Supplementary Information

Sterically (un)encumbered *mer*-tridentate N-heterocyclic carbene complexes of titanium(IV) for the copolymerization of cyclohexene oxide with CO_2

Julie Hessevik, Ralte Lalrempuia, Hajar Nsiri, Karl W. Törnroos, Vidar R. Jensen

and Erwan Le Roux*

TABLE OF CONTENTS

Synthesis of onium salts

[PPN]O*i*Pr

In a glovebox, a solution of LiO*i*Pr (5.7 mg, 87 μmol, 1 equiv) in CH_2Cl_2 (2 mL) was added at -30 °C to a stirring solution of [PPN]Cl (50 mg, 87 μmol) in CH_2Cl_2 (2 mL). The colorless solution was stirred overnight, and then centrifuged, filtered and all volatile removed under vacuum (92% yield). Anal. Calcd. for [PPN]O*i*Pr-1.2CH_2Cl_2, $C_{40.2}H_{39.4}Cl_{2.4}NOP_2$: C, 69.02; H, 5.68; Cl, 12.16; N, 2.00; O, 2.29; P, 8.85%. Found: C, 69.00; H, 5.22; N, 2.19%. ^{1}H NMR (500.13 MHz, 25 °C, chloroform-*d*) *δ* 7.70-7.64 (m, 6H, Ar-*H*), 7.50-7.40 (m, 24H, Ar-*H*), 3.99 (bsept, 1H, OC*H*(CH_3)$_2$), 1.16 (bd, 6H, OCH(C*H*$_3$)$_2$) ppm. ^{13}C NMR (125.75 MHz, 25 °C, chloroform-*d*) *δ* 134.0 (Ar), 132.2 (Ar), 132.1 (Ar), 132.1 (Ar), 132.1 (Ar), 132.0 (Ar), 132.0 (Ar), 129.8 (Ar), 129.7 (Ar), 129.7 (Ar), 129.6 (Ar), 129.6 (Ar), 127.4 (Ar), 126.6 (Ar), 77.7 (O*C*H(CH_3)$_2$), 25.4 (OCH(*C*H$_3$)$_2$) ppm.

[PPN]OAr'

In a glovebox, a solution of LiOAr' (9.1 mg, 139 μmol, 1 equiv) in CH_2Cl_2 (2 mL) was added at -30 °C to a stirring solution of [PPN]Cl (80 mg, 139 μmol) in CH_2Cl_2 (2 mL). The colorless solution was stirred overnight, and then centrifuged, filtered and all volatile removed under vacuum (85% yield). Anal. Calcd. for [PPN]OAr'-1.2CH_2Cl_2, $C_{52.2}H_{55.4}Cl_{2.4}NOP_2$: C, 72.92; H, 6.49; Cl, 9.90; N, 1.63; O, 1.86; P, 7.20%. Found: C, 72.72; H, 6.13; N, 1.81%. ^{1}H NMR (500.13 MHz, 25 °C, chloroform-*d*) *δ* 7.71-7.63 (m, 6H, Ar-*H*), 7.52-7.39 (m, 24H, Ar-*H*), 6.97 (s, 2H, Ar-*H*), 2.26 (s, 3H, Ar'-C*H*$_3$), 1.42 (s, 18H, Ar'-C(C*H*$_3$)$_3$) ppm. ^{13}C NMR (125.75 MHz, 25 °C, chloroform-*d*) *δ* 135.7 (Ar'), 134.0 (Ar), 132.2 (Ar), 132.2 (Ar), 132.1 (Ar), 132.1 (Ar),, 132.1 (Ar), 129.8 (Ar), 129.8 (Ar), 129.7 (Ar), 129.7 (Ar), 129.6 (Ar), 128.3 (Ar'), 127.5 (Ar'), 127.4 (Ar), 126.6 (Ar'), 126.6 (Ar), 125.6 (Ar'), 34.3 (Ar'-*C*(CH_3)$_3$), 30.4 (Ar'-C(*C*H$_3$)$_3$), 21.3 (Ar'-*C*H$_3$) ppm.

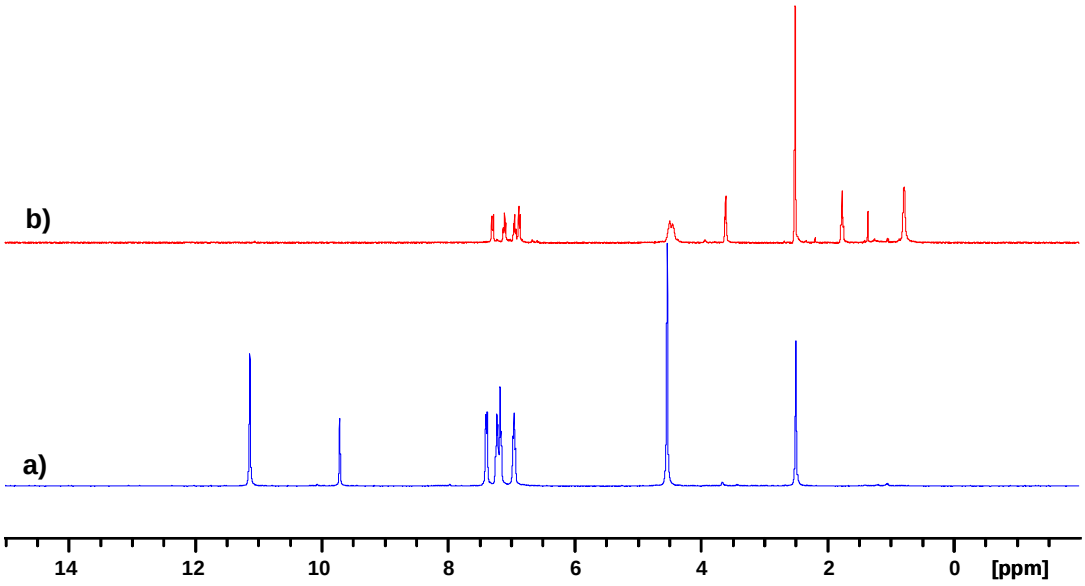

Fig. S1. a) ^{1}H NMR spectra of proligand **A** and b) complex **1-THF** in dmso-d_6.

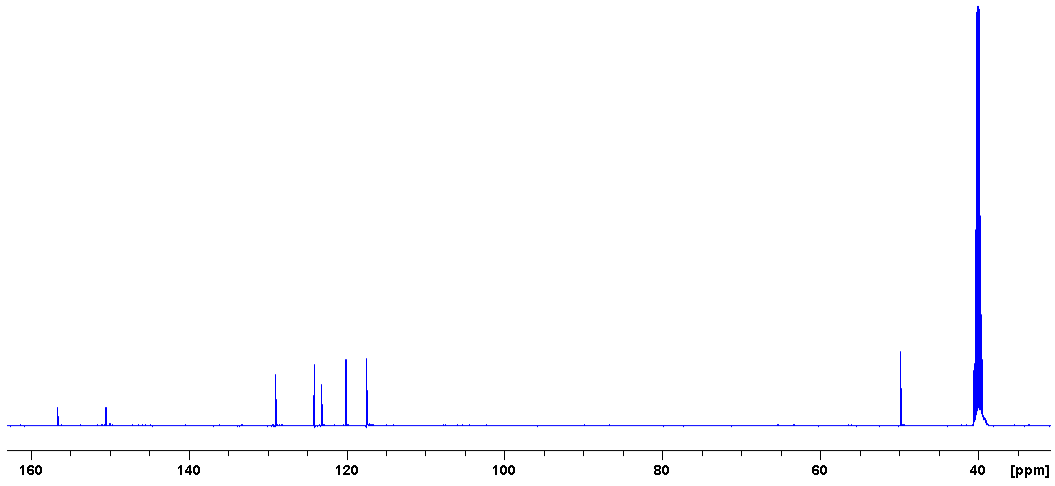

Fig. S2. ^{13}C NMR of proligand **A** in dmso-d_6.

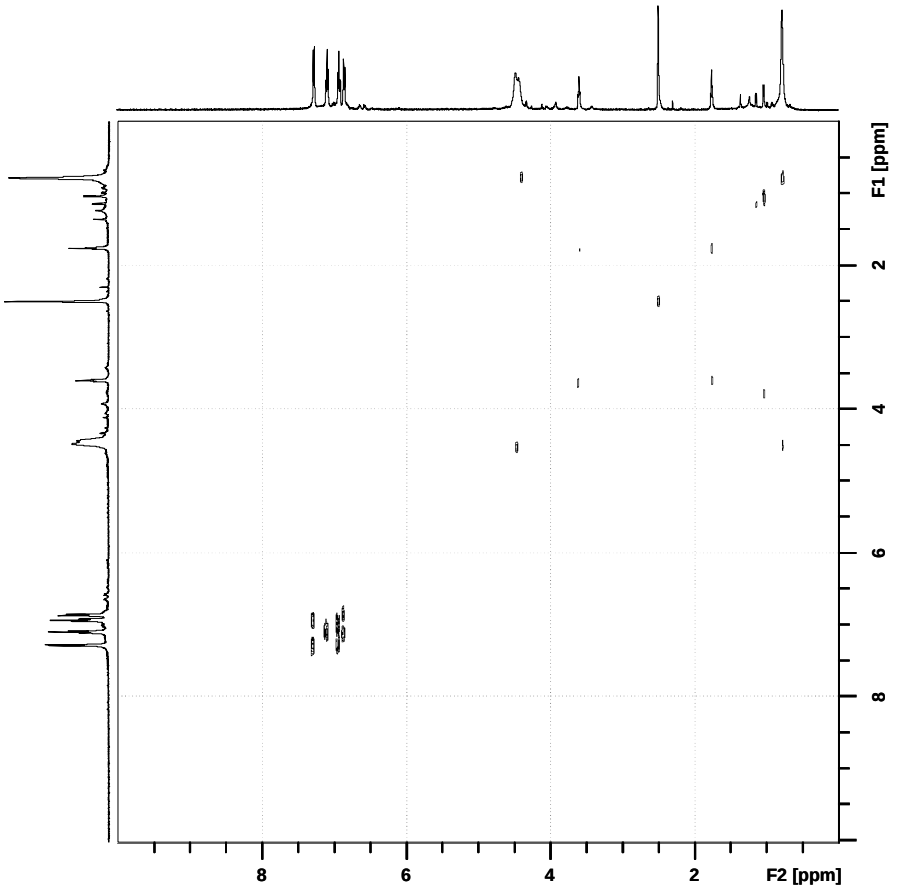

Fig. S3. 2D ^{1}H-^{1}H COSY NMR spectrum of complex **1-THF** in dmso-d_6.

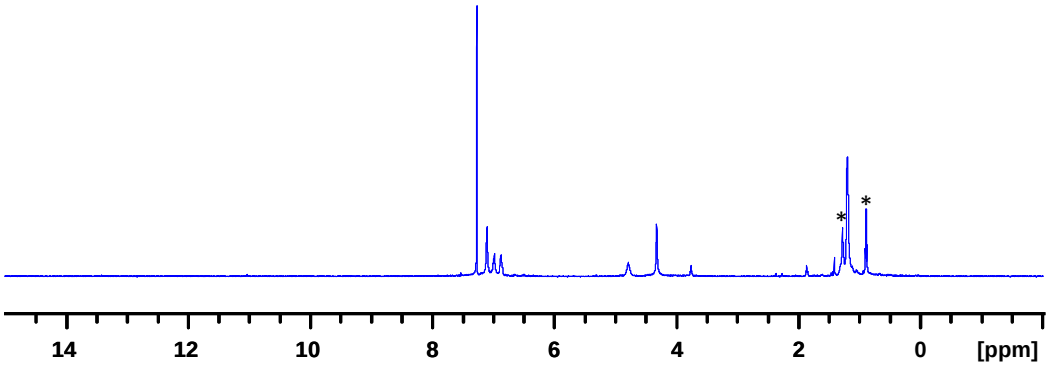

Fig. S4. ^{1}H NMR spectrum of complex **2** in chloroform-*d* (* = hexane).

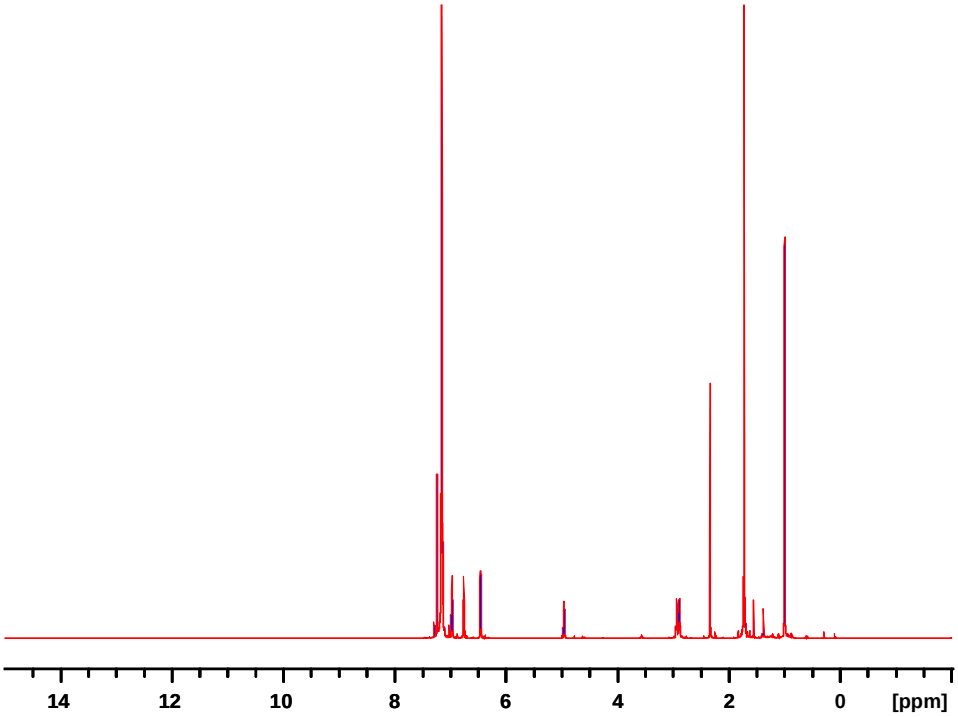

Fig. S5. ^{1}H NMR spectrum of complex **3** in benzene-d_6.

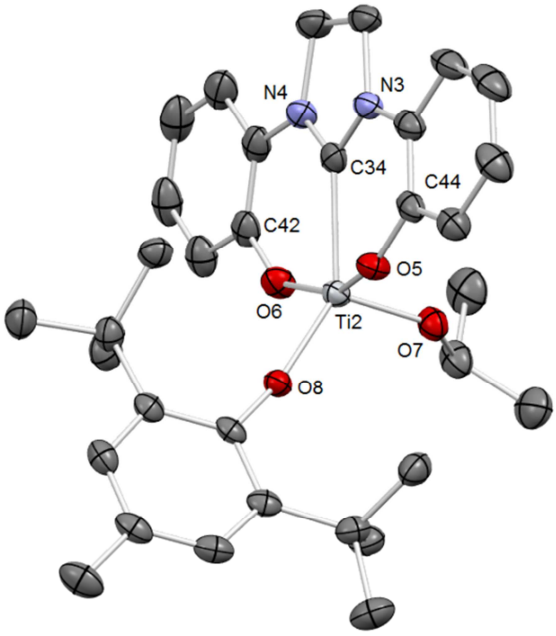

Fig. S6. Molecular structure of complex **5** (isomer B) with anisotropic displacement parameters at the 50% probability level. Hydrogen atoms and co-recrystallized hexane molecules were removed for clarity. Selected bond lengths (Å): Ti2-C34 = 2.222(3), Ti2-O5 = 1.868(2), Ti2-O6 = 1.889(2), Ti2-O7 = 1.792(2), Ti2-O8 = 1.8397(19), C34-N3 = 1.344(4), C34-N4 = 1.347(4). Selected angle (°): O5-Ti2-O6 = 157.75(9), C34-Ti2-O8 = 143.43(9).

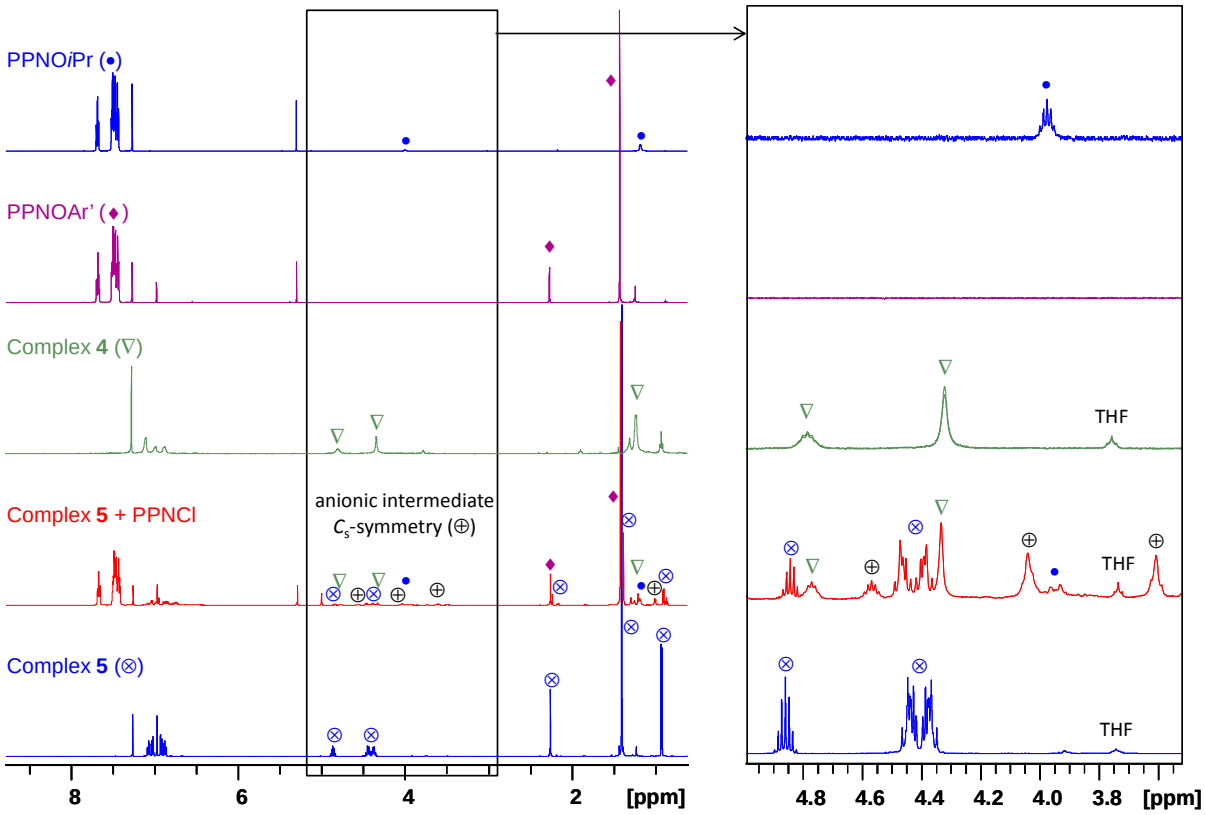

Fig. S7. ^{1}H NMR spectra of **5**, **5**/[PPN]Cl, **4**, [PPN]OAr' and [PPN]O*i*Pr complexes in chloroform-*d*.

X-Ray crystallography details and data

Table S1. Crystal data and structure refinement for **3**-**CH_3CN**.

Identification code	Compound3 (3-CH_3CN)	
Empirical formula	$C_{26}H_{27}ClFN_3O_3Ti$	
Formula weight	531.85	
Temperature	103(2) K	
Wavelength (λ)	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 17.700(10) Å	α= 90°.
	b = 7.391(4) Å	β= 111.032(8)°.
	c = 19.676(12) Å	γ = 90°.
Volume	2403(2) $Å^3$	
Z	4	
Density (calculated)	1.470 Mg/m^3	
Linear absorption coefficient (μ)	0.510 mm^{-1}	
F(000)	1104	
Crystal size	0.408 x 0.083 x 0.016 mm^3	
Crystal habit/color	Lath/Brown	
Theta range for data collection	2.116 to 18.932°.	
Index ranges	-16<=h<=16, -6<=k<=6, -17<=l<=17	
Reflections collected	13120	
Independent reflections	1905 [R(int) = 0.1282]	
Completeness to theta = 18.932°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1905 / 448 / 328	
Goodness-of-fit on F^2	1.060	
Final R indices [I>2sigma(I)]	R1 = 0.0645, wR2 = 0.1593	
R indices (all data)	R1 = 0.0879, wR2 = 0.1785	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.747 and -0.287 $e.Å^{-3}$	

Table S2. Bond lengths [Å] and angles [°] for **3**-**CH_3CN**.

Ti(1)-O(3)	1.762(5)	Ti(1)-N(3)	2.276(7)
Ti(1)-O(1)	1.835(6)	Ti(1)-Cl(1)	2.354(3)
Ti(1)-O(2)	1.850(5)	O(1)-C(5)	1.327(9)
Ti(1)-C(1)	2.175(8)	N(1)-C(1)	1.327(9)

N(1)-C(4)	1.382(9)	C(18)-H(18)	1.0000
N(1)-C(3)	1.477(9)	C(19)-H(19A)	0.9800
C(1)-N(2)	1.307(9)	C(19)-H(19B)	0.9800
O(2)-C(11)	1.328(9)	C(19)-H(19C)	0.9800
N(2)-C(10)	1.388(9)	C(20)-H(20A)	0.9800
N(2)-C(2)	1.472(9)	C(20)-H(20B)	0.9800
C(2)-C(3)	1.501(10)	C(20)-H(20C)	0.9800
C(2)-H(2A)	0.9900	C(18A)-C(20A)	1.498(8)
C(2)-H(2B)	0.9900	C(18A)-C(19A)	1.498(8)
O(3)-C(18A)	1.447(9)	C(18A)-H(18A)	1.0000
O(3)-C(18)	1.447(9)	C(19A)-H(19D)	0.9800
N(3)-C(16)	1.145(9)	C(19A)-H(19E)	0.9800
C(3)-H(3A)	0.9900	C(19A)-H(19F)	0.9800
C(3)-H(3B)	0.9900	C(20A)-H(20D)	0.9800
C(4)-C(9)	1.359(10)	C(20A)-H(20E)	0.9800
C(4)-C(5)	1.412(11)	C(20A)-H(20F)	0.9800
C(5)-C(6)	1.354(10)	C(21)-F(1)	1.198(10)
C(6)-C(7)	1.352(11)	C(21)-C(22)	1.3900
C(6)-H(6)	0.9500	C(21)-C(26)	1.3900
C(7)-C(8)	1.397(11)	C(22)-C(23)	1.3900
C(7)-H(7)	0.9500	C(22)-H(22)	0.9500
C(8)-C(9)	1.360(10)	C(23)-C(24)	1.3900
C(8)-H(8)	0.9500	C(23)-H(23)	0.9500
C(9)-H(9)	0.9500	C(24)-C(25)	1.3900
C(10)-C(15)	1.374(10)	C(24)-H(24)	0.9500
C(10)-C(11)	1.394(10)	C(25)-C(26)	1.3900
C(11)-C(12)	1.371(10)	C(25)-H(25)	0.9500
C(12)-C(13)	1.354(10)	C(26)-H(26)	0.9500
C(12)-H(12)	0.9500	C(21A)-C(22A)	1.3900
C(13)-C(14)	1.388(11)	C(21A)-C(26A)	1.3900
C(13)-H(13)	0.9500	C(21A)-H(21A)	0.9500
C(14)-C(15)	1.344(11)	C(22A)-C(23A)	1.3900
C(14)-H(14)	0.9500	C(22A)-H(22A)	0.9500
C(15)-H(15)	0.9500	C(23A)-C(24A)	1.3900
C(16)-C(17)	1.416(11)	C(23A)-H(23A)	0.9500
C(17)-H(17A)	0.9800	C(24A)-F(1A)	1.198(10)
C(17)-H(17B)	0.9800	C(24A)-C(25A)	1.3900
C(17)-H(17C)	0.9800	C(25A)-C(26A)	1.3900
C(18)-C(19)	1.498(8)	C(25A)-H(25A)	0.9500
C(18)-C(20)	1.498(8)	C(26A)-H(26A)	0.9500

O(3)-Ti(1)-O(1)	95.0(2)	O(3)-Ti(1)-C(1)	96.3(3)
O(3)-Ti(1)-O(2)	95.9(2)	O(1)-Ti(1)-C(1)	81.9(3)
O(1)-Ti(1)-O(2)	161.5(2)	O(2)-Ti(1)-C(1)	82.1(3)

O(3)-Ti(1)-N(3)	179.5(2)	C(6)-C(7)-C(8)	119.9(8)
O(1)-Ti(1)-N(3)	85.3(2)	C(6)-C(7)-H(7)	120.1
O(2)-Ti(1)-N(3)	83.9(2)	C(8)-C(7)-H(7)	120.1
C(1)-Ti(1)-N(3)	84.0(2)	C(9)-C(8)-C(7)	117.7(8)
O(3)-Ti(1)-Cl(1)	98.00(17)	C(9)-C(8)-H(8)	121.1
O(1)-Ti(1)-Cl(1)	96.82(17)	C(7)-C(8)-H(8)	121.1
O(2)-Ti(1)-Cl(1)	96.46(17)	C(4)-C(9)-C(8)	122.9(8)
C(1)-Ti(1)-Cl(1)	165.7(2)	C(4)-C(9)-H(9)	118.5
N(3)-Ti(1)-Cl(1)	81.66(16)	C(8)-C(9)-H(9)	118.5
C(5)-O(1)-Ti(1)	141.4(5)	C(15)-C(10)-N(2)	120.4(7)
C(1)-N(1)-C(4)	129.1(7)	C(15)-C(10)-C(11)	118.2(7)
C(1)-N(1)-C(3)	111.3(6)	N(2)-C(10)-C(11)	121.3(7)
C(4)-N(1)-C(3)	119.5(6)	O(2)-C(11)-C(12)	120.7(7)
N(2)-C(1)-N(1)	110.2(7)	O(2)-C(11)-C(10)	120.6(7)
N(2)-C(1)-Ti(1)	125.7(6)	C(12)-C(11)-C(10)	118.7(7)
N(1)-C(1)-Ti(1)	124.1(6)	C(13)-C(12)-C(11)	122.4(7)
C(11)-O(2)-Ti(1)	142.0(5)	C(13)-C(12)-H(12)	118.8
C(1)-N(2)-C(10)	128.1(7)	C(11)-C(12)-H(12)	118.8
C(1)-N(2)-C(2)	112.4(6)	C(12)-C(13)-C(14)	118.6(7)
C(10)-N(2)-C(2)	119.5(6)	C(12)-C(13)-H(13)	120.7
N(2)-C(2)-C(3)	102.8(6)	C(14)-C(13)-H(13)	120.7
N(2)-C(2)-H(2A)	111.2	C(15)-C(14)-C(13)	119.8(7)
C(3)-C(2)-H(2A)	111.2	C(15)-C(14)-H(14)	120.1
N(2)-C(2)-H(2B)	111.2	C(13)-C(14)-H(14)	120.1
C(3)-C(2)-H(2B)	111.2	C(14)-C(15)-C(10)	122.3(8)
H(2A)-C(2)-H(2B)	109.1	C(14)-C(15)-H(15)	118.9
C(18A)-O(3)-Ti(1)	126.3(6)	C(10)-C(15)-H(15)	118.9
C(18)-O(3)-Ti(1)	156.2(7)	N(3)-C(16)-C(17)	178.5(9)
C(16)-N(3)-Ti(1)	167.3(6)	C(16)-C(17)-H(17A)	109.5
N(1)-C(3)-C(2)	102.8(6)	C(16)-C(17)-H(17B)	109.5
N(1)-C(3)-H(3A)	111.2	H(17A)-C(17)-H(17B)	109.5
C(2)-C(3)-H(3A)	111.2	C(16)-C(17)-H(17C)	109.5
N(1)-C(3)-H(3B)	111.2	H(17A)-C(17)-H(17C)	109.5
C(2)-C(3)-H(3B)	111.2	H(17B)-C(17)-H(17C)	109.5
H(3A)-C(3)-H(3B)	109.1	O(3)-C(18)-C(19)	107.5(9)
C(9)-C(4)-N(1)	121.6(7)	O(3)-C(18)-C(20)	107.4(11)
C(9)-C(4)-C(5)	118.7(8)	C(19)-C(18)-C(20)	113.2(13)
N(1)-C(4)-C(5)	119.5(7)	O(3)-C(18)-H(18)	109.6
O(1)-C(5)-C(6)	121.1(7)	C(19)-C(18)-H(18)	109.6
O(1)-C(5)-C(4)	120.7(7)	C(20)-C(18)-H(18)	109.6
C(6)-C(5)-C(4)	118.1(8)	C(18)-C(19)-H(19A)	109.5
C(7)-C(6)-C(5)	122.6(8)	C(18)-C(19)-H(19B)	109.5
C(7)-C(6)-H(6)	118.7	H(19A)-C(19)-H(19B)	109.5
C(5)-C(6)-H(6)	118.7	C(18)-C(19)-H(19C)	109.5

H(19A)-C(19)-H(19C)	109.5	C(23)-C(22)-H(22)	120.0
H(19B)-C(19)-H(19C)	109.5	C(24)-C(23)-C(22)	120.0
C(18)-C(20)-H(20A)	109.5	C(24)-C(23)-H(23)	120.0
C(18)-C(20)-H(20B)	109.5	C(22)-C(23)-H(23)	120.0
H(20A)-C(20)-H(20B)	109.5	C(25)-C(24)-C(23)	120.0
C(18)-C(20)-H(20C)	109.5	C(25)-C(24)-H(24)	120.0
H(20A)-C(20)-H(20C)	109.5	C(23)-C(24)-H(24)	120.0
H(20B)-C(20)-H(20C)	109.5	C(24)-C(25)-C(26)	120.0
O(3)-C(18A)-C(20A)	107.6(9)	C(24)-C(25)-H(25)	120.0
O(3)-C(18A)-C(19A)	106.5(9)	C(26)-C(25)-H(25)	120.0
C(20A)-C(18A)-C(19A)	114.0(13)	C(25)-C(26)-C(21)	120.0
O(3)-C(18A)-H(18A)	109.5	C(25)-C(26)-H(26)	120.0
C(20A)-C(18A)-H(18A)	109.5	C(21)-C(26)-H(26)	120.0
C(19A)-C(18A)-H(18A)	109.5	C(22A)-C(21A)-C(26A)	120.0
C(18A)-C(19A)-H(19D)	109.5	C(22A)-C(21A)-H(21A)	120.0
C(18A)-C(19A)-H(19E)	109.5	C(26A)-C(21A)-H(21A)	120.0
H(19D)-C(19A)-H(19E)	109.5	C(23A)-C(22A)-C(21A)	120.0
C(18A)-C(19A)-H(19F)	109.5	C(23A)-C(22A)-H(22A)	120.0
H(19D)-C(19A)-H(19F)	109.5	C(21A)-C(22A)-H(22A)	120.0
H(19E)-C(19A)-H(19F)	109.5	C(22A)-C(23A)-C(24A)	120.0
C(18A)-C(20A)-H(20D)	109.5	C(22A)-C(23A)-H(23A)	120.0
C(18A)-C(20A)-H(20E)	109.5	C(24A)-C(23A)-H(23A)	120.0
H(20D)-C(20A)-H(20E)	109.5	F(1A)-C(24A)-C(23A)	121.6(7)
C(18A)-C(20A)-H(20F)	109.5	F(1A)-C(24A)-C(25A)	118.4(7)
H(20D)-C(20A)-H(20F)	109.5	C(23A)-C(24A)-C(25A)	120.0
H(20E)-C(20A)-H(20F)	109.5	C(26A)-C(25A)-C(24A)	120.0
F(1)-C(21)-C(22)	124.5(7)	C(26A)-C(25A)-H(25A)	120.0
F(1)-C(21)-C(26)	115.3(7)	C(24A)-C(25A)-H(25A)	120.0
C(22)-C(21)-C(26)	120.0	C(25A)-C(26A)-C(21A)	120.0
C(21)-C(22)-C(23)	120.0	C(25A)-C(26A)-H(26A)	120.0
C(21)-C(22)-H(22)	120.0	C(21A)-C(26A)-H(26A)	120.0

Symmetry transformations used to generate equivalent atoms:

Table S3. Torsion angles [°] for **3**-**CH_3CN**.

O(3)-Ti(1)-O(1)-C(5)	74.4(8)	C(4)-N(1)-C(1)-Ti(1)	-2.9(10)
O(2)-Ti(1)-O(1)-C(5)	-51.4(12)	C(3)-N(1)-C(1)-Ti(1)	173.4(5)
C(1)-Ti(1)-O(1)-C(5)	-21.2(8)	O(3)-Ti(1)-O(2)-C(11)	-102.0(7)
N(3)-Ti(1)-O(1)-C(5)	-105.9(8)	O(1)-Ti(1)-O(2)-C(11)	23.7(12)
Cl(1)-Ti(1)-O(1)-C(5)	173.1(8)	C(1)-Ti(1)-O(2)-C(11)	-6.4(7)
C(4)-N(1)-C(1)-N(2)	178.0(6)	N(3)-Ti(1)-O(2)-C(11)	78.4(7)
C(3)-N(1)-C(1)-N(2)	-5.7(8)	Cl(1)-Ti(1)-O(2)-C(11)	159.2(7)

N(1)-C(1)-N(2)-C(10)	-179.8(6)	C(1)-N(2)-C(10)-C(11)	-3.4(11)
Ti(1)-C(1)-N(2)-C(10)	1.1(11)	C(2)-N(2)-C(10)-C(11)	175.4(6)
N(1)-C(1)-N(2)-C(2)	1.3(8)	Ti(1)-O(2)-C(11)-C(12)	-174.3(5)
Ti(1)-C(1)-N(2)-C(2)	-177.8(5)	Ti(1)-O(2)-C(11)-C(10)	6.0(11)
C(1)-N(2)-C(2)-C(3)	3.5(8)	C(15)-C(10)-C(11)-O(2)	178.4(6)
C(10)-N(2)-C(2)-C(3)	-175.6(6)	N(2)-C(10)-C(11)-O(2)	0.6(10)
O(1)-Ti(1)-O(3)-C(18A)	15.9(6)	C(15)-C(10)-C(11)-C(12)	-1.4(10)
O(2)-Ti(1)-O(3)-C(18A)	-179.2(6)	N(2)-C(10)-C(11)-C(12)	-179.1(6)
C(1)-Ti(1)-O(3)-C(18A)	98.2(6)	O(2)-C(11)-C(12)-C(13)	-177.8(6)
Cl(1)-Ti(1)-O(3)-C(18A)	-81.8(6)	C(10)-C(11)-C(12)-C(13)	2.0(11)
O(1)-Ti(1)-O(3)-C(18)	10.6(14)	C(11)-C(12)-C(13)-C(14)	-1.9(11)
O(2)-Ti(1)-O(3)-C(18)	175.6(13)	C(12)-C(13)-C(14)-C(15)	1.2(11)
C(1)-Ti(1)-O(3)-C(18)	93.0(14)	C(13)-C(14)-C(15)-C(10)	-0.7(11)
Cl(1)-Ti(1)-O(3)-C(18)	-87.0(13)	N(2)-C(10)-C(15)-C(14)	178.6(7)
C(1)-N(1)-C(3)-C(2)	7.5(8)	C(11)-C(10)-C(15)-C(14)	0.8(11)
C(4)-N(1)-C(3)-C(2)	-175.8(6)	Ti(1)-O(3)-C(18)-C(19)	49(2)
N(2)-C(2)-C(3)-N(1)	-6.2(7)	Ti(1)-O(3)-C(18)-C(20)	-73(2)
C(1)-N(1)-C(4)-C(9)	174.4(7)	Ti(1)-O(3)-C(18A)-C(20A)	-122.3(14)
C(3)-N(1)-C(4)-C(9)	-1.5(10)	Ti(1)-O(3)-C(18A)-C(19A)	115.1(10)
C(1)-N(1)-C(4)-C(5)	-9.0(11)	F(1)-C(21)-C(22)-C(23)	175.2(9)
C(3)-N(1)-C(4)-C(5)	175.1(6)	C(26)-C(21)-C(22)-C(23)	0.0
Ti(1)-O(1)-C(5)-C(6)	-160.8(6)	C(21)-C(22)-C(23)-C(24)	0.0
Ti(1)-O(1)-C(5)-C(4)	16.0(12)	C(22)-C(23)-C(24)-C(25)	0.0
C(9)-C(4)-C(5)-O(1)	-178.2(7)	C(23)-C(24)-C(25)-C(26)	0.0
N(1)-C(4)-C(5)-O(1)	5.1(10)	C(24)-C(25)-C(26)-C(21)	0.0
C(9)-C(4)-C(5)-C(6)	-1.3(11)	F(1)-C(21)-C(26)-C(25)	-175.6(8)
N(1)-C(4)-C(5)-C(6)	-178.1(6)	C(22)-C(21)-C(26)-C(25)	0.0
O(1)-C(5)-C(6)-C(7)	178.8(7)	C(26A)-C(21A)-C(22A)-C(23A)	0.0
C(4)-C(5)-C(6)-C(7)	2.0(11)	C(21A)-C(22A)-C(23A)-C(24A)	0.0
C(5)-C(6)-C(7)-C(8)	-2.1(12)	C(22A)-C(23A)-C(24A)-F(1A)	-178.9(9)
C(6)-C(7)-C(8)-C(9)	1.6(11)	C(22A)-C(23A)-C(24A)-C(25A)	0.0
N(1)-C(4)-C(9)-C(8)	177.6(7)	F(1A)-C(24A)-C(25A)-C(26A)	178.9(8)
C(5)-C(4)-C(9)-C(8)	1.0(11)	C(23A)-C(24A)-C(25A)-C(26A)	0.0
C(7)-C(8)-C(9)-C(4)	-1.1(11)	C(24A)-C(25A)-C(26A)-C(21A)	0.0
C(1)-N(2)-C(10)-C(15)	178.9(7)	C(22A)-C(21A)-C(26A)-C(25A)	0.0
C(2)-N(2)-C(10)-C(15)	-2.3(10)		

Symmetry transformations used to generate equivalent atoms:

Table S4. Crystal data and structure refinement for **4**.

Identification code	Compound4	
Empirical formula	$C_{46}H_{60}N_4O_9Ti_2$	
Formula weight	908.78	
Temperature	103(2) K	
Wavelength (λ)	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 29.100(4) Å	α= 90°.
	b = 19.218(3) Å	β= 130.641(2)°.
	c = 20.797(3) Å	γ = 90°.
Volume	8825(2) $Å^3$	
Z	8	
Density (calculated)	1.368 Mg/m^3	
Linear absorption coefficient (μ)	0.422 mm^{-1}	
F(000)	3840	
Crystal size	0.480 x 0.340 x 0.320 mm^3	
Crystal habit/color	Prism/Yellow	
Theta range for data collection	1.845 to 26.372°.	
Index ranges	-36<=h<=36, -24<=k<=24, -25<=l<=25	
Reflections collected	55583	
Independent reflections	9018 [R(int) = 0.0630]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9018 / 36 / 615	
Goodness-of-fit on F^2	1.057	
Final R indices [I>2sigma(I)]	R1 = 0.0458, wR2 = 0.1176	
R indices (all data)	R1 = 0.0590, wR2 = 0.1269	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.691 and -0.489 $e.Å^{-3}$	

Table S5. Bond lengths [Å] and angles [°] for **4**.

Ti(1)-O(3)	1.8413(17)	Ti(2)-O(6)	1.8772(16)
Ti(1)-O(5)	1.8465(17)	Ti(2)-O(7)	1.8844(16)
Ti(1)-O(1)	1.8811(16)	Ti(2)-O(4)	1.9646(16)
Ti(1)-O(2)	2.0122(16)	Ti(2)-C(25)	2.210(2)
Ti(1)-O(4)	2.1126(16)	Ti(2)-O(2)	2.2332(16)
Ti(1)-C(1)	2.231(2)	O(1)-C(11)	1.336(3)
Ti(1)-Ti(2)	3.3332(6)	O(2)-C(9)	1.358(3)
Ti(2)-O(8)	1.8145(16)	O(3)-C(16)	1.411(3)

O(4)-C(19)	1.442(3)	C(16)-C(17)	1.516(4)
O(5)-C(22)	1.404(4)	C(16)-H(16)	1.0000
O(5)-C(22A)	1.404(4)	C(17)-H(17A)	0.9800
O(6)-C(35)	1.331(3)	C(17)-H(17B)	0.9800
O(7)-C(33)	1.327(3)	C(17)-H(17C)	0.9800
O(8)-C(40)	1.431(3)	C(18)-H(18A)	0.9800
N(1)-C(1)	1.336(3)	C(18)-H(18B)	0.9800
N(1)-C(10)	1.410(3)	C(18)-H(18C)	0.9800
N(1)-C(2)	1.478(3)	C(19)-C(21)	1.512(4)
N(2)-C(1)	1.340(3)	C(19)-C(20)	1.515(4)
N(2)-C(4)	1.408(3)	C(19)-H(19)	1.0000
N(2)-C(3)	1.485(3)	C(20)-H(20A)	0.9800
N(3)-C(25)	1.345(3)	C(20)-H(20B)	0.9800
N(3)-C(34)	1.415(3)	C(20)-H(20C)	0.9800
N(3)-C(26)	1.474(3)	C(21)-H(21A)	0.9800
N(4)-C(25)	1.348(3)	C(21)-H(21B)	0.9800
N(4)-C(28)	1.412(3)	C(21)-H(21C)	0.9800
N(4)-C(27)	1.479(3)	C(22)-C(23)	1.524(4)
C(2)-C(3)	1.515(3)	C(22)-C(24)	1.524(4)
C(2)-H(2A)	0.9900	C(22)-H(22)	1.0000
C(2)-H(2B)	0.9900	C(23)-H(23A)	0.9800
C(3)-H(3A)	0.9900	C(23)-H(23B)	0.9800
C(3)-H(3B)	0.9900	C(23)-H(23C)	0.9800
C(4)-C(5)	1.396(3)	C(24)-H(24A)	0.9800
C(4)-C(9)	1.406(3)	C(24)-H(24B)	0.9800
C(5)-C(6)	1.381(4)	C(24)-H(24C)	0.9800
C(5)-H(5)	0.9500	C(22A)-C(24A)	1.524(4)
C(6)-C(7)	1.380(4)	C(22A)-C(23A)	1.524(4)
C(6)-H(6)	0.9500	C(22A)-H(22A)	1.0000
C(7)-C(8)	1.392(4)	C(23A)-H(23D)	0.9800
C(7)-H(7)	0.9500	C(23A)-H(23E)	0.9800
C(8)-C(9)	1.390(3)	C(23A)-H(23F)	0.9800
C(8)-H(8)	0.9500	C(24A)-H(24D)	0.9800
C(10)-C(15)	1.391(3)	C(24A)-H(24E)	0.9800
C(10)-C(11)	1.415(3)	C(24A)-H(24F)	0.9800
C(11)-C(12)	1.397(3)	C(26)-C(27)	1.511(4)
C(12)-C(13)	1.381(4)	C(26)-H(26A)	0.9900
C(12)-H(12)	0.9500	C(26)-H(26B)	0.9900
C(13)-C(14)	1.382(4)	C(27)-H(27A)	0.9900
C(13)-H(13)	0.9500	C(27)-H(27B)	0.9900
C(14)-C(15)	1.380(4)	C(28)-C(29)	1.398(3)
C(14)-H(14)	0.9500	C(28)-C(33)	1.409(3)
C(15)-H(15)	0.9500	C(29)-C(30)	1.381(4)
C(16)-C(18)	1.511(4)	C(29)-H(29)	0.9500

C(30)-C(31)	1.381(4)	O(1S)-C(4S)	1.424(7)
C(30)-H(30)	0.9500	C(1S)-C(2S)	1.533(5)
C(31)-C(32)	1.380(4)	C(1S)-H(1S1)	0.9900
C(31)-H(31)	0.9500	C(1S)-H(1S2)	0.9900
C(32)-C(33)	1.398(3)	C(2S)-C(3S)	1.524(5)
C(32)-H(32)	0.9500	C(2S)-H(2S1)	0.9900
C(34)-C(39)	1.396(3)	C(2S)-H(2S2)	0.9900
C(34)-C(35)	1.402(4)	C(3S)-C(4S)	1.525(5)
C(35)-C(36)	1.401(4)	C(3S)-H(3S1)	0.9900
C(36)-C(37)	1.392(4)	C(3S)-H(3S2)	0.9900
C(36)-H(36)	0.9500	C(4S)-H(4S1)	0.9900
C(37)-C(38)	1.372(4)	C(4S)-H(4S2)	0.9900
C(37)-H(37)	0.9500	O(2S)-C(8S)	1.397(11)
C(38)-C(39)	1.388(4)	O(2S)-C(5S)	1.415(8)
C(38)-H(38)	0.9500	C(5S)-C(6S)	1.526(5)
C(39)-H(39)	0.9500	C(5S)-H(5S1)	0.9900
C(40)-C(42)	1.513(4)	C(5S)-H(5S2)	0.9900
C(40)-C(41)	1.515(4)	C(6S)-C(7S)	1.526(5)
C(40)-H(40)	1.0000	C(6S)-H(6S1)	0.9900
C(41)-H(41A)	0.9800	C(6S)-H(6S2)	0.9900
C(41)-H(41B)	0.9800	C(7S)-C(8S)	1.524(5)
C(41)-H(41C)	0.9800	C(7S)-H(7S1)	0.9900
C(42)-H(42A)	0.9800	C(7S)-H(7S2)	0.9900
C(42)-H(42B)	0.9800	C(8S)-H(8S1)	0.9900
C(42)-H(42C)	0.9800	C(8S)-H(8S2)	0.9900
O(1S)-C(1S)	1.397(10)		

O(3)-Ti(1)-O(5)	96.01(8)	O(1)-Ti(1)-Ti(2)	119.97(5)
O(3)-Ti(1)-O(1)	98.67(7)	O(2)-Ti(1)-Ti(2)	40.68(5)
O(5)-Ti(1)-O(1)	102.83(7)	O(4)-Ti(1)-Ti(2)	33.72(4)
O(3)-Ti(1)-O(2)	95.53(7)	C(1)-Ti(1)-Ti(2)	81.74(6)
O(5)-Ti(1)-O(2)	96.96(7)	O(8)-Ti(2)-O(6)	92.02(7)
O(1)-Ti(1)-O(2)	154.18(7)	O(8)-Ti(2)-O(7)	93.02(7)
O(3)-Ti(1)-O(4)	168.39(7)	O(6)-Ti(2)-O(7)	163.13(7)
O(5)-Ti(1)-O(4)	91.03(7)	O(8)-Ti(2)-O(4)	108.29(7)
O(1)-Ti(1)-O(4)	88.71(7)	O(6)-Ti(2)-O(4)	96.69(7)
O(2)-Ti(1)-O(4)	74.40(6)	O(7)-Ti(2)-O(4)	96.99(7)
O(3)-Ti(1)-C(1)	83.55(8)	O(8)-Ti(2)-C(25)	96.01(8)
O(5)-Ti(1)-C(1)	175.19(8)	O(6)-Ti(2)-C(25)	81.38(8)
O(1)-Ti(1)-C(1)	81.96(8)	O(7)-Ti(2)-C(25)	82.08(8)
O(2)-Ti(1)-C(1)	78.34(7)	O(4)-Ti(2)-C(25)	155.69(8)
O(4)-Ti(1)-C(1)	88.67(7)	O(8)-Ti(2)-O(2)	178.27(7)
O(3)-Ti(1)-Ti(2)	135.83(5)	O(6)-Ti(2)-O(2)	89.32(7)
O(5)-Ti(1)-Ti(2)	95.37(5)	O(7)-Ti(2)-O(2)	85.39(7)

O(4)-Ti(2)-O(2)	72.62(6)	C(2)-C(3)-H(3A)	111.4
C(25)-Ti(2)-O(2)	83.11(7)	N(2)-C(3)-H(3B)	111.4
O(8)-Ti(2)-Ti(1)	144.95(5)	C(2)-C(3)-H(3B)	111.4
O(6)-Ti(2)-Ti(1)	93.04(5)	H(3A)-C(3)-H(3B)	109.3
O(7)-Ti(2)-Ti(1)	92.05(5)	C(5)-C(4)-C(9)	119.0(2)
O(4)-Ti(2)-Ti(1)	36.66(5)	C(5)-C(4)-N(2)	120.0(2)
C(25)-Ti(2)-Ti(1)	119.05(6)	C(9)-C(4)-N(2)	121.0(2)
O(2)-Ti(2)-Ti(1)	35.97(4)	C(6)-C(5)-C(4)	120.9(2)
C(11)-O(1)-Ti(1)	138.29(15)	C(6)-C(5)-H(5)	119.5
C(9)-O(2)-Ti(1)	123.81(14)	C(4)-C(5)-H(5)	119.5
C(9)-O(2)-Ti(2)	121.97(13)	C(7)-C(6)-C(5)	120.2(2)
Ti(1)-O(2)-Ti(2)	103.34(7)	C(7)-C(6)-H(6)	119.9
C(16)-O(3)-Ti(1)	144.91(16)	C(5)-C(6)-H(6)	119.9
C(19)-O(4)-Ti(2)	127.61(14)	C(6)-C(7)-C(8)	119.5(2)
C(19)-O(4)-Ti(1)	120.47(13)	C(6)-C(7)-H(7)	120.2
Ti(2)-O(4)-Ti(1)	109.62(7)	C(8)-C(7)-H(7)	120.2
C(22)-O(5)-Ti(1)	134.8(2)	C(9)-C(8)-C(7)	121.1(2)
C(22A)-O(5)-Ti(1)	141.6(3)	C(9)-C(8)-H(8)	119.5
C(35)-O(6)-Ti(2)	142.11(16)	C(7)-C(8)-H(8)	119.5
C(33)-O(7)-Ti(2)	141.81(15)	O(2)-C(9)-C(8)	119.2(2)
C(40)-O(8)-Ti(2)	134.86(14)	O(2)-C(9)-C(4)	121.7(2)
C(1)-N(1)-C(10)	125.86(19)	C(8)-C(9)-C(4)	119.0(2)
C(1)-N(1)-C(2)	112.90(19)	C(15)-C(10)-N(1)	119.5(2)
C(10)-N(1)-C(2)	121.07(19)	C(15)-C(10)-C(11)	119.4(2)
C(1)-N(2)-C(4)	124.7(2)	N(1)-C(10)-C(11)	121.2(2)
C(1)-N(2)-C(3)	113.30(19)	O(1)-C(11)-C(12)	119.2(2)
C(4)-N(2)-C(3)	121.70(19)	O(1)-C(11)-C(10)	122.4(2)
C(25)-N(3)-C(34)	127.0(2)	C(12)-C(11)-C(10)	118.3(2)
C(25)-N(3)-C(26)	113.0(2)	C(13)-C(12)-C(11)	121.3(2)
C(34)-N(3)-C(26)	119.9(2)	C(13)-C(12)-H(12)	119.3
C(25)-N(4)-C(28)	126.8(2)	C(11)-C(12)-H(12)	119.3
C(25)-N(4)-C(27)	112.7(2)	C(12)-C(13)-C(14)	119.9(2)
C(28)-N(4)-C(27)	120.2(2)	C(12)-C(13)-H(13)	120.0
N(1)-C(1)-N(2)	108.1(2)	C(14)-C(13)-H(13)	120.0
N(1)-C(1)-Ti(1)	125.96(16)	C(15)-C(14)-C(13)	120.0(2)
N(2)-C(1)-Ti(1)	125.41(17)	C(15)-C(14)-H(14)	120.0
N(1)-C(2)-C(3)	103.16(19)	C(13)-C(14)-H(14)	120.0
N(1)-C(2)-H(2A)	111.1	C(14)-C(15)-C(10)	121.0(2)
C(3)-C(2)-H(2A)	111.1	C(14)-C(15)-H(15)	119.5
N(1)-C(2)-H(2B)	111.1	C(10)-C(15)-H(15)	119.5
C(3)-C(2)-H(2B)	111.1	O(3)-C(16)-C(18)	108.2(2)
H(2A)-C(2)-H(2B)	109.1	O(3)-C(16)-C(17)	110.6(2)
N(2)-C(3)-C(2)	101.89(18)	C(18)-C(16)-C(17)	112.7(2)
N(2)-C(3)-H(3A)	111.4	O(3)-C(16)-H(16)	108.4

C(18)-C(16)-H(16)	108.4	C(22)-C(24)-H(24A)	109.5
C(17)-C(16)-H(16)	108.4	C(22)-C(24)-H(24B)	109.5
C(16)-C(17)-H(17A)	109.5	H(24A)-C(24)-H(24B)	109.5
C(16)-C(17)-H(17B)	109.5	C(22)-C(24)-H(24C)	109.5
H(17A)-C(17)-H(17B)	109.5	H(24A)-C(24)-H(24C)	109.5
C(16)-C(17)-H(17C)	109.5	H(24B)-C(24)-H(24C)	109.5
H(17A)-C(17)-H(17C)	109.5	O(5)-C(22A)-C(24A)	112.1(5)
H(17B)-C(17)-H(17C)	109.5	O(5)-C(22A)-C(23A)	107.3(10)
C(16)-C(18)-H(18A)	109.5	C(24A)-C(22A)-C(23A)	110.9(6)
C(16)-C(18)-H(18B)	109.5	O(5)-C(22A)-H(22A)	108.8
H(18A)-C(18)-H(18B)	109.5	C(24A)-C(22A)-H(22A)	108.8
C(16)-C(18)-H(18C)	109.5	C(23A)-C(22A)-H(22A)	108.8
H(18A)-C(18)-H(18C)	109.5	C(22A)-C(23A)-H(23D)	109.5
H(18B)-C(18)-H(18C)	109.5	C(22A)-C(23A)-H(23E)	109.5
O(4)-C(19)-C(21)	109.2(2)	H(23D)-C(23A)-H(23E)	109.5
O(4)-C(19)-C(20)	110.4(2)	C(22A)-C(23A)-H(23F)	109.5
C(21)-C(19)-C(20)	113.6(3)	H(23D)-C(23A)-H(23F)	109.5
O(4)-C(19)-H(19)	107.8	H(23E)-C(23A)-H(23F)	109.5
C(21)-C(19)-H(19)	107.8	C(22A)-C(24A)-H(24D)	109.5
C(20)-C(19)-H(19)	107.8	C(22A)-C(24A)-H(24E)	109.5
C(19)-C(20)-H(20A)	109.5	H(24D)-C(24A)-H(24E)	109.5
C(19)-C(20)-H(20B)	109.5	C(22A)-C(24A)-H(24F)	109.5
H(20A)-C(20)-H(20B)	109.5	H(24D)-C(24A)-H(24F)	109.5
C(19)-C(20)-H(20C)	109.5	H(24E)-C(24A)-H(24F)	109.5
H(20A)-C(20)-H(20C)	109.5	N(3)-C(25)-N(4)	107.9(2)
H(20B)-C(20)-H(20C)	109.5	N(3)-C(25)-Ti(2)	126.07(17)
C(19)-C(21)-H(21A)	109.5	N(4)-C(25)-Ti(2)	125.86(17)
C(19)-C(21)-H(21B)	109.5	N(3)-C(26)-C(27)	103.1(2)
H(21A)-C(21)-H(21B)	109.5	N(3)-C(26)-H(26A)	111.2
C(19)-C(21)-H(21C)	109.5	C(27)-C(26)-H(26A)	111.2
H(21A)-C(21)-H(21C)	109.5	N(3)-C(26)-H(26B)	111.2
H(21B)-C(21)-H(21C)	109.5	C(27)-C(26)-H(26B)	111.2
O(5)-C(22)-C(23)	109.0(5)	H(26A)-C(26)-H(26B)	109.1
O(5)-C(22)-C(24)	109.4(3)	N(4)-C(27)-C(26)	102.9(2)
C(23)-C(22)-C(24)	110.9(6)	N(4)-C(27)-H(27A)	111.2
O(5)-C(22)-H(22)	109.2	C(26)-C(27)-H(27A)	111.2
C(23)-C(22)-H(22)	109.2	N(4)-C(27)-H(27B)	111.2
C(24)-C(22)-H(22)	109.2	C(26)-C(27)-H(27B)	111.2
C(22)-C(23)-H(23A)	109.5	H(27A)-C(27)-H(27B)	109.1
C(22)-C(23)-H(23B)	109.5	C(29)-C(28)-C(33)	118.6(2)
H(23A)-C(23)-H(23B)	109.5	C(29)-C(28)-N(4)	119.9(2)
C(22)-C(23)-H(23C)	109.5	C(33)-C(28)-N(4)	121.4(2)
H(23A)-C(23)-H(23C)	109.5	C(30)-C(29)-C(28)	121.2(3)
H(23B)-C(23)-H(23C)	109.5	C(30)-C(29)-H(29)	119.4

C(28)-C(29)-H(29)	119.4	C(40)-C(42)-H(42B)	109.5
C(29)-C(30)-C(31)	120.2(2)	H(42A)-C(42)-H(42B)	109.5
C(29)-C(30)-H(30)	119.9	C(40)-C(42)-H(42C)	109.5
C(31)-C(30)-H(30)	119.9	H(42A)-C(42)-H(42C)	109.5
C(32)-C(31)-C(30)	119.5(3)	H(42B)-C(42)-H(42C)	109.5
C(32)-C(31)-H(31)	120.2	C(1S)-O(1S)-C(4S)	107.6(5)
C(30)-C(31)-H(31)	120.2	O(1S)-C(1S)-C(2S)	105.2(5)
C(31)-C(32)-C(33)	121.4(3)	O(1S)-C(1S)-H(1S1)	110.7
C(31)-C(32)-H(32)	119.3	C(2S)-C(1S)-H(1S1)	110.7
C(33)-C(32)-H(32)	119.3	O(1S)-C(1S)-H(1S2)	110.7
O(7)-C(33)-C(32)	119.2(2)	C(2S)-C(1S)-H(1S2)	110.7
O(7)-C(33)-C(28)	121.8(2)	H(1S1)-C(1S)-H(1S2)	108.8
C(32)-C(33)-C(28)	119.0(2)	C(3S)-C(2S)-C(1S)	100.9(5)
C(39)-C(34)-C(35)	119.6(2)	C(3S)-C(2S)-H(2S1)	111.6
C(39)-C(34)-N(3)	119.9(2)	C(1S)-C(2S)-H(2S1)	111.6
C(35)-C(34)-N(3)	120.5(2)	C(3S)-C(2S)-H(2S2)	111.6
O(6)-C(35)-C(36)	118.9(2)	C(1S)-C(2S)-H(2S2)	111.6
O(6)-C(35)-C(34)	122.0(2)	H(2S1)-C(2S)-H(2S2)	109.4
C(36)-C(35)-C(34)	119.1(2)	C(2S)-C(3S)-C(4S)	104.0(5)
C(37)-C(36)-C(35)	120.2(3)	C(2S)-C(3S)-H(3S1)	111.0
C(37)-C(36)-H(36)	119.9	C(4S)-C(3S)-H(3S1)	111.0
C(35)-C(36)-H(36)	119.9	C(2S)-C(3S)-H(3S2)	111.0
C(38)-C(37)-C(36)	120.5(3)	C(4S)-C(3S)-H(3S2)	111.0
C(38)-C(37)-H(37)	119.8	H(3S1)-C(3S)-H(3S2)	109.0
C(36)-C(37)-H(37)	119.8	O(1S)-C(4S)-C(3S)	107.5(5)
C(37)-C(38)-C(39)	120.1(2)	O(1S)-C(4S)-H(4S1)	110.2
C(37)-C(38)-H(38)	119.9	C(3S)-C(4S)-H(4S1)	110.2
C(39)-C(38)-H(38)	119.9	O(1S)-C(4S)-H(4S2)	110.2
C(38)-C(39)-C(34)	120.4(3)	C(3S)-C(4S)-H(4S2)	110.2
C(38)-C(39)-H(39)	119.8	H(4S1)-C(4S)-H(4S2)	108.5
C(34)-C(39)-H(39)	119.8	C(8S)-O(2S)-C(5S)	105.4(7)
O(8)-C(40)-C(42)	108.5(2)	O(2S)-C(5S)-C(6S)	106.2(7)
O(8)-C(40)-C(41)	109.6(2)	O(2S)-C(5S)-H(5S1)	110.5
C(42)-C(40)-C(41)	112.0(2)	C(6S)-C(5S)-H(5S1)	110.5
O(8)-C(40)-H(40)	108.9	O(2S)-C(5S)-H(5S2)	110.5
C(42)-C(40)-H(40)	108.9	C(6S)-C(5S)-H(5S2)	110.5
C(41)-C(40)-H(40)	108.9	H(5S1)-C(5S)-H(5S2)	108.7
C(40)-C(41)-H(41A)	109.5	C(7S)-C(6S)-C(5S)	104.0(8)
C(40)-C(41)-H(41B)	109.5	C(7S)-C(6S)-H(6S1)	111.0
H(41A)-C(41)-H(41B)	109.5	C(5S)-C(6S)-H(6S1)	111.0
C(40)-C(41)-H(41C)	109.5	C(7S)-C(6S)-H(6S2)	111.0
H(41A)-C(41)-H(41C)	109.5	C(5S)-C(6S)-H(6S2)	111.0
H(41B)-C(41)-H(41C)	109.5	H(6S1)-C(6S)-H(6S2)	109.0
C(40)-C(42)-H(42A)	109.5	C(8S)-C(7S)-C(6S)	102.6(7)

C(8S)-C(7S)-H(7S1)	111.2	O(2S)-C(8S)-H(8S1)	110.6
C(6S)-C(7S)-H(7S1)	111.2	C(7S)-C(8S)-H(8S1)	110.6
C(8S)-C(7S)-H(7S2)	111.2	O(2S)-C(8S)-H(8S2)	110.6
C(6S)-C(7S)-H(7S2)	111.2	C(7S)-C(8S)-H(8S2)	110.6
H(7S1)-C(7S)-H(7S2)	109.2	H(8S1)-C(8S)-H(8S2)	108.7
O(2S)-C(8S)-C(7S)	105.6(8)		

Symmetry transformations used to generate equivalent atoms:

Table S6. Torsion angles [°] for **4**.

O(3)-Ti(1)-O(1)-C(11)	-104.7(2)	O(2)-Ti(2)-O(7)-C(33)	85.1(2)
O(5)-Ti(1)-O(1)-C(11)	157.0(2)	Ti(1)-Ti(2)-O(7)-C(33)	120.5(2)
O(2)-Ti(1)-O(1)-C(11)	17.9(3)	O(6)-Ti(2)-O(8)-C(40)	-20.0(2)
O(4)-Ti(1)-O(1)-C(11)	66.3(2)	O(7)-Ti(2)-O(8)-C(40)	143.9(2)
C(1)-Ti(1)-O(1)-C(11)	-22.6(2)	O(4)-Ti(2)-O(8)-C(40)	-117.7(2)
Ti(2)-Ti(1)-O(1)-C(11)	53.0(2)	C(25)-Ti(2)-O(8)-C(40)	61.6(2)
O(5)-Ti(1)-O(3)-C(16)	161.6(3)	Ti(1)-Ti(2)-O(8)-C(40)	-118.19(19)
O(1)-Ti(1)-O(3)-C(16)	57.6(3)	C(10)-N(1)-C(1)-N(2)	-178.5(2)
O(2)-Ti(1)-O(3)-C(16)	-100.7(3)	C(2)-N(1)-C(1)-N(2)	-3.1(3)
O(4)-Ti(1)-O(3)-C(16)	-71.3(5)	C(10)-N(1)-C(1)-Ti(1)	9.5(3)
C(1)-Ti(1)-O(3)-C(16)	-23.2(3)	C(2)-N(1)-C(1)-Ti(1)	-175.11(16)
Ti(2)-Ti(1)-O(3)-C(16)	-94.3(3)	C(4)-N(2)-C(1)-N(1)	-176.18(19)
O(3)-Ti(1)-O(5)-C(22)	75.2(3)	C(3)-N(2)-C(1)-N(1)	-2.5(3)
O(1)-Ti(1)-O(5)-C(22)	175.5(3)	C(4)-N(2)-C(1)-Ti(1)	-4.2(3)
O(2)-Ti(1)-O(5)-C(22)	-21.2(3)	C(3)-N(2)-C(1)-Ti(1)	169.51(15)
O(4)-Ti(1)-O(5)-C(22)	-95.6(3)	C(1)-N(1)-C(2)-C(3)	7.1(3)
Ti(2)-Ti(1)-O(5)-C(22)	-62.1(3)	C(10)-N(1)-C(2)-C(3)	-177.24(19)
O(3)-Ti(1)-O(5)-C(22A)	28.8(5)	C(1)-N(2)-C(3)-C(2)	6.7(2)
O(1)-Ti(1)-O(5)-C(22A)	129.1(5)	C(4)-N(2)-C(3)-C(2)	-179.43(19)
O(2)-Ti(1)-O(5)-C(22A)	-67.6(5)	N(1)-C(2)-C(3)-N(2)	-7.6(2)
O(4)-Ti(1)-O(5)-C(22A)	-142.0(5)	C(1)-N(2)-C(4)-C(5)	165.2(2)
Ti(2)-Ti(1)-O(5)-C(22A)	-108.5(5)	C(3)-N(2)-C(4)-C(5)	-8.0(3)
O(8)-Ti(2)-O(6)-C(35)	87.2(2)	C(1)-N(2)-C(4)-C(9)	-15.8(3)
O(7)-Ti(2)-O(6)-C(35)	-20.1(4)	C(3)-N(2)-C(4)-C(9)	171.0(2)
O(4)-Ti(2)-O(6)-C(35)	-164.1(2)	C(9)-C(4)-C(5)-C(6)	3.0(3)
C(25)-Ti(2)-O(6)-C(35)	-8.5(2)	N(2)-C(4)-C(5)-C(6)	-178.0(2)
O(2)-Ti(2)-O(6)-C(35)	-91.7(2)	C(4)-C(5)-C(6)-C(7)	1.4(4)
Ti(1)-Ti(2)-O(6)-C(35)	-127.5(2)	C(5)-C(6)-C(7)-C(8)	-3.1(4)
O(8)-Ti(2)-O(7)-C(33)	-94.2(2)	C(6)-C(7)-C(8)-C(9)	0.2(4)
O(6)-Ti(2)-O(7)-C(33)	12.9(4)	Ti(1)-O(2)-C(9)-C(8)	-128.51(19)
O(4)-Ti(2)-O(7)-C(33)	156.9(2)	Ti(2)-O(2)-C(9)-C(8)	93.3(2)
C(25)-Ti(2)-O(7)-C(33)	1.4(2)	Ti(1)-O(2)-C(9)-C(4)	54.4(3)

Ti(2)-O(2)-C(9)-C(4)	-83.8(2)	C(25)-N(4)-C(27)-C(26)	6.2(3)
C(7)-C(8)-C(9)-O(2)	-173.0(2)	C(28)-N(4)-C(27)-C(26)	-179.2(2)
C(7)-C(8)-C(9)-C(4)	4.2(3)	N(3)-C(26)-C(27)-N(4)	-5.3(2)
C(5)-C(4)-C(9)-O(2)	171.4(2)	C(25)-N(4)-C(28)-C(29)	-175.5(2)
N(2)-C(4)-C(9)-O(2)	-7.6(3)	C(27)-N(4)-C(28)-C(29)	10.8(3)
C(5)-C(4)-C(9)-C(8)	-5.7(3)	C(25)-N(4)-C(28)-C(33)	4.4(4)
N(2)-C(4)-C(9)-C(8)	175.3(2)	C(27)-N(4)-C(28)-C(33)	-169.3(2)
C(1)-N(1)-C(10)-C(15)	168.4(2)	C(33)-C(28)-C(29)-C(30)	0.8(4)
C(2)-N(1)-C(10)-C(15)	-6.6(3)	N(4)-C(28)-C(29)-C(30)	-179.3(2)
C(1)-N(1)-C(10)-C(11)	-12.0(3)	C(28)-C(29)-C(30)-C(31)	1.2(4)
C(2)-N(1)-C(10)-C(11)	173.0(2)	C(29)-C(30)-C(31)-C(32)	-1.5(4)
Ti(1)-O(1)-C(11)-C(12)	-155.08(18)	C(30)-C(31)-C(32)-C(33)	-0.1(4)
Ti(1)-O(1)-C(11)-C(10)	26.3(3)	Ti(2)-O(7)-C(33)-C(32)	179.10(17)
C(15)-C(10)-C(11)-O(1)	176.0(2)	Ti(2)-O(7)-C(33)-C(28)	-0.1(4)
N(1)-C(10)-C(11)-O(1)	-3.7(3)	C(31)-C(32)-C(33)-O(7)	-177.1(2)
C(15)-C(10)-C(11)-C(12)	-2.6(3)	C(31)-C(32)-C(33)-C(28)	2.1(3)
N(1)-C(10)-C(11)-C(12)	177.7(2)	C(29)-C(28)-C(33)-O(7)	176.8(2)
O(1)-C(11)-C(12)-C(13)	-176.8(2)	N(4)-C(28)-C(33)-O(7)	-3.1(3)
C(10)-C(11)-C(12)-C(13)	1.9(4)	C(29)-C(28)-C(33)-C(32)	-2.4(3)
C(11)-C(12)-C(13)-C(14)	-0.1(4)	N(4)-C(28)-C(33)-C(32)	177.7(2)
C(12)-C(13)-C(14)-C(15)	-1.0(4)	C(25)-N(3)-C(34)-C(39)	174.3(2)
C(13)-C(14)-C(15)-C(10)	0.2(4)	C(26)-N(3)-C(34)-C(39)	-2.7(3)
N(1)-C(10)-C(15)-C(14)	-178.7(2)	C(25)-N(3)-C(34)-C(35)	-5.5(4)
C(11)-C(10)-C(15)-C(14)	1.6(4)	C(26)-N(3)-C(34)-C(35)	177.4(2)
Ti(1)-O(3)-C(16)-C(18)	166.8(2)	Ti(2)-O(6)-C(35)-C(36)	-167.68(18)
Ti(1)-O(3)-C(16)-C(17)	-69.3(3)	Ti(2)-O(6)-C(35)-C(34)	12.0(4)
Ti(2)-O(4)-C(19)-C(21)	73.7(3)	C(39)-C(34)-C(35)-O(6)	177.1(2)
Ti(1)-O(4)-C(19)-C(21)	-125.36(19)	N(3)-C(34)-C(35)-O(6)	-3.1(3)
Ti(2)-O(4)-C(19)-C(20)	-51.8(3)	C(39)-C(34)-C(35)-C(36)	-3.2(3)
Ti(1)-O(4)-C(19)-C(20)	109.1(2)	N(3)-C(34)-C(35)-C(36)	176.6(2)
Ti(1)-O(5)-C(22)-C(23)	171.4(7)	O(6)-C(35)-C(36)-C(37)	-177.4(2)
Ti(1)-O(5)-C(22)-C(24)	-67.2(5)	C(34)-C(35)-C(36)-C(37)	2.8(4)
Ti(1)-O(5)-C(22A)-C(24A)	54.2(9)	C(35)-C(36)-C(37)-C(38)	-0.3(4)
Ti(1)-O(5)-C(22A)-C(23A)	176.1(10)	C(36)-C(37)-C(38)-C(39)	-1.7(4)
C(34)-N(3)-C(25)-N(4)	-176.8(2)	C(37)-C(38)-C(39)-C(34)	1.3(4)
C(26)-N(3)-C(25)-N(4)	0.5(3)	C(35)-C(34)-C(39)-C(38)	1.2(4)
C(34)-N(3)-C(25)-Ti(2)	7.3(3)	N(3)-C(34)-C(39)-C(38)	-178.6(2)
C(26)-N(3)-C(25)-Ti(2)	-175.44(16)	Ti(2)-O(8)-C(40)-C(42)	-96.1(2)
C(28)-N(4)-C(25)-N(3)	-178.5(2)	Ti(2)-O(8)-C(40)-C(41)	141.41(19)
C(27)-N(4)-C(25)-N(3)	-4.3(3)	C(4S)-O(1S)-C(1S)-C(2S)	-36.6(9)
C(28)-N(4)-C(25)-Ti(2)	-2.6(3)	O(1S)-C(1S)-C(2S)-C(3S)	37.9(9)
C(27)-N(4)-C(25)-Ti(2)	171.56(16)	C(1S)-C(2S)-C(3S)-C(4S)	-24.7(9)
C(25)-N(3)-C(26)-C(27)	3.3(3)	C(1S)-O(1S)-C(4S)-C(3S)	19.9(9)
C(34)-N(3)-C(26)-C(27)	-179.2(2)	C(2S)-C(3S)-C(4S)-O(1S)	4.8(10)

C(8S)-O(2S)-C(5S)-C(6S)	-36.2(9)	C(5S)-O(2S)-C(8S)-C(7S)	41.6(13)
O(2S)-C(5S)-C(6S)-C(7S)	16.3(16)	C(6S)-C(7S)-C(8S)-O(2S)	-30(2 (2)
C(5S)-C(6S)-C(7S)-C(8S)	8(2)		

Symmetry transformations used to generate equivalent atoms:

Table S7. Crystal data and structure refinement for **5**.

Identification code	Compound5	
Empirical formula	$C_{81}H_{119}N_4O_8Ti_2$	
Formula weight	1372.59	
Temperature	103(2) K	
Wavelength (λ)	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 16.7643(16) Å	α = 90°.
	b = 27.625(3) Å	β = 112.6230(10)°.
	c = 17.7509(17) Å	γ = 90°.
Volume	7588.2(13) $Å^3$	
Z	4	
Density (calculated)	1.201 Mg/m^3	
Linear absorption coefficient (μ)	0.267 mm^{-1}	
F(000)	2964	
Crystal size	0.484 x 0.252 x 0.118 mm^3	
Crystal habit/colour	Elongated prism/Pale yellow	
Theta range for data collection	1.928 to 25.290°.	
Index ranges	-20<=h<=20, -33<=k<=33, -21<=l<=21	
Reflections collected	88763	
Independent reflections	13786 [R(int) = 0.0648]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13786 / 9 / 879	
Goodness-of-fit on F^2	1.088	
Final R indices [I>2sigma(I)]	R1 = 0.0587, wR2 = 0.1672	
R indices (all data)	R1 = 0.0739, wR2 = 0.1785	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.990 and -0.773 $e.Å^{-3}$	

Table S8. Bond lengths [Å] and angles [°] for **5**.

C(1)-N(1)	1.341(4)	C(8)-C(9)	1.393(4)
C(1)-N(2)	1.348(4)	C(8)-H(8)	0.9500
C(1)-Ti(1)	2.212(3)	O(8)-C(52)	1.357(3)
N(1)-C(10)	1.411(4)	C(10)-C(15)	1.395(4)
N(1)-C(2)	1.476(4)	C(10)-C(11)	1.406(4)
O(1)-C(11)	1.337(3)	C(11)-C(12)	1.394(4)
O(1)-Ti(1)	1.892(2)	C(12)-C(13)	1.384(4)
Ti(1)-O(3)	1.769(2)	C(12)-H(12)	0.9500
Ti(1)-O(4)	1.8598(18)	C(13)-C(14)	1.382(5)
Ti(1)-O(2)	1.876(2)	C(13)-H(13)	0.9500
C(2)-C(3)	1.518(4)	C(14)-C(15)	1.384(5)
C(2)-H(2A)	0.9900	C(14)-H(14)	0.9500
C(2)-H(2B)	0.9900	C(15)-H(15)	0.9500
N(2)-C(4)	1.411(4)	C(16)-C(17)	1.502(5)
N(2)-C(3)	1.482(4)	C(16)-C(18)	1.514(4)
O(2)-C(9)	1.331(3)	C(16)-H(16)	1.0000
Ti(2)-O(7)	1.792(2)	C(17)-H(17A)	0.9800
Ti(2)-O(8)	1.8397(19)	C(17)-H(17B)	0.9800
Ti(2)-O(5)	1.868(2)	C(17)-H(17C)	0.9800
Ti(2)-O(6)	1.889(2)	C(18)-H(18A)	0.9800
Ti(2)-C(34)	2.222(3)	C(18)-H(18B)	0.9800
C(3)-H(3A)	0.9900	C(18)-H(18C)	0.9800
C(3)-H(3B)	0.9900	C(19)-C(24)	1.422(4)
N(3)-C(34)	1.344(4)	C(19)-C(20)	1.422(4)
N(3)-C(43)	1.409(4)	C(20)-C(21)	1.395(4)
N(3)-C(35)	1.479(4)	C(20)-C(26)	1.542(4)
O(3)-C(16)	1.429(4)	C(21)-C(22)	1.388(4)
C(4)-C(5)	1.393(4)	C(21)-H(21)	0.9500
C(4)-C(9)	1.409(4)	C(22)-C(23)	1.382(4)
N(4)-C(34)	1.347(4)	C(22)-C(25)	1.511(4)
N(4)-C(37)	1.410(4)	C(23)-C(24)	1.397(4)
N(4)-C(36)	1.478(4)	C(23)-H(23)	0.9500
O(4)-C(19)	1.348(3)	C(24)-C(30)	1.541(4)
C(5)-C(6)	1.377(5)	C(25)-H(25A)	0.9800
C(5)-H(5)	0.9500	C(25)-H(25B)	0.9800
O(5)-C(44)	1.339(4)	C(25)-H(25C)	0.9800
C(6)-C(7)	1.381(5)	C(26)-C(29)	1.527(4)
C(6)-H(6)	0.9500	C(26)-C(28)	1.528(4)
O(6)-C(42)	1.329(3)	C(26)-C(27)	1.543(4)
C(7)-C(8)	1.384(4)	C(27)-H(27A)	0.9800
C(7)-H(7)	0.9500	C(27)-H(27B)	0.9800
O(7)-C(49)	1.436(4)	C(27)-H(27C)	0.9800

C(28)-H(28A)	0.9800	C(49)-C(50)	1.514(5)
C(28)-H(28B)	0.9800	C(49)-H(49)	1.0000
C(28)-H(28C)	0.9800	C(50)-H(50A)	0.9800
C(29)-H(29A)	0.9800	C(50)-H(50B)	0.9800
C(29)-H(29B)	0.9800	C(50)-H(50C)	0.9800
C(29)-H(29C)	0.9800	C(51)-H(51A)	0.9800
C(30)-C(32)	1.537(4)	C(51)-H(51B)	0.9800
C(30)-C(33)	1.538(4)	C(51)-H(51C)	0.9800
C(30)-C(31)	1.544(4)	C(52)-C(53)	1.411(4)
C(31)-H(31A)	0.9800	C(52)-C(57)	1.411(4)
C(31)-H(31B)	0.9800	C(53)-C(54)	1.393(4)
C(31)-H(31C)	0.9800	C(53)-C(59)	1.539(4)
C(32)-H(32A)	0.9800	C(54)-C(55)	1.384(4)
C(32)-H(32B)	0.9800	C(54)-H(54)	0.9500
C(32)-H(32C)	0.9800	C(55)-C(56)	1.379(4)
C(33)-H(33A)	0.9800	C(55)-C(58)	1.513(4)
C(33)-H(33B)	0.9800	C(56)-C(57)	1.396(4)
C(33)-H(33C)	0.9800	C(56)-H(56)	0.9500
C(35)-C(36)	1.510(5)	C(57)-C(63)	1.543(4)
C(35)-H(35A)	0.9900	C(58)-H(58A)	0.9800
C(35)-H(35B)	0.9900	C(58)-H(58B)	0.9800
C(36)-H(36A)	0.9900	C(58)-H(58C)	0.9800
C(36)-H(36B)	0.9900	C(59)-C(62)	1.537(4)
C(37)-C(38)	1.393(4)	C(59)-C(60)	1.539(4)
C(37)-C(42)	1.408(4)	C(59)-C(61)	1.543(4)
C(38)-C(39)	1.381(5)	C(60)-H(60A)	0.9800
C(38)-H(38)	0.9500	C(60)-H(60B)	0.9800
C(39)-C(40)	1.386(5)	C(60)-H(60C)	0.9800
C(39)-H(39)	0.9500	C(61)-H(61A)	0.9800
C(40)-C(41)	1.381(4)	C(61)-H(61B)	0.9800
C(40)-H(40)	0.9500	C(61)-H(61C)	0.9800
C(41)-C(42)	1.393(4)	C(62)-H(62A)	0.9800
C(41)-H(41)	0.9500	C(62)-H(62B)	0.9800
C(43)-C(44)	1.399(5)	C(62)-H(62C)	0.9800
C(43)-C(48)	1.406(4)	C(63)-C(64)	1.531(4)
C(44)-C(45)	1.394(5)	C(63)-C(66)	1.535(4)
C(45)-C(46)	1.385(5)	C(63)-C(65)	1.539(4)
C(45)-H(45)	0.9500	C(64)-H(64A)	0.9800
C(46)-C(47)	1.375(6)	C(64)-H(64B)	0.9800
C(46)-H(46)	0.9500	C(64)-H(64C)	0.9800
C(47)-C(48)	1.377(5)	C(65)-H(65A)	0.9800
C(47)-H(47)	0.9500	C(65)-H(65B)	0.9800
C(48)-H(48)	0.9500	C(65)-H(65C)	0.9800
C(49)-C(51)	1.511(5)	C(66)-H(66A)	0.9800

C(66)-H(66B)	0.9800	C(11S)-H(11A)	0.9900
C(66)-H(66C)	0.9800	C(11S)-H(11B)	0.9900
C(1S)-C(2S)	1.497(15)	C(12S)-H(12A)	0.9800
C(1S)-H(1SA)	0.9800	C(12S)-H(12B)	0.9800
C(1S)-H(1SB)	0.9800	C(12S)-H(12C)	0.9800
C(1S)-H(1SC)	0.9800	C(13S)-C(14S)	1.531(6)
C(2S)-C(3S)	1.586(15)	C(13S)-H(13A)	0.9800
C(2S)-H(2SA)	0.9900	C(13S)-H(13B)	0.9800
C(2S)-H(2SB)	0.9900	C(13S)-H(13C)	0.9800
C(3S)-C(3S)#1	1.57(2)	C(14S)-C(15S)	1.512(6)
C(3S)-H(3SA)	0.9900	C(14S)-H(14A)	0.9900
C(3S)-H(3SB)	0.9900	C(14S)-H(14B)	0.9900
C(7S)-C(8S)	1.448(8)	C(15S)-C(16S)	1.504(6)
C(7S)-H(7SA)	0.9800	C(15S)-H(15A)	0.9900
C(7S)-H(7SB)	0.9800	C(15S)-H(15B)	0.9900
C(7S)-H(7SC)	0.9800	C(16S)-C(17S)	1.500(6)
C(8S)-C(9S)	1.488(7)	C(16S)-H(16A)	0.9900
C(8S)-H(8A)	0.9900	C(16S)-H(16B)	0.9900
C(8S)-H(8B)	0.9900	C(17S)-C(18S)	1.536(6)
C(9S)-C(10S)	1.468(7)	C(17S)-H(17D)	0.9900
C(9S)-H(9SA)	0.9900	C(17S)-H(17E)	0.9900
C(9S)-H(9SB)	0.9900	C(18S)-H(18D)	0.9800
C(10S)-C(11S)	1.493(7)	C(18S)-H(18E)	0.9800
C(10S)-H(10A)	0.9900	C(18S)-H(18F)	0.9800
C(10S)-H(10B)	0.9900		
C(11S)-C(12S)	1.411(7)		

N(1)-C(1)-N(2)	108.3(2)	N(1)-C(2)-C(3)	102.9(2)
N(1)-C(1)-Ti(1)	125.26(19)	N(1)-C(2)-H(2A)	111.2
N(2)-C(1)-Ti(1)	126.3(2)	C(3)-C(2)-H(2A)	111.2
C(1)-N(1)-C(10)	126.5(2)	N(1)-C(2)-H(2B)	111.2
C(1)-N(1)-C(2)	113.1(2)	C(3)-C(2)-H(2B)	111.2
C(10)-N(1)-C(2)	120.4(2)	H(2A)-C(2)-H(2B)	109.1
C(11)-O(1)-Ti(1)	135.71(18)	C(1)-N(2)-C(4)	127.7(2)
O(3)-Ti(1)-O(4)	113.53(9)	C(1)-N(2)-C(3)	112.6(2)
O(3)-Ti(1)-O(2)	101.23(9)	C(4)-N(2)-C(3)	119.7(2)
O(4)-Ti(1)-O(2)	94.62(8)	C(9)-O(2)-Ti(1)	144.14(19)
O(3)-Ti(1)-O(1)	99.26(10)	O(7)-Ti(2)-O(8)	111.39(9)
O(4)-Ti(1)-O(1)	91.76(8)	O(7)-Ti(2)-O(5)	97.63(9)
O(2)-Ti(1)-O(1)	153.96(9)	O(8)-Ti(2)-O(5)	94.73(9)
O(3)-Ti(1)-C(1)	99.75(10)	O(7)-Ti(2)-O(6)	98.46(9)
O(4)-Ti(1)-C(1)	146.64(9)	O(8)-Ti(2)-O(6)	93.60(8)
O(2)-Ti(1)-C(1)	80.46(9)	O(5)-Ti(2)-O(6)	157.75(9)
O(1)-Ti(1)-C(1)	80.38(9)	O(7)-Ti(2)-C(34)	105.17(10)

O(8)-Ti(2)-C(34)	143.43(9)	C(12)-C(11)-C(10)	118.8(3)
O(5)-Ti(2)-C(34)	80.50(10)	C(13)-C(12)-C(11)	121.3(3)
O(6)-Ti(2)-C(34)	80.52(10)	C(13)-C(12)-H(12)	119.3
N(2)-C(3)-C(2)	102.8(2)	C(11)-C(12)-H(12)	119.3
N(2)-C(3)-H(3A)	111.2	C(14)-C(13)-C(12)	119.7(3)
C(2)-C(3)-H(3A)	111.2	C(14)-C(13)-H(13)	120.2
N(2)-C(3)-H(3B)	111.2	C(12)-C(13)-H(13)	120.2
C(2)-C(3)-H(3B)	111.2	C(13)-C(14)-C(15)	120.1(3)
H(3A)-C(3)-H(3B)	109.1	C(13)-C(14)-H(14)	120.0
C(34)-N(3)-C(43)	127.0(3)	C(15)-C(14)-H(14)	120.0
C(34)-N(3)-C(35)	113.0(3)	C(14)-C(15)-C(10)	120.9(3)
C(43)-N(3)-C(35)	119.9(3)	C(14)-C(15)-H(15)	119.6
C(16)-O(3)-Ti(1)	146.57(19)	C(10)-C(15)-H(15)	119.6
C(5)-C(4)-C(9)	119.4(3)	O(3)-C(16)-C(17)	109.2(3)
C(5)-C(4)-N(2)	120.6(3)	O(3)-C(16)-C(18)	109.2(3)
C(9)-C(4)-N(2)	120.0(2)	C(17)-C(16)-C(18)	113.3(3)
C(34)-N(4)-C(37)	127.1(2)	O(3)-C(16)-H(16)	108.3
C(34)-N(4)-C(36)	112.6(3)	C(17)-C(16)-H(16)	108.3
C(37)-N(4)-C(36)	120.1(2)	C(18)-C(16)-H(16)	108.3
C(19)-O(4)-Ti(1)	160.30(17)	C(16)-C(17)-H(17A)	109.5
C(6)-C(5)-C(4)	120.7(3)	C(16)-C(17)-H(17B)	109.5
C(6)-C(5)-H(5)	119.7	H(17A)-C(17)-H(17B)	109.5
C(4)-C(5)-H(5)	119.7	C(16)-C(17)-H(17C)	109.5
C(44)-O(5)-Ti(2)	143.9(2)	H(17A)-C(17)-H(17C)	109.5
C(5)-C(6)-C(7)	120.4(3)	H(17B)-C(17)-H(17C)	109.5
C(5)-C(6)-H(6)	119.8	C(16)-C(18)-H(18A)	109.5
C(7)-C(6)-H(6)	119.8	C(16)-C(18)-H(18B)	109.5
C(42)-O(6)-Ti(2)	140.63(19)	H(18A)-C(18)-H(18B)	109.5
C(6)-C(7)-C(8)	119.6(3)	C(16)-C(18)-H(18C)	109.5
C(6)-C(7)-H(7)	120.2	H(18A)-C(18)-H(18C)	109.5
C(8)-C(7)-H(7)	120.2	H(18B)-C(18)-H(18C)	109.5
C(49)-O(7)-Ti(2)	133.47(19)	O(4)-C(19)-C(24)	119.4(2)
C(7)-C(8)-C(9)	121.2(3)	O(4)-C(19)-C(20)	119.8(2)
C(7)-C(8)-H(8)	119.4	C(24)-C(19)-C(20)	120.8(2)
C(9)-C(8)-H(8)	119.4	C(21)-C(20)-C(19)	117.7(2)
C(52)-O(8)-Ti(2)	158.87(17)	C(21)-C(20)-C(26)	119.4(2)
O(2)-C(9)-C(8)	120.1(3)	C(19)-C(20)-C(26)	122.9(2)
O(2)-C(9)-C(4)	121.2(3)	C(22)-C(21)-C(20)	122.8(3)
C(8)-C(9)-C(4)	118.7(3)	C(22)-C(21)-H(21)	118.6
C(15)-C(10)-C(11)	119.3(3)	C(20)-C(21)-H(21)	118.6
C(15)-C(10)-N(1)	120.5(3)	C(23)-C(22)-C(21)	118.1(3)
C(11)-C(10)-N(1)	120.2(2)	C(23)-C(22)-C(25)	120.9(3)
O(1)-C(11)-C(12)	119.3(3)	C(21)-C(22)-C(25)	121.0(3)
O(1)-C(11)-C(10)	121.8(3)	C(22)-C(23)-C(24)	123.1(3)

C(22)-C(23)-H(23)	118.5	C(30)-C(31)-H(31C)	109.5
C(24)-C(23)-H(23)	118.5	H(31A)-C(31)-H(31C)	109.5
C(23)-C(24)-C(19)	117.5(2)	H(31B)-C(31)-H(31C)	109.5
C(23)-C(24)-C(30)	119.8(2)	C(30)-C(32)-H(32A)	109.5
C(19)-C(24)-C(30)	122.7(2)	C(30)-C(32)-H(32B)	109.5
C(22)-C(25)-H(25A)	109.5	H(32A)-C(32)-H(32B)	109.5
C(22)-C(25)-H(25B)	109.5	C(30)-C(32)-H(32C)	109.5
H(25A)-C(25)-H(25B)	109.5	H(32A)-C(32)-H(32C)	109.5
C(22)-C(25)-H(25C)	109.5	H(32B)-C(32)-H(32C)	109.5
H(25A)-C(25)-H(25C)	109.5	C(30)-C(33)-H(33A)	109.5
H(25B)-C(25)-H(25C)	109.5	C(30)-C(33)-H(33B)	109.5
C(29)-C(26)-C(28)	105.7(2)	H(33A)-C(33)-H(33B)	109.5
C(29)-C(26)-C(20)	112.9(2)	C(30)-C(33)-H(33C)	109.5
C(28)-C(26)-C(20)	111.3(2)	H(33A)-C(33)-H(33C)	109.5
C(29)-C(26)-C(27)	106.2(2)	H(33B)-C(33)-H(33C)	109.5
C(28)-C(26)-C(27)	110.5(2)	N(3)-C(34)-N(4)	108.1(2)
C(20)-C(26)-C(27)	110.1(2)	N(3)-C(34)-Ti(2)	126.3(2)
C(26)-C(27)-H(27A)	109.5	N(4)-C(34)-Ti(2)	125.5(2)
C(26)-C(27)-H(27B)	109.5	N(3)-C(35)-C(36)	102.7(2)
H(27A)-C(27)-H(27B)	109.5	N(3)-C(35)-H(35A)	111.2
C(26)-C(27)-H(27C)	109.5	C(36)-C(35)-H(35A)	111.2
H(27A)-C(27)-H(27C)	109.5	N(3)-C(35)-H(35B)	111.2
H(27B)-C(27)-H(27C)	109.5	C(36)-C(35)-H(35B)	111.2
C(26)-C(28)-H(28A)	109.5	H(35A)-C(35)-H(35B)	109.1
C(26)-C(28)-H(28B)	109.5	N(4)-C(36)-C(35)	103.2(2)
H(28A)-C(28)-H(28B)	109.5	N(4)-C(36)-H(36A)	111.1
C(26)-C(28)-H(28C)	109.5	C(35)-C(36)-H(36A)	111.1
H(28A)-C(28)-H(28C)	109.5	N(4)-C(36)-H(36B)	111.1
H(28B)-C(28)-H(28C)	109.5	C(35)-C(36)-H(36B)	111.1
C(26)-C(29)-H(29A)	109.5	H(36A)-C(36)-H(36B)	109.1
C(26)-C(29)-H(29B)	109.5	C(38)-C(37)-C(42)	119.4(3)
H(29A)-C(29)-H(29B)	109.5	C(38)-C(37)-N(4)	120.0(3)
C(26)-C(29)-H(29C)	109.5	C(42)-C(37)-N(4)	120.6(3)
H(29A)-C(29)-H(29C)	109.5	C(39)-C(38)-C(37)	120.7(3)
H(29B)-C(29)-H(29C)	109.5	C(39)-C(38)-H(38)	119.7
C(32)-C(30)-C(33)	110.9(3)	C(37)-C(38)-H(38)	119.7
C(32)-C(30)-C(24)	111.5(2)	C(38)-C(39)-C(40)	120.2(3)
C(33)-C(30)-C(24)	109.8(2)	C(38)-C(39)-H(39)	119.9
C(32)-C(30)-C(31)	106.2(2)	C(40)-C(39)-H(39)	119.9
C(33)-C(30)-C(31)	106.2(2)	C(41)-C(40)-C(39)	119.7(3)
C(24)-C(30)-C(31)	112.0(2)	C(41)-C(40)-H(40)	120.1
C(30)-C(31)-H(31A)	109.5	C(39)-C(40)-H(40)	120.1
C(30)-C(31)-H(31B)	109.5	C(40)-C(41)-C(42)	121.2(3)
H(31A)-C(31)-H(31B)	109.5	C(40)-C(41)-H(41)	119.4

C(42)-C(41)-H(41)	119.4	C(54)-C(53)-C(59)	120.4(3)
O(6)-C(42)-C(41)	119.8(3)	C(52)-C(53)-C(59)	121.4(2)
O(6)-C(42)-C(37)	121.3(3)	C(55)-C(54)-C(53)	122.3(3)
C(41)-C(42)-C(37)	118.8(3)	C(55)-C(54)-H(54)	118.9
C(44)-C(43)-C(48)	118.8(3)	C(53)-C(54)-H(54)	118.9
C(44)-C(43)-N(3)	120.9(3)	C(56)-C(55)-C(54)	118.1(3)
C(48)-C(43)-N(3)	120.3(3)	C(56)-C(55)-C(58)	121.4(3)
O(5)-C(44)-C(45)	119.5(3)	C(54)-C(55)-C(58)	120.5(3)
O(5)-C(44)-C(43)	121.1(3)	C(55)-C(56)-C(57)	123.1(3)
C(45)-C(44)-C(43)	119.4(3)	C(55)-C(56)-H(56)	118.5
C(46)-C(45)-C(44)	121.0(3)	C(57)-C(56)-H(56)	118.5
C(46)-C(45)-H(45)	119.5	C(56)-C(57)-C(52)	117.4(3)
C(44)-C(45)-H(45)	119.5	C(56)-C(57)-C(63)	120.4(3)
C(47)-C(46)-C(45)	119.4(3)	C(52)-C(57)-C(63)	122.3(2)
C(47)-C(46)-H(46)	120.3	C(55)-C(58)-H(58A)	109.5
C(45)-C(46)-H(46)	120.3	C(55)-C(58)-H(58B)	109.5
C(46)-C(47)-C(48)	120.9(3)	H(58A)-C(58)-H(58B)	109.5
C(46)-C(47)-H(47)	119.6	C(55)-C(58)-H(58C)	109.5
C(48)-C(47)-H(47)	119.6	H(58A)-C(58)-H(58C)	109.5
C(47)-C(48)-C(43)	120.4(3)	H(58B)-C(58)-H(58C)	109.5
C(47)-C(48)-H(48)	119.8	C(62)-C(59)-C(60)	106.7(3)
C(43)-C(48)-H(48)	119.8	C(62)-C(59)-C(53)	112.2(2)
O(7)-C(49)-C(51)	109.4(3)	C(60)-C(59)-C(53)	108.7(2)
O(7)-C(49)-C(50)	107.9(3)	C(62)-C(59)-C(61)	105.5(3)
C(51)-C(49)-C(50)	112.8(3)	C(60)-C(59)-C(61)	111.2(2)
O(7)-C(49)-H(49)	108.9	C(53)-C(59)-C(61)	112.5(2)
C(51)-C(49)-H(49)	108.9	C(59)-C(60)-H(60A)	109.5
C(50)-C(49)-H(49)	108.9	C(59)-C(60)-H(60B)	109.5
C(49)-C(50)-H(50A)	109.5	H(60A)-C(60)-H(60B)	109.5
C(49)-C(50)-H(50B)	109.5	C(59)-C(60)-H(60C)	109.5
H(50A)-C(50)-H(50B)	109.5	H(60A)-C(60)-H(60C)	109.5
C(49)-C(50)-H(50C)	109.5	H(60B)-C(60)-H(60C)	109.5
H(50A)-C(50)-H(50C)	109.5	C(59)-C(61)-H(61A)	109.5
H(50B)-C(50)-H(50C)	109.5	C(59)-C(61)-H(61B)	109.5
C(49)-C(51)-H(51A)	109.5	H(61A)-C(61)-H(61B)	109.5
C(49)-C(51)-H(51B)	109.5	C(59)-C(61)-H(61C)	109.5
H(51A)-C(51)-H(51B)	109.5	H(61A)-C(61)-H(61C)	109.5
C(49)-C(51)-H(51C)	109.5	H(61B)-C(61)-H(61C)	109.5
H(51A)-C(51)-H(51C)	109.5	C(59)-C(62)-H(62A)	109.5
H(51B)-C(51)-H(51C)	109.5	C(59)-C(62)-H(62B)	109.5
O(8)-C(52)-C(53)	119.6(2)	H(62A)-C(62)-H(62B)	109.5
O(8)-C(52)-C(57)	119.4(2)	C(59)-C(62)-H(62C)	109.5
C(53)-C(52)-C(57)	120.9(2)	H(62A)-C(62)-H(62C)	109.5
C(54)-C(53)-C(52)	118.2(3)	H(62B)-C(62)-H(62C)	109.5

C(64)-C(63)-C(66)	110.7(3)	H(7SA)-C(7S)-H(7SB)	109.5
C(64)-C(63)-C(65)	106.4(2)	C(8S)-C(7S)-H(7SC)	109.5
C(66)-C(63)-C(65)	106.5(3)	H(7SA)-C(7S)-H(7SC)	109.5
C(64)-C(63)-C(57)	110.4(2)	H(7SB)-C(7S)-H(7SC)	109.5
C(66)-C(63)-C(57)	110.8(2)	C(7S)-C(8S)-C(9S)	115.2(5)
C(65)-C(63)-C(57)	111.9(3)	C(7S)-C(8S)-H(8A)	108.5
C(63)-C(64)-H(64A)	109.5	C(9S)-C(8S)-H(8A)	108.5
C(63)-C(64)-H(64B)	109.5	C(7S)-C(8S)-H(8B)	108.5
H(64A)-C(64)-H(64B)	109.5	C(9S)-C(8S)-H(8B)	108.5
C(63)-C(64)-H(64C)	109.5	H(8A)-C(8S)-H(8B)	107.5
H(64A)-C(64)-H(64C)	109.5	C(10S)-C(9S)-C(8S)	118.8(5)
H(64B)-C(64)-H(64C)	109.5	C(10S)-C(9S)-H(9SA)	107.6
C(63)-C(65)-H(65A)	109.5	C(8S)-C(9S)-H(9SA)	107.6
C(63)-C(65)-H(65B)	109.5	C(10S)-C(9S)-H(9SB)	107.6
H(65A)-C(65)-H(65B)	109.5	C(8S)-C(9S)-H(9SB)	107.6
C(63)-C(65)-H(65C)	109.5	H(9SA)-C(9S)-H(9SB)	107.1
H(65A)-C(65)-H(65C)	109.5	C(9S)-C(10S)-C(11S)	116.3(5)
H(65B)-C(65)-H(65C)	109.5	C(9S)-C(10S)-H(10A)	108.2
C(63)-C(66)-H(66A)	109.5	C(11S)-C(10S)-H(10A)	108.2
C(63)-C(66)-H(66B)	109.5	C(9S)-C(10S)-H(10B)	108.2
H(66A)-C(66)-H(66B)	109.5	C(11S)-C(10S)-H(10B)	108.2
C(63)-C(66)-H(66C)	109.5	H(10A)-C(10S)-H(10B)	107.4
H(66A)-C(66)-H(66C)	109.5	C(12S)-C(11S)-C(10S)	119.1(5)
H(66B)-C(66)-H(66C)	109.5	C(12S)-C(11S)-H(11A)	107.5
C(2S)-C(1S)-H(1SA)	109.5	C(10S)-C(11S)-H(11A)	107.5
C(2S)-C(1S)-H(1SB)	109.5	C(12S)-C(11S)-H(11B)	107.5
H(1SA)-C(1S)-H(1SB)	109.5	C(10S)-C(11S)-H(11B)	107.5
C(2S)-C(1S)-H(1SC)	109.5	H(11A)-C(11S)-H(11B)	107.0
H(1SA)-C(1S)-H(1SC)	109.5	C(11S)-C(12S)-H(12A)	109.5
H(1SB)-C(1S)-H(1SC)	109.5	C(11S)-C(12S)-H(12B)	109.5
C(1S)-C(2S)-C(3S)	116.9(13)	H(12A)-C(12S)-H(12B)	109.5
C(1S)-C(2S)-H(2SA)	108.1	C(11S)-C(12S)-H(12C)	109.5
C(3S)-C(2S)-H(2SA)	108.1	H(12A)-C(12S)-H(12C)	109.5
C(1S)-C(2S)-H(2SB)	108.1	H(12B)-C(12S)-H(12C)	109.5
C(3S)-C(2S)-H(2SB)	108.1	C(14S)-C(13S)-H(13A)	109.5
H(2SA)-C(2S)-H(2SB)	107.3	C(14S)-C(13S)-H(13B)	109.5
C(3S)#1-C(3S)-C(2S)	107.2(12)	H(13A)-C(13S)-H(13B)	109.5
C(3S)#1-C(3S)-H(3SA)	110.3	C(14S)-C(13S)-H(13C)	109.5
C(2S)-C(3S)-H(3SA)	110.3	H(13A)-C(13S)-H(13C)	109.5
C(3S)#1-C(3S)-H(3SB)	110.3	H(13B)-C(13S)-H(13C)	109.5
C(2S)-C(3S)-H(3SB)	110.3	C(15S)-C(14S)-C(13S)	112.7(4)
H(3SA)-C(3S)-H(3SB)	108.5	C(15S)-C(14S)-H(14A)	109.0
C(8S)-C(7S)-H(7SA)	109.5	C(13S)-C(14S)-H(14A)	109.0
C(8S)-C(7S)-H(7SB)	109.5	C(15S)-C(14S)-H(14B)	109.0

C(13S)-C(14S)-H(14B)	109.0	H(16A)-C(16S)-H(16B)	107.5
H(14A)-C(14S)-H(14B)	107.8	C(16S)-C(17S)-C(18S)	113.6(4)
C(16S)-C(15S)-C(14S)	114.5(4)	C(16S)-C(17S)-H(17D)	108.8
C(16S)-C(15S)-H(15A)	108.6	C(18S)-C(17S)-H(17D)	108.8
C(14S)-C(15S)-H(15A)	108.6	C(16S)-C(17S)-H(17E)	108.8
C(16S)-C(15S)-H(15B)	108.6	C(18S)-C(17S)-H(17E)	108.8
C(14S)-C(15S)-H(15B)	108.6	H(17D)-C(17S)-H(17E)	107.7
H(15A)-C(15S)-H(15B)	107.6	C(17S)-C(18S)-H(18D)	109.5
C(17S)-C(16S)-C(15S)	115.3(4)	C(17S)-C(18S)-H(18E)	109.5
C(17S)-C(16S)-H(16A)	108.4	H(18D)-C(18S)-H(18E)	109.5
C(15S)-C(16S)-H(16A)	108.4	C(17S)-C(18S)-H(18F)	109.5
C(17S)-C(16S)-H(16B)	108.4	H(18D)-C(18S)-H(18F)	109.5
C(15S)-C(16S)-H(16B)	108.4	H(18E)-C(18S)-H(18F)	109.5

Symmetry transformations used to generate equivalent atoms:

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

Table S9. Torsion angles [°] for **5**.

N(2)-C(1)-N(1)-C(10)	-179.0(2)	C(1)-Ti(1)-O(3)-C(16)	58.1(4)
Ti(1)-C(1)-N(1)-C(10)	4.7(4)	C(1)-N(2)-C(4)-C(5)	-177.0(3)
N(2)-C(1)-N(1)-C(2)	-0.7(3)	C(3)-N(2)-C(4)-C(5)	5.4(4)
Ti(1)-C(1)-N(1)-C(2)	-177.09(19)	C(1)-N(2)-C(4)-C(9)	3.1(4)
C(11)-O(1)-Ti(1)-O(3)	-60.6(3)	C(3)-N(2)-C(4)-C(9)	-174.4(2)
C(11)-O(1)-Ti(1)-O(4)	-174.7(3)	O(3)-Ti(1)-O(4)-C(19)	-125.1(5)
C(11)-O(1)-Ti(1)-O(2)	81.0(3)	O(2)-Ti(1)-O(4)-C(19)	130.5(5)
C(11)-O(1)-Ti(1)-C(1)	37.9(3)	O(1)-Ti(1)-O(4)-C(19)	-24.2(5)
C(1)-N(1)-C(2)-C(3)	4.1(3)	C(1)-Ti(1)-O(4)-C(19)	50.8(6)
C(10)-N(1)-C(2)-C(3)	-177.6(2)	C(9)-C(4)-C(5)-C(6)	-2.1(4)
N(1)-C(1)-N(2)-C(4)	179.1(2)	N(2)-C(4)-C(5)-C(6)	178.1(3)
Ti(1)-C(1)-N(2)-C(4)	-4.6(4)	O(7)-Ti(2)-O(5)-C(44)	-106.9(3)
N(1)-C(1)-N(2)-C(3)	-3.2(3)	O(8)-Ti(2)-O(5)-C(44)	140.8(3)
Ti(1)-C(1)-N(2)-C(3)	173.11(19)	O(6)-Ti(2)-O(5)-C(44)	29.1(5)
O(3)-Ti(1)-O(2)-C(9)	101.2(3)	C(34)-Ti(2)-O(5)-C(44)	-2.7(3)
O(4)-Ti(1)-O(2)-C(9)	-143.7(3)	C(4)-C(5)-C(6)-C(7)	1.0(5)
O(1)-Ti(1)-O(2)-C(9)	-40.0(4)	O(7)-Ti(2)-O(6)-C(42)	78.5(3)
C(1)-Ti(1)-O(2)-C(9)	3.1(3)	O(8)-Ti(2)-O(6)-C(42)	-169.3(3)
C(1)-N(2)-C(3)-C(2)	5.5(3)	O(5)-Ti(2)-O(6)-C(42)	-57.4(4)
C(4)-N(2)-C(3)-C(2)	-176.6(2)	C(34)-Ti(2)-O(6)-C(42)	-25.6(3)
N(1)-C(2)-C(3)-N(2)	-5.3(3)	C(5)-C(6)-C(7)-C(8)	0.4(5)
O(4)-Ti(1)-O(3)-C(16)	-124.1(3)	O(8)-Ti(2)-O(7)-C(49)	76.8(3)
O(2)-Ti(1)-O(3)-C(16)	-24.0(4)	O(5)-Ti(2)-O(7)-C(49)	-21.3(3)
O(1)-Ti(1)-O(3)-C(16)	139.9(3)	O(6)-Ti(2)-O(7)-C(49)	174.1(3)

C(34)-Ti(2)-O(7)-C(49)	-103.5(3)	C(25)-C(22)-C(23)-C(24)	178.7(3)
C(6)-C(7)-C(8)-C(9)	-0.7(5)	C(22)-C(23)-C(24)-C(19)	1.7(4)
O(7)-Ti(2)-O(8)-C(52)	134.9(5)	C(22)-C(23)-C(24)-C(30)	-177.2(3)
O(5)-Ti(2)-O(8)-C(52)	-125.0(5)	O(4)-C(19)-C(24)-C(23)	176.8(2)
O(6)-Ti(2)-O(8)-C(52)	34.4(5)	C(20)-C(19)-C(24)-C(23)	-1.1(4)
C(34)-Ti(2)-O(8)-C(52)	-44.6(6)	O(4)-C(19)-C(24)-C(30)	-4.3(4)
Ti(1)-O(2)-C(9)-C(8)	174.7(2)	C(20)-C(19)-C(24)-C(30)	177.8(2)
Ti(1)-O(2)-C(9)-C(4)	-4.9(5)	C(21)-C(20)-C(26)-C(29)	-1.4(4)
C(7)-C(8)-C(9)-O(2)	-180.0(3)	C(19)-C(20)-C(26)-C(29)	179.4(3)
C(7)-C(8)-C(9)-C(4)	-0.4(4)	C(21)-C(20)-C(26)-C(28)	-120.1(3)
C(5)-C(4)-C(9)-O(2)	-178.6(3)	C(19)-C(20)-C(26)-C(28)	60.8(3)
N(2)-C(4)-C(9)-O(2)	1.2(4)	C(21)-C(20)-C(26)-C(27)	117.1(3)
C(5)-C(4)-C(9)-C(8)	1.8(4)	C(19)-C(20)-C(26)-C(27)	-62.1(3)
N(2)-C(4)-C(9)-C(8)	-178.4(3)	C(23)-C(24)-C(30)-C(32)	-122.6(3)
C(1)-N(1)-C(10)-C(15)	-172.1(3)	C(19)-C(24)-C(30)-C(32)	58.5(3)
C(2)-N(1)-C(10)-C(15)	9.8(4)	C(23)-C(24)-C(30)-C(33)	114.0(3)
C(1)-N(1)-C(10)-C(11)	9.3(4)	C(19)-C(24)-C(30)-C(33)	-64.8(3)
C(2)-N(1)-C(10)-C(11)	-168.8(3)	C(23)-C(24)-C(30)-C(31)	-3.8(4)
Ti(1)-O(1)-C(11)-C(12)	145.4(2)	C(19)-C(24)-C(30)-C(31)	177.4(3)
Ti(1)-O(1)-C(11)-C(10)	-36.3(4)	C(43)-N(3)-C(34)-N(4)	-176.7(3)
C(15)-C(10)-C(11)-O(1)	-176.2(3)	C(35)-N(3)-C(34)-N(4)	0.5(3)
N(1)-C(10)-C(11)-O(1)	2.5(4)	C(43)-N(3)-C(34)-Ti(2)	6.7(4)
C(15)-C(10)-C(11)-C(12)	2.2(4)	C(35)-N(3)-C(34)-Ti(2)	-176.1(2)
N(1)-C(10)-C(11)-C(12)	-179.2(2)	C(37)-N(4)-C(34)-N(3)	-179.1(3)
O(1)-C(11)-C(12)-C(13)	176.9(3)	C(36)-N(4)-C(34)-N(3)	-3.9(3)
C(10)-C(11)-C(12)-C(13)	-1.5(4)	C(37)-N(4)-C(34)-Ti(2)	-2.5(4)
C(11)-C(12)-C(13)-C(14)	-0.3(5)	C(36)-N(4)-C(34)-Ti(2)	172.68(19)
C(12)-C(13)-C(14)-C(15)	1.3(5)	C(34)-N(3)-C(35)-C(36)	2.9(3)
C(13)-C(14)-C(15)-C(10)	-0.6(5)	C(43)-N(3)-C(35)-C(36)	-179.7(2)
C(11)-C(10)-C(15)-C(14)	-1.2(5)	C(34)-N(4)-C(36)-C(35)	5.6(3)
N(1)-C(10)-C(15)-C(14)	-179.8(3)	C(37)-N(4)-C(36)-C(35)	-178.9(2)
Ti(1)-O(3)-C(16)-C(17)	65.7(4)	N(3)-C(35)-C(36)-N(4)	-4.7(3)
Ti(1)-O(3)-C(16)-C(18)	-58.7(4)	C(34)-N(4)-C(37)-C(38)	173.0(3)
Ti(1)-O(4)-C(19)-C(24)	109.6(5)	C(36)-N(4)-C(37)-C(38)	-1.9(4)
Ti(1)-O(4)-C(19)-C(20)	-72.5(6)	C(34)-N(4)-C(37)-C(42)	-7.2(4)
O(4)-C(19)-C(20)-C(21)	-178.5(2)	C(36)-N(4)-C(37)-C(42)	178.0(3)
C(24)-C(19)-C(20)-C(21)	-0.6(4)	C(42)-C(37)-C(38)-C(39)	1.0(5)
O(4)-C(19)-C(20)-C(26)	0.7(4)	N(4)-C(37)-C(38)-C(39)	-179.2(3)
C(24)-C(19)-C(20)-C(26)	178.6(2)	C(37)-C(38)-C(39)-C(40)	0.2(5)
C(19)-C(20)-C(21)-C(22)	1.8(4)	C(38)-C(39)-C(40)-C(41)	-1.2(5)
C(26)-C(20)-C(21)-C(22)	-177.4(3)	C(39)-C(40)-C(41)-C(42)	1.1(5)
C(20)-C(21)-C(22)-C(23)	-1.3(4)	Ti(2)-O(6)-C(42)-C(41)	-155.4(2)
C(20)-C(21)-C(22)-C(25)	179.5(3)	Ti(2)-O(6)-C(42)-C(37)	23.8(4)
C(21)-C(22)-C(23)-C(24)	-0.6(4)	C(40)-C(41)-C(42)-O(6)	179.2(3)

C(40)-C(41)-C(42)-C(37)	0.0(4)	C(53)-C(54)-C(55)-C(56)	0.4(4)
C(38)-C(37)-C(42)-O(6)	179.7(3)	C(53)-C(54)-C(55)-C(58)	-179.7(3)
N(4)-C(37)-C(42)-O(6)	-0.1(4)	C(54)-C(55)-C(56)-C(57)	0.5(4)
C(38)-C(37)-C(42)-C(41)	-1.1(4)	C(58)-C(55)-C(56)-C(57)	-179.4(3)
N(4)-C(37)-C(42)-C(41)	179.1(3)	C(55)-C(56)-C(57)-C(52)	0.0(4)
C(34)-N(3)-C(43)-C(44)	-5.2(4)	C(55)-C(56)-C(57)-C(63)	179.9(3)
C(35)-N(3)-C(43)-C(44)	177.7(3)	O(8)-C(52)-C(57)-C(56)	-179.7(2)
C(34)-N(3)-C(43)-C(48)	174.5(3)	C(53)-C(52)-C(57)-C(56)	-1.4(4)
C(35)-N(3)-C(43)-C(48)	-2.5(4)	O(8)-C(52)-C(57)-C(63)	0.4(4)
Ti(2)-O(5)-C(44)-C(45)	-176.0(2)	C(53)-C(52)-C(57)-C(63)	178.7(2)
Ti(2)-O(5)-C(44)-C(43)	4.3(5)	C(54)-C(53)-C(59)-C(62)	5.4(4)
C(48)-C(43)-C(44)-O(5)	-179.8(3)	C(52)-C(53)-C(59)-C(62)	-178.4(3)
N(3)-C(43)-C(44)-O(5)	0.0(4)	C(54)-C(53)-C(59)-C(60)	-112.3(3)
C(48)-C(43)-C(44)-C(45)	0.6(4)	C(52)-C(53)-C(59)-C(60)	63.9(3)
N(3)-C(43)-C(44)-C(45)	-179.7(3)	C(54)-C(53)-C(59)-C(61)	124.2(3)
O(5)-C(44)-C(45)-C(46)	-179.7(3)	C(52)-C(53)-C(59)-C(61)	-59.6(3)
C(43)-C(44)-C(45)-C(46)	-0.1(4)	C(56)-C(57)-C(63)-C(64)	122.2(3)
C(44)-C(45)-C(46)-C(47)	-0.4(5)	C(52)-C(57)-C(63)-C(64)	-57.9(3)
C(45)-C(46)-C(47)-C(48)	0.3(5)	C(56)-C(57)-C(63)-C(66)	-114.7(3)
C(46)-C(47)-C(48)-C(43)	0.2(5)	C(52)-C(57)-C(63)-C(66)	65.2(3)
C(44)-C(43)-C(48)-C(47)	-0.7(5)	C(56)-C(57)-C(63)-C(65)	3.9(4)
N(3)-C(43)-C(48)-C(47)	179.6(3)	C(52)-C(57)-C(63)-C(65)	-176.2(3)
Ti(2)-O(7)-C(49)-C(51)	85.2(3)	C(1S)-C(2S)-C(3S)-C(3S)#1	-64.7(19)
Ti(2)-O(7)-C(49)-C(50)	-151.6(2)	C(7S)-C(8S)-C(9S)-C(10S)	177.0(6)
Ti(2)-O(8)-C(52)-C(53)	67.6(6)	C(8S)-C(9S)-C(10S)-C(11S)	178.0(6)
Ti(2)-O(8)-C(52)-C(57)	-114.0(5)	C(9S)-C(10S)-C(11S)-C(12S)	176.4(6)
O(8)-C(52)-C(53)-C(54)	-179.4(2)	C(13S)-C(14S)-C(15S)-C(16S)	-178.4(4)
C(57)-C(52)-C(53)-C(54)	2.2(4)	C(14S)-C(15S)-C(16S)-C(17S)	-68.2(5)
O(8)-C(52)-C(53)-C(59)	4.2(4)	C(15S)-C(16S)-C(17S)-C(18S)	-176.4(4)
C(57)-C(52)-C(53)-C(59)	-174.1(2)		
C(52)-C(53)-C(54)-C(55)	-1.7(4)		
C(59)-C(53)-C(54)-C(55)	174.7(3)		

Symmetry transformations used to generate equivalent atoms:

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

Table S10. Coupling of propylene oxide (PO) and styrene oxide (SO) with CO_2 catalyzed by NHC-Ti complexes[a]

Run	Complex/Cocat. (equiv.)[b]	Epoxide	Conv.[c] (%)	Carbonate linkage[c] (%)	Selectivity[c] cyclic carbonate (%)	TOF[d] (h^{-1})
1	**1**/[PPN]Cl (1)	PO	10	99	99	10
2	**2**/[PPN]Cl (1)	PO	15	99	99	15
3	**3**/[PPN]Cl (1)	PO	6	99	99	7
4	**1**/[PPN]Cl (1)	SO	5	99	99	5
5	**2**/[PPN]Cl (1)	SO	7	99	99	7
6	**3**/[PPN]Cl (1)	SO	2	99	99	2

[a] Polymerization procedure: 8 µmol of precursor, 20 mmol of monomer, P_{CO2} < 1 bar at 60 °C for 24 h. [b] Catalyst pre-formation 15 min in CH_2Cl_2 at 30 °C and dried 2 h under vacuum. [c] Determined by ^{1}H NMR spectroscopy of the crude product in chloroform-*d*. [d] Turnover frequency = $mol_{CHO}\ mol_{Ti}^{-1}\ h^{-1}$.

Calculated absolute energies

Table S11. Calculated absolute energies with the PBE-D3BJ functional.

T = 298.15 K	Hartree				
	G_{corr} [a]	$E_{solvent}$ [b]	$\Delta G^{1atm\rightarrow 1M}$ [c]	G^{nodisp} [d]	G [e]
THF	8.53E-002	-232.2678682	0.003011906	-232.2586416	-232.1795762
3	0.284436543	-1550.427047	0.003011906	-1550.36224	-1550.139598
3-THF	0.393684118	-1782.711542	0.003011906	-1782.625587	-1782.314846
3'-μ-Cl	0.597851299	-3100.875134	0.003011906	-3100.711724	-3100.27427
3'-μ-O*i*Pr	0.599229402	-3100.879455	0.003011906	-3100.709639	-3100.277214
3''-μ-Cl/Cl	0.596663489	-3100.868752	0.003011906	-3100.71831	-3100.269076
3''-μ-Cl/O*i*Pr	0.597831544	-3100.866494	0.003011906	-3100.710409	-3100.265651
3''-μ-O*i*Pr/O*i*Pr	0.598431419	-3100.871029	0.003011906	-3100.711537	-3100.269585

[a] Gas-phase-calculated thermochemical correction due to translation, rotation and vibration. [b] The SCF energy of the SMD SP calculation. [c] The correction to change standard state from 1 atm to 1 M infinitely diluted solution. [d] $G^{nodisp} = G - E_{disp}$, E_{disp} is the Grimme D3(BJ) dispersion correction, which is included in $E_{solvent}$. [e] The total Gibbs free energy, obtained as $G = E_{solvent} + G_{corr} + \Delta G^{1atm\rightarrow 1M}$.

Table S12. Calculated absolute energies with the M06-D3 functional.

T = 298.15 K	Hartree				
	G_{corr} [a]	$E_{solvent}$ [b]	$\Delta G^{1atm\rightarrow 1M}$ [c]	G^{nodisp} [d]	G [e]
THF	8.53E-002	-232.3966389	0.003011906	-232.3959064	-232.308347
3	0.284436543	-1551.053933	0.003011906	-1551.043895	-1550.766484
3-THF	0.393684118	-1783.473523	0.003011906	-1783.458389	-1783.076827
3'-μ-Cl	0.597851299	-3102.140236	0.003011906	-3102.107447	-3101.539373
3'-μ-O*i*Pr	0.599229402	-3102.149996	0.003011906	-3102.114847	-3101.547754
3''-μ-Cl/Cl	0.596663489	-3102.127979	0.003011906	-3102.099948	-3101.528304
3''-μ-Cl/O*i*Pr	0.597831544	-3102.128357	0.003011906	-3101.497282	-3101.533475
3''-μ-O*i*Pr/O*i*Pr	0.598431419	-3102.134318	0.003011906	-3101.501214	-3101.532875

[a] Gas-phase-calculated thermochemical correction due to translation, rotation and vibration. [b] The SCF energy of the SMD SP calculation. [c] The correction to change standard state from 1 atm to 1 M infinitely diluted solution. [d] $G^{nodisp} = G - E_{disp}$, E_{disp} is the Grimme D3 dispersion correction, which is included in $E_{solvent}$. [e] The total Gibbs free energy, obtained as $G = E_{solvent} + G_{corr} + \Delta G^{1atm\rightarrow 1M}$.

Table S13. Calculated absolute energies with the M06L-D3 functional:

T=298.15 K	Hartree				
	G_{corr} [a]	$E_{solvent}$ [b]	$\Delta G^{1atm\rightarrow 1M}$ [c]	G^{nodisp} [d]	G [e]
THF	8.53E-002	-232.520169	0.003011906	-232.431727	-232.431877
3	0.284436543	-1551.701921	0.003011906	-1551.410375	-1551.414473
3-THF	0.393684118	-1784.245791	0.003011906	-1783.842575	-1783.849095
3'-μ-Cl	0.597851299	-3103.43535	0.003011906	-3102.819840	-3102.834494
3'-μ-O*i*Pr	0.599229402	-3103.44417	0.003011906	-3102.826396	-3102.841929
3''-μ-Cl/Cl	0.596663489	-3103.426907	0.003011906	-3102.814336	-3102.827232
3''-μ-Cl/O*i*Pr	0.597831544	-3103.426813	0.003011906	-3102.812196	-3102.825969
3''-μ-O*i*Pr/O*i*Pr	0.598431419	-3103.433617	0.003011906	-3102.817738	-3102.832174

[a] Gas-phase-calculated thermochemical correction due to translation, rotation and vibration. [b] The SCF energy of the SMD SP calculation. [c] The correction to change standard state from 1 atm to 1 M infinitely diluted solution. [d] $G^{nodisp} = G - E_{disp}$, E_{disp} is the Grimme D3 dispersion correction, which is included in $E_{solvent}$. [e] The total Gibbs free energy, obtained as $G = E_{solvent} + G_{corr} + \Delta G^{1atm\rightarrow 1M}$.

Table S14. Calculated absolute energies with the PBE-D3M(BJ) functional:

T=298.15 K	Hartree			
	G_{corr} [a]	$E_{solvent}$ [b]	$\Delta G^{1atm\rightarrow 1M}$ [c]	G [d]
THF	8.53E-002	-232,269619	0.003011906	-232,181327
3	0.284436543	-1550,454530	0.003011906	-1550,167081
3-THF	0.393684118	-1782,743418	0.003011906	-1782,346722
3'-μ-Cl	0.597851299	-3100,940091	0.003011906	-3100,339228
3'-μ-O*i*Pr	0.599229402	-3100,944943	0.003011906	-3100,342702
3''-μ-Cl/Cl	0.596663489	-3100,932594	0.003011906	-3100,332918
3''-μ-Cl/O*i*Pr	0.597831544	-3100,932303	0.003011906	-3100,331459
3''-μ-O*i*Pr/O*i*Pr	0.598431419	-3100,937430	0.003011906	-3100,335987

[a] Gas-phase-calculated thermochemical correction due to translation, rotation and vibration. [b] The SCF energy of the SMD SP calculation. [c] The correction to change standard state from 1 atm to 1 M infinitely diluted solution. [d] The total Gibbs free energy, obtained as $G = E_{solvent} + G_{corr} + \Delta G^{1atm\rightarrow 1M}$.

Table S15. Calculated absolute energies with the B3LYP-D3M(BJ) functional:

T=298.15 K	Hartree				
	G_{corr} [a]	$E_{solvent}$ [b]	$\Delta G^{1atm\rightarrow 1M}$ [c]	G^{nodisp} [d]	G [e]
THF	8.53E-002	-232.581028	0.003011906	-232.481759	-232.492736
3	0.284436543	-1551.959338	0.003011906	-1551.533936	-1551.671889
3-THF	0.393684118	-1784.563781	0.003011906	-1783.989374	-1784.167085
3'-μ-Cl	0.597851299	-3103.956119	0.003011906	-3103.020059	-3103.355255
3'-μ-O*i*Pr	0.599229402	-3103.964905	0.003011906	-3103,017092	-3103.362664
3''-μ-Cl/Cl	0.596663489	-3103.943344	0.003011906	-3103.028749	-3103.343669
3''-μ-Cl/O*i*Pr	0.597831544	-3103.944785	0.003011906	-3103.018964	-3103.343941
3''-μ-O*i*Pr/O*i*Pr	0.598431419	-3103.952879	0.003011906	-3103.021208	-3103.351436

[a] Gas-phase-calculated thermochemical correction due to translation, rotation and vibration. [b] The SCF energy of the SMD SP calculation. [c] The correction to change standard state from 1 atm to 1 M infinitely diluted solution. [d] $G^{nodisp} = G - E_{disp}$, E_{disp} is the Grimme D3 dispersion correction with the revised damping parameters, which is included in $E_{solvent}$. [e] The total Gibbs free energy, obtained as $G = E_{solvent} + G_{corr} + \Delta G^{1atm\rightarrow 1M}$.

Calculated relatives energies:

Table S16. Calculated relative Gibbs free energies for the coordination of THF to **3**.

kcal mol^{-1}	With E_{disp}					Without E_{disp}				
	PBE-D3(BJ)	M06-D3	M06L-D3	PBE-D3M(BJ)	B3LYP-D3M(BJ)	PBE	M06	M06L	PBE-D3M(BJ)	B3LYP-D3M(BJ)
ΔG_r [a]	2.7	-1.3	-1.7	1.1	-1.5	10.2	1.5	-0.3	5.1	16.5

[a] ΔG_r = G(**3-THF**) –G(**3**) –G(**THF**).

Table S17. Calculated relative Gibbs free energies of dimerization, including E_{disp}.[a]

kcal mol^{-1}	$\Delta G_{r,\mathbf{3}}$[b]					$\Delta G_{r,\mathbf{3\text{-}THF}}$[c]				
	PBE D3(BJ)	M06 D3	M06L D3	PBE D3M(BJ)	B3LYP D3M(BJ)	PBE D3(BJ)	M06 D3	M06L D3	PBE D3M(BJ)	B3LYP D3M(BJ)
3'-μ-Cl	3.1	-4.0	-3.5	-3.2	-7.2	-2.3	-1.5	0.0	-5.3	-4.1
3'-μ-O*i*Pr	1.2	-9.3	-8.1	-5.4	-11.9	-4.2	-6.8	-4.7	-7,5	-8.8
3''-μ-Cl/Cl	6.4	2.9	1.1	0.8	0.1	0.9	5.4	4.5	-1,3	3.2
3''-μ-Cl/O*i*Pr	8.5	3.4	1.9	1.7	-0.1	3.1	5.9	5.3	-0,4	3.0
3''-μ-O*i*Pr/O*i*Pr	6.0	0.1	-2.0	-1.1	-4.8	0.6	2.6	1.4	-3,3	-1.7

[a] E_{disp} is the Grimme D3(BJ) for PBE, D3M(BJ) for PBE and B3LYP, D3 for M06 and M06L dispersion correction, which is included in $E_{solvent}$. [b] $\Delta G_{r,\mathbf{3}}$ = G(dimer) – 2·G(**3**), [c] $\Delta G_{r,\mathbf{3\text{-}THF}}$ = G(dimer)+ 2·G(THF) – 2·G(**3-THF**).

Table S18. Calculated relative Gibbs free energies of dimerization, excluding E_{disp}.[a]

kcal mol^{-1}	$\Delta G^{nodisp}_{r,\mathbf{3}}$[b]				$\Delta G^{nodisp}_{r,\mathbf{3-THF}}$[c]			
	PBE	M06	M06L	B3LYP	PBE	M06	M06L	B3LYP
3'-μ-Cl	24.3	4.0	0.6	30.0	3.9	1.0	1.2	-3.0
3'-μ-O*i*Pr	26.5	0.2	-3.5	31.9	6.1	-2.8	-2.9	-1.2
3''-μ-Cl/Cl	19.4	7.9	4.0	24.6	-1.0	4.9	4.6	-8.5
3''-μ-Cl/O*i*Pr	25.1	9.8	5.4	30.7	4.7	6.8	6.0	-2.3
3''-μ-O*i*Pr/O*i*Pr	24.8	7.3	1.9	29.3	4.4	4.4	2.5	-3.8

[a] E_{disp} is the Grimme D3(BJ) for PBE, D3M(BJ) for PBE and B3LYP, D3 for M06 and M06L dispersion correction, which is included in $E_{solvent}$. [b] $\Delta G^{nodisp}_{r,\mathbf{3}} = G^{nodisp}(\text{dimer}) - 2\,G^{nodisp}(\mathbf{3})$, [c] $\Delta G^{nodisp}_{r,\mathbf{3-THF}} = G^{nodisp}(\text{dimer}) + 2 \cdot G^{nodisp}(\text{THF}) - 2 \cdot G^{nodisp}(\mathbf{3-THF})$.

Sample input files

Input file for geometry optimization of **3**:

%mem=25GB

%chk=complex1_opt

PBEPBE/gen EmpiricalDispersion=GD3BJ opt=(calcfc,maxcycle=180)

int=UltraFine nosymm SCF=(vshift=300) pseudo=read

gfinput gfprint freq

Title,

0 1

Ti	0.859375	6.366195	10.327120
O	1.164549	6.666067	8.482577
O	1.218627	5.924311	12.134462
Cl	-0.678754	4.719852	10.042852
N	3.835941	6.110401	9.139588
N	3.906777	6.147376	11.337814
C	3.075180	6.202504	10.263064
C	5.269855	5.908553	9.439874
H	5.885056	6.633781	8.875619
H	5.570384	4.884667	9.136386
C	5.333639	6.114082	10.951999
H	5.851965	5.288972	11.475178
H	5.819497	7.069182	11.239254
C	3.543385	6.138214	12.697228
C	4.523923	6.232502	13.706605
H	5.581418	6.362074	13.441111
C	4.163581	6.169408	15.058370
H	4.941963	6.248054	15.829713
C	2.815438	6.002728	15.417817
H	2.528959	5.945445	16.477781
C	1.832301	5.911245	14.428124
H	0.770709	5.779191	14.678289
C	2.170318	5.987704	13.058008
C	3.390398	6.105901	7.801633
C	2.021972	6.393592	7.513016
C	1.599295	6.408602	6.164881
H	0.542182	6.636703	5.972232
C	2.496656	6.138312	5.128651
H	2.145736	6.150815	4.086744
C	3.841604	5.849033	5.417184
H	4.551951	5.630503	4.608006
C	4.284992	5.834844	6.745406
H	5.337043	5.600745	6.954550
O	0.075516	7.955308	10.600900
C	-0.906876	8.624808	11.400824
H	-0.554031	9.679661	11.476472
C	-1.018507	8.031045	12.804533
C	-2.234080	8.581394	10.642498
H	-2.120217	9.023714	9.634272
H	-3.017951	9.142985	11.190130
H	-2.565129	7.528416	10.527954
H	-0.047216	8.066708	13.334013
H	-1.348355	6.973267	12.755153
H	-1.761791	8.606239	13.392023

H 0

S 3 1.00

13.0100000 0.0196850

1.9620000 0.1379770

0.4446000 0.4781480

S 1 1.00

0.1220000 1.0000000

P 1 1.00

0.7270000 1.0000000

****

C 0

S 8 1.00

6665.0000000 0.0006920

1000.0000000 0.0053290

228.0000000 0.0270770

64.7100000 0.1017180

21.0600000 0.2747400

7.4950000 0.4485640

2.7970000 0.2850740

0.5215000 0.0152040

S 8 1.00

6665.0000000 -0.0001460

1000.0000000 -0.0011540

228.0000000 -0.0057250

64.7100000 -0.0233120

21.0600000 -0.0639550

7.4950000 -0.1499810

2.7970000 -0.1272620

0.5215000 0.5445290

S 1 1.00

0.1596000 1.0000000

P 3 1.00

9.4390000 0.0381090

2.0020000 0.2094800

0.5456000 0.5085570

P 1 1.00

0.1517000 1.0000000

D 1 1.00

0.5500000 1.0000000

****

N 0

S 8 1.00

9046.0000000 0.0007000

1357.0000000 0.0053890

309.3000000 0.0274060

87.7300000 0.1032070

28.5600000 0.2787230

10.2100000 0.4485400

3.8380000 0.2782380

0.7466000 0.0154400

S 8 1.00

9046.0000000 -0.0001530

1357.0000000 -0.0012080

309.3000000 -0.0059920

87.7300000 -0.0245440

28.5600000 -0.0674590

10.2100000 -0.1580780

3.8380000 -0.1218310

0.7466000 0.5490030

S 1 1.00

0.2248000 1.0000000

P 3 1.00

13.5500000 0.0399190

2.9170000 0.2171690

0.7973000 0.5103190

P 1 1.00

0.2185000 1.0000000

D 1 1.00

0.8170000 1.0000000

****

O 0

S 8 1.00

11720.0000000 0.0007100

1759.0000000 0.0054700

400.8000000 0.0278370

113.7000000 0.1048000

37.0300000 0.2830620

13.2700000 0.4487190

5.0250000 0.2709520

1.0130000 0.0154580

S 8 1.00

11720.0000000 -0.0001600

1759.0000000 -0.0012630

400.8000000 -0.0062670

113.7000000 -0.0257160

37.0300000 -0.0709240

13.2700000 -0.1654110

5.0250000 -0.1169550

1.0130000 0.5573680

S 1 1.00

0.3023000 1.0000000

P 3 1.00

17.7000000 0.0430180

3.8540000 0.2289130

1.0460000 0.5087280

P 1 1.00

0.2753000 1.0000000

D 1 1.00

1.1850000 1.0000000

****

Cl 0

S 11 1.00

127900.0000000 0.241153D-03

19170.0000000 0.187095D-02

4363.0000000 0.970827D-02

1236.0000000 0.393153D-01

403.6000000 0.125932D+00

145.7000000 0.299341D+00

56.8100000 0.421886D+00

23.2300000 0.237201D+00

6.6440000 0.191531D-01

2.5750000 -0.334792D-02

0.5371000 0.929883D-03

S 11 1.00

127900.0000000 -0.678922D-04

19170.0000000 -0.521836D-03

4363.0000000 -0.276513D-02

1236.0000000 -0.111537D-01

403.6000000 -0.385919D-01

145.7000000 -0.994848D-01

56.8100000 -0.201392D+00

23.2300000 -0.130313D+00

6.6440000 0.509443D+00

2.5750000 0.610725D+00

0.5371000 0.421549D-01

S 11 1.00

127900.0000000 0.204986D-04

19170.0000000 0.158298D-03

4363.0000000 0.833639D-03

1236.0000000 0.339880D-02

403.6000000 0.116738D-01

145.7000000 0.309622D-01

56.8100000 0.629533D-01

23.2300000 0.460257D-01

6.6440000 -0.219312D+00

2.5750000 -0.408773D+00

0.5371000 0.638465D+00

S 1 1.00

0.1938000 1.0000000

P 7 1.00

417.6000000 0.525982D-02

98.3300000 0.398332D-01

31.0400000 0.164655D+00

11.1900000 0.387322D+00

4.2490000 0.457072D+00

1.6240000 0.151636D+00

0.5322000 0.181615D-02

P 7 1.00

417.6000000 -0.143570D-02

98.3300000 -0.107796D-01

31.0400000 -0.470075D-01

11.1900000 -0.111030D+00

4.2490000 -0.153275D+00

1.6240000 0.894609D-01

0.5322000 0.579444D+00

P 1 1.00

0.1620000 1.0000000

D 1 1.00

0.6000000 1.0000000

****

Ti 0

S 3 1.00

10.7803650 1.7838920

9.7170130 -2.0006890

4.5077550 -0.7563330

S 1 1.00

1.2467080 1.0

S 1 1.00

0.5087070 1.0

S 1 1.00

0.0734380 1.0

S 1 1.00

0.0300480 1.0

S 1 1.00

0.0100000 1.0

P 2 1.00

17.5663810 0.0886010

7.7058440 -1.0707460

P 2 1.00

3.3291380 0.2001090

1.3081040 0.8379860

P 1 1.00

0.4544820 1.0

P 1 1.00

0.0717720 1.0

P 1 1.00

0.0237840 1.0

D 4 1.00

19.5191940 0.0358140

5.8646130 0.1723730

1.9280380 0.4251360

0.6065630 0.6025950

D 1 1.00

0.1639610 1.0

D 1 1.00

0.0500000 1.0

******

Ti 0

ECP10MDF 3 10

F-Komponente

1

2 1.000000 0.000000

S-F

2

2 13.010000 158.241593

2 5.862000 17.511824

P-F

2

2 12.460000 95.235127

2 5.217000 10.047856

D-F

2

2 15.350000 -17.568861

2 4.980000 -0.587256

Input file for SP calculation of **3** with PBEGD3BJ functional:

%mem=25GB

%chk=complex3_SP

#P PBEPBE/gen EmpiricalDispersion=GD3BJ SP guess=read geom=check

#P int=UltraFine nosymm SCF=(vshift=300,conver=5) pseudo=read

#P gfinput gfprint scrf=(solvent=TetraHydroFuran,smd)

Title,

0 1

H 0

S 3 1.00

82.6400000 0.0020060

12.4100000 0.0153430

2.8240000 0.0755790

S 1 1.00

0.7977000 1.0000000

S 1 1.00

0.2581000 1.0000000

S 1 1.00

0.0898900 1.0000000

P 1 1.00

2.2920000 1.0000000

P 1 1.00

0.8380000 1.0000000

P 1 1.00

0.2920000 1.0000000

D 1 1.00

2.0620000 1.0000000

D 1 1.00

0.6620000 1.0000000

F 1 1.00

1.3970000 1.0000000

****

C 0

S 9 1.00

33980.0000000 0.0000910

5089.0000000 0.0007040

1157.0000000 0.0036930

326.6000000 0.0153600

106.1000000 0.0529290

38.1100000 0.1470430

14.7500000 0.3056310

6.0350000 0.3993450

2.5300000 0.2170510

S 9 1.00

33980.0000000 -0.0000190

5089.0000000 -0.0001510

1157.0000000 -0.0007850

326.6000000 -0.0033240

106.1000000 -0.0115120

38.1100000 -0.0341600

14.7500000 -0.0771730

6.0350000 -0.1414930

2.5300000 -0.1180190

S 1 1.00

0.7355000 1.0000000

S 1 1.00

0.2905000 1.0000000

S 1 1.00

0.1111000 1.0000000

P 3 1.00

34.5100000 0.0053780

7.9150000 0.0361320

2.3680000 0.1424930

P 1 1.00

0.8132000 1.0000000

P 1 1.00

0.2890000 1.0000000

P 1 1.00

0.1007000 1.0000000

D 1 1.00

1.8480000 1.0000000

D 1 1.00

0.6490000 1.0000000

D 1 1.00

0.2280000 1.0000000

F 1 1.00

1.4190000 1.0000000

```
F   1   1.00
0.4850000          1.0000000
G   1   1.00
1.0110000          1.0000000
****
N    0
S   9   1.00
45840.0000000           0.0000920
6868.0000000           0.0007170
1563.0000000           0.0037490
442.4000000           0.0155320
144.3000000           0.0531460
52.1800000           0.1467870
20.3400000           0.3046630
8.3810000           0.3976840
3.5290000           0.2176410
S   9   1.00
45840.0000000          -0.0000200
6868.0000000          -0.0001590
1563.0000000          -0.0008240
442.4000000          -0.0034780
144.3000000          -0.0119660
52.1800000          -0.0353880
20.3400000          -0.0800770
8.3810000          -0.1467220
3.5290000          -0.1163600
S   1   1.00
1.0540000          1.0000000
S   1   1.00
0.4118000          1.0000000
S   1   1.00
0.1552000          1.0000000
S   1   1.00
0.0546400          1.0000000
P   3   1.00
49.3300000           0.0055330
11.3700000           0.0379620
3.4350000           0.1490280
P   1   1.00
1.1820000          1.0000000
P   1   1.00
0.4173000          1.0000000
P   1   1.00
0.1428000          1.0000000
P   1   1.00
0.0440200          1.0000000
D   1   1.00
2.8370000          1.0000000
D   1   1.00
0.9680000          1.0000000
D   1   1.00
0.3350000          1.0000000
D   1   1.00
0.1110000          1.0000000
F   1   1.00
2.0270000          1.0000000
F   1   1.00
0.6850000          1.0000000
F   1   1.00
0.2450000          1.0000000
```

```
G   1   1.00
1.4270000          1.0000000
G   1   1.00
0.5590000          1.0000000
****
O    0
S   9   1.00
61420.0000000           0.0000900
9199.0000000            0.0006980
2091.0000000            0.0036640
590.9000000             0.0152180
192.3000000             0.0524230
69.3200000              0.1459210
26.9700000              0.3052580
11.1000000              0.3985080
4.6820000               0.2169800
S   9   1.00
61420.0000000          -0.0000200
9199.0000000           -0.0001590
2091.0000000           -0.0008290
590.9000000            -0.0035080
192.3000000            -0.0121560
69.3200000             -0.0362610
26.9700000             -0.0829920
11.1000000             -0.1520900
4.6820000              -0.1153310
S   1   1.00
1.4280000          1.0000000
S   1   1.00
0.5547000          1.0000000
S   1   1.00
0.2067000          1.0000000
S   1   1.00
0.0695900          1.0000000
P   3   1.00
63.4200000           0.0060440
14.6600000           0.0417990
4.4590000            0.1611430
P   1   1.00
1.5310000          1.0000000
P   1   1.00
0.5302000          1.0000000
P   1   1.00
0.1750000          1.0000000
P   1   1.00
0.0534800          1.0000000
D   1   1.00
3.7750000          1.0000000
D   1   1.00
1.3000000          1.0000000
D   1   1.00
0.4440000          1.0000000
D   1   1.00
0.1540000          1.0000000
F   1   1.00
2.6660000          1.0000000
F   1   1.00
0.8590000          1.0000000
F   1   1.00
0.3240000          1.0000000
```

G 1 1.00

1.8460000 1.0000000

G 1 1.00

0.7140000 1.0000000

****

Cl 0

S 13 1.00

834900.0000000 0.231688D-04

125000.0000000 0.180154D-03

28430.0000000 0.947782D-03

8033.0000000 0.400139D-02

2608.0000000 0.144629D-01

933.9000000 0.456586D-01

360.0000000 0.123248D+00

147.0000000 0.264369D+00

62.8800000 0.382989D+00

27.6000000 0.270934D+00

11.0800000 0.471404D-01

5.0750000 -0.371766D-02

2.2780000 0.219158D-02

S 13 1.00

834900.0000000 -0.649649D-05

125000.0000000 -0.504895D-04

28430.0000000 -0.266113D-03

8033.0000000 -0.112499D-02

2608.0000000 -0.410497D-02

933.9000000 -0.131987D-01

360.0000000 -0.375342D-01

147.0000000 -0.897233D-01

62.8800000 -0.167671D+00

27.6000000 -0.174763D+00

11.0800000 0.114909D+00

5.0750000 0.563618D+00

2.2780000 0.441606D+00

S 13 1.00

834900.0000000 0.196645D-05

125000.0000000 0.152620D-04

28430.0000000 0.806086D-04

8033.0000000 0.339960D-03

2608.0000000 0.124551D-02

933.9000000 0.399612D-02

360.0000000 0.114751D-01

147.0000000 0.275504D-01

62.8800000 0.532917D-01

27.6000000 0.571246D-01

11.0800000 -0.395201D-01

5.0750000 -0.264343D+00

2.2780000 -0.349291D+00

S 1 1.00

0.7775000 1.0000000

S 1 1.00

0.3527000 1.0000000

S 1 1.00

0.1431000 1.0000000

S 1 1.00

0.0519000 1.0000000

P 8 1.00

1703.0000000 0.474039D-03

403.6000000 0.406412D-02

130.3000000 0.213355D-01

49.0500000 0.794611D-01
20.2600000 0.208927D+00
8.7870000 0.364945D+00
3.9190000 0.371725D+00
1.7650000 0.146292D+00
P 8 1.00
1703.0000000 -0.128266D-03
403.6000000 -0.109356D-02
130.3000000 -0.583429D-02
49.0500000 -0.219258D-01
20.2600000 -0.601385D-01
8.7870000 -0.106929D+00
3.9190000 -0.122454D+00
1.7650000 0.383619D-01
P 1 1.00
0.7207000 1.0000000
P 1 1.00
0.2839000 1.0000000
P 1 1.00
0.1060000 1.0000000
P 1 1.00
0.0376000 1.0000000
D 1 1.00
0.2540000 1.0000000
D 1 1.00
0.6280000 1.0000000
D 1 1.00
1.5510000 1.0000000
D 1 1.00
0.0952000 1.0000000
F 1 1.00
0.4230000 1.0000000
F 1 1.00
1.0890000 1.0000000
F 1 1.00
0.2170000 1.0000000
G 1 1.00
0.8270000 1.0000000
G 1 1.00
0.3780000 1.0000000
****
Ti 0
S 3 1.00
10.7803650 1.7838920
9.7170130 -2.0006890
4.5077550 -0.7563330
S 1 1.00
1.2467080 1.0
S 1 1.00
0.5087070 1.0
S 1 1.00
0.0734380 1.0
S 1 1.00
0.0300480 1.0
S 1 1.00
0.0100000 1.0
P 2 1.00
17.5663810 0.0886010
7.7058440 -1.0707460
P 2 1.00

3.3291380 0.2001090

1.3081040 0.8379860

P 1 1.00

0.4544820 1.0

P 1 1.00

0.0717720 1.0

P 1 1.00

0.0237840 1.0

D 4 1.00

19.5191940 0.0358140

5.8646130 0.1723730

1.9280380 0.4251360

0.6065630 0.6025950

D 1 1.00

0.1639610 1.0

D 1 1.00

0.0500000 1.0

F 1 1.00

1.2640000 1.0

F 1 1.00

0.2850000 1.0

G 1 1.00

0.6360000 1.0

*****

Ti 0

ECP10MDF 3 10

F-Komponente

1

2 1.000000 0.000000

S-F

2

2 13.010000 158.241593

2 5.862000 17.511824

P-F

2

2 12.460000 95.235127

2 5.217000 10.047856

D-F

2

2 15.350000 -17.568861

2 4.980000 -0.587256

Optimized Cartesian coordinates

3

Ti	0.596783	6.076487	10.027413
O	1.027058	6.226433	8.196202
O	0.823737	5.614734	11.849987
Cl	-1.020195	4.496573	9.713868
N	3.679568	6.161374	9.114697
N	3.534293	6.129415	11.312474
C	2.808368	6.107196	10.159092
C	5.093063	6.178741	9.550256
H	5.618055	7.041427	9.098197
H	5.596706	5.250144	9.213309
C	4.985436	6.278076	11.070893
H	5.540501	5.478246	11.596881
H	5.330574	7.256225	11.462847
C	3.052819	6.028728	12.631590
C	3.922355	6.186303	13.731301
H	4.981244	6.426232	13.570728
C	3.448291	6.046548	15.041250
H	4.141584	6.176152	15.883304
C	2.096501	5.739736	15.269389

H	1.720811	5.623911	16.295866
C	1.222966	5.583850	14.189259
H	0.160242	5.346081	14.333835
C	1.676715	5.734143	12.859948
C	3.376019	6.140599	7.738178
C	2.015043	6.171092	7.314567
C	1.730402	6.154962	5.931118
H	0.672644	6.177707	5.636358
C	2.759740	6.112004	4.987172
H	2.516162	6.100376	3.915318
C	4.100149	6.083244	5.407467
H	4.915786	6.047553	4.672633
C	4.404775	6.097959	6.773794
H	5.457009	6.071091	7.084399
O	-0.011810	7.747428	10.272846
C	-0.649722	8.579207	11.250523
H	-1.090548	9.422246	10.669944
C	0.400718	9.136098	12.212346
C	-1.770374	7.820745	11.959850
H	-2.490755	7.412775	11.224434
H	-2.314162	8.497505	12.649684
H	-1.355077	6.975134	12.543591
H	1.213802	9.637008	11.650841
H	0.840112	8.324871	12.827239
H	-0.060113	9.878745	12.895021

THF

C	-0.597061	-0.528449	0.023255
C	-0.156717	0.952062	0.025675
C	-2.148494	-0.433864	0.011371
C	-2.405272	1.088980	0.003429
O	-1.246623	1.679462	0.592014
H	-0.242164	-1.045669	0.935829
H	-0.193612	-1.076477	-0.850542
H	0.041758	1.299918	-1.019794
H	0.741978	1.159250	0.638087
H	-3.284432	1.406166	0.596800
H	-2.538132	1.455040	-1.046249
H	-2.576993	-0.899494	0.920147
H	-2.602696	-0.933016	-0.866791

3_THF

Ti	0.809107	10.726117	10.923360
O	0.756026	10.874054	9.037572
O	0.297308	10.755953	12.742916
Cl	1.801283	12.807795	11.179831
N	-1.840567	11.890233	9.542504
N	-1.886046	12.250263	11.713438
C	-1.165657	11.694838	10.703615
C	-3.140691	12.565216	9.747095
H	-3.967043	11.863853	9.510539
H	-3.223951	13.441357	9.076640
C	-3.096866	12.947734	11.228027
H	-2.985655	14.039888	11.386009
H	-3.986522	12.602384	11.787840
C	-1.570756	12.234452	13.086548
C	-2.356726	12.960137	14.006134
H	-3.192325	13.576585	13.650425
C	-2.081665	12.915359	15.377705
H	-2.705178	13.493325	16.073266
C	-1.013457	12.135968	15.853196
H	-0.793085	12.096291	16.929408
C	-0.223508	11.413650	14.955839
H	0.624571	10.801276	15.292013
C	-0.474833	11.451543	13.565629
C	-1.426214	11.510137	8.250634
C	-0.097833	11.028757	8.038728
C	0.305408	10.715319	6.720183
H	1.338036	10.366587	6.585070
C	-0.576462	10.842158	5.643896
H	-0.239250	10.587169	4.629028
C	-1.889390	11.293712	5.860935
H	-2.593458	11.390913	5.023456
C	-2.305925	11.629644	7.154610
H	-3.333066	11.984968	7.309017
Ti	1.574208	7.646402	10.708566
O	1.837796	7.722136	8.848522
O	1.861726	7.369197	12.549904
Cl	0.498254	5.582382	10.464540
N	3.972535	5.943590	9.445201
N	4.124952	5.928188	11.640276
C	3.430581	6.439587	10.589307
C	5.065058	4.980692	9.702959
H	5.973514	5.271868	9.142219
H	4.753849	3.971020	9.366114
C	5.251602	5.069634	11.217868
H	5.188371	4.085335	11.719625
H	6.211660	5.546470	11.503050
C	3.894736	6.173472	13.008560
C	4.799461	5.699090	13.981231
H	5.695130	5.142689	13.676591
C	4.577638	5.934857	15.343242
H	5.297807	5.556532	16.081400

C	3.441804	6.652410	15.754784
H	3.262809	6.840597	16.822942
C	2.535441	7.128471	14.804327
H	1.637398	7.693354	15.090025
C	2.738016	6.901866	13.423743
C	3.527458	6.169693	8.127452
C	2.450623	7.072781	7.870301
C	2.036937	7.278678	6.534658
H	1.195457	7.966146	6.374749
C	2.664070	6.620005	5.474748
H	2.320155	6.791387	4.444782
C	3.726124	5.735973	5.729061
H	4.226242	5.210209	4.904321
C	4.150746	5.514376	7.043993
H	4.977393	4.815460	7.223598
O	-0.028665	8.833752	10.859081
O	2.415667	9.536130	10.899813
C	-1.389478	8.583490	11.316573
H	-1.809880	9.582868	11.559832
C	-1.404991	7.749271	12.593069
C	-2.184789	7.987339	10.158818
H	-2.146916	8.658069	9.277256
H	-3.244680	7.850578	10.457472
H	-1.770373	7.002438	9.867648
H	-0.787771	8.235585	13.371751
H	-1.013044	6.730036	12.413555
H	-2.446832	7.668839	12.965311
C	3.769985	10.029399	10.686976
C	4.281958	9.670632	9.296438
C	4.664673	9.535717	11.819055
H	3.692586	11.134616	10.756827
H	4.464186	8.583068	9.192992
H	5.238747	10.199771	9.110007
H	3.552169	9.978475	8.524428
H	4.802308	8.437588	11.773826
H	4.225278	9.790337	12.802478
H	5.663213	10.012908	11.745048

3'-μ-Cl

Ti	-0.191178	9.854560	10.225722
Ti	-2.831090	8.265555	12.083313
O	-0.255406	10.288756	8.391201
O	-0.988003	9.628418	12.081006
O	0.998490	11.071044	10.780077
Cl	-2.391429	8.453288	9.709516
Cl	0.976763	7.870989	10.225162
O	-3.892729	9.862517	12.131672
O	-1.639577	6.912801	12.562876
O	-4.296811	7.212747	11.997589
N	-2.408998	11.929448	9.227252
N	-2.065990	12.137018	11.383784
N	-3.558550	9.519867	14.930676
N	-1.975181	8.004021	15.137983
C	-1.720519	11.434532	10.277243
C	-3.404151	12.944553	9.640972
H	-4.422374	12.505401	9.586003
H	-3.360531	13.825110	8.973793
C	-2.981216	13.256444	11.081198
H	-2.436697	14.221532	11.159515
H	-3.829186	13.259524	11.791282
C	-1.531477	11.914778	12.665316
C	-1.579007	12.916809	13.653075
H	-2.070145	13.874903	13.436443
C	-0.987993	12.709162	14.907621
H	-1.027165	13.505773	15.663349
C	-0.321457	11.501986	15.173625
H	0.193179	11.353228	16.134610
C	-0.293962	10.487410	14.204959
H	0.224343	9.534412	14.380501
C	-0.933153	10.656371	12.963062
C	-2.288265	11.494392	7.891592
C	-1.177908	10.681029	7.508196
C	-1.054927	10.301817	6.155283
H	-0.194514	9.674038	5.886769
C	-1.999079	10.702798	5.204115
H	-1.883068	10.389123	4.156927
C	-3.092280	11.496084	5.587349
H	-3.842797	11.809067	4.848756
C	-3.231812	11.889640	6.924340
H	-4.094375	12.502089	7.219434
C	1.485256	12.407154	10.703174
H	0.596650	13.073939	10.581392
C	2.384087	12.540759	9.474757
H	2.730283	13.587902	9.359473
H	1.834492	12.242166	8.560909
H	3.271164	11.883774	9.578229
C	2.187563	12.749774	12.015579
H	2.549185	13.798147	11.996803
H	3.057570	12.079482	12.168044
H	1.496094	12.628005	12.871938
C	-2.788850	8.630377	14.250512
C	-3.292273	9.507564	16.384487
H	-4.194552	9.165827	16.930736
H	-3.035428	10.529740	16.722486

C	-2.121104	8.533589	16.510055
H	-1.181828	9.042971	16.806022
H	-2.314685	7.707458	17.220301
C	-0.935105	7.095489	14.844090
C	-0.033153	6.690460	15.851026
H	-0.142845	7.064396	16.876924
C	1.017034	5.813065	15.555452
H	1.710878	5.513923	16.352893
C	1.181648	5.330124	14.246092
H	2.014092	4.653450	14.006774
C	0.290642	5.712286	13.240253
H	0.397364	5.369535	12.203007
C	-0.781928	6.584579	13.521418
C	-4.513810	10.403945	14.394652
C	-4.652698	10.540382	12.979016
C	-5.635692	11.429472	12.483297
H	-5.750790	11.484577	11.391074
C	-6.437778	12.187366	13.343512
H	-7.195922	12.867006	12.928509
C	-6.277733	12.066879	14.733131
H	-6.899146	12.654834	15.421996
C	-5.325891	11.178124	15.249126
H	-5.222492	11.084688	16.337661
C	-5.663135	7.399185	11.619370
H	-5.773990	8.439750	11.234127
C	-5.988720	6.409499	10.502687
H	-7.030368	6.553383	10.150195
H	-5.877079	5.367381	10.864753
H	-5.301663	6.559134	9.647418
C	-6.541838	7.227017	12.857529
H	-7.610157	7.366950	12.595041
H	-6.274526	7.974254	13.631207
H	-6.412984	6.211351	13.284202

3'-μ-O*i*Pr

Ti	-0.177865	9.858643	10.229403
Ti	-2.634108	8.240639	11.829220
O	-0.358578	10.296185	8.393821
O	-0.874006	9.616742	12.110893
O	0.982378	11.138929	10.735227
O	-1.834915	8.526269	10.070573
Cl	1.262369	8.032850	10.111780
O	-3.793323	9.740783	11.701545
O	-1.490525	6.919413	12.484468
Cl	-4.422682	6.822575	11.744818
N	-2.389622	12.029908	9.372958
N	-1.955818	12.165780	11.516525
N	-3.627097	9.641784	14.535380
N	-2.138384	8.082704	14.980936
C	-1.695488	11.467217	10.382447
C	-3.260937	13.139583	9.825755
H	-4.324462	12.837846	9.749637
H	-3.098428	14.032009	9.192365
C	-2.823742	13.339950	11.281609
H	-2.241872	14.274738	11.422431
H	-3.675297	13.331969	11.988372
C	-1.402174	11.884159	12.778672
C	-1.425973	12.848813	13.805237
H	-1.905787	13.820725	13.630597
C	-0.826719	12.588503	15.046097
H	-0.847157	13.359324	15.828963
C	-0.177428	11.362864	15.265484
H	0.337943	11.169307	16.217736
C	-0.171241	10.385541	14.259162
H	0.327804	9.416485	14.398471
C	-0.811680	10.611230	13.027302
C	-2.344420	11.625434	8.022030
C	-1.296546	10.765406	7.569715
C	-1.262894	10.409560	6.203890
H	-0.445933	9.750969	5.878352
C	-2.233533	10.872812	5.309022
H	-2.185361	10.574876	4.251965
C	-3.264045	11.711958	5.760966
H	-4.034030	12.077114	5.067938
C	-3.312696	12.087382	7.109949
H	-4.125001	12.738639	7.459402
C	1.453993	12.473296	10.801468
H	0.558302	13.139543	10.873617
C	2.212037	12.797515	9.513434
H	2.545564	13.855129	9.513016
H	1.565831	12.625240	8.630617
H	3.103115	12.144259	9.422142
C	2.298122	12.646770	12.063600
H	2.654077	13.693597	12.150566
H	3.179916	11.975617	12.026237
H	1.705493	12.398004	12.965322
C	-2.021675	7.694696	8.877914
H	-1.241237	8.041083	8.168555
C	-1.766419	6.224400	9.196407
H	-1.804913	5.636090	8.257123
H	-2.532102	5.820631	9.888470
H	-0.765427	6.102363	9.650245
C	-3.403029	7.965745	8.290250
H	-3.525042	7.401270	7.343519

H	-3.534109	9.042417	8.068811
H	-4.198989	7.645316	8.992684
C	-2.825057	8.693888	13.983564
C	-3.500803	9.709081	16.007265
H	-4.475124	9.473806	16.479616
H	-3.193999	10.730504	16.304465
C	-2.428394	8.662916	16.309653
H	-1.504319	9.116702	16.719487
H	-2.774976	7.871592	17.001731
C	-1.135225	7.100459	14.849270
C	-0.413632	6.662193	15.980332
H	-0.642172	7.068057	16.973811
C	0.604218	5.709627	15.854148
H	1.153271	5.385228	16.748585
C	0.921325	5.182397	14.590544
H	1.728911	4.444339	14.485347
C	0.212844	5.599644	13.461815
H	0.441873	5.222310	12.456505
C	-0.826382	6.549575	13.569098
C	-4.530453	10.486942	13.866525
C	-4.609718	10.473559	12.440109
C	-5.580377	11.285498	11.807921
H	-5.658573	11.202837	10.714667
C	-6.408230	12.138407	12.544903
H	-7.155602	12.758271	12.029121
C	-6.285737	12.190685	13.943598
H	-6.922730	12.860969	14.536508
C	-5.360795	11.364639	14.594861
H	-5.294476	11.402821	15.689338

3''-μ-Cl/Cl

Ti	1.294059	11.015649	10.803504
O	0.957046	10.779399	8.962953
O	1.026007	11.163791	12.656361
O	2.241299	12.536787	10.634028
N	-1.488027	12.034509	9.635716
N	-1.522069	12.075040	11.839188
C	-0.753052	11.795761	10.754887
C	-2.837008	12.554247	9.943379
H	-3.604248	11.922209	9.456499
H	-2.939228	13.588061	9.555777
C	-2.893763	12.484848	11.469335
H	-3.142093	13.457596	11.935084
H	-3.614359	11.726703	11.837099
C	-1.209400	11.839285	13.195802
C	-2.172588	12.068934	14.200323
H	-3.166431	12.452816	13.937454
C	-1.883089	11.807295	15.545251
H	-2.651665	11.990659	16.308414
C	-0.620617	11.308612	15.906438
H	-0.390721	11.094140	16.959938
C	0.348365	11.084863	14.924699
H	1.345976	10.694785	15.169099
C	0.079777	11.351653	13.564162
C	-1.129764	11.761634	8.299952
C	0.096179	11.091267	8.006286
C	0.400831	10.783199	6.661207
H	1.346627	10.257459	6.471098
C	-0.468479	11.137367	5.624913
H	-0.209068	10.889268	4.585697
C	-1.665202	11.813146	5.914174
H	-2.352959	12.103664	5.108359
C	-1.990409	12.120888	7.241446
H	-2.928114	12.652146	7.449133
C	2.868914	13.377976	9.663730
H	3.505630	14.078999	10.252320
C	1.808784	14.190544	8.917243
H	2.293766	14.943846	8.263558
H	1.153594	14.722331	9.635329
H	1.182175	13.532247	8.282644
C	3.760721	12.557438	8.731758
H	4.315337	13.228447	8.044547
H	3.149880	11.854156	8.132235
H	4.491783	11.967019	9.317615
Ti	1.159614	7.107168	10.876180
O	1.304775	7.281357	9.003562
O	1.619026	7.021146	12.695238
O	0.200954	5.583947	10.856838
N	3.803083	6.033803	9.462217
N	4.068607	6.075196	11.649852
C	3.190137	6.317626	10.642612
C	5.175405	5.516644	9.645986
H	5.888878	6.122767	9.055499
H	5.232350	4.467390	9.291900
C	5.393695	5.646277	11.153359
H	5.690756	4.691939	11.628472
H	6.148602	6.416022	11.412130
C	3.899817	6.361522	13.022115
C	4.963541	6.167069	13.927733
H	5.925291	5.772600	13.576117
C	4.815919	6.477820	15.285206
H	5.660647	6.321258	15.969803
C	3.597021	6.991065	15.758347
H	3.478214	7.243854	16.821689

C	2.530007	7.180632	14.876086
H	1.562636	7.580887	15.209411
C	2.655279	6.864433	13.505433
C	3.305869	6.257522	8.162286
C	2.058141	6.925734	7.974112
C	1.613793	7.183932	6.657708
H	0.655213	7.709490	6.548147
C	2.366859	6.782854	5.549938
H	1.999563	6.992628	4.535094
C	3.584831	6.109107	5.737121
H	4.181978	5.781990	4.875057
C	4.047832	5.850468	7.033589
H	5.000124	5.319985	7.161669
C	-0.522832	4.710299	9.987659
H	-1.098789	4.035926	10.663516
C	0.455625	3.863687	9.170837
H	-0.094439	3.092835	8.593624
H	1.174654	3.350960	9.840034
H	1.021136	4.494837	8.456308
C	-1.501933	5.499985	9.118807
H	-2.122988	4.806645	8.515750
H	-0.952979	6.177586	8.435749
H	-2.170375	6.115334	9.751884
Cl	-0.492684	8.825698	11.093751
Cl	2.962345	9.301215	10.903147

3''-μ-Cl/O*i*Pr

Ti	0.933372	10.623596	10.983239
O	0.868566	10.711495	9.083234
O	0.363492	10.596520	12.798470
O	1.806097	12.199109	11.177629
N	-1.684995	11.804687	9.590910
N	-1.651395	12.282449	11.740019
C	-0.990403	11.638074	10.744778
C	-2.953677	12.535163	9.797808
H	-3.810089	11.845263	9.648549
H	-3.041421	13.362998	9.069199
C	-2.832299	13.021330	11.244384
H	-2.646897	14.113319	11.314025
H	-3.720264	12.778901	11.857959
C	-1.304381	12.304695	13.108071
C	-1.978779	13.164030	13.999454
H	-2.743958	13.856148	13.623600
C	-1.679941	13.154911	15.367369
H	-2.214248	13.835956	16.043581
C	-0.701978	12.275596	15.861489
H	-0.463527	12.260609	16.934660
C	-0.023479	11.419059	14.989785
H	0.749948	10.724298	15.345177
C	-0.297776	11.418746	13.603602
C	-1.320668	11.335449	8.312109
C	-0.010914	10.806555	8.097737
C	0.345990	10.397495	6.793208
H	1.361092	10.002760	6.653950
C	-0.563673	10.481409	5.735121
H	-0.262100	10.150003	4.730925
C	-1.857423	10.983819	5.955422
H	-2.581570	11.047205	5.131946
C	-2.228460	11.412623	7.235840
H	-3.241701	11.803686	7.396915
C	2.420215	13.270034	10.466621
H	2.904071	13.914335	11.237618
C	1.344435	14.089312	9.747849
H	1.794823	14.982068	9.268685
H	0.574769	14.431286	10.468852
H	0.854051	13.478146	8.963541
C	3.491011	12.731780	9.516496
H	4.017737	13.570100	9.016528
H	3.027245	12.083223	8.747271
H	4.233250	12.128909	10.074596
Ti	1.188651	7.155106	10.598188
O	1.405296	7.404038	8.745771
O	1.503974	6.767831	12.409028
Cl	0.062244	5.200048	10.256176
N	3.839929	6.039531	9.231077
N	4.031235	5.971004	11.423303
C	3.201950	6.301038	10.400320
C	5.172791	5.434445	9.437222
H	5.938308	5.996401	8.869438
H	5.166188	4.386181	9.074702
C	5.362001	5.533691	10.951378
H	5.635396	4.566849	11.414423
H	6.121300	6.289247	11.239750
C	3.780456	6.116488	12.801510
C	4.797995	5.861164	13.744120
H	5.799821	5.564388	13.408530
C	4.552442	5.987987	15.116577
H	5.362503	5.786792	15.830788
C	3.279269	6.372148	15.569525
H	3.081597	6.473704	16.646098
C	2.260518	6.629485	14.648739
H	1.255378	6.937917	14.966903
C	2.487265	6.511060	13.259768
C	3.337350	6.228753	7.928933

C	2.104192	6.919854	7.727919
C	1.623770	7.084736	6.409242
H	0.662003	7.600773	6.289488
C	2.343259	6.601076	5.313041
H	1.947262	6.738399	4.296631
C	3.564893	5.937277	5.512974
H	4.139617	5.553172	4.659170
C	4.053940	5.751736	6.811765
H	5.002809	5.218229	6.951975
O	-0.030691	8.675740	10.852618
Cl	2.901014	9.179831	11.015450
C	-1.428616	8.548266	11.247522
H	-1.744739	9.578323	11.520144
C	-1.587702	7.679701	12.492850
C	-2.258013	8.083666	10.052636
H	-2.100800	8.753057	9.184133
H	-3.336697	8.085827	10.313651
H	-1.976750	7.054206	9.752791
H	-0.944994	8.063953	13.307218
H	-1.314569	6.624700	12.293689
H	-2.644730	7.707061	12.828185

3''-μ- O*i*Pr /O*i*Pr

Ti	0.809107	10.726117	10.923360
O	0.756026	10.874054	9.037572
O	0.297308	10.755953	12.742916
Cl	1.801283	12.807795	11.179831
N	-1.840567	11.890233	9.542504
N	-1.886046	12.250263	11.713438
C	-1.165657	11.694838	10.703615
C	-3.140691	12.565216	9.747095
H	-3.967043	11.863853	9.510539
H	-3.223951	13.441357	9.076640
C	-3.096866	12.947734	11.228027
H	-2.985655	14.039888	11.386009
H	-3.986522	12.602384	11.787840
C	-1.570756	12.234452	13.086548
C	-2.356726	12.960137	14.006134
H	-3.192325	13.576585	13.650425
C	-2.081665	12.915359	15.377705
H	-2.705178	13.493325	16.073266
C	-1.013457	12.135968	15.853196
H	-0.793085	12.096291	16.929408
C	-0.223508	11.413650	14.955839
H	0.624571	10.801276	15.292013
C	-0.474833	11.451543	13.565629
C	-1.426214	11.510137	8.250634
C	-0.097833	11.028757	8.038728
C	0.305408	10.715319	6.720183
H	1.338036	10.366587	6.585070
C	-0.576462	10.842158	5.643896
H	-0.239250	10.587169	4.629028
C	-1.889390	11.293712	5.860935
H	-2.593458	11.390913	5.023456
C	-2.305925	11.629644	7.154610
H	-3.333066	11.984968	7.309017
Ti	1.574208	7.646402	10.708566
O	1.837796	7.722136	8.848522
O	1.861726	7.369197	12.549904
Cl	0.498254	5.582382	10.464540
N	3.972535	5.943590	9.445201
N	4.124952	5.928188	11.640276
C	3.430581	6.439587	10.589307
C	5.065058	4.980692	9.702959
H	5.973514	5.271868	9.142219
H	4.753849	3.971020	9.366114
C	5.251602	5.069634	11.217868
H	5.188371	4.085335	11.719625
H	6.211660	5.546470	11.503050
C	3.894736	6.173472	13.008560
C	4.799461	5.699090	13.981231
H	5.695130	5.142689	13.676591
C	4.577638	5.934857	15.343242
H	5.297807	5.556532	16.081400
C	3.441804	6.652410	15.754784
H	3.262809	6.840597	16.822942
C	2.535441	7.128471	14.804327
H	1.637398	7.693354	15.090025
C	2.738016	6.901866	13.423743
C	3.527458	6.169693	8.127452
C	2.450623	7.072781	7.870301
C	2.036937	7.278678	6.534658
H	1.195457	7.966146	6.374749
C	2.664070	6.620005	5.474748
H	2.320155	6.791387	4.444782
C	3.726124	5.735973	5.729061
H	4.226242	5.210209	4.904321
C	4.150746	5.514376	7.043993
H	4.977393	4.815460	7.223598
O	-0.028665	8.833752	10.859081
O	2.415667	9.536130	10.899813
C	-1.389478	8.583490	11.316573
H	-1.809880	9.582868	11.559832
C	-1.404991	7.749271	12.593069

C	-2.184789	7.987339	10.158818
H	-2.146916	8.658069	9.277256
H	-3.244680	7.850578	10.457472
H	-1.770373	7.002438	9.867648
H	-0.787771	8.235585	13.371751
H	-1.013044	6.730036	12.413555
H	-2.446832	7.668839	12.965311
C	3.769985	10.029399	10.686976
C	4.281958	9.670632	9.296438
C	4.664673	9.535717	11.819055
H	3.692586	11.134616	10.756827
H	4.464186	8.583068	9.192992
H	5.238747	10.199771	9.110007
H	3.552169	9.978475	8.524428
H	4.802308	8.437588	11.773826
H	4.225278	9.790337	12.802478
H	5.663213	10.012908	11.745048