $CDCl_3$, 400MHz): δ in ppm 207.84, 139.06, 131.68, 105.71, 104.08, 52.41, 35.45, 29.58, 27.15, 24.48; LCMS m/z calcd for $C_{30}H_{36}N_4O_2$ (M+H) 485.63, found 485.55; Elemental analysis for $C_{30}H_{36}N_4O_2$ calcd (found); C 74.35 (74.25), H 7.49 (7.51), N 11.56 (11.68).

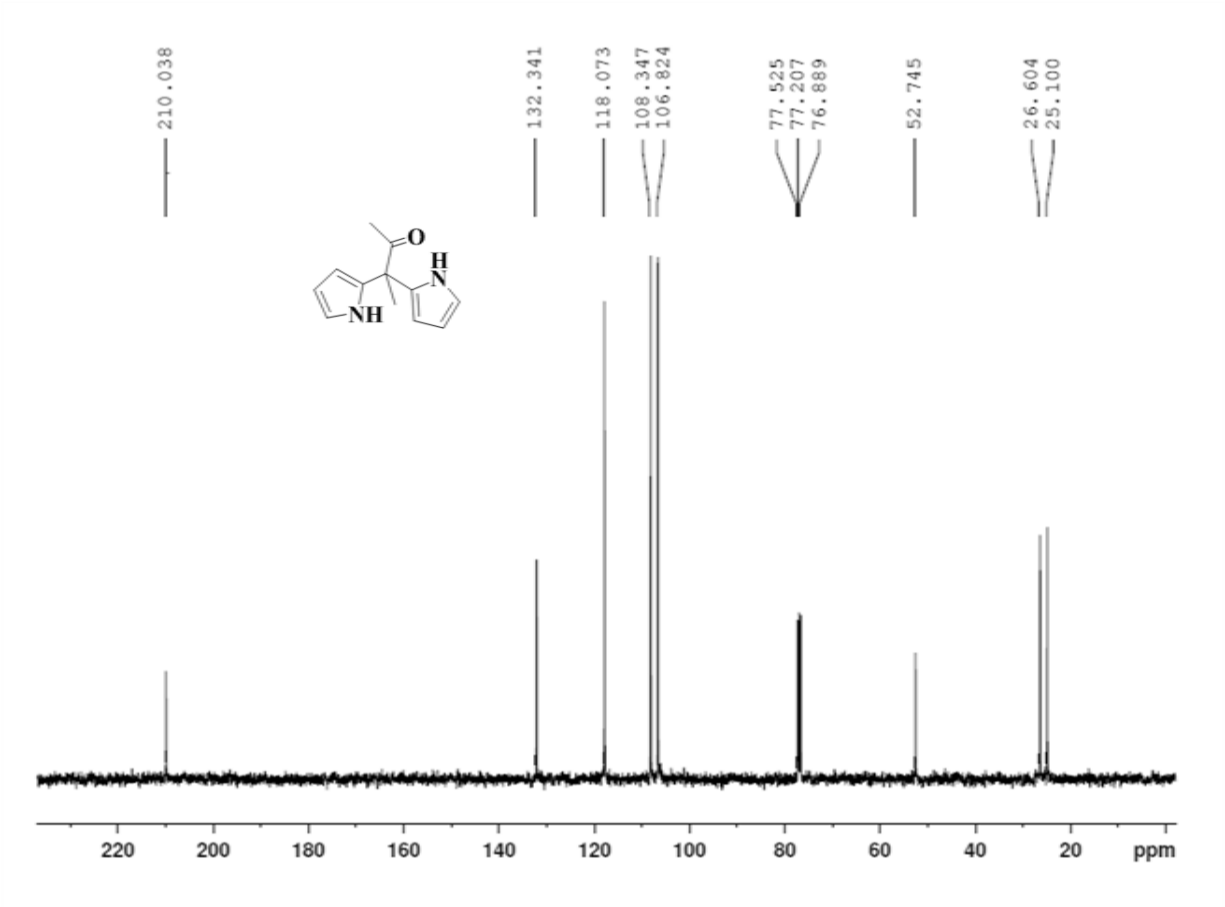
Cis-**6** isomer: mp- 208-210^o C; FT-IR Data (KBr) - 1699.44 cm^{-1}; ^1H NMR (in $CDCl_3$, 400MHz): δ in ppm 7.44 (br, s, 4H, NH), 5.90-5.97 (m, 8H, pyrrole CH), 2.15 (d, 6H, CH_3), 1.74 (d, 6H, CH_3), 1.52 (s, 12H, CH_3); ^1H NMR (in CD_3CN, 400MHz): δ in ppm 8.29 (br, s, 4H, NH), 5.80-5.88 (m, 8H, pyrrole CH), 2.02 (s, 6H, CH_3), 1.67 (s, 6H, CH_3), 1.53 (s, 6H, CH_3), 1.57 (s, 6H, CH_3) ; ^{13}C NMR (in $CDCl_3$, 400MHz): δ in ppm 207.39, 139.22, 131.70, 105.74, 103.98, 52.47, 35.45, 29.92, 29.10, 27.12, 24.08; LCMS m/z calcd for $C_{30}H_{36}N_4O_2$ (M+H) 485.63, found 485.50; Elemental analysis for $C_{30}H_{36}N_4O_2$ calcd (found); C 74.35 (74.41), H 7.49 (7.55), N 11.56 (11.45).

^{1}H and ^{13}C NMR spectra of compounds:

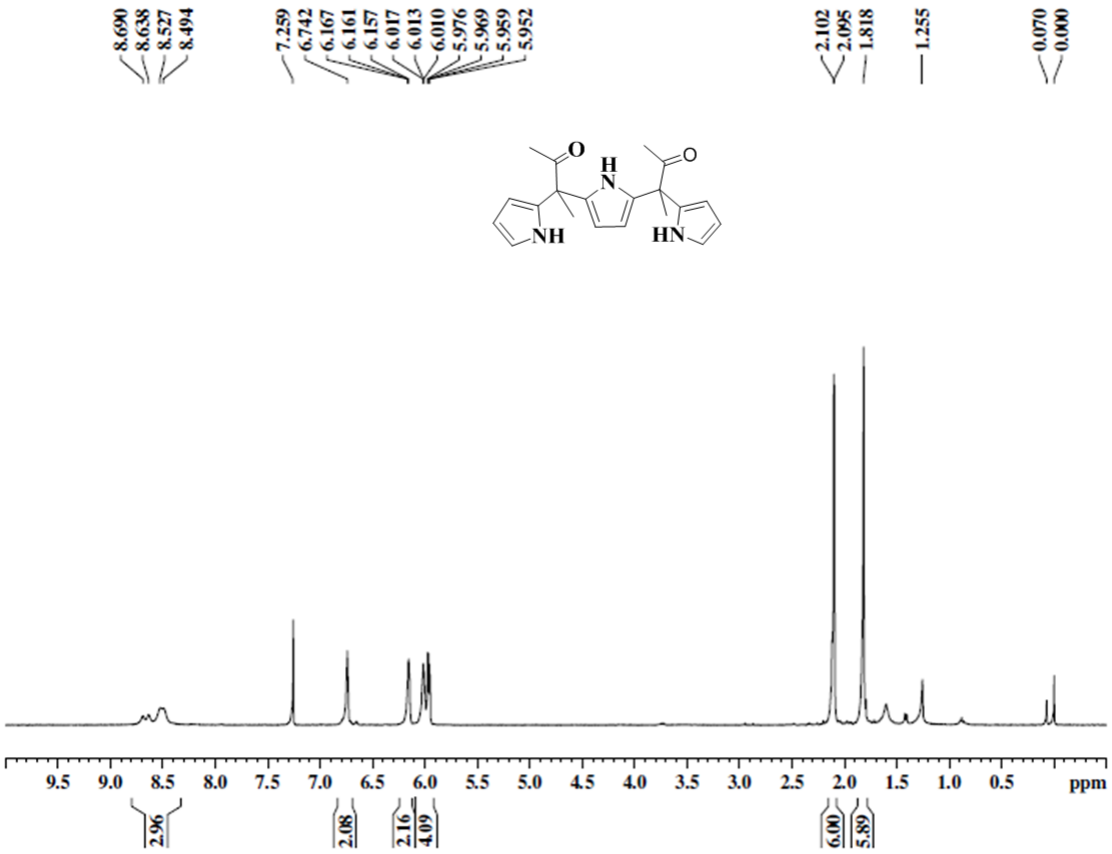
^{1}H NMR spectra of compound **4 (**In $CDCl_3$**)**:



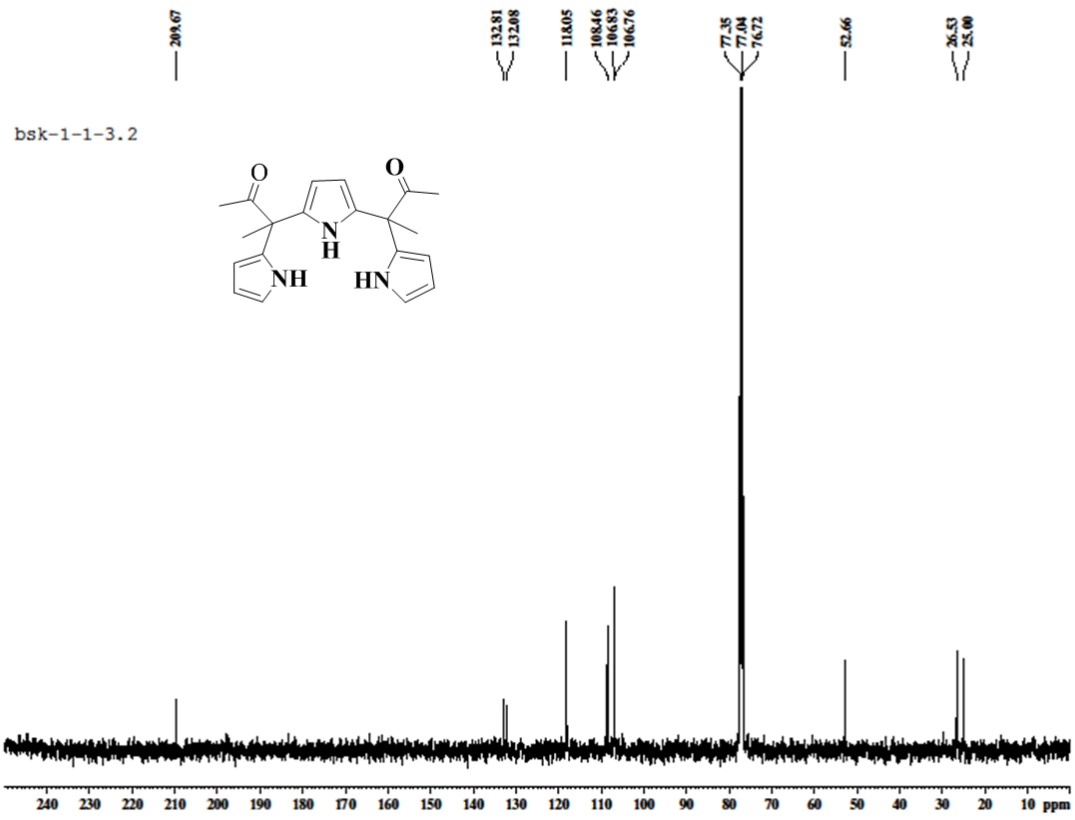
^{13}C NMR spectra of compound **4 (**In $CDCl_3$**)**:



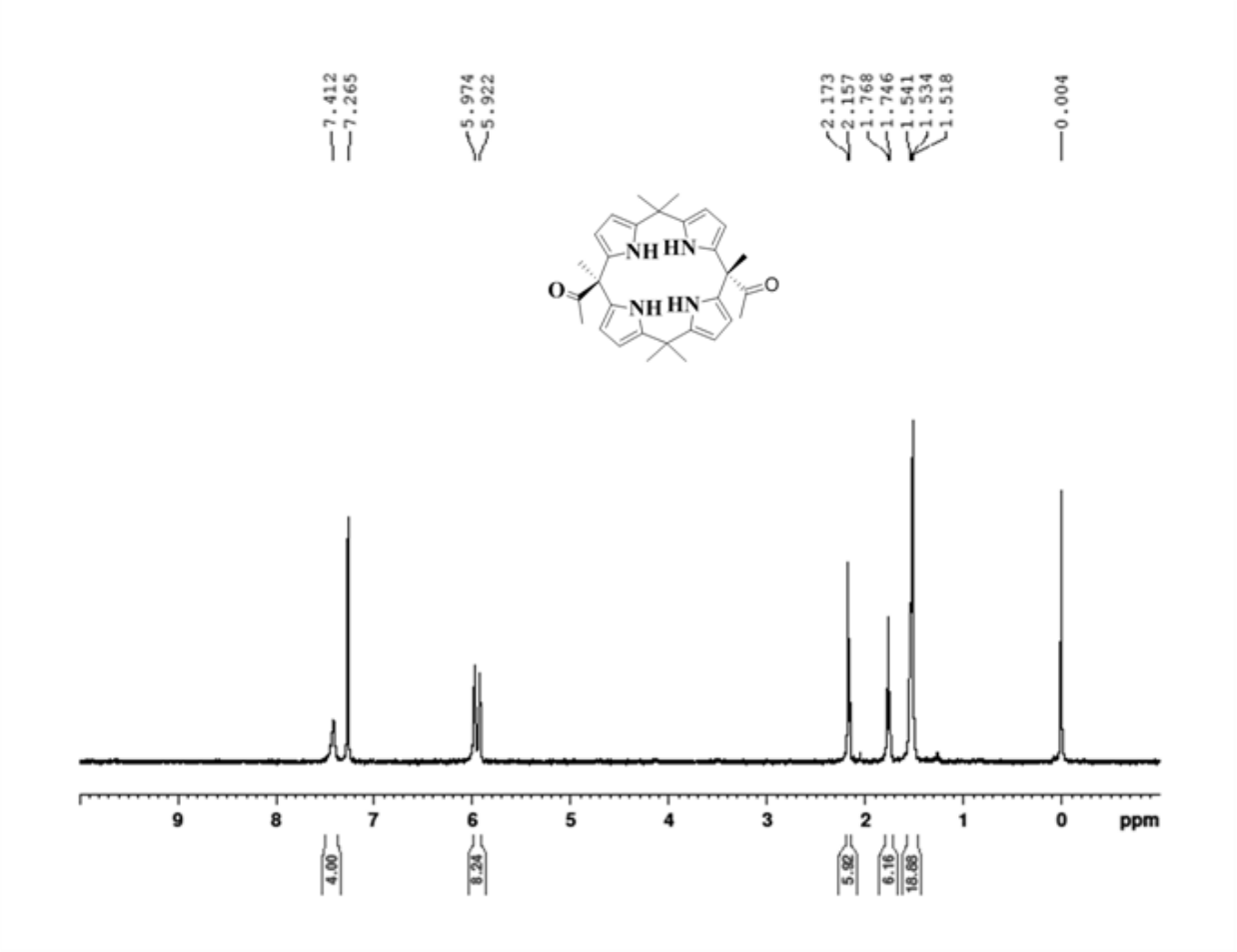
^{1}H NMR spectra of compound **5 (**In $CDCl_3$**)**:



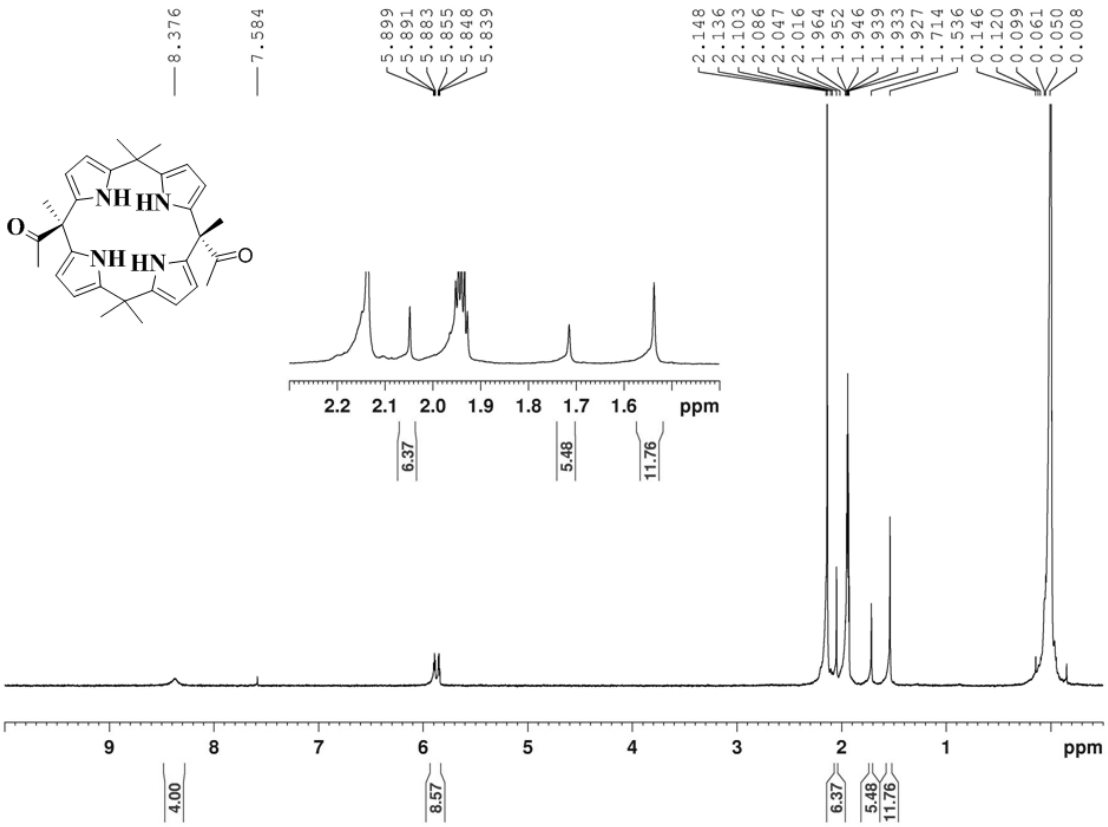
^{13}C NMR spectra of compound **5 (**In $CDCl_3$**)**:



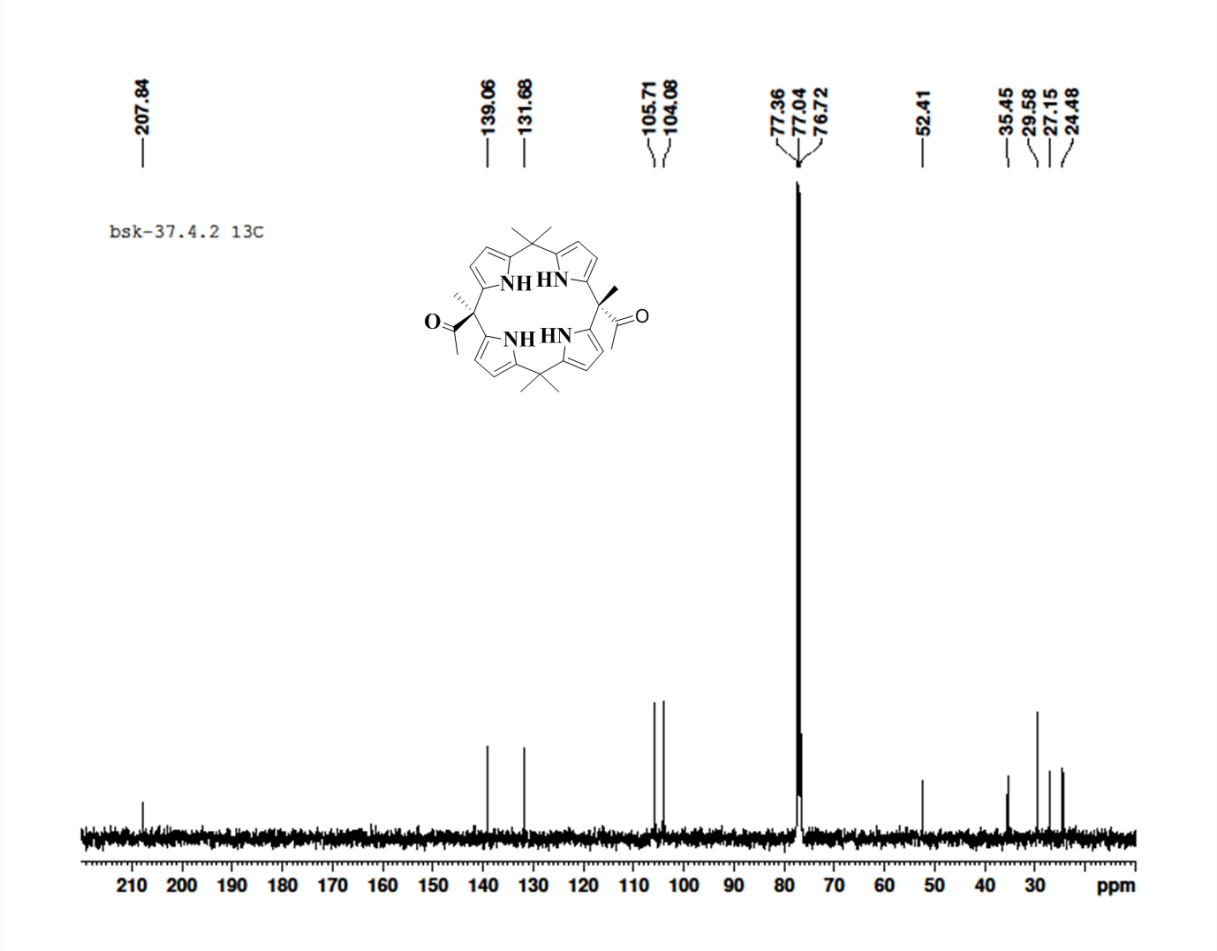
^{1}H NMR spectra of *trans*-**6** (In $CDCl_3$):



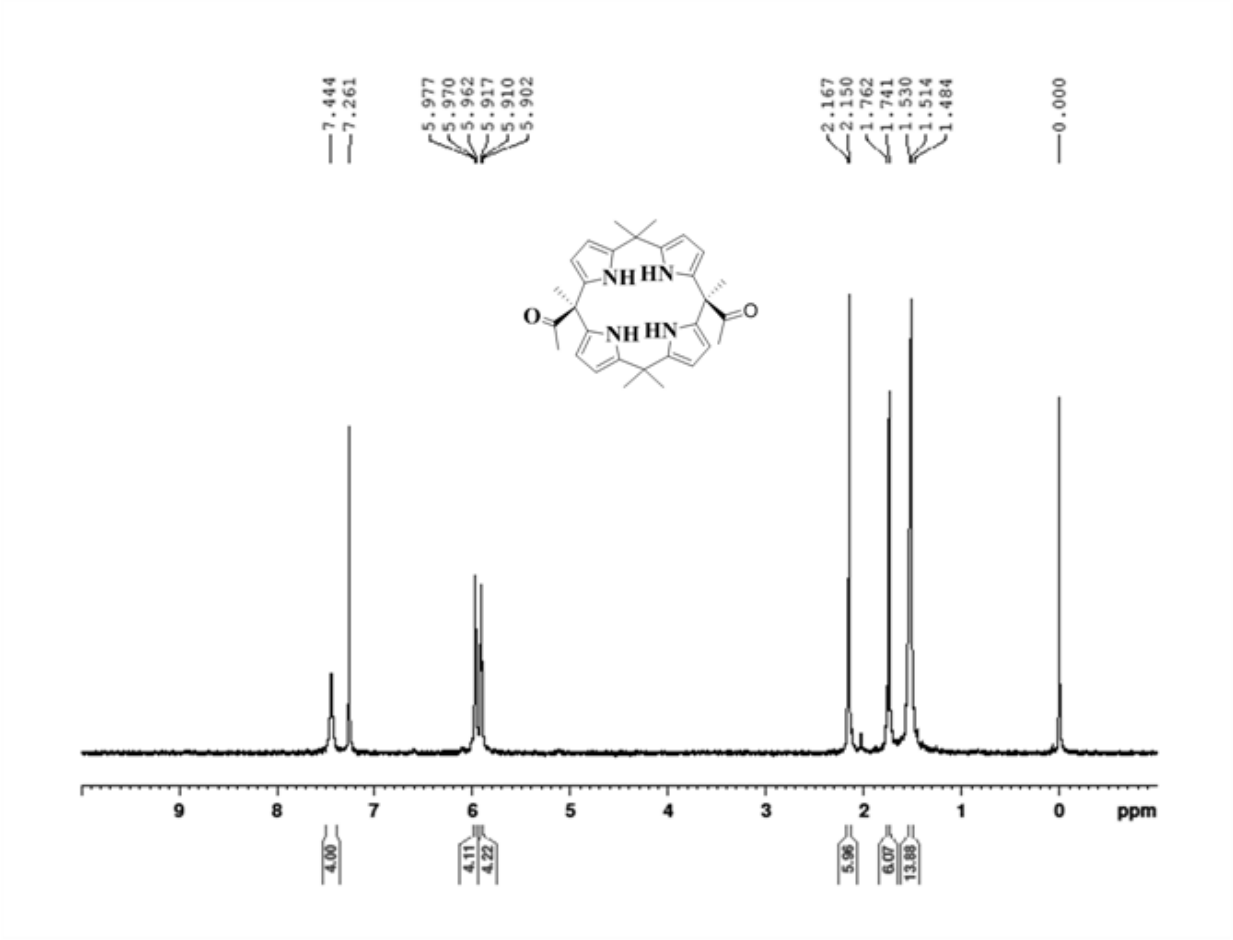
^{1}H NMR spectra of *trans*-**6** (In CD_3CN):



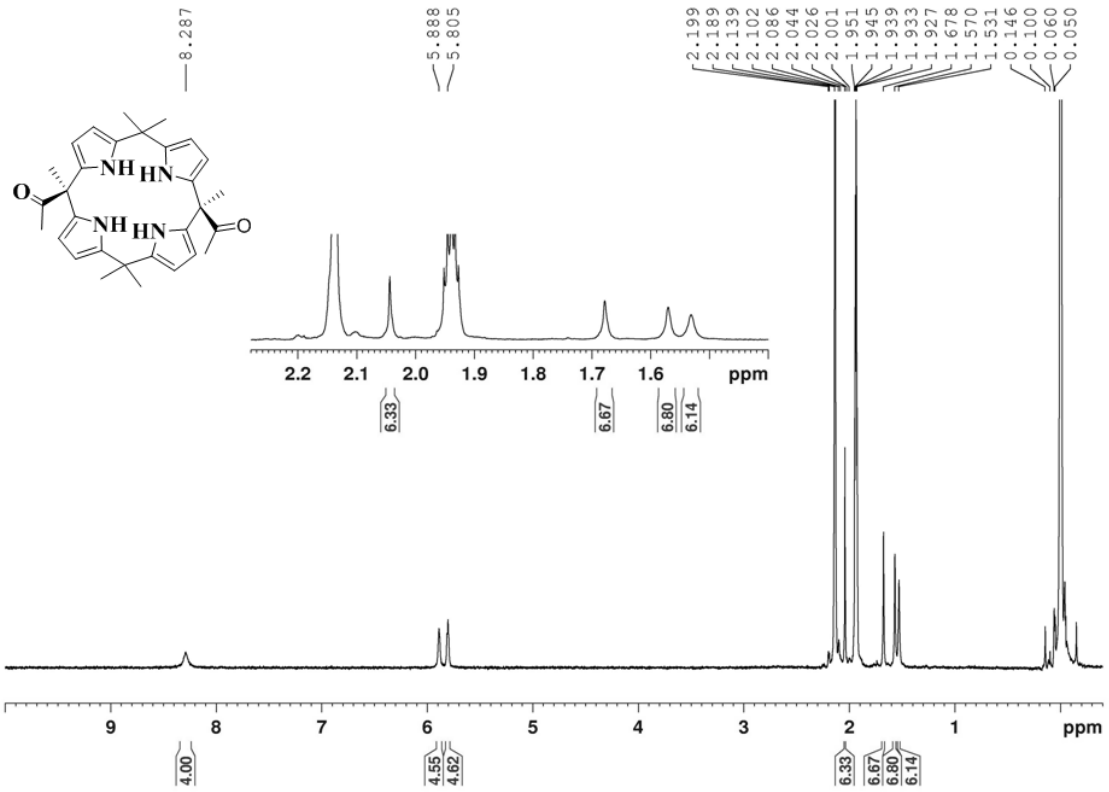
^{13}C NMR spectra of *trans*-**6 (**In $CDCl_3$**)**:



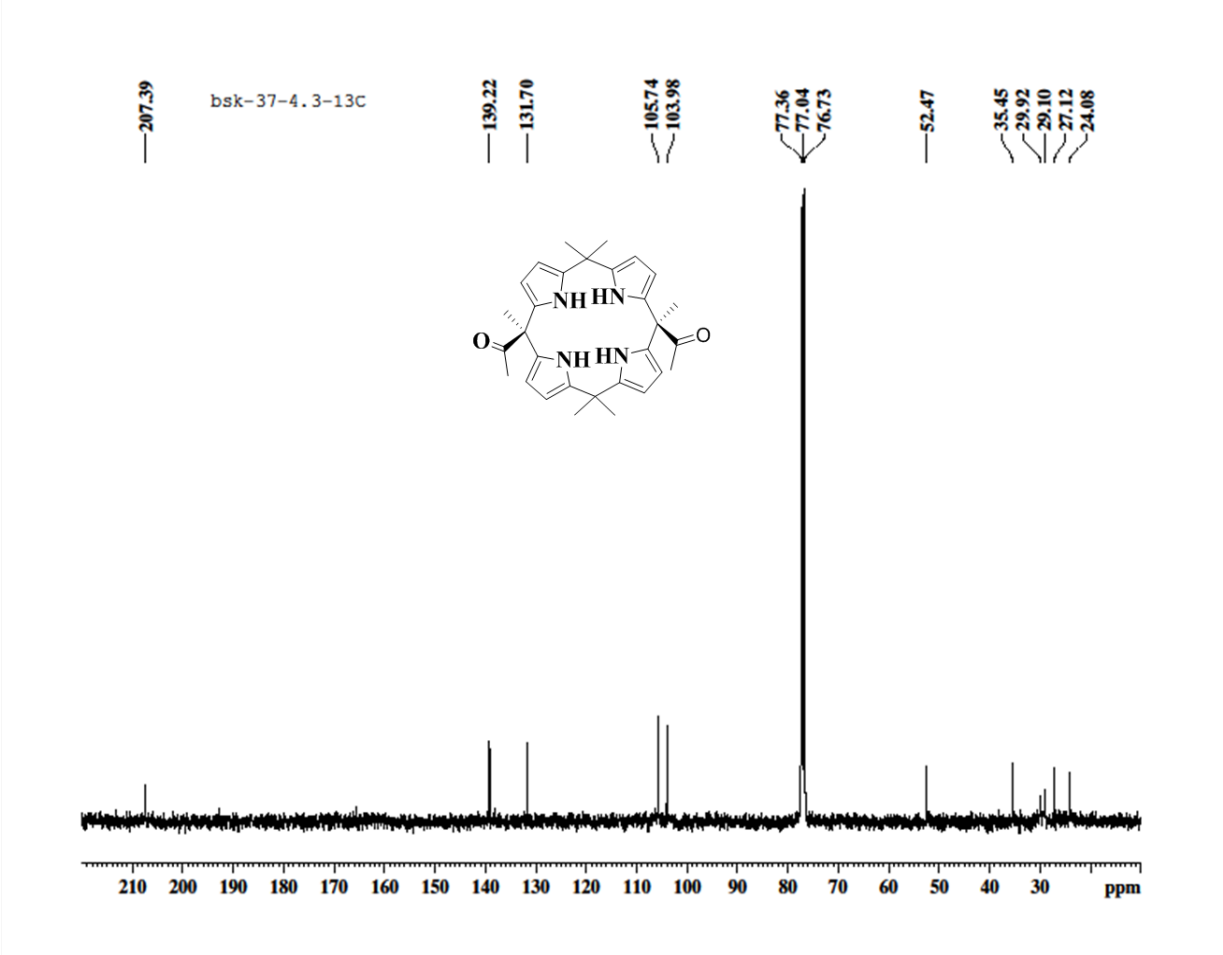
^{1}H NMR spectra of *cis*-**6** (In $CDCl_3$):



^{1}H NMR spectra of *cis*-**6** (In CD_3CN):

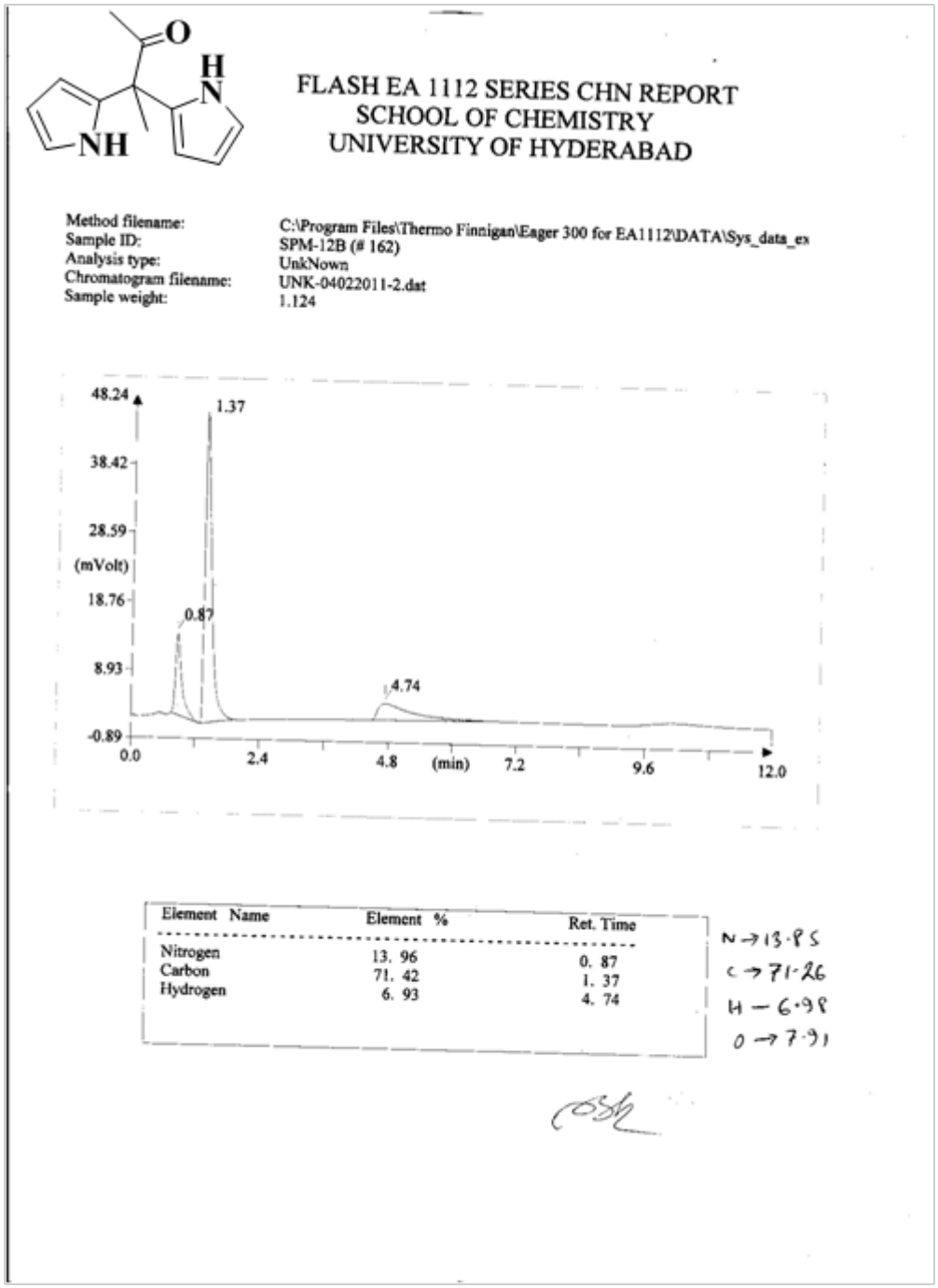


^{13}C NMR spectra of *cis*-**6 (**In $CDCl_3$**)**:



ELEMENTAL ANALYSIS:

Compound **4**:



FLASH EA 1112 SERIES CHN REPORT
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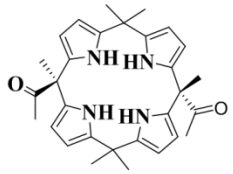
Analysis type: UnkNown
Chromatogram filename: UNK-04022011-2.dat
Sample weight: 1.124

Element Name	Element %	Ret. Time
Nitrogen	13. 96	0. 87
Carbon	71. 42	1. 37
Hydrogen	6. 93	4. 74

N → 13·95
C → 71·26
H — 6·98
O → 7·91

trans-**6**:



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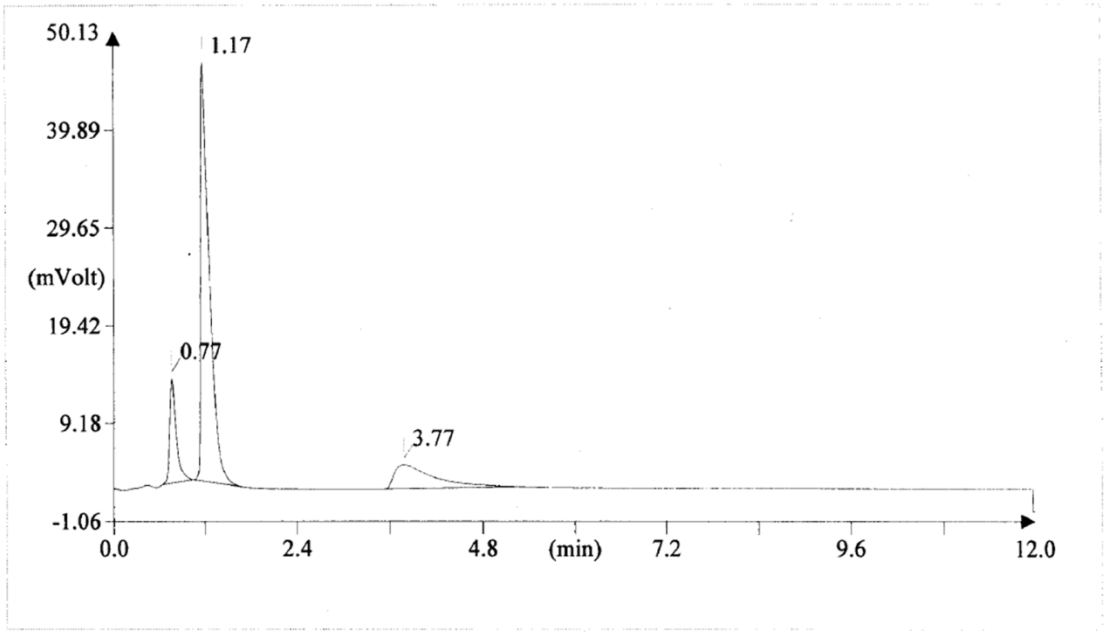
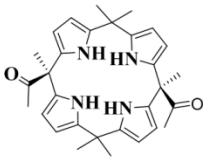


Element Name	Element %	Ret. Time
Nitrogen	11. 75	0. 77
Carbon	74. 21	1. 17
Hydrogen	7. 36	3. 77

cis-**6**:



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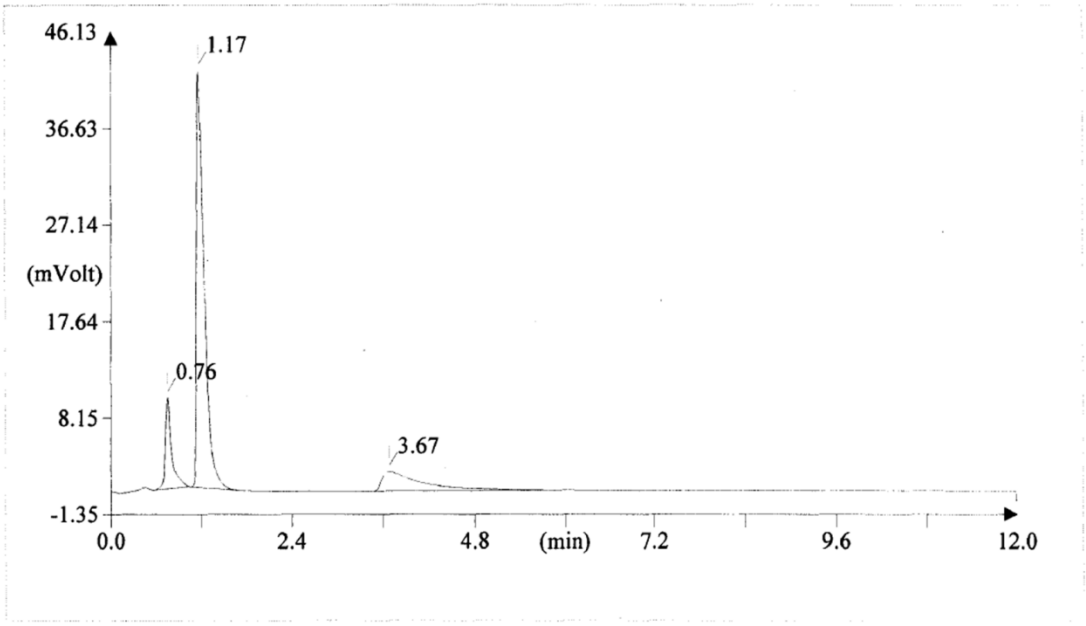


Element Name	Element %	Ret. Time
Nitrogen	11. 45	0. 76
Carbon	74. 41	1. 17
Hydrogen	7. 55	3. 67

Solid state analysis:

Crystal Structure analysis:

Compound **4**:

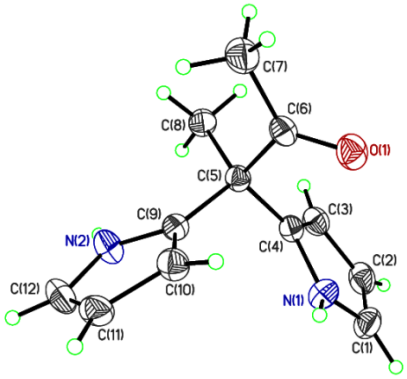


Figure S1: Ortep diagram of compound **4**. Thermal ellipsoid are scaled upto 25% probability level.

trans-**6**:

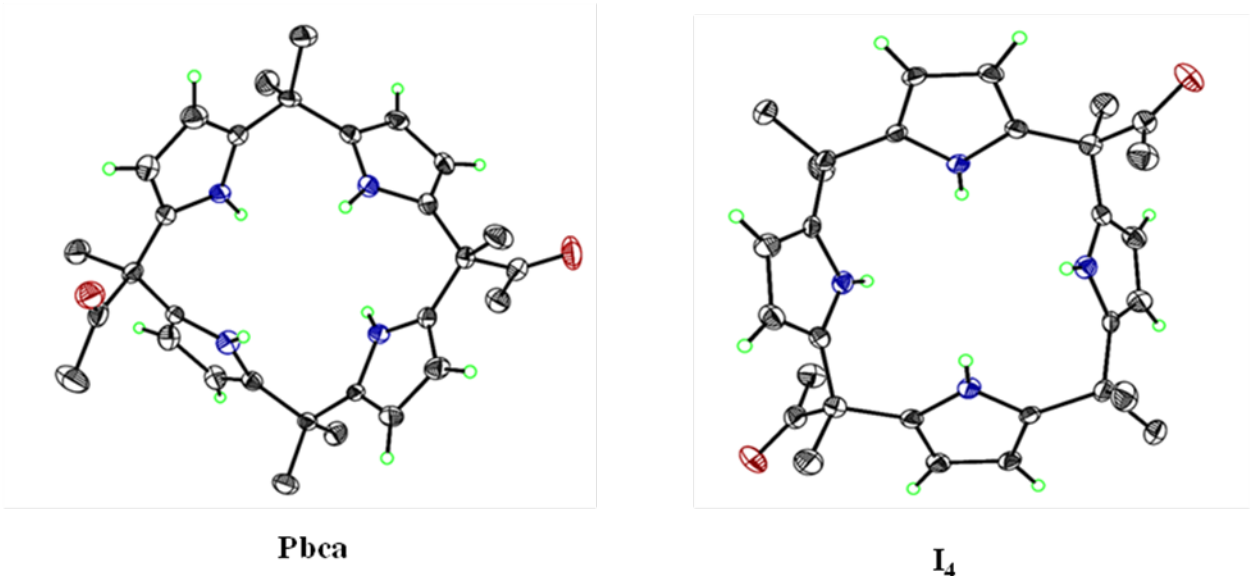
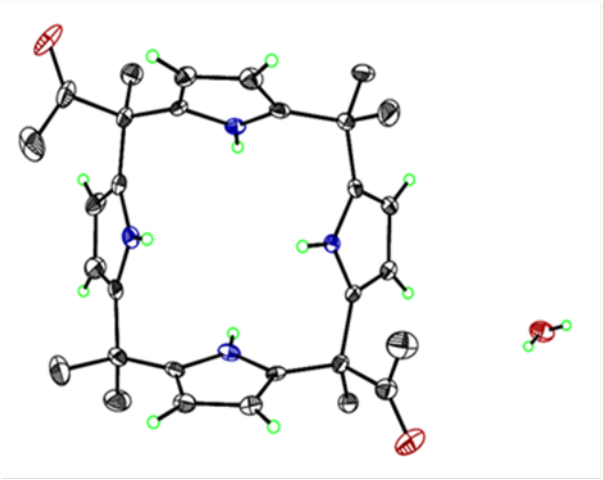
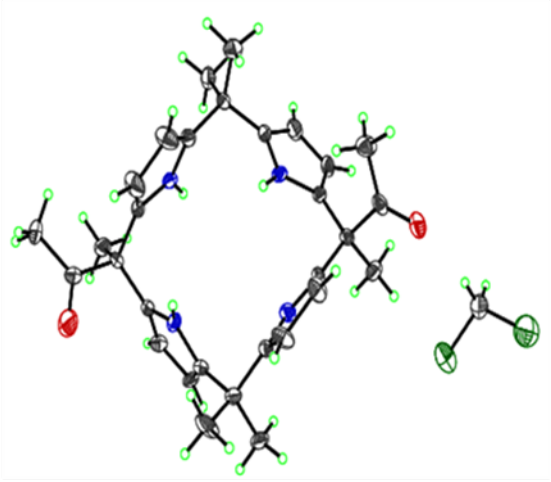


Figure S2: Ortep diagram of the two forms of trans-6 (1,3-alternate (left) and 1,2-alternate (right)). Thermal ellipsoid are scaled upto 25% probability level. All methyl hydrogens has removed for clarity.

cis-**6**:



Cis-6. H_2O



Cis-6. CH_2Cl_2

Figure S3: Ortep diagram of *cis*-**6**.H_2O (left) and *cis*-**6**.CH_2Cl_2 (right). Thermal ellipsoid are scaled upto 25% probability level. All methyl hydrogens has removed for clarity.

Author's comment on IUCR check .cif alert:

cis-**6**.CH_2Cl_2:

RINTA01_ALERT_3_A: The value of Rint is greater than 0.25.

PLAT020_ALERT_3_A: The value of Rint is greater than 0.12 .....0.26

Author Response: The Crystal quality was not good. After several attempt of data collection, the reported one is found to be the best one.

PLAT026_ALERT_3_A: Ratio Observed / Unique Reflections too Low ...27 Perc.

Author Response: The crystal quality and data was not good enough so a sufficient fraction of the unique data is above the 2 sigma level.

trans-**6**(Pbca):

RINTA01_ALERT_3_A The value of Rint is greater than 0.25 Rint given 0.503

PLAT020_ALERT_3_A The value of Rint is greater than 0.12 .....0.50

Author Response: The Crystal quality was not good. After several attempt of data collection, the reported one is found to be the best one.

SHFSU01_ALERT_2_A The absolute value of parameter shift to su ratio >0.20
Absolute value of the parameter shift to su ratio given 1.195
Additional refinement cycles may be required.

PLAT080_ALERT_2_A Maximum Shift/Error 1.20

PLAT222_ALERT_3_A Large Non-Solvent H Uiso(max)/Uso(min)..10.00 Ratio

Author Response: The Crystal quality was not good. These alert comes due to nonconvergent refinement of one of the N-H hydrogen atom.

Overlay diagram:

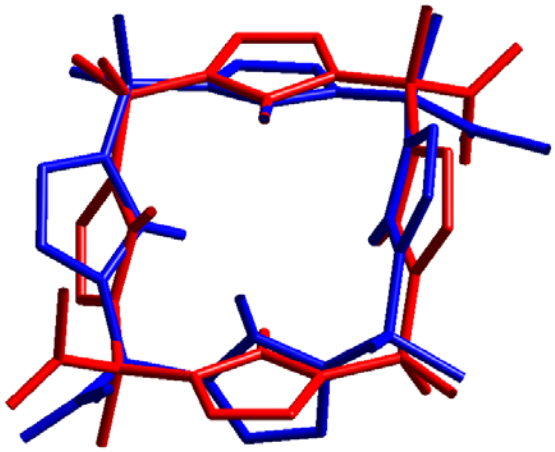


Figure S4: Overlay diagram showing the different orientation of the pyrrole rings in the two forms of the *trans*-**6** isomer. Red: 1,2-alternate (I_4). Blue: 1,3-alternate (Pbca).

Confirmational analysis of *trans*-6 (powder XRD):

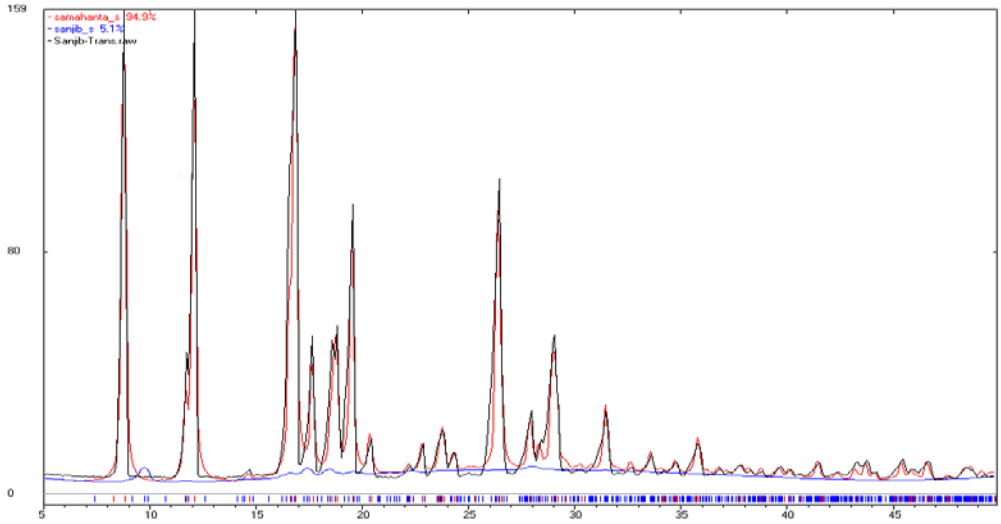


Figure S5: Comparison of the powder XRD pattern of the column purified *trans*-**6** (black) with the simulated pattern of the I4 (red) and Pbca (blue) crystals. The powdercell refinement shows I4 one resembles ~95% and the Pbca one ~5% with the column purified one.

Thermal Analysis: (Differential Scanning calorimetry)

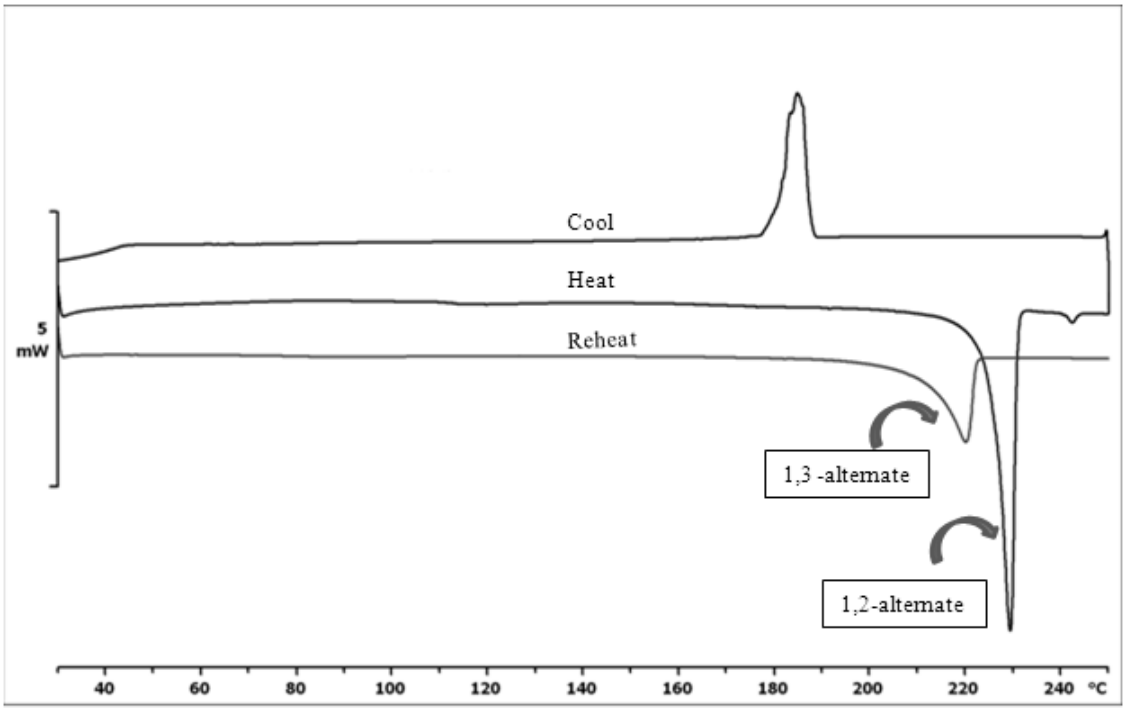


Figure S6: DSC pattern of the *trans*-**6** showing polymorphic transition.

Packing Diagram:

trans-**6**:

I_4 (1,2-alternate):

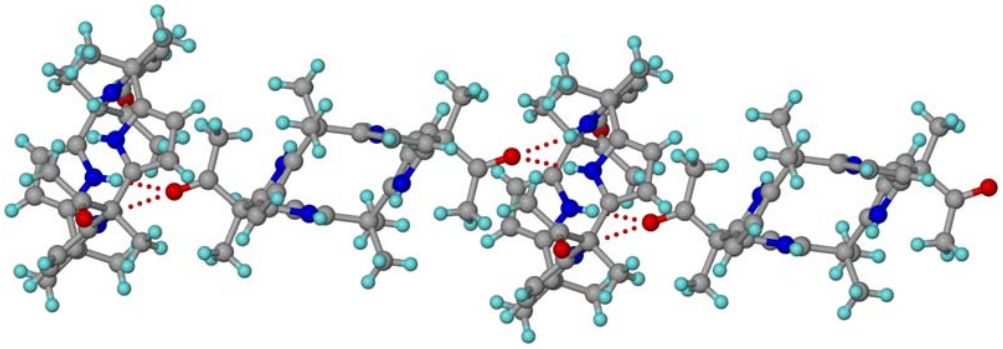


Figure S7: POV ray picture of Hydrogen bonding pattern in I_4 form of *trans*-**6**.

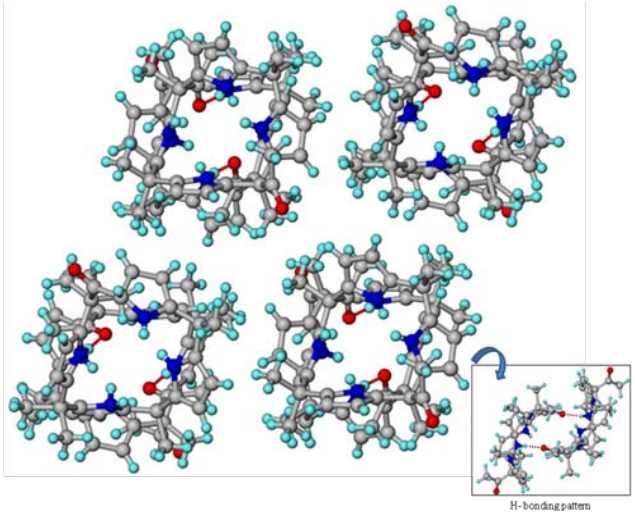


Figure S8: POV ray picture of hydrogen bonding pattern in Pbca form of *trans*-**6**.

cis-**6**.H_2O

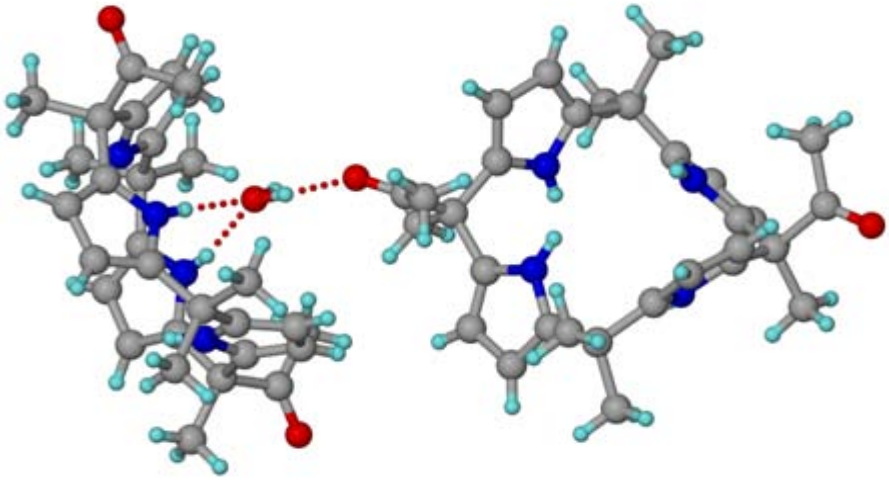


Figure S9: POV ray picture showing the hydrogen bonding pattern of *cis*-**6**.H_2O.

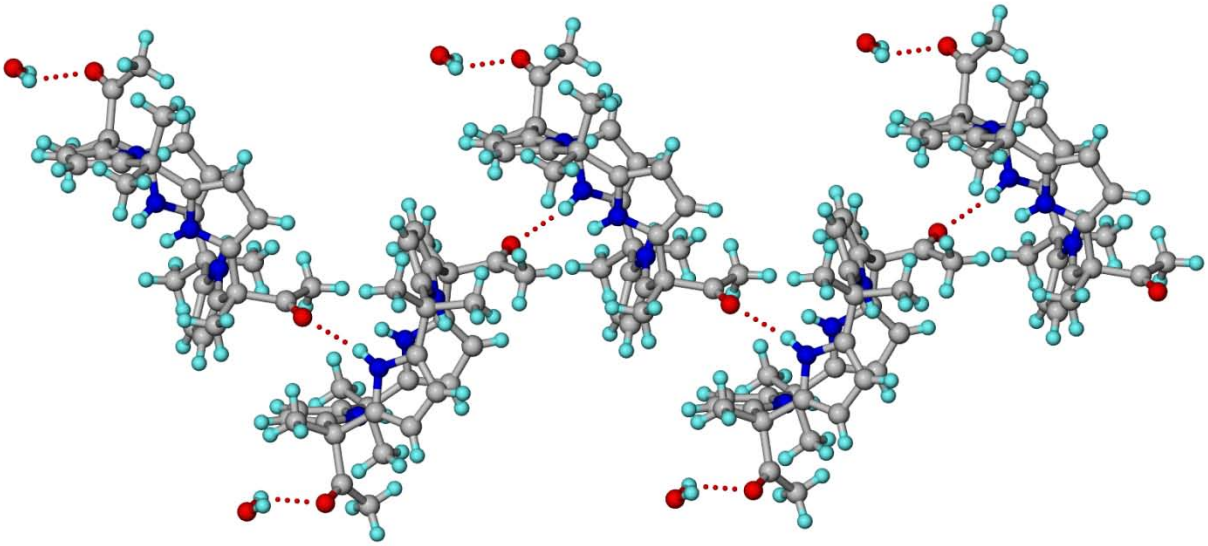


Figure S10: POV ray picture showing the chiral helix in the crystal structure of *cis*-**6**.H_2O.

cis-**6**.DCM solvate:

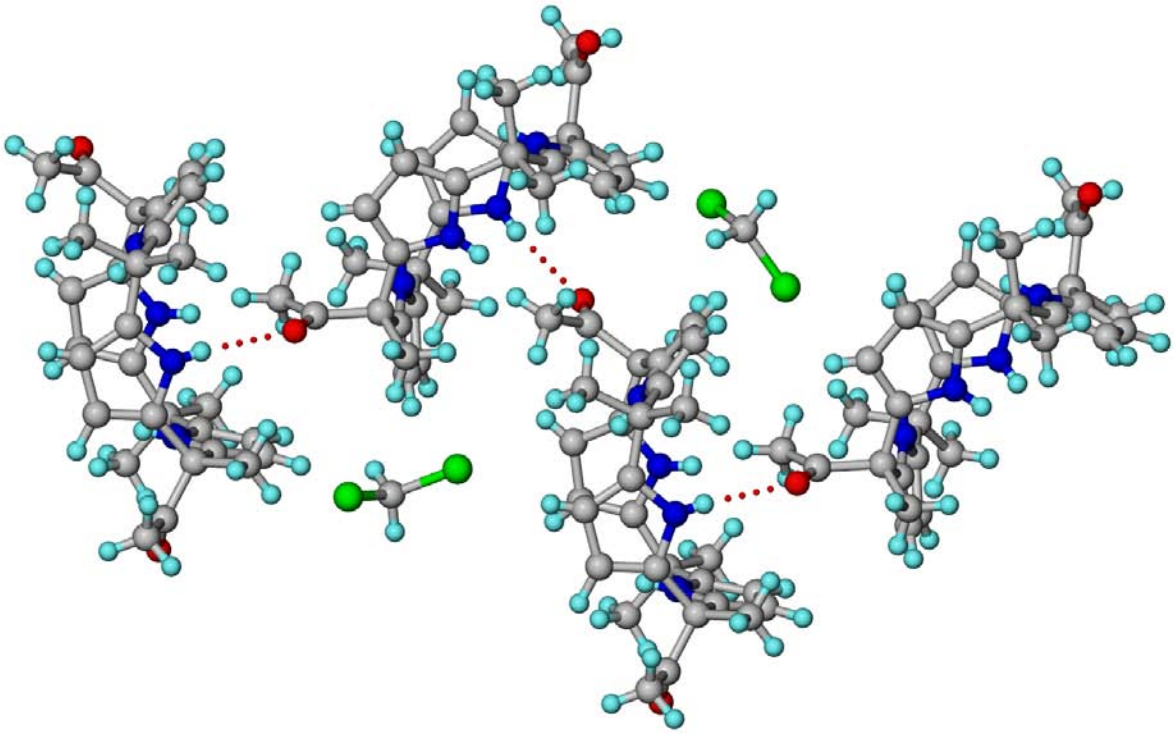


Figure S11: POV ray picture of the hydrogen bonding pattern in *cis*-**6**.CH_2Cl_2.

trans-**6**:

I_4 (1,2-alternate):

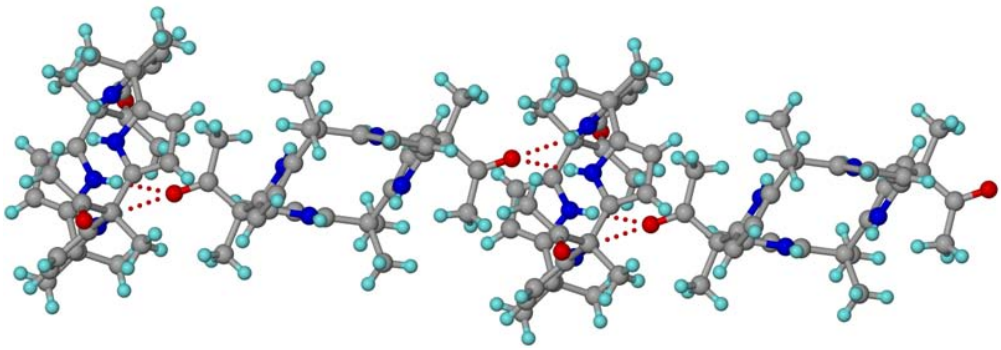


Figure S12: POV ray picture of Hydrogen bonding pattern in I_4 form of *trans*-**6**.

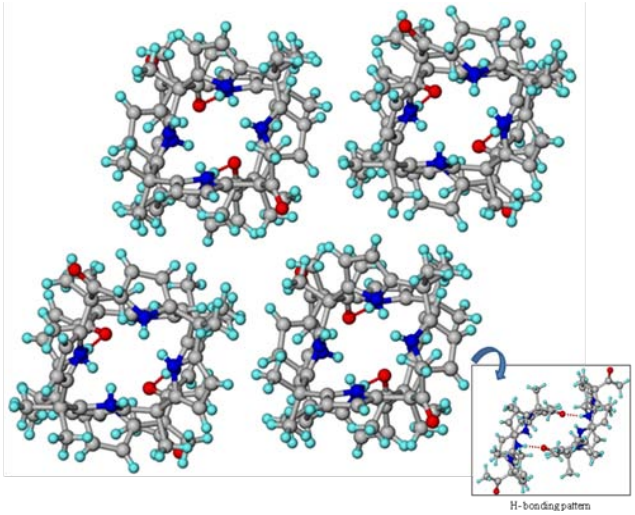


Figure S13: POV ray picture of hydrogen bonding pattern in Pbca form of *trans*-**6**.

Lattice Energy Calculation:

Lattice energies of the two polymorphs of *trans*-**6** (1,3- alternate and 1,2-alternate) were computed using the Dreiding force fields in the Cerius2 program package. The calculations yielded an overall energy of -474.159 kcal.mol^{-1} for 1,3-alternate (Pbca) conformation and -466.228 kcal.mol^{-1} for 1,2-alternate (I_4) conformation. Therefore, the 1,3-alternate form is thermodynamically more stable than the 1,2-form.

Anion binding study:

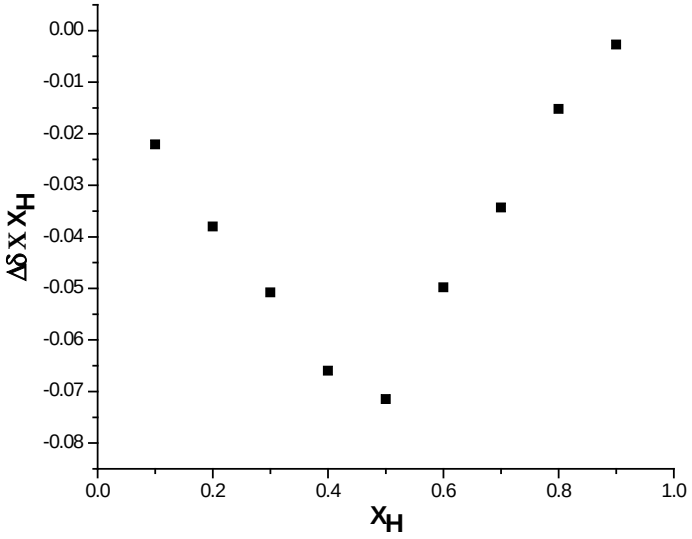
^{1}H NMR spectral titration plot:

Job's plot analysis for determination of stoichiometry:

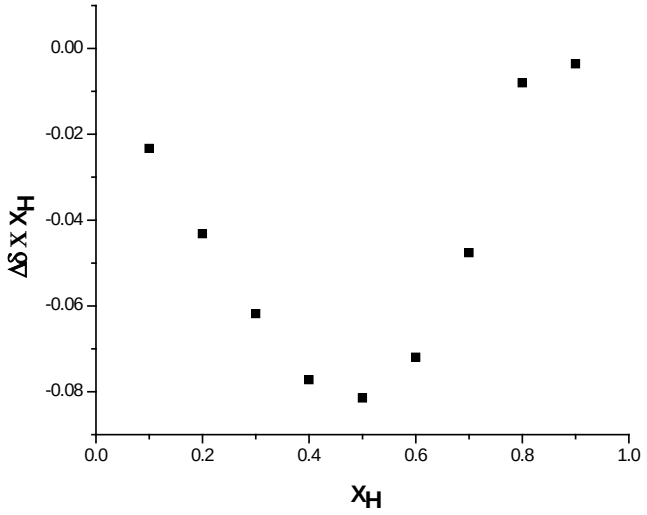
With Fluoride:

Job's plot for fluoride anion was done in $CDCl_3$. 8 mM of compound-**6** and 8 mM of the tetrabutylammonium fluoride salt was mixed in ratios from 1:10 ratios to 10:1 and chemical shift was collected vs the residual $CDCl_3$ (7.26 ppm) resonance. In this experiment pyrrole CH proton resonance are monitored.

With *cis*-**6**:



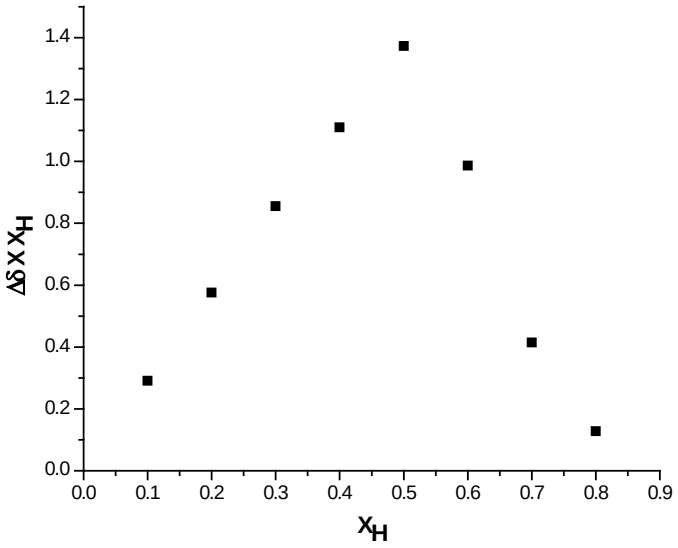
With *trans*-**6**:



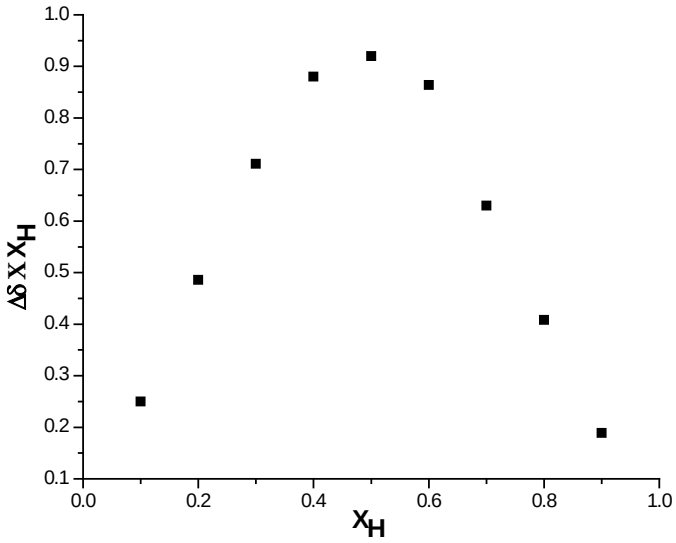
With Dihydrogenphosphate:

Job's plot for phosphate anion was done in CD_3CN. 1 mM of compound-**6** and 1 mM of the tetrabutylammonium dihydrogenphosphate salt was mixed in ratios from 1:10 ratios to 10:1 and chemical shift was collected vs the TMS resonance. In this experiment NH proton resonance is monitored.

With *cis*-**6**:



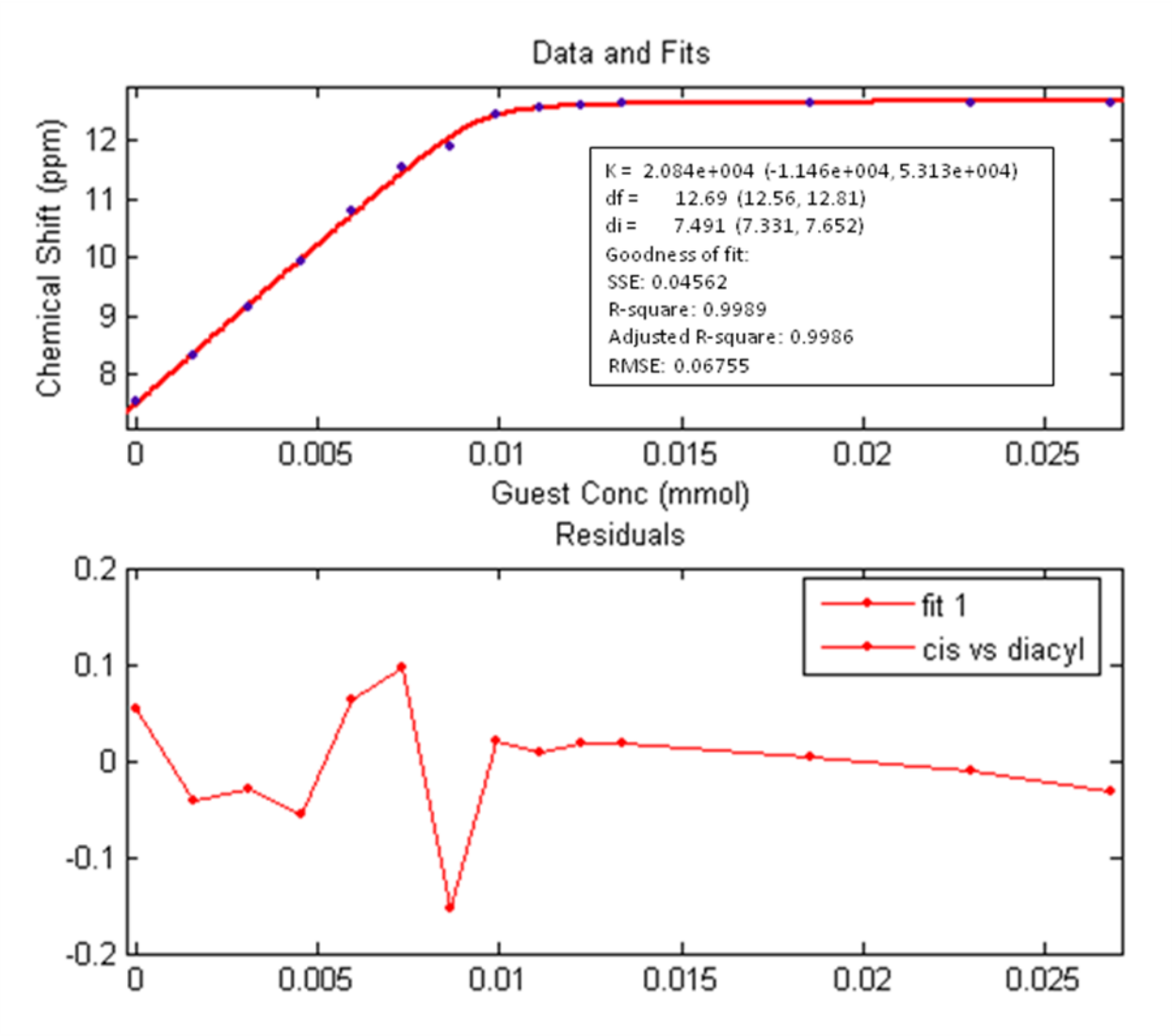
With *trans*-**6**:



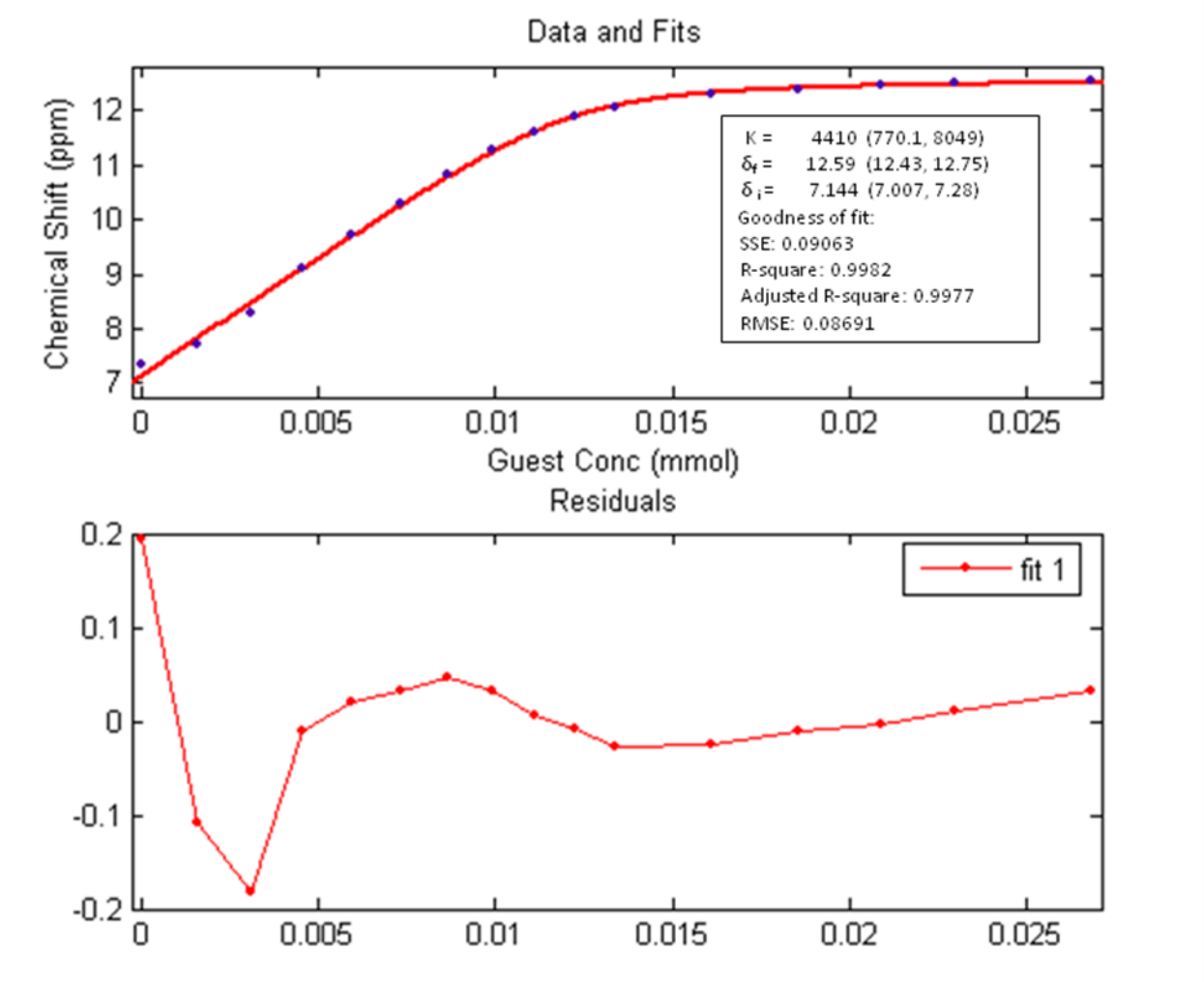
Binding constant determination by ^{1}H NMR spectroscopy:

All the titrations were carried out with 8 x 10^{-3} M solution of the host.

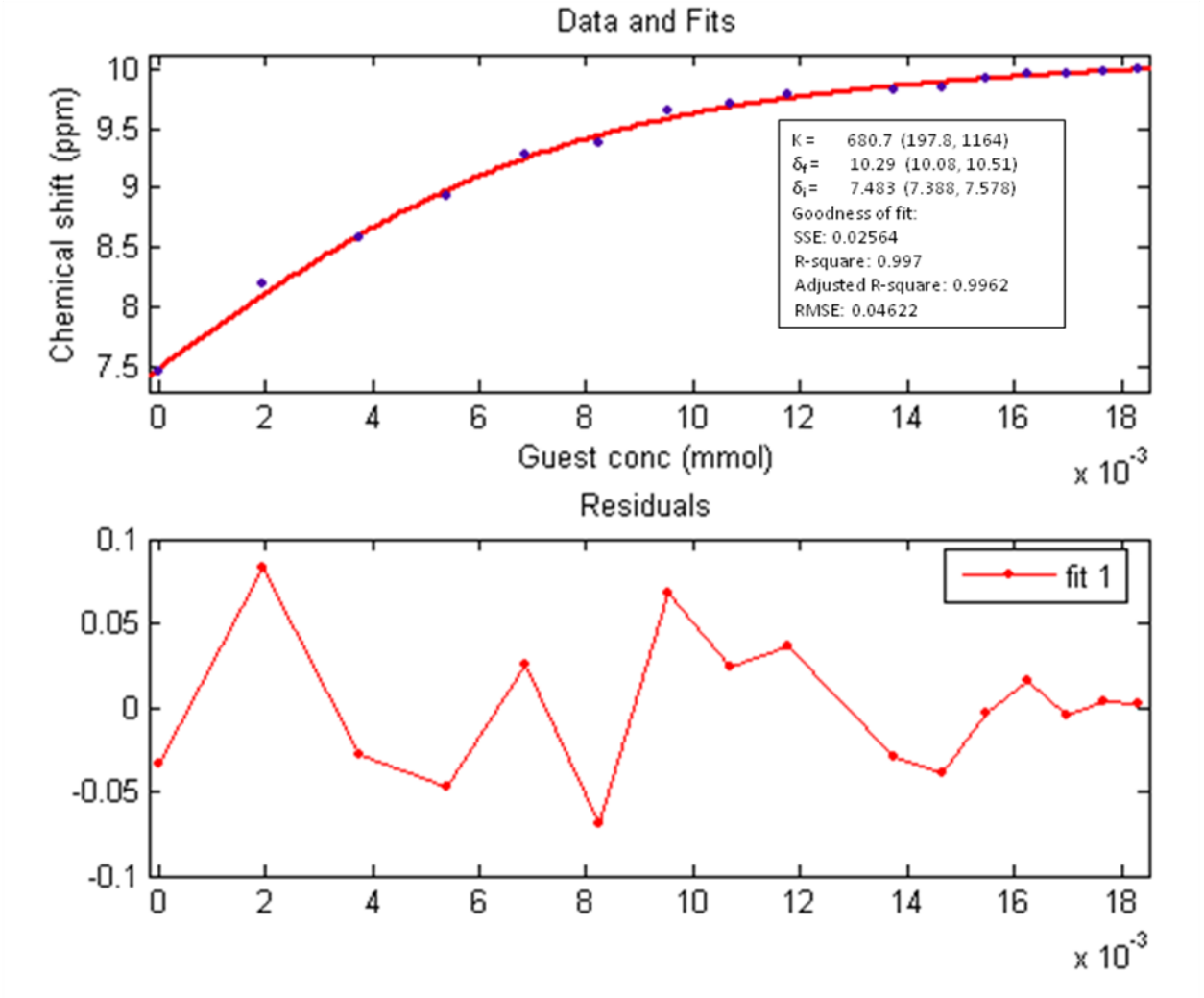
cis-**6** vs fluoride :



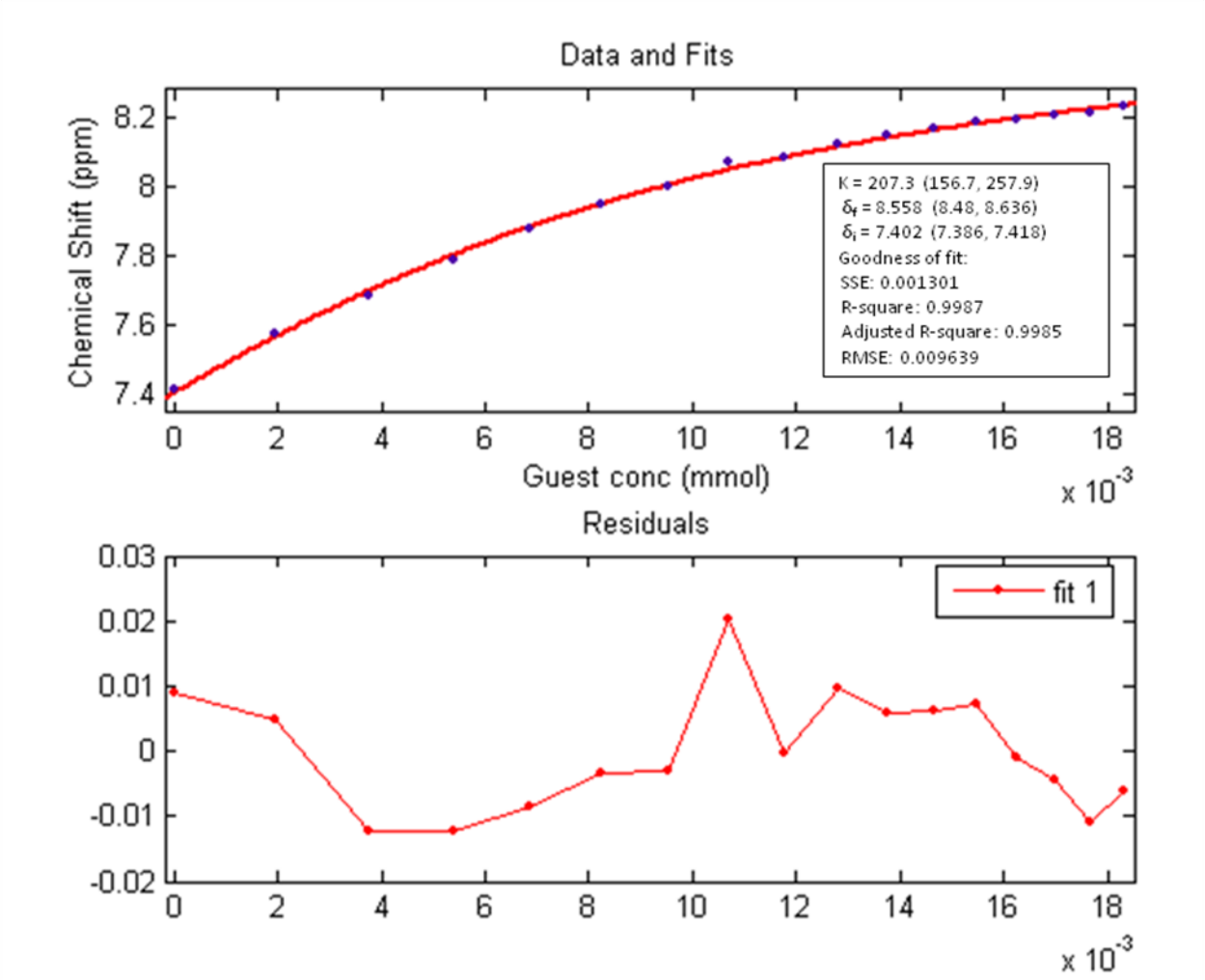
trans-**6** vs fluoride:



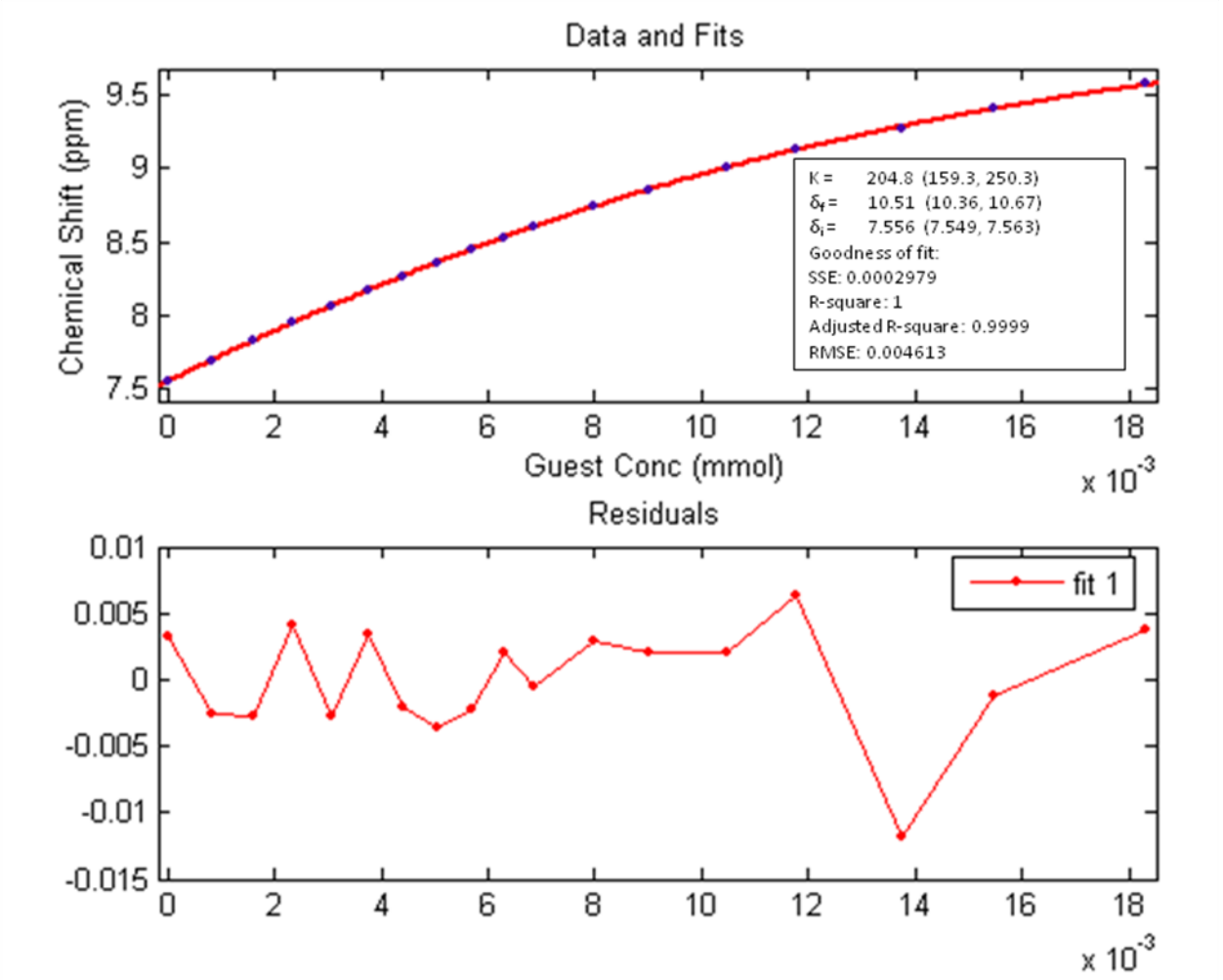
cis-**6** vs dihydrogenphosphate:



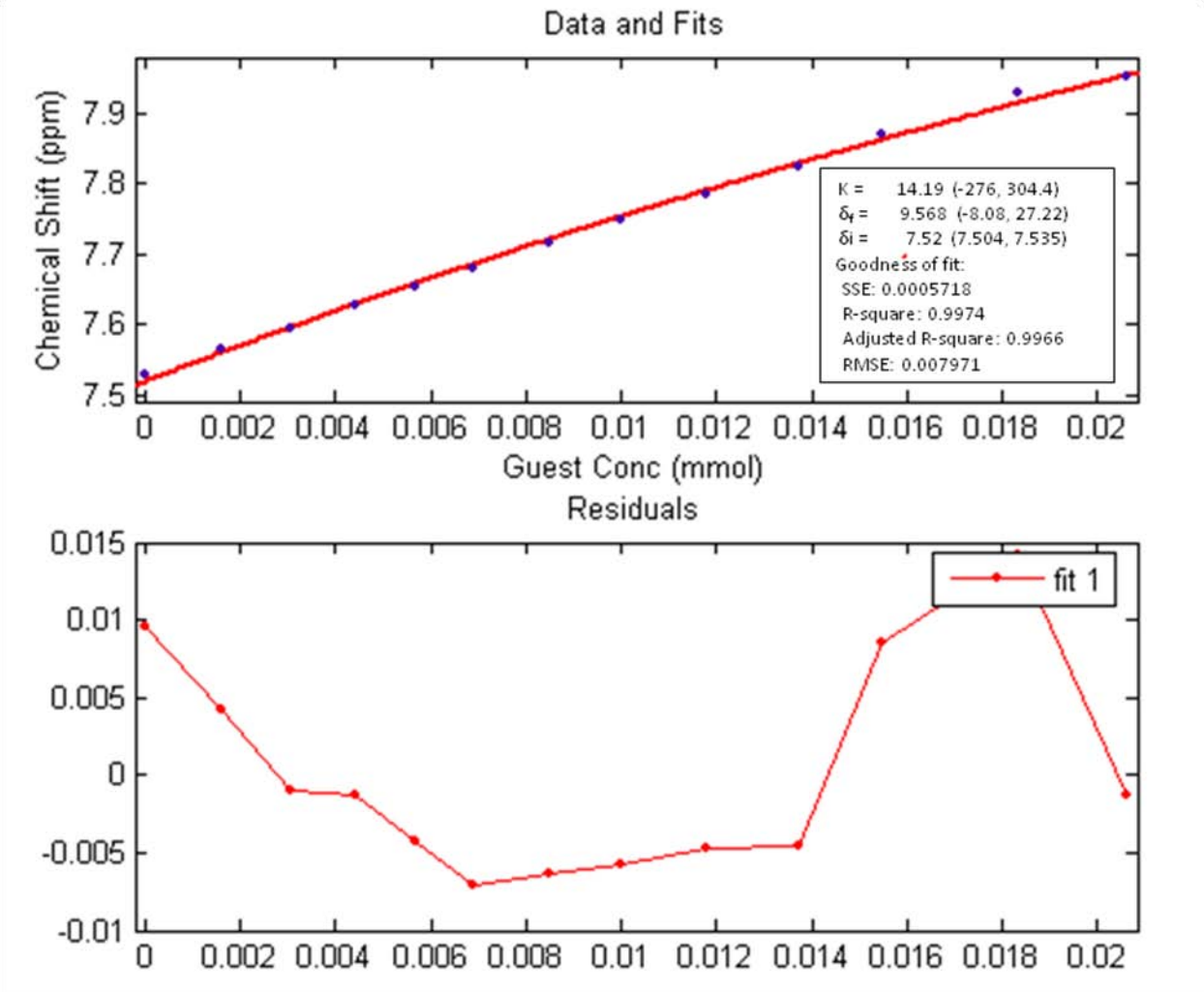
trans-**6** vs dihydrogenphosphate:



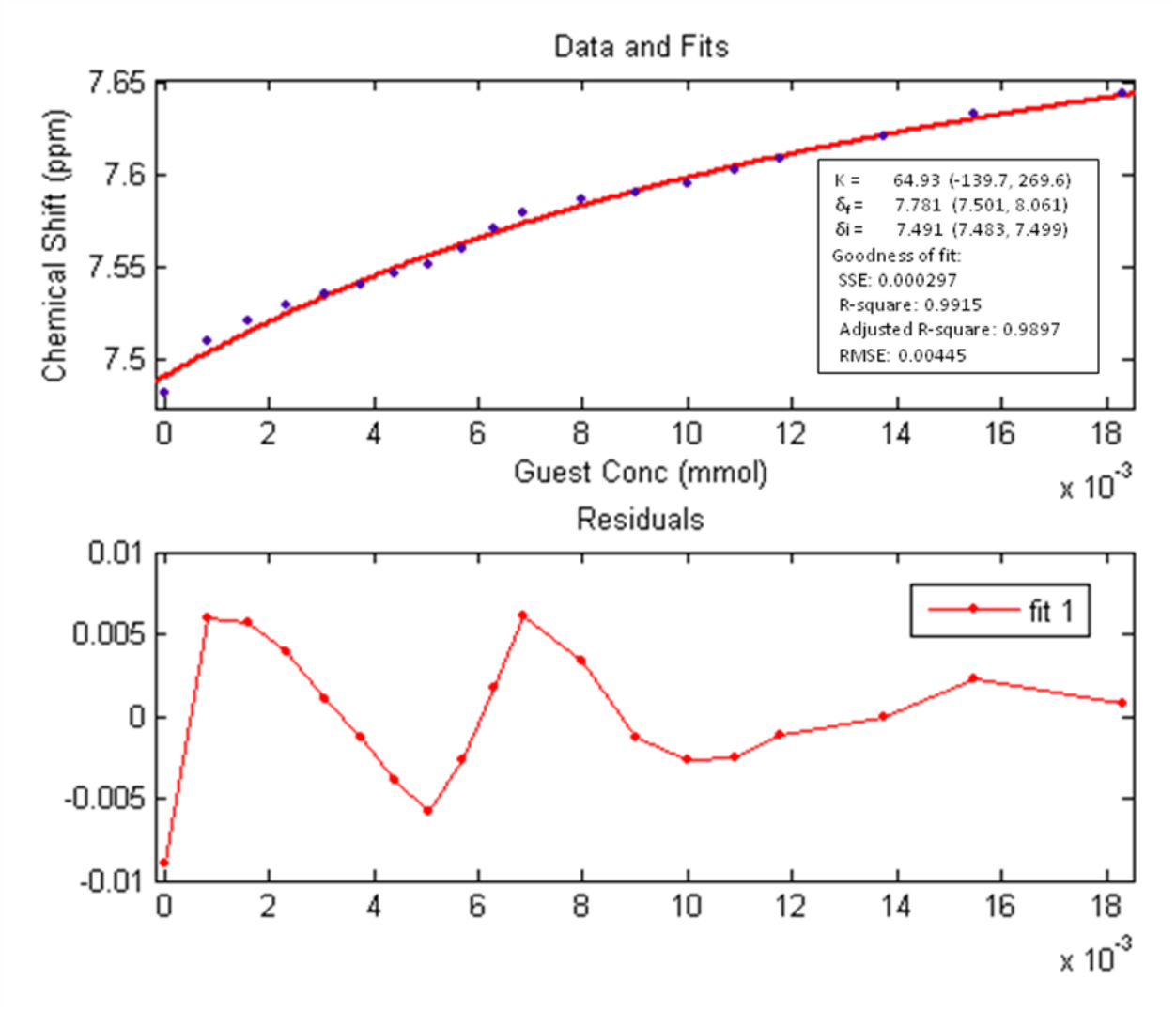
cis-**6** vs chloride:



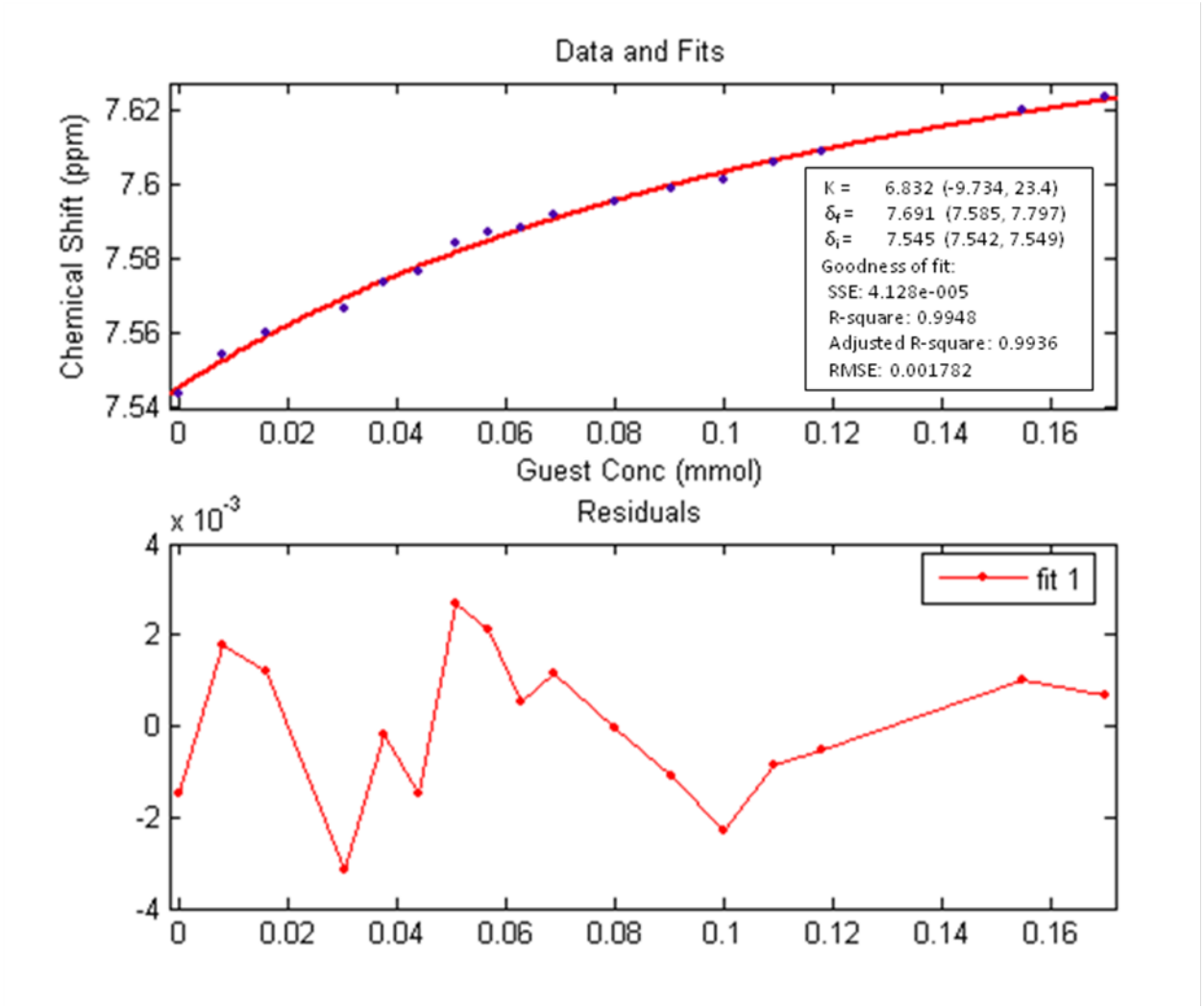
trans-**6** vs chloride:



cis-**6** vs bisulphate:



trans-**6** vs bisulphate:



Binding constant determination by ITC:

Octamethylcalix[**4**]pyrrole **1** vs dihydrogenphosphate:

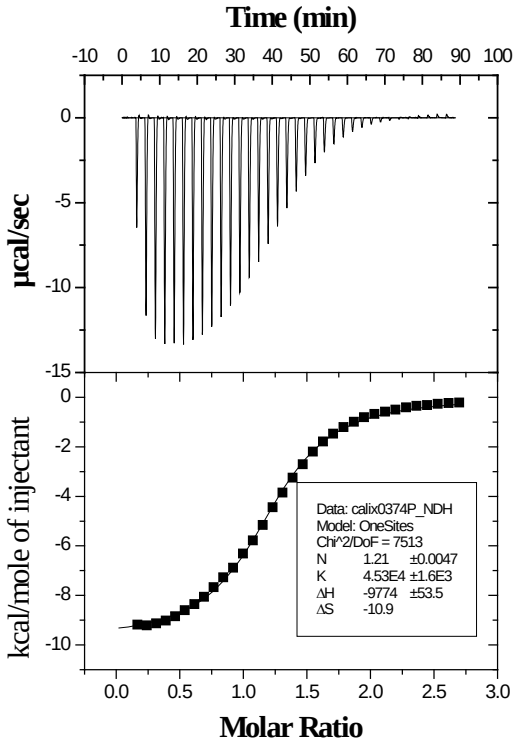


Figure S14: Isothermal calorimetric titration in acetonitrile at 303 K of tetrabutylammonium dihydrogenphosphate (5.6 mM) added into the solution of **1** at 0.37 mM. The curve shows the fit of the experimental data to a 1:1 binding profile.

cis-**6** vs dihydrogenphosphate :

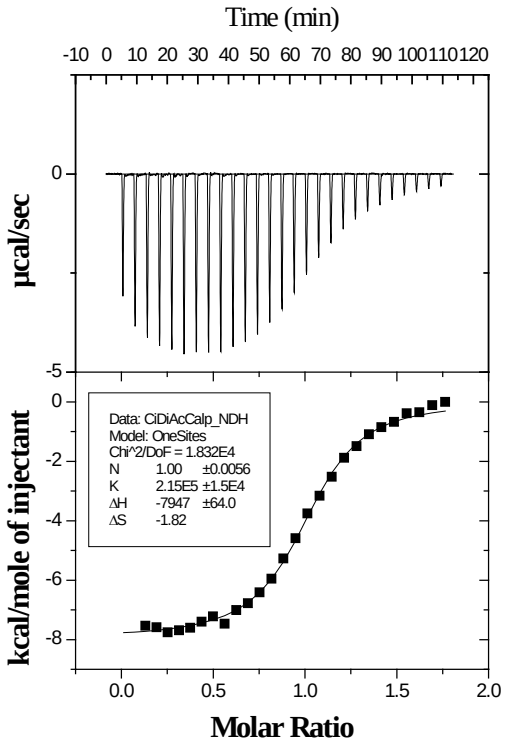


Figure S15: Isothermal calorimetric titration in acetonitrile at 303 K of tetrabutylammonium dihydrogenphosphate (1.7 mM) added into the solution of *cis*-**6** isomer at 0.2 mM. The curve shows the fit of the experimental data to a 1:1 binding profile.

trans-**6** vs dihydrogenphosphate:

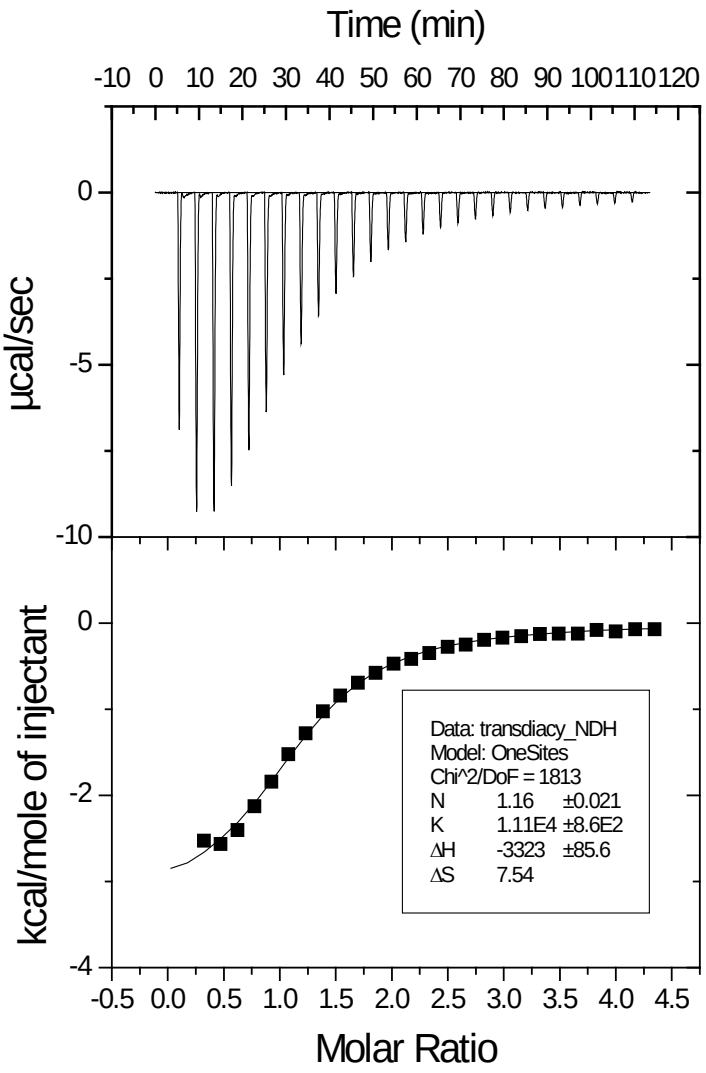


Figure S16: Isothermal calorimetric titration in acetonitrile at 303K of tetrabutylammonium dihydrogenphosphate (10 mM) added into the solution of *trans*-**6** isomer at 0.47 mM. The curve shows the fit of the experimental data to a 1:1 binding profile.

cis-**6** vs chloride:

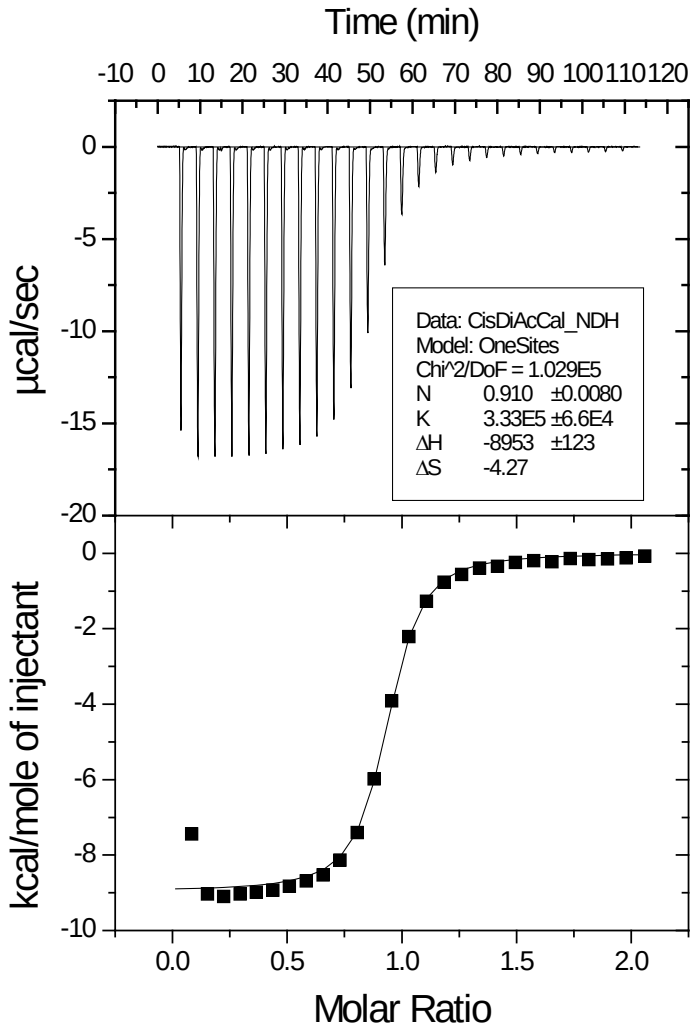


Figure S17: Isothermal calorimetric titration in acetonitrile at 303 K of tetrabutylammonium chloride (5 mM) added into the solution of *cis*-**6** isomer at 0.5mM. The curve shows the fit of the experimental data to a 1:1 binding profile.

trans-**6** vs chloride:

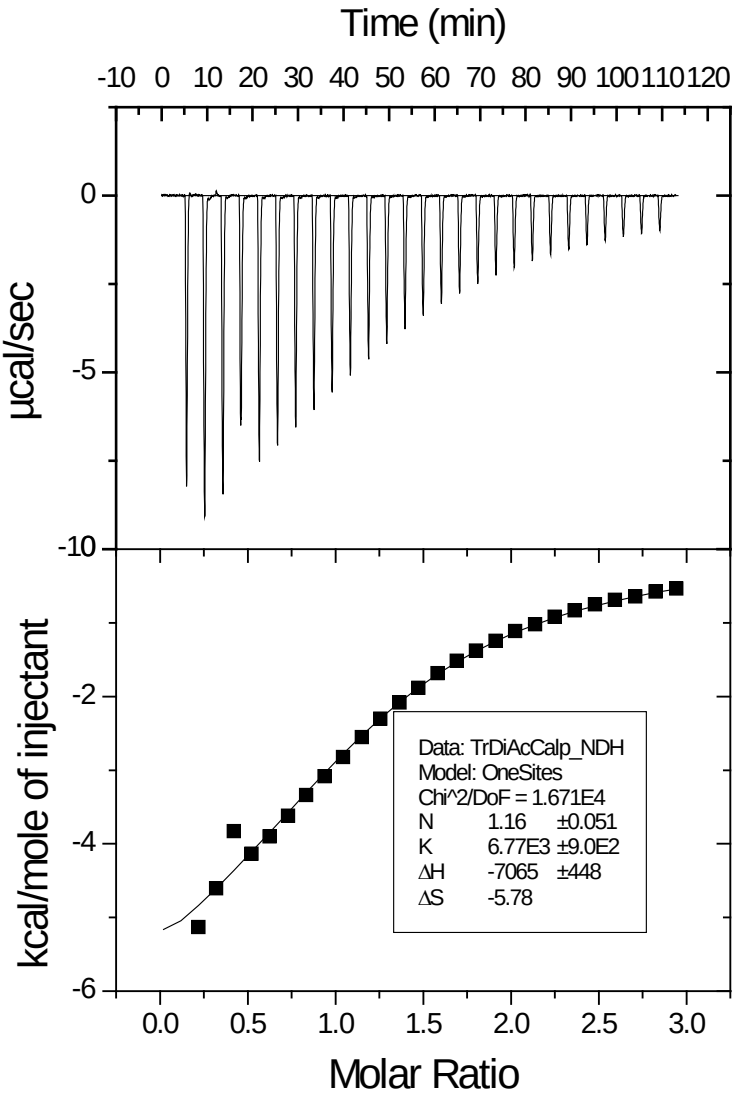


Figure S18: Isothermal calorimetric titration in acetonitrile at 303 K of tetrabutylammonium chloride (5 mM) added into the solution of *trans*-**6** isomer at 0.35 mM. The curve shows the fit of the experimental data to a 1:1 binding profile.

cis-**6** vs bromide:

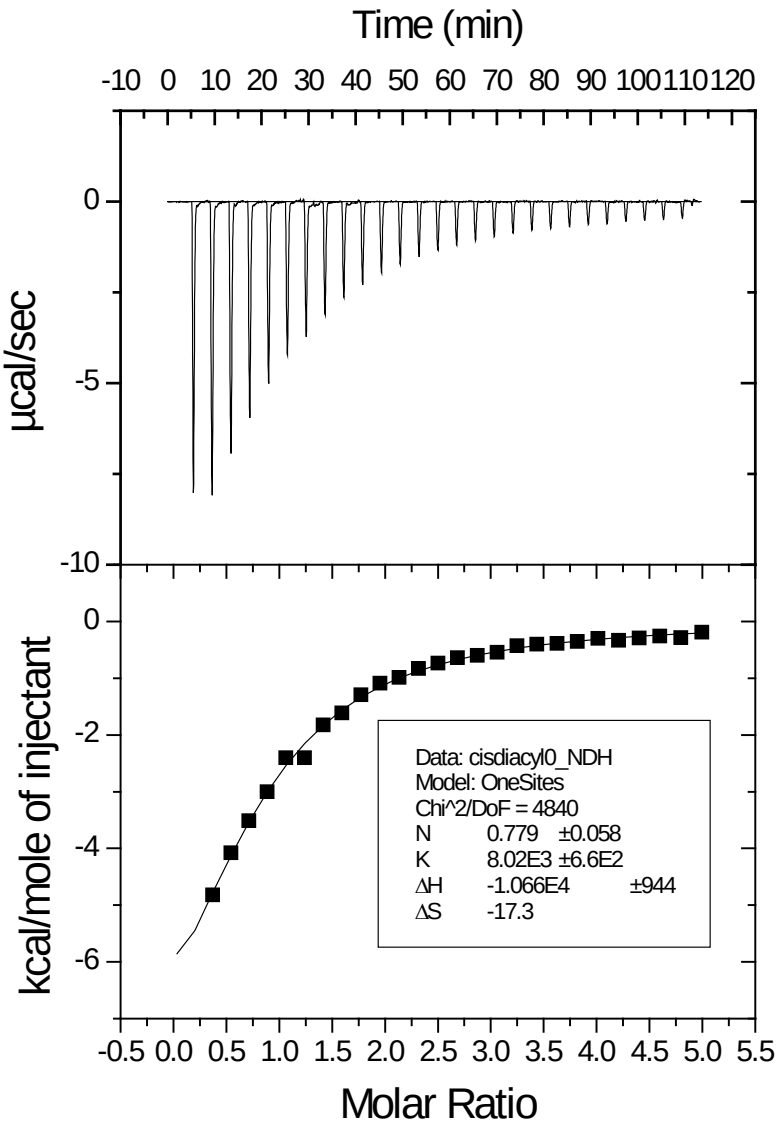


Figure S19: Isothermal calorimetric titration in acetonitrile at 303 K of tetrabutylammonium bromide (4.85 mM) added into the solution of *cis*-**6** isomer at 0.2 mM. The curve shows the fit of the experimental data to a 1:1 binding profile.

trans-**6** vs bromide:

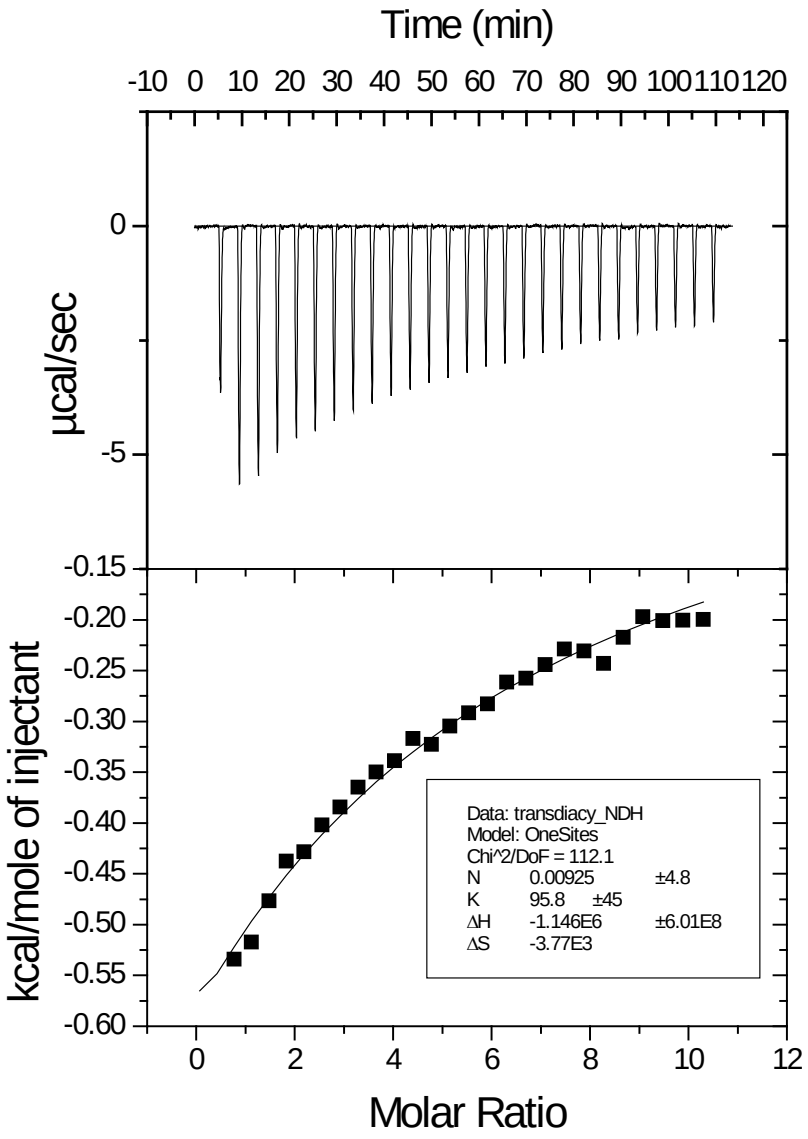


Figure S20: Isothermal calorimetric titration in acetonitrile at 303 K of tetrabutylammonium bromide (28 mM) added into the solution of *trans*-**6** isomer at 0.56 mM. The curve shows the fit of the experimental data to a 1:1 binding profile.

Table 1: Association constants K_a, and thermodynamic parameters for the binding of chloride, bromide, and dihydrogenphosphate by hosts *cis*-**6**, *trans*-**6** and octamethycalix[**4**]pyrrole **1** as measured by ITC (Isothermal Titration Calorimetry) at 30 °C using the corresponding tetrabutylammonium salts (TBA)

Anion	Host	TΔS (kcalmol^{-}1)	ΔH (kcalmol^{-}1)	ΔG (kcalmol^{-}1)	K_a(ITC) (M^{-1})
Cl^-	*cis*-**6**	-1.29	-8.95	-7.66	3.3 X 10^5
	trans-**6**	-1.75	-7.06	-5.31	6.77 X 10^3
	1	-2.91	-10.16	-7.29	2.2 X 10^5
Br^-	*cis*-**6**	-1.245	-6.84	-8.09	1.10 X 10^4
	trans-**6**	ND	ND	ND	ND
$H_2PO_4^-$	*cis*-**6**	-0.546	-7.947	-7.401	2.15 X 10^5
	trans-**6**	2.262	-3.32	-5.58	1.11 X 10^4
	1	-3.27	-9.774	-6.504	4.53 X 10^4

ND: observed no binding in ITC.

Computational (DFT) analysis:

[*cis*-6.H_2PO_4]$^-$ and [*trans*-6.H_2PO_4]$^-$:

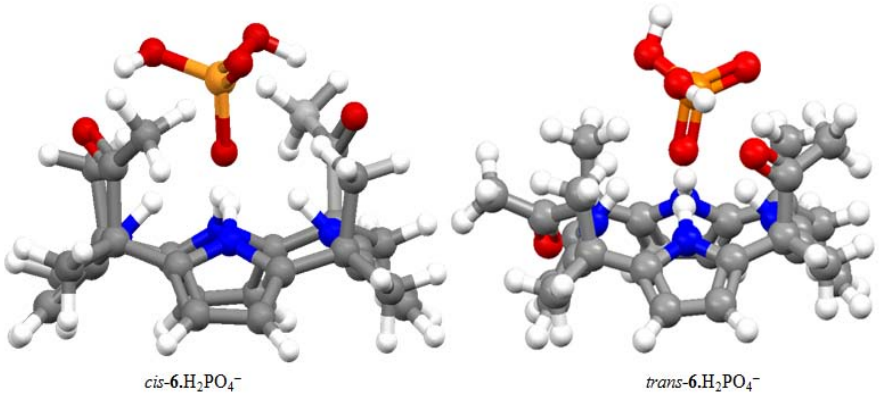


Figure S21: Ball and stick view of the DFT optimized structure of the two isomers of **6** with dihydrogenphosphate.

In case of *cis*-**6**, the O-H…O 'd' values ranges from 1.98 Å (155.05), 1.94 (157.14) N-H…O 'd' values ranges from 1.90Å (169.02), 1.85 Å (169.14), 1.90 Å (166.55), 1.93 Å (168.6); C-H...O (methyl) d values ranges from 2.52 Å (160.02), 2.74 Å (157.1) and the C-H…O (acyl methyl) d values 2.29 Å (152.4), 2.89 Å (123.2)

In case of *trans*-**6**, the O-H…O 'd' values ranges from 1.94 Å (158.14), N-H…O 'd' values ranges from 1.92 Å (172.3), 1.94 Å (170.7), 2.02 Å (169.03), 1.99 Å (157.3); C-H...O (methyl) d values ranges from 2.6 Å (154.8), 2.58 Å (151.1), 2.94 Å (144.2) and the C-H…O (acyl methyl) d values 2.34 Å (152.2).

[*cis*-**6**.F]$^-$ and [*trans*-**6**.F]$^-$:

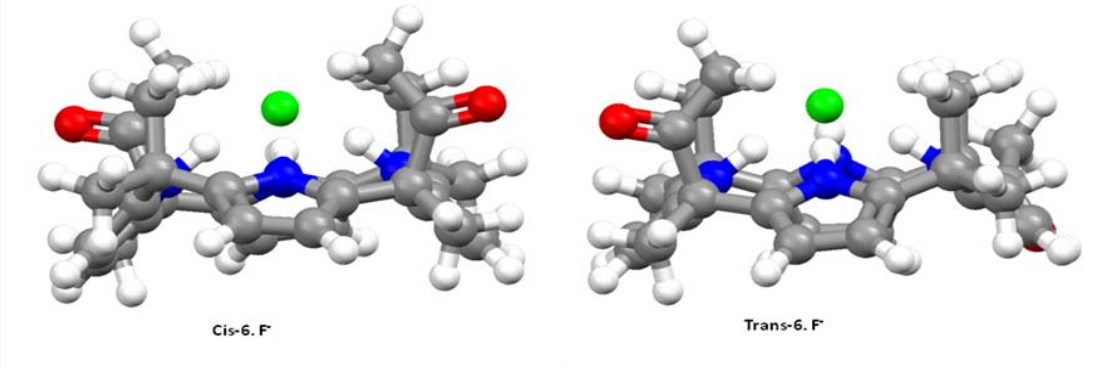


Figure S22: Ball and stick view of the DFT optimized structure of the two isomers of **6** with fluoride.

In case of *cis*-**6**, The N-H…F, d values ranges from 1.72 Å (176.5), 1.73 Å (166.7), 1.72 Å (176.6), 1.73 Å (166.8); C-H...F (methyl) d values ranges from 2.51(145.8), 2.51(145.8) and the C-H…F (acyl methyl) d values 2.42(158.1), 2.42(158.1).

In case of *trans*-**6**, the N-H…F 'd' values ranges from 1.740 Å (177.17), 1.752 Å (171.74), 1.728 Å (163.7), 1.726 Å (173.8); C-H...F (methyl) d values ranges from 2.67 Å (144.7), 2.67 Å (143.25), 2.69 Å (145.1) and the C-H…F (acyl methyl) d values 2.31 Å (157.0).

[*cis*-6.Cl]$^-$ and [*cis*-6.Cl]$^-$:

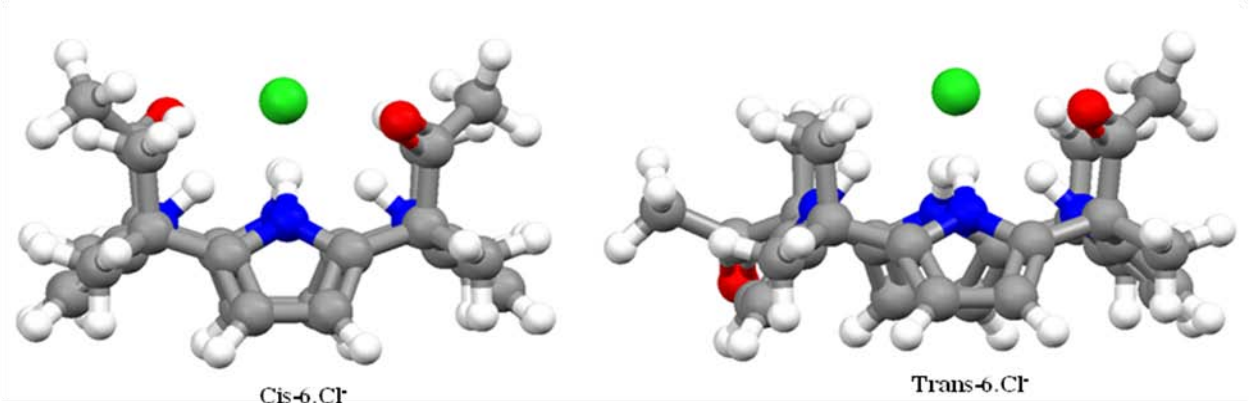


Figure S23: Ball and stick view of the DFT optimized structure of the two isomers of **6** with chloride.

In case of *cis*-**6**, The N-H…Cl, d values ranges from 2.28 Å (175.8), 2.33 Å (162.1), 2.28 Å (175.8), 2.33 Å (162.1); C-H...Cl (methyl) d values ranges from 2.85 (157.4), 2.85 (157.4) and the C-H…Cl (acyl methyl) d values 3.18 (136.8), 3.18 (136.8).

In case of *trans*-**6**, The N-H…Cl, d values ranges from 2.31 Å (169.3), 2.26 Å (177.4), 2.35 Å (172.3), 2.35 Å (164.7); C-H...Cl (methyl) d values ranges from 2.86 (157.9), 2.7 (161.69), 2.9(156.9) and the C-H…Cl (acyl methyl) d values 3.12(136.7).

Cartesian coordinates for the DFT optimized geometry:

[*cis*-**6**.F]$^-$:

C	0.0202830271	-0.0498348454	-0.0155299618
C	0.0443561721	-0.0192945838	1.3697270018
H	0.9267340874	-0.0235849443	1.9936171772
C	-1.3034104838	0.0261628449	1.8225938059
H	-1.6233534553	0.063261205	2.8533884016
C	-2.1304450698	0.0269857831	0.7065540117
C	-3.6568351847	-0.0087170759	0.65749938
C	-4.1929177292	0.2991809458	2.0724719202

H	-3.8090770649	-0.4295392516	2.7895970134
H	-5.2798544749	0.2299514656	2.086207041
H	-3.8815348509	1.2994281187	2.3825057665
C	-4.307486948	0.9745499724	-0.318974663
C	-5.2565594454	1.9519765033	-0.057906065
H	-5.6506202516	2.2132988276	0.9128470978
C	-5.6362946306	2.5354700708	-1.297409652
H	-6.3578481742	3.3284899311	-1.433584626
C	-4.9210426719	1.8999228619	-2.2993980303
C	-4.9481305673	2.0954507773	-3.8126065454
C	-6.2089267076	2.9034831348	-4.182448482
H	-7.1041579747	2.3774639796	-3.8377210175
H	-6.273044455	3.0253444222	-5.2681835236
H	-6.1994616891	3.8986416454	-3.7285756662
C	-5.0477050773	0.7129327187	-4.5190900611
H	-4.1732585003	0.0879340303	-4.3215050858
H	-5.1227160652	0.8569795824	-5.6029147861
H	-5.9383233372	0.176544509	-4.1721842166
C	-3.7193573962	2.8403478176	-4.327385908
C	-3.6128872303	4.0501706077	-4.9948138406
H	-4.4249568722	4.7225920148	-5.2319480409
C	-2.239261539	4.2509407443	-5.3053316483
H	-1.8255666624	5.105343172	-5.820240039
C	-1.5266315744	3.1624393562	-4.8186933882
C	-0.0353983561	2.864234395	-4.9629091046
C	0.6681608434	4.1469977047	-5.4567620992
H	0.2413473188	4.4703824111	-6.4085266322
H	1.7275457731	3.95515308	-5.6220332174
H	0.5467414294	4.9477401793	-4.7235170662
C	0.2200439566	1.7578027177	-6.056429161
C	0.6700392102	2.3998107679	-3.686127188
C	1.7806598959	2.949739572	-3.0629914613
H	2.297366036	3.8496669045	-3.3614518551
C	2.1330491949	2.1074845181	-1.9732969505
H	2.9547561005	2.2621698504	-1.2885177785
C	1.2386889004	1.0496105084	-1.9514952789
C	1.1587869885	-0.1611390601	-1.0260315722
C	2.4917818938	-0.2843327035	-0.2597242309
H	2.6794711894	0.590698519	0.3691822376
H	3.3211282955	-0.383484281	-0.9663538243
H	2.4754321638	-1.1690033545	0.3843775209
C	0.9761930329	-1.4555504353	-1.8695833087
H	0.973901882	-2.3295581085	-1.2084093159
H	1.7997424584	-1.557208499	-2.585606411
H	0.0363654167	-1.4519614701	-2.4272967513
N	-1.3027489327	-0.0163271465	-0.3980511156

H	-1.6014765562,	-0.0442471246	-1.3812047587
N	-4.1279460007	0.9506240864	-1.690480716
H	-3.4091976915	0.4192265215	-2.1962169812
N	-2.4474457979	2.3207624424	-4.2263508849
H	-2.2466713536	1.4150674719	-3.783835457
N	0.3650246111	1.2369131804	-3.0015593766
H	-0.470776095	0.6567411748	-3.1398705847
C	-4.1804770484	-1.4462994453	0.2775149163
F	-2.0109034063	-0.1258515789	-3.0508880028
C	-0.7369810354	0.5884582926	-6.1877690756
H	-0.9872712899	0.1214419626	-5.2315244083
H	-1.6805970111	0.9470473344	-6.6152668653
H	-0.2920917949	-0.1478944602	-6.8601467662
O	1.1749804904	1.8500556661	-6.811546594
C	-3.4327372304	-2.2774935029	-0.7473452385
H	-3.1736675821	-1.7215736499	-1.6523902737
H	-2.4868252326	-2.6168583228	-0.3094191625
H	-4.0453806682	-3.1447169341	-1.0019282578
O	-5.1750645323	-1.9006241856	0.820684254

[*trans*-**6**.F]$^-$:

C	-0.000798722	-0.098618476	-1.3511123846
H	0.9119518034	-0.1538986379	0.0345568835
C	0.0272264549	-0.1106189693	1.9706983185
C	-1.318861483	-0.0609100713	1.8183313003
H	-1.6470860341	-0.0425630554	2.8446861097
C	-2.1443880516	-0.0233055863	0.70642434
C	-3.6600418085	-0.0590746433	0.5153284555
C	-4.2191653138	1.2259284403	-0.1009192026
C	-4.9206449128	2.2759590912	0.4695043103
H	-5.1616773345	2.3817782716	1.5182439675
C	-5.2542365783	3.1855439441	-0.5759409403
H	-5.8063654154	4.1082092276	-0.4660453456
C	-4.7427995299	2.6742353081	-1.7584297547
C	-4.777557648	3.2155943942	-3.1836537436
C	-5.8809662321	4.2895299274	-3.2787796323
H	-6.8483914764	3.8554185722	-3.0080817335
H	-5.9441244954	4.6759536952	-4.3007443912
H	-5.6860016461	5.1314911406	-2.608364672
C	-5.1402601079	2.0747225193	-4.1746311386
H	-4.3954405548	1.2745305006	-4.1744640128
H	-5.2017491816	2.4751682605	-5.1925799553
H	-6.1093272236	1.6376815821	-3.9075062119
C	-3.4458992995	3.8397920936	-3.5904353349
C	-3.1244533487	5.1575218443	-3.8725457424

H	-3.7967641998	6.0024015856	-3.826301708
C	-1.7510673622	5.198944077	-4.2349605417
H	-1.1986054347	6.0797534392	-4.5257038209
C	-1.251217491	3.9069466753	-4.1601831017
C	0.1479196628	3.4080581059	-4.5329171801
C	1.0008009813	4.6364046884	-4.9197245005
H	0.5335334628	5.1739880178	-5.7434658082
H	1.9904944394	4.3184378138	-5.2546499192
H	1.1128170621	5.3019363709	-4.0607579247
C	-0.0066648241	2.5408201777	-5.8415527203
C	0.8857461319	2.6474683981	-3.4313902647
C	2.1689738335	2.8691303469	-2.9491026544
H	2.83609307	3 .6620760643	-3.2524562301
C	2.4501380106	1.8730689532	-1.9746344766
H	3.3674550916	1.7734653725	-1.4124038753
C	1.3372454143	1.053429673	-1.8767642791
C	1.1228842908	-0.2180826344	-1.0590983561
C	2.4322176858	-0.5536347322	-0.3158529204
H	2.7144858692	0.2399521467	0.3822522028
H	3.2492522373	-0.6879194031	-1.0313408732
H	2.3117348081	-1.481239984	0.2516285485
C	0.813193793	-1.398175438	-2.0259707147
H	0.6933452193	-2.3270142041	-1.4564913458
H	1.6380356685	-1.5234609631	-2.7370306243
H	-0.1038172407	-1.2294515443	-2.5967950216
N	-1.3251210943	-0.048085102	-0.406889402
H	-1.646400544	0.0475526905	-1.3779504501
N	-4.1337224546	1.4761567555	-1.4535568666
H	-3.5071534595	0.97295598	-2.0979080088
N	-2.3014956365	3.092977949	-3.7757517693
H	-2.237992392	2.0894416698	-3.5566856017
N	0.3984194185	1.5400284588	-2.7624975892
H	-0.5351957329	1.1282955344	-2.8846981342
O	0.1209903794	3.0631351825	-6.938217276
C	-0.2979190392	1.0566790234	-5.7438083089
H	-0.5317283939	0.6861900545	-6.7440277139
H	0.5915912743	0.5410174338	-5.3640334386
H	-1.1126395426	0.8185100329	-5.053681211
C	-4.4215213264	-0.2035620721	1.8596213686
C	-5.7967062737	-0.8625844502	1.8387543381
H	-6.4138698954	-0.4832944166	1.020002801
H	-5.6953783734	-1.9462426827	1.7064187135
H	-6.2836127027	-0.6660774587	2.7957057268
O	-3.9838061013	0.224789718	2.912776263
C	-4.0030832382	-1.2716624799	-0.4054116677
H	-3.6882087522	-2.2060189466	0.0713712853

H	-5.0714878055	-1.3214814839	-0.6288017353
H	-3.4743925198	-1.1942126102	-1.3568034579
F	-2.1348615784	0.4547532455	-3.0109388001

[*cis*-**6**.Cl]$^{-}$:

C	-0.0081413707	-0.1213074343	-0.0221282544
C	0.0030012688	-0.3496869784	1.3447356397
H	0.8802203693	-0.513951114	1.954182991
C	-1.346123752	-0.3347681134	1.8002849537
H	-1.6773250109	-0.4873624054	2.8177314056
C	-2.1565686389	-0.0954888929	0.7038889365
C	-3.6684229328	0.0374529983	0.6076598179
C	-4.3080770336	-0.6216369866	1.8607127514
H	-3.9851581326	-1.6620396102	1.930001958
H	-5.4004748312	-0.5864937099	1.8034706699
H	-3.9998790249	-0.0923159333	2.7659995523
C	-4.1197419532	1.4890220323	0.5367056256
C	-4.8622798178	2.2367698366	1.4366811002
H	-5.2484452687	1.8927075752	2.3855629304
C	-5.0170934856	3.5437849603	0.892557809
H	-5.5406075371	4.3683462848	1.3548539559
C	-4.3689394285	3.5732205834	-0.3318838741
C	-4.2438325085	4.6953661853	-1.3588115571
C	-5.0847733971	5.8978453852	-0.8805324181
H	-6.1344280993	5.605628478	-0.7765427639
H	-5.018954116	6.7103977975	-1.6098862612
H	-4.7397696281	6.2768720967	0.0857334667
C	-4.8254703015	4.2283386471	-2.7221811736
H	-4.3018985637	3.35793791	-3.126074699
H	-4.7520739011	5.03641266	-3.4581923449
H	-5.8800485001	3.9569499173	-2.5986895622
C	-2.7988503213	5.1521470957	-1.5338724446
C	-2.140403599	6.2678488742	-1.0416751666
H	-2.5681809674	7.0277083538	-0.4032857076
C	-0.8036027744	6.2365566515	-1.5314405613
H	-0.0344514283	6.9694866923	-1.3329532058
C	-0.6692431095	5.1013884923	-2.3121436859
C	0.536270625	4.5625078801	-3.0664509714
C	1.5516629439	5.7195068896	-3.2762797025
H	1.0637401117	6.5412315143	-3.8037395098
H	2.413822704	5.3792416836	-3.8582986001
H	1.9167735083	6.0824717008	-2.3120901772
C	0.1426863445	4.1767546603	-4.5356013832
C	1.2313046491	3.4338892043	-2.3188366833
C	2.4988588881	3.38185746	-1.7611211412

H	3.2275919353	4.1798684431	-1.7588694959
C	2.6664027253	2.0916295621	-1.1818399442
H	3.5440276787	1.7362491934	-0.6611047141
C	1.4998145222	1.3752762988	-1.396635687
C	1.1378796034	-0.0606850403	-1.027227443
C	2.3764230452	-0.7362949595	-0.4015685541
H	2.7060492548	-0.2213491302	0.5053692606
H	3.2066610782	-0.7348091146	-1.1147884502
H	2.1419565536	-1.7723536758	-0.1405352175
C	0.7666129323	-0.8563552657	-2.3095152308
H	0.5213261928	-1.8921808516	-2.0507048803
H	1.6164377466	-0.8563035532	-3.0014941038
H	-0.0916418836	-0.4294493741	-2.8348770298
N	-1.3279775058	0.0350505254	-0.3880353187
H	-1.6511090812	0.2176732098	-1.3380365411
N	-3.8274907435	2.3192354945	-0.5265138769
H	-3.313864613	2.0307676583	-1.3623617239
N	-1.8858236397	4.4567031775	-2.297445959
H	-2.0822994464	3.5855189119	-2.7900961462
N	0.6409900636	2.2086952453	-2.0831919296
H	-0.2910590297	1.9426988775	-2.4090685564
C	-5.4418662156	-0.3492602925	-1.3296043681
H	-5.1002165409	0.3210805193	-2.127332141
H	-5.9442605298	-1.205388663	-1.7849567183
H	-6.1250229956	0.2213296463	-0.6942654901
O	-3.7276639214	-1.9221244465	-0.8139479044
C	-4.2273561679	-0.8389721046	-0.5677475651
O	-0.6663827021	4.8499124516	-5.1486203023
C	0.8447718813	3.008058231	-5.1962819358
H	0.3148330525	2.0883139129	-4.9211734704
H	0.7927067322	3.1294455522	-6.2803746983
H	1.8789999065	2.902638474	-4.8568822587
C	-2.306351002	1.3190391646	-3.284717526

[*trans*-**6**.Cl]$^-$:

C	-0.0004301504	0.000674102	-0.0001019186
C	-0.0003922011	-0.0003735814	1.3849986393
H	0.8737015834	-0.0006013478	2.0207411779
C	-1.3538947728	-0.017533048	1.8283887405
H	-1.6996433463	-0.0303809167	2.8485300759
C	-2.1636338245	-0.0334257324	0.7049380465
C	-3.6747887314	0.0062847826	0.496984485
C	-4.1314345357	1.4165703369	0.1294970634
C	-4.569542567	2.4465527513	0.9437073254

H	-4.6746904284	2.3996846241	2.0197259647
C	-4.8402303261	3.5693253498	0.1110379535
H	-5.1967317342	4.5354553085	0.4390833816
C	-4.5519363685	3.2088762307	-1.1959622273
C	-4.6024403466	4.0259801835	-2.4841034788
C	-5.5586986086	5.2189430932	-2.2736429728
H	-6.5594931754	4.8551321753	-2.0212730438
H	-5.620800667	5.815241378	-3.1891142499
H	-5.2212535752	5.8732654996	-1.4652603219
C	-5.1665553642	3.1702560896	-3.6497031375
H	-4.5437469545	2.3016605383	-3.8796378126
H	-5.2286816078	3.7800410021	-4.5571965716
H	-6.1702290604	2.8090716372	-3.3973914489
C	-3.2212175167	4.5622793946	-2.8482230652
C	-2.7017825316	5.8444804251	-2.7721360237
H	-3.2242979362	6.7225985834	-2.4200222751
C	-1.3568479466	5.7974920525	-3.2389260628
H	-0.6780751329	6.6354301489	-3.3108040754
C	-1.0794258321	4.4873296111	-3.5890944126
C	0.1923603373	3.864732796	-4.1432417805
C	1.1235783182	5.0021943916	-4.6467464024
H	0.5974836186	5.6007917581	-5.3927944663
H	2.0335513391	4.5894059105	-5.0928859596
H	1.4168915509	5.6489544399	-3.8158455987
C	-0.1132236436	3.0675310451	-5.4605782598
C	0.9459819001	3.0437707527	-3.1052177163
C	2.1733299189	3.2798660987	-2.5066442694
H	2.8135806454	4.1327726695	-2.6804231033
C	2.4384174089	2.2011010077	-1.6161793584
H	3.3154038797	2.0894035521	-0.9950782429
C	1.3707954752	1.3202577089	-1.6854714464
C	1.1562087405	-0.0256761589	-0.9954668398
C	2.446857574	-0.3979130167	-0.2348349637
H	2.6900496952	0.3378011837	0.5372159963
H	3.2904804809	-0.4554739862	-0.9296019196
H	2.3255088155	-1.3716784479	0.2486547851
C	0.9101395671	-1.1267043132	-2.0651056053
H	0.7888824722	-2.1003991718	-1.5770283278
H	1.7664190914	-1.1787406829	-2.7472184044
H	0.0158796897	-0.9366339977	-2.6643161699
N	-1.3211855024	-0.0210284025	-0.3948312181
H	-1.6310670511	0.0235993621	-1.3645175242
N	-4.1368114034	1.8925897235	-1.1654314749
H	-3.7523195772	1.389070411	-1.9654119721
N	-2.2188022058	3.7543597466	-3.3406806825
H	-2.3146929672	2.7557336765	-3.5284402756

N	0.4738273055	1.8533319526	-2.5890569642
H	-0.4049285087	1.4109727901	-2.8676384568
O	-0.9531160381	3.4773937865	-6.2412388446
C	0.7109874544	1.8365890715	-5.780337369
H	0.2380643841	0.9730697753	-5.2977984102
H	0.7038341003	1.6770842891	-6.8608642863
H	1.7322543236	1.9095023548	-5.3965392533
C	-4.4835099289	-0.3818031751	1.7638929812
C	-5.9936999044	-0.5535073882	1.605228763
H	-6.4143688543	0.0465379552	0.7974891839
H	-6.2060458635	-1.6111360701	1.4047613659
H	-6.4687069573	-0.2898892478	2.5528044395
O	-3.9827103414	-0.5772602621	2.8568816368
C	-4.0775259372	-1.0266061651	-0.60185815
H	-3.8106588422	-2.0361593183	-0.2723297209
H	-5.1491371685	-0.9909585208	-0.8113368019
H	-3.5596357675	-0.8365678106	-1.5436263057
C	-2.3230442214	0.440686397	-3.58097154

[*cis*-**6**.H_2PO_4]$^-$:

C	0.0081334338	-0.0270384054	-0.0058734513
C	0.0121495124	0.0019401491	1.3806188855
H	0.8868952313	0.0132894426	2.0145660016
C	-1.3417872318	0.004205999	1.8201899684
H	-1.6775131552	0.0292225196	2.847216284
C	-2.1467178223	-0.0214308022	0.693015448
C	-3.6606751239	0.0040004106	0.5759001338
C	-4.2759706681	-0.2771478696	1.9726178038
H	-3.9236370825	-1.239912527	2.3520473502
H	-5.3676136155	-0.2837458496	1.9300413273
H	-3.9710992501	0.5016521183	2.6760365217
C	-4.1910138157	1.3320227653	0.0524824683
C	-4.8752961273	2.3485448572	0.6964175129
H	-5.1355948321	2.3788393761	1.7451634828
C	-5.1703499425	3.3475782752	-0.2743861301
H	-5.6946154823	4.2748329588	-0.0936826136
C	-4.6689526356	2.9193034406	-1.494372976
C	-4.7607715437	3.5580879348	-2.8771004781
C	-5.679292276	4.7940689111	-2.7873491162
H	-6.67003543	4.4996593083	-2.4282834952
H	-5.7914738056	5.247992683	-3.7762428121
H	-5.2769773559	5.5506031074	-2.1070377572
C	-5.4146740715	2.5561194416	-3.8713837199
H	-4.8189952032	1.6516098517	-4.014517271

H	-5.5287066664	3.0298833513	-4.852440936
H	-6.404180099	2.2580297086	-3.505710795
C	-3.4044345392	3.9958600936	-3.4199411203
C	-2.9376022861	5.2535870803	-3.7698030456
H	-3.4682224529	6.1868935797	-3.6470762521
C	-1.6384788028	5.0936810534	-4.3316850329
H	-1.0036413584	5.8852933067	-4.7038225467
C	-1.3374709825	3.7418585873	-4.3114702744
C	-0.093530559	3.0038305316	-4.7755261016
C	0.7778787549	3.9723270244	-5.6191044313
H	0.2018447882	4.3549117056	-6.4655889699
H	1.6743355046	3.4701180327	-5.9907494737
H	1.0941778531	4.8198181721	-5.0054422432
C	-0.4488047688	1.8461930805	-5.7621160905
C	0.7360079003	2.4667128765	-3.618421866
C	1.9625164881	2.8753580711	-3.1222024944
H	2.5537376435	3.7046349225	-3.4845404572
C	2.3033091822	2.0042640606	-2.0485276739
H	3.201510026	2.0535046125	-1.450007581
C	1.2830011197	1.0750319389	-1.9123128684
C	1.1679225037	-0.1363279573	-0.9915018797
C	2.4797900107	-0.2694849406	-0.1902584362
H	2.660441113	0.6032975256	0.4446852639
H	3.325989698	-0.3783786175	-0.874923859
H	2.4385968081	-1.1565494366	0.4487033709
C	1.0078287194	-1.4243649852	-1.8496168152
H	0.9225312051	-2.298183393	-1.1940602183
H	1.8863560618	-1.5506040922	-2.4927644411
H	0.1328772192	-1.4018885883	-2.5037212156
N	-1.3113118708	-0.0326180359	-0.4010652399
H	-1.6408443807	-0.0767589514	-1.3676506022
N	-4.0786466933	1.692053133	-1.2757408277
H	-3.57497995	1.1426221802	-1.9824947928
N	-2.4140438073	3.0967727797	-3.7477159187
H	-2.4717663177	2.0843542922	-3.6212348161
N	0.3395469538	1.3760911004	-2.8716908047
H	-0.5473750579	0.8817515446	-3.0001903571
C	-5.6699779924	-1.1387519972	-0.7032566112
H	-5.7493033048	-1.0693796411	-1.7933564176
H	-6.0981019121	-2.1020901753	-0.4064481807
H	-6.229192584	-0.3177204001	-0.2537126047
O	-3.4652390367	-2.02230741	-0.7598869473
C	-4.1945769672	-1.1350860383	-0.3392460409
O	-1.5563808362	1.7776749754	-6.2797069526
C	0.6075466071	0.813260137	-6.0827504192
H	0.3025253273	-0.1202499371	-5.5875274017

H	0.6039449954	0.6290076213	-7.1612863185
H	1.603771135	1.0925487841	-5.7358802218
O	-2.3798586496	0.2610777673	-3.087778012
P	-2.5472391917	-0.8595072134	-4.1601886081
O	-3.6668897356	-1.9122223182	-3.6225288616
O	-3.4246081047	-0.2604213075	-5.3962446682
O	-1.2610538846	-1.4924542553	-4.6098596775
H	-3.4946349378	-2.1818656048	-2.7006973453
H	-2.8623751348	0.3152605761	-5.9480746214

[*trans*-**6**.H_2PO_4]$^-$:

C	0.0014696797	0.0104543221	-0.0011883178
C	-0.0000840256	0.0299637111	1.3835341404
H	0.8730614252	0.0429700792	2.0203000244
C	-1.3537409978	0.014047275	1.8268422116
H	-1.7015980318	0.021177162	2.8460487341
C	-2.1614685366	-0.0209223705	0.7033708612
C	-3.6714669282	-0.0066779174	0.4898805952
C	-4.1386673685	1.3680971119	0.0163252187
C	-4.5901402871	2.4512262716	0.7493811574
H	-4.6893936957	2.4872420164	1.8261658168
C	-4.8900730295	3.496925919	-0.1690214041
H	-5.2710998288	4.4765250896	0.0814606936
C	-4.6069745097	3.0366952047	-1.4448753678
C	-4.7236941387	3.7346186444	-2.79574487
C	-5.6702593029	4.9440537493	-2.6464409193
H	-6.6507553313	4.6089319662	-2.2951097016
H	-5.797807936	5.4422800779	-3.6123678299
H	-5.2830562484	5.6780659313	-1.9339813934
C	-5.3481498119	2.7739624323	-3.8448424611
H	-4.7267525524	1.8977357058	-4.0445986957
H	-5.4759715891	3.3017949978	-4.7959830934
H	-6.328204406	2.424886782	-3.4998637466
C	-3.3707378097	4.2291601922	-3.2963088094
C	-2.9220215739	5.5111503796	-3.571057983
H	-3.479306609	6.4257045039	-3.4269585987
C	-1.5959391817	5.4063301514	-4.080733801
H	-0.9669512991	6.2286737617	-4.3908685331
C	-1.2604436379	4.0629260534	-4.1044024175
C	0.0182145699	3.380172352	-4.5583428742
C	0.9146473884	4.4256402427	-5.2756412845
H	0.3747972061	4.8688022837	-6.1162408892
H	1.8360721514	3.9664278892	-5.6416576399
H	1.1854332795	5.2233802929	-4.5792860928
C	-0.2682906451	2.3091958165	-5.6564615625

C	0.8031963532	2.7553825741	-3.4135892213
C	2.013525976	3.1218623778	-2.8498530617
H	2.6128035994	3.9775999769	-3.126699806
C	2.3268850188	2.1653707961	-1.843094774
H	3.2066478042	2.1667007055	-1.2161164535
C	1.3067581577	1.2271068444	-1.8128011439
C	1.1635773365	-0.0492018751	-0.9874217337
C	2.4679641881	-0.2660985521	-0.1914636828
H	2.6586221601	0.5521800866	0.5091443211
H	3.3183650503	-0.3371597181	-0.8763669354
H	2.404591937	-1.1970421129	0.3794878163
C	0.9898361091	-1.2660820699	-1.9396951823
H	0.8885576855	-2.1847700024	-1.3508869428
H	1.8682057931	-1.358784671	-2.5884278801
H	0.1183591736	-1.182236912	-2.5926991211
N	-1.3193951131	-0.0226878903	-0.3979027593
H	-1.6350243496	0.0101233518	-1.3657744021
N	-4.1635325248	1.7349644291	-1.3135525815
H	-3.7457718796	1.1842229227	-2.0638958451
N	-2.3450961646	3.3678987175	-3.6173033398
H	-2.3922019617	2.3505614337	-3.5425818537
N	0.3894107647	1.6052237054	-2.7712124716
H	-0.4885508878	1.119525367	-2.9664074893
O	-1.3486513011	2.2717427971	-6.232279984
C	0.8211884443	1.3248373976	-6.0190165256
H	0.5059067883	0.341131982	-5.6436731843
H	0.881908845	1.2544663611	-7.1093639481
H	1.7913680353	1.5775077164	-5.5882241755
O	-2.2971864871	0.4548280074	-3.2235384383
P	-2.3918514073	-0.5289722922	-4.4095549069
O	-3.4905754755	-1.6601494947	-3.9509194306
O	-3.229518369	0.1949771613	-5.6114914102
O	-1.1235374752	-1.1680794706	-4.9024424054
H	-3.3248775407	-2.4744289453	-4.4454373073
H	-2.6735610249	0.8661993144	-6.05319074
C	-4.4854508355	-0.2933470324	1.7798089973
C	-5.9851762501	-0.5360319356	1.6202036508
H	-6.4182855677	-0.001879968	0.7732630337
H	-6.1550293674	-1.6105476839	1.4777896619
H	-6.4802226332	-0.2351025962	2.5459907688
O	-3.996756065	-0.3466400812	2.8945429556
C	-4.057564276	-1.1183857945	-0.5331926158
H	-3.7921378259	-2.0999252005	-0.1269285984
H	-5.1250461241	-1.1046097318	-0.7638683859
H	-3.5296288682	-1.0036593793	-1.4793815926