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Supporting Information

Molecular Titanium-Hydroxamate Complexes as Models for TiO_2 Surface Binding

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Experimental

Instrumentation

NMR spectra were obtained on a 400/100 MHz or 600/150 MHz ($^{1}H/^{13}C$) instrument, with chemical shifts reported as δ ppm from an internal TMS standard. Elemental analysis was performed by Robertson Microlit Laboratories (Ledgewood, NJ). UV-Visible spectra were obtained using a Shimadzu UV-2600 spectrophotometer or a Varian Cary 50 scan. IR spectra were obtained using an Agilent Cary 660 FTIR with a diamond ATR attachment from Pike Technologies or a NXR FT-Raman module with a Smart Orbit diamond ATR attachment from Thermo Scientific. IR spectra of molecular species were obtained of the isolated powders. IR spectra of functionalized TiO_2 were obtained by pressing the TiO_2 substrate onto the ATR diamond surface. The IR background spectra were obtained from non-functionalized TiO_2 unless otherwise stated.

Crystallography

Single crystals of compounds **2**, **3**, and **4** were grown by slow cooling in ethylene glycol or DMSO, or by diffusion of diethyl ether into dichloromethane, respectively. Low-temperature diffraction data (ω-scans) were collected on a Rigaku R-AXIS RAPID diffractometer coupled to an R-AXIS RAPID imaging plate detector with Mo Kα radiation (λ = 0.71073 Å) for the structure of compounds **2**, **3**, and **4**. All structures were solved by direct methods using SHELXS and were refined against F^2 on all data by full-matrix least squares with SHELXL. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The full numbering scheme of compounds **2**, **3**, and **4** can be found in the Supporting Information.

Materials

Phenylhydroxamic acid (NH-PHA) was obtained from TCI Chemicals, and titanium(IV) isopropoxide was obtained from Strem Chemicals. N-methyl phenylhydroxamic acid (NMe-PHA) was synthesized from N-methylhydroxylamine hydrochloride and benzoyl chloride

according to a previously reported procedure.[1] TiO_2 paste was obtained from Solaronix (14411, T-SP, 15-20 nm particles). Rutile TiO_2 was obtained from US Research Nanomaterials Inc. (99.9+%, 30 nm particles). Fluorine-doped tin oxide (FTO, TEC 15) glass was obtained from Hartford Glass. All other chemicals were obtained from commercial sources and used as received. Solvents were dried using molecular sieves.

Nanoparticulate anatase TiO_2 films were prepared by spreading a film of Solaronix TiO_2 paste with a glass rod on FTO glass masked by a single layer of Scotch© Magic tape. The films were dried at 80 °C for 8 minutes, and then sintered in an oven at 370 °C for 10 min and 470 °C for 30 min followed by slow cooling to room temperature. These films were soaked in a dilute solution containing NH-PHA (10 mM ethanol or a saturated toluene solution) or NMe-PHA (10 mM toluene) overnight, rinsed, and dried under vacuum prior to experimentation.

Synthetic Procedures

Titanium(IV)-*cis*-bis-phenylhydroxamate-*cis*-bis-isopropoxide (1). In a dry flask was dissolved 185 mg phenylhydroxamic acid (1.35 mmol) in 5 mL anhydrous isopropanol. Separately, 200 μL titanium(IV) isopropoxide (0.675 mmol) was dissolved in 2 mL anhydrous isopropanol, and the solution was added to the stirred solution of phenylhydroxamic acid. The reaction was stirred overnight under a nitrogen atmosphere at room temperature, over which time a yellow-orange solid precipitated. The reaction was cooled to 0 °C and the precipitate obtained by filtration. The solid was washed with ethyl acetate and diethyl ether to yield a yellow powder. Yield: 235 mg, 79%.

^{1}H NMR (400 MHz, [D_4] methanol, 25 °C, TMS): δ = 7.78-7.76 (m, 4H; Ar-H), 7.53 (t, J = 7.5 Hz, 2H; Ar-H), 7.46 (t, J = 7.5 Hz, 4H; Ar-H), 3.92 (sept, J = 6.1 Hz, 2H; O-CH) 1.15 (d, J = 6.1 Hz, 12H; CH_3); ^{13}C NMR (100 MHz, [D_4] methanol, 25 °C, TMS): δ = 165.26 (C=O), 133.19 (Ar-C), 129.97 (Ar-C), 128.72 (Ar-C), 127.94 (Ar-C), 64.78 (O-CH), 25.29 (CH_3).

IR (solid): 3190 (w, br ν(NH)), 3153 (w), 3114 (w), 3085 (w), 3064 (w, ν(CH)), 3029 (w), 2960 (m, ν(CH)), 2925 (w, ν(CH)), 2862 (w, ν(CH)), 1597 (m, ν(C=O)), 1566 (m), 1517 (m, δ(NH)), 1482 (m), 1440 (w), 1330 (m), 1151 (m), 1118 (m), 1062 (m), 970 (s), 914 (m), 843 (m), 781 (m, ν(TiO)), 688 (s), 611 (m), 590 (m), 545 (m), 495 (m), 470 (m) cm^{-1};

UV/Vis (isopropanol): $\lambda_{max}(\varepsilon)$= 226 (38400), 294sh (11200); Elemental Analysis for $C_{20}H_{26}N_2O_6Ti$: Calculated: C 54.81; H 5.98; N 6.39; Ti 10.92. Measured: C 54.92; H 6.11; N 6.27; Ti 11.07.

Titanium(IV)-*cis*-bis-phenylhydroxamate-*cis*-bis-ethylene glycoxide (2).

Titanium complex **1** (32 mg, 0.073 mmol) was dissolved in 1 mL hot ethylene glycol. The solution was kept in the dark at room temperature for 1 week, over which time a precipitate formed. The solid was filtered, washed with anhydrous acetonitrile and diethyl ether to yield a pale yellow powder. Yield 21 mg, 65%.

IR (solid): 3434 (m), 3338 (m), 3189 (w, br ν(NH)), 3164 (w), 3105 (w), 3068 (w), 3025 (w), 2998 (w), 2912 (w, ν(CH)), 2838 (w, ν(CH)), 1602 (m, ν(C=O)), 1566 (m, ν(C=O)), 1518 (m, δ(NH)), 1487 (m), 1443 (w), 1360 (m), 1256 (m), 1220 (m), 1149 (m), 1122 (m), 1085 (m), 1051 (s), 906 (m), 862 (m), 783 (m, ν(TiO)), 688 (s), 669 (m), 545 (m), 490 (m), 459 (m) cm^{-1}.

Elemental Analysis for $C_{18}H_{22}N_2O_8Ti$: Calculated: C 48.89; H 5.01; N 6.33; Ti 10.82. Measured: C 48.71; H 4.77; N 6.05; Ti 10.63.

Titanium(IV)-*cis*-bis-phenylhydroxamate-*μ*-oxo trimer (3).

Titanium complex **1** (32 mg, 0.073 mmol) was dissolved in 1 mL hot DMSO. The red solution was hydrated with a small amount of water vapor, and kept in the dark at room temperature for 1 week. The solution gradually turned yellow with the concomitant formation of a precipitate. The solid was filtered, washed with anhydrous acetonitrile and diethyl ether to yield a yellow-orange powder. Yield 23 mg, 94%.

IR (solid): 3180 (w, br ν(NH)), 3155 (w,sh), 3058 (w, ν(CH)), 2996 (w), 2912 (w), 2827 (w), 2705 (w), 1594 (m, ν(C=O)), 1558 (m, ν(C=O)), 1523 (m, δ(NH)), 1483 (m), 1442 (w), 1355 (m), 1315 (m), 1150 (m), 1058 (m), 1024 (m), 912 (m), 800 (s, ν(TiOTi)), 783 (m, sh), 683 (s), 530 (m), 470 (m), 408 (m) cm^{-1}.

Elemental Analysis for $C_{54}H_{72}N_6O_{21}S_6Ti_3$ (**3** • 6 DMSO): Calculated: C 43.91; H 4.91; N 5.69; Ti 9.72. Measured: C 45.47; H 4.12; N 6.47; Ti 9.34.

Titanium(IV)-*cis*-bis-N-methyl-phenylhydroxamate-μ-oxo dimer (4). In a flask was placed 194 mg N-methylphenylhydroxamic acid (1.26 mmol) in 10 mL toluene. 185 μL Titanium(IV) isopropoxide (176 mg, 0.621 mmol) was added to the flask, and the solution immediately became dark yellow. The solution was stirred overnight under air at room temperature. The solvent was removed in vacuo to yield a yellow oil, which was purified by recrystallization with diethyl ether into dichloromethane to yield a pale yellow powder. Yield: 118 mg, 52.2%.
^{1}H NMR (400 MHz, [D_4] methanol, 25 ^{o}C): δ = 7.66-7.49 (m, 5H; Ar-H), δ = 3.50 (s, 3H, CH_3).
^{13}C NMR (150 MHz, [D_4] methanol, 25 ^{o}C): δ = 165.25 (C=O), 132.54 (Ar-C), 130.87 (Ar-C), 129.90 (Ar-C), 129.32 (Ar-C), 40.89 (CH_3).
UV/Vis (methanol): $\lambda_{max}(\varepsilon)$= 224 (63900)
IR (solid): 3477 (w, br), 3062 (w, ν(CH)), 3033 (w, ν(CH)), 2988 (w), 2940 (w), 2854 (w), 2792 (w), 1586 (m, ν(C=O)), 1564 (m, ν(C=O)), 1503 (m), 1463 (m), 1442 (m), 1406 (w), 1198 (s), 1076 (w), 1058 (m), 958 (s), 912 (m), 781 (s, ν(TiOTi)), 738 (w), 698 (m), 530 (m), 677 (m), 653 (m), 586 (m), 528 (m), 438 (m), 410 (m) cm^{-1}.
Elemental Analysis for $C_{32}H_{32}N_4O_{10}Ti_2$(4 • CH_2Cl_2): Calculated: C 40.48; H 3.78; N 5.24. Measured: C 38.11; H 3.73, N 5.34.

Theoretical Methods.

All calculations were conducted using the Gaussian 09[2] suite of programs. The B3LYP functional[3] was used for both the geometry optimizations and frequency calculations in conjunction with the 6-311G(d,p) basis set[4-6] for nonmetal atoms and the LANL2DZ basis set[7-9] for Ti. For the simulations of coordination complexes, the crystal structure was used as the starting geometry (solvent molecules were not included). The 9[TiO_2] cluster models were carved from the appropriate (same binding mode) larger slab of 4x4x3{101} facet anatase TiO_2 with hydrating water molecules at the surface.[10] This larger slab with the NH hydroxamate bound was optimized using DFT via SIESTA 3.1.[11] The functional used was PBE, an exchange-correlation functional[12], within the generalized gradient approximation (GGA). The basis set used was polarized double-ζ basis set[13] together with GGA Pseudopotential Database pseudopotentials based on the work of Troullier and Martins.[14] The Γ-point was used for the Monkhorst-Pack k-point grid for the Brillouin zone.[15, 16] During optimization the atoms of the

two bottom layers were fixed with a real space grid energy cutoff of 200 Ry until the residual force met the criterion of less than 0.04 eV/Å per atom.

This cluster model is similar to that in our previous work with siloxane anchors.[17] The valence of the model was filled using hydroxide ions and water molecules to make the cluster a singly positively charged singlet with the adsorbate, the hydroxamate. With the monodeprotonated adsorbate, the system would be neutral. For the reference blank TiO_2 simulation, from which the theoretical IR for the binding mode was subtracted, the dye molecule was simply removed. The artificial vibrations arising from the water molecules that just fill the valence is mostly removed by the subtraction. For the simulation of binding through an oxygen vacancy, the oxygen atom that would have been there was moved to the side as a water molecule (two protons were removed elsewhere) to allow for energetic comparisons. Similarly, a surface water molecule was moved to the side to allow for bridging bidentate binding while keeping the number of atoms the same.

During the geometry optimizations, only the adsorbate and the surface waters were allowed to relax using the default optimization criteria and integration grid provided by Gaussian 09.[2] This restriction mimics the effect of a large surface, but also follows the assumption that there is no significant surface rearrangement. For the free energy comparisons of binding modes, partial Hessians (only including the adsorbate and surface waters) were calculated using the ideal gas rigid rotor and harmonic oscillator approximations to the entropy as described by Cramer.[18] For visualization of the normal modes and generation of the IR spectra, the full Hessian was calculated. The IR spectra were created by convoluting the theoretical amplitudes with Lorentzians with a full-width at half-maximum of 8 cm^{-1} for the model complexes or 12 cm^{-1} for the clusters. A 0.975 scaling factor was used for the IR frequencies, based on aligning the spectra of the model complexes. The images of geometries were generated using Mercury.[19]

Notes for IR spectra: TiO_2 contains significant IR peaks between 3000-3500 and at ~1600 cm^{-1} due to surface hydroxo species and hydration. These peaks, upon binding a monolayer of organic molecules, are significantly removed, causing inverted peaks in those regions. In addition, binding of an organic molecule will disrupt the Ti-O network on the surface, causing an inverted peak at ~800 cm^{-1} due to a loss of Ti-O and Ti-O-Ti vibrations. The TiO_2 skeletal stretches limit the observable window to > ~500 cm^{-1}.

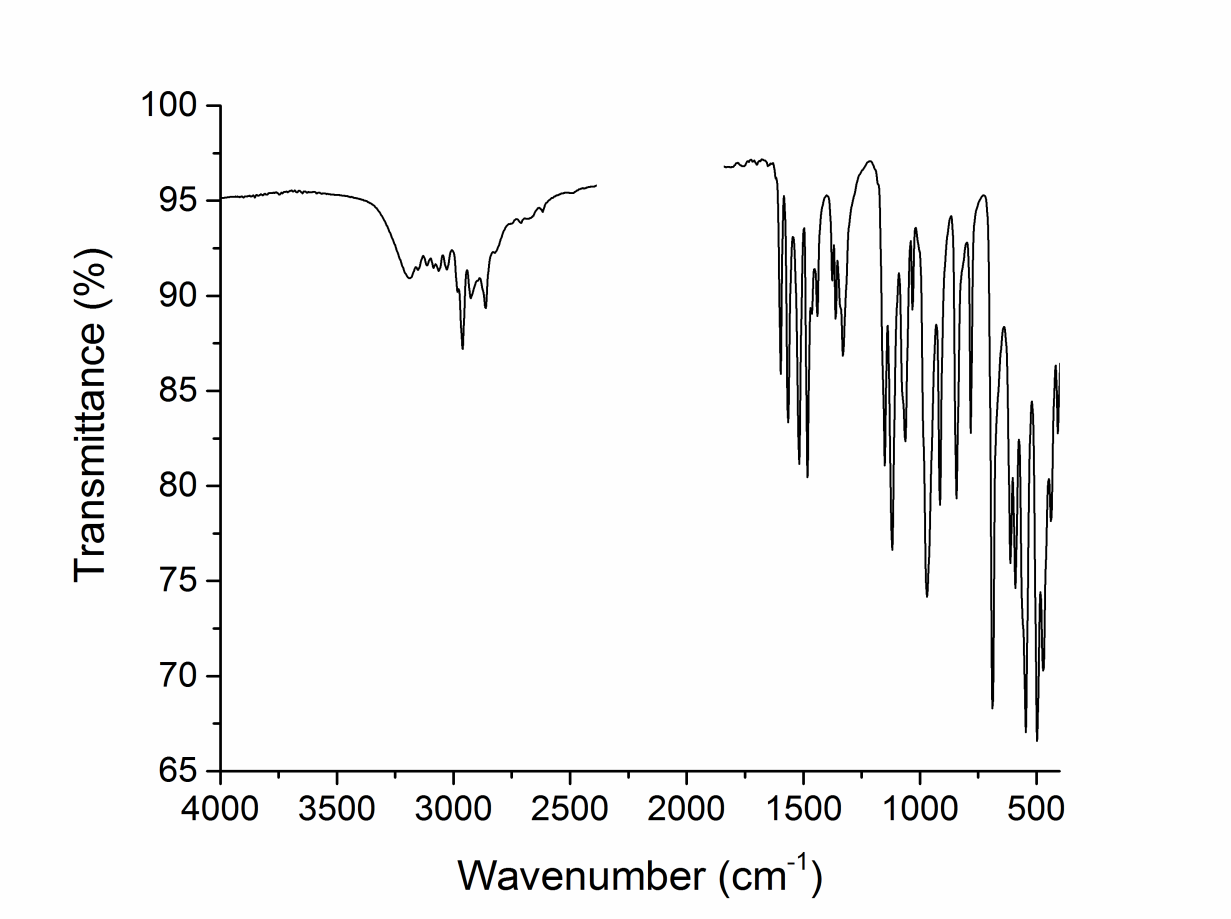


Figure S1. FTIR-ATR spectrum of compound **1**.

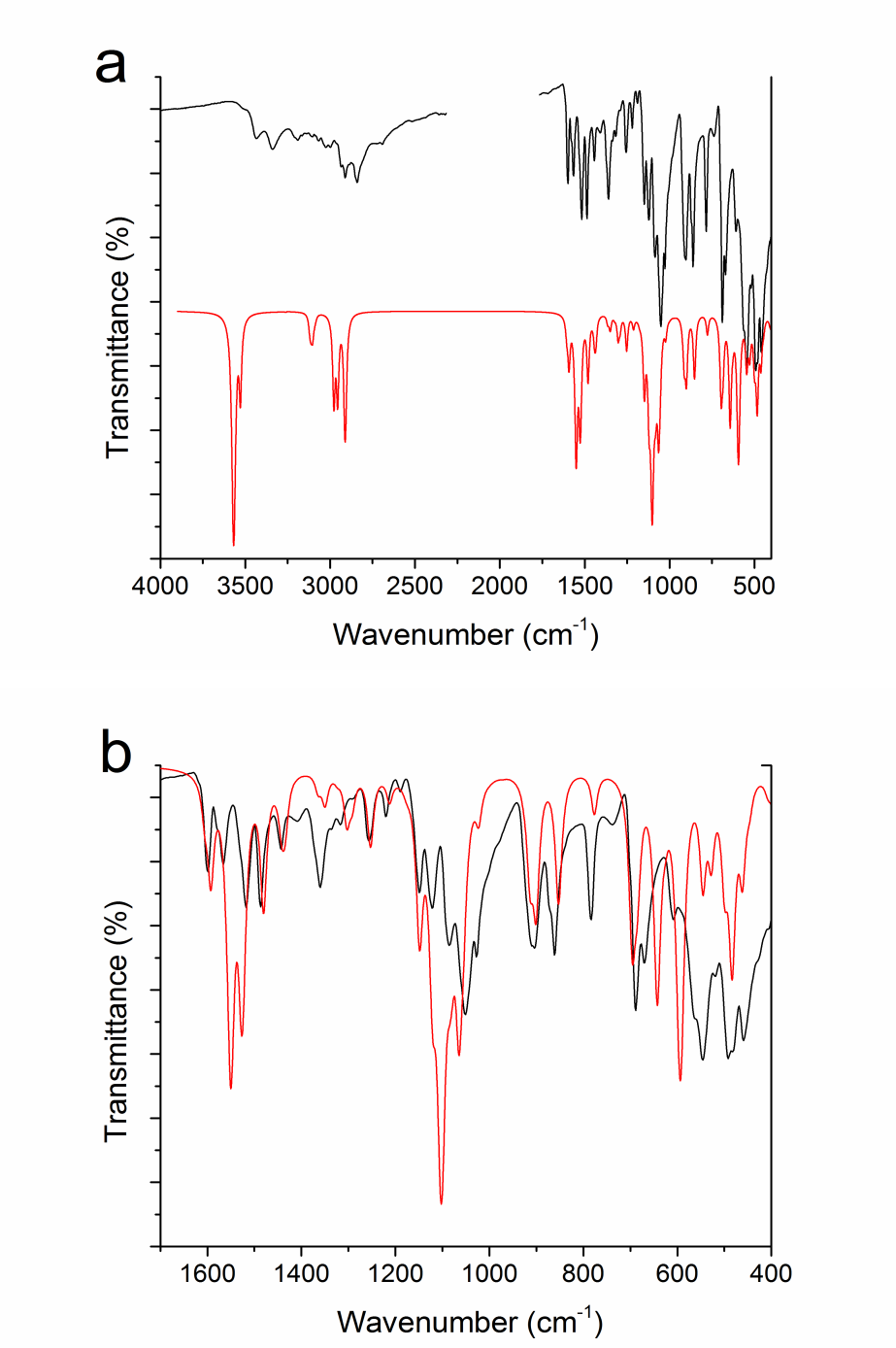


Figure S2. IR spectra of compound **2**, with experimental (black) and theoretical (red). Full range offset spectra (a) and 1700-400 cm^{-1} region highlighted (b).

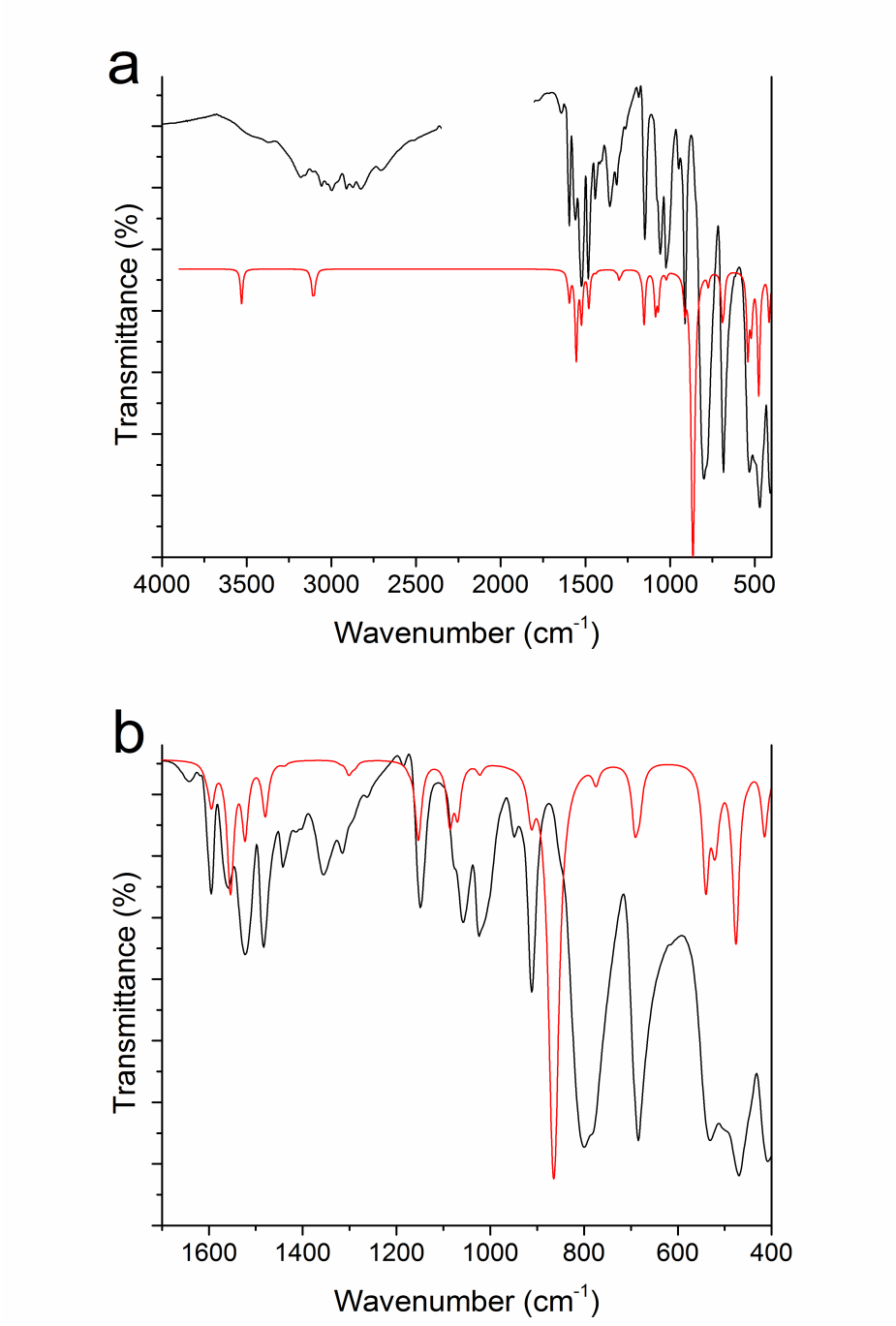


Figure S3. IR spectra of compound **3**, with experimental (black) and theoretical (red). Full range offset spectra (a) and 1700-400 cm^{-1} region highlighted (b).

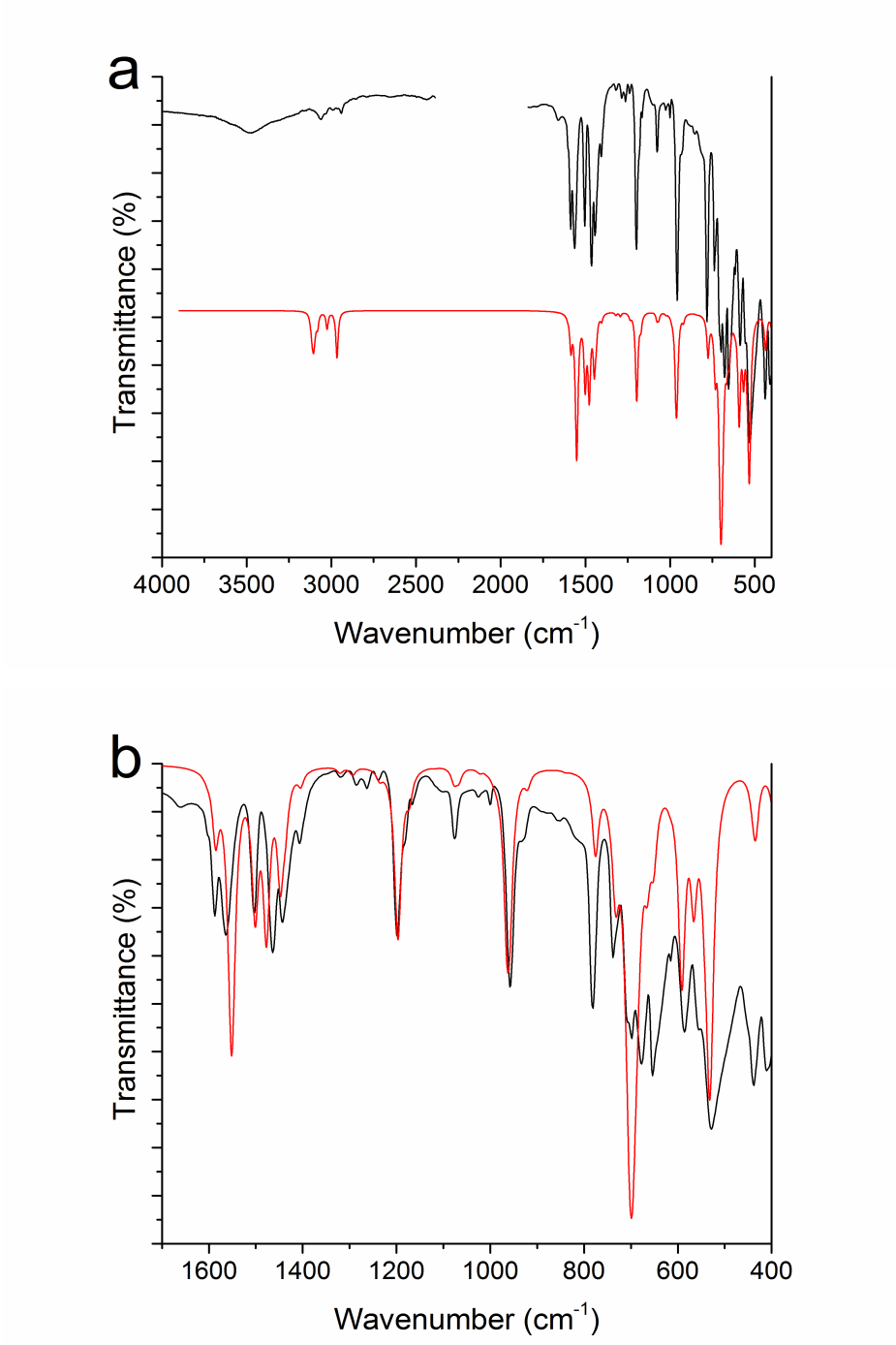


Figure S4. IR spectra of compound **4**, with experimental (black) and theoretical (red). Full range offset spectra (a) and 1700-400 cm^{-1} region highlighted (b).

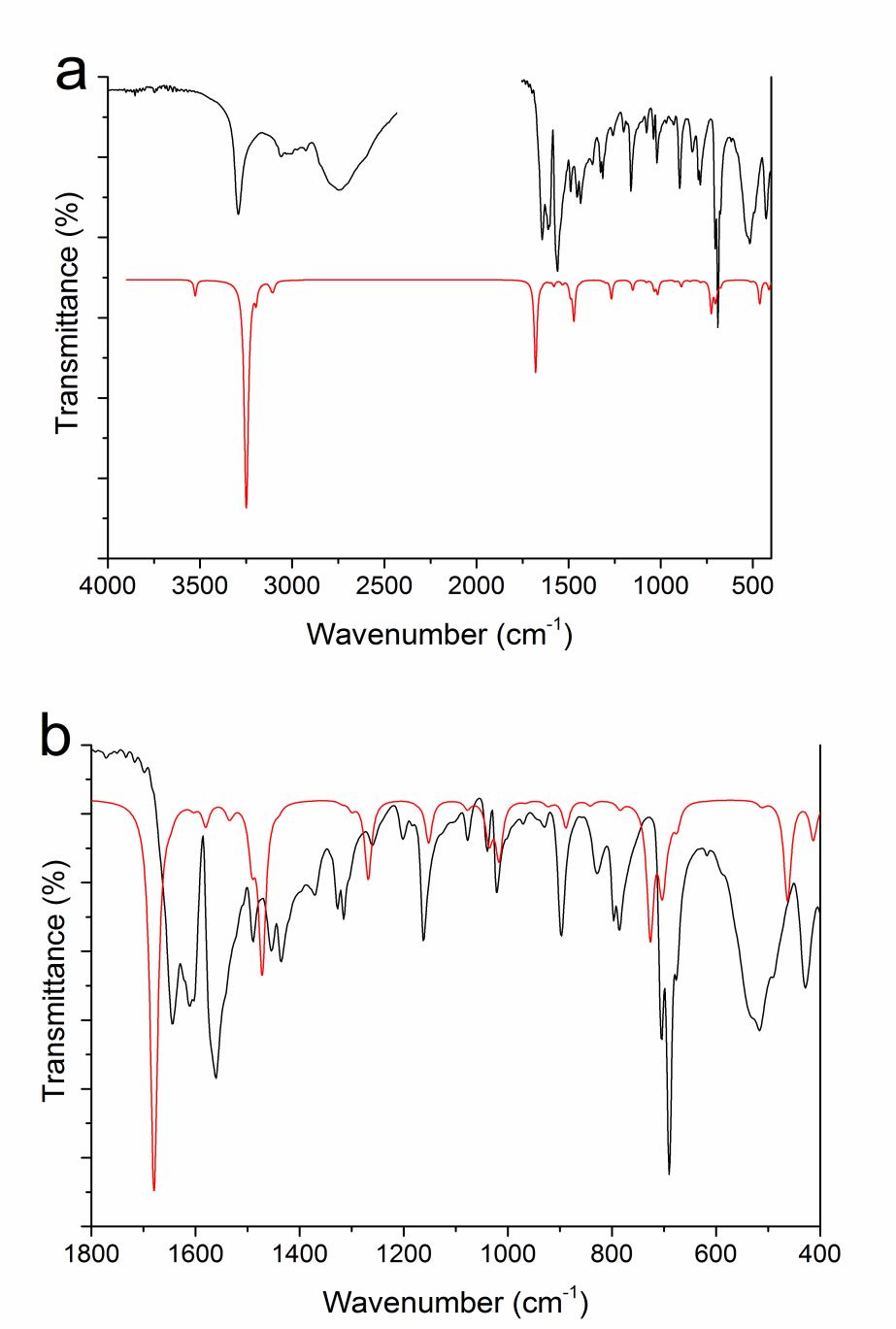


Figure S5. IR spectra of ligand NH-PHA with experimental (black) and theoretical (red). Full range offset spectra (a) and 1800-400 cm^{-1} region highlighted (b).

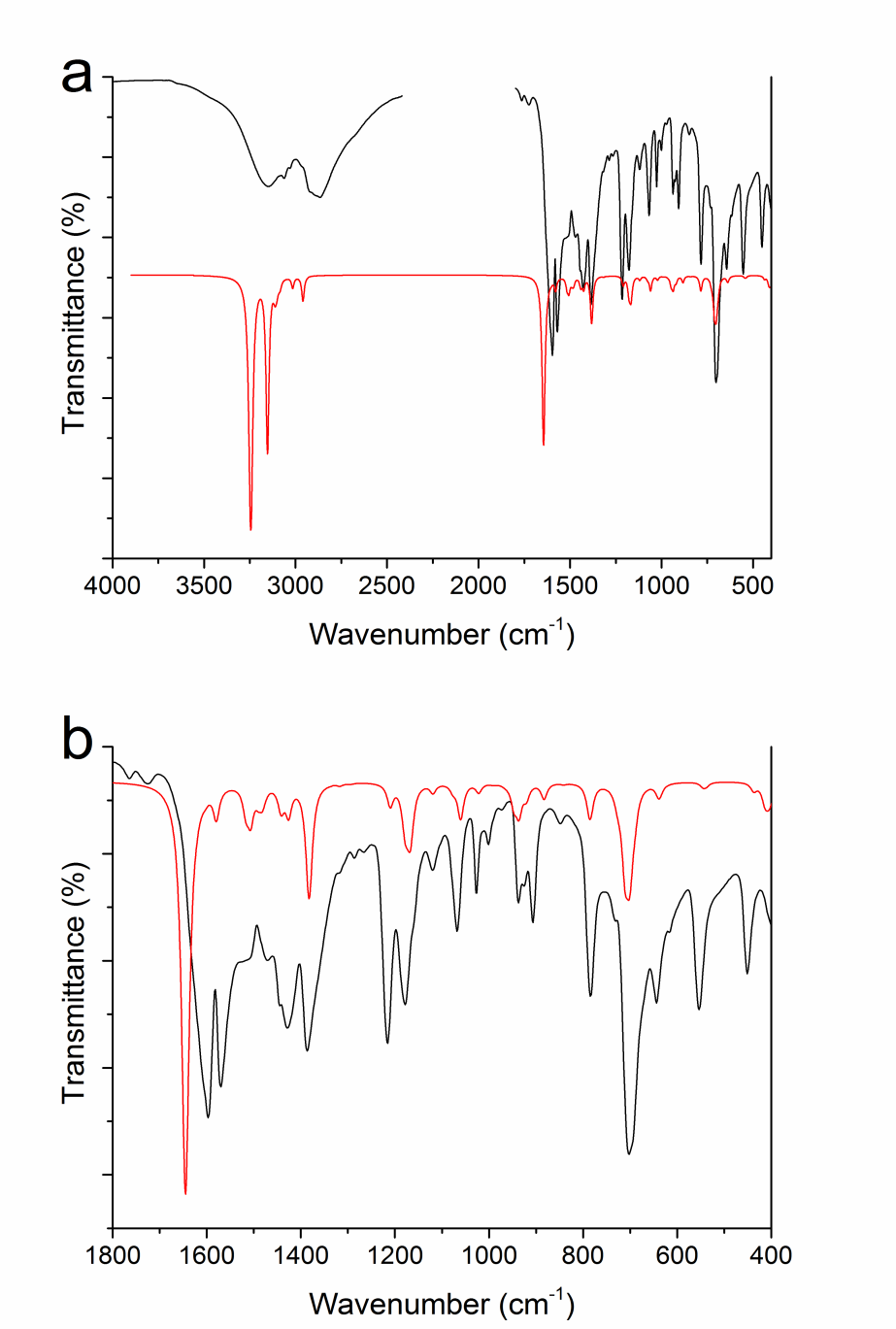


Figure S6. IR spectra of ligand NMe-PHA with experimental (black) and theoretical (red). Full range offset spectra (a) and 1800-400 cm^{-1} region highlighted (b).

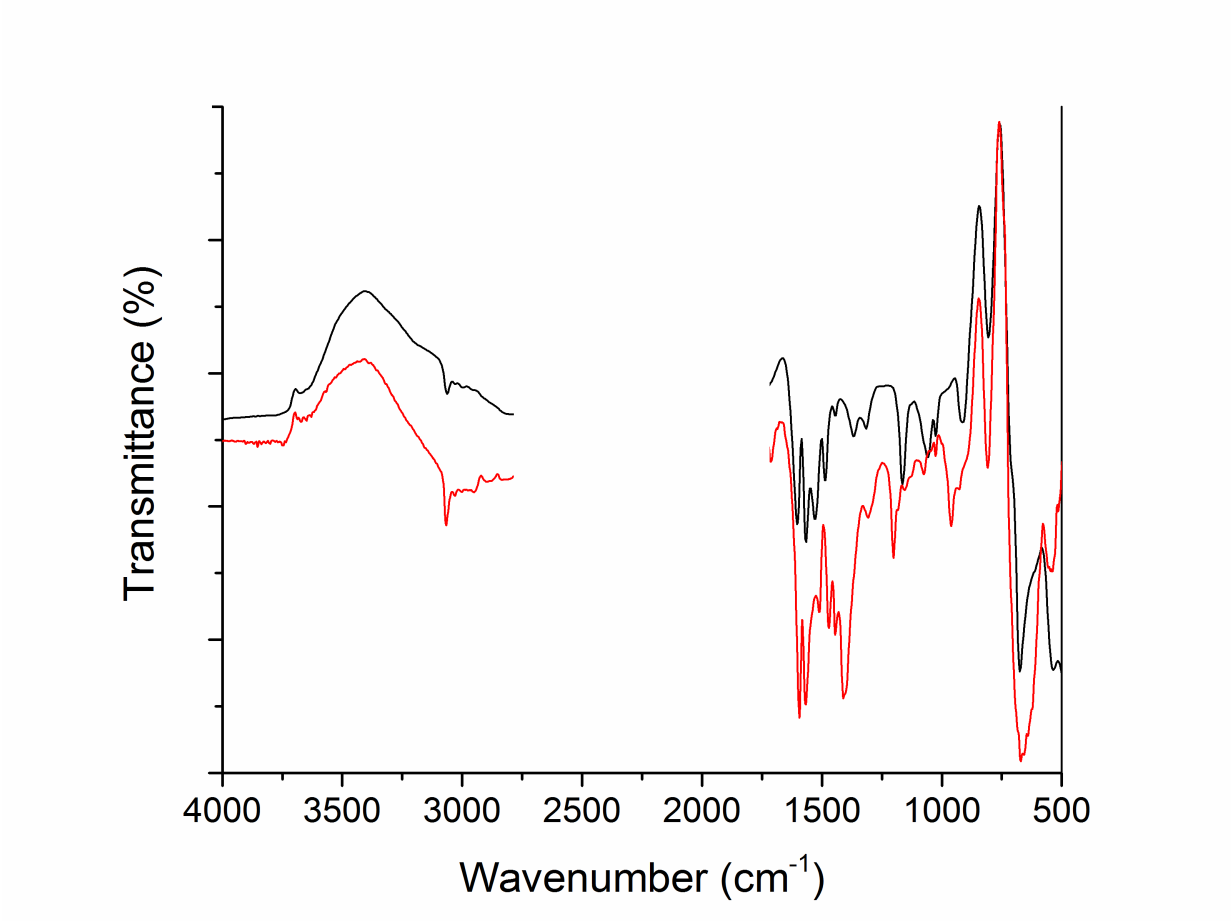


Figure S7. FT-IR-ATR overlay spectra of NH-PHA (black) and NMe-PHA (red) on nanoparticulate TiO_2 films. Bare TiO_2 was used as an internal background.

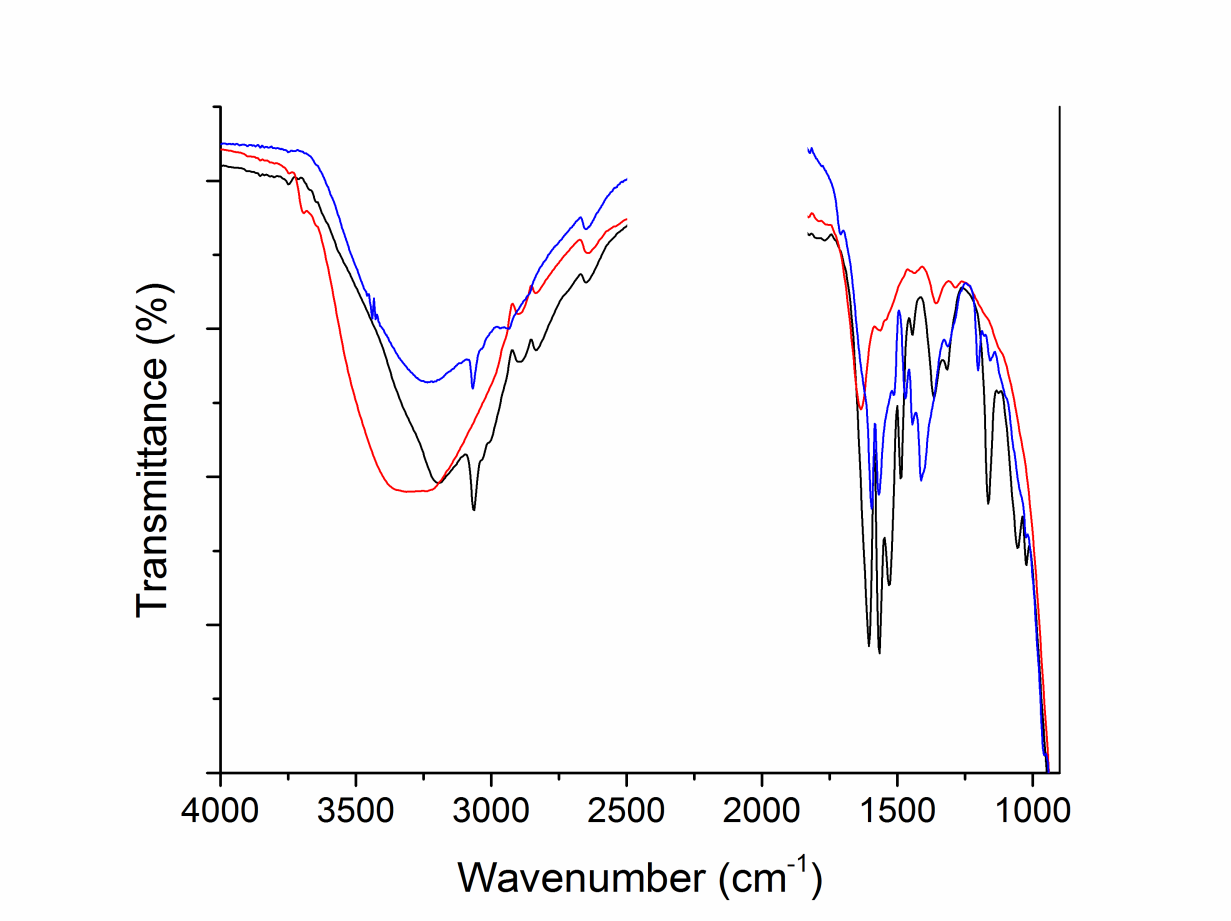


Figure S8. FT-IR-ATR overlay spectra of NH-PHA (black) and NMe-PHA (blue) on nanoparticulate TiO_2 films, and bare TiO_2 (red). Air was used as an internal background.

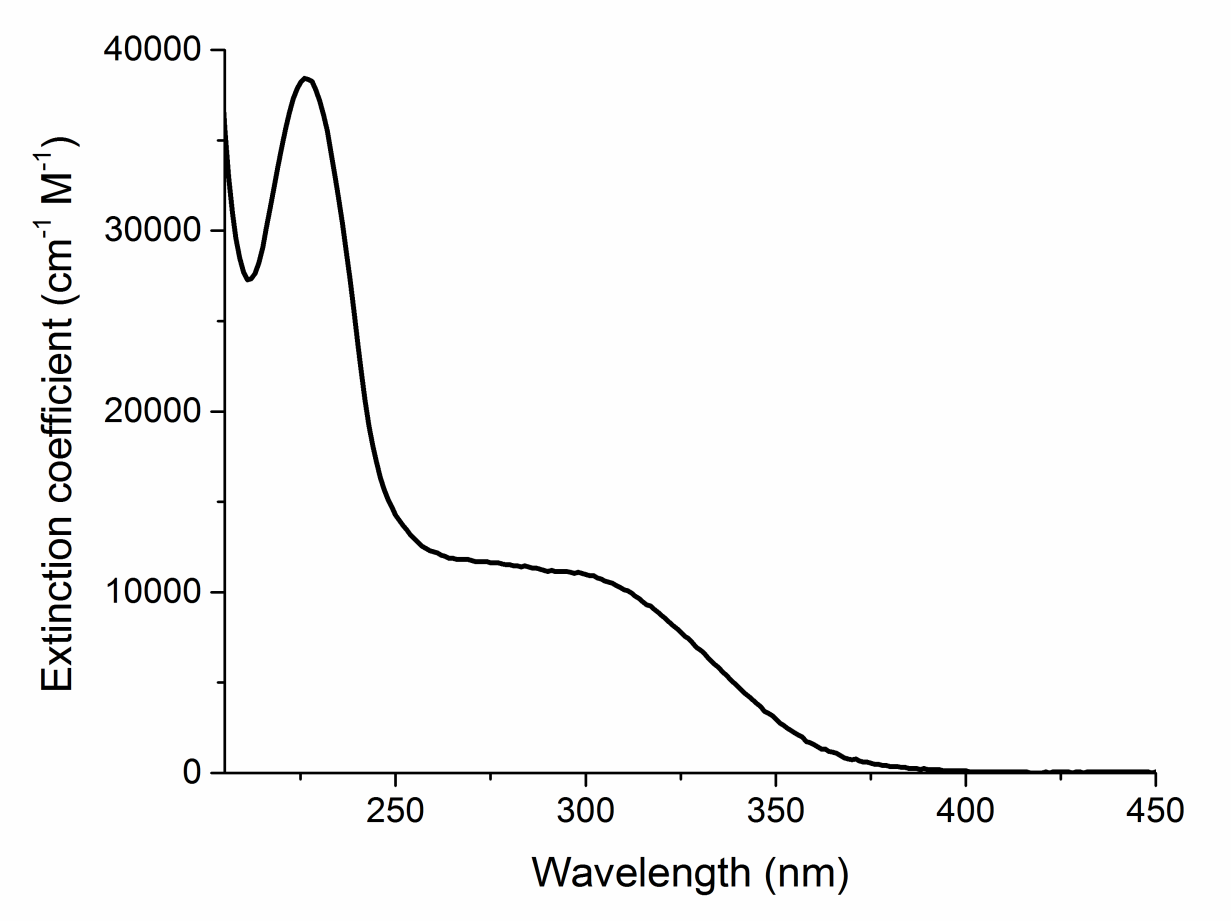


Figure S9. UV-visible spectrum of compound **1** in isopropanol.

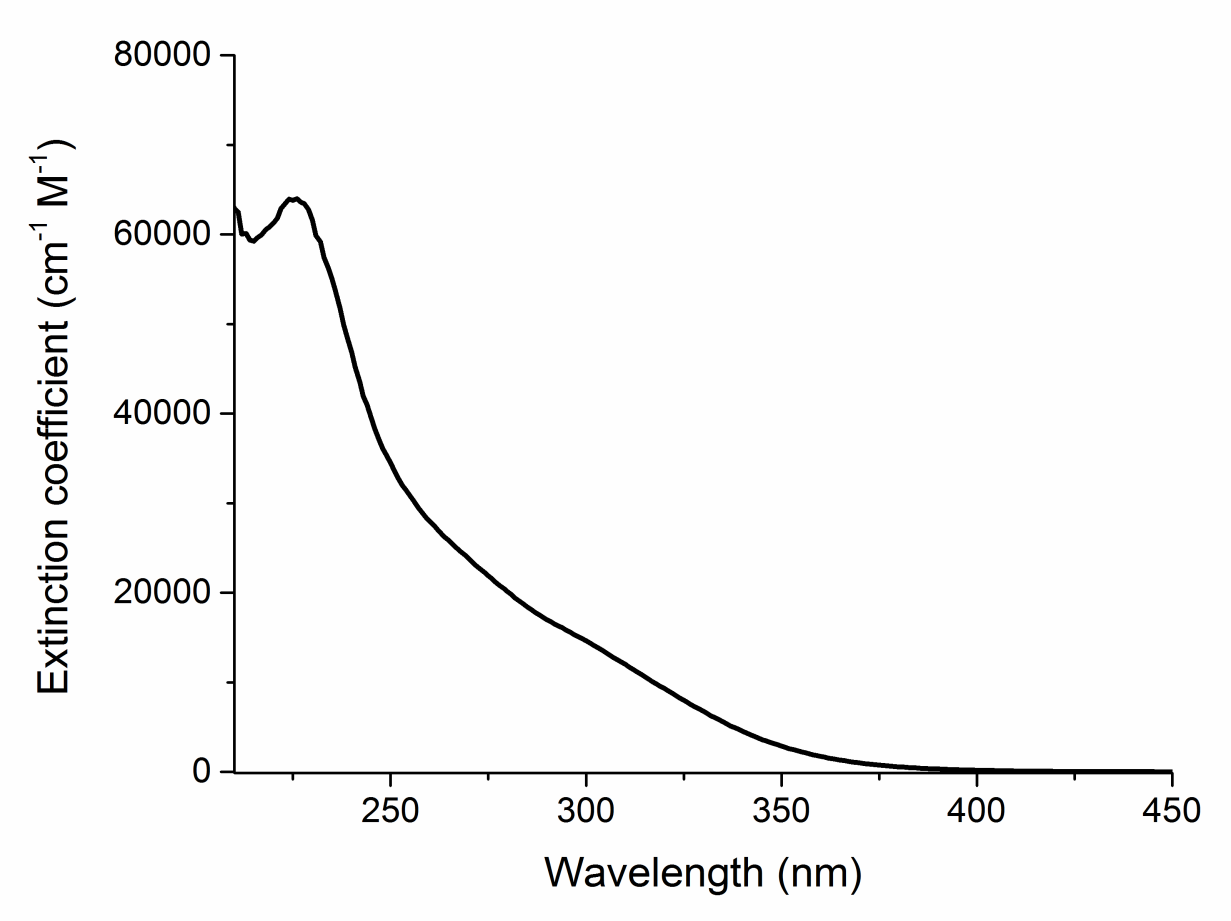


Figure S10. UV-visible spectrum of compound **4** in methanol.

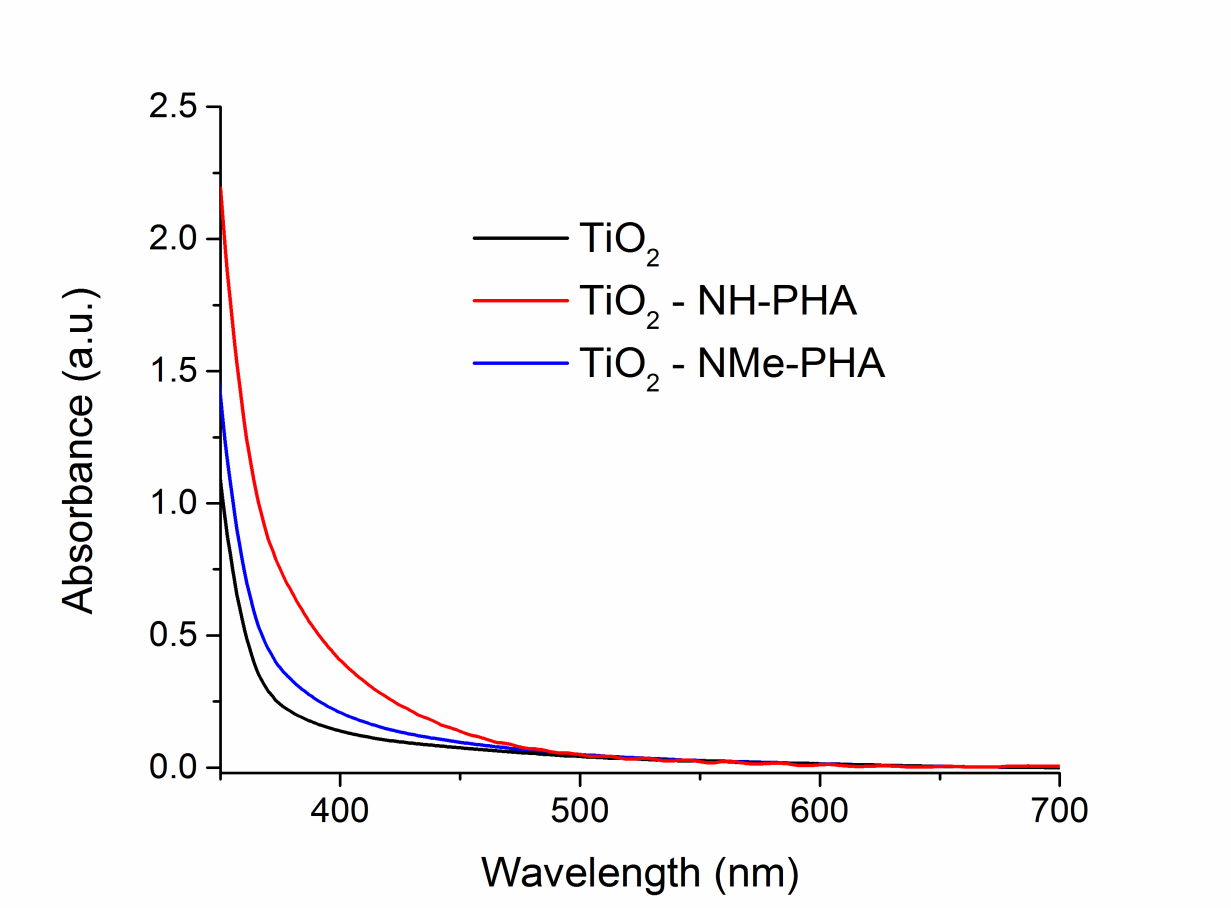


Figure S11. UV-visible spectra of TiO_2 nanoparticulate thin films (black) with surface-bound NH-PHA (red) and NMe-PHA (blue).

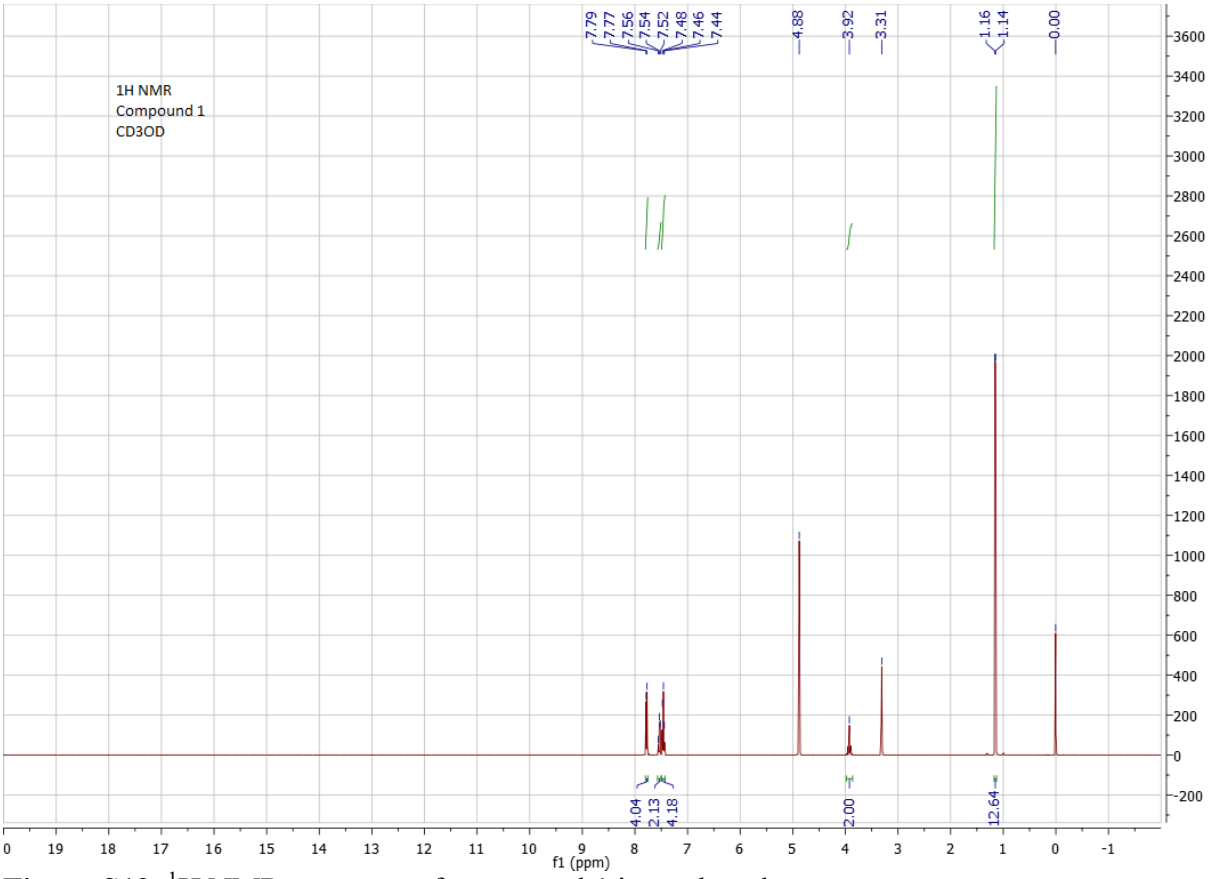


Figure S12. ^{1}H NMR spectrum of compound **1** in methanol.

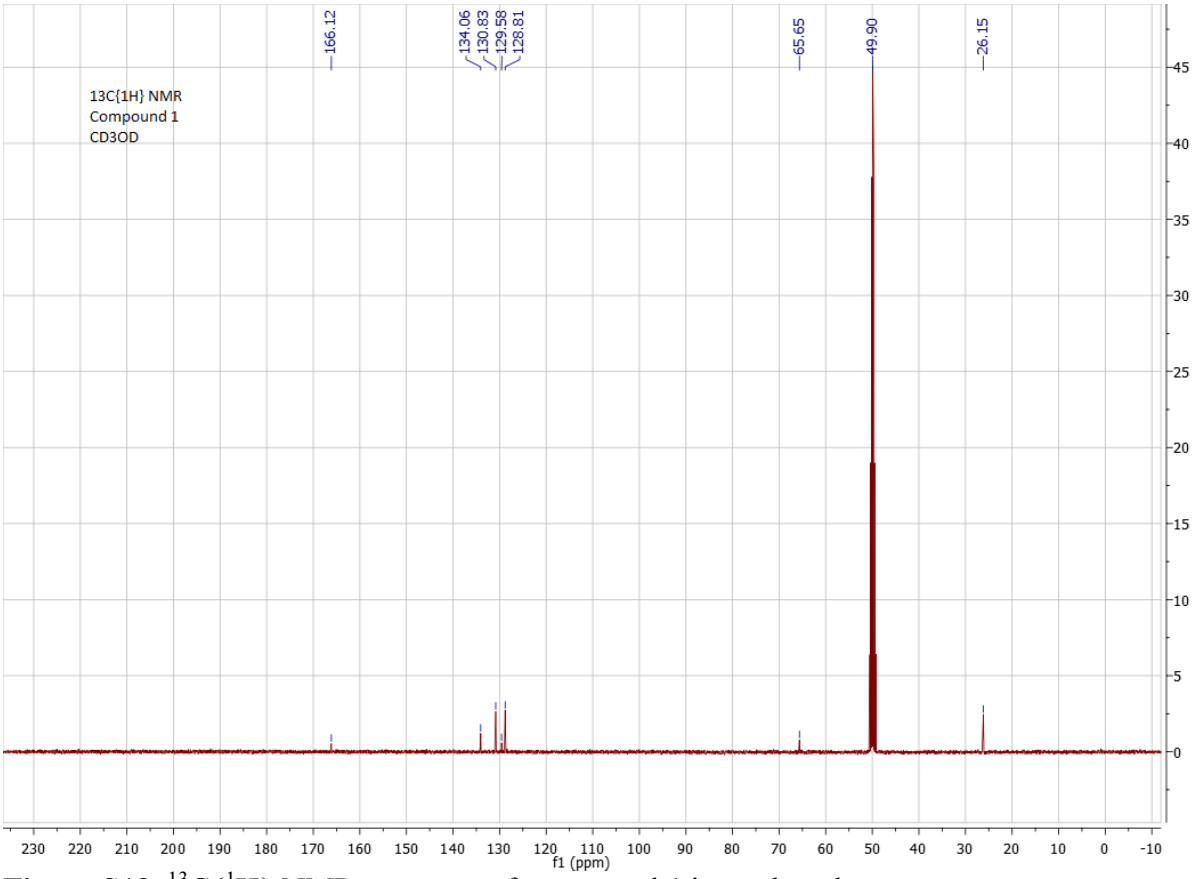


Figure S13. $^{13}C\{^{1}H\}$ NMR spectrum of compound **1** in methanol.

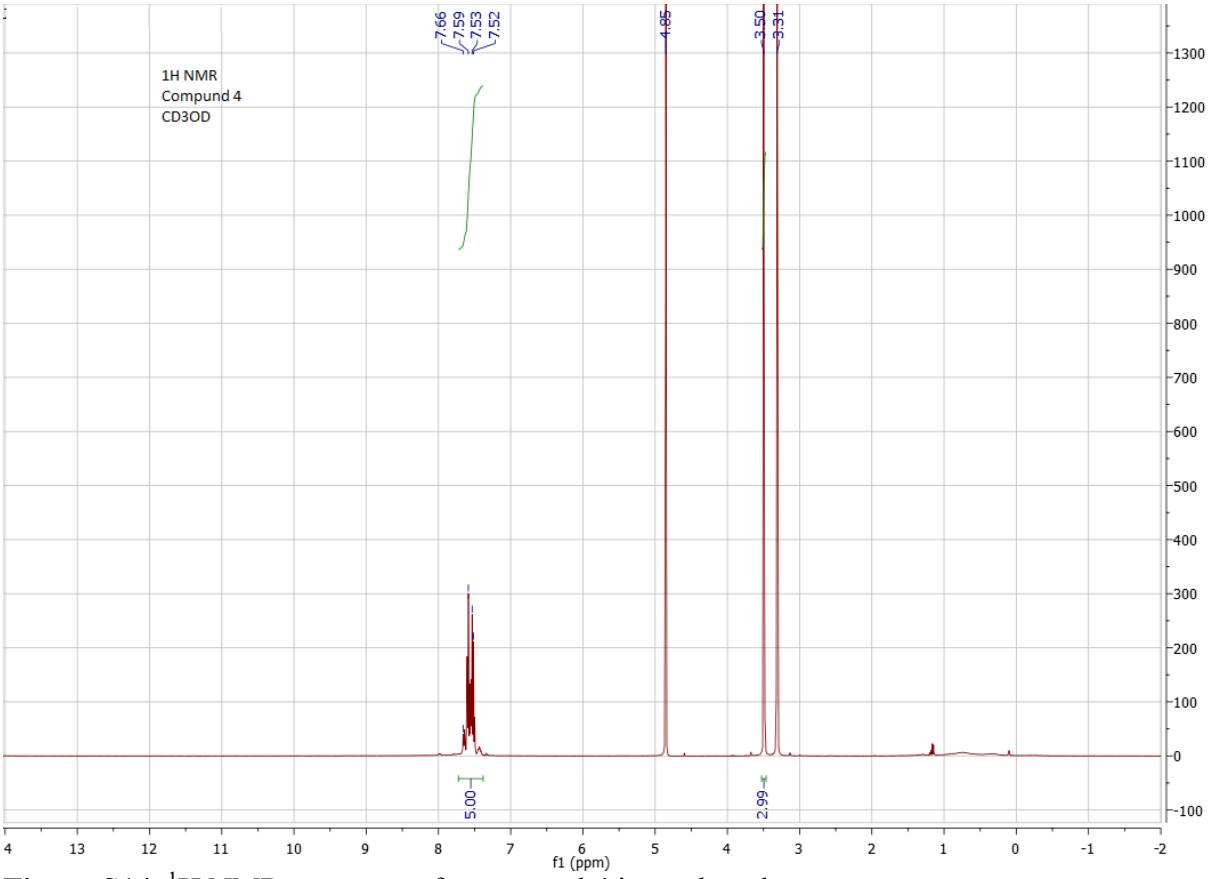


Figure S14. ^{1}H NMR spectrum of compound **4** in methanol.

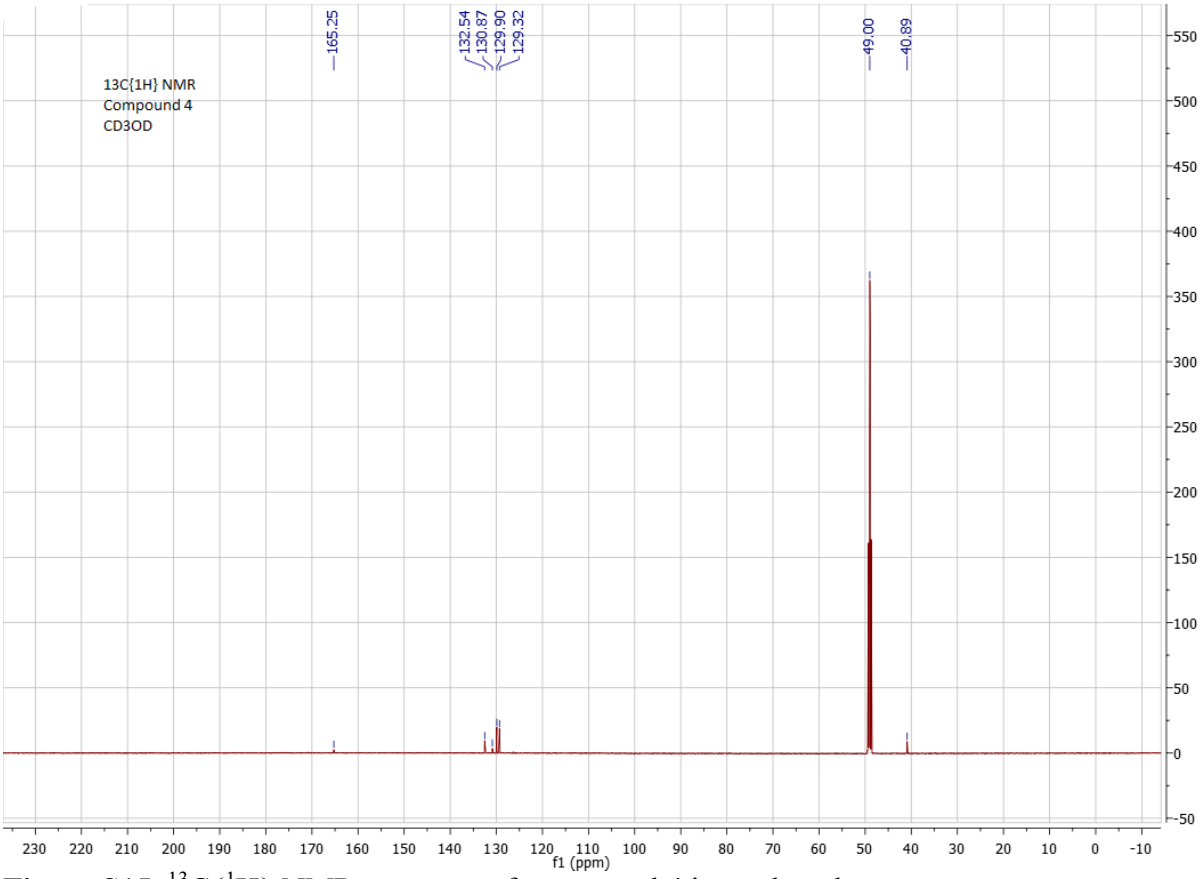


Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4** in methanol.

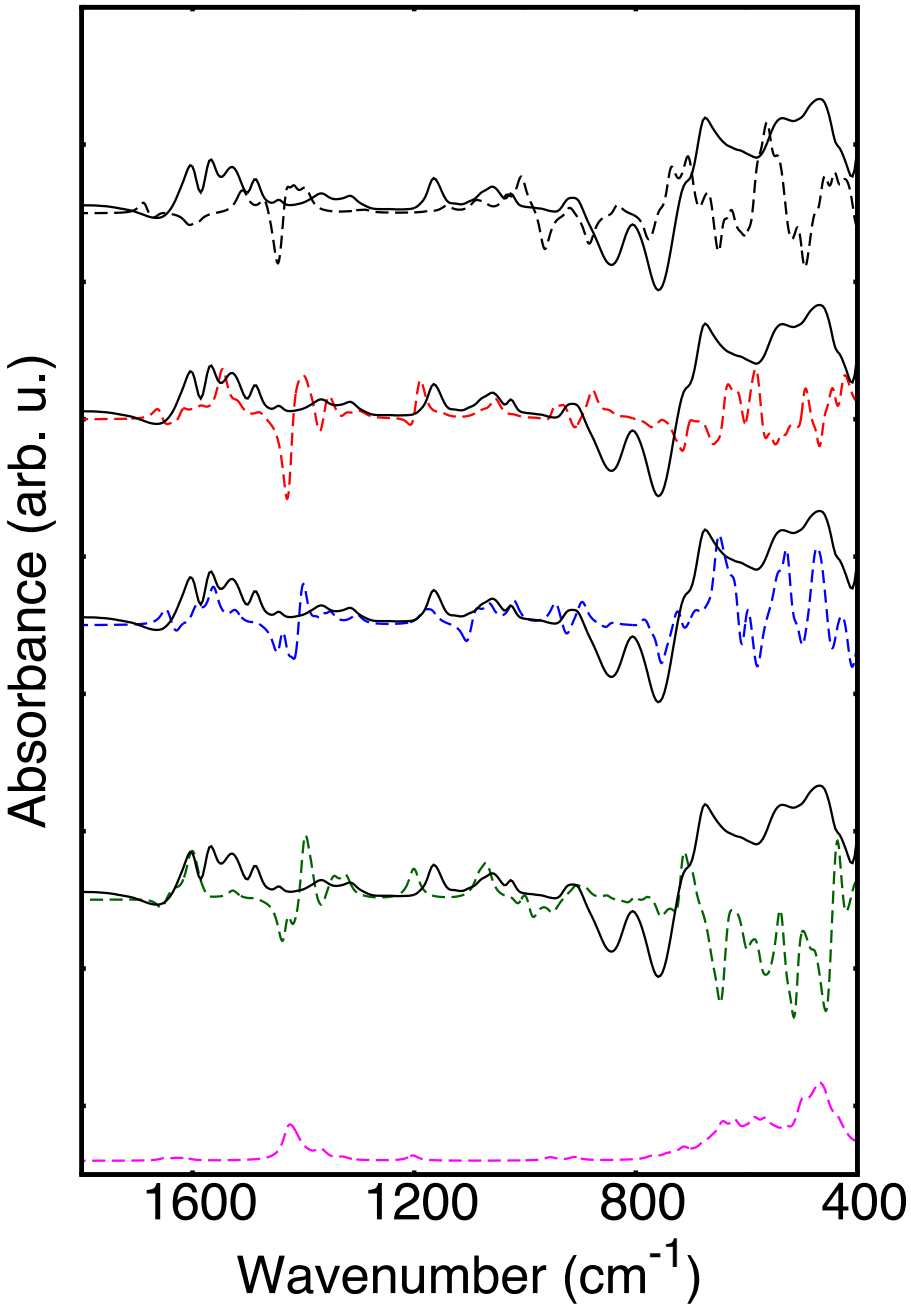


Figure S16. Theoretical IR spectra (frequency scaling factor of 0.975) of NH-PHA anchored to TiO_2 a) in a chelate binding mode at an oxygen vacancy site with the N-O occupying it (black dashed), b) in a chelate binding mode at 7-coordinate Ti (red dashed), c) in a monodentate binding mode (blue dashed), and d) in a bridging bidentate binding mode (green) as compared to the experimental spectrum (black solid). In magenta, a typical spectrum for the reference TiO_2 is given, scaled by several orders of magnitude to compare to the other difference spectra.

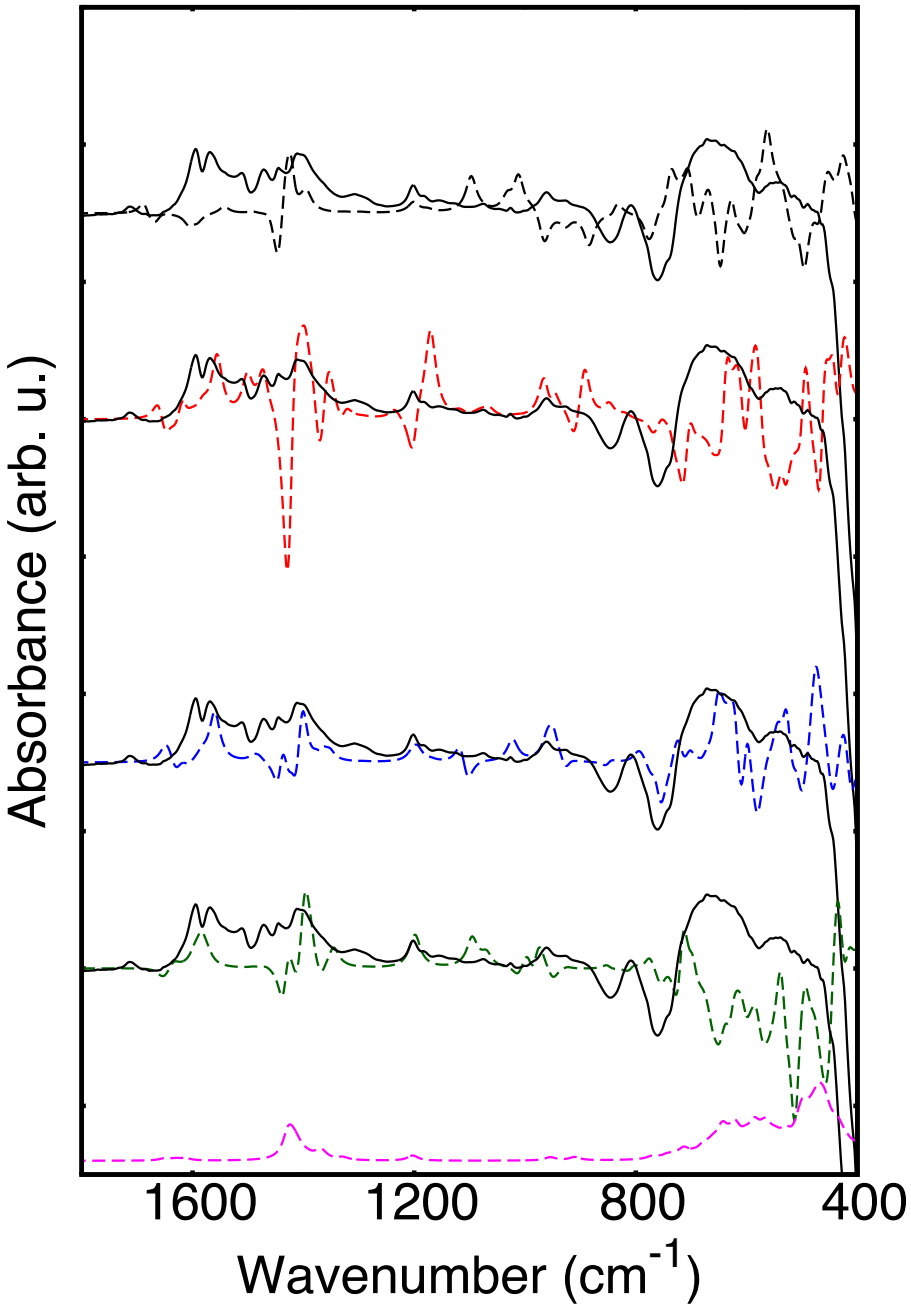
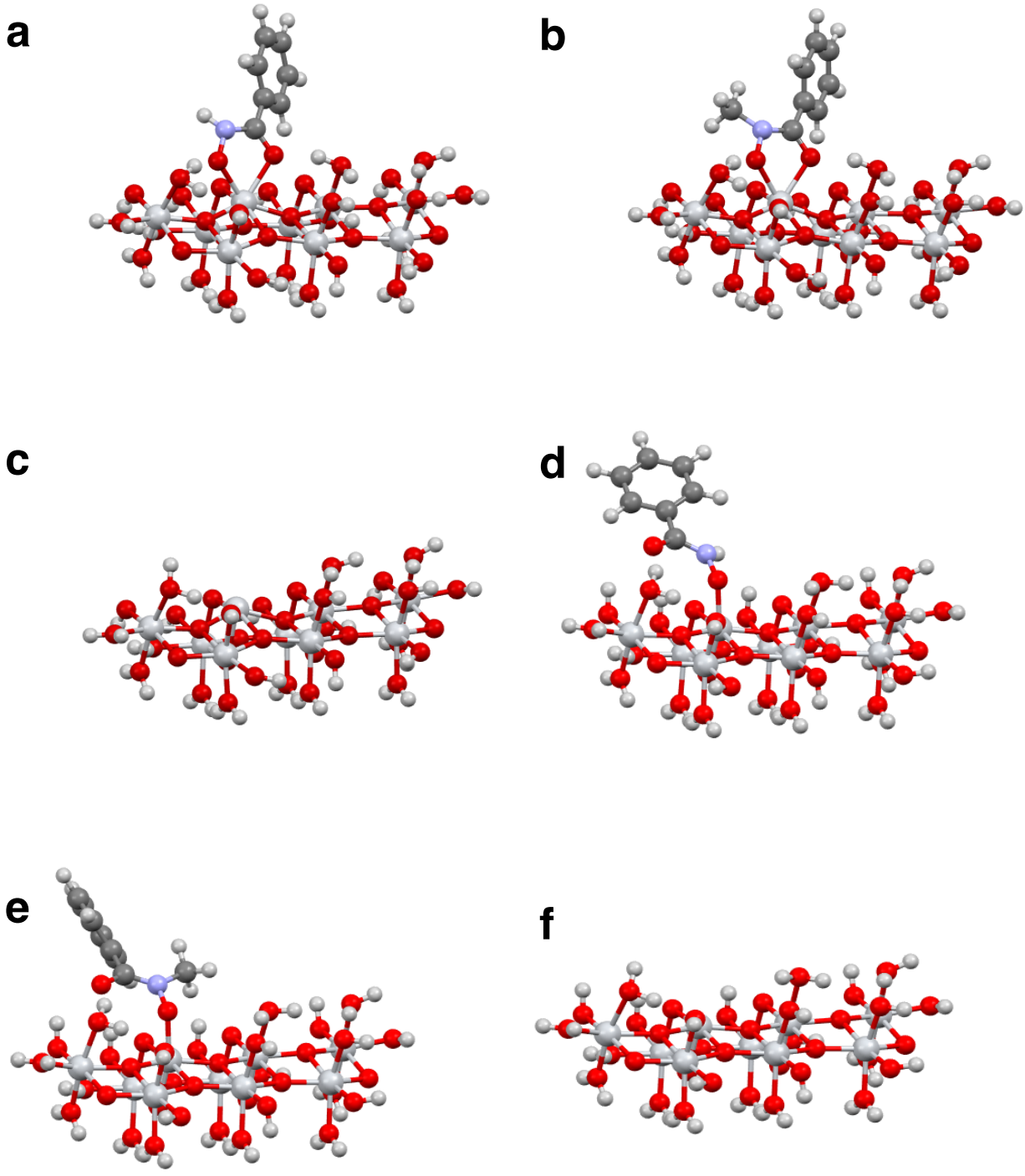


Figure S17. Theoretical IR spectra (frequency scaling factor of 0.975) of NMe-PHA anchored to TiO_2 a) in a chelate binding mode at an oxygen vacancy site with the N-O occupying it (black dashed), b) in a chelate binding mode at 7-coordinate Ti (red dashed), c) in a monodentate binding mode (blue dashed), and d) in a bridging bidentate binding mode (green dashed) as compared to the experimental spectrum (black solid). In magenta, a typical spectrum for the reference TiO_2 is given, scaled by several orders of magnitude to compare to the other difference spectra.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b
c
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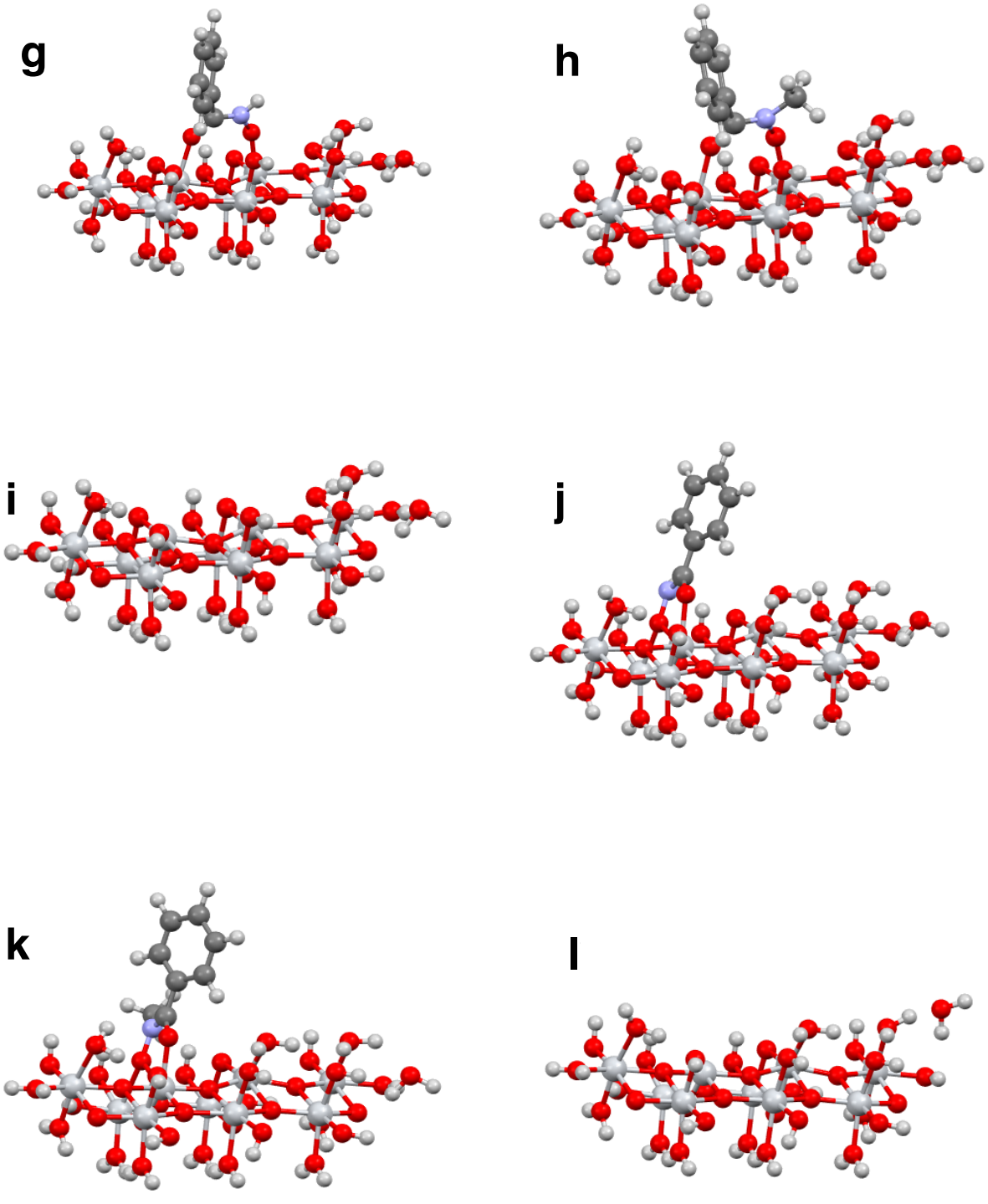
g
h
i
j
k
l

Figure S18. Geometries for simulations of cluster models for adsorption onto TiO_2. The panels depict the clusters used in this study as follows: a) chelate binding for NH-PHA, b) chelate binding for NMe-PHA, c) blank used for chelate binding, d) monodentate binding for NH-PHA, e) monodentate binding for NMe-PHA, f) blank used for monodentate binding, g) bridging bidentate binding for NH-PHA, h) bridging bidentate binding for NMe-PHA, i) blank used for bridging bidentate binding, j) chelate binding for NH-PHA at an oxygen vacancy, k) chelate binding for NMe-PHA at an oxygen vacancy, l) blank for chelate binding for NMe-PHA at an oxygen vacancy. The color code is as follows: red = O, light gray = Ti, dark gray = C, white = H, violet = N.

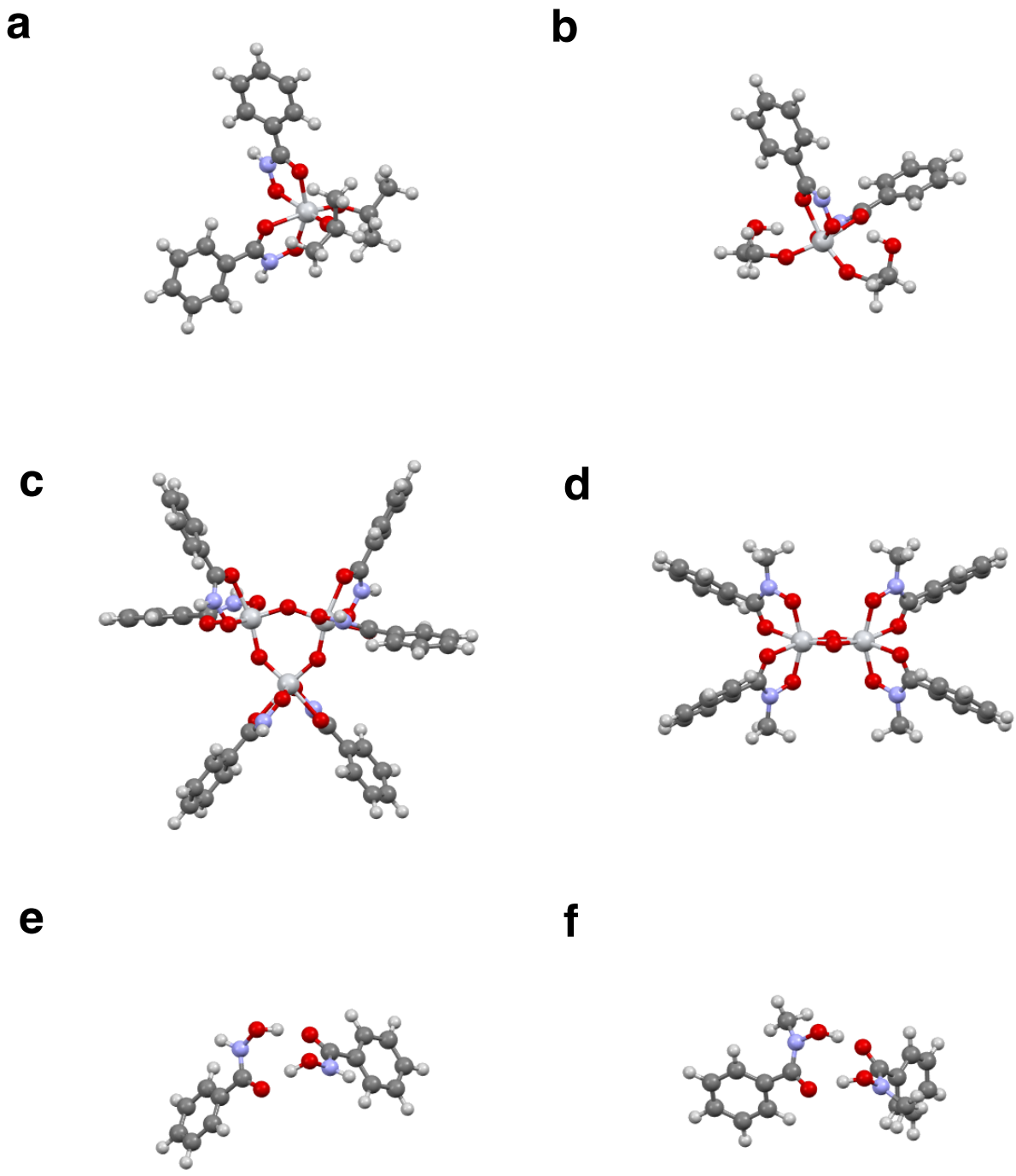

Figure S19. Geometries for simulations of the coordination complexes as well as free ligand dimers in this study. The panels depict the clusters used in this study as follows: a) monomer **1**, b) monomer **2**, c) dimer **3**, d) trimer **4**, e) dimer of the NH-PHA ligand, f) dimer of the NMe-PHA ligand. The color code is as follows: red = O, light gray = Ti, dark gray = C, white = H, violet = N.

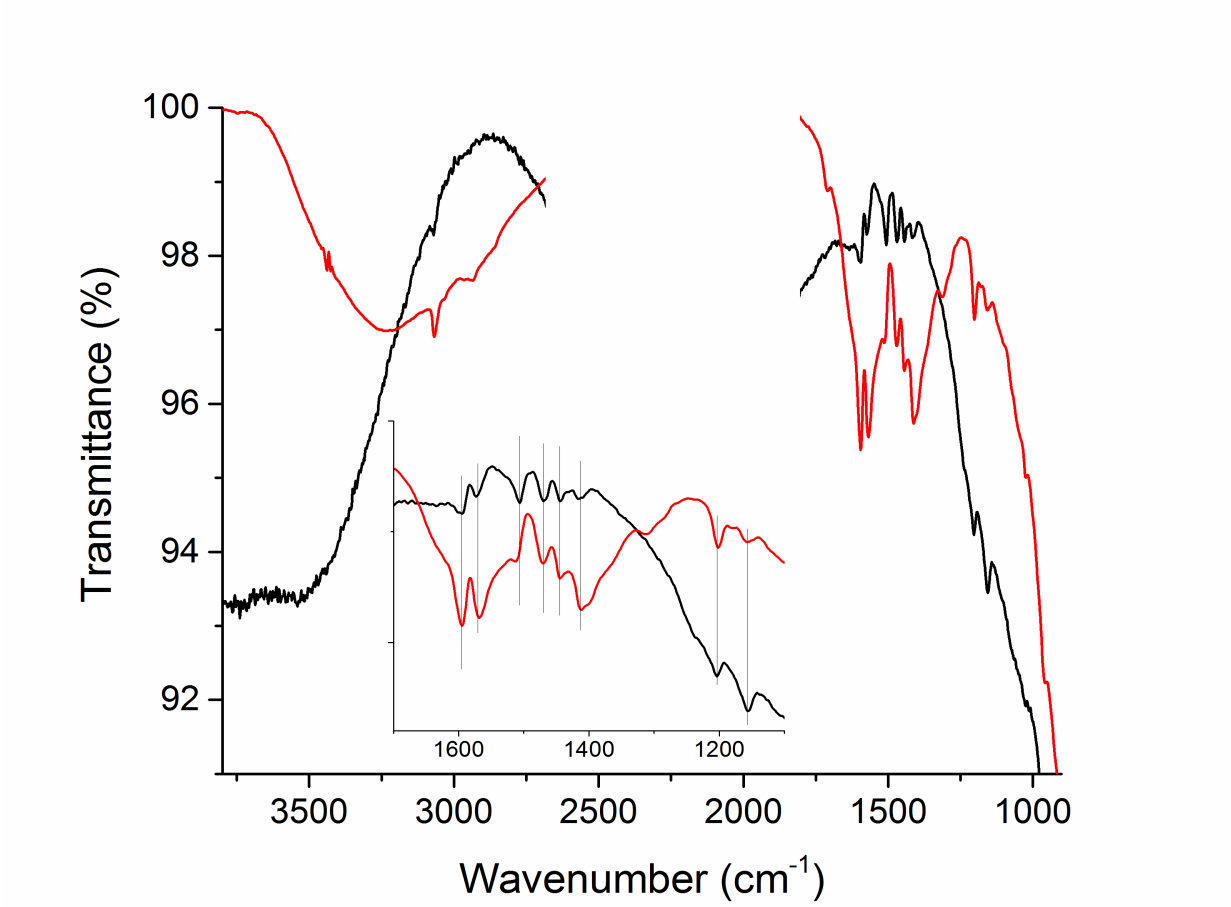

Figure S20. NMe-PHA on rutile TiO_2 nanoparticles (30 nm particles, black) *vs.* TiO_2 anatase thin film (fused 15-20 nm particles, red). Inset highlights region between 1700-1100 cm^{-1} with vertical lines showing alignment of observable bands. Nonfunctionalized TiO_2 used as experimental background. A significantly decreased signal to noise ratio occurs for the larger particle rutile nanoparticles due to their lower relative surface area compared to the anatase particle films.

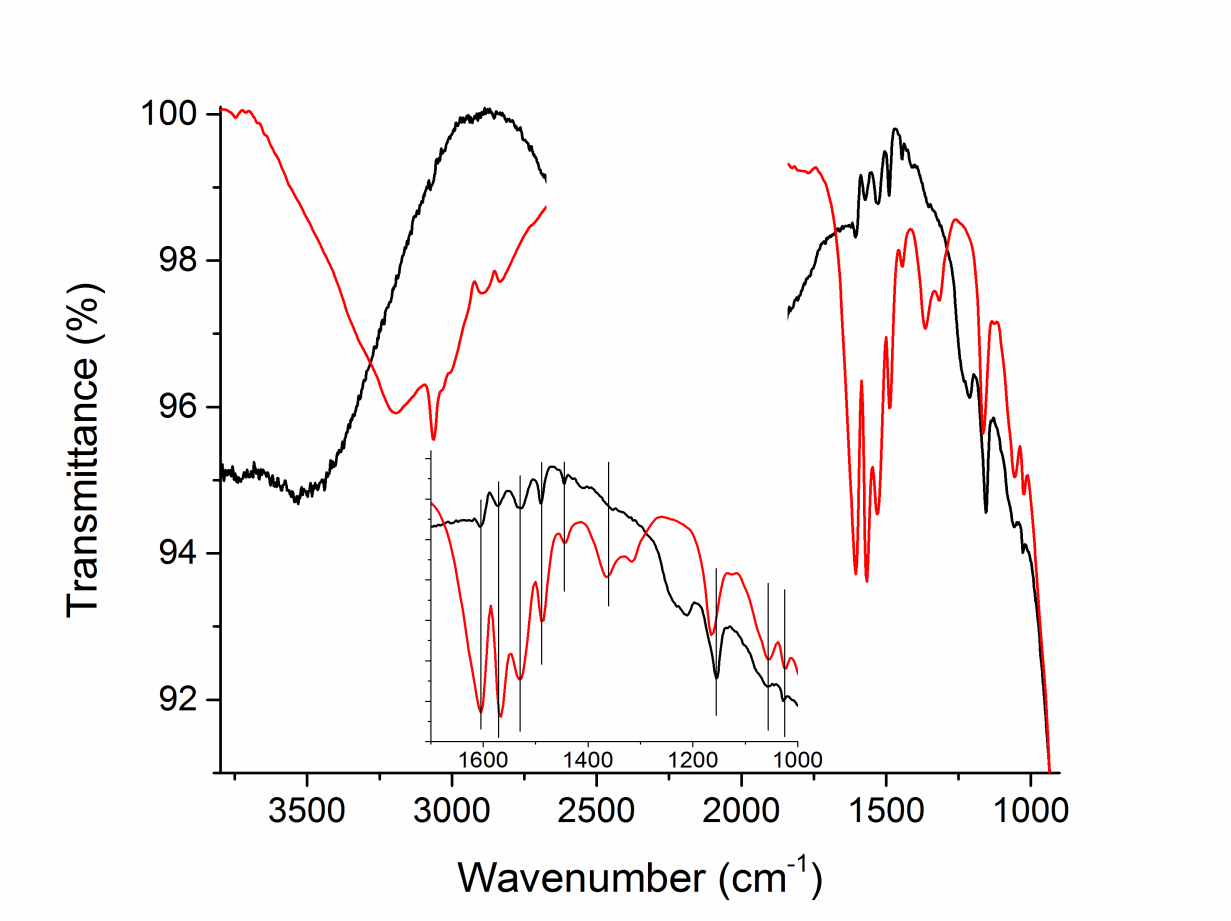

Figure S21. NH-PHA on rutile TiO_2 nanoparticles (30 nm particles, black) *vs.* TiO_2 anatase thin film (fused 15-20 nm particles, red). Inset highlights region between 1700-1100 cm^{-1} with vertical lines showing alignment of observable bands. Nonfunctionalized TiO_2 used as experimental background. A significantly decreased signal to noise ratio occurs for the larger particle rutile nanoparticles due to their lower relative surface area compared to the anatase particle films.

Table S1. C=O, C-N, and N-O experimental and theoretical (in parentheses) bond lengths in Å of compounds **2**, **3**, and **4**.

Bond	TiNH Monomer (2)	TiNH Trimer (3)	TiNMe Dimer (4)
C=O	1.277 (1.26)	1.263 (1.26)	1.277 (1.26)
C-N	1.309 (1.33)	1.304 (1.33)	1.309 (1.33)
N-O	1.372 (1.36)	1.379 (1.35)	1.362 (1.36)

Table S2. Bond lengths of the C-O, C-N, and N-O bonds derived from CSD structure search of organometallic compounds containing hydroxamate ligands.

Name	Count	Minimum	Maximum	Mean	Variance	Std. Dev.
C-O	329	1.191	1.440	1.276	0.001	0.027
C-N	329	1.187	1.431	1.32	0.001	0.027
N-O	329	1.277	1.449	1.376	0.001	0.022

Table S3. Free energies calculated from doing a Hessian calculation only for the surface bound water and hydroxamate for the different binding modes on a pristine surface with N-R^2 = N-H or N-Me. These energies are referenced against the monodentate mode.

Binding Mode	R^2	ΔG (kcal/mol)
chelate on pristine surface	H	63.33
chelate through an oxygen vacancy	H	23.41
bridging bidentate	H	30.10
monodentate	H	0
chelate on pristine surface	Me	61.85
chelate through an oxygen vacancy	Me	18.96
bridging bidentate	Me	26.68
monodentate	Me	0

Table S4. Summary of experimental and theoretical values for IR carbonyl stretches

	$\nu_{C=O}$ **experimental (calculation)** cm^{-1}
NH-PHA / TiO_2	1565, 1604 (1514, 1562, 1598)
2	1566, 1602 (1552, 1593)
3	1558, 1594 (1556, 1594)
NH-PHA ligand	1645 (1679)
NMe-PHA / TiO_2	1565, 1595 (1424, 1428, 1584)
4	1564, 1586 (1551, 1586)
NMe-PHA ligand	1597 (1646)

Crystal Structure Details

Single crystals of spider-15003 were grown from slow cooling of a hot DMSO solution containing compound 1. Low-temperature diffraction data (ω-scans) were collected on a Rigaku R-AXIS RAPID diffractometer coupled to an R-AXIS RAPID imaging plate detector with Mo Kα radiation (λ = 0.71073 Å) for the structure of spider-15003. All structures were solved by direct methods using SHELXS and were refined against F^2 on all data by full-matrix least squares with SHELXL. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The only exception is H1. The U_{iso} is freely refining, but the distance to N1 is fixed near a value of 0.90 Å. The N1-H1 distance is fixed, the refined donor/acceptor distance between N1 and O4 is listed in Table S11. The full numbering scheme of compound spider-15003 can be found in Figure S21. Full details of the X-ray structure determination are in the CIF included as Supporting Information. CCDC number 1402798 (spider-15003) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Refinement Information

One DMSO solvent was involved in a hydrogen bond, but the modeled is disordered over a major and minor position, denoted by the atom label suffixes "a" and "b", respectively. The site occupancy factors were freely refined and subsequently fixed at their converged values of 0.64 and 0.36. A rigid bond restraint was needed due to the near superposition of the atomic position

parameters. The use of rigid bond restraints also aided in the convergence of the DMSO disordered model.

The program SQUEEZE was used to compensate for the contribution of disordered solvents contained in voids within the crystal lattice from the diffraction intensities. This procedure was applied to the data file, and the submitted model is based on the solvent removed data. Based on the total electron density found in the voids (401.4 e/Å^3), it is likely that ~10 additional DMSO molecules are present in the unit cell. See "_platon_squeeze_details" in this .cif for more information.

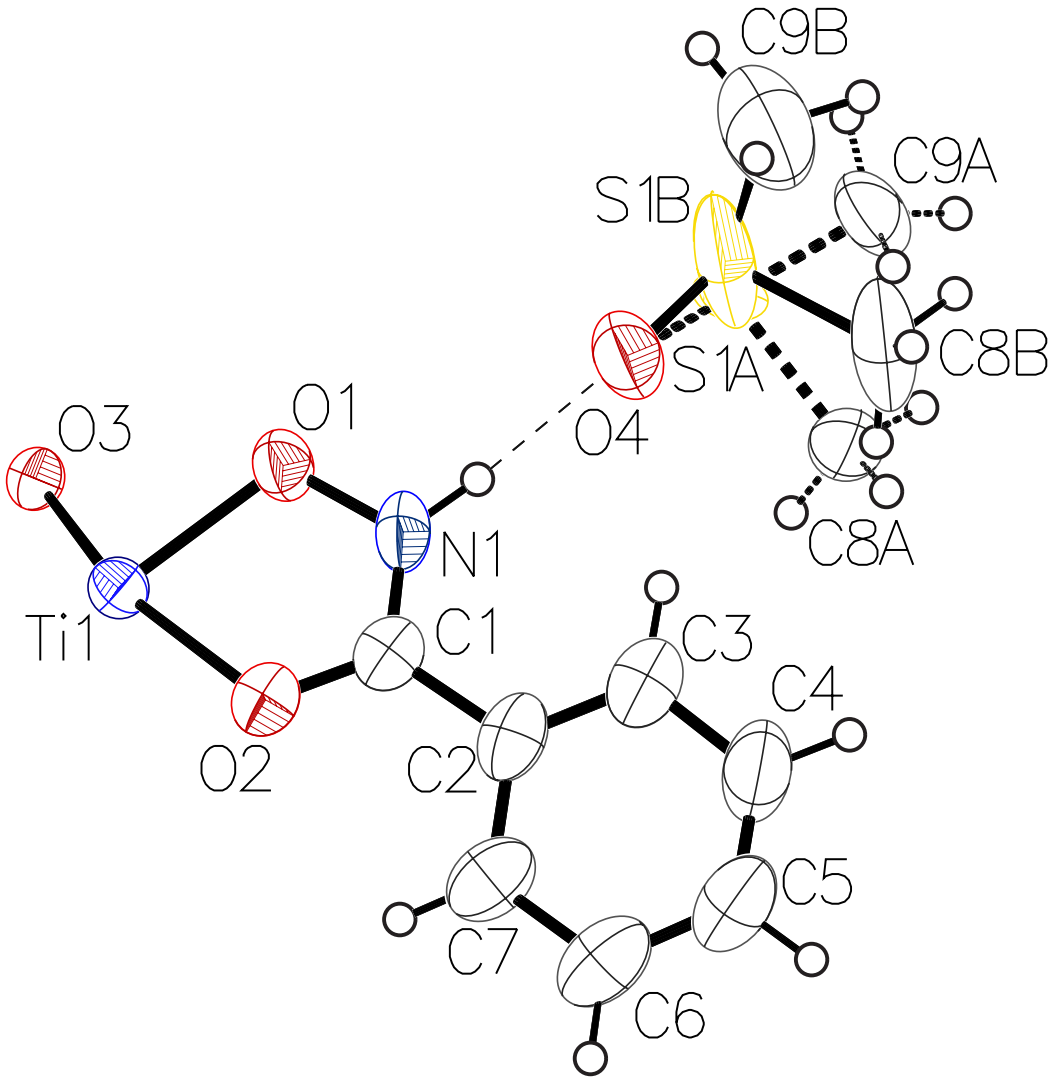

Figure S22. The full numbering scheme of spider-15003. All atoms shown are depicted with 50% thermal contours. The hydrogen atoms are shown as spheres.

Table S5. Crystal data and structure refinement for spider-15003.

Identification code	spider-15003	
Empirical formula	$C_{54}H_{72}N_6O_{21}S_6Ti_3$	
Formula weight	1477.23	
Temperature	93(2) K	
Wavelength	0.71075 Å	
Crystal system	Trigonal	
Space group	R -3 c	
Unit cell dimensions	a = 15.7049(9) Å	α = 90°.
	b = 15.7049(9) Å	β = 90°.
	c = 53.457(4) Å	γ = 120°.
Volume	11418.5(15) $Å^3$	
Z	6	
Density (calculated)	1.289 Mg/m^3	
Absorption coefficient	0.538 mm^{-1}	
F(000)	4608	
Crystal size	0.150 x 0.150 x 0.150 mm^3	
Crystal color and habit	Colorless Block	
Diffractometer	Rigaku R-AXIS RAPID imaging plate	
Θ range for data collection	3.091 to 25.349°.	
Index ranges	$-18 \le h \le 18, -18 \le k \le 18, -64 \le l \le 64$	
Reflections collected	59502	
Independent reflections	2324 [R(int) = 0.1488]	
Observed reflections (I > 2σ(I))	1682	
Completeness to θ = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.714	
Solution method	SHELXS-2013 (Sheldrick, 2013)	
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)	
Data / restraints / parameters	2324 / 37 / 172	
Goodness-of-fit on F^2	1.037	
Final R indices [I>2σ(I)]	R1 = 0.0744, wR2 = 0.1801	
R indices (all data)	R1 = 0.1024, wR2 = 0.1986	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.750 and -0.295 $e.Å^{-3}$	

Table S6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for spider-15003. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ti(1)	5404(1)	3333	5833	36(1)
O(1)	5252(2)	3557(2)	5481(1)	45(1)
O(2)	3877(2)	2397(2)	5764(1)	44(1)
O(3)	6667	4354(3)	5833	35(1)
N(1)	4289(3)	3213(3)	5410(1)	47(1)
C(1)	3604(4)	2623(3)	5564(1)	44(1)
C(2)	2554(4)	2272(4)	5512(1)	53(1)
C(3)	2218(5)	2379(5)	5286(1)	72(2)
C(4)	1202(5)	2033(6)	5254(2)	83(2)
C(5)	577(5)	1597(5)	5439(2)	81(2)
C(6)	894(4)	1503(5)	5670(2)	76(2)
C(7)	1884(4)	1838(4)	5710(1)	65(2)
S(1A)	4244(6)	4313(8)	4751(1)	48(2)
S(1B)	4348(5)	4179(5)	4704(1)	116(3)
O(4)	4095(3)	3458(3)	4914(1)	69(1)
C(8A)	3232(12)	4577(15)	4826(4)	71(4)
C(8B)	3227(9)	4034(9)	4620(3)	103(4)
C(9A)	3741(15)	3872(15)	4448(3)	72(5)
C(9B)	4467(15)	3631(15)	4447(3)	154(6)

Table S7. Bond lengths [Å] and angles [°] for spider-15003.

Ti(1)-O(3)	1.8223(16)
Ti(1)-O(3)#1	1.8224(16)
Ti(1)-O(1)#2	1.955(3)
Ti(1)-O(1)	1.955(3)
Ti(1)-O(2)#2	2.128(3)
Ti(1)-O(2)	2.128(3)
O(1)-N(1)	1.379(5)
O(2)-C(1)	1.263(6)
O(3)-Ti(1)#3	1.8223(16)
N(1)-C(1)	1.304(7)
N(1)-H(1)	0.87(2)
C(1)-C(2)	1.480(7)
C(2)-C(3)	1.363(8)
C(2)-C(7)	1.405(8)
C(3)-C(4)	1.417(9)
C(3)-H(3)	0.9500
C(4)-C(5)	1.319(10)
C(4)-H(4)	0.9500
C(5)-C(6)	1.366(10)
C(5)-H(5)	0.9500
C(6)-C(7)	1.386(8)
C(6)-H(6)	0.9500
C(7)-H(7)	0.9500
S(1A)-O(4)	1.517(11)
S(1A)-C(9A)	1.782(18)
S(1A)-C(8A)	1.877(18)
S(1B)-O(4)	1.500(7)
S(1B)-C(9B)	1.68(2)
S(1B)-C(8B)	1.718(13)
C(8A)-H(8AA)	0.9800
C(8A)-H(8AB)	0.9800
C(8A)-H(8AC)	0.9800
C(8B)-H(8BA)	0.9800
C(8B)-H(8BB)	0.9800

C(8B)-H(8BC)	0.9800
C(9A)-H(9AA)	0.9800
C(9A)-H(9AB)	0.9800
C(9A)-H(9AC)	0.9800
C(9B)-H(9BA)	0.9800
C(9B)-H(9BB)	0.9800
C(9B)-H(9BC)	0.9800

O(3)-Ti(1)-O(3)#1	99.2(3)
O(3)-Ti(1)-O(1)#2	104.86(10)
O(3)#1-Ti(1)-O(1)#2	91.10(10)
O(3)-Ti(1)-O(1)	91.10(10)
O(3)#1-Ti(1)-O(1)	104.87(10)
O(1)#2-Ti(1)-O(1)	155.4(2)
O(3)-Ti(1)-O(2)#2	92.93(15)
O(3)#1-Ti(1)-O(2)#2	164.21(14)
O(1)#2-Ti(1)-O(2)#2	75.98(13)
O(1)-Ti(1)-O(2)#2	84.81(14)
O(3)-Ti(1)-O(2)	164.21(14)
O(3)#1-Ti(1)-O(2)	92.93(15)
O(1)#2-Ti(1)-O(2)	84.81(14)
O(1)-Ti(1)-O(2)	75.97(14)
O(2)#2-Ti(1)-O(2)	77.11(17)
N(1)-O(1)-Ti(1)	113.7(3)
C(1)-O(2)-Ti(1)	112.2(3)
Ti(1)#3-O(3)-Ti(1)	140.8(3)
C(1)-N(1)-O(1)	117.3(4)
C(1)-N(1)-H(1)	130(4)
O(1)-N(1)-H(1)	112(4)
O(2)-C(1)-N(1)	117.2(4)
O(2)-C(1)-C(2)	121.7(5)
N(1)-C(1)-C(2)	121.1(5)
C(3)-C(2)-C(7)	119.1(6)
C(3)-C(2)-C(1)	123.2(6)
C(7)-C(2)-C(1)	117.6(5)
C(2)-C(3)-C(4)	119.4(6)

C(2)-C(3)-H(3)	120.3
C(4)-C(3)-H(3)	120.3
C(5)-C(4)-C(3)	120.7(7)
C(5)-C(4)-H(4)	119.6
C(3)-C(4)-H(4)	119.6
C(4)-C(5)-C(6)	121.2(7)
C(4)-C(5)-H(5)	119.4
C(6)-C(5)-H(5)	119.4
C(5)-C(6)-C(7)	120.0(7)
C(5)-C(6)-H(6)	120.0
C(7)-C(6)-H(6)	120.0
C(6)-C(7)-C(2)	119.5(6)
C(6)-C(7)-H(7)	120.3
C(2)-C(7)-H(7)	120.3
O(4)-S(1A)-C(9A)	109.6(9)
O(4)-S(1A)-C(8A)	107.4(6)
C(9A)-S(1A)-C(8A)	91.2(10)
O(4)-S(1B)-C(9B)	106.3(8)
O(4)-S(1B)-C(8B)	103.1(6)
C(9B)-S(1B)-C(8B)	95.1(9)
S(1A)-C(8A)-H(8AA)	109.5
S(1A)-C(8A)-H(8AB)	109.5
H(8AA)-C(8A)-H(8AB)	109.5
S(1A)-C(8A)-H(8AC)	109.5
H(8AA)-C(8A)-H(8AC)	109.5
H(8AB)-C(8A)-H(8AC)	109.5
S(1B)-C(8B)-H(8BA)	109.5
S(1B)-C(8B)-H(8BB)	109.5
H(8BA)-C(8B)-H(8BB)	109.5
S(1B)-C(8B)-H(8BC)	109.5
H(8BA)-C(8B)-H(8BC)	109.5
H(8BB)-C(8B)-H(8BC)	109.5
S(1A)-C(9A)-H(9AA)	109.5
S(1A)-C(9A)-H(9AB)	109.5
H(9AA)-C(9A)-H(9AB)	109.5
S(1A)-C(9A)-H(9AC)	109.5

H(9AA)-C(9A)-H(9AC)	109.5
H(9AB)-C(9A)-H(9AC)	109.5
S(1B)-C(9B)-H(9BA)	109.5
S(1B)-C(9B)-H(9BB)	109.5
H(9BA)-C(9B)-H(9BB)	109.5
S(1B)-C(9B)-H(9BC)	109.5
H(9BA)-C(9B)-H(9BC)	109.5
H(9BB)-C(9B)-H(9BC)	109.5

Symmetry transformations used to generate equivalent atoms:

#1 -y+1,x-y,z #2 x-y+1/3,-y+2/3,-z+7/6 #3 -x+y+1,-x+1,z

Table S8. Anisotropic displacement parameters ($Å^2$ x 10^3) for spider-15003. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ti(1)	37(1)	38(1)	34(1)	-2(1)	-1(1)	19(1)
O(1)	43(2)	49(2)	38(2)	-1(1)	-7(1)	20(2)
O(2)	42(2)	37(2)	53(2)	-5(2)	-4(2)	21(2)
O(3)	31(2)	36(2)	37(2)	-2(1)	-3(2)	16(1)
N(1)	50(3)	53(3)	45(2)	-10(2)	-18(2)	32(2)
C(1)	43(3)	33(2)	55(3)	-10(2)	-5(2)	19(2)
C(2)	55(3)	41(3)	74(4)	-14(3)	-14(3)	33(3)
C(3)	57(4)	86(5)	81(4)	1(4)	-7(3)	41(4)
C(4)	64(4)	94(5)	94(5)	17(4)	-16(4)	42(4)
C(5)	54(4)	85(5)	108(6)	2(4)	-6(4)	38(4)
C(6)	49(3)	63(4)	112(6)	-2(4)	4(4)	25(3)
C(7)	43(3)	51(3)	91(5)	-4(3)	2(3)	15(3)
S(1A)	32(3)	61(3)	28(2)	-2(2)	8(2)	6(2)
S(1B)	75(4)	90(4)	112(4)	55(3)	-56(3)	-13(2)
O(4)	68(3)	81(3)	50(2)	5(2)	-11(2)	32(2)
C(8A)	55(9)	91(12)	67(9)	34(8)	15(7)	38(9)
C(8B)	76(6)	68(7)	120(9)	38(7)	-52(6)	2(5)
C(9A)	68(11)	86(11)	40(6)	3(6)	-11(6)	21(9)
C(9B)	146(13)	206(16)	104(8)	47(8)	-11(8)	83(13)

Table S9. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for spider-15003.

	x	y	z	U(eq)
H(3)	2663	2682	5151	87
H(4)	967	2115	5097	99
H(5)	-105	1345	5412	97
H(6)	437	1207	5803	91
H(7)	2107	1774	5871	78
H(8AA)	3316	4831	4997	106
H(8AB)	2595	3971	4812	106
H(8AC)	3256	5068	4709	106
H(8BA)	2802	3364	4558	155
H(8BB)	3319	4508	4489	155
H(8BC)	2919	4146	4766	155
H(9AA)	4229	3822	4344	108
H(9AB)	3567	4329	4370	108
H(9AC)	3152	3223	4463	108
H(9BA)	5159	3820	4425	232
H(9BB)	4242	3838	4301	232
H(9BC)	4069	2916	4466	232
H(1)	4240(40)	3390(40)	5258(5)	56(16)

Table S10. Torsion angles [°] for spider-15003.

O(3)#1-Ti(1)-O(3)-Ti(1)#3	-0.003(1)
O(1)#2-Ti(1)-O(3)-Ti(1)#3	93.62(11)
O(1)-Ti(1)-O(3)-Ti(1)#3	-105.26(10)
O(2)#2-Ti(1)-O(3)-Ti(1)#3	169.89(9)
O(2)-Ti(1)-O(3)-Ti(1)#3	-139.9(4)
Ti(1)-O(1)-N(1)-C(1)	-13.5(5)
Ti(1)-O(2)-C(1)-N(1)	14.4(5)
Ti(1)-O(2)-C(1)-C(2)	-162.8(3)
O(1)-N(1)-C(1)-O(2)	-1.5(6)
O(1)-N(1)-C(1)-C(2)	175.8(4)
O(2)-C(1)-C(2)-C(3)	-170.1(5)
N(1)-C(1)-C(2)-C(3)	12.7(8)
O(2)-C(1)-C(2)-C(7)	11.9(7)
N(1)-C(1)-C(2)-C(7)	-165.2(5)
C(7)-C(2)-C(3)-C(4)	-1.2(9)
C(1)-C(2)-C(3)-C(4)	-179.1(6)
C(2)-C(3)-C(4)-C(5)	-1.0(11)
C(3)-C(4)-C(5)-C(6)	2.7(12)
C(4)-C(5)-C(6)-C(7)	-2.2(11)
C(5)-C(6)-C(7)-C(2)	-0.1(9)
C(3)-C(2)-C(7)-C(6)	1.7(8)
C(1)-C(2)-C(7)-C(6)	179.8(5)

Symmetry transformations used to generate equivalent atoms:

#1 -y+1,x-y,z #2 x-y+1/3,-y+2/3,-z+7/6 #3 -x+y+1,-x+1,z

Table S11. Hydrogen bonds for spider-15003 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(4)	0.87(2)	1.86(2)	2.720(6)	166(5)

Symmetry transformations used to generate equivalent atoms:

#1 -y+1,x-y,z #2 x-y+1/3,-y+2/3,-z+7/6 #3 -x+y+1,-x+1,z

Crystal Structure Details

Single crystals of spider-15007 were grown from slow cooling of a hot ethylene glycol solution containing compound 1. Low-temperature diffraction data (ω-scans) were collected on a Rigaku R-AXIS RAPID diffractometer coupled to an R-AXIS RAPID imaging plate detector with Mo Kα radiation (λ = 0.71073 Å) for the structure of spider-15007. All structures were solved by direct methods using SHELXS and were refined against F^2 on all data by full-matrix least squares with SHELXL. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). Hydrogen atoms H2 and H6 are freely refining and participate in refined hydrogen bonding interactions between N2...O6_$1, O6...O3, O8A...O1, and N1...O5_$2, where $1 and $2 denote the symmetry operations -X, 1-Y, -Z and 1-X, 1-Y, 1-Z. The O8A and H8A bond distance required the use of a similarity restraint due to the atoms' proximity. Atom H8a is semi-freely refining. H8b is geometrically placed, fixed and riding on O8b. The refined donor/acceptor distances are listed in Table S18. The full numbering scheme of compound spider-15007 can be found in Figure S22. Full details of the X-ray structure determination are in the CIF included as Supporting Information. CCDC number 1402797 (spider-15007) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Refinement Information

Atoms C17, C18 and O8 are disordered over two positions. The major and minor positions are denoted with the suffixes "a" and "b." The site occupancies were freely refined and subsequently fixed at their converged values of 0.7 and 0.3. Due to the small amount of electron density in the minor portion of the disordered model, rigid bond restraints were required for a stable refinement.

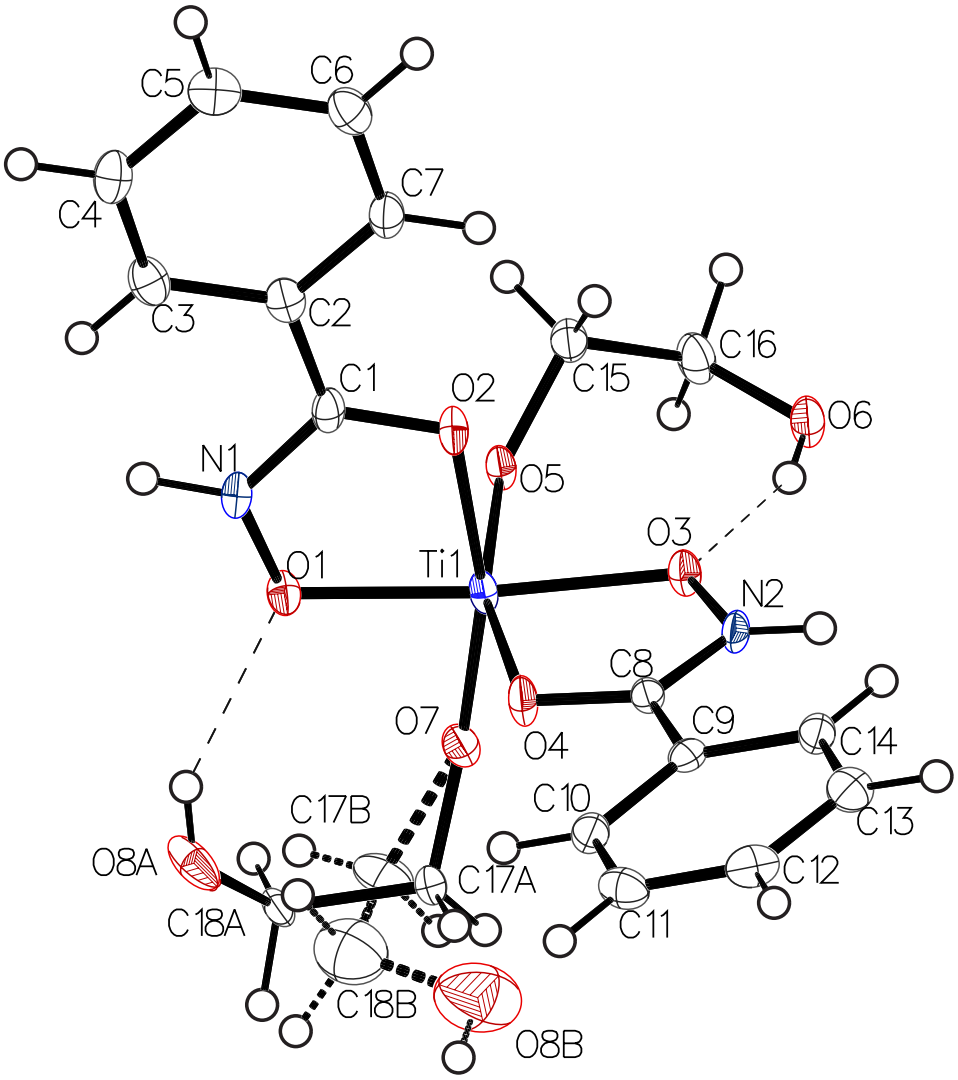

Figure S23. The full numbering scheme of spider-15007. All atoms shown are depicted with 50% thermal contours. The hydrogen atoms are shown as spheres.

Table S12. Crystal data and structure refinement for spider-15007

Identification code	spider-15007	
Empirical formula	$C_{18}H_{22}N_2O_8Ti$	
Formula weight	442.27	
Temperature	93(2) K	
Wavelength	0.71075 Å	
Crystal system	Monoclinic	
Space group	P 2_1/n	
Unit cell dimensions	a = 10.9669(3) Å	α = 90°
	b = 14.7049(4) Å	β = 113.016(8)°
	c = 13.0353(9) Å	γ = 90°
Volume	1934.82(19) Å^3	
Z	4	
Density (calculated)	1.518 Mg/m^3	
Absorption coefficient	0.492 mm^{-1}	
F(000)	920	
Crystal size	0.150 x 0.150 x 0.080 mm^3	
Crystal color and habit	Colorless Block	
Diffractometer	Rigaku R-AXIS RAPID imaging plate	
θ range for data collection	3.104 to 25.348°.	
Index ranges	$-13 \le h \le 13$, $-17 \le k \le 17$, $-15 \le l \le 15$	
Reflections collected	21555	
Independent reflections	3533 [R(int) = 0.0494]	
Observed reflections (I > 2σ(I))	2877	
Completeness to θ = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.962 and 0.824	
Solution method	SHELXS-2013 (Sheldrick, 2013)	
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)	
Data / restraints / parameters	3533 / 10 / 305	
Goodness-of-fit on F^2	1.056	
Final R indices [I>2σ(I)]	R1 = 0.0384, wR2 = 0.0943	
R indices (all data)	R1 = 0.0516, wR2 = 0.1021	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.538 and -0.346 e.Å^{-3}	

Table S13. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for spider-15007. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ti(1)	3802(1)	5071(1)	2659(1)	14(1)
O(1)	5410(2)	5303(1)	3997(1)	16(1)
O(2)	3312(2)	6216(1)	3384(1)	17(1)
O(3)	2146(1)	5245(1)	1317(1)	15(1)
O(4)	4296(2)	6053(1)	1751(1)	18(1)
O(5)	2809(2)	4327(1)	3201(1)	16(1)
O(6)	108(2)	4134(1)	1304(1)	21(1)
O(7)	4705(2)	4212(1)	2292(1)	18(1)
O(8A)	7539(2)	4550(2)	3581(3)	30(1)
O(8B)	6164(9)	4839(6)	1008(8)	61(2)
N(1)	5351(2)	6031(1)	4638(2)	16(1)
N(2)	2204(2)	5910(1)	599(2)	15(1)
C(0AA)	4222(2)	6473(2)	4294(2)	16(1)
C(1AA)	4068(2)	7261(2)	4943(2)	16(1)
C(3)	5078(2)	7536(2)	5933(2)	19(1)
C(4)	4898(2)	8282(2)	6510(2)	21(1)
C(5)	3700(2)	8755(2)	6104(2)	21(1)
C(6)	2698(2)	8482(2)	5116(2)	20(1)
C(7)	2872(2)	7741(2)	4532(2)	18(1)
C(8)	3344(2)	6324(2)	870(2)	14(1)
C(9)	3514(2)	7085(2)	203(2)	14(1)
C(10)	4785(2)	7440(2)	478(2)	17(1)
C(11)	4975(2)	8172(2)	-114(2)	21(1)
C(12)	3909(2)	8558(2)	-981(2)	21(1)
C(13)	2642(2)	8207(2)	-1260(2)	20(1)
C(14)	2442(2)	7479(2)	-668(2)	17(1)
C(15)	1553(2)	4378(2)	3276(2)	19(1)
C(16)	553(2)	3779(2)	2413(2)	21(1)
C(17A)	5712(5)	3986(4)	1935(4)	21(1)
C(18A)	6991(3)	3782(2)	2919(3)	16(1)
C(17B)	5995(14)	3794(10)	2362(12)	30(3)

C(18B)	6817(12)	4467(8)	2152(10)	49(3)

Table S14. Bond lengths [Å] and angles [°] for spider-15007.

Ti(1)-O(7)	1.7831(16)
Ti(1)-O(5)	1.8661(16)
Ti(1)-O(1)	1.9654(16)
Ti(1)-O(3)	1.9847(15)
Ti(1)-O(4)	2.0685(16)
Ti(1)-O(2)	2.1001(16)
O(1)-N(1)	1.375(2)
O(2)-C(0AA)	1.273(3)
O(3)-N(2)	1.372(2)
O(4)-C(8)	1.277(3)
O(5)-C(15)	1.421(3)
O(6)-C(16)	1.432(3)
O(6)-H(6)	0.75(3)
O(7)-C(17A)	1.396(6)
O(7)-C(17B)	1.513(15)
O(8A)-C(18A)	1.405(4)
O(8A)-H(8A)	0.73(3)
O(8B)-C(18B)	1.484(14)
O(8B)-H(8B)	0.8400
N(1)-C(0AA)	1.312(3)
N(1)-H(1)	0.90(3)
N(2)-C(8)	1.309(3)
N(2)-H(2)	0.84(3)
C(0AA)-C(1AA)	1.483(3)
C(1AA)-C(3)	1.391(3)
C(1AA)-C(7)	1.399(3)
C(3)-C(4)	1.388(3)
C(3)-H(3)	0.9500
C(4)-C(5)	1.395(3)
C(4)-H(4)	0.9500
C(5)-C(6)	1.385(3)
C(5)-H(5)	0.9500
C(6)-C(7)	1.385(3)
C(6)-H(6A)	0.9500

C(7)-H(7)	0.9500
C(8)-C(9)	1.473(3)
C(9)-C(10)	1.398(3)
C(9)-C(14)	1.400(3)
C(10)-C(11)	1.386(3)
C(10)-H(10)	0.9500
C(11)-C(12)	1.390(3)
C(11)-H(11)	0.9500
C(12)-C(13)	1.390(3)
C(12)-H(12)	0.9500
C(13)-C(14)	1.386(3)
C(13)-H(13)	0.9500
C(14)-H(14)	0.9500
C(15)-C(16)	1.510(3)
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(17A)-C(18A)	1.515(5)
C(17A)-H(17A)	0.9900
C(17A)-H(17B)	0.9900
C(18A)-H(18A)	0.9900
C(18A)-H(18B)	0.9900
C(17B)-C(18B)	1.435(18)
C(17B)-H(17C)	0.9900
C(17B)-H(17D)	0.9900
C(18B)-H(18C)	0.9900
C(18B)-H(18D)	0.9900

O(7)-Ti(1)-O(5)	98.83(7)
O(7)-Ti(1)-O(1)	87.78(7)
O(5)-Ti(1)-O(1)	102.71(7)
O(7)-Ti(1)-O(3)	105.50(7)
O(5)-Ti(1)-O(3)	86.61(6)
O(1)-Ti(1)-O(3)	162.58(7)
O(7)-Ti(1)-O(4)	92.48(7)

O(5)-Ti(1)-O(4)	161.41(7)
O(1)-Ti(1)-O(4)	92.37(6)
O(3)-Ti(1)-O(4)	76.13(6)
O(7)-Ti(1)-O(2)	162.84(7)
O(5)-Ti(1)-O(2)	90.60(7)
O(1)-Ti(1)-O(2)	76.12(6)
O(3)-Ti(1)-O(2)	89.25(6)
O(4)-Ti(1)-O(2)	82.44(7)
N(1)-O(1)-Ti(1)	115.80(12)
C(0AA)-O(2)-Ti(1)	114.34(14)
N(2)-O(3)-Ti(1)	114.96(12)
C(8)-O(4)-Ti(1)	115.34(14)
C(15)-O(5)-Ti(1)	136.04(14)
C(16)-O(6)-H(6)	109(3)
C(17A)-O(7)-Ti(1)	148.6(3)
C(17B)-O(7)-Ti(1)	151.3(6)
C(18A)-O(8A)-H(8A)	109(4)
C(18B)-O(8B)-H(8B)	109.5
C(0AA)-N(1)-O(1)	116.11(18)
C(0AA)-N(1)-H(1)	126.1(19)
O(1)-N(1)-H(1)	115.2(19)
C(8)-N(2)-O(3)	116.26(18)
C(8)-N(2)-H(2)	127.8(17)
O(3)-N(2)-H(2)	115.7(17)
O(2)-C(0AA)-N(1)	117.6(2)
O(2)-C(0AA)-C(1AA)	122.8(2)
N(1)-C(0AA)-C(1AA)	119.7(2)
C(3)-C(1AA)-C(7)	119.7(2)
C(3)-C(1AA)-C(0AA)	121.9(2)
C(7)-C(1AA)-C(0AA)	118.3(2)
C(4)-C(3)-C(1AA)	120.1(2)
C(4)-C(3)-H(3)	119.9
C(1AA)-C(3)-H(3)	119.9
C(3)-C(4)-C(5)	120.1(2)
C(3)-C(4)-H(4)	120.0
C(5)-C(4)-H(4)	120.0

C(6)-C(5)-C(4)	119.7(2)
C(6)-C(5)-H(5)	120.2
C(4)-C(5)-H(5)	120.2
C(7)-C(6)-C(5)	120.6(2)
C(7)-C(6)-H(6A)	119.7
C(5)-C(6)-H(6A)	119.7
C(6)-C(7)-C(1AA)	119.8(2)
C(6)-C(7)-H(7)	120.1
C(1AA)-C(7)-H(7)	120.1
O(4)-C(8)-N(2)	117.1(2)
O(4)-C(8)-C(9)	121.4(2)
N(2)-C(8)-C(9)	121.5(2)
C(10)-C(9)-C(14)	119.4(2)
C(10)-C(9)-C(8)	118.5(2)
C(14)-C(9)-C(8)	122.2(2)
C(11)-C(10)-C(9)	119.9(2)
C(11)-C(10)-H(10)	120.0
C(9)-C(10)-H(10)	120.0
C(10)-C(11)-C(12)	120.5(2)
C(10)-C(11)-H(11)	119.8
C(12)-C(11)-H(11)	119.8
C(13)-C(12)-C(11)	119.9(2)
C(13)-C(12)-H(12)	120.1
C(11)-C(12)-H(12)	120.1
C(14)-C(13)-C(12)	120.0(2)
C(14)-C(13)-H(13)	120.0
C(12)-C(13)-H(13)	120.0
C(13)-C(14)-C(9)	120.3(2)
C(13)-C(14)-H(14)	119.8
C(9)-C(14)-H(14)	119.8
O(5)-C(15)-C(16)	111.02(19)
O(5)-C(15)-H(15A)	109.4
C(16)-C(15)-H(15A)	109.4
O(5)-C(15)-H(15B)	109.4
C(16)-C(15)-H(15B)	109.4
H(15A)-C(15)-H(15B)	108.0

O(6)-C(16)-C(15)	113.65(19)
O(6)-C(16)-H(16A)	108.8
C(15)-C(16)-H(16A)	108.8
O(6)-C(16)-H(16B)	108.8
C(15)-C(16)-H(16B)	108.8
H(16A)-C(16)-H(16B)	107.7
O(7)-C(17A)-C(18A)	110.9(4)
O(7)-C(17A)-H(17A)	109.5
C(18A)-C(17A)-H(17A)	109.5
O(7)-C(17A)-H(17B)	109.5
C(18A)-C(17A)-H(17B)	109.5
H(17A)-C(17A)-H(17B)	108.1
O(8A)-C(18A)-C(17A)	113.2(3)
O(8A)-C(18A)-H(18A)	108.9
C(17A)-C(18A)-H(18A)	108.9
O(8A)-C(18A)-H(18B)	108.9
C(17A)-C(18A)-H(18B)	108.9
H(18A)-C(18A)-H(18B)	107.8
C(18B)-C(17B)-O(7)	110.5(10)
C(18B)-C(17B)-H(17C)	109.5
O(7)-C(17B)-H(17C)	109.5
C(18B)-C(17B)-H(17D)	109.5
O(7)-C(17B)-H(17D)	109.5
H(17C)-C(17B)-H(17D)	108.1
C(17B)-C(18B)-O(8B)	110.7(10)
C(17B)-C(18B)-H(18C)	109.5
O(8B)-C(18B)-H(18C)	109.5
C(17B)-C(18B)-H(18D)	109.5
O(8B)-C(18B)-H(18D)	109.5
H(18C)-C(18B)-H(18D)	108.1

Symmetry transformations used to generate equivalent atoms:

Table S15. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for spider-15007. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ti(1)	10(1)	16(1)	12(1)	1(1)	0(1)	-1(1)
O(1)	13(1)	16(1)	15(1)	-1(1)	1(1)	0(1)
O(2)	13(1)	18(1)	14(1)	1(1)	-1(1)	0(1)
O(3)	13(1)	17(1)	12(1)	4(1)	1(1)	-2(1)
O(4)	12(1)	22(1)	15(1)	5(1)	-1(1)	-2(1)
O(5)	11(1)	18(1)	15(1)	2(1)	1(1)	0(1)
O(6)	14(1)	28(1)	15(1)	5(1)	0(1)	-5(1)
O(7)	13(1)	22(1)	18(1)	-1(1)	4(1)	1(1)
O(8A)	11(1)	22(1)	50(2)	-19(1)	6(1)	-2(1)
O(8B)	65(5)	62(5)	69(5)	21(4)	39(4)	10(4)
N(1)	14(1)	15(1)	13(1)	1(1)	1(1)	-2(1)
N(2)	12(1)	17(1)	11(1)	3(1)	1(1)	0(1)
C(0AA)	14(1)	18(1)	14(1)	6(1)	3(1)	-3(1)
C(1AA)	16(1)	16(1)	15(1)	4(1)	5(1)	-2(1)
C(3)	16(1)	17(1)	22(1)	4(1)	5(1)	0(1)
C(4)	21(1)	19(1)	17(1)	0(1)	2(1)	-4(1)
C(5)	26(1)	15(1)	24(1)	2(1)	12(1)	0(1)
C(6)	18(1)	21(1)	21(1)	4(1)	6(1)	2(1)
C(7)	15(1)	23(1)	16(1)	4(1)	4(1)	-2(1)
C(8)	12(1)	16(1)	14(1)	-3(1)	4(1)	2(1)
C(9)	16(1)	15(1)	12(1)	-3(1)	6(1)	0(1)
C(10)	17(1)	17(1)	16(1)	-1(1)	6(1)	2(1)
C(11)	20(1)	20(1)	25(1)	-2(1)	12(1)	-3(1)
C(12)	28(1)	16(1)	23(1)	2(1)	15(1)	2(1)
C(13)	23(1)	17(1)	19(1)	1(1)	8(1)	5(1)
C(14)	16(1)	16(1)	16(1)	-2(1)	5(1)	2(1)
C(15)	14(1)	26(1)	17(1)	2(1)	4(1)	-1(1)
C(16)	15(1)	29(1)	17(1)	6(1)	2(1)	-5(1)
C(17A)	10(2)	36(3)	13(3)	-1(2)	2(2)	7(2)
C(18A)	8(2)	17(2)	19(2)	-6(1)	2(2)	2(1)
C(17B)	32(9)	28(6)	30(8)	-1(5)	15(7)	11(5)

C(18B)	50(6)	43(5)	58(6)	-5(5)	25(5)	1(5)

Table S16. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for spider-15007.

	x	y	z	U(eq)
H(2)	1520(30)	5968(17)	10(20)	14(6)
H(6)	670(30)	4380(20)	1240(30)	37(10)
H(8A)	7100(40)	4700(30)	3840(40)	44
H(8B)	6617	5272	924	92
H(1)	5980(30)	6046(19)	5330(30)	33(8)
H(3)	5892	7212	6213	23
H(4)	5591	8470	7183	25
H(5)	3573	9263	6502	25
H(6A)	1884	8806	4838	25
H(7)	2181	7559	3855	22
H(10)	5518	7181	1070	20
H(11)	5840	8411	73	25
H(12)	4045	9060	-1381	25
H(13)	1914	8466	-1856	24
H(14)	1574	7246	-853	20
H(15A)	1237	5015	3165	23
H(15B)	1640	4185	4030	23
H(16A)	954	3173	2430	26
H(16B)	-222	3696	2614	26
H(17A)	5855	4497	1499	25
H(17B)	5443	3447	1442	25
H(18A)	6821	3309	3386	19
H(18B)	7643	3535	2640	19
H(17C)	6467	3530	3113	36
H(17D)	5810	3297	1809	36
H(18C)	7676	4190	2242	59
H(18D)	6995	4966	2701	59

Table S17. Torsion angles [°] for spider-15007.

O(7)-Ti(1)-O(5)-C(15)	-151.2(2)
O(1)-Ti(1)-O(5)-C(15)	119.1(2)
O(3)-Ti(1)-O(5)-C(15)	-46.0(2)
O(4)-Ti(1)-O(5)-C(15)	-24.4(3)
O(2)-Ti(1)-O(5)-C(15)	43.2(2)
O(5)-Ti(1)-O(7)-C(17A)	-172.0(4)
O(1)-Ti(1)-O(7)-C(17A)	-69.5(4)
O(3)-Ti(1)-O(7)-C(17A)	99.1(4)
O(4)-Ti(1)-O(7)-C(17A)	22.8(4)
O(2)-Ti(1)-O(7)-C(17A)	-49.4(5)
O(5)-Ti(1)-O(7)-C(17B)	-125.2(11)
O(1)-Ti(1)-O(7)-C(17B)	-22.7(11)
O(3)-Ti(1)-O(7)-C(17B)	145.9(11)
O(4)-Ti(1)-O(7)-C(17B)	69.6(11)
O(2)-Ti(1)-O(7)-C(17B)	-2.6(12)
Ti(1)-O(1)-N(1)-C(0AA)	1.3(2)
Ti(1)-O(3)-N(2)-C(8)	1.9(2)
Ti(1)-O(2)-C(0AA)-N(1)	2.9(3)
Ti(1)-O(2)-C(0AA)-C(1AA)	-179.26(16)
O(1)-N(1)-C(0AA)-O(2)	-2.8(3)
O(1)-N(1)-C(0AA)-C(1AA)	179.27(18)
O(2)-C(0AA)-C(1AA)-C(3)	-179.6(2)
N(1)-C(0AA)-C(1AA)-C(3)	-1.8(3)
O(2)-C(0AA)-C(1AA)-C(7)	-0.3(3)
N(1)-C(0AA)-C(1AA)-C(7)	177.5(2)
C(7)-C(1AA)-C(3)-C(4)	0.1(3)
C(0AA)-C(1AA)-C(3)-C(4)	179.4(2)
C(1AA)-C(3)-C(4)-C(5)	0.4(3)
C(3)-C(4)-C(5)-C(6)	-0.6(4)
C(4)-C(5)-C(6)-C(7)	0.3(4)
C(5)-C(6)-C(7)-C(1AA)	0.2(3)
C(3)-C(1AA)-C(7)-C(6)	-0.4(3)
C(0AA)-C(1AA)-C(7)-C(6)	-179.7(2)
Ti(1)-O(4)-C(8)-N(2)	-4.9(3)

Ti(1)-O(4)-C(8)-C(9)	173.65(15)
O(3)-N(2)-C(8)-O(4)	2.1(3)
O(3)-N(2)-C(8)-C(9)	-176.45(18)
O(4)-C(8)-C(9)-C(10)	7.5(3)
N(2)-C(8)-C(9)-C(10)	-174.1(2)
O(4)-C(8)-C(9)-C(14)	-170.5(2)
N(2)-C(8)-C(9)-C(14)	8.0(3)
C(14)-C(9)-C(10)-C(11)	-0.4(3)
C(8)-C(9)-C(10)-C(11)	-178.3(2)
C(9)-C(10)-C(11)-C(12)	0.1(3)
C(10)-C(11)-C(12)-C(13)	-0.2(4)
C(11)-C(12)-C(13)-C(14)	0.6(3)
C(12)-C(13)-C(14)-C(9)	-0.9(3)
C(10)-C(9)-C(14)-C(13)	0.7(3)
C(8)-C(9)-C(14)-C(13)	178.6(2)
Ti(1)-O(5)-C(15)-C(16)	104.6(2)
O(5)-C(15)-C(16)-O(6)	-73.8(3)
Ti(1)-O(7)-C(17A)-C(18A)	94.3(5)
O(7)-C(17A)-C(18A)-O(8A)	-67.2(5)
Ti(1)-O(7)-C(17B)-C(18B)	-50.2(17)
O(7)-C(17B)-C(18B)-O(8B)	-62.2(13)

Symmetry transformations used to generate equivalent atoms:

Table S18. Hydrogen bonds for spider-15007 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2)...O(6)#1	0.84(3)	1.94(3)	2.770(3)	169(2)
O(6)-H(6)...O(3)	0.75(3)	2.03(3)	2.762(2)	167(3)
O(8A)-H(8A)...O(1)	0.73(3)	2.13(4)	2.822(3)	158(5)
N(1)-H(1)...O(5)#2	0.90(3)	1.94(3)	2.800(2)	162(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z #2 -x+1,-y+1,-z+1

Crystallographic details

Single crystals of $C_{36}H_{40}Cl_8N_4O_{10}Ti_2$ spider-15013 were grown by diffusion of diethyl ether into a solution of compound 4 in dichloromethane. For the structure of spider-15013, low-temperature diffraction data (ω-scans) were collected on a Rigaku R-AXIS RAPID diffractometer coupled to an R-AXIS RAPID imaging plate detector with Mo Kα radiation (λ = 0.71073 Å). All structures were solved by direct methods using SHELXT and were refined against F^2 on all data by full-matrix least squares with SHELXL (Sheldrick, G. M. Acta Cryst. 2008, A64, 112–122). All non-hydrogen atoms were refined anisotropically. Unless stated otherwise, hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The overall quality of the data was poor due to crystal quality. The dichloromethane solvent molecules in the crystal lattice caused the crystals to dissolve and crack while screening. This fact affected the material's crystallinity. The crystal was also very small, which exacerbated the already weak diffraction. A high-resolution cut-off of 0.95 Å was applied to the data. The full numbering scheme of spider-15013 can be found in the Figure S23. Full details of the X-ray structure determination are located in the CIF, also included in the Supporting Information. CCDC number 1402799 (spider-15013) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

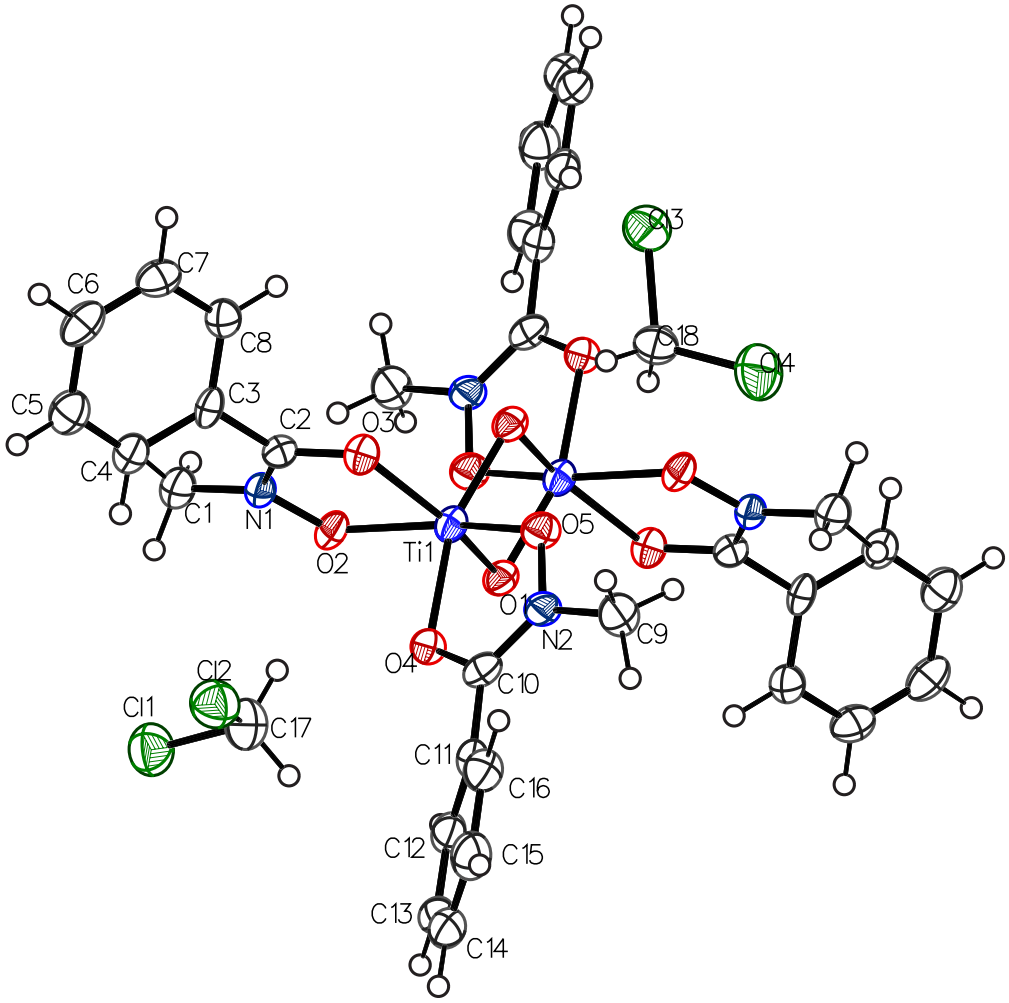

Figure S24. The full numbering scheme of spider-15013. Only the asymmetric unit is numbered and half of the Ti complex is generated by the crystallographic inversion center. All atoms shown are depicted with 50% thermal contours. The hydrogen atoms are shown as spheres.

Table S19. Crystal data and structure refinement for spider-15013

Identification code	spider-15013	
Empirical formula	$C_{36}H_{40}Cl_8N_4O_{10}Ti_2$	
Formula weight	1068.12	
Temperature	93(2) K	
Wavelength	0.71075 Å	
Crystal system	Monoclinic	
Space group	$P\,2_1/n$	
Unit cell dimensions	a = 12.1927(9) Å	α = 90°
	b = 10.0654(8) Å	β = 102.042(7)°
	c = 19.3484(15) Å	γ = 90°
Volume	2322.3(3) $Å^3$	
Z	2	
Density (calculated)	1.528 Mg/m^3	
Absorption coefficient	0.860 mm^{-1}	
F(000)	1088	
Crystal size	0.200 x 0.200 x 0.040 mm^3	
Crystal color and habit	Colorless Block	
Diffractometer	Rigaku R-AXIS RAPID imaging plate	
Theta range for data collection	2.990 to 21.964°.	
Index ranges	$-12 \le h \le 12, -10 \le k \le 10, -20 \le l \le 20$	
Reflections collected	31353	
Independent reflections	2831 [R(int) = 0.1328]	
Observed reflections ($I > 2\sigma(I)$)	2258	
Completeness to θ = 21.965°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.966 and 0.648	
Solution method	SHELXS-2013 (Sheldrick, 2013)	
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)	
Data / restraints / parameters	2831 / 0 / 273	
Goodness-of-fit on F^2	1.124	
Final R indices [$I>2\sigma(I)$]	R1 = 0.0886, wR2 = 0.2478	
R indices (all data)	R1 = 0.1033, wR2 = 0.2587	
Largest diff. peak and hole	0.998 and -0.647 $e.Å^{-3}$	

Table S20. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for spider-15013. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ti(1)	5193(1)	8826(2)	4692(1)	27(1)
O(1)	3994(5)	9807(5)	4818(3)	27(1)
O(2)	5655(5)	9514(6)	3828(3)	30(1)
O(3)	4309(5)	7696(6)	3863(3)	31(1)
O(4)	6540(4)	7567(5)	4895(3)	26(1)
O(5)	4837(5)	7536(6)	5386(3)	31(1)
N(1)	5202(6)	8906(7)	3204(3)	26(2)
N(2)	5642(6)	6612(7)	5638(4)	30(2)
C(1)	5466(8)	9520(9)	2587(4)	35(2)
C(2)	4496(7)	7948(9)	3251(4)	27(2)
C(3)	3956(7)	7153(9)	2628(4)	30(2)
C(4)	4583(8)	6496(9)	2198(4)	35(2)
C(5)	4060(8)	5718(9)	1646(5)	40(2)
C(6)	2901(8)	5608(9)	1496(5)	39(2)
C(7)	2286(8)	6237(9)	1906(5)	37(2)
C(8)	2783(7)	7001(9)	2480(4)	32(2)
C(9)	5403(8)	5839(9)	6221(5)	40(2)
C(10)	6545(7)	6667(9)	5367(4)	30(2)
C(11)	7509(7)	5753(8)	5562(4)	29(2)
C(12)	8580(8)	6271(9)	5590(4)	34(2)
C(13)	9492(8)	5487(10)	5750(5)	39(2)
C(14)	9382(9)	4141(10)	5890(5)	42(2)
C(15)	8334(9)	3624(10)	5868(5)	46(3)
C(16)	7384(8)	4418(9)	5699(5)	36(2)
Cl(1)	8608(2)	8511(3)	3152(1)	56(1)
Cl(2)	7465(2)	6156(3)	3527(2)	54(1)
C(17)	7947(9)	7764(10)	3784(5)	49(3)
Cl(3)	1101(2)	9001(3)	5275(1)	56(1)
Cl(4)	2401(3)	7652(3)	6518(2)	66(1)
C(18)	2402(8)	8273(11)	5682(5)	44(2)

Table S21. Bond lengths [Å] and angles [°] for spider-15013.

Ti(1)-O(1)	1.822(6)
Ti(1)-O(1)#1	1.839(6)
Ti(1)-O(5)	1.981(6)
Ti(1)-O(2)	1.996(6)
Ti(1)-O(4)	2.046(5)
Ti(1)-O(3)	2.075(6)
Ti(1)-Ti(1)#1	2.732(3)
O(1)-Ti(1)#1	1.839(5)
O(2)-N(1)	1.362(8)
O(3)-C(2)	1.277(10)
O(4)-C(10)	1.287(10)
O(5)-N(2)	1.366(9)
N(1)-C(2)	1.309(11)
N(1)-C(1)	1.439(11)
N(2)-C(10)	1.315(11)
N(2)-C(9)	1.450(11)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(2)-C(3)	1.483(12)
C(3)-C(8)	1.406(12)
C(3)-C(4)	1.407(12)
C(4)-C(5)	1.370(13)
C(4)-H(4)	0.9500
C(5)-C(6)	1.386(13)
C(5)-H(5)	0.9500
C(6)-C(7)	1.357(13)
C(6)-H(6)	0.9500
C(7)-C(8)	1.383(13)
C(7)-H(7)	0.9500
C(8)-H(8)	0.9500
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800

C(10)-C(11)	1.478(13)
C(11)-C(16)	1.384(13)
C(11)-C(12)	1.397(13)
C(12)-C(13)	1.346(13)
C(12)-H(12)	0.9500
C(13)-C(14)	1.393(14)
C(13)-H(13)	0.9500
C(14)-C(15)	1.372(15)
C(14)-H(14)	0.9500
C(15)-C(16)	1.389(14)
C(15)-H(15)	0.9500
C(16)-H(16)	0.9500
Cl(1)-C(17)	1.766(10)
Cl(2)-C(17)	1.758(10)
C(17)-H(17A)	0.9900
C(17)-H(17B)	0.9900
Cl(3)-C(18)	1.776(10)
Cl(4)-C(18)	1.734(10)
C(18)-H(18A)	0.9900
C(18)-H(18B)	0.9900

O(1)-Ti(1)-O(1)#1	83.5(3)
O(1)-Ti(1)-O(5)	88.2(2)
O(1)#1-Ti(1)-O(5)	108.2(2)
O(1)-Ti(1)-O(2)	107.4(2)
O(1)#1-Ti(1)-O(2)	87.5(2)
O(5)-Ti(1)-O(2)	159.3(2)
O(1)-Ti(1)-O(4)	160.7(2)
O(1)#1-Ti(1)-O(4)	92.3(2)
O(5)-Ti(1)-O(4)	75.2(2)
O(2)-Ti(1)-O(4)	91.1(2)
O(1)-Ti(1)-O(3)	95.7(2)
O(1)#1-Ti(1)-O(3)	161.1(2)
O(5)-Ti(1)-O(3)	90.7(2)
O(2)-Ti(1)-O(3)	74.6(2)
O(4)-Ti(1)-O(3)	94.3(2)

O(1)-Ti(1)-Ti(1)#1	41.98(17)
O(1)#1-Ti(1)-Ti(1)#1	41.49(18)
O(5)-Ti(1)-Ti(1)#1	100.91(18)
O(2)-Ti(1)-Ti(1)#1	99.81(18)
O(4)-Ti(1)-Ti(1)#1	131.01(18)
O(3)-Ti(1)-Ti(1)#1	134.64(18)
Ti(1)-O(1)-Ti(1)#1	96.5(3)
N(1)-O(2)-Ti(1)	116.9(5)
C(2)-O(3)-Ti(1)	116.3(5)
C(10)-O(4)-Ti(1)	117.2(5)
N(2)-O(5)-Ti(1)	116.4(4)
C(2)-N(1)-O(2)	114.8(6)
C(2)-N(1)-C(1)	129.7(7)
O(2)-N(1)-C(1)	115.0(7)
C(10)-N(2)-O(5)	115.4(7)
C(10)-N(2)-C(9)	130.8(7)
O(5)-N(2)-C(9)	113.4(7)
N(1)-C(1)-H(1A)	109.5
N(1)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
N(1)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
O(3)-C(2)-N(1)	117.3(7)
O(3)-C(2)-C(3)	120.8(8)
N(1)-C(2)-C(3)	121.9(7)
C(8)-C(3)-C(4)	119.0(8)
C(8)-C(3)-C(2)	118.9(7)
C(4)-C(3)-C(2)	122.0(8)
C(5)-C(4)-C(3)	120.5(9)
C(5)-C(4)-H(4)	119.8
C(3)-C(4)-H(4)	119.8
C(4)-C(5)-C(6)	119.8(9)
C(4)-C(5)-H(5)	120.1
C(6)-C(5)-H(5)	120.1
C(7)-C(6)-C(5)	120.2(9)

C(7)-C(6)-H(6)	119.9
C(5)-C(6)-H(6)	119.9
C(6)-C(7)-C(8)	121.8(9)
C(6)-C(7)-H(7)	119.1
C(8)-C(7)-H(7)	119.1
C(7)-C(8)-C(3)	118.7(8)
C(7)-C(8)-H(8)	120.7
C(3)-C(8)-H(8)	120.7
N(2)-C(9)-H(9A)	109.5
N(2)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
N(2)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
O(4)-C(10)-N(2)	115.6(8)
O(4)-C(10)-C(11)	120.4(8)
N(2)-C(10)-C(11)	124.0(8)
C(16)-C(11)-C(12)	119.6(8)
C(16)-C(11)-C(10)	122.7(8)
C(12)-C(11)-C(10)	117.7(8)
C(13)-C(12)-C(11)	120.7(9)
C(13)-C(12)-H(12)	119.7
C(11)-C(12)-H(12)	119.7
C(12)-C(13)-C(14)	120.4(9)
C(12)-C(13)-H(13)	119.8
C(14)-C(13)-H(13)	119.8
C(15)-C(14)-C(13)	119.3(9)
C(15)-C(14)-H(14)	120.3
C(13)-C(14)-H(14)	120.3
C(14)-C(15)-C(16)	121.0(10)
C(14)-C(15)-H(15)	119.5
C(16)-C(15)-H(15)	119.5
C(11)-C(16)-C(15)	119.0(9)
C(11)-C(16)-H(16)	120.5
C(15)-C(16)-H(16)	120.5
Cl(2)-C(17)-Cl(1)	111.7(6)

Cl(2)-C(17)-H(17A)	109.3
Cl(1)-C(17)-H(17A)	109.3
Cl(2)-C(17)-H(17B)	109.3
Cl(1)-C(17)-H(17B)	109.3
H(17A)-C(17)-H(17B)	107.9
Cl(4)-C(18)-Cl(3)	112.9(5)
Cl(4)-C(18)-H(18A)	109.0
Cl(3)-C(18)-H(18A)	109.0
Cl(4)-C(18)-H(18B)	109.0
Cl(3)-C(18)-H(18B)	109.0
H(18A)-C(18)-H(18B)	107.8

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+2,-z+1

Table S22. Anisotropic displacement parameters ($Å^2$ x 10^3) for spider-15013. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ti(1)	30(1)	29(1)	21(1)	2(1)	4(1)	-1(1)
O(1)	26(3)	29(3)	25(3)	0(2)	2(2)	-3(3)
O(2)	35(4)	32(3)	20(3)	-3(3)	0(3)	0(3)
O(3)	36(4)	31(3)	26(4)	1(3)	6(3)	-1(3)
O(4)	27(3)	23(3)	27(3)	3(3)	6(2)	-1(3)
O(5)	31(3)	29(3)	33(3)	6(3)	6(3)	2(3)
N(1)	26(4)	32(4)	20(4)	2(3)	5(3)	-1(3)
N(2)	28(4)	31(4)	29(4)	9(3)	6(3)	6(3)
C(1)	38(6)	40(5)	26(5)	3(4)	6(4)	0(4)
C(2)	26(5)	31(5)	24(5)	2(4)	3(4)	5(4)
C(3)	40(6)	35(5)	15(4)	7(4)	5(4)	1(4)
C(4)	36(6)	44(6)	25(5)	-1(4)	4(4)	-1(4)
C(5)	45(6)	38(6)	34(5)	-5(4)	4(4)	-1(5)
C(6)	47(7)	33(5)	32(5)	-2(4)	-5(5)	-9(5)
C(7)	30(5)	37(5)	39(6)	1(4)	0(4)	-6(4)
C(8)	33(5)	36(5)	28(5)	1(4)	8(4)	-1(4)
C(9)	47(6)	37(5)	39(6)	15(4)	16(5)	13(5)
C(10)	29(5)	31(5)	26(5)	-3(4)	-3(4)	-2(4)
C(11)	34(5)	33(5)	21(4)	-1(4)	7(4)	0(4)
C(12)	40(6)	35(5)	24(5)	-2(4)	4(4)	5(5)
C(13)	28(5)	63(7)	26(5)	-3(5)	3(4)	-5(5)
C(14)	43(6)	52(7)	29(5)	3(4)	6(4)	13(5)
C(15)	60(7)	41(6)	36(6)	6(4)	13(5)	14(6)
C(16)	39(6)	36(6)	33(5)	1(4)	7(4)	-7(5)
Cl(1)	59(2)	62(2)	48(2)	1(1)	17(1)	-5(1)
Cl(2)	49(2)	58(2)	56(2)	-4(1)	12(1)	-4(1)
C(17)	58(7)	46(6)	43(6)	-5(5)	14(5)	-2(5)
Cl(3)	52(2)	61(2)	53(2)	-7(1)	8(1)	13(1)
Cl(4)	69(2)	78(2)	55(2)	19(2)	25(2)	2(2)
C(18)	28(5)	59(7)	44(6)	-2(5)	7(4)	-10(5)

Table S23. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for spider-15013.

	x	y	z	U(eq)
H(1A)	5296	10471	2588	53
H(1B)	5017	9109	2162	53
H(1C)	6264	9397	2591	53
H(4)	5375	6592	2292	43
H(5)	4490	5255	1367	48
H(6)	2536	5091	1104	47
H(7)	1493	6151	1795	44
H(8)	2342	7414	2770	38
H(9A)	5074	6416	6532	60
H(9B)	6100	5451	6489	60
H(9C)	4874	5127	6037	60
H(12)	8666	7187	5495	40
H(13)	10215	5853	5767	47
H(14)	10026	3587	6000	50
H(15)	8257	2710	5970	55
H(16)	6660	4050	5677	43
H(17A)	8484	7718	4244	58
H(17B)	7305	8321	3847	58
H(18A)	2576	7542	5380	52
H(18B)	3001	8948	5718	52

Table S24. Torsion angles [°] for spider-15013.

O(1)#1-Ti(1)-O(1)-Ti(1)#1	-0.004(2)
O(5)-Ti(1)-O(1)-Ti(1)#1	108.5(3)
O(2)-Ti(1)-O(1)-Ti(1)#1	-85.3(3)
O(4)-Ti(1)-O(1)-Ti(1)#1	78.1(8)
O(3)-Ti(1)-O(1)-Ti(1)#1	-161.0(2)
Ti(1)-O(2)-N(1)-C(2)	1.1(8)
Ti(1)-O(2)-N(1)-C(1)	173.8(5)
Ti(1)-O(5)-N(2)-C(10)	-2.3(9)
Ti(1)-O(5)-N(2)-C(9)	170.8(6)
Ti(1)-O(3)-C(2)-N(1)	-1.5(9)
Ti(1)-O(3)-C(2)-C(3)	176.8(6)
O(2)-N(1)-C(2)-O(3)	0.3(10)
C(1)-N(1)-C(2)-O(3)	-171.1(8)
O(2)-N(1)-C(2)-C(3)	-177.9(7)
C(1)-N(1)-C(2)-C(3)	10.6(13)
O(3)-C(2)-C(3)-C(8)	53.0(11)
N(1)-C(2)-C(3)-C(8)	-128.8(9)
O(3)-C(2)-C(3)-C(4)	-124.0(9)
N(1)-C(2)-C(3)-C(4)	54.2(12)
C(8)-C(3)-C(4)-C(5)	-0.1(13)
C(2)-C(3)-C(4)-C(5)	176.9(8)
C(3)-C(4)-C(5)-C(6)	1.9(14)
C(4)-C(5)-C(6)-C(7)	-1.9(14)
C(5)-C(6)-C(7)-C(8)	0.0(14)
C(6)-C(7)-C(8)-C(3)	1.8(13)
C(4)-C(3)-C(8)-C(7)	-1.7(12)
C(2)-C(3)-C(8)-C(7)	-178.8(8)
Ti(1)-O(4)-C(10)-N(2)	3.9(9)
Ti(1)-O(4)-C(10)-C(11)	-177.7(6)
O(5)-N(2)-C(10)-O(4)	-1.1(10)
C(9)-N(2)-C(10)-O(4)	-172.7(8)
O(5)-N(2)-C(10)-C(11)	-179.5(7)
C(9)-N(2)-C(10)-C(11)	8.9(14)
O(4)-C(10)-C(11)-C(16)	-140.7(9)

N(2)-C(10)-C(11)-C(16)	37.6(13)
O(4)-C(10)-C(11)-C(12)	37.7(11)
N(2)-C(10)-C(11)-C(12)	-144.0(8)
C(16)-C(11)-C(12)-C(13)	-0.2(13)
C(10)-C(11)-C(12)-C(13)	-178.6(8)
C(11)-C(12)-C(13)-C(14)	0.0(13)
C(12)-C(13)-C(14)-C(15)	-0.4(14)
C(13)-C(14)-C(15)-C(16)	0.9(14)
C(12)-C(11)-C(16)-C(15)	0.7(13)
C(10)-C(11)-C(16)-C(15)	179.0(8)
C(14)-C(15)-C(16)-C(11)	-1.0(14)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+2,-z+1

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Coordinates for Theoretical Calculations.
Below are the .xyz files for the molecules (separated by blank lines) in this study with the comment line indicating the name of the molecule and the absolute SCF energy in kcal/mol.

```
55
Complex 1      Energy: -876791.5486352
Ti      -0.16745      1.23012      -0.29099
O       -1.62472     -0.15896       0.26784
O       -0.05036      1.77499       1.42533
O        1.51160      1.84383      -1.10686
O       -1.11979      2.62992      -0.91845
O       -0.42876      0.04934      -1.92985
O        1.35024     -0.34820       0.21929
C       -1.93539     -1.03225      -0.60191
C        2.45656     -0.11143      -0.32028
C        3.61333     -1.03571      -0.21959
C        3.35664     -2.38022       0.07017
C        4.40570     -3.28731       0.16925
C        5.72070     -2.86018      -0.00986
C        5.98429     -1.51857      -0.28067
C        4.93742     -0.60792      -0.38044
C       -2.94466     -2.07965      -0.34597
C       -2.98673     -3.27564      -1.07529
C       -3.96555     -4.22568      -0.80577
C       -4.90400     -3.99747       0.19970
C       -4.85508     -2.81754       0.94020
```

C	-3.87868	-1.86408	0.67411
N	2.58522	1.02170	-1.01106
N	-1.32240	-0.94197	-1.76883
C	0.01474	1.69607	2.83110
C	-1.14194	0.85689	3.37612
C	1.38142	1.16157	3.26408
C	-1.37955	3.96991	-0.53954
C	-0.51407	4.90407	-1.38492
C	-2.87415	4.24312	-0.69885
H	2.32995	-2.69109	0.21599
H	4.19841	-4.32822	0.38983
H	6.53819	-3.56753	0.07133
H	7.00649	-1.17836	-0.40010
H	5.15922	0.43986	-0.54963
H	-2.23985	-3.48544	-1.83304
H	-3.98798	-5.15010	-1.37123
H	-5.66409	-4.74100	0.41064
H	-5.57799	-2.64067	1.72823
H	-3.82274	-0.94529	1.24339
H	3.35006	1.23426	-1.63407
H	-1.53851	-1.49508	-2.58599
H	-0.09247	2.72332	3.20876
H	-2.09783	1.27102	3.04842
H	-1.12208	0.84673	4.47031
H	-1.07279	-0.16886	3.00834
H	2.17780	1.78807	2.85551
H	1.46526	1.16280	4.35523
H	1.52239	0.14276	2.89705
H	-1.10082	4.08077	0.51819
H	0.54047	4.64787	-1.26684
H	-0.66158	5.94592	-1.08357
H	-0.77439	4.80460	-2.44233
H	-3.45526	3.55265	-0.08346
H	-3.11481	5.26667	-0.39558
H	-3.17234	4.10851	-1.74226

51

Complex 2 Energy: -921866.0219909

Ti	0.00018	-1.60881	-0.00048
O	-0.68355	-1.17023	1.84331
O	-1.36484	0.00864	-0.27813
H	2.03353	-0.01441	-2.80162
O	0.68328	-1.16830	-1.84421
O	1.36616	0.00760	0.27847
O	-1.21276	-2.72765	-0.71543
O	-1.73842	-1.38443	-3.33328

H	-0.88789	-1.18457	-2.90914
O	1.21311	-2.72839	0.71363
O	1.73636	-1.39064	3.33499
H	0.88578	-1.19145	2.91062
N	-1.57899	-0.14942	1.91057
H	-2.03552	-0.01869	2.80110
N	1.57841	-0.14722	-1.91063
C	-1.91825	0.43823	0.76923
C	-2.92217	1.52299	0.73687
C	-3.23386	2.30046	1.85907
H	-2.70678	2.15423	2.79551
C	-4.19678	3.29961	1.76734
H	-4.43035	3.90367	2.63631
C	-4.84764	3.53343	0.55663
H	-5.59639	4.31431	0.48754
C	-4.52727	2.77172	-0.56632
H	-5.02667	2.95794	-1.50996
C	-3.56437	1.77234	-0.48202
H	-3.29417	1.17339	-1.34336
C	1.91842	0.43896	-0.76881
C	2.92186	1.52418	-0.73582
C	3.56384	1.77326	0.48323
H	3.29373	1.17387	1.34428
C	4.52631	2.77300	0.56813
H	5.02550	2.95898	1.51194
C	4.84652	3.53537	-0.55441
H	5.59495	4.31651	-0.48487
C	4.19585	3.30186	-1.76528
H	4.42925	3.90644	-2.63394
C	3.23335	2.30237	-1.85759
H	2.70650	2.15647	-2.79421
C	-2.36104	-2.90226	-1.50753
H	-3.12819	-2.17877	-1.20194
H	-2.74491	-3.91633	-1.33361
C	-2.06707	-2.71782	-2.99509
H	-1.27148	-3.41788	-3.28747
H	-2.96982	-2.97824	-3.55775
C	2.36304	-2.90038	1.50397
H	2.75111	-3.91225	1.32659
C	2.06940	-2.72177	2.99232
H	1.27643	-3.42562	3.28282
H	2.97335	-2.98082	3.55369
H	3.12671	-2.17253	1.20004

102
Complex 3 Energy: -2042295.7231883

Ti	0.90291	1.77652	0.00142
O	1.32749	2.03850	-1.90549
O	0.42915	3.88616	-0.42118
O	1.56459	0.08653	-0.00226
N	1.13013	3.27020	-2.42154
C	0.64430	4.20938	-1.61556
C	0.40126	5.57611	-2.13544
C	0.17941	5.83718	-3.49348
H	0.13944	5.02358	-4.20917
C	-0.03761	7.14007	-3.93004
H	-0.21532	7.33254	-4.98194
C	-0.04576	8.19174	-3.01530
H	-0.21923	9.20603	-3.35669
C	0.15494	7.93431	-1.65989
H	0.13767	8.74858	-0.94442
C	0.37209	6.63343	-1.21964
H	0.51730	6.41212	-0.16995
H	1.45897	3.41281	-3.36456
Ti	-1.98219	-0.11312	-0.01852
O	-2.40166	0.14798	-1.92758
O	-3.57799	-1.56017	-0.47097
O	-0.84937	1.30470	-0.00053
N	-3.37880	-0.61833	-2.45718
C	-3.96274	-1.51282	-1.66574
C	-5.03561	-2.38510	-2.19978
C	-5.16137	-2.67703	-3.56387
H	-4.43708	-2.29691	-4.27567
C	-6.19201	-3.49634	-4.01273
H	-6.27818	-3.72269	-5.06935
C	-7.09909	-4.03999	-3.10462
H	-7.89938	-4.68161	-3.45576
C	-6.96601	-3.76849	-1.74366
H	-7.66287	-4.19911	-1.03360
C	-5.93737	-2.94977	-1.29116
H	-5.81029	-2.73695	-0.23738
H	-3.66253	-0.38641	-3.39709
Ti	1.09544	-1.66659	0.00438
O	1.12986	-2.18166	-1.89780
O	3.16182	-2.31769	-0.39029
O	-0.69998	-1.39813	-0.01752
N	2.29756	-2.64228	-2.39491
C	3.34514	-2.68475	-1.57730
C	4.65403	-3.17265	-2.07339
C	5.00200	-3.15698	-3.43002
H	4.32322	-2.74174	-4.16665
C	6.24264	-3.63378	-3.84055

H	6.50620	-3.61216	-4.89184
C	7.15083	-4.11982	-2.90146
H	8.11890	-4.48718	-3.22286
C	6.81676	-4.11896	-1.54800
H	7.52519	-4.48545	-0.81378
C	5.57747	-3.64386	-1.13385
H	5.30431	-3.62380	-0.08656
H	2.26393	-3.01211	-3.33286
O	-2.40462	-0.41384	1.88319
O	-3.72790	1.16325	0.40427
N	-3.45986	0.25324	2.39743
C	-4.11999	1.08237	1.59458
C	-5.27980	1.84696	2.11195
C	-5.44535	2.13802	3.47193
H	-4.69280	1.83848	4.19284
C	-6.55583	2.85569	3.90434
H	-6.67276	3.08288	4.95784
C	-7.50464	3.29790	2.98396
H	-8.36725	3.86066	3.32250
C	-7.33398	3.02748	1.62695
H	-8.06404	3.37984	0.90717
C	-6.22550	2.31039	1.19090
H	-6.06900	2.10108	0.14038
H	-3.73068	-0.00205	3.33508
O	0.85447	2.26846	1.90991
O	2.87608	2.65416	0.43117
N	1.95675	2.85036	2.42825
C	3.00184	3.02372	1.62490
C	4.23788	3.65448	2.14594
C	4.57610	3.64016	3.50503
H	3.95009	3.11894	4.22071
C	5.74369	4.25682	3.94275
H	6.00122	4.23564	4.99554
C	6.58887	4.88322	3.02833
H	7.50027	5.36012	3.37085
C	6.26684	4.88201	1.67187
H	6.92790	5.35799	0.95656
C	5.10072	4.26678	1.23046
H	4.83960	4.24507	0.18008
H	1.86992	3.20428	3.36897
O	1.52581	-1.85627	1.91870
O	0.87009	-3.81255	0.44620
N	1.47836	-3.09871	2.44446
C	1.11656	-4.09704	1.64445
C	1.04145	-5.47904	2.17526
C	0.85266	-5.75462	3.53550

H	0.71244	-4.94626	4.24456
C	0.79812	-7.07076	3.98258
H	0.64509	-7.27534	5.03608
C	0.92074	-8.12261	3.07621
H	0.87438	-9.14783	3.42579
C	1.08855	-7.85321	1.71865
H	1.17266	-8.66913	1.00982
C	1.14368	-6.53905	1.26790
H	1.26191	-6.30977	0.21655
H	1.81838	-3.19289	3.38957

80

Complex 4 Energy: -1460214.1100913

Ti	-1.37428	0.00032	0.00072
O	0.00022	0.81041	0.91095
O	-1.79615	1.20117	-1.50429
O	-2.96095	1.28306	0.69062
O	-2.96161	-1.28230	-0.69009
O	-1.79594	-1.20176	1.50451
N	-2.83318	2.06667	-1.37549
N	-2.83298	-2.06722	1.37549
C	-2.96450	2.97454	-2.50009
H	-1.97435	3.38210	-2.71151
H	-3.65301	3.77975	-2.25601
H	-3.31577	2.42935	-3.37941
C	-3.42647	2.06753	-0.18263
C	-4.58331	2.94452	0.13347
C	-5.66242	3.12186	-0.73999
H	-5.67495	2.61469	-1.69730
C	-6.74333	3.91642	-0.36620
H	-7.57942	4.03995	-1.04513
C	-6.75634	4.53865	0.87994
H	-7.59726	5.15935	1.16811
C	-5.69246	4.34872	1.76158
H	-5.70445	4.82107	2.73724
C	-4.61726	3.54628	1.39758
H	-3.79650	3.37024	2.08169
C	-2.96454	-2.97528	2.49990
H	-1.97415	-3.38173	2.71231
H	-3.65184	-3.78128	2.25497
H	-3.31739	-2.43069	3.37898
C	-3.42673	-2.06730	0.18280
C	-4.58354	-2.94432	-0.13342
C	-4.61780	-3.54538	-1.39785
H	-3.79729	-3.36886	-2.08212
C	-5.69305	-4.34771	-1.76197

H	-5.70530	-4.81954	-2.73789
C	-6.75665	-4.53823	-0.88012
H	-7.59761	-5.15883	-1.16840
C	-6.74331	-3.91673	0.36638
H	-7.57918	-4.04073	1.04549
C	-5.66235	-3.12230	0.74030
H	-5.67460	-2.61573	1.69794
Ti	1.37428	-0.00032	-0.00072
O	-0.00022	-0.81041	-0.91094
O	1.79615	-1.20118	1.50429
O	2.96095	-1.28306	-0.69062
O	2.96160	1.28229	0.69009
O	1.79594	1.20176	-1.50450
N	2.83318	-2.06667	1.37549
N	2.83298	2.06722	-1.37548
C	2.96450	-2.97454	2.50009
H	1.97434	-3.38210	2.71151
H	3.65301	-3.77976	2.25602
H	3.31577	-2.42936	3.37941
C	3.42647	-2.06753	0.18264
C	4.58331	-2.94452	-0.13347
C	5.66244	-3.12184	0.73998
H	5.67497	-2.61466	1.69728
C	6.74334	-3.91641	0.36617
H	7.57944	-4.03992	1.04510
C	6.75634	-4.53864	-0.87996
H	7.59726	-5.15934	-1.16814
C	5.69245	-4.34872	-1.76159
H	5.70443	-4.82108	-2.73725
C	4.61725	-3.54628	-1.39758
H	3.79649	-3.37025	-2.08168
C	2.96454	2.97528	-2.49990
H	1.97415	3.38173	-2.71230
H	3.65185	3.78128	-2.25497
H	3.31740	2.43069	-3.37897
C	3.42673	2.06730	-0.18279
C	4.58354	2.94432	0.13342
C	4.61781	3.54537	1.39786
H	3.79730	3.36885	2.08213
C	5.69305	4.34771	1.76197
H	5.70531	4.81953	2.73789
C	6.75665	4.53823	0.88011
H	7.59761	5.15883	1.16839
C	6.74331	3.91674	-0.36638
H	7.57917	4.04074	-1.04550
C	5.66234	3.12230	-0.74030

H 5.67458 2.61574 -1.69794

34
Dimer of free NH-PHA Energy: -597708.9884212
O -1.45131 1.08540 1.06910
C -2.05109 0.82832 0.02390
N -1.74068 1.38673 -1.17169
C -3.17130 -0.16637 -0.00833
C -3.89234 -0.36736 1.17310
C -3.49881 -0.90969 -1.14861
C -4.94605 -1.27354 1.20497
H -3.60795 0.19370 2.05432
C -4.55027 -1.82167 -1.11130
H -2.91185 -0.80970 -2.05440
C -5.27931 -2.00018 0.06233
H -5.50555 -1.41729 2.12223
H -4.79113 -2.40136 -1.99502
O -0.85967 2.45036 -1.23702
H -6.09767 -2.71074 0.08947
H -2.40499 1.37778 -1.93094
H 0.04141 2.04004 -1.19680
O 1.45243 1.08714 -1.06903
C 2.05149 0.82888 -0.02371
N 1.74080 1.38630 1.17223
C 3.17135 -0.16628 0.00821
C 3.89297 -0.36641 -1.17301
C 3.49795 -0.91083 1.14794
C 4.94632 -1.27299 -1.20520
H 3.60929 0.19562 -2.05385
C 4.54906 -1.82322 1.11031
H 2.91057 -0.81146 2.05352
C 5.27866 -2.00088 -0.06310
H 5.50627 -1.41606 -2.12230
H 4.78922 -2.40386 1.99359
O 0.85973 2.44980 1.23849
H 6.09673 -2.71177 -0.09049
H 2.40470 1.37627 1.93180
H -0.04130 2.03936 1.19775

40
Dimer of free NMe-PHA Energy: -647051.5995310
O -1.34939 -0.98660 -1.20643
C -1.99342 -0.77063 -0.17404
N -1.82890 -1.49090 0.96612
C -3.04947 0.29519 -0.17628
C -2.77752 1.48997 -0.85003

C	-4.31920	0.09200	0.37463
C	-3.74664	2.48362	-0.93511
H	-1.80544	1.62187	-1.30867
C	-5.29421	1.08086	0.27243
H	-4.55156	-0.84865	0.86011
C	-5.00666	2.28162	-0.37311
H	-3.52322	3.41242	-1.44763
H	-6.27994	0.91016	0.69008
O	-0.99573	-2.59930	0.89279
H	-5.76498	3.05289	-0.44755
H	-0.07650	-2.23056	0.87716
O	1.26018	-1.13301	0.95368
C	1.98337	-0.79624	0.00901
N	1.86774	-1.34115	-1.23001
C	2.98235	0.30630	0.20339
C	3.72062	0.31618	1.39139
C	3.11987	1.36699	-0.69839
C	4.61432	1.34896	1.65299
H	3.57718	-0.48705	2.10353
C	4.00158	2.40979	-0.42494
H	2.52067	1.38992	-1.60125
C	4.75731	2.39778	0.74521
H	5.19291	1.34119	2.56969
H	4.09276	3.23428	-1.12295
O	0.93714	-2.36517	-1.37759
H	5.44713	3.20756	0.95434
H	0.04626	-1.92569	-1.33470
C	2.88225	-1.41671	-2.26997
H	2.45647	-1.11170	-3.22837
H	3.72783	-0.78150	-2.02114
H	3.21831	-2.45414	-2.34953
C	-2.05285	-1.05184	2.33703
H	-2.65437	-0.14667	2.35153
H	-2.55912	-1.84210	2.89481
H	-1.08423	-0.84849	2.80284

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monodentate binding for NH-PHA Energy: -2341416.7913079

O	8.73780	3.74880	5.95740
O	3.62850	5.62290	5.88900
O	8.77270	7.50917	5.95310
O	3.64130	9.41080	5.89110
O	8.77658	11.29396	5.93350
O	5.75800	1.83471	7.23350
O	5.74411	5.62295	7.22670
O	5.75199	9.49933	7.21270

O	5.78241	13.18499	7.24728
Ti	8.92960	3.73400	7.91560
Ti	3.88200	5.66684	7.82830
Ti	9.02200	7.52716	7.98369
Ti	3.83440	9.43066	7.83710
Ti	9.01774	11.30162	7.92419
O	8.57870	1.84150	8.01870
O	3.42890	3.72710	7.87200
O	8.57109	5.62560	8.12561
O	3.46970	7.52920	7.86940
O	8.59020	9.41611	8.02540
O	3.45680	11.31440	7.89290
O	8.58390	13.19280	7.92610
O	7.11982	3.72710	8.89388
O	2.08840	5.62880	8.90190
O	7.11053	7.54023	8.81376
O	2.08370	9.42110	8.92550
O	7.19893	11.29722	8.97526
Ti	6.63079	1.83020	8.99030
Ti	6.64621	5.65532	9.03862
Ti	6.60829	9.42438	8.90901
Ti	6.68241	13.19016	8.98471
O	4.84740	1.83969	9.64230
O	4.79890	5.62489	9.62370
O	4.84150	9.40838	9.61831
O	4.90940	13.19229	9.65100
O	7.91053	12.92659	10.78228
H	8.70040	12.38805	10.48317
H	8.24237	13.76725	11.11699
O	7.66661	2.07308	10.77964
H	8.46197	2.62204	10.54146
H	7.10168	2.65295	11.41135
O	5.98137	3.18649	12.30123
C	5.57676	4.36152	12.49587
N	6.06212	5.44586	11.88953
C	4.48623	4.61878	13.48734
H	5.46101	6.26013	11.81120
O	7.02846	5.38692	10.95803
C	4.31949	5.85448	14.12656
C	3.61951	3.56820	13.80709
H	5.01091	6.66598	13.93427
C	3.28498	6.04040	15.03867
C	2.58645	3.75619	14.71835
H	3.77440	2.60631	13.33570
C	2.41277	4.99487	15.33371
H	3.16815	7.00134	15.52661

H	1.91652	2.93575	14.95107
O	7.99089	9.30914	10.74504
H	8.57114	10.08487	10.71444
H	8.62965	8.57362	10.59858
H	1.60792	5.14198	16.04528
H	2.27894	5.59552	9.84221
H	2.28983	9.41283	9.86307
H	4.39067	5.60969	5.30546
H	2.74193	5.61457	5.52087
H	4.42123	9.40508	5.33139
H	2.76658	9.40676	5.49556
H	9.51844	3.75302	5.39866
H	7.86359	3.75180	5.56074
H	9.53940	7.50411	5.37539
H	7.88902	7.50589	5.57800
H	9.54424	11.29143	5.35703
H	7.89353	11.29225	5.55695
H	4.12934	3.07077	7.88679
H	2.51014	3.44882	7.87827
H	4.17768	11.94810	7.91167
H	2.54732	11.62157	7.90200
H	6.28899	1.83677	6.43372
H	4.79988	1.83483	7.17354
H	4.75255	13.19410	10.59810
H	4.85767	1.85369	10.60214
H	6.29983	13.18250	6.43868
H	4.82340	13.18522	7.20351
O	7.08403	-0.06727	9.32881
O	7.19892	15.08179	9.26092
H	8.00322	-0.33991	9.37744
H	6.38460	-0.71461	9.44430
H	8.15617	15.15376	9.27140
O	10.87960	11.23468	7.25397
H	11.29174	12.09446	7.36586
O	10.90015	7.47061	7.35940
H	10.92402	7.57514	6.40541
O	10.76679	3.80508	7.18071
H	11.15860	2.92924	7.21209
O	10.02444	11.38463	9.62729
H	10.79546	11.94574	9.51651
O	9.93189	3.65910	9.62153
H	10.73812	3.15291	9.49756
O	9.98217	7.58662	9.71429
H	10.92597	7.66041	9.55478

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blank used monodentate binding for NH-PHA Energy: -2042795.3948909

O	8.73780	3.74880	5.95740
O	3.62850	5.62290	5.88900
O	8.77270	7.50920	5.95310
O	3.64130	9.41080	5.89110
O	8.77660	11.29380	5.93350
O	5.75800	1.83476	7.23349
O	5.74410	5.62300	7.22670
O	5.75200	9.49930	7.21270
O	5.78260	13.18533	7.24720
Ti	8.92960	3.73400	7.91560
Ti	3.88200	5.66680	7.82830
Ti	9.02200	7.52710	7.98370
Ti	3.83440	9.43070	7.83710
Ti	9.01769	11.30200	7.92418
O	8.57870	1.84150	8.01870
O	3.42890	3.72710	7.87200
O	8.57110	5.62560	8.12560
O	3.46970	7.52920	7.86940
O	8.59020	9.41610	8.02540
O	3.45680	11.31440	7.89290
O	8.58387	13.19280	7.92604
O	7.11980	3.72710	8.89388
O	2.08840	5.62880	8.90190
O	7.11050	7.54020	8.81380
O	2.08370	9.42110	8.92550
O	7.19912	11.29723	8.97508
Ti	6.63080	1.83019	8.99031
Ti	6.64620	5.65530	9.03861
Ti	6.60820	9.42429	8.90921
Ti	6.68209	13.19024	8.98492
O	4.84740	1.83970	9.64230
O	4.79890	5.62490	9.62370
O	4.84150	9.40840	9.61830
O	4.90941	13.19186	9.65103
O	7.88013	12.91527	10.78424
H	8.66498	12.35904	10.51586
H	8.21454	13.74311	11.14801
O	7.97990	2.04200	10.71310
H	8.76348	2.61343	10.37638
H	7.71513	2.43879	11.55221
O	7.87469	9.23863	10.80657
H	8.66920	9.78492	10.67051
H	8.23788	8.33851	10.87058
H	2.27894	5.59552	9.84221
H	2.28983	9.41283	9.86307

H	4.39067	5.60969	5.30546
H	2.74193	5.61457	5.52087
H	4.42123	9.40508	5.33139
H	2.76658	9.40676	5.49556
H	9.51844	3.75302	5.39866
H	7.86359	3.75180	5.56074
H	9.53940	7.50411	5.37539
H	7.88902	7.50589	5.57800
H	9.54424	11.29143	5.35703
H	7.89353	11.29225	5.55695
H	4.12934	3.07077	7.88679
H	2.51014	3.44882	7.87827
H	4.17768	11.94810	7.91167
H	2.54732	11.62157	7.90200
H	6.28900	1.83674	6.43372
H	4.79988	1.83481	7.17354
H	4.75255	13.19439	10.59810
H	4.85767	1.85369	10.60214
H	6.29983	13.18257	6.43869
H	4.82340	13.18497	7.20350
O	7.08403	-0.06727	9.32881
O	7.19896	15.08176	9.26093
H	8.00322	-0.33991	9.37745
H	6.38460	-0.71461	9.44429
H	8.15617	15.15383	9.27131
O	10.87960	11.23468	7.25397
H	11.29174	12.09446	7.36586
O	10.90015	7.47062	7.35940
H	10.92402	7.57514	6.40541
O	10.76679	3.80508	7.18071
H	11.15860	2.92924	7.21209
O	10.02453	11.38445	9.62711
H	10.79546	11.94578	9.51672
O	9.93189	3.65910	9.62153
H	10.73812	3.15291	9.49756
O	9.98221	7.58642	9.71429
H	10.92595	7.66048	9.55473

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monodentate binding for NMe-PHA Energy: -2366090.8303455

O	8.73780	3.74880	5.95740
O	3.62850	5.62290	5.88900
O	8.77270	7.50920	5.95310
O	3.64130	9.41080	5.89110
O	8.77660	11.29380	5.93350

O	5.75800	1.83468	7.23350
O	5.74410	5.62300	7.22670
O	5.75200	9.49930	7.21270
O	5.78246	13.18525	7.24727
Ti	8.92960	3.73400	7.91560
Ti	3.88200	5.66680	7.82830
Ti	9.02200	7.52710	7.98370
Ti	3.83440	9.43070	7.83710
Ti	9.01770	11.30200	7.92420
O	8.57870	1.84150	8.01870
O	3.42890	3.72710	7.87200
O	8.57110	5.62560	8.12560
O	3.46970	7.52920	7.86940
O	8.59020	9.41610	8.02540
O	3.45680	11.31440	7.89290
O	8.58389	13.19280	7.92607
O	7.11980	3.72710	8.89391
O	2.08840	5.62880	8.90190
O	7.11050	7.54020	8.81380
O	2.08370	9.42110	8.92550
O	7.19904	11.29721	8.97516
Ti	6.63080	1.83020	8.99030
Ti	6.64620	5.65530	9.03860
Ti	6.60820	9.42430	8.90913
Ti	6.68231	13.19032	8.98478
O	4.84740	1.83970	9.64230
O	4.79890	5.62490	9.62370
O	4.84150	9.40840	9.61830
O	4.90940	13.19190	9.65101
O	7.91527	12.92472	10.78106
H	8.70528	12.38753	10.47808
H	8.24670	13.76481	11.11769
O	7.64885	2.08583	10.78221
H	8.45312	2.61996	10.54400
H	7.05266	2.71428	11.35152
O	5.86398	3.27290	12.06431
C	5.51270	4.45418	12.35334
N	6.13430	5.54678	11.91992
C	4.31028	4.61493	13.23223
O	7.07102	5.43612	10.94993
C	4.22362	3.86897	14.41171
C	3.22428	5.40054	12.83124
H	5.05595	3.23712	14.69853
C	3.08126	3.93982	15.20312
C	2.07510	5.45476	13.61674
H	3.28691	5.94903	11.89849

C	2.00442	4.73267	14.80668
H	3.02806	3.37298	16.12633
H	1.23466	6.05911	13.29416
O	8.01012	9.29974	10.74661
H	8.55342	10.10176	10.74684
H	8.68137	8.59888	10.56010
H	1.11142	4.78220	15.42030
H	2.27894	5.59552	9.84221
H	2.28983	9.41283	9.86307
H	4.39067	5.60969	5.30546
H	2.74193	5.61457	5.52087
H	4.42123	9.40508	5.33139
H	2.76658	9.40676	5.49556
H	9.51844	3.75302	5.39866
H	7.86359	3.75180	5.56074
H	9.53940	7.50411	5.37539
H	7.88902	7.50589	5.57800
H	9.54424	11.29143	5.35703
H	7.89353	11.29225	5.55695
H	4.12934	3.07077	7.88679
H	2.51014	3.44882	7.87827
H	4.17768	11.94810	7.91167
H	2.54732	11.62157	7.90200
H	6.28899	1.83675	6.43372
H	4.79988	1.83486	7.17353
H	4.75255	13.19435	10.59810
H	4.85767	1.85369	10.60214
H	6.29983	13.18259	6.43869
H	4.82340	13.18495	7.20350
O	7.08403	-0.06727	9.32880
O	7.19894	15.08178	9.26088
H	8.00322	-0.33991	9.37745
H	6.38460	-0.71461	9.44429
H	8.15617	15.15382	9.27138
O	10.87960	11.23468	7.25397
H	11.29174	12.09446	7.36586
O	10.90015	7.47062	7.35940
H	10.92402	7.57514	6.40541
O	10.76679	3.80508	7.18071
H	11.15860	2.92924	7.21209
O	10.02453	11.38445	9.62711
H	10.79546	11.94578	9.51672
O	9.93189	3.65910	9.62153
H	10.73812	3.15291	9.49756
O	9.98220	7.58643	9.71428
H	10.92596	7.66047	9.55474

C	5.87945	6.93381	12.31183
H	5.35987	6.96686	13.26662
H	6.84921	7.42260	12.39976
H	5.29701	7.43582	11.53651

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bridging bidentate binding for NH-PHA Energy: -2341385.6281711

O	8.74700	3.82420	5.93530
O	3.64600	5.62520	5.88730
O	8.78900	7.51520	5.95530
O	3.64900	9.41420	5.89430
O	8.78400	11.29220	5.94330
O	5.80998	1.84324	7.24831
O	5.75599	5.53916	7.21831
O	5.75598	9.50625	7.23832
O	5.80100	13.19820	7.25430
Ti	8.96200	3.74920	7.85031
Ti	3.87800	5.67921	7.82730
Ti	9.04299	7.53720	7.99428
Ti	3.87500	9.44217	7.84430
Ti	9.03201	11.29220	7.95932
O	8.59201	1.85120	7.92731
O	3.42600	3.71620	7.86930
O	8.61100	5.62019	8.13330
O	3.48400	7.52420	7.86130
O	8.61600	9.42121	8.08431
O	3.46700	11.32420	7.89130
O	8.58300	13.19820	7.92630
O	7.21300	-0.04780	8.96031
O	7.20200	3.74120	8.96634
O	2.09500	5.61920	8.93130
O	7.09102	7.52020	8.59431
O	2.09300	9.42520	8.92430
O	7.19601	11.29820	8.97733
Ti	6.71602	1.84917	8.99626
Ti	6.64799	5.66429	8.95226
Ti	6.65800	9.39110	9.03724
Ti	6.70000	13.18321	8.99729
O	4.93000	1.84216	9.64730
O	4.83300	5.63119	9.59030
O	4.81200	9.41122	9.60930
O	7.98723	12.99665	10.73350
H	8.67796	12.30419	10.51121
H	8.48787	13.81532	10.85665
O	8.02127	2.02942	10.68895
H	8.37641	1.42155	11.34424

H	8.76441	2.66061	10.39996
O	7.36949	6.02449	10.83813
C	7.96917	6.81499	11.61664
N	7.90738	8.14063	11.63160
C	8.84266	6.24514	12.69109
H	8.58347	8.61517	12.21724
O	7.25699	8.97076	10.82314
C	8.68454	6.60788	14.03171
C	9.82214	5.31197	12.33075
H	7.90956	7.31323	14.31085
C	9.50214	6.04457	15.01120
C	10.63926	4.76216	13.31367
H	9.95210	5.04890	11.28696
C	10.48180	5.12253	14.65348
H	9.36946	6.32540	16.05024
H	11.41596	4.05947	13.02959
H	11.12409	4.69043	15.41363
H	9.51960	3.84650	5.36600
H	9.55460	7.50900	5.37620
H	9.55050	11.29220	5.36530
H	7.86720	3.83930	5.55120
H	7.90460	7.51120	5.58170
H	7.90020	11.29220	5.56840
H	4.41450	5.60920	5.31220
H	2.76350	5.61470	5.50950
H	4.41960	9.40600	5.32180
H	2.76780	9.40870	5.51320
H	2.28850	9.41040	9.86400
H	2.30000	5.56830	9.86770
H	6.31980	13.20520	6.44660
H	4.84200	13.19859	7.20880
H	6.32720	1.84039	6.43950
H	4.85090	1.84310	7.20470
H	8.13880	-0.30140	8.95540
H	6.53030	-0.72270	8.94750
H	4.93930	1.83193	10.60720
H	4.17780	11.96920	7.90740
H	2.55280	11.61710	7.89860
H	4.12850	3.06210	7.88330
H	2.50810	3.43500	7.87530
O	10.89810	11.18360	7.30660
H	11.30340	12.05290	7.34850
O	10.94070	7.53060	7.42960
H	10.99100	7.43230	6.47600
O	10.76420	3.83150	7.03460
H	11.16080	2.95730	7.04470

O 10.04930 3.61010 9.49910
H 10.83070 3.08060 9.32400
O 9.92890 7.57060 9.76470
H 10.87550 7.67910 9.64730
O 10.02600 11.41590 9.66720
H 10.74090 12.05020 9.57670
O 4.84250 13.19991 9.68279
H 4.61360 14.08800 9.96661
O 7.25740 15.07000 9.14910
H 8.21610 15.12110 9.15320
O 10.11255 14.67608 9.35381
H 10.54879 15.37931 8.86510
H 9.65015 14.09905 8.67074

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blank used for bridging bidentate binding for NH-PHA Energy: -2042772.7226098
O 8.74700 3.82420 5.93530
O 3.64600 5.62520 5.88730
O 8.78900 7.51520 5.95530
O 3.64900 9.41420 5.89430
O 8.78400 11.29220 5.94330
O 5.81001 1.84319 7.24829
O 5.75600 5.53920 7.21830
O 5.75600 9.50620 7.23830
O 5.80101 13.19823 7.25429
Ti 8.96200 3.74920 7.85030
Ti 3.87800 5.67920 7.82730
Ti 9.04300 7.53720 7.99430
Ti 3.87500 9.44220 7.84430
Ti 9.03199 11.29220 7.95929
O 8.59200 1.85120 7.92729
O 3.42600 3.71620 7.86930
O 8.61100 5.62020 8.13330
O 3.48400 7.52420 7.86130
O 8.61600 9.42120 8.08430
O 3.46700 11.32420 7.89130
O 8.58300 13.19820 7.92631
O 7.21300 -0.04780 8.96030
O 7.20200 3.74120 8.96631
O 2.09500 5.61920 8.93130
O 7.09100 7.52020 8.59430
O 2.09300 9.42520 8.92430
O 7.19600 11.29820 8.97730
Ti 6.71600 1.84921 8.99630
Ti 6.64800 5.66420 8.95230
Ti 6.65800 9.39120 9.03729

Ti	6.69999	13.18321	8.99730
O	4.93000	1.84221	9.64730
O	4.83300	5.63120	9.59030
O	4.81200	9.41120	9.60930
O	7.97503	12.97943	10.72415
H	8.70724	12.32859	10.50452
H	8.43101	13.81229	10.91416
O	8.02888	2.04179	10.67539
H	8.37256	1.40522	11.31172
H	8.79775	2.64829	10.38117
H	9.51960	3.84650	5.36600
H	9.55460	7.50900	5.37620
H	9.55050	11.29220	5.36530
H	7.86720	3.83930	5.55120
H	7.90460	7.51120	5.58170
H	7.90020	11.29220	5.56840
H	4.41450	5.60920	5.31220
H	2.76350	5.61470	5.50950
H	4.41960	9.40600	5.32180
H	2.76780	9.40870	5.51320
H	2.28850	9.41040	9.86400
H	2.30000	5.56830	9.86770
H	6.31980	13.20517	6.44660
H	4.84200	13.19857	7.20880
H	6.32720	1.84040	6.43950
H	4.85090	1.84310	7.20470
H	8.13880	-0.30140	8.95540
H	6.53030	-0.72270	8.94750
H	4.93930	1.83190	10.60720
H	4.17780	11.96920	7.90740
H	2.55280	11.61710	7.89860
H	4.12850	3.06210	7.88330
H	2.50810	3.43500	7.87530
O	10.89810	11.18360	7.30660
H	11.30340	12.05290	7.34850
O	10.94070	7.53060	7.42960
H	10.99100	7.43230	6.47600
O	10.76420	3.83150	7.03460
H	11.16080	2.95730	7.04470
O	10.04930	3.61010	9.49910
H	10.83070	3.08060	9.32400
O	9.92890	7.57060	9.76470
H	10.87550	7.67910	9.64730
O	10.02600	11.41590	9.66720
H	10.74090	12.05020	9.57670
O	4.84250	13.19992	9.68281

H 4.61360 14.08800 9.96660
O 7.25739 15.07000 9.14911
H 8.21610 15.12110 9.15321
O 10.07210 14.68206 9.43040
H 10.60160 15.37939 9.03353
H 9.68787 14.13918 8.68998

101
bridging bidentate binding for NMe-PHA Energy: -2366062.9098262
O 8.74700 3.82420 5.93530
O 3.64600 5.62520 5.88730
O 8.78900 7.51520 5.95530
O 3.64900 9.41420 5.89430
O 8.78400 11.29220 5.94330
O 5.81003 1.84313 7.24829
O 5.75602 5.53912 7.21830
O 5.75593 9.50641 7.23835
O 5.80100 13.19822 7.25430
Ti 8.96201 3.74920 7.85032
Ti 3.87800 5.67914 7.82730
Ti 9.04295 7.53720 7.99419
Ti 3.87500 9.44219 7.84429
Ti 9.03206 11.29220 7.95942
O 8.59198 1.85120 7.92727
O 3.42600 3.71620 7.86930
O 8.61100 5.62015 8.13329
O 3.48400 7.52420 7.86130
O 8.61603 9.42127 8.08436
O 3.46700 11.32420 7.89130
O 8.58297 13.19819 7.92625
O 7.21300 -0.04780 8.96028
O 7.20204 3.74120 8.96642
O 2.09500 5.61920 8.93130
O 7.09102 7.52019 8.59432
O 2.09300 9.42520 8.92430
O 7.19609 11.29819 8.97748
Ti 6.71596 1.84926 8.99628
Ti 6.64800 5.66468 8.95238
Ti 6.65793 9.39067 9.03689
Ti 6.69995 13.18318 8.99729
O 4.93000 1.84225 9.64730
O 4.83300 5.63119 9.59029
O 4.81201 9.41121 9.60935
O 7.98828 13.00169 10.73480
H 8.68146 12.31443 10.50814
H 8.48455 13.82346 10.85585

O	8.08292	1.99594	10.69562
H	7.78469	2.60554	11.38760
H	8.86582	2.51287	10.29058
O	7.30984	6.07911	10.84875
C	7.96656	6.82996	11.63307
N	7.97598	8.15795	11.63255
C	8.74530	6.12062	12.70189
O	7.23201	8.91264	10.81494
C	9.76382	5.24053	12.31991
C	8.39338	6.23677	14.04957
H	10.02455	5.14654	11.27190
C	10.43427	4.50201	13.29276
C	9.06191	5.48647	15.01553
H	7.59363	6.90971	14.33859
C	10.08675	4.62067	14.63919
H	11.23780	3.83604	12.99616
H	8.78210	5.58006	16.05922
H	10.61412	4.04369	15.39147
H	9.51960	3.84650	5.36600
H	9.55460	7.50900	5.37620
H	9.55050	11.29220	5.36530
H	7.86720	3.83930	5.55120
H	7.90460	7.51120	5.58170
H	7.90020	11.29220	5.56840
H	4.41450	5.60920	5.31220
H	2.76350	5.61470	5.50950
H	4.41960	9.40600	5.32180
H	2.76780	9.40870	5.51320
H	2.28850	9.41040	9.86400
H	2.30000	5.56830	9.86770
H	6.31980	13.20519	6.44660
H	4.84200	13.19861	7.20880
H	6.32720	1.84041	6.43950
H	4.85090	1.84309	7.20470
H	8.13880	-0.30140	8.95539
H	6.53030	-0.72270	8.94752
H	4.93930	1.83186	10.60720
H	4.17780	11.96920	7.90740
H	2.55280	11.61710	7.89860
H	4.12850	3.06210	7.88330
H	2.50810	3.43500	7.87530
O	10.89810	11.18360	7.30660
H	11.30340	12.05290	7.34850
O	10.94070	7.53060	7.42960
H	10.99100	7.43230	6.47600
O	10.76420	3.83150	7.03460

H 11.16080 2.95730 7.04470
O 10.04930 3.61010 9.49910
H 10.83070 3.08060 9.32400
O 9.92890 7.57060 9.76470
H 10.87550 7.67910 9.64730
O 10.02600 11.41590 9.66720
H 10.74090 12.05020 9.57670
O 4.84251 13.19989 9.68281
H 4.61360 14.08800 9.96659
O 7.25743 15.06999 9.14908
H 8.21610 15.12110 9.15319
O 10.11577 14.66798 9.35922
H 10.55350 15.37435 8.87636
H 9.65197 14.09734 8.67202
C 8.95331 8.99242 12.33813
H 9.60673 8.38572 12.95700
H 9.53338 9.50735 11.57061
H 8.41005 9.71780 12.94654

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chelate binding for NH-PHA at an oxygen vacancy Energy: -2341407.1221086
O 8.78900 3.74600 5.93700
O 3.59813 5.62264 5.84599
O 8.78200 7.52100 5.95700
O 3.64400 9.40700 5.90300
O 8.78100 11.29000 5.93300
O 5.78800 1.83195 7.25100
O 5.60599 5.61011 7.43201
O 5.75200 9.42500 7.25200
O 5.77400 13.21400 7.24300
Ti 9.05099 3.66200 7.93698
Ti 3.71975 5.62745 7.67404
Ti 9.04500 7.59900 8.00200
Ti 3.88801 9.42500 7.84401
Ti 9.00700 11.30800 7.93800
O 8.59200 1.83100 7.90800
O 3.47004 3.72399 7.90997
O 8.58200 5.62002 8.03600
O 3.47297 7.51400 7.90199
O 8.60500 9.42400 8.06899
O 3.46800 11.31400 7.89200
O 8.58500 13.19900 7.91200
O 7.20900 -0.05000 8.94699
O 7.20401 3.71100 8.91801
O 2.11600 5.61894 8.95001
O 7.13105 7.52500 8.80912

O	2.08000	9.42600	8.91500
O	7.14000	11.32400	8.85998
Ti	6.68800	1.83102	8.98500
Ti	6.85909	5.64279	8.87892
Ti	6.65597	9.42700	9.18797
Ti	6.67300	13.18499	8.98701
O	4.91400	1.84003	9.65800
O	4.99690	5.77147	9.70608
O	4.80400	9.41200	9.65500
O	4.90500	13.19799	9.65200
O	7.98387	13.11334	10.70044
H	8.70417	12.45710	10.46983
H	8.46478	13.95824	10.73036
O	7.99791	2.00954	10.71947
H	8.33008	1.36654	11.35253
H	8.76802	2.62184	10.46391
O	7.10896	5.76900	10.94978
C	6.12761	6.25021	11.59283
N	4.95117	6.27517	10.96184
C	6.26328	6.74206	12.97445
H	4.24875	6.99531	11.10639
C	5.15596	6.90304	13.81838
C	7.54619	7.05371	13.44128
H	4.16383	6.63049	13.47785
C	5.33132	7.39178	15.10776
C	7.71396	7.53766	14.73348
H	8.39028	6.92147	12.77677
C	6.60926	7.71132	15.56610
H	4.47264	7.51708	15.75702
H	8.70711	7.78775	15.08796
O	8.18343	9.37654	10.75068
H	8.76108	10.16296	10.66989
H	6.74270	8.09320	16.57205
H	2.42910	5.61330	9.85750
H	2.26600	9.42690	9.85680
H	4.39560	5.62188	5.31170
H	2.73650	5.62207	5.42240
H	4.40900	9.40160	5.32310
H	2.75920	9.40350	5.53050
H	6.30480	1.83252	6.44200
H	4.82900	1.83201	7.20800
H	6.29310	13.22740	6.43560
H	4.81510	13.21481	7.19720
H	8.13830	-0.29070	8.94210
H	6.53590	-0.73430	8.93320
H	4.93590	1.85278	10.61770

H 9.55340 11.28490 5.36290
H 7.90110 11.28660 5.54920
H 9.54540 7.49880 5.37540
H 7.89620 7.50690 5.58720
H 9.55110 3.77050 5.35370
H 7.90240 3.76140 5.56930
H 4.17540 11.96270 7.90850
H 4.23240 3.14500 7.98181
O 10.04210 3.56150 9.64810
H 10.88870 3.13260 9.50340
O 9.97910 7.59350 9.74780
H 10.92270 7.70010 9.60670
O 9.95070 11.41200 9.67550
H 10.74660 11.93960 9.57690
O 10.88660 11.22480 7.32100
H 11.20930 12.11370 7.15590
O 10.93360 7.69870 7.41590
H 11.02490 7.28110 6.55640
O 10.92690 3.66090 7.30350
H 11.19840 2.76120 7.10730
H 4.92420 13.21681 10.61160
O 7.23200 15.08020 8.85979
H 8.19060 15.13150 8.85631
H 8.83855 8.64854 10.55133
O 10.13760 14.56501 9.49174
H 10.55941 15.32921 9.08976
H 9.69646 14.05596 8.75183

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blank used for chelate binding for NH-PHA at an oxygen vacancy Energy: -2042750.1824572
O 8.78900 3.74600 5.93700
O 3.59800 5.62300 5.84600
O 8.78200 7.52100 5.95700
O 3.64400 9.40700 5.90300
O 8.78100 11.29000 5.93300
O 5.78800 1.83200 7.25100
O 5.60600 5.61000 7.43200
O 5.75200 9.42500 7.25200
O 5.77406 13.21405 7.24297
Ti 9.05100 3.66200 7.93700
Ti 3.72000 5.62700 7.67400
Ti 9.04500 7.59900 8.00198
Ti 3.88800 9.42503 7.84400
Ti 9.00700 11.30800 7.93800
O 8.59200 1.83100 7.90800
O 3.47000 3.72400 7.91000

O	8.58200	5.62000	8.03600
O	3.47300	7.51400	7.90200
O	8.60500	9.42392	8.06900
O	3.46800	11.31400	7.89200
O	8.58498	13.19898	7.91197
O	7.20900	-0.05000	8.94700
O	7.20400	3.71100	8.91801
O	2.11600	5.61900	8.95000
O	7.13107	7.52503	8.80895
O	2.08000	9.42600	8.91500
O	7.13993	11.32404	8.86004
Ti	6.68800	1.83100	8.98500
Ti	6.85902	5.64300	8.87902
Ti	6.65603	9.42690	9.18804
Ti	6.67293	13.18492	8.98704
O	4.91400	1.84000	9.65800
O	4.80399	9.41209	9.65498
O	4.90500	13.19796	9.65201
O	7.75390	13.03149	10.78750
H	8.61420	12.59507	10.57077
H	7.88597	13.90227	11.24556
O	7.98257	2.00991	10.69874
H	8.25039	1.38277	11.37929
H	8.78429	2.58745	10.46150
O	8.16280	9.39049	10.73742
H	8.70363	10.20821	10.68298
H	2.42910	5.61330	9.85750
H	2.26600	9.42690	9.85680
H	4.39560	5.62180	5.31170
H	2.73650	5.62210	5.42240
H	4.40900	9.40160	5.32310
H	2.75920	9.40350	5.53050
H	6.30480	1.83250	6.44200
H	4.82900	1.83200	7.20800
H	6.29310	13.22741	6.43560
H	4.81510	13.21483	7.19720
H	8.13830	-0.29070	8.94210
H	6.53590	-0.73430	8.93320
H	4.93590	1.85280	10.61770
H	9.55340	11.28490	5.36290
H	7.90110	11.28660	5.54920
H	9.54540	7.49880	5.37540
H	7.89620	7.50690	5.58720
H	9.55110	3.77050	5.35370
H	7.90240	3.76140	5.56930
H	4.17540	11.96270	7.90850

H	4.23240	3.14500	7.98180
O	10.04210	3.56150	9.64810
H	10.88870	3.13260	9.50340
O	9.97910	7.59350	9.74780
H	10.92270	7.70010	9.60670
O	9.95070	11.41200	9.67550
H	10.74660	11.93960	9.57690
O	10.88660	11.22480	7.32100
H	11.20930	12.11370	7.15590
O	10.93360	7.69870	7.41590
H	11.02490	7.28110	6.55640
O	10.92690	3.66090	7.30350
H	11.19840	2.76120	7.10730
H	4.92420	13.21683	10.61160
O	7.23198	15.08020	8.85979
H	8.19060	15.13150	8.85629
H	8.85486	8.69433	10.57034
O	7.43116	15.51609	11.52788
H	7.20632	15.70471	10.58921
H	7.92179	16.26939	11.86748

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chelate binding for NMe-PHA at an oxygen vacancy Energy: -2366086.4075144

O	8.78900	3.74600	5.93700
O	3.59800	5.62297	5.84600
O	8.78200	7.52100	5.95700
O	3.64400	9.40700	5.90300
O	8.78100	11.29000	5.93300
O	5.78801	1.83207	7.25099
O	5.60600	5.61005	7.43199
O	5.75200	9.42500	7.25200
O	5.77400	13.21402	7.24300
Ti	9.05100	3.66200	7.93699
Ti	3.72003	5.62705	7.67404
Ti	9.04500	7.59900	8.00201
Ti	3.88800	9.42500	7.84400
Ti	9.00700	11.30800	7.93800
O	8.59201	1.83102	7.90801
O	3.47000	3.72400	7.90999
O	8.58201	5.62000	8.03601
O	3.47299	7.51400	7.90199
O	8.60500	9.42400	8.06900
O	3.46800	11.31400	7.89200
O	8.58500	13.19900	7.91199
O	7.20901	-0.05000	8.94702
O	7.20404	3.71100	8.91799

O	2.11600	5.61899	8.95000
O	7.13103	7.52500	8.80900
O	2.08000	9.42600	8.91500
O	7.14001	11.32400	8.86001
Ti	6.68795	1.83096	8.98501
Ti	6.85895	5.64294	8.87894
Ti	6.65597	9.42699	9.18800
Ti	6.67300	13.18499	8.98701
O	4.91400	1.83991	9.65800
O	5.04033	5.76444	9.79268
O	4.80400	9.41201	9.65500
O	4.90500	13.19796	9.65200
O	7.98427	13.11242	10.70020
H	8.70575	12.45764	10.46802
H	8.46407	13.95792	10.73191
O	8.02356	2.00240	10.73283
H	7.69506	2.65969	11.36301
H	8.84915	2.47792	10.36937
O	7.19672	5.64973	10.91518
C	6.24107	6.06185	11.65911
N	5.05207	6.18748	11.08213
C	6.49961	6.34828	13.08619
C	5.55135	6.12561	14.09332
C	7.78168	6.79893	13.43140
H	4.57107	5.73844	13.84553
C	5.87348	6.37692	15.42354
C	8.09344	7.05550	14.76136
H	8.51487	6.94416	12.64843
C	7.14116	6.84869	15.75888
H	5.13559	6.19974	16.19756
H	9.08181	7.41794	15.01881
O	8.18306	9.37140	10.75311
H	8.75540	10.16224	10.67980
H	7.38779	7.04956	16.79538
H	2.42910	5.61330	9.85750
H	2.26600	9.42690	9.85680
H	4.39560	5.62181	5.31170
H	2.73650	5.62209	5.42240
H	4.40900	9.40160	5.32310
H	2.75920	9.40350	5.53050
H	6.30480	1.83248	6.44200
H	4.82900	1.83199	7.20800
H	6.29310	13.22740	6.43560
H	4.81510	13.21480	7.19720
H	8.13830	-0.29070	8.94208
H	6.53590	-0.73430	8.93321

H 4.93590 1.85287 10.61770
H 9.55340 11.28490 5.36290
H 7.90110 11.28660 5.54920
H 9.54540 7.49880 5.37540
H 7.89620 7.50690 5.58720
H 9.55110 3.77050 5.35370
H 7.90240 3.76140 5.56930
H 4.17540 11.96270 7.90850
H 4.23240 3.14500 7.98180
O 10.04210 3.56150 9.64810
H 10.88870 3.13260 9.50340
O 9.97910 7.59350 9.74780
H 10.92270 7.70010 9.60670
O 9.95070 11.41200 9.67550
H 10.74660 11.93960 9.57690
O 10.88660 11.22480 7.32100
H 11.20930 12.11370 7.15590
O 10.93360 7.69870 7.41590
H 11.02490 7.28110 6.55640
O 10.92690 3.66090 7.30350
H 11.19840 2.76120 7.10730
H 4.92420 13.21682 10.61160
O 7.23200 15.08020 8.85977
H 8.19060 15.13150 8.85632
H 8.84297 8.64977 10.54310
O 10.13609 14.56560 9.49355
H 10.56070 15.32916 9.09328
H 9.69711 14.05706 8.75234
C 3.86488 6.92562 11.50991
H 3.07957 6.23515 11.82980
H 4.13040 7.59457 12.32501
H 3.53674 7.50892 10.64889

98
chelate binding for NH-PHA Energy: -2341354.4571528
O 8.74718 3.83663 5.93160
O 3.66630 5.62260 5.91250
O 8.77890 7.43190 5.96370
O 3.63500 9.40960 5.89090
O 8.78140 11.29270 5.93340
O 5.78493 1.76126 7.24020
O 5.77538 5.61920 7.28531
O 5.74840 9.50620 7.20400
O 5.78931 13.19699 7.24740
Ti 8.92201 3.75846 7.83714
Ti 3.95721 5.68102 7.84939

Ti	9.01420	7.50870	7.99851
Ti	3.84890	9.42760	7.83090
Ti	9.01650	11.28380	7.92729
O	8.59790	1.84907	7.91770
O	3.46020	3.72440	7.89020
O	8.60392	5.61941	8.26543
O	3.48179	7.52340	7.87731
O	8.59290	9.40620	8.01620
O	3.46300	11.31640	7.89320
O	8.58859	13.19252	7.92119
O	7.21293	-0.05282	8.95248
O	7.11985	3.73109	8.78010
O	2.08920	5.61609	8.94920
O	7.08003	7.52320	8.73921
O	2.09560	9.42130	8.91290
O	7.19550	11.30560	8.93958
Ti	6.69907	1.85172	8.98682
Ti	6.70858	5.64708	9.35290
Ti	6.61009	9.42030	8.91975
Ti	6.69580	13.19244	8.98337
O	4.92590	1.83712	9.64770
O	4.83980	5.70310	9.67780
O	4.84450	9.41050	9.61370
O	4.91580	13.19582	9.64971
O	7.87031	12.88692	10.76836
H	8.60134	12.24688	10.52411
H	8.28375	13.70408	11.06551
O	7.85853	2.11346	10.66988
H	7.45471	2.97873	11.05284
H	8.73716	2.48203	10.32091
O	6.82613	6.84352	11.19132
C	6.30094	6.28938	12.19243
N	6.34287	4.95943	12.22356
C	5.63198	7.05023	13.26239
H	5.63954	4.42600	12.71866
O	6.83212	4.38116	11.08776
C	5.70465	6.65990	14.60514
C	4.88847	8.17821	12.88735
H	6.30943	5.80549	14.88910
C	5.03306	7.39689	15.57482
C	4.21576	8.90210	13.86675
H	4.81834	8.46434	11.84164
C	4.28775	8.51642	15.20468
H	5.10017	7.10653	16.61729
H	3.63331	9.76812	13.57585
O	7.79678	9.28666	10.76330

H 8.73115 9.15318 10.49881
H 7.52968 8.41386 11.12080
H 3.76607 9.09102 15.96239
H 1.25050 9.42395 8.45749
H 1.25340 5.64392 8.47775
H 4.40877 9.40433 5.32271
H 2.75602 9.40602 5.50492
H 4.41721 5.60457 5.31467
H 2.77287 5.61201 5.56140
H 9.55086 11.29526 5.35935
H 7.89953 11.29439 5.55406
H 9.54969 7.41032 5.39184
H 7.89791 7.41751 5.58258
H 9.53130 3.85928 5.37819
H 7.87548 3.85307 5.52982
O 7.24187 15.07536 9.21673
H 8.17360 15.30489 9.24525
H 4.17480 13.19278 9.03936
H 6.30408 13.19851 6.43709
H 4.83016 13.19670 7.20674
H 4.18154 11.95268 7.91419
H 2.55239 11.62020 7.90322
H 4.14786 3.05467 7.90416
H 2.53625 3.46386 7.89563
H 4.18572 1.85069 9.03653
H 6.29933 1.71762 6.43089
H 4.82574 1.75726 7.20017
H 8.14071 -0.29966 8.94779
H 6.53533 -0.73266 8.93989
O 10.88591 11.20255 7.27992
O 10.88890 7.42043 7.36754
O 10.72053 3.95945 7.03391
O 9.97151 3.53018 9.50057
H 10.81541 3.07322 9.47676
O 9.95805 7.65309 9.73306
H 10.91174 7.76110 9.75305
O 9.99940 11.35049 9.64481
H 10.77444 11.91009 9.73290
H 11.25773 10.36613 6.99052
H 11.07586 7.29277 6.43461
H 11.04098 4.82976 6.78595

82
blank used for chelate binding for NH-PHA Energy: -2042724.6268517
O 8.74719 3.83661 5.93160
O 3.66630 5.62260 5.91250

O	8.77890	7.43190	5.96370
O	3.63500	9.40960	5.89090
O	8.78140	11.29270	5.93340
O	5.78479	1.76042	7.24035
O	5.77540	5.61920	7.28530
O	5.74840	9.50620	7.20400
O	5.78909	13.19664	7.24751
Ti	8.92199	3.75850	7.83719
Ti	3.95720	5.68100	7.84940
Ti	9.01420	7.50870	7.99850
Ti	3.84890	9.42759	7.83089
Ti	9.01650	11.28380	7.92729
O	8.59791	1.84912	7.91771
O	3.46020	3.72440	7.89020
O	8.60391	5.61940	8.26541
O	3.48180	7.52340	7.87730
O	8.59290	9.40619	8.01620
O	3.46300	11.31640	7.89321
O	8.58865	13.19250	7.92129
O	7.21295	-0.05281	8.95237
O	7.11985	3.73110	8.78023
O	2.08920	5.61610	8.94920
O	7.07996	7.52320	8.73917
O	2.09560	9.42130	8.91290
O	7.19536	11.30556	8.93968
Ti	6.69924	1.85192	8.98662
Ti	6.70858	5.64710	9.35288
Ti	6.61013	9.42032	8.91970
Ti	6.69615	13.19282	8.98312
O	4.92590	1.83694	9.64768
O	4.83980	5.70310	9.67780
O	4.84450	9.41050	9.61370
O	4.91579	13.19558	9.64968
O	7.91324	12.88488	10.76025
H	8.72031	12.37275	10.45287
H	8.21343	13.71021	11.15800
O	8.09768	1.99600	10.56123
H	7.91291	2.20892	11.48380
H	8.91241	2.58078	10.22938
O	7.92723	9.26137	10.72149
H	8.26013	10.14561	10.93031
H	8.74496	8.74357	10.50559
H	1.25050	9.42395	8.45749
H	1.25340	5.64392	8.47775
H	4.40877	9.40433	5.32271
H	2.75602	9.40602	5.50492

H 4.41721 5.60457 5.31467
H 2.77287 5.61201 5.56140
H 9.55086 11.29526 5.35935
H 7.89953 11.29439 5.55406
H 9.54969 7.41032 5.39184
H 7.89791 7.41751 5.58258
H 9.53130 3.85928 5.37819
H 7.87548 3.85307 5.52982
O 7.24184 15.07538 9.21668
H 8.17360 15.30488 9.24536
H 4.17480 13.19296 9.03936
H 6.30408 13.19860 6.43710
H 4.83016 13.19670 7.20674
H 4.18154 11.95268 7.91419
H 2.55239 11.62020 7.90322
H 4.14786 3.05467 7.90416
H 2.53625 3.46386 7.89563
H 4.18572 1.85077 9.03653
H 6.29932 1.71754 6.43089
H 4.82574 1.75795 7.20013
H 8.14071 -0.29966 8.94787
H 6.53533 -0.73266 8.93988
O 10.88591 11.20255 7.27992
O 10.88890 7.42043 7.36754
O 10.72054 3.95945 7.03390
O 9.97150 3.53020 9.50058
H 10.81541 3.07322 9.47676
O 9.95805 7.65309 9.73306
H 10.91174 7.76110 9.75305
O 9.99940 11.35049 9.64481
H 10.77444 11.91009 9.73290
H 11.25773 10.36613 6.99052
H 11.07586 7.29277 6.43461
H 11.04098 4.82976 6.78595

101
chelate binding for NMe-PHA Energy: -2366029.3489381
O 8.74718 3.83663 5.93160
O 3.66630 5.62260 5.91250
O 8.77890 7.43190 5.96370
O 3.63500 9.40960 5.89090
O 8.78140 11.29270 5.93340
O 5.78493 1.76126 7.24020
O 5.77538 5.61920 7.28531
O 5.74840 9.50620 7.20400
O 5.78931 13.19699 7.24740

Ti	8.92201	3.75846	7.83714
Ti	3.95721	5.68102	7.84939
Ti	9.01420	7.50870	7.99851
Ti	3.84890	9.42760	7.83090
Ti	9.01650	11.28380	7.92729
O	8.59790	1.84907	7.91770
O	3.46020	3.72440	7.89020
O	8.60392	5.61941	8.26543
O	3.48179	7.52340	7.87731
O	8.59290	9.40620	8.01620
O	3.46300	11.31640	7.89320
O	8.58859	13.19252	7.92119
O	7.21293	-0.05282	8.95248
O	7.11985	3.73109	8.78010
O	2.08920	5.61609	8.94920
O	7.08003	7.52320	8.73921
O	2.09560	9.42130	8.91290
O	7.19550	11.30560	8.93958
Ti	6.69907	1.85172	8.98682
Ti	6.70858	5.64708	9.35290
Ti	6.61009	9.42030	8.91975
Ti	6.69580	13.19244	8.98337
O	4.92590	1.83712	9.64770
O	4.83980	5.70310	9.67780
O	4.84450	9.41050	9.61370
O	4.91580	13.19582	9.64971
O	7.87079	12.88713	10.76818
H	8.60183	12.24715	10.52364
H	8.28435	13.70432	11.06501
O	7.85943	2.11579	10.67164
H	7.45066	2.97632	11.05399
H	8.73728	2.48719	10.32193
O	6.85832	6.81279	11.17153
C	6.30967	6.28249	12.18322
N	6.27174	4.95573	12.20413
C	5.72041	7.12874	13.24305
O	6.81093	4.38462	11.08428
C	5.95542	6.90436	14.60466
C	4.93409	8.21327	12.82896
H	6.59666	6.08750	14.91682
C	5.39605	7.75529	15.55279
C	4.37011	9.04978	13.78768
H	4.76065	8.39226	11.77140
C	4.59893	8.82430	15.14418
H	5.59072	7.59136	16.60681
H	3.75735	9.88284	13.46455

O	7.79022	9.27512	10.76381
H	8.72656	9.15440	10.50132
H	7.53179	8.39185	11.10584
H	4.16427	9.48697	15.88474
C	5.35195	4.09396	12.92762
H	5.90318	3.26238	13.37340
H	4.85337	4.66449	13.70743
H	4.61706	3.71348	12.21519
H	1.25050	9.42395	8.45749
H	1.25340	5.64392	8.47775
H	4.40877	9.40433	5.32271
H	2.75602	9.40602	5.50492
H	4.41721	5.60457	5.31467
H	2.77287	5.61201	5.56140
H	9.55086	11.29526	5.35935
H	7.89953	11.29439	5.55406
H	9.54969	7.41032	5.39184
H	7.89791	7.41751	5.58258
H	9.53130	3.85928	5.37819
H	7.87548	3.85307	5.52982
O	7.24187	15.07536	9.21673
H	8.17360	15.30489	9.24525
H	4.17480	13.19278	9.03936
H	6.30408	13.19851	6.43709
H	4.83016	13.19670	7.20674
H	4.18154	11.95268	7.91419
H	2.55239	11.62020	7.90322
H	4.14786	3.05467	7.90416
H	2.53625	3.46386	7.89563
H	4.18572	1.85069	9.03653
H	6.29933	1.71762	6.43089
H	4.82574	1.75726	7.20017
H	8.14071	-0.29966	8.94779
H	6.53533	-0.73266	8.93989
O	10.88591	11.20255	7.27992
O	10.88890	7.42043	7.36754
O	10.72053	3.95945	7.03391
O	9.97151	3.53018	9.50057
H	10.81541	3.07322	9.47676
O	9.95805	7.65309	9.73306
H	10.91174	7.76110	9.75305
O	9.99940	11.35049	9.64481
H	10.77444	11.91009	9.73290
H	11.25773	10.36613	6.99052
H	11.07586	7.29277	6.43461
H	11.04098	4.82976	6.78595