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# Syntheses of Tungsten t-Butylimido and Adamantylimido Alkylidene Complexes Employing Pyridinium Chloride as the Acid

Hyangsoo Jeong,[‡] Jonathan C. Axtell,[‡] Béla Török,[†] Richard R. Schrock,*[,‡] Peter Müller[‡]

[‡] Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139; [†] Department of Chemistry, University of Massachusetts Boston, Boston, Massachusetts 02125.

*RECEIVED DATE (automatically inserted by publisher);* ***rrs@mit.edu***

**ABSTRACT:** Routes to new tungsten alkylidene complexes that contain t-butylimido or adamantylimido ligands have been devised that begin with a reaction between $WCl_6$ and four equivalents of HNR(TMS) to give $[W(NR)_2Cl(\mu\text{-}Cl)(RNH_2)]_2$ (R = t-Bu or 1-adamantyl). Alkylation leads to $W(NR)_2(CH_2R')_2$ (R' = t-Bu or $CMe_2Ph$) which upon treatment with pyridinium chloride yields $W(NR)(CHR')Cl_2py_2$ complexes, from which $W(NR)(CHR')(Pyrrolide)_2$ and two W(NR)(CHR')(Pyrrolide)(OAr) complexes (OAr = hexamethyl- or hexaisopropylterphenoxide) have been prepared.

Olefin metathesis catalyzed by well-defined Mo, W, Ru catalysts is the only way to prepare olefins from olefins catalytically and with a high degree of control.[1] Arylimido ligands usually have been employed in high oxidation state imido alkylidene complexes of molybdenum and tungsten, especially aryls that are mono- or disubstituted in the ortho position(s).[2] However, it has become clear that (i) adamantylimido alkylidene complexes of molybdenum often are the catalysts of choice in some circumstances such as *Z*-selective ring-opening metathesis reactions,[3] and (ii) tungsten arylimido alkylidene complexes are often more selective than molybdenum complexes for *Z*- selective reactions.[4] However, no *tungsten-based alkylimido* alkylidene complexes have been reported to our knowledge. Therefore, we were compelled to explore routes to tungsten t-butylimido or adamantylimido alkylidene complexes.

A logical starting material for the synthesis of t-butylimido alkylidene complexes of tungsten would be W(N-t-Bu)$_2$Cl$_2$(DME). However, attempts to prepare W(N-t-Bu)$_2$Cl$_2$(DME) through reactions between $WO_2Cl_2$(DME), t-butylamine, $Me_3SiCl$, and $NEt_3$ under conditions analogous to those employed to prepare W(NAryl)$_2$Cl$_2$(DME) and Mo(NAryl)$_2$Cl$_2$(DME) complexes[2] have failed so far in our hands; similar reactions to synthesize the 1-adamantyl analogue, including conditions in which an *N*-sulfinylamine is employed as the imido source,[5] were also unsuccessful. As far as we are aware, W(N-t-Bu)$_2$Cl$_2$(DME) is still unknown, although adducts such as W(N-t-Bu)$_2$Cl$_2$(pyridine)$_2$ have been reported (*vide infra*).[6]

In 1987 Nielson[7] found that addition of four equivalents of t-BuNH(TMS) to $WCl_6$ gave a compound with the formula W(N-t-Bu)$_2$(t-BuNH$_2$)Cl$_2$.[8] This compound has also been prepared in 30% yield in a reaction between $WO_2Cl_2$(DME) and t-BuNH(TMS) in heptane or dimethoxyethane.[9] On the basis of IR studies and by analogy with {W(N-t-Bu)(μ-NPh)(t-BuNH$_2$)Cl$_2$}$_2$ and {W(N-t-Bu)(μ-Ntolyl)(t-BuNH$_2$)Cl$_2$}$_2$,[10] W(N-t-Bu)$_2$Cl$_2$(t-BuNH$_2$) was proposed to be a dimer that contains bridging t-butylimido groups. We have confirmed that W(N-t-Bu)$_2$(t-BuNH$_2$)Cl$_2$ can be prepared conveniently on a 15 g scale as described by Nielson, but have found through an X-ray structural study that it contains bridging chlorides, not bridging imido groups, as has been assumed in the literature. The structure of $[W(N\text{-}t\text{-}Bu)_2Cl(\mu\text{-}Cl)(t\text{-}BuNH_2)]_2$ (**1a**, Figure 1) can be viewed as essentially two square pyramids with

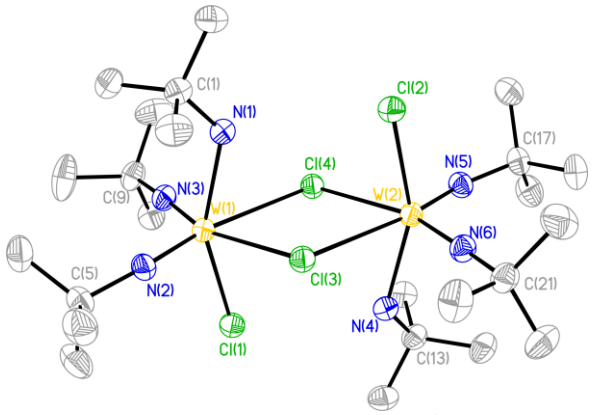



**Figure 1.** Thermal ellipsoid drawing (50%) of **1a**. Selected bond distances (Å) and angles(°): W(1)-Cl(1) = 2.3942(6), W(1)-Cl(3) = 2.6104(6), W(1)-Cl(4) = 2.8063(6), W(1)-N(1) = 2.210(2), W(1)-N(2) = 1.754(2), W(1)-N(3) = 1.743(2), W(1)-N(1)-C(1) = 126.63(15), W(1)-N(2)-C(5) = 159.36(18), W(1)-N(3)-C(9) = 177.24(19), W(1)-Cl(3)-W(2) = 106.72(2), W(1)-Cl(4)-W(2) = 106.14(2).

slightly bent imido groups in the apical positions (those that contain N(2) and N(5) in Figure 1) "joined" through relatively long W-Cl bridges (e.g., W(1)-Cl(4) = 2.8063(6) Å). However, the N(1)···Cl(2) and N(4)···Cl(1) distances (3.34 Å) are in the range observed when a hydrogen bond is present between an NH proton and chloride (N···Cl = 3.30 Å).[11] Also, one proton on each amine nitrogen points toward the terminal chloride on the neighboring tungsten (e.g., H···Cl(1) = 2.448 Å). Therefore, we propose that two hydrogen bonds stabilize the structure of **1a** to a considerable degree. The fact that **1a** can be prepared in dimethoxyethane,[9] as noted earlier, attests to the integrity of the dimeric structure of **1a**, at least toward dimethoxyethane, although addition of nitrogen donors to **1a**, e.g., pyridine[6] or di-t-butyl-l,4-diaza-1,3-butadiene,[9] leads to formation of monomeric complexes of the type W(N-t-Bu)$_2$Cl$_2$L$_2$. The 1-adamantylimido analog of **1a** (**1b**) was prepared similarly and has a structure that is closely analogous to that of **1a** (see Supporting Information). Heating a solution of **1b** in DME at 120 ˚C for 24 h in a high pressure vessel results in neither replacement of the amines by dimethoxyethane nor decomposition of **1b**.

In spite of the presence of t-butylamine in **1a**, we find that it reacts cleanly with two equivalents of t-BuCH$_2$MgCl (per W) to give W(N-t-Bu)$_2$(CH$_2$-t-Bu)$_2$ (**2a**) in 87% yield. W(N-t-Bu)$_2$(CH$_2$-t-Bu)$_2$ so far has been obtained only as a light brown oil that becomes solid at ~ -20 °C. However, the analogous reaction between **1b** and $Me_2PhCCH_2MgCl$ yielded crystalline W(NAd)$_2$(CH$_2$CMe$_2$Ph)$_2$ (**2b**), an X-ray structural study of

which revealed the expected pseudotetrahedral structure shown

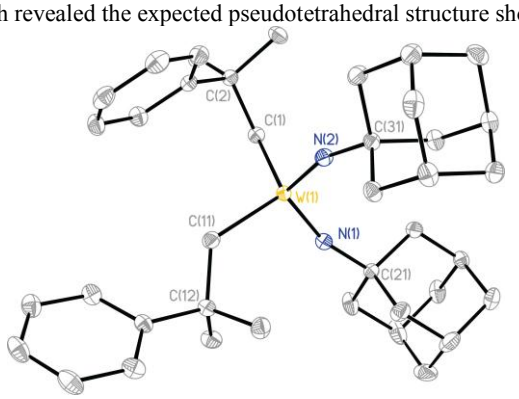
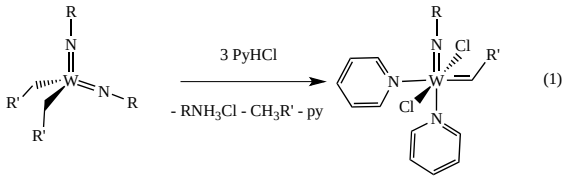



**Figure 2.** Thermal ellipsoid drawing (50%) of **2b**. Selected bond distances (Å) and angles (°): W(1)-N(1) = 1.7520(15), W(1)-N(2) = 1.7564(16), W(1)-C(1) = 2.1467(18), W(1)-C(11) = 2.1256(19), W(1)-N(1)-C(21) = 159.84(13), W(1)-N(2)-C(31) = 162.84(13), W(1)-C(1)-C(2) = 119.70(12), W(1)-C(11)-C(12) = 127.92(12).

in Figure 2. The neopentyl analogue of **2b** (**2c**) has also been synthesized and can be isolated as a solid in 53% yield.

Addition of three equivalents of triflic acid to **2a**, **2b,** or **2c** in a mixture of 1,2-dimethoxyethane and ether, which is the method employed to form M(NR)(CHR')$(OTf)_2$(DME) complexes of Mo and W,[2b] in our hands has not yet led to W(NR)(CHR)$(OTf)_2$(DME) complexes (R = t-Bu or Ad). We also found that triflic acid could not be employed to remove the t-butylimido group selectively from Mo(NAr*)(N-t-Bu)$(CH_2CMe_2Ph)_2$ (Ar* = 2,6-dimesitylphenyl) to give Mo(NAr*)$(CHCMe_2Ph)(OTf)_2$(DME).[12] Instead, three equivalents of 3,5-lutidinium chloride, was found to give Mo(NAr*)$(CHCMe_2Ph)Cl_2$(3,5-lutidine) in good yield. Therefore we turned to reactions employing pyridinium chloride, a mild acid compared to triflic acid. Addition of three equivalents of pyridinium chloride to **2a** or **2c** led to formation of W(NR)(CHR')$Cl_2(py)_2$ (R = t-Bu (**3a**) or 1-Ad (**3b**)) in good yield (equation 1).




(1)

R = t-Bu (**3a**, 64%) or adamantyl (**3b**, 75%)

An X-ray structural study of crystals obtained through recrystallization of **3a** from a mixture of methylene chloride and pentane showed the crystal to be [W(NR)(CHR')Cl(μ-Cl)py]$_2$ formed through loss of one pyridine from **3a** (Figure 3). The W=N and W=C bond lengths and W-N-C and W-C-C angles are normal, as are the terminal, approximately equal, and longer bridging W-Cl bond lengths. The W(1)-N(2) bond length (2.207(5) Å) is also within the expected range. In contrast, although a solid-state structure of **3b** has not been determined, there is no evidence for formation of a dimer analogous to **3a**.

The reaction between **3a** and two equivalents of lithium 2,5-dimethylpyrrolide led to formation of W(N-t-Bu)$(CHCMe_3)(2,5\text{-}Me_2pyr)_2$ (**4a**) in 58% isolated yield. We propose that the one pyrrolide is bound to the metal in **4a** in an $\eta^1$ fashion, while the other is bound in an $\eta^5$ fashion, as found in bispyrrolide complexes of this general type that do not contain donor ligands,[13] unless the pyrrolide cannot bind readily in an $\eta^5$ fashion, as in the case of 2-mesitylpyrrolide.[14] Compound **4a** was treated with 1 equivalent of HMTOH (2,6-(2,4,6-$Me_3C_6H_2)_2C_6H_3OH$) in benzene to generate the MAP complex, W(N-t-Bu)$(CHCMe_3)$(pyr)(OHMT) (**5a**).

An attempted synthesis of W(N-t-Bu)$(CHCMe_3)(pyr)_2$ (where pyr is the parent, unsubstituted pyrrolide) in a manner similar to that described for **4a** was not successful. Isolation and storage of parent bispyrrolide complexes of Mo has also

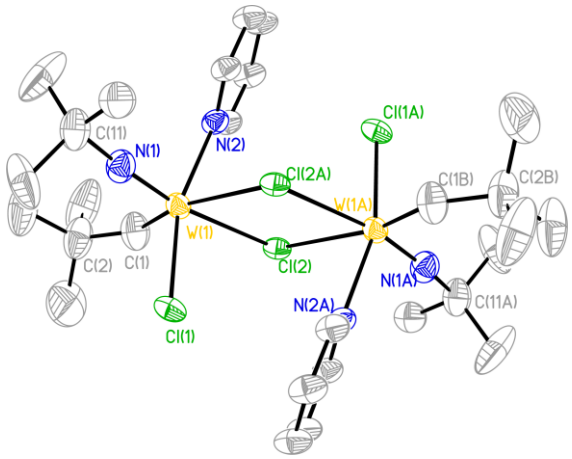
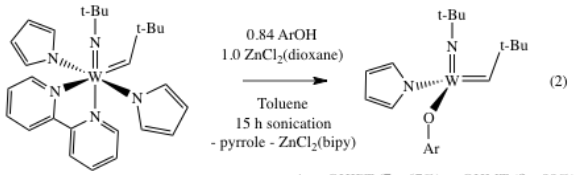



**Figure 3.** Thermal ellipsoid drawing (50%) of **3a**. Selected bond distances (Å) and angles(°) : W(1)-Cl(1) = 2.4056(13), W(1)-Cl(2) = 2.6085(13), W(1)-Cl(2A) = 2.6781(13), W(1)-N(1) = 1.687(6), W(1)-N(2) = 2.207(5), W(1)-C(1) = 1.928(8), W(1)-Cl(2)-W(1A) = 105.28(4), W(1)-N(1)-C(11) = 169.8(5), W(1)-C(1)-C(2) = 145.1(7).

been problematic, but a solution to their synthesis and use was provided through formation of 2,2'-bipyridine adducts as intermediates.[15] As in Mo chemistry, we find that W(N-t-Bu)$(CHCMe_3)(pyr)_2$(bipy) (**6a**) can be prepared in 83% yield. The $^1$H NMR spectrum of **6a** obtained in $CD_2Cl_2$ showed four alkylidene resonances at room temperature. However, after the sample was heated to 100 ºC overnight in $CD_2Cl_2$ in a sealed tube the $^1$H NMR spectrum at room temperature showed just one isomer to be present. Limited solubility of **6a** prevents the determination of whether the alkylidene is the *syn* or *anti* isomer.

Compound **6a** was treated with 1 equivalent of $ZnCl_2$(dioxane) and 0.84 equivalents of HIPTOH (2,6-(2,4,6-i-$Pr_3C_6H_2)_2C_6H_3OH$) in toluene and the mixture was placed in an ultrasonic sonicator for 16 h. The yellow-brown mixture was filtered through a pad of Celite and W(N-*t*-Bu)$(CHCMe_3)$(pyr)(OHIPT) (**7a**) isolated in good yield from the filtrate (eq 2). Exchange of the pyrrolide ligand with chloride is minimal during formation of **7a**. W(N-*t*-Bu)$(CHCMe_3)$(pyr)(OHMT) (**8a**) can be synthesized in an analogous manner.




(2)

Ar = OHIPT (**7a**, 67%) or OHMT (**8a**, 99%)

The solid state structure of **8a** was determined in an X-ray study (Figure 4). It is interesting to note that the distance between tungsten and the imido nitrogen is relatively short compared W-N distances in MAP complexes of arylimido tungsten species. Compound **8a** has W=N distance 1.670 Å, whereas several 2,6-diisopropylimido and 3,5-dimethylphenylimido MAP compounds have W=N distances of ~1.75-1.77 Å.[3, 16] We attribute this difference to the greater electron donating ability of the t-butylimido ligand compared

to arylimido ligands.

The use of pyridinium chloride as shown in equation 1 would be of significant benefit for the syntheses of the chloride analogs of known *arylimido* alkylidene bistriflate complexes. Although a cursory exploration has not looked promising, we have found that the addition of one equivalent of 2,2'-bipyridine to $W(NAr)_2(CH_2CMe_2Ph)_2$ (Ar = 2,6-$Me_2C_6H_3$, 2,6-i-$Pr_2C_6H_3$, 2,6-$Cl_2C_6H_3$, or 2-i-$PrC_6H_4$) complexes followed by two equivalents of HCl in diethyl ether led to formation of $W(NAr)(CHCMe_2Ph)Cl_2$(bipy) complexes **9a-12a** (equation 3). Compounds **9a-12a** are essentially insoluble and therefore isolated readily in good yields and high purity simply through

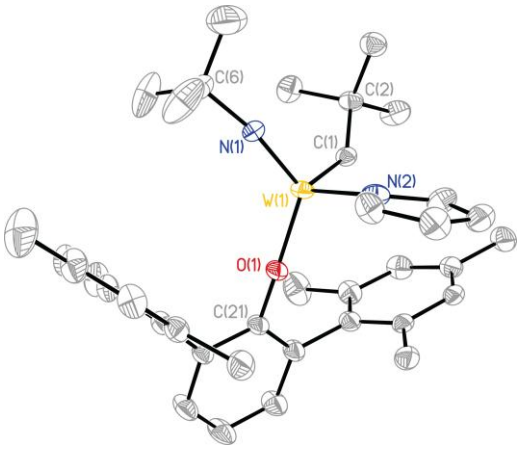
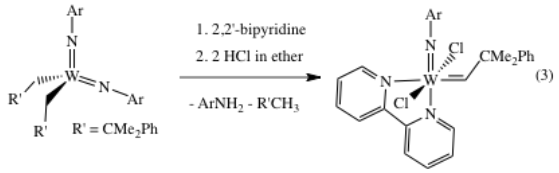



**Figure 4**. Thermal ellipsoid drawing (50%) of **8a**. Selected bond distances (Å) and angles(°): W(1)-N(1) = 1.670(3), W(1)-N(2) = 2.0214(16), W(1)-C(1) = 1.916(3), W(1)-O(1) = 1.8691(12), W(1)-N(1)-C(6) = 169.5(5), W(1)-C(1)-C(2) = 141.9(3), W(1)-O(1)-C(21) = 173.81(13), N(1)-W(1)-C(1) = 105.63(14), O(1)-W(1)-C(1) = 108.10(10), N(2)-W(1)-N(1) = 105.42(10), O(1)-W(1)-N(2) = 109.29(6), C(1)-W(1)-N(2) = 100.62(10), N(1)-W(1)-O(1) = 125.10(12).




Ar = 2,6-$Me_2C_6H_3$ (**9a**, 90%), 2,6-i-$Pr_2C_6H_3$ (**10a**, 60%), 2,6-$Cl_2C_6H_3$ (**11a**, 54%), 2-i-$PrC_6H_4$ (**12a**, 57%)

filtration. The aniline ($ArNH_2$) and alkane ($R'CH_3$) were the only byproducts observed (in high yields versus an internal standard) in $^1$H NMR spectra of the filtrates of the reaction mixtures from which ether had been removed *in vacuo*. Proton NMR spectra of **9a-12a** (in $CD_2Cl_2$) are consistent with the presence of two isomers, one that contains *trans* chlorides and another (out of two possible) that contains *cis* chlorides. A spectrum of $W(N\text{-}2,6\text{-}Me_2C_6H_3)(CHCMe_2Ph)Cl_2$(bipy), for example, has alkylidene α proton resonances at 11.29 ppm and 10.48 ppm for *cis* and *trans* isomers, respectively, the ratio of which varies with reaction conditions. Limited solubility of **9a-12a** in $CD_2Cl_2$ prevented confirmation (either by $^1$H or $^{13}$C NMR studies) of the proposal that the alkylidene in each case is the *syn* isomer.

We conclude that t-butylimido and adamantylimido alkylidene complexes of tungsten are now readily accessible from tungsten hexachloride, that pyridinium chloride can be employed to initiate an α abstraction reaction that generates the alkylidene, and that HCl can be employed in the presence of 2,2'-bipyridine to make several tungsten arylimido alkylidene complexes. Therefore, the use of $WCl_6$ and HCl in some form (in place of triflic acid) in order to prepare tungsten imido alkylidene complexes seems promising. We also are in the process of exploring the chemistry of hitherto unknown t-butylimido and adamantylimido alkylidene complexes of tungsten from a fundamental perspective and in terms of various applications that involve olefin metathesis reactions, especially metathesis reactions that are likely to be Z-selective.

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**Supporting Information Available.** Experimental details for the synthesis of all compounds and details of the X-ray structural studies. Supporting Information is available free of charge via the Internet at http://pubs.acs.org.

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Supporting Information for

# Synthesis of Tungsten t-Butylimido and Adamantylimido Alkylidene Complexes Employing Pyridinium Chloride as the Acid

Hyangsoo Jeong,[‡] Jonathan C. Axtell,[‡] Béla Török,[†] Richard R. Schrock,*[‡] Peter Müller[‡]



**Abbreviations**

t-Bu : tert-Butyl

Ad : 1-Adamantyl

Ar : 2,6-diisopropylphenyl

Ar' : 2,6-dimethylphenyl

$Ar^{Cl2}$ : 2,6-dichlorophenyl

$Ar^{iPr}$ : 2-isopropylphenyl

2,5-$Me_2$pyr : 2,5-dimethylpyrrolide

Pyr : pyrrolide

OHIPT : 2,6-bis-(2,4,6-triisopropylphenyl)-phenoxide

OHMT : 2,6-bis-(2,4,6-trimethylphenyl)-phenoxide

2,2'-bipy : 2,2'-bipyridine

DME : 1,2-dimethoxyethane

**Experimental Section**

**General.** All air and moisture sensitive materials were manipulated under a nitrogen atmosphere in a Vacuum Atmospheres glovebox or on a dual-manifold Schlenk line. All glassware, including NMR tubes, was oven-dried prior to use. Diethyl ether, pentane, toluene, dichloromethane, 1,2-dimethoxyethane, and benzene were degassed and passed through activated alumina columns and stored over 4 Å Linde-type molecular sieves prior to use. Deuterated solvents were dried over 4 Å Linde-type molecular sieves prior to use. $^{1}$H and $^{13}$C NMR spectra were acquired at room temperature using Varian 300MHz or 500MHz spectrometers. Chemical shifts for $^{1}$H and $^{13}$C spectra are reported as parts per million relative to tetramethylsilane and referenced to the residual $^{1}$H/$^{13}$C resonances of the deuterated solvent ($^{1}$H (δ) : benzene 7.16, chloroform 7.26, methylene chloride 5.32; $^{13}$C (δ) : benzene 128.06, chloroform 77.16, methylene chloride 53.84). *N*-t-butyltrimethylsilylamine was either prepared from TMSCl and *t*-BuNHLi in ether or purchased from Sigma-Aldrich. The synthesis of *N*-trimethylsilyl(1-adamantyl)amine has been reported previously;[i] our preparation employed the *n*-butyllithium and chlorotrimethylsilane. Pyridinium chloride was purchased from Sigma-Aldrich or Alfa Aesar and sublimed before use. Ethereal solutions of HCl were prepared by bubbling HCl gas into diethyl ether; these solutions were titrated before use. Neopentyl Grignard[ii], HMTOH[iii], HIPTOH[iv], and $ZnCl_2$(dioxane)[v] were prepared according to literature procedures. All other reagents were used as received.

**[W(N-t-Bu)$_2$Cl($\mu$-Cl)(t-BuNH$_2$)]$_2$ (1a).** The following procedure was adapted from a recent publication.[vi] A solution of *N*-t-butyltrimethylsilylamine (25 g, 172 mmol) in 30 mL toluene was added slowly over a period of 50 min to $WCl_6$ (15.2 g, 38.33 mmol) in 150 mL of toluene. The reaction mixture was stirred for 24 h at room temperature. The dark green mixture was filtered through a pad of Celite, and the solvent was removed from the filtrate *in vacuo*. Pentane was added and the yellow suspension was cooled at -30 °C and filtered to yield 12.03 g of the yellow product (67%). X-ray quality crystals were grown from a mixture of methylene chloride and pentane at -30 °C.

**[W(NAd)$_2$Cl($\mu$-Cl)(AdNH$_2$)]$_2$ (1b).** *N*-trimethylsilyl(1-adamantyl)amine (28.2 g, 126 mmol) was added to a stirred suspension of $WCl_6$ (12.51 g, 31.6 mmol) in benzene (400 mL) in a roundbottom flask. After 24 h, the mixture was filtered through Celite and the Celite pad was washed with methylene chloride. All volatile components wer removed from the filtrate *in vacuo*. The resulting tan solid (16.68 g, 75%) was washed on a glass frit with cold $Et_2O$ and dried *in vacuo*. A sample for elemental analysis was isolated from a concentrated solution in $Et_2O$ at -30 °C: $^{1}$H NMR (500 MHz, $C_6D_6$) δ 2.61 (s, 4H, $NH_2$), 2.26 (br s, 24H, $CH_2$), 2.07 (br s, 12H, CH), 1.94 (br s, 6H, CH), 1.86 (br s, 12H, ax/eq $CH_2$), 1.54 (m, 24H, ax/eq $CH_2$), 1.46 (br s, 12H, CH); $^{13}$C NMR (125Hz, $CD_2Cl_2$); 49.83, 45.32, 45.12, 43.58, 36.49, 36.41, 35.90, 30.20, 30.18, 30.00. Anal. Calcd for $C_{60}H_{94}Cl_4N_6W_2$ %C 51.15, %H 6.72, %N 5.96; Found %C 50.86, %H 6.47, %N 6.01.

**W(N-t-Bu)$_2$(CH$_2$-t-Bu)$_2$ (2a)** An ether solution of $Me_3CCH_2MgCl$ (2.83 M, 14.2 mL, 40.16 mmol) was added to a −30 °C solution of [W(N-t-Bu)$_2$Cl$_2$(H$_2$N-t-Bu)]$_2$ (9.44 g, 20.08 mmol) in 60 mL of diethyl ether. The reaction mixture was stirred for 6 h at room temperature. A white precipitate formed and the yellow solution turned to an ivory color. The mixture was filtered through a pad of Celite and the solvent was removed from the filtrate *in vacuo* to yield a brown oil. Pentane was added to the oil and the mixture was cooled to −30 °C. A light yellow powder was filtered off and a brown oil (8.20 g, 87%) was obtained: $^{1}$H NMR (500 MHz, $C_6D_6$) δ 1.55 (s, 4H, $CH_2$, $J_{WH}$ = 10 Hz), 1.44 (s, 18H, Me), 1.18 (s, 18H, Me); $^{13}$C NMR (125 MHz, $C_6D_6$) δ 84.59, 66.36, 34.62, 34.37, 33.50. Anal. Calcd for $C_{18}H_{40}N_2W$ %C 46.16, %H 8.61, %N 5.98; Found %C 45.94, %H 8.56, %N 5.87.

**W(NAd)$_2$(CH$_2$CMe$_2$Ph)$_2$ (2b).** A solution of [W(NAd)$_2$Cl($\mu$-Cl)(AdNH$_2$)]$_2$ (6.0 g, 8.18 mmol) in 60 mL of diethyl ether was chilled at -30 ˚C for 1 h. Ethereal $ClMgCH_2CMe_2Ph$ (0.5 M, 33.5 mL, 16.8 mmol) was added to the stirred mixture and the resulting mixture was allowed to stir for 6 h. The suspension was filtered over Celite and washed with ether. The filtrate was dried under vacuum and pentane was added to the residue. The resulting pale yellow solid (3.82 g, 56%) was isolated by filtration: $^{1}$H NMR (500 MHz, $C_6D_6$) δ 7.42 (d, 4H, Ar), 7.24 (t, 4H, Ar), 7.09 (t, 2H, Ar), 2.04 (br s, 6H, CH), 1.95 (d, 12H, $CH_2$), 1.58 (m, 6H, ax/eq $CH_2$), 1.57 (s, 4H, W$CH_2$), 1.56 (s, 12H, C$Me_2$Ph); $^{13}$C NMR (125 MHz, $C_6D_6$)

152.84, 128.51, 126.35, 125.78, 83.26, 67.07, 47.00, 40.41, 36.69, 34.07, 30.48. Anal. Calcd for $C_{40}H_{56}N_2W$ %C 64.17, %H 7.54, %N 3.74. Found %C 64.27, %H 7.57, %N 3.62.

**W(NAd)$_2$(CH$_2$-t-Bu)$_2$ (2c).** [W(NAd)$_2$Cl($\mu$-Cl)(AdNH$_2$)]$_2$ (3.62 g, 2.57 mmol) was added to 60 mL of diethyl ether and the solution was to -30˚C for 1 h. Ethereal $Me_3CCH_2MgCl$ (2.32 M, 4.98 mL, 11.6 mmol) was added to the stirred mixture and the whole was stirred for 6 h. The solvent was removed *in vacuo*, the residue was extracted with benzene, and the extract was filtered through Celite. Solvents were removed from the filtrate *in vacuo*. Cold ether was added to the product, and the pale product (1.71 g, 53%) was isolated by filtration: $^1$H NMR (500 MHz, $C_6D_6$) δ 2.11 (d, 12H, $CH_2$), 2.05 (br s, 6H, CH), 1.66 (s, 4H, WC*H*$_2$, $^2J_{WH}$ = 10.5 Hz), 1.58 (m, 12H, ax/eq $CH_2$); $^{13}$C NMR (125 MHz, $C_6D_6$) 84.42, 67.05, 47.40, 36.70, 34.79, 34.35, 30.51. Anal. Calcd for $C_{30}H_{52}N_2W$ %C 57.69, %H 8.39, %N 4.49. Found %C 57.66, %H 8.14, %N 4.39.

**W(N-t-Bu)(CH-t-Bu)Cl$_2$(py)$_2$ (3a)**. W(N-t-Bu)$_2$(CH$_2$-t-Bu)$_2$ (0.70 g, 1.49 mmol) was dissolved in ether (15 mL) and the solution was chilled at -30 ºC for 2 h. Pyridinium chloride (0.52 g, 4.46 mmol) was added and the mixture was allowed to stir at room temperature for 15 h. The color of the solution turned from yellow to brown and a precipitate formed. All volatile components were removed from the reaction mixture and the residue was extracted with a mixture of toluene and methylene chloride. The extract was filtered through a pad of Celite on a glass frit and all solvents removed from the filtrate to yield a yellow residue. Pentane was added and the yellow solid was collected; yield 0.53 g (64%): $^1$H NMR (500 MHz, $C_6D_6$) δ 11.86 (s, 1H, W=C*H*), 9.63 (d, 4H, py), 6.69 (t, 2H, py), 6.39 (t, 4H, py), 1.38 (s, 9H, Me), 1.34 (s, 9H, Me); $^{13}$C NMR (125 MHz, $C_6D_6$) δ 297.03, 156.69, 138.08, 123.78, 68.94, 43.70, 34.31, 30.98. The $^1$H NMR spectrum in $C_6D_6$ showed traces of [W(N-t-Bu)(CH-t-Bu)Cl$_2$(py)]$_2$. A pure sample of [W(N-t-Bu)(CH-t-Bu)Cl$_2$(py)]$_2$ was obtained by recrystallization from methylene chloride and pentane at -30 °C and an X-ray diffraction study was carried out: $^1$H NMR (500 MHz, $CD_2Cl_2$) δ 10.86 (s, 1H, W=C*H*), 8.78 (d, 2H, py), 7.98 (t, 2H, py), 7.54 (t, 2H, py), 1.34 (s, 9H, Me), 1.30 (s, 9H, Me). $^{13}$C NMR (125 MHz, $CD_2Cl_2$) δ 282.20, 154.72, 139.91, 125.98, 70.54, 44.02, 32.29, 30.78. Anal. Calcd for $C_{28}H_{48}Cl_4N_4W_2$ %C 35.39, %H 5.09, %N 5.90. Found %C 35.46, %H 5.15, %N 5.90.

**W(NAd)(CH-t-Bu)Cl$_2$(py)$_2$ (3b).** A solution of **2c** (3.84 g, 6.15 mmol) in ether was chilled to -30 ˚C. Pyridinium chloride (2.13 g, 18.4 mmol) was added and the mixture was stirred for 24 h. The resulting suspension was filtered through Celite and the filter cake was washed with toluene and methylene chloride. The filtrate was concentrated *in vacuo* and pentane was added in order to precipitate the yellow product (2.12 g, 75%): $^1$H NMR (500 MHz, $C_6D_6$) δ 11.88 (s, 1H, WC*H*), 9.70 (d, 4H, py), 6.68 (t, 2H, py), 6.41 (t, 4H, py), 2.20 (br s, 6H, $CH_2$), 1.90 (br s, 3H, CH), 1.42 (m, 6H, ax/eq $CH_2$), 1.40 (s, 9H, -t-Bu); $^{13}$C NMR (125 MHz, $CD_2Cl_2$) 299.21 ($^1J_{WC}$ = 155 Hz), 156.58, 138.93, 124.41, 70.63, 43.32, 43.25, 35.91, 33.79, 29.48. Anal. Calcd for $C_{25}H_{35}Cl_2N_3W$ %C 47.49, %H 5.58, %N 6.65. Found %C 47.49, %H 5.79, %N 6.54.

**W(N-t-Bu)(CH-t-Bu)(2,5-Me$_2$pyr)$_2$ (4a).** Solid Li-2,5-Me$_2$pyr (0.182 g, 1.80 mmol) was added portion-wise to a -30 ºC solution of W(N-t-Bu)(CH-t-Bu)Cl$_2$(py)$_2$ (0.499 g, 0.90 mmol) in toluene (40 mL). The reaction mixture was stirred for 15 h at room temperature. The solution became dark yellow. The reaction mixture was filtered through a pad of Celite on a glass frit and the solvents were removed from the yellow filtrate *in vacuo* to give a brown oil. Pentane was added and the yellow precipitate was filtered off. The filtrate was concentrated, cooled to -30 ºC and a second crop was collected; total yield 0.270 g (58%): $^1$H NMR (500 MHz, $C_6D_6$) δ 10.12 (s, 1H, *syn*-W=C*H*, $J_{CH}$ = 110 Hz), 5.95 (br, 4H, NC$_4$*H*$_2$), 2.26 (s, 12H, Me), 1.28 (s, 9H, Me), 1.20 (s, 9H, Me). $^{13}$C NMR (125 MHz, $C_6D_6$) δ 273.0, 107.1, 70.22, 45.05, 34.20, 33.29, 32.33, 18.73. Anal. Calcd for $C_{21}H_{35}N_3W$ %C 49.13, %H 6.87, %N 8.19. Found %C 49.25, %H 6.89, %N 8.08.

**W(N-t-Bu)(CH-t-Bu)(2,5-Me$_2$pyr)(OHMT) (5a).** A J. Young NMR tube was charged with a solution of W(N-t-Bu)(CH-t-Bu)(2,5-Me$_2$pyr)$_2$ (65 mg, 0.127 mmol) and HMTOH (42 mg, 0.126 mmol) in a total of 1.2 mL $C_6D_6$. The NMR tube was heated at 60 °C until the starting material was consumed (~3h). Formation of W(N-t-Bu)(CH-t-Bu)(2,5-Me$_2$pyr)(OHMT) was observed by $^1$H NMR spectroscopy. The

volatiles were removed *in vacuo* and the residue was extracted with pentane to yield a light yellow powder (63 mg, 67%): $^1$H NMR (500 MHz, $C_6D_6$) δ 8.34 (s, 1H, *syn*-W=C*H*, $J_{CH}$ = 110 Hz, $J_{WH}$ = 15 Hz), 6.96-6.91 (m, 3H, Ar), 6.86 (s, 2H, Ar), 6.77 (s, 2H, Ar), 6.11 (s, 2H, $NC_4H_2$), 2.23 (s, 6H, OHMT Me), 2.16-2.13 (br, 12H, OHMT Me + pyr Me), 2.00 (s, 6H, OHMT Me), 1.24 (s, 9H, Me), 1.05 (s, 9H, Me); $^{13}$C NMR (125 MHz, $C_6D_6$) δ 259.11, 157.92, 136.90, 136.53, 135.24, 131.96, 130.20, 129.37, 128.54, 122.97, 109.81, 70.59, 43.75, 33.97, 32.00, 21.42, 21.22, 20.19. Anal. Calcd for $C_{39}H_{52}N_2OW$ %C 62.57, %H 7.00, %N 3.74. Found %C 62.43, %H 6.84, %N 3.67.

**W(N-t-Bu)(CH-t-Bu)(pyr)$_2$(bipy) (6a).** W(N-t-Bu)(CH-t-Bu)Cl$_2$(py)$_2$ (1 g, 1.804 mmol) was suspended in toluene (50 ml) and the suspension was chilled at -30 ºC for 1 h. Lipyr (0.264 g, 3.61 mmol) was added in one portion and the mixture was allowed to stir at room temperature for 3 h, during which time salts precipitated out. The precipitate was filtered off on a pad of Celite on a glass frit and washed with toluene. 2,2'-Bipyidyl (0.268 g, 1.72 mmol) was added to the solution and the mixture was allowed to stir at room temperature overnight. The resulting precipitate was collected by filtration and dried *in vacuo* to give a red powder (0.876 g, 83%). A sample of this red powder was used for elemental analysis. At room temperature, four isomers were observed. (Alkylidene peaks in $^1$H NMR spectrum: 500 MHz, $CD_2Cl_2$, δ 11.08, 10.85, 10.57, 10.46) Heating the NMR sample to 100 ºC overnight generated one major isomer: $^1$H NMR (500 MHz, $CD_2Cl_2$) δ 10.27 (s, 1H), 9.20 (d, 1H, bipy), 8.24 (d, 1H, bipy), 8.19 (d, 1H, bipy), 8.05 (q, 2H, bipy), 7.59 (d, 1H, bipy), 7.51 (t, 1H, bipy), 7.45 (t, 1H, bipy), 6.80 (m, 2H, $NC_4H_2$), 6.19 (m, 2H, $NC_4H_2$), 6.07 (br, 2H, $NC_4H_2$), 1.52 (s, 9H, Me), 1.17 (s, 9H, Me); $^{13}$C NMR could not be obtained due to insolubility of the sample. Anal. Calcd for $C_{27}H_{35}N_5W$ %C 52.86, %H 5.75, %N 11.42. Found %C 53.01, %H 5.82, %N 11.34.

**W(N-t-Bu)(CH-t-Bu)(pyr)(OHIPT) (7a).** W(N-t-Bu)(CH-t-Bu)(pyr)$_2$(bipy) (200 mg, 0.326 mmol), ZnCl$_2$(dioxane) (73.2 mg, 0.326 mmol) and HIPTOH (136.6 mg, 0.274 mmol) were dissolved in toluene (~ 40 mL) in a 100 mL Schlenk bomb. The bomb was sonicated for 16 h (water bath reached 60 °C) and the mixture was filtered through a pad of Celite on a glass frit. All solvents were removed from the filtrate *in vacuo*. The residue was extracted with minimal pentane and the extract was filtered through a pad of Celite on a glass frit. All solvents were removed *in vacuo* to generate a yellow foam (163.7 mg, 67%): $^1$H NMR (500 MHz, $C_6D_6$) δ 9.11 (s, 1H, *syn*-W=C*H*, $J_{CH}$ = 110 Hz, $J_{WH}$ = 20 Hz), 7.24 (d, 2H, Ar), 7.20 (d, 2H, Ar), 7.07 (dd, 2H, Ar), 6.86 (tt, 1H, Ar), 6.66 (m, 2H, $NC_4H_2$), 6.37 (m, 2H, $NC_4H_2$), 3.02 (sept, 2H, MeC*H*Me), 2.95-2.84 (m, 4H, MeC*H*Me), 1.37-1.33 (m, 18H, OHIPT Me), 1.21 (s, 9H, Me), 1.20 (d, 6H, OHIPT Me), 1.33 (d, 6H, OHIPT Me), 1.04 (s, 9H, Me), 1.03 (s, 9H, Me): $^{13}$C NMR (125 MHz, $C_6D_6$) δ 259.05, 159.30, 148.59, 147.59, 147.54, 135.66, 134.23, 132.32, 131.53, 122.46, 122.04, 121.82, 111.43, 71.06, 43.94, 35.01, 34.32, 32.45, 31.70, 25.44, 25.20, 24.92, 24.86, 24.68, 23.59. Anal. Calcd for $C_{49}H_{72}N_2OW$ %C, 66.20; %H, 8.16; %N, 3.15; Found %C 66.31, %H 8.20, %N 3.09.

**W(N-t-Bu)(CH-t-Bu)(pyr)(OHMT) (8a).** W(N-t-Bu)(CH-t-Bu)(pyr)$_2$(bipy) (200 mg, 0.326 mmol), ZnCl$_2$(dioxane) (73.2 mg, 0.326 mmol) and HMTOH (90.5 mg, 0.274 mmol) were dissolved in toluene (~ 25 mL) in a 100 mL Schlenk bomb. The bomb was sonicated for 15 h, (the water bath reached 60 °C) and the mixture was filtered through a pad of Celite on a glass frit. All solvents were removed from the filtrate *in vacuo*. The residue was extracted with minimal pentane and the mixture was filtered through a pad of Celite on a glass frit to yield a yellow powder (197.3 mg, 99%): $^1$H NMR (500 MHz, $C_6D_6$) δ 8.34 (s, 1H, *syn*-W=C*H*, $J_{CH}$ = 115 Hz, $J_{WH}$ = 15 Hz), 6.95-6.84 (m, 7H, Ar), 6.69 (m, 2H, $NC_4H_2$), 6.40 (m, 2H, $NC_4H_2$), 2.24 (s, 6H, OHMT Me), 2.14 (s, 6H, OHMT Me), 1.97 (s, 6H, OHMT Me), 1.15 (s, 9H, Me), 1.04 (s, 9H, Me); $^{13}$C NMR (125 MHz, $C_6D_6$) δ 255.02, 157.80, 136.97, 136.84, 136.75, 135.40, 133.98, 132.13, 130.05, 129.51, 128.71, 123.23, 111.06, 70.48, 43.41, 33.38, 31.76, 21.23, 21.03, 20.17. Anal. Calcd for $C_{37}H_{48}N_2OW$ %C, 61.67; %H, 6.71; %N, 3.89. Found %C, 61.33; %H, 6.68; %N, 3.84.

**W(NAr')(CHCMe$_2$Ph)Cl$_2$(bipy) (9a).** W(NAr')$_2$(CH$_2$CMe$_2$Ph)$_2$ (420.3 mg, 0.61 mmol) and *2,2*'-bipyridyl (95.3 mg, 0.61 mmol) were dissolved in Et$_2$O (20 mL)/DME (~1.5 mL) and the solution was chilled at -30 ºC for 2 h. An ethereal solution of HCl (1.0 M, 1.22 mL, 1.22 mmol) was added dropwise to the chilled suspension and the reaction mixture was allowed to stir at room temperature overnight. The solution slowly turned pink and a precipitate formed. The reaction mixture was filtered, and the resulting

pink powder was washed with ether and dried *in vacuo*; yield 367 mg (91%). The compound is a mixture of *cis* and *trans* isomers in a ratio of 4:3. $^1$H NMR (500 MHz, $CD_2Cl_2$) δ 11.27 (s, 1H, W=C*H*, cis), 10.46 (s, 1H, W=C*H*, trans), 9.65 (dd, 1H, cis Ar), 9.48 (dd, 1H, trans Ar), 8.73 (dd, 1H, cis Ar), 8.61 (dd, 1H, trans Ar), 8.07-8.29 (overlapping peaks, 8H, Ar), 6.77-7.68 (overlapping peaks, 20H, Ar), 2.88 (s, 3H, cis CH*Me*2), 2.61 (s, 9H, trans and cis CH*Me*2), 1.75 (s, 3H, cis CHC*Me*$_2$Ph), 1.66 (s, 6H, trans CHC*Me*$_2$Ph), 1.62 (s, 3H, cis CHC*Me*$_2$Ph); a $^{13}$C NMR spectrum could not be obtained due to the insolubility of **9a**. Anal. Calcd for $C_{28}H_{29}Cl_2N_3W$: %C, 50.78; %H, 4.41; %N, 6.34. Found %C, 50.61; %H, 4.53; %N, 6.44.

**W(NAr)(CHCMe$_2$Ph)Cl$_2$(bipy) (10a).** Compound **10a** was prepared as described for **9a** from $W(NAr)_2(CH_2CMe_2Ph)_2$ (200 mg, 0.25 mmol), *2,2*'-bipyridyl (39mg, 0.25 mmol), and an ethereal solution of HCl (1.0 M 0.5 mL, 0.5 mmol). The reaction mixture was filtered, and the resulting yellow powder (107.5 mg, 60%) was washed with $Et_2O$ and dried *in vacuo*: $^1$H NMR (500 MHz, $CDCl_3$) δ 11.48 (s, 1H, W=C*H, major isomer*, cis), 9.74 (dd, 1H, Ar), 8.62 (dd, 1H, Ar), 8.18 (d, 1H, Ar), 8.08-8.13 (overlapping peaks, 2H, Ar), 8.04 (t, 1H, Ar), 7.61 (t, 1H, Ar), 7.54 (d, 2H, Ar), 7.36 (t, 2H, Ar), 7.19 (t, 2H, Ar), 7.10 (d, 1H, Ar), 6.98 (t, 1H, Ar), 6.90 (d, 1H, Ar), 4.39 (m, 1H, *i*-Pr C*H*), 2.83 (m, 1H, *i*-Pr C*H*), 1.79 (s, 3H, CHC*Me*$_2$Ph), 1.62 (s, 3H, CHC*Me*$_2$Ph), 1.26 (d, 3H, *i*-Pr Me), 1.17 (d, 3H, *i*-Pr Me), 1.01 (d, 3H, *i*-Pr Me), 0.04 (d, 3H, *i*-Pr Me); a $^{13}$C NMR spectrum could not be obtained due to insolubility of **10a**. Anal. Calcd for $C_{32}H_{37}Cl_2N_3W$ %C, 53.50; %H, 5.19; %N, 5.85. Found %C, 53.13; %H, 5.17; %N, 5.78.

**W(NAr$^{Cl2}$)(CHCMe$_2$Ph)Cl$_2$(bipy) (11a).** Compound **11a** was prepared as described for **9a** from $W(NAr^{Cl2})_2(CH_2CMe_2Ph)_2$ (128.8 mg, 0.17 mmol), *2,2*'-bipy (26.1mg, 0.17 mmol), and an ethereal solution of HCl (3.82 M 0.088 mL, 0.33 mmol). The solution slowly turned yellow and a precipitate formed. The reaction mixture was filtered, and the resulting yellow powder (63 mg, 54%) was washed with $Et_2O$ and dried *in vacuo*: $^1$H NMR (500 MHz, $CD_2Cl_2$) δ 11.10 (s, 1H, W=C*H, major isomer*), 9.66 (dd, 1H, Ar), 8.95 (dd, 1H, Ar), 8.25 (d, 1H, Ar), 8.16 (m, 2H, Ar), 8.06 (t, 1H, Ar), 7.63 (t, 1H, Ar), 7.58 (d, 2H, Ar), 7.35 (t, 1H, Ar), 7.27 (t, 2H, Ar), 7.07 (t, 3H, Ar), 6.80 (t, 1H, Ar), 1.74 (s, 3H, CHC*Me*$_2$Ph), 1.67 (s, 3H, CHC*Me*$_2$Ph); a $^{13}$C NMR spectrum could not be obtained due to the insolubility of **11a**: Anal. Calcd for $C_{26}H_{23}Cl_4N_3W$ %C, 44.41; %H, 3.30; %N, 5.98. Found %C, 44.33; %H, 3.32; %N, 6.02.

**W(NAr$^{iPr}$)(CHCMe$_2$Ph)Cl$_2$(bipy) (12a).** Compound **12a** was prepared as described for **9a** from $W(NAr^{iPr})_2(CH_2CMe_2Ph)_2$ (100 mg, 0.14 mmol), *2,2*'-bipy (21.8mg, 0.14 mmol), and ethereal HCl (1.0 M 0.28 mL, 0.28 mmol). The reaction mixture was then filtered, and the resulting pink powder (53.4 mg, 57%) was washed with $Et_2O$ and dried *in vacuo*. The compound is a mixture of cis and trans isomers in a ratio of 1:1.2: $^1$H NMR (500 MHz, $CD_2Cl_2$) δ 11.20 (s, 1H, W=C*H*, cis), 10.46 (s, 1H, W=C*H*, trans), 9.62 (dd, 1H, cis Ar), 9.48 (dd, 1H, trans Ar), 8.62 (dd, 1H, trans Ar), 8.59 (dd, 1H, cis Ar), 8.03-8.29 (overlapping peaks, 8H, Ar), 6.95-7.70 (overlapping peaks, 22H, Ar), 3.98 (m, 1H, trans *i*-Pr C*H*), 3.35 (m, 1H, cis *i*-Pr C*H*), 1.81 (s, 3H, cis CHC*Me*$_2$Ph), 1.68 (s, 6H, trans CHC*Me*$_2$Ph), 1.63 (s, 3H, cis CHC*Me*$_2$Ph), 1.23 (d, 6H, trans *i*-Pr *Me*), 1.00 (d, 3H, cis *i*-Pr *Me*), 0.77 (d, 3H, cis *i*-Pr *Me*); a $^{13}$C NMR spectrum could not be obtained due to the insolubility of **12a**. Anal. Calcd for $C_{29}H_{31}Cl_2N_3W$ %C, 51.50; %H, 4.62; %N, 6.21. Found %C, 51.50; %H, 4.70; %N, 6.23.

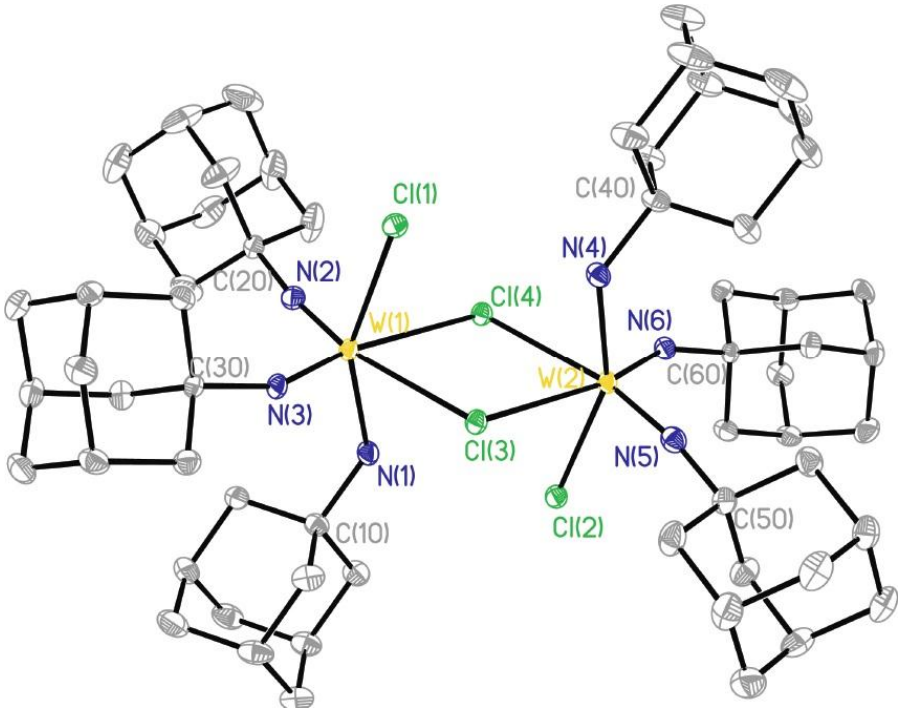


**Figure S1**. Thermal ellipsoid drawing of $[W(NAd)_2Cl(\mu\text{-}Cl)(AdNH_2)]_2$ (**1b**). Selected distances (Å) and angles (°) : W(1)-N(1) = 2.206(2), W(1)-N(2) = 1.732(2), W(1)-N(3) = 1.762(2), W(1)-Cl(1) = 2.4048(7), W(1)-Cl(3) = 2.6023(7), W(1)-Cl(4) = 2.8155(7), W(2)-N(4) = 2.212(2), W(2)-N(5) = 1.739(2), W(2)-N(6) = 1.764(2), W(2)-Cl(2) = 2.4001(7), W(2)-Cl(3) = 2.8172(6), W(1)-Cl(4) = 2.5997(7), W(1)-N(1)-C(10) = 128.80(16), W(1)-N(2)-C(20) = 172.53(18), W(1)-N(3)-C(30) = 153.22(18), W(1)-Cl(3)-W(2) = 105.81(2), W(1)-Cl(4)-W(2) = 105.93(2), W(2)-N(4)-C(40) = 126.86(16), W(2)-N(5)-C(50) = 171.01(19), W(2)-N(6)-C(60) = 152.40(19).

**Crystal data and structure refinement**

Low-temperature diffraction data were collected on a Bruker-AXS X8 Kappa Duo diffractometer coupled to a SMART Apex2 CCD detector with Mo $K_\alpha$ radiation ($\lambda$ = 0.71073 Å) from an $I\mu S$ micro-source, for the structures of **1a**, **1b**, **3a**, and **8a** and on a Siemens Platform diffractometer coupled to a SMART Apex detector with graphite-monochromated Mo $K_\alpha$ radiation ($\lambda$ = 0.71073 Å) for the structure of **2b**, performing $\phi$-and $\omega$-scans. The structures were solved by direct methods using SHELXS[vii] and refined against $F^2$ on all data by full-matrix least squares with SHELXL-97[viii] following established refinement strategies[ix]. All non-hydrogen atoms were refined anisotropically. Except when noted otherwise below, all hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the $U$ value of the atoms they are linked to (1.5 times for methyl groups). Details of the data quality and a summary of the residual values of the refinements are listed in tables below.

**[W(N-t-Bu)$_2$Cl($\mu$-Cl)(t-BuNH$_2$)]$_2$ (1a)** crystallizes in the triclinic space group P1 with 2.5 molecules of **1a** and five molecules of dichloromethane per asymmetric unit. The half molecule is completed by the crystallographic inversion center and each unit cell contains thus 5 molecules of **1a** and 10 molecules of $CH_2Cl_2$. Two of the t-Bu groups in the molecule containing tungsten atoms W3 and W4 as well as two of the solvent molecules are disordered over two positions. Those disorders were refined with the help of similarity restraints on 1-2 and 1-3 distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters. Coordinates for the nitrogen bound hydrogen atoms were taken from the difference Fourier Synthesis. The hydrogen atoms in question were subsequently refined semi-freely with the help of distance restraints (target N—H distance 0.91(2) Å, while constraining their $U_{iso}$ to 1.2 times the value of the $U_{eq}$ of the nitrogen atom to which they bind.

**[W(NAd)$_2$Cl($\mu$-Cl)(AdNH$_2$)]$_2$ (1b)** crystallizes in the triclinic space group P1 with 1.5 molecules of **1b** and 7.5 molecules of dichloromethane in the asymmetric unit. The half molecule is completed by the crystallographic inversion center and the half-occupied solvent molecule is located near a crystallographic inversion center and disordered over four positions (that is two independent positions); thus the unit cell contains 3 target molecules and 15 solvent molecules. Besides the solvent molecule near the inversion center, one further dichloromethane molecule is disordered over two positions. Those solvent disorders were refined with the help of similarity restraints on 1-2 and 1-3 distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters. The crystal was non-merohedrally twinned. Two independent orientation matrices for the unit cell were found using the program CELL_NOW[x], and data reduction taking into account the twinning was performed with SAINT[xi]. The program TWINABS[xii] was used to perform absorption correction and to set up a detwinned HKLF4 format file for structure refinement. Coordinates for the nitrogen bound hydrogen atoms were taken from the difference Fourier Synthesis. The hydrogen atoms in question were subsequently refined semi-freely with the help of distance restraints (target N—H distance 0.91(2) Å, while constraining their $U_{iso}$ to 1.2 times the value of the $U_{eq}$ of the nitrogen atom to which they bind.

**W(NAd)$_2$(CH$_2$CMe$_2$Ph)$_2$ (2b)** crystallizes in the triclinic space group P1 with 1 molecules of **2b** in the asymmetric unit. The crystal was split (domain 2 is rotated from domain 1 by 3.4 degrees about reciprocal axis 1.000 -0.466 0.568 and real axis 1.000 -0.637 0.260) and treated as non-merohedrally twinned as described above.

**[W(N-t-Bu)(CH-t-Bu)Cl$_2$(py)]$_2$ (3a)** crystallizes in the monoclinic space group $P2_1/c$ with half a molecule **3a** of in the asymmetric unit. The second half is generated by the crystallographic inversion center. The crystallographically independent alkylidene ligand (C1 to C5) is disordered over two positions and disorder was refined with the help of similarity restraints on 1-2 and 1-3 distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters. The ratio between the two components was refined freely and converged at 0.744(14).

**W(N-t-Bu)(CH-t-Bu)(pyr)(OHMT) (8a)** crystallizes in the monoclinic space group $P2_1/n$ with one molecule **8a** of in the asymmetric unit. The alkylidene and the N-t-Bu ligand are engaged in a disorder that makes them swap places. The disorder was refined with the help of similarity restraints on 1-2 and 1-3 distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters. The ratio between the two components was refined freely and converged at 0.552(5). In spite of this disorder, coordinates the two independent hydrogen atoms on C1 and C1A (the carbon atoms binding directly to tungsten) could be taken from the difference Fourier Synthesis. The

hydrogen atoms in question were subsequently refined semi-freely with the help of distance restraints (target C—H distance 0.95(2) Å, while constraining their $U_{iso}$ to 1.2 times the value of the $U_{eq}$ of the carbon atom to which they bind.

**Table S1**. Crystal data and structure refinement for $[W(N\text{-}t\text{-}Bu)_2Cl(\mu\text{-}Cl)(t\text{-}BuNH_2)]_2$ (**1a**).

| | | |
|---|---|---|
| Identification code | X8_12060 | |
| Empirical formula | $C_{26}\ H_{62}\ Cl_8\ N_6\ W_2$ | |
| Formula weight | 1110.12 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | P1 | |
| Unit cell dimensions | $a$ = 12.5147(14) Å | $\alpha$= 98.741(2)°. |
| | $b$ = 19.130(2) Å | $\beta$= 93.348(2)°. |
| | $c$ = 22.909(3) Å | $\gamma$ = 99.364(2)°. |
| Volume | 5329.1(10) Å$^3$ | |
| $Z$ | 5 | |
| Density (calculated) | 1.730 Mg/m$^3$ | |
| Absorption coefficient | 5.918 mm$^{-1}$ | |
| $F$(000) | 2720 | |
| Crystal size | 0.30 x 0.28 x 0.18 mm$^3$ | |
| Theta range for data collection | 0.90 to 31.00°. | |
| Index ranges | -18<=$h$<=18, -27<=$k$<=27, -33<=$l$<=33 | |
| Reflections collected | 504483 | |
| Independent reflections | 33880 [$R_{int}$ = 0.0395] | |
| Completeness to theta = 31.00° | 99.8 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.4155 and 0.2733 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 33880 / 590 / 1132 | |
| Goodness-of-fit on $F^2$ | 1.052 | |
| Final $R$ indices [$I$>2$\sigma$($I$)] | $R$1 = 0.0259, $wR$2 = 0.0660 | |
| $R$ indices (all data) | $R$1 = 0.0320, $wR$2 = 0.0709 | |
| Largest diff. peak and hole | 2.379 and -0.995 e.Å$^{-3}$ | |

Table S2. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for **X8_12060**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Cl(1) | 1166(1) | 916(1) | 4252(1) | 30(1) |
| W(1) | 1519(1) | 190(1) | 3361(1) | 26(1) |
| Cl(3) | -105(1) | 655(1) | 2870(1) | 27(1) |
| N(1) | 1807(2) | -24(1) | 2413(1) | 30(1) |
| C(1) | 1647(2) | -750(1) | 2022(1) | 32(1) |
| C(2) | 2357(2) | -1216(2) | 2292(1) | 38(1) |
| C(3) | 447(2) | -1076(2) | 1968(1) | 41(1) |
| C(4) | 2009(3) | -628(2) | 1412(1) | 43(1) |
| N(2) | 686(2) | -599(1) | 3476(1) | 30(1) |
| C(5) | 305(2) | -1228(1) | 3738(1) | 33(1) |
| C(6) | -844(2) | -1557(2) | 3468(2) | 48(1) |
| C(7) | 1057(2) | -1783(2) | 3633(1) | 43(1) |
| C(8) | 294(3) | -967(2) | 4404(1) | 51(1) |
| N(3) | 2848(2) | 137(1) | 3598(1) | 30(1) |
| C(9) | 3931(2) | 92(1) | 3823(1) | 35(1) |
| C(10) | 3995(3) | -649(2) | 3967(2) | 60(1) |
| C(11) | 4706(3) | 279(2) | 3353(1) | 52(1) |
| C(12) | 4222(2) | 655(2) | 4384(1) | 40(1) |
| Cl(2) | 1093(1) | 1307(1) | 1691(1) | 31(1) |
| W(2) | 722(1) | 1998(1) | 2600(1) | 26(1) |
| Cl(4) | 2364(1) | 1532(1) | 3069(1) | 28(1) |
| N(4) | 424(2) | 2188(1) | 3547(1) | 28(1) |
| C(13) | 683(2) | 2892(1) | 3968(1) | 32(1) |
| C(14) | 1906(2) | 3151(1) | 4019(1) | 35(1) |
| C(15) | 303(2) | 2751(2) | 4568(1) | 39(1) |
| C(16) | 54(2) | 3427(2) | 3732(1) | 40(1) |
| N(5) | 1530(2) | 2814(1) | 2522(1) | 30(1) |
| C(17) | 1771(2) | 3467(1) | 2263(1) | 33(1) |
| C(18) | 2226(3) | 4109(2) | 2744(1) | 44(1) |
| C(19) | 2643(3) | 3347(2) | 1835(1) | 45(1) |
| C(20) | 755(2) | 3607(2) | 1929(1) | 42(1) |
| N(6) | -608(2) | 2042(1) | 2357(1) | 29(1) |
| C(21) | -1727(2) | 2013(1) | 2143(1) | 32(1) |
| C(22) | -2357(2) | 1261(2) | 2152(2) | 48(1) |
| C(23) | -1763(2) | 2178(2) | 1511(1) | 50(1) |
| C(24) | -2202(2) | 2568(2) | 2555(1) | 46(1) |
| Cl(5) | 7244(1) | 6857(1) | 2307(1) | 33(1) |
| W(3) | 7554(1) | 6168(1) | 1386(1) | 26(1) |
| Cl(7) | 5774(1) | 6540(1) | 982(1) | 28(1) |
| N(7) | 7773(2) | 5986(1) | 426(1) | 28(1) |
| C(31) | 7642(2) | 5276(1) | 20(1) | 32(1) |
| C(32) | 6442(2) | 4952(2) | -56(1) | 44(1) |
| C(33) | 8341(3) | 4801(2) | 279(1) | 42(1) |
| C(34) | 8037(3) | 5427(2) | -578(1) | 42(1) |
| N(8) | 6834(2) | 5348(1) | 1502(1) | 32(1) |
| C(35) | 6484(2) | 4691(2) | 1740(1) | 42(1) |
| C(36) | 6364(16) | 4943(8) | 2401(4) | 86(4) |
| C(37) | 7315(8) | 4191(6) | 1683(6) | 48(2) |
| C(38) | 5398(7) | 4304(7) | 1424(7) | 68(3) |

| | | | | |
|---|---|---|---|---|
| C(36A) | 6050(20) | 4897(17) | 2342(7) | 58(4) |
| C(37A) | 7425(18) | 4299(15) | 1812(15) | 61(5) |
| C(38A) | 5544(18) | 4239(13) | 1319(10) | 53(4) |
| N(9) | 8926(2) | 6180(1) | 1581(1) | 31(1) |
| C(39) | 10046(2) | 6193(1) | 1776(1) | 32(1) |
| C(40) | 10210(2) | 5465(2) | 1926(2) | 47(1) |
| C(41) | 10329(3) | 6775(2) | 2324(1) | 47(1) |
| C(42) | 10745(2) | 6396(2) | 1281(1) | 43(1) |
| Cl(6) | 6697(1) | 7181(1) | -252(1) | 33(1) |
| W(4) | 6384(1) | 7873(1) | 669(1) | 28(1) |
| Cl(8) | 8168(1) | 7515(1) | 1079(1) | 29(1) |
| N(10) | 6226(2) | 8089(1) | 1635(1) | 31(1) |
| C(43) | 6433(2) | 8813(1) | 2030(1) | 35(1) |
| C(44) | 5676(3) | 9277(2) | 1793(2) | 49(1) |
| C(45) | 7627(2) | 9135(2) | 2027(1) | 40(1) |
| C(46) | 6184(3) | 8697(2) | 2656(1) | 44(1) |
| N(11) | 7069(2) | 8700(1) | 533(1) | 35(1) |
| C(47) | 7158(5) | 9316(3) | 212(3) | 36(1) |
| C(48) | 6056(4) | 9435(3) | -29(2) | 54(1) |
| C(49) | 7716(5) | 9986(3) | 645(2) | 57(2) |
| C(50) | 7862(6) | 9173(4) | -302(3) | 58(2) |
| C(47A) | 7348(9) | 9393(6) | 347(5) | 36(1) |
| C(48A) | 8472(8) | 9779(6) | 615(5) | 54(3) |
| C(49A) | 7317(12) | 9159(7) | -318(5) | 59(3) |
| C(50A) | 6497(9) | 9848(5) | 509(6) | 59(3) |
| N(12) | 5006(2) | 7850(1) | 487(1) | 31(1) |
| C(51) | 3857(2) | 7762(1) | 318(1) | 33(1) |
| C(52) | 3551(3) | 8447(2) | 144(2) | 49(1) |
| C(53) | 3594(2) | 7148(2) | -206(1) | 42(1) |
| C(54) | 3252(2) | 7567(2) | 848(1) | 45(1) |
| Cl(9) | 4681(1) | 5259(1) | 3736(1) | 32(1) |
| W(5) | 4781(1) | 5984(1) | 4700(1) | 26(1) |
| Cl(10) | 6285(1) | 5260(1) | 4936(1) | 28(1) |
| N(13) | 5134(2) | 6252(1) | 5677(1) | 28(1) |
| C(61) | 4582(2) | 6711(1) | 6117(1) | 31(1) |
| C(62) | 5203(2) | 6783(2) | 6724(1) | 36(1) |
| C(63) | 4641(3) | 7450(1) | 5929(1) | 41(1) |
| C(64) | 3426(2) | 6330(2) | 6127(1) | 38(1) |
| N(14) | 5689(2) | 6717(1) | 4548(1) | 28(1) |
| C(65) | 6025(2) | 7375(1) | 4313(1) | 29(1) |
| C(66) | 7003(2) | 7818(1) | 4701(1) | 38(1) |
| C(67) | 5092(2) | 7805(2) | 4290(1) | 41(1) |
| C(68) | 6334(2) | 7153(2) | 3685(1) | 37(1) |
| N(15) | 3477(2) | 6182(1) | 4598(1) | 30(1) |
| C(69) | 2393(2) | 6278(2) | 4409(1) | 37(1) |
| C(70) | 2316(3) | 6218(2) | 3728(1) | 46(1) |
| C(71) | 1561(2) | 5688(2) | 4589(2) | 52(1) |
| C(72) | 2194(2) | 7016(2) | 4689(1) | 44(1) |
| C(1S) | 8241(6) | 5638(3) | 3885(4) | 51(2) |
| Cl(1S) | 8819(4) | 4917(2) | 3567(4) | 84(1) |
| Cl(2S) | 9047(6) | 6460(3) | 3811(3) | 48(1) |
| C(1T) | 8136(9) | 5685(6) | 3582(11) | 67(4) |
| Cl(1T) | 8797(8) | 4931(4) | 3427(3) | 58(1) |
| Cl(2T) | 9052(11) | 6451(6) | 3898(6) | 56(2) |

| | | | | |
|---|---|---|---|---|
| C(2S) | 9622(10) | 7791(4) | 9730(11) | 45(2) |
| Cl(3S) | 10437(2) | 8551(2) | 10150(4) | 66(1) |
| Cl(4S) | 10248(5) | 7022(4) | 9764(3) | 54(1) |
| C(2T) | 9497(16) | 7859(7) | 9760(20) | 47(4) |
| Cl(3T) | 10449(3) | 8657(3) | 9875(5) | 57(2) |
| Cl(4T) | 10138(10) | 7112(7) | 9838(6) | 65(2) |
| C(3S) | 8206(3) | 467(2) | 3972(2) | 50(1) |
| Cl(5S) | 7755(1) | 1296(1) | 3990(1) | 64(1) |
| Cl(6S) | 7347(1) | -130(1) | 4322(1) | 54(1) |
| C(4S) | 5723(2) | 3673(2) | 7634(1) | 44(1) |
| Cl(7S) | 6215(1) | 2846(1) | 7540(1) | 53(1) |
| Cl(8S) | 6577(1) | 4320(1) | 8157(1) | 50(1) |
| C(5S) | 3962(2) | 1709(2) | 1826(2) | 46(1) |
| Cl(9S) | 4351(1) | 882(1) | 1888(1) | 70(1) |
| Cl(15) | 5008(1) | 2298(1) | 1593(1) | 52(1) |

Table S3. Bond lengths [Å] and angles [°] for **X8_12060**.

| | |
|---|---|
| Cl(1)-W(1) | 2.3942(6) |
| W(1)-N(3) | 1.743(2) |
| W(1)-N(2) | 1.754(2) |
| W(1)-N(1) | 2.210(2) |
| W(1)-Cl(3) | 2.6104(6) |
| W(1)-Cl(4) | 2.8063(6) |
| Cl(3)-W(2) | 2.7825(6) |
| N(1)-C(1) | 1.511(3) |
| N(1)-H(1A) | 0.910(17) |
| N(1)-H(1B) | 0.900(17) |
| C(1)-C(3) | 1.520(4) |
| C(1)-C(2) | 1.525(4) |
| C(1)-C(4) | 1.532(4) |
| C(2)-H(2A) | 0.9800 |
| C(2)-H(2B) | 0.9800 |
| C(2)-H(2C) | 0.9800 |
| C(3)-H(3A) | 0.9800 |
| C(3)-H(3B) | 0.9800 |
| C(3)-H(3C) | 0.9800 |
| C(4)-H(4C) | 0.9800 |
| C(4)-H(4D) | 0.9800 |
| C(4)-H(4E) | 0.9800 |
| N(2)-C(5) | 1.449(3) |
| C(5)-C(6) | 1.525(4) |
| C(5)-C(7) | 1.531(4) |
| C(5)-C(8) | 1.534(4) |
| C(6)-H(6A) | 0.9800 |
| C(6)-H(6B) | 0.9800 |
| C(6)-H(6C) | 0.9800 |
| C(7)-H(7C) | 0.9800 |
| C(7)-H(7D) | 0.9800 |
| C(7)-H(7E) | 0.9800 |
| C(8)-H(8A) | 0.9800 |
| C(8)-H(8B) | 0.9800 |
| C(8)-H(8C) | 0.9800 |
| N(3)-C(9) | 1.442(3) |
| C(9)-C(10) | 1.518(4) |
| C(9)-C(12) | 1.530(4) |
| C(9)-C(11) | 1.533(4) |
| C(10)-H(10C) | 0.9800 |
| C(10)-H(10D) | 0.9800 |
| C(10)-H(10E) | 0.9800 |
| C(11)-H(11A) | 0.9800 |
| C(11)-H(11B) | 0.9800 |
| C(11)-H(11C) | 0.9800 |
| C(12)-H(12A) | 0.9800 |
| C(12)-H(12B) | 0.9800 |
| C(12)-H(12C) | 0.9800 |
| Cl(2)-W(2) | 2.4034(6) |
| W(2)-N(6) | 1.744(2) |
| W(2)-N(5) | 1.758(2) |
| W(2)-N(4) | 2.208(2) |

| | |
|---|---|
| W(2)-Cl(4) | 2.6065(6) |
| N(4)-C(13) | 1.508(3) |
| N(4)-H(4A) | 0.907(17) |
| N(4)-H(4B) | 0.891(17) |
| C(13)-C(14) | 1.522(4) |
| C(13)-C(15) | 1.529(4) |
| C(13)-C(16) | 1.530(4) |
| C(14)-H(14A) | 0.9800 |
| C(14)-H(14B) | 0.9800 |
| C(14)-H(14C) | 0.9800 |
| C(15)-H(15A) | 0.9800 |
| C(15)-H(15B) | 0.9800 |
| C(15)-H(15C) | 0.9800 |
| C(16)-H(16A) | 0.9800 |
| C(16)-H(16B) | 0.9800 |
| C(16)-H(16C) | 0.9800 |
| N(5)-C(17) | 1.457(3) |
| C(17)-C(18) | 1.527(4) |
| C(17)-C(20) | 1.528(4) |
| C(17)-C(19) | 1.532(4) |
| C(18)-H(18A) | 0.9800 |
| C(18)-H(18B) | 0.9800 |
| C(18)-H(18C) | 0.9800 |
| C(19)-H(19A) | 0.9800 |
| C(19)-H(19B) | 0.9800 |
| C(19)-H(19C) | 0.9800 |
| C(20)-H(20A) | 0.9800 |
| C(20)-H(20B) | 0.9800 |
| C(20)-H(20C) | 0.9800 |
| N(6)-C(21) | 1.447(3) |
| C(21)-C(23) | 1.527(4) |
| C(21)-C(22) | 1.528(4) |
| C(21)-C(24) | 1.530(4) |
| C(22)-H(22A) | 0.9800 |
| C(22)-H(22B) | 0.9800 |
| C(22)-H(22C) | 0.9800 |
| C(23)-H(23A) | 0.9800 |
| C(23)-H(23B) | 0.9800 |
| C(23)-H(23C) | 0.9800 |
| C(24)-H(24A) | 0.9800 |
| C(24)-H(24B) | 0.9800 |
| C(24)-H(24C) | 0.9800 |
| Cl(5)-W(3) | 2.4000(6) |
| W(3)-N(8) | 1.743(2) |
| W(3)-N(9) | 1.744(2) |
| W(3)-N(7) | 2.213(2) |
| W(3)-Cl(7) | 2.6073(6) |
| W(3)-Cl(8) | 2.7741(6) |
| Cl(7)-W(4) | 2.7553(6) |
| N(7)-C(31) | 1.505(3) |
| N(7)-H(7A) | 0.904(17) |
| N(7)-H(7B) | 0.913(17) |
| C(31)-C(32) | 1.518(4) |
| C(31)-C(33) | 1.518(4) |

| | |
|---|---|
| C(31)-C(34) | 1.534(4) |
| C(32)-H(32A) | 0.9800 |
| C(32)-H(32B) | 0.9800 |
| C(32)-H(32C) | 0.9800 |
| C(33)-H(33A) | 0.9800 |
| C(33)-H(33B) | 0.9800 |
| C(33)-H(33C) | 0.9800 |
| C(34)-H(34A) | 0.9800 |
| C(34)-H(34B) | 0.9800 |
| C(34)-H(34C) | 0.9800 |
| N(8)-C(35) | 1.458(3) |
| C(35)-C(37A) | 1.511(11) |
| C(35)-C(38) | 1.522(7) |
| C(35)-C(37) | 1.522(7) |
| C(35)-C(36A) | 1.530(11) |
| C(35)-C(38A) | 1.531(11) |
| C(35)-C(36) | 1.540(7) |
| C(36)-H(36A) | 0.9800 |
| C(36)-H(36B) | 0.9800 |
| C(36)-H(36C) | 0.9800 |
| C(37)-H(37A) | 0.9800 |
| C(37)-H(37B) | 0.9800 |
| C(37)-H(37C) | 0.9800 |
| C(38)-H(38A) | 0.9800 |
| C(38)-H(38B) | 0.9800 |
| C(38)-H(38C) | 0.9800 |
| C(36A)-H(36D) | 0.9800 |
| C(36A)-H(36E) | 0.9800 |
| C(36A)-H(36F) | 0.9800 |
| C(37A)-H(37D) | 0.9800 |
| C(37A)-H(37E) | 0.9800 |
| C(37A)-H(37F) | 0.9800 |
| C(38A)-H(38D) | 0.9800 |
| C(38A)-H(38E) | 0.9800 |
| C(38A)-H(38F) | 0.9800 |
| N(9)-C(39) | 1.442(3) |
| C(39)-C(40) | 1.525(4) |
| C(39)-C(41) | 1.528(4) |
| C(39)-C(42) | 1.531(4) |
| C(40)-H(40A) | 0.9800 |
| C(40)-H(40B) | 0.9800 |
| C(40)-H(40C) | 0.9800 |
| C(41)-H(41A) | 0.9800 |
| C(41)-H(41B) | 0.9800 |
| C(41)-H(41C) | 0.9800 |
| C(42)-H(42A) | 0.9800 |
| C(42)-H(42B) | 0.9800 |
| C(42)-H(42C) | 0.9800 |
| Cl(6)-W(4) | 2.4023(6) |
| W(4)-N(12) | 1.742(2) |
| W(4)-N(11) | 1.752(2) |
| W(4)-N(10) | 2.216(2) |
| W(4)-Cl(8) | 2.6049(6) |
| N(10)-C(43) | 1.509(3) |

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|---|---|
| N(10)-H(10A) | 0.890(17) |
| N(10)-H(10B) | 0.884(17) |
| C(43)-C(45) | 1.521(4) |
| C(43)-C(46) | 1.527(4) |
| C(43)-C(44) | 1.528(4) |
| C(44)-H(44A) | 0.9800 |
| C(44)-H(44B) | 0.9800 |
| C(44)-H(44C) | 0.9800 |
| C(45)-H(45A) | 0.9800 |
| C(45)-H(45B) | 0.9800 |
| C(45)-H(45C) | 0.9800 |
| C(46)-H(46A) | 0.9800 |
| C(46)-H(46B) | 0.9800 |
| C(46)-H(46C) | 0.9800 |
| N(11)-C(47A) | 1.450(12) |
| N(11)-C(47) | 1.475(6) |
| C(47)-C(48) | 1.520(7) |
| C(47)-C(50) | 1.529(7) |
| C(47)-C(49) | 1.535(7) |
| C(48)-H(48A) | 0.9800 |
| C(48)-H(48B) | 0.9800 |
| C(48)-H(48C) | 0.9800 |
| C(49)-H(49A) | 0.9800 |
| C(49)-H(49B) | 0.9800 |
| C(49)-H(49C) | 0.9800 |
| C(50)-H(50A) | 0.9800 |
| C(50)-H(50B) | 0.9800 |
| C(50)-H(50C) | 0.9800 |
| C(47A)-C(50A) | 1.510(11) |
| C(47A)-C(49A) | 1.517(11) |
| C(47A)-C(48A) | 1.525(11) |
| C(48A)-H(48D) | 0.9800 |
| C(48A)-H(48E) | 0.9800 |
| C(48A)-H(48F) | 0.9800 |
| C(49A)-H(49D) | 0.9800 |
| C(49A)-H(49E) | 0.9800 |
| C(49A)-H(49F) | 0.9800 |
| C(50A)-H(50D) | 0.9800 |
| C(50A)-H(50E) | 0.9800 |
| C(50A)-H(50F) | 0.9800 |
| N(12)-C(51) | 1.443(3) |
| C(51)-C(53) | 1.526(4) |
| C(51)-C(52) | 1.526(4) |
| C(51)-C(54) | 1.530(4) |
| C(52)-H(52A) | 0.9800 |
| C(52)-H(52B) | 0.9800 |
| C(52)-H(52C) | 0.9800 |
| C(53)-H(53A) | 0.9800 |
| C(53)-H(53B) | 0.9800 |
| C(53)-H(53C) | 0.9800 |
| C(54)-H(54A) | 0.9800 |
| C(54)-H(54B) | 0.9800 |
| C(54)-H(54C) | 0.9800 |
| Cl(9)-W(5) | 2.4075(6) |

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|---|---|
| W(5)-N(15) | 1.745(2) |
| W(5)-N(14) | 1.749(2) |
| W(5)-N(13) | 2.219(2) |
| W(5)-Cl(10) | 2.5897(6) |
| W(5)-Cl(10)#1 | 2.7986(6) |
| Cl(10)-W(5)#1 | 2.7986(6) |
| N(13)-C(61) | 1.509(3) |
| N(13)-H(13A) | 0.881(17) |
| N(13)-H(13B) | 0.905(17) |
| C(61)-C(64) | 1.513(4) |
| C(61)-C(62) | 1.529(3) |
| C(61)-C(63) | 1.531(4) |
| C(62)-H(62A) | 0.9800 |
| C(62)-H(62B) | 0.9800 |
| C(62)-H(62C) | 0.9800 |
| C(63)-H(63A) | 0.9800 |
| C(63)-H(63B) | 0.9800 |
| C(63)-H(63C) | 0.9800 |
| C(64)-H(64A) | 0.9800 |
| C(64)-H(64B) | 0.9800 |
| C(64)-H(64C) | 0.9800 |
| N(14)-C(65) | 1.451(3) |
| C(65)-C(66) | 1.520(4) |
| C(65)-C(68) | 1.527(3) |
| C(65)-C(67) | 1.537(3) |
| C(66)-H(66A) | 0.9800 |
| C(66)-H(66B) | 0.9800 |
| C(66)-H(66C) | 0.9800 |
| C(67)-H(67A) | 0.9800 |
| C(67)-H(67B) | 0.9800 |
| C(67)-H(67C) | 0.9800 |
| C(68)-H(68A) | 0.9800 |
| C(68)-H(68B) | 0.9800 |
| C(68)-H(68C) | 0.9800 |
| N(15)-C(69) | 1.449(3) |
| C(69)-C(72) | 1.525(4) |
| C(69)-C(71) | 1.528(4) |
| C(69)-C(70) | 1.543(4) |
| C(70)-H(70A) | 0.9800 |
| C(70)-H(70B) | 0.9800 |
| C(70)-H(70C) | 0.9800 |
| C(71)-H(71A) | 0.9800 |
| C(71)-H(71B) | 0.9800 |
| C(71)-H(71C) | 0.9800 |
| C(72)-H(72A) | 0.9800 |
| C(72)-H(72B) | 0.9800 |
| C(72)-H(72C) | 0.9800 |
| C(1S)-Cl(1S) | 1.742(7) |
| C(1S)-Cl(2S) | 1.762(7) |
| C(1S)-H(1S1) | 0.9900 |
| C(1S)-H(1S2) | 0.9900 |
| C(1T)-Cl(2T) | 1.737(11) |
| C(1T)-Cl(1T) | 1.777(10) |
| C(1T)-H(1T1) | 0.9900 |

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|---|---|
| C(1T)-H(1T2) | 0.9900 |
| C(2S)-Cl(3S) | 1.748(10) |
| C(2S)-Cl(4S) | 1.785(8) |
| C(2S)-H(2S1) | 0.9900 |
| C(2S)-H(2S2) | 0.9900 |
| C(2T)-Cl(3T) | 1.751(13) |
| C(2T)-Cl(4T) | 1.777(12) |
| C(2T)-H(2T1) | 0.9900 |
| C(2T)-H(2T2) | 0.9900 |
| C(3S)-Cl(6S) | 1.756(3) |
| C(3S)-Cl(5S) | 1.763(3) |
| C(3S)-H(3S1) | 0.9900 |
| C(3S)-H(3S2) | 0.9900 |
| C(4S)-Cl(8S) | 1.754(3) |
| C(4S)-Cl(7S) | 1.776(3) |
| C(4S)-H(4S1) | 0.9900 |
| C(4S)-H(4S2) | 0.9900 |
| C(5S)-Cl(15) | 1.747(3) |
| C(5S)-Cl(9S) | 1.751(3) |
| C(5S)-H(5S1) | 0.9900 |
| C(5S)-H(5S2) | 0.9900 |

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|---|---|
| N(3)-W(1)-N(2) | 107.33(10) |
| N(3)-W(1)-N(1) | 93.29(9) |
| N(2)-W(1)-N(1) | 103.80(9) |
| N(3)-W(1)-Cl(1) | 95.75(7) |
| N(2)-W(1)-Cl(1) | 95.88(7) |
| N(1)-W(1)-Cl(1) | 154.79(6) |
| N(3)-W(1)-Cl(3) | 159.95(7) |
| N(2)-W(1)-Cl(3) | 92.47(7) |
| N(1)-W(1)-Cl(3) | 78.51(6) |
| Cl(1)-W(1)-Cl(3) | 85.129(19) |
| N(3)-W(1)-Cl(4) | 86.89(7) |
| N(2)-W(1)-Cl(4) | 165.78(7) |
| N(1)-W(1)-Cl(4) | 74.55(6) |
| Cl(1)-W(1)-Cl(4) | 82.490(19) |
| Cl(3)-W(1)-Cl(4) | 73.332(18) |
| W(1)-Cl(3)-W(2) | 106.72(2) |
| C(1)-N(1)-W(1) | 126.63(15) |
| C(1)-N(1)-H(1A) | 110(2) |
| W(1)-N(1)-H(1A) | 105(2) |
| C(1)-N(1)-H(1B) | 106.3(19) |
| W(1)-N(1)-H(1B) | 104.9(19) |
| H(1A)-N(1)-H(1B) | 101(3) |
| N(1)-C(1)-C(3) | 108.4(2) |
| N(1)-C(1)-C(2) | 108.7(2) |
| C(3)-C(1)-C(2) | 112.3(2) |
| N(1)-C(1)-C(4) | 107.4(2) |
| C(3)-C(1)-C(4) | 110.0(2) |
| C(2)-C(1)-C(4) | 109.9(2) |
| C(1)-C(2)-H(2A) | 109.5 |
| C(1)-C(2)-H(2B) | 109.5 |
| H(2A)-C(2)-H(2B) | 109.5 |
| C(1)-C(2)-H(2C) | 109.5 |

| | |
|---|---|
| H(2A)-C(2)-H(2C) | 109.5 |
| H(2B)-C(2)-H(2C) | 109.5 |
| C(1)-C(3)-H(3A) | 109.5 |
| C(1)-C(3)-H(3B) | 109.5 |
| H(3A)-C(3)-H(3B) | 109.5 |
| C(1)-C(3)-H(3C) | 109.5 |
| H(3A)-C(3)-H(3C) | 109.5 |
| H(3B)-C(3)-H(3C) | 109.5 |
| C(1)-C(4)-H(4C) | 109.5 |
| C(1)-C(4)-H(4D) | 109.5 |
| H(4C)-C(4)-H(4D) | 109.5 |
| C(1)-C(4)-H(4E) | 109.5 |
| H(4C)-C(4)-H(4E) | 109.5 |
| H(4D)-C(4)-H(4E) | 109.5 |
| C(5)-N(2)-W(1) | 159.36(18) |
| N(2)-C(5)-C(6) | 109.0(2) |
| N(2)-C(5)-C(7) | 111.1(2) |
| C(6)-C(5)-C(7) | 109.9(2) |
| N(2)-C(5)-C(8) | 106.6(2) |
| C(6)-C(5)-C(8) | 110.0(3) |
| C(7)-C(5)-C(8) | 110.1(2) |
| C(5)-C(6)-H(6A) | 109.5 |
| C(5)-C(6)-H(6B) | 109.5 |
| H(6A)-C(6)-H(6B) | 109.5 |
| C(5)-C(6)-H(6C) | 109.5 |
| H(6A)-C(6)-H(6C) | 109.5 |
| H(6B)-C(6)-H(6C) | 109.5 |
| C(5)-C(7)-H(7C) | 109.5 |
| C(5)-C(7)-H(7D) | 109.5 |
| H(7C)-C(7)-H(7D) | 109.5 |
| C(5)-C(7)-H(7E) | 109.5 |
| H(7C)-C(7)-H(7E) | 109.5 |
| H(7D)-C(7)-H(7E) | 109.5 |
| C(5)-C(8)-H(8A) | 109.5 |
| C(5)-C(8)-H(8B) | 109.5 |
| H(8A)-C(8)-H(8B) | 109.5 |
| C(5)-C(8)-H(8C) | 109.5 |
| H(8A)-C(8)-H(8C) | 109.5 |
| H(8B)-C(8)-H(8C) | 109.5 |
| C(9)-N(3)-W(1) | 177.24(19) |
| N(3)-C(9)-C(10) | 111.4(2) |
| N(3)-C(9)-C(12) | 107.2(2) |
| C(10)-C(9)-C(12) | 110.0(2) |
| N(3)-C(9)-C(11) | 107.9(2) |
| C(10)-C(9)-C(11) | 110.8(3) |
| C(12)-C(9)-C(11) | 109.4(2) |
| C(9)-C(10)-H(10C) | 109.5 |
| C(9)-C(10)-H(10D) | 109.5 |
| H(10C)-C(10)-H(10D) | 109.5 |
| C(9)-C(10)-H(10E) | 109.5 |
| H(10C)-C(10)-H(10E) | 109.5 |
| H(10D)-C(10)-H(10E) | 109.5 |
| C(9)-C(11)-H(11A) | 109.5 |
| C(9)-C(11)-H(11B) | 109.5 |

| | |
|---|---|
| H(11A)-C(11)-H(11B) | 109.5 |
| C(9)-C(11)-H(11C) | 109.5 |
| H(11A)-C(11)-H(11C) | 109.5 |
| H(11B)-C(11)-H(11C) | 109.5 |
| C(9)-C(12)-H(12A) | 109.5 |
| C(9)-C(12)-H(12B) | 109.5 |
| H(12A)-C(12)-H(12B) | 109.5 |
| C(9)-C(12)-H(12C) | 109.5 |
| H(12A)-C(12)-H(12C) | 109.5 |
| H(12B)-C(12)-H(12C) | 109.5 |
| N(6)-W(2)-N(5) | 106.90(10) |
| N(6)-W(2)-N(4) | 93.77(8) |
| N(5)-W(2)-N(4) | 101.92(9) |
| N(6)-W(2)-Cl(2) | 94.87(7) |
| N(5)-W(2)-Cl(2) | 97.26(7) |
| N(4)-W(2)-Cl(2) | 155.66(6) |
| N(6)-W(2)-Cl(4) | 160.36(7) |
| N(5)-W(2)-Cl(4) | 92.58(7) |
| N(4)-W(2)-Cl(4) | 79.40(5) |
| Cl(2)-W(2)-Cl(4) | 84.93(2) |
| N(6)-W(2)-Cl(3) | 86.66(7) |
| N(5)-W(2)-Cl(3) | 166.27(7) |
| N(4)-W(2)-Cl(3) | 74.42(6) |
| Cl(2)-W(2)-Cl(3) | 83.410(19) |
| Cl(4)-W(2)-Cl(3) | 73.792(18) |
| W(2)-Cl(4)-W(1) | 106.14(2) |
| C(13)-N(4)-W(2) | 127.09(15) |
| C(13)-N(4)-H(4A) | 107(2) |
| W(2)-N(4)-H(4A) | 106.3(19) |
| C(13)-N(4)-H(4B) | 106.9(19) |
| W(2)-N(4)-H(4B) | 102.8(19) |
| H(4A)-N(4)-H(4B) | 104(3) |
| N(4)-C(13)-C(14) | 108.5(2) |
| N(4)-C(13)-C(15) | 107.3(2) |
| C(14)-C(13)-C(15) | 110.5(2) |
| N(4)-C(13)-C(16) | 108.6(2) |
| C(14)-C(13)-C(16) | 112.1(2) |
| C(15)-C(13)-C(16) | 109.7(2) |
| C(13)-C(14)-H(14A) | 109.5 |
| C(13)-C(14)-H(14B) | 109.5 |
| H(14A)-C(14)-H(14B) | 109.5 |
| C(13)-C(14)-H(14C) | 109.5 |
| H(14A)-C(14)-H(14C) | 109.5 |
| H(14B)-C(14)-H(14C) | 109.5 |
| C(13)-C(15)-H(15A) | 109.5 |
| C(13)-C(15)-H(15B) | 109.5 |
| H(15A)-C(15)-H(15B) | 109.5 |
| C(13)-C(15)-H(15C) | 109.5 |
| H(15A)-C(15)-H(15C) | 109.5 |
| H(15B)-C(15)-H(15C) | 109.5 |
| C(13)-C(16)-H(16A) | 109.5 |
| C(13)-C(16)-H(16B) | 109.5 |
| H(16A)-C(16)-H(16B) | 109.5 |
| C(13)-C(16)-H(16C) | 109.5 |

| | |
|---|---|
| H(16A)-C(16)-H(16C) | 109.5 |
| H(16B)-C(16)-H(16C) | 109.5 |
| C(17)-N(5)-W(2) | 153.56(18) |
| N(5)-C(17)-C(18) | 110.5(2) |
| N(5)-C(17)-C(20) | 110.8(2) |
| C(18)-C(17)-C(20) | 110.2(2) |
| N(5)-C(17)-C(19) | 106.4(2) |
| C(18)-C(17)-C(19) | 108.8(2) |
| C(20)-C(17)-C(19) | 110.1(2) |
| C(17)-C(18)-H(18A) | 109.5 |
| C(17)-C(18)-H(18B) | 109.5 |
| H(18A)-C(18)-H(18B) | 109.5 |
| C(17)-C(18)-H(18C) | 109.5 |
| H(18A)-C(18)-H(18C) | 109.5 |
| H(18B)-C(18)-H(18C) | 109.5 |
| C(17)-C(19)-H(19A) | 109.5 |
| C(17)-C(19)-H(19B) | 109.5 |
| H(19A)-C(19)-H(19B) | 109.5 |
| C(17)-C(19)-H(19C) | 109.5 |
| H(19A)-C(19)-H(19C) | 109.5 |
| H(19B)-C(19)-H(19C) | 109.5 |
| C(17)-C(20)-H(20A) | 109.5 |
| C(17)-C(20)-H(20B) | 109.5 |
| H(20A)-C(20)-H(20B) | 109.5 |
| C(17)-C(20)-H(20C) | 109.5 |
| H(20A)-C(20)-H(20C) | 109.5 |
| H(20B)-C(20)-H(20C) | 109.5 |
| C(21)-N(6)-W(2) | 175.18(18) |
| N(6)-C(21)-C(23) | 109.0(2) |
| N(6)-C(21)-C(22) | 108.8(2) |
| C(23)-C(21)-C(22) | 110.2(2) |
| N(6)-C(21)-C(24) | 108.3(2) |
| C(23)-C(21)-C(24) | 110.7(2) |
| C(22)-C(21)-C(24) | 109.9(2) |
| C(21)-C(22)-H(22A) | 109.5 |
| C(21)-C(22)-H(22B) | 109.5 |
| H(22A)-C(22)-H(22B) | 109.5 |
| C(21)-C(22)-H(22C) | 109.5 |
| H(22A)-C(22)-H(22C) | 109.5 |
| H(22B)-C(22)-H(22C) | 109.5 |
| C(21)-C(23)-H(23A) | 109.5 |
| C(21)-C(23)-H(23B) | 109.5 |
| H(23A)-C(23)-H(23B) | 109.5 |
| C(21)-C(23)-H(23C) | 109.5 |
| H(23A)-C(23)-H(23C) | 109.5 |
| H(23B)-C(23)-H(23C) | 109.5 |
| C(21)-C(24)-H(24A) | 109.5 |
| C(21)-C(24)-H(24B) | 109.5 |
| H(24A)-C(24)-H(24B) | 109.5 |
| C(21)-C(24)-H(24C) | 109.5 |
| H(24A)-C(24)-H(24C) | 109.5 |
| H(24B)-C(24)-H(24C) | 109.5 |
| N(8)-W(3)-N(9) | 107.61(10) |
| N(8)-W(3)-N(7) | 103.48(9) |

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|---|---|
| N(9)-W(3)-N(7) | 92.69(9) |
| N(8)-W(3)-Cl(5) | 96.75(7) |
| N(9)-W(3)-Cl(5) | 94.90(7) |
| N(7)-W(3)-Cl(5) | 155.11(6) |
| N(8)-W(3)-Cl(7) | 91.01(7) |
| N(9)-W(3)-Cl(7) | 161.27(7) |
| N(7)-W(3)-Cl(7) | 80.69(6) |
| Cl(5)-W(3)-Cl(7) | 84.64(2) |
| N(8)-W(3)-Cl(8) | 164.89(7) |
| N(9)-W(3)-Cl(8) | 87.44(7) |
| N(7)-W(3)-Cl(8) | 73.75(6) |
| Cl(5)-W(3)-Cl(8) | 82.93(2) |
| Cl(7)-W(3)-Cl(8) | 73.909(18) |
| W(3)-Cl(7)-W(4) | 106.15(2) |
| C(31)-N(7)-W(3) | 127.27(15) |
| C(31)-N(7)-H(7A) | 109(2) |
| W(3)-N(7)-H(7A) | 108(2) |
| C(31)-N(7)-H(7B) | 107.9(19) |
| W(3)-N(7)-H(7B) | 102.0(19) |
| H(7A)-N(7)-H(7B) | 99(3) |
| N(7)-C(31)-C(32) | 107.7(2) |
| N(7)-C(31)-C(33) | 109.2(2) |
| C(32)-C(31)-C(33) | 112.9(2) |
| N(7)-C(31)-C(34) | 107.3(2) |
| C(32)-C(31)-C(34) | 110.1(2) |
| C(33)-C(31)-C(34) | 109.4(2) |
| C(31)-C(32)-H(32A) | 109.5 |
| C(31)-C(32)-H(32B) | 109.5 |
| H(32A)-C(32)-H(32B) | 109.5 |
| C(31)-C(32)-H(32C) | 109.5 |
| H(32A)-C(32)-H(32C) | 109.5 |
| H(32B)-C(32)-H(32C) | 109.5 |
| C(31)-C(33)-H(33A) | 109.5 |
| C(31)-C(33)-H(33B) | 109.5 |
| H(33A)-C(33)-H(33B) | 109.5 |
| C(31)-C(33)-H(33C) | 109.5 |
| H(33A)-C(33)-H(33C) | 109.5 |
| H(33B)-C(33)-H(33C) | 109.5 |
| C(31)-C(34)-H(34A) | 109.5 |
| C(31)-C(34)-H(34B) | 109.5 |
| H(34A)-C(34)-H(34B) | 109.5 |
| C(31)-C(34)-H(34C) | 109.5 |
| H(34A)-C(34)-H(34C) | 109.5 |
| H(34B)-C(34)-H(34C) | 109.5 |
| C(35)-N(8)-W(3) | 163.1(2) |
| N(8)-C(35)-C(37A) | 110.3(11) |
| N(8)-C(35)-C(38) | 109.7(6) |
| C(37A)-C(35)-C(38) | 121.1(13) |
| N(8)-C(35)-C(37) | 112.1(6) |
| C(37A)-C(35)-C(37) | 12.9(13) |
| C(38)-C(35)-C(37) | 109.7(5) |
| N(8)-C(35)-C(36A) | 108.2(12) |
| C(37A)-C(35)-C(36A) | 110.1(11) |
| C(38)-C(35)-C(36A) | 96.0(12) |

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| C(37)-C(35)-C(36A) | 119.8(13) |
| N(8)-C(35)-C(38A) | 107.5(10) |
| C(37A)-C(35)-C(38A) | 112.5(11) |
| C(38)-C(35)-C(38A) | 12.4(12) |
| C(37)-C(35)-C(38A) | 100.2(12) |
| C(36A)-C(35)-C(38A) | 108.1(10) |
| N(8)-C(35)-C(36) | 105.0(6) |
| C(37A)-C(35)-C(36) | 98.5(13) |
| C(38)-C(35)-C(36) | 110.6(6) |
| C(37)-C(35)-C(36) | 109.6(6) |
| C(36A)-C(35)-C(36) | 15.0(12) |
| C(38A)-C(35)-C(36) | 122.4(11) |
| C(35)-C(36)-H(36A) | 109.5 |
| C(35)-C(36)-H(36B) | 109.5 |
| H(36A)-C(36)-H(36B) | 109.5 |
| C(35)-C(36)-H(36C) | 109.5 |
| H(36A)-C(36)-H(36C) | 109.5 |
| H(36B)-C(36)-H(36C) | 109.5 |
| C(35)-C(37)-H(37A) | 109.5 |
| C(35)-C(37)-H(37B) | 109.5 |
| H(37A)-C(37)-H(37B) | 109.5 |
| C(35)-C(37)-H(37C) | 109.5 |
| H(37A)-C(37)-H(37C) | 109.5 |
| H(37B)-C(37)-H(37C) | 109.5 |
| C(35)-C(38)-H(38A) | 109.5 |
| C(35)-C(38)-H(38B) | 109.5 |
| H(38A)-C(38)-H(38B) | 109.5 |
| C(35)-C(38)-H(38C) | 109.5 |
| H(38A)-C(38)-H(38C) | 109.5 |
| H(38B)-C(38)-H(38C) | 109.5 |
| C(35)-C(36A)-H(36D) | 109.5 |
| C(35)-C(36A)-H(36E) | 109.5 |
| H(36D)-C(36A)-H(36E) | 109.5 |
| C(35)-C(36A)-H(36F) | 109.5 |
| H(36D)-C(36A)-H(36F) | 109.5 |
| H(36E)-C(36A)-H(36F) | 109.5 |
| C(35)-C(37A)-H(37D) | 109.5 |
| C(35)-C(37A)-H(37E) | 109.5 |
| H(37D)-C(37A)-H(37E) | 109.5 |
| C(35)-C(37A)-H(37F) | 109.5 |
| H(37D)-C(37A)-H(37F) | 109.5 |
| H(37E)-C(37A)-H(37F) | 109.5 |
| C(35)-C(38A)-H(38D) | 109.5 |
| C(35)-C(38A)-H(38E) | 109.5 |
| H(38D)-C(38A)-H(38E) | 109.5 |
| C(35)-C(38A)-H(38F) | 109.5 |
| H(38D)-C(38A)-H(38F) | 109.5 |
| H(38E)-C(38A)-H(38F) | 109.5 |
| C(39)-N(9)-W(3) | 176.84(18) |
| N(9)-C(39)-C(40) | 110.8(2) |
| N(9)-C(39)-C(41) | 106.8(2) |
| C(40)-C(39)-C(41) | 110.7(2) |
| N(9)-C(39)-C(42) | 108.1(2) |
| C(40)-C(39)-C(42) | 110.8(2) |

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| C(41)-C(39)-C(42) | 109.6(2) |
| C(39)-C(40)-H(40A) | 109.5 |
| C(39)-C(40)-H(40B) | 109.5 |
| H(40A)-C(40)-H(40B) | 109.5 |
| C(39)-C(40)-H(40C) | 109.5 |
| H(40A)-C(40)-H(40C) | 109.5 |
| H(40B)-C(40)-H(40C) | 109.5 |
| C(39)-C(41)-H(41A) | 109.5 |
| C(39)-C(41)-H(41B) | 109.5 |
| H(41A)-C(41)-H(41B) | 109.5 |
| C(39)-C(41)-H(41C) | 109.5 |
| H(41A)-C(41)-H(41C) | 109.5 |
| H(41B)-C(41)-H(41C) | 109.5 |
| C(39)-C(42)-H(42A) | 109.5 |
| C(39)-C(42)-H(42B) | 109.5 |
| H(42A)-C(42)-H(42B) | 109.5 |
| C(39)-C(42)-H(42C) | 109.5 |
| H(42A)-C(42)-H(42C) | 109.5 |
| H(42B)-C(42)-H(42C) | 109.5 |
| N(12)-W(4)-N(11) | 106.77(10) |
| N(12)-W(4)-N(10) | 93.28(9) |
| N(11)-W(4)-N(10) | 102.43(9) |
| N(12)-W(4)-Cl(6) | 95.62(7) |
| N(11)-W(4)-Cl(6) | 96.34(8) |
| N(10)-W(4)-Cl(6) | 155.92(6) |
| N(12)-W(4)-Cl(8) | 160.41(7) |
| N(11)-W(4)-Cl(8) | 92.58(8) |
| N(10)-W(4)-Cl(8) | 79.25(6) |
| Cl(6)-W(4)-Cl(8) | 85.03(2) |
| N(12)-W(4)-Cl(7) | 86.35(7) |
| N(11)-W(4)-Cl(7) | 166.83(8) |
| N(10)-W(4)-Cl(7) | 75.04(6) |
| Cl(6)-W(4)-Cl(7) | 83.24(2) |
| Cl(8)-W(4)-Cl(7) | 74.263(18) |
| W(4)-Cl(8)-W(3) | 105.67(2) |
| C(43)-N(10)-W(4) | 126.81(17) |
| C(43)-N(10)-H(10A) | 106(2) |
| W(4)-N(10)-H(10A) | 107(2) |
| C(43)-N(10)-H(10B) | 109(2) |
| W(4)-N(10)-H(10B) | 101(2) |
| H(10A)-N(10)-H(10B) | 106(3) |
| N(10)-C(43)-C(45) | 108.0(2) |
| N(10)-C(43)-C(46) | 108.0(2) |
| C(45)-C(43)-C(46) | 109.8(2) |
| N(10)-C(43)-C(44) | 108.2(2) |
| C(45)-C(43)-C(44) | 112.4(3) |
| C(46)-C(43)-C(44) | 110.4(2) |
| C(43)-C(44)-H(44A) | 109.5 |
| C(43)-C(44)-H(44B) | 109.5 |
| H(44A)-C(44)-H(44B) | 109.5 |
| C(43)-C(44)-H(44C) | 109.5 |
| H(44A)-C(44)-H(44C) | 109.5 |
| H(44B)-C(44)-H(44C) | 109.5 |
| C(43)-C(45)-H(45A) | 109.5 |

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| C(43)-C(45)-H(45B) | 109.5 |
| H(45A)-C(45)-H(45B) | 109.5 |
| C(43)-C(45)-H(45C) | 109.5 |
| H(45A)-C(45)-H(45C) | 109.5 |
| H(45B)-C(45)-H(45C) | 109.5 |
| C(43)-C(46)-H(46A) | 109.5 |
| C(43)-C(46)-H(46B) | 109.5 |
| H(46A)-C(46)-H(46B) | 109.5 |
| C(43)-C(46)-H(46C) | 109.5 |
| H(46A)-C(46)-H(46C) | 109.5 |
| H(46B)-C(46)-H(46C) | 109.5 |
| C(47A)-N(11)-C(47) | 14.7(5) |
| C(47A)-N(11)-W(4) | 164.4(5) |
| C(47)-N(11)-W(4) | 151.3(3) |
| N(11)-C(47)-C(48) | 112.3(4) |
| N(11)-C(47)-C(50) | 108.2(4) |
| C(48)-C(47)-C(50) | 109.4(5) |
| N(11)-C(47)-C(49) | 107.7(4) |
| C(48)-C(47)-C(49) | 109.6(5) |
| C(50)-C(47)-C(49) | 109.6(5) |
| C(47)-C(48)-H(48A) | 109.5 |
| C(47)-C(48)-H(48B) | 109.5 |
| H(48A)-C(48)-H(48B) | 109.5 |
| C(47)-C(48)-H(48C) | 109.5 |
| H(48A)-C(48)-H(48C) | 109.5 |
| H(48B)-C(48)-H(48C) | 109.5 |
| C(47)-C(49)-H(49A) | 109.5 |
| C(47)-C(49)-H(49B) | 109.5 |
| H(49A)-C(49)-H(49B) | 109.5 |
| C(47)-C(49)-H(49C) | 109.5 |
| H(49A)-C(49)-H(49C) | 109.5 |
| H(49B)-C(49)-H(49C) | 109.5 |
| C(47)-C(50)-H(50A) | 109.5 |
| C(47)-C(50)-H(50B) | 109.5 |
| H(50A)-C(50)-H(50B) | 109.5 |
| C(47)-C(50)-H(50C) | 109.5 |
| H(50A)-C(50)-H(50C) | 109.5 |
| H(50B)-C(50)-H(50C) | 109.5 |
| N(11)-C(47A)-C(50A) | 110.1(9) |
| N(11)-C(47A)-C(49A) | 100.1(8) |
| C(50A)-C(47A)-C(49A) | 111.8(10) |
| N(11)-C(47A)-C(48A) | 111.5(8) |
| C(50A)-C(47A)-C(48A) | 110.7(9) |
| C(49A)-C(47A)-C(48A) | 112.2(10) |
| C(47A)-C(48A)-H(48D) | 109.5 |
| C(47A)-C(48A)-H(48E) | 109.5 |
| H(48D)-C(48A)-H(48E) | 109.5 |
| C(47A)-C(48A)-H(48F) | 109.5 |
| H(48D)-C(48A)-H(48F) | 109.5 |
| H(48E)-C(48A)-H(48F) | 109.5 |
| C(47A)-C(49A)-H(49D) | 109.5 |
| C(47A)-C(49A)-H(49E) | 109.5 |
| H(49D)-C(49A)-H(49E) | 109.5 |
| C(47A)-C(49A)-H(49F) | 109.5 |

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| H(49D)-C(49A)-H(49F) | 109.5 |
| H(49E)-C(49A)-H(49F) | 109.5 |
| C(47A)-C(50A)-H(50D) | 109.5 |
| C(47A)-C(50A)-H(50E) | 109.5 |
| H(50D)-C(50A)-H(50E) | 109.5 |
| C(47A)-C(50A)-H(50F) | 109.5 |
| H(50D)-C(50A)-H(50F) | 109.5 |
| H(50E)-C(50A)-H(50F) | 109.5 |
| C(51)-N(12)-W(4) | 174.72(19) |
| N(12)-C(51)-C(53) | 107.1(2) |
| N(12)-C(51)-C(52) | 111.4(2) |
| C(53)-C(51)-C(52) | 110.2(2) |
| N(12)-C(51)-C(54) | 107.6(2) |
| C(53)-C(51)-C(54) | 110.5(2) |
| C(52)-C(51)-C(54) | 110.0(2) |
| C(51)-C(52)-H(52A) | 109.5 |
| C(51)-C(52)-H(52B) | 109.5 |
| H(52A)-C(52)-H(52B) | 109.5 |
| C(51)-C(52)-H(52C) | 109.5 |
| H(52A)-C(52)-H(52C) | 109.5 |
| H(52B)-C(52)-H(52C) | 109.5 |
| C(51)-C(53)-H(53A) | 109.5 |
| C(51)-C(53)-H(53B) | 109.5 |
| H(53A)-C(53)-H(53B) | 109.5 |
| C(51)-C(53)-H(53C) | 109.5 |
| H(53A)-C(53)-H(53C) | 109.5 |
| H(53B)-C(53)-H(53C) | 109.5 |
| C(51)-C(54)-H(54A) | 109.5 |
| C(51)-C(54)-H(54B) | 109.5 |
| H(54A)-C(54)-H(54B) | 109.5 |
| C(51)-C(54)-H(54C) | 109.5 |
| H(54A)-C(54)-H(54C) | 109.5 |
| H(54B)-C(54)-H(54C) | 109.5 |
| N(15)-W(5)-N(14) | 106.89(10) |
| N(15)-W(5)-N(13) | 102.37(8) |
| N(14)-W(5)-N(13) | 95.10(8) |
| N(15)-W(5)-Cl(9) | 94.09(7) |
| N(14)-W(5)-Cl(9) | 96.68(7) |
| N(13)-W(5)-Cl(9) | 156.01(5) |
| N(15)-W(5)-Cl(10) | 158.61(7) |
| N(14)-W(5)-Cl(10) | 94.49(7) |
| N(13)-W(5)-Cl(10) | 75.52(5) |
| Cl(9)-W(5)-Cl(10) | 82.78(2) |
| N(15)-W(5)-Cl(10)#1 | 84.58(7) |
| N(14)-W(5)-Cl(10)#1 | 167.97(7) |
| N(13)-W(5)-Cl(10)#1 | 78.53(6) |
| Cl(9)-W(5)-Cl(10)#1 | 85.882(19) |
| Cl(10)-W(5)-Cl(10)#1 | 74.12(2) |
| W(5)-Cl(10)-W(5)#1 | 105.88(2) |
| C(61)-N(13)-W(5) | 128.50(15) |
| C(61)-N(13)-H(13A) | 110.5(18) |
| W(5)-N(13)-H(13A) | 99.6(18) |
| C(61)-N(13)-H(13B) | 104.3(19) |
| W(5)-N(13)-H(13B) | 106.2(19) |

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| H(13A)-N(13)-H(13B) | 106(2) |
| N(13)-C(61)-C(64) | 107.9(2) |
| N(13)-C(61)-C(62) | 107.5(2) |
| C(64)-C(61)-C(62) | 110.1(2) |
| N(13)-C(61)-C(63) | 108.2(2) |
| C(64)-C(61)-C(63) | 112.7(2) |
| C(62)-C(61)-C(63) | 110.1(2) |
| C(61)-C(62)-H(62A) | 109.5 |
| C(61)-C(62)-H(62B) | 109.5 |
| H(62A)-C(62)-H(62B) | 109.5 |
| C(61)-C(62)-H(62C) | 109.5 |
| H(62A)-C(62)-H(62C) | 109.5 |
| H(62B)-C(62)-H(62C) | 109.5 |
| C(61)-C(63)-H(63A) | 109.5 |
| C(61)-C(63)-H(63B) | 109.5 |
| H(63A)-C(63)-H(63B) | 109.5 |
| C(61)-C(63)-H(63C) | 109.5 |
| H(63A)-C(63)-H(63C) | 109.5 |
| H(63B)-C(63)-H(63C) | 109.5 |
| C(61)-C(64)-H(64A) | 109.5 |
| C(61)-C(64)-H(64B) | 109.5 |
| H(64A)-C(64)-H(64B) | 109.5 |
| C(61)-C(64)-H(64C) | 109.5 |
| H(64A)-C(64)-H(64C) | 109.5 |
| H(64B)-C(64)-H(64C) | 109.5 |
| C(65)-N(14)-W(5) | 156.45(17) |
| N(14)-C(65)-C(66) | 108.82(19) |
| N(14)-C(65)-C(68) | 106.8(2) |
| C(66)-C(65)-C(68) | 110.4(2) |
| N(14)-C(65)-C(67) | 110.9(2) |
| C(66)-C(65)-C(67) | 110.5(2) |
| C(68)-C(65)-C(67) | 109.4(2) |
| C(65)-C(66)-H(66A) | 109.5 |
| C(65)-C(66)-H(66B) | 109.5 |
| H(66A)-C(66)-H(66B) | 109.5 |
| C(65)-C(66)-H(66C) | 109.5 |
| H(66A)-C(66)-H(66C) | 109.5 |
| H(66B)-C(66)-H(66C) | 109.5 |
| C(65)-C(67)-H(67A) | 109.5 |
| C(65)-C(67)-H(67B) | 109.5 |
| H(67A)-C(67)-H(67B) | 109.5 |
| C(65)-C(67)-H(67C) | 109.5 |
| H(67A)-C(67)-H(67C) | 109.5 |
| H(67B)-C(67)-H(67C) | 109.5 |
| C(65)-C(68)-H(68A) | 109.5 |
| C(65)-C(68)-H(68B) | 109.5 |
| H(68A)-C(68)-H(68B) | 109.5 |
| C(65)-C(68)-H(68C) | 109.5 |
| H(68A)-C(68)-H(68C) | 109.5 |
| H(68B)-C(68)-H(68C) | 109.5 |
| C(69)-N(15)-W(5) | 169.89(18) |
| N(15)-C(69)-C(72) | 110.1(2) |
| N(15)-C(69)-C(71) | 109.2(2) |
| C(72)-C(69)-C(71) | 110.3(3) |

| | |
|---|---|
| N(15)-C(69)-C(70) | 107.6(2) |
| C(72)-C(69)-C(70) | 109.7(2) |
| C(71)-C(69)-C(70) | 109.9(3) |
| C(69)-C(70)-H(70A) | 109.5 |
| C(69)-C(70)-H(70B) | 109.5 |
| H(70A)-C(70)-H(70B) | 109.5 |
| C(69)-C(70)-H(70C) | 109.5 |
| H(70A)-C(70)-H(70C) | 109.5 |
| H(70B)-C(70)-H(70C) | 109.5 |
| C(69)-C(71)-H(71A) | 109.5 |
| C(69)-C(71)-H(71B) | 109.5 |
| H(71A)-C(71)-H(71B) | 109.5 |
| C(69)-C(71)-H(71C) | 109.5 |
| H(71A)-C(71)-H(71C) | 109.5 |
| H(71B)-C(71)-H(71C) | 109.5 |
| C(69)-C(72)-H(72A) | 109.5 |
| C(69)-C(72)-H(72B) | 109.5 |
| H(72A)-C(72)-H(72B) | 109.5 |
| C(69)-C(72)-H(72C) | 109.5 |
| H(72A)-C(72)-H(72C) | 109.5 |
| H(72B)-C(72)-H(72C) | 109.5 |
| Cl(1S)-C(1S)-Cl(2S) | 110.7(4) |
| Cl(1S)-C(1S)-H(1S1) | 109.5 |
| Cl(2S)-C(1S)-H(1S1) | 109.5 |
| Cl(1S)-C(1S)-H(1S2) | 109.5 |
| Cl(2S)-C(1S)-H(1S2) | 109.5 |
| H(1S1)-C(1S)-H(1S2) | 108.1 |
| Cl(2T)-C(1T)-Cl(1T) | 111.3(8) |
| Cl(2T)-C(1T)-H(1T1) | 109.4 |
| Cl(1T)-C(1T)-H(1T1) | 109.4 |
| Cl(2T)-C(1T)-H(1T2) | 109.4 |
| Cl(1T)-C(1T)-H(1T2) | 109.4 |
| H(1T1)-C(1T)-H(1T2) | 108.0 |
| Cl(3S)-C(2S)-Cl(4S) | 109.7(7) |
| Cl(3S)-C(2S)-H(2S1) | 109.7 |
| Cl(4S)-C(2S)-H(2S1) | 109.7 |
| Cl(3S)-C(2S)-H(2S2) | 109.7 |
| Cl(4S)-C(2S)-H(2S2) | 109.7 |
| H(2S1)-C(2S)-H(2S2) | 108.2 |
| Cl(3T)-C(2T)-Cl(4T) | 110.8(11) |
| Cl(3T)-C(2T)-H(2T1) | 109.5 |
| Cl(4T)-C(2T)-H(2T1) | 109.5 |
| Cl(3T)-C(2T)-H(2T2) | 109.5 |
| Cl(4T)-C(2T)-H(2T2) | 109.5 |
| H(2T1)-C(2T)-H(2T2) | 108.1 |
| Cl(6S)-C(3S)-Cl(5S) | 111.88(17) |
| Cl(6S)-C(3S)-H(3S1) | 109.2 |
| Cl(5S)-C(3S)-H(3S1) | 109.2 |
| Cl(6S)-C(3S)-H(3S2) | 109.2 |
| Cl(5S)-C(3S)-H(3S2) | 109.2 |
| H(3S1)-C(3S)-H(3S2) | 107.9 |
| Cl(8S)-C(4S)-Cl(7S) | 110.83(16) |
| Cl(8S)-C(4S)-H(4S1) | 109.5 |
| Cl(7S)-C(4S)-H(4S1) | 109.5 |

| | |
|---|---|
| Cl(8S)-C(4S)-H(4S2) | 109.5 |
| Cl(7S)-C(4S)-H(4S2) | 109.5 |
| H(4S1)-C(4S)-H(4S2) | 108.1 |
| Cl(15)-C(5S)-Cl(9S) | 111.48(16) |
| Cl(15)-C(5S)-H(5S1) | 109.3 |
| Cl(9S)-C(5S)-H(5S1) | 109.3 |
| Cl(15)-C(5S)-H(5S2) | 109.3 |
| Cl(9S)-C(5S)-H(5S2) | 109.3 |
| H(5S1)-C(5S)-H(5S2) | 108.0 |

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **X8_12060**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Cl(1) | 32(1) | 31(1) | 27(1) | 4(1) | 3(1) | 6(1) |
| W(1) | 27(1) | 26(1) | 28(1) | 6(1) | 4(1) | 7(1) |
| Cl(3) | 25(1) | 28(1) | 30(1) | 5(1) | 3(1) | 4(1) |
| N(1) | 32(1) | 28(1) | 31(1) | 6(1) | 7(1) | 8(1) |
| C(1) | 36(1) | 31(1) | 31(1) | 4(1) | 7(1) | 8(1) |
| C(2) | 43(1) | 33(1) | 40(1) | 4(1) | 6(1) | 14(1) |
| C(3) | 38(1) | 45(2) | 35(1) | -2(1) | 0(1) | 3(1) |
| C(4) | 55(2) | 42(2) | 35(1) | 6(1) | 16(1) | 13(1) |
| N(2) | 35(1) | 24(1) | 30(1) | 6(1) | 6(1) | 4(1) |
| C(5) | 36(1) | 30(1) | 32(1) | 8(1) | 4(1) | 0(1) |
| C(6) | 38(2) | 46(2) | 59(2) | 16(1) | 4(1) | -1(1) |
| C(7) | 43(2) | 32(1) | 56(2) | 14(1) | 2(1) | 6(1) |
| C(8) | 80(2) | 40(2) | 32(1) | 9(1) | 12(1) | -1(2) |
| N(3) | 29(1) | 31(1) | 33(1) | 6(1) | 2(1) | 9(1) |
| C(9) | 29(1) | 30(1) | 44(1) | 2(1) | -4(1) | 7(1) |
| C(10) | 53(2) | 35(2) | 87(3) | 8(2) | -30(2) | 11(1) |
| C(11) | 34(1) | 71(2) | 48(2) | -4(2) | 7(1) | 10(1) |
| C(12) | 41(1) | 38(1) | 39(1) | 4(1) | 0(1) | 4(1) |
| Cl(2) | 33(1) | 33(1) | 28(1) | 4(1) | 4(1) | 8(1) |
| W(2) | 25(1) | 25(1) | 27(1) | 5(1) | 2(1) | 6(1) |
| Cl(4) | 24(1) | 28(1) | 32(1) | 7(1) | 3(1) | 5(1) |
| N(4) | 28(1) | 28(1) | 28(1) | 3(1) | 3(1) | 6(1) |
| C(13) | 33(1) | 31(1) | 32(1) | 1(1) | 2(1) | 7(1) |
| C(14) | 33(1) | 36(1) | 34(1) | 3(1) | 0(1) | 3(1) |
| C(15) | 39(1) | 46(2) | 31(1) | 0(1) | 6(1) | 9(1) |
| C(16) | 43(2) | 34(1) | 42(1) | -2(1) | -1(1) | 14(1) |
| N(5) | 32(1) | 27(1) | 30(1) | 7(1) | 3(1) | 3(1) |
| C(17) | 38(1) | 29(1) | 34(1) | 10(1) | 1(1) | 5(1) |
| C(18) | 51(2) | 33(1) | 46(2) | 10(1) | 0(1) | -2(1) |
| C(19) | 48(2) | 45(2) | 48(2) | 19(1) | 16(1) | 9(1) |
| C(20) | 45(2) | 36(1) | 47(2) | 15(1) | -4(1) | 9(1) |
| N(6) | 28(1) | 31(1) | 29(1) | 5(1) | 0(1) | 7(1) |
| C(21) | 26(1) | 35(1) | 37(1) | 6(1) | 0(1) | 7(1) |
| C(22) | 35(1) | 41(2) | 65(2) | 9(1) | -8(1) | 1(1) |
| C(23) | 37(1) | 76(2) | 37(1) | 15(1) | -3(1) | 10(1) |
| C(24) | 36(1) | 53(2) | 47(2) | -2(1) | 0(1) | 20(1) |
| Cl(5) | 33(1) | 39(1) | 28(1) | 2(1) | 4(1) | 10(1) |
| W(3) | 27(1) | 27(1) | 27(1) | 5(1) | 4(1) | 7(1) |
| Cl(7) | 25(1) | 28(1) | 32(1) | 6(1) | 3(1) | 5(1) |
| N(7) | 31(1) | 28(1) | 28(1) | 5(1) | 4(1) | 7(1) |
| C(31) | 35(1) | 29(1) | 30(1) | 1(1) | 3(1) | 5(1) |
| C(32) | 37(1) | 45(2) | 44(2) | -4(1) | 0(1) | -3(1) |
| C(33) | 53(2) | 37(1) | 38(1) | 4(1) | 5(1) | 20(1) |
| C(34) | 50(2) | 43(2) | 33(1) | 2(1) | 8(1) | 10(1) |
| N(8) | 37(1) | 31(1) | 33(1) | 9(1) | 8(1) | 9(1) |
| C(35) | 49(2) | 36(1) | 48(1) | 18(1) | 19(1) | 13(1) |
| C(36) | 157(10) | 63(5) | 57(3) | 32(3) | 55(5) | 34(6) |
| C(37) | 44(3) | 34(3) | 68(4) | 14(3) | -3(3) | 9(2) |
| C(38) | 32(2) | 52(4) | 127(8) | 34(4) | 17(3) | 5(2) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(36A) | 80(11) | 67(10) | 46(5) | 31(5) | 27(5) | 36(7) |
| C(37A) | 59(8) | 44(9) | 94(14) | 35(9) | 33(8) | 24(7) |
| C(38A) | 60(8) | 34(6) | 66(7) | 17(5) | 22(5) | -4(6) |
| N(9) | 30(1) | 35(1) | 29(1) | 4(1) | 3(1) | 11(1) |
| C(39) | 26(1) | 39(1) | 33(1) | 9(1) | 2(1) | 8(1) |
| C(40) | 36(1) | 49(2) | 64(2) | 26(2) | 2(1) | 14(1) |
| C(41) | 38(2) | 58(2) | 40(1) | -3(1) | -2(1) | 8(1) |
| C(42) | 35(1) | 53(2) | 44(2) | 14(1) | 8(1) | 8(1) |
| Cl(6) | 34(1) | 38(1) | 30(1) | 6(1) | 5(1) | 11(1) |
| W(4) | 27(1) | 27(1) | 32(1) | 7(1) | 5(1) | 8(1) |
| Cl(8) | 26(1) | 27(1) | 34(1) | 5(1) | 4(1) | 4(1) |
| N(10) | 30(1) | 28(1) | 34(1) | 2(1) | 6(1) | 6(1) |
| C(43) | 35(1) | 28(1) | 40(1) | 0(1) | 0(1) | 7(1) |
| C(44) | 50(2) | 40(2) | 56(2) | -6(1) | -6(1) | 22(1) |
| C(45) | 36(1) | 39(1) | 42(1) | 5(1) | -2(1) | -3(1) |
| C(46) | 46(2) | 42(2) | 40(1) | -4(1) | 10(1) | 4(1) |
| N(11) | 36(1) | 28(1) | 44(1) | 10(1) | 10(1) | 8(1) |
| C(47) | 36(2) | 29(2) | 47(3) | 12(2) | 7(2) | 4(2) |
| C(48) | 49(3) | 57(3) | 65(3) | 33(3) | 5(2) | 16(2) |
| C(49) | 74(4) | 38(2) | 56(3) | 15(2) | 5(3) | -7(2) |
| C(50) | 75(4) | 63(4) | 54(3) | 35(3) | 32(3) | 31(4) |
| C(47A) | 36(2) | 29(2) | 47(3) | 12(2) | 7(2) | 4(2) |
| C(48A) | 45(5) | 49(5) | 63(6) | 10(5) | 8(4) | -10(4) |
| C(49A) | 82(10) | 49(6) | 47(5) | 19(4) | 1(6) | 6(7) |
| C(50A) | 58(6) | 38(5) | 91(8) | 26(5) | 20(6) | 20(4) |
| N(12) | 29(1) | 33(1) | 33(1) | 8(1) | 5(1) | 9(1) |
| C(51) | 28(1) | 38(1) | 35(1) | 11(1) | 4(1) | 10(1) |
| C(52) | 49(2) | 53(2) | 54(2) | 15(1) | 3(1) | 28(1) |
| C(53) | 38(1) | 46(2) | 41(1) | 4(1) | 1(1) | 7(1) |
| C(54) | 34(1) | 60(2) | 42(1) | 14(1) | 10(1) | 8(1) |
| Cl(9) | 40(1) | 30(1) | 26(1) | 3(1) | 2(1) | 6(1) |
| W(5) | 27(1) | 25(1) | 26(1) | 4(1) | 3(1) | 6(1) |
| Cl(10) | 26(1) | 28(1) | 30(1) | 5(1) | 3(1) | 5(1) |
| N(13) | 28(1) | 27(1) | 29(1) | 3(1) | 3(1) | 6(1) |
| C(61) | 34(1) | 31(1) | 28(1) | 1(1) | 5(1) | 7(1) |
| C(62) | 38(1) | 38(1) | 30(1) | -1(1) | 4(1) | 3(1) |
| C(63) | 53(2) | 29(1) | 41(1) | 3(1) | 6(1) | 11(1) |
| C(64) | 33(1) | 45(2) | 35(1) | 1(1) | 8(1) | 6(1) |
| N(14) | 32(1) | 26(1) | 27(1) | 5(1) | 3(1) | 6(1) |
| C(65) | 32(1) | 26(1) | 30(1) | 7(1) | 2(1) | 6(1) |
| C(66) | 40(1) | 34(1) | 39(1) | 6(1) | -1(1) | -1(1) |
| C(67) | 41(1) | 36(1) | 52(2) | 14(1) | 4(1) | 14(1) |
| C(68) | 43(1) | 40(1) | 29(1) | 9(1) | 6(1) | 8(1) |
| N(15) | 30(1) | 31(1) | 32(1) | 4(1) | 0(1) | 9(1) |
| C(69) | 29(1) | 44(1) | 38(1) | 9(1) | -3(1) | 9(1) |
| C(70) | 42(2) | 60(2) | 37(1) | 8(1) | -4(1) | 17(1) |
| C(71) | 34(1) | 59(2) | 63(2) | 22(2) | -4(1) | -1(1) |
| C(72) | 39(1) | 53(2) | 47(2) | 12(1) | 6(1) | 22(1) |
| C(1S) | 40(3) | 61(3) | 51(3) | 13(3) | 6(3) | -5(2) |
| Cl(1S) | 44(1) | 45(1) | 164(4) | 24(2) | -3(2) | 3(1) |
| Cl(2S) | 45(2) | 48(2) | 54(2) | 16(1) | 11(1) | 6(1) |
| C(1T) | 39(5) | 53(5) | 97(11) | -9(7) | -11(6) | 4(3) |
| Cl(1T) | 62(3) | 50(2) | 59(3) | 0(2) | 16(2) | 11(2) |
| Cl(2T) | 45(4) | 49(3) | 65(4) | -10(3) | -13(3) | 10(2) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(2S) | 28(3) | 62(3) | 44(4) | 13(4) | 1(3) | 2(2) |
| Cl(3S) | 49(1) | 64(1) | 77(3) | 1(1) | -7(1) | -3(1) |
| Cl(4S) | 44(2) | 61(2) | 59(1) | 21(1) | 4(2) | 6(1) |
| C(2T) | 34(7) | 57(5) | 51(8) | 16(6) | 2(6) | 3(3) |
| Cl(3T) | 41(1) | 56(2) | 66(4) | 0(2) | 12(1) | -3(1) |
| Cl(4T) | 53(3) | 68(3) | 85(5) | 33(3) | 25(2) | 19(2) |
| C(3S) | 39(2) | 56(2) | 56(2) | 17(2) | 15(1) | 7(1) |
| Cl(5S) | 50(1) | 53(1) | 90(1) | 17(1) | 11(1) | 4(1) |
| Cl(6S) | 43(1) | 64(1) | 59(1) | 25(1) | 14(1) | 3(1) |
| C(4S) | 35(1) | 48(2) | 46(2) | 10(1) | -5(1) | 0(1) |
| Cl(7S) | 56(1) | 46(1) | 56(1) | 9(1) | 1(1) | 6(1) |
| Cl(8S) | 40(1) | 50(1) | 54(1) | 3(1) | -4(1) | 1(1) |
| C(5S) | 33(1) | 44(2) | 59(2) | 6(1) | 11(1) | 3(1) |
| Cl(9S) | 51(1) | 53(1) | 116(1) | 32(1) | 26(1) | 11(1) |
| Cl(15) | 42(1) | 60(1) | 62(1) | 29(1) | 16(1) | 11(1) |

Table S5. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^{-3}$) for **X8_12060**.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1A) | 1450(20) | 278(14) | 2240(13) | 36 |
| H(1B) | 2503(15) | 179(15) | 2396(13) | 36 |
| H(2A) | 3124 | -998 | 2299 | 57 |
| H(2B) | 2232 | -1697 | 2054 | 57 |
| H(2C) | 2171 | -1251 | 2698 | 57 |
| H(3A) | 223 | -1153 | 2360 | 62 |
| H(3B) | 323 | -1537 | 1699 | 62 |
| H(3C) | 21 | -749 | 1811 | 62 |
| H(4C) | 1567 | -315 | 1247 | 65 |
| H(4D) | 1915 | -1090 | 1147 | 65 |
| H(4E) | 2776 | -401 | 1454 | 65 |
| H(6A) | -1314 | -1194 | 3525 | 72 |
| H(6B) | -1126 | -1962 | 3664 | 72 |
| H(6C) | -828 | -1727 | 3044 | 72 |
| H(7C) | 1032 | -1962 | 3208 | 65 |
| H(7D) | 816 | -2183 | 3842 | 65 |
| H(7E) | 1802 | -1558 | 3782 | 65 |
| H(8A) | 1037 | -771 | 4576 | 77 |
| H(8B) | -5 | -1371 | 4597 | 77 |
| H(8C) | -157 | -594 | 4466 | 77 |
| H(10C) | 3493 | -757 | 4267 | 89 |
| H(10D) | 4738 | -662 | 4119 | 89 |
| H(10E) | 3794 | -1007 | 3607 | 89 |
| H(11A) | 4538 | -91 | 2999 | 78 |
| H(11B) | 5458 | 302 | 3512 | 78 |
| H(11C) | 4618 | 745 | 3248 | 78 |
| H(12A) | 4147 | 1129 | 4291 | 60 |
| H(12B) | 4974 | 663 | 4534 | 60 |
| H(12C) | 3732 | 533 | 4686 | 60 |
| H(4A) | 730(20) | 1863(14) | 3718(12) | 34 |
| H(4B) | -289(14) | 2035(15) | 3540(13) | 34 |
| H(14A) | 2277 | 2792 | 4169 | 53 |
| H(14B) | 2087 | 3607 | 4293 | 53 |
| H(14C) | 2140 | 3219 | 3628 | 53 |
| H(15A) | -478 | 2557 | 4523 | 59 |
| H(15B) | 441 | 3202 | 4851 | 59 |
| H(15C) | 701 | 2404 | 4716 | 59 |
| H(16A) | 242 | 3477 | 3330 | 60 |
| H(16B) | 245 | 3895 | 3991 | 60 |
| H(16C) | -729 | 3253 | 3726 | 60 |
| H(18A) | 1663 | 4205 | 3010 | 66 |
| H(18B) | 2456 | 4532 | 2559 | 66 |
| H(18C) | 2851 | 4002 | 2971 | 66 |
| H(19A) | 3303 | 3281 | 2057 | 68 |
| H(19B) | 2808 | 3764 | 1635 | 68 |
| H(19C) | 2376 | 2917 | 1539 | 68 |
| H(20A) | 461 | 3188 | 1628 | 63 |
| H(20B) | 944 | 4029 | 1736 | 63 |

| | | | | |
|---|---|---|---|---|
| H(20C) | 208 | 3694 | 2208 | 63 |
| H(22A) | -2047 | 908 | 1889 | 72 |
| H(22B) | -3121 | 1238 | 2017 | 72 |
| H(22C) | -2308 | 1155 | 2557 | 72 |
| H(23A) | -1420 | 2677 | 1516 | 74 |
| H(23B) | -2521 | 2107 | 1347 | 74 |
| H(23C) | -1372 | 1856 | 1266 | 74 |
| H(24A) | -2130 | 2471 | 2962 | 68 |
| H(24B) | -2972 | 2539 | 2429 | 68 |
| H(24C) | -1808 | 3050 | 2538 | 68 |
| H(7A) | 7410(20) | 6281(15) | 250(13) | 34 |
| H(7B) | 8468(16) | 6220(15) | 417(13) | 34 |
| H(32A) | 6189 | 4881 | 331 | 67 |
| H(32B) | 6332 | 4488 | -321 | 67 |
| H(32C) | 6030 | 5277 | -227 | 67 |
| H(33A) | 9103 | 5041 | 329 | 62 |
| H(33B) | 8272 | 4342 | 10 | 62 |
| H(33C) | 8101 | 4713 | 665 | 62 |
| H(34A) | 7610 | 5754 | -736 | 63 |
| H(34B) | 7946 | 4975 | -857 | 63 |
| H(34C) | 8806 | 5649 | -522 | 63 |
| H(36A) | 7069 | 5193 | 2597 | 129 |
| H(36B) | 6109 | 4526 | 2588 | 129 |
| H(36C) | 5837 | 5271 | 2437 | 129 |
| H(37A) | 8030 | 4456 | 1852 | 72 |
| H(37B) | 7353 | 4005 | 1263 | 72 |
| H(37C) | 7098 | 3790 | 1895 | 72 |
| H(38A) | 4853 | 4617 | 1484 | 102 |
| H(38B) | 5166 | 3863 | 1585 | 102 |
| H(38C) | 5476 | 4183 | 999 | 102 |
| H(36D) | 5470 | 5178 | 2295 | 88 |
| H(36E) | 6640 | 5185 | 2620 | 88 |
| H(36F) | 5759 | 4461 | 2496 | 88 |
| H(37D) | 7694 | 4167 | 1424 | 91 |
| H(37E) | 7183 | 3863 | 1979 | 91 |
| H(37F) | 8010 | 4611 | 2079 | 91 |
| H(38D) | 4962 | 4520 | 1279 | 79 |
| H(38E) | 5264 | 3805 | 1480 | 79 |
| H(38F) | 5804 | 4104 | 930 | 79 |
| H(40A) | 9761 | 5348 | 2246 | 71 |
| H(40B) | 10977 | 5484 | 2053 | 71 |
| H(40C) | 9996 | 5096 | 1574 | 71 |
| H(41A) | 10211 | 7237 | 2221 | 70 |
| H(41B) | 11093 | 6810 | 2466 | 70 |
| H(41C) | 9864 | 6652 | 2636 | 70 |
| H(42A) | 10564 | 6021 | 931 | 65 |
| H(42B) | 11515 | 6443 | 1415 | 65 |
| H(42C) | 10604 | 6854 | 1180 | 65 |
| H(10A) | 6640(20) | 7823(15) | 1801(13) | 37 |
| H(10B) | 5546(16) | 7883(15) | 1654(14) | 37 |
| H(44A) | 5819 | 9326 | 1384 | 74 |
| H(44B) | 5806 | 9753 | 2040 | 74 |
| H(44C) | 4919 | 9049 | 1804 | 74 |
| H(45A) | 8079 | 8813 | 2170 | 61 |

| | | | | |
|---|---|---|---|---|
| H(45B) | 7784 | 9603 | 2287 | 61 |
| H(45C) | 7787 | 9198 | 1623 | 61 |
| H(46A) | 5415 | 8487 | 2655 | 66 |
| H(46B) | 6340 | 9158 | 2924 | 66 |
| H(46C) | 6637 | 8370 | 2790 | 66 |
| H(48A) | 5606 | 9532 | 300 | 81 |
| H(48B) | 5696 | 9004 | -301 | 81 |
| H(48C) | 6155 | 9846 | -242 | 81 |
| H(49A) | 7270 | 10071 | 978 | 86 |
| H(49B) | 7803 | 10402 | 440 | 86 |
| H(49C) | 8432 | 9911 | 794 | 86 |
| H(50A) | 7511 | 8740 | -574 | 87 |
| H(50B) | 8577 | 9104 | -147 | 87 |
| H(50C) | 7950 | 9584 | -514 | 87 |
| H(48D) | 9012 | 9474 | 508 | 81 |
| H(48E) | 8473 | 9879 | 1048 | 81 |
| H(48F) | 8654 | 10231 | 463 | 81 |
| H(49D) | 7891 | 8876 | -407 | 88 |
| H(49E) | 7432 | 9585 | -513 | 88 |
| H(49F) | 6608 | 8867 | -464 | 88 |
| H(50D) | 5782 | 9592 | 331 | 89 |
| H(50E) | 6669 | 10303 | 360 | 89 |
| H(50F) | 6488 | 9944 | 941 | 89 |
| H(52A) | 3761 | 8844 | 476 | 74 |
| H(52B) | 2764 | 8375 | 44 | 74 |
| H(52C) | 3931 | 8563 | -201 | 74 |
| H(53A) | 4025 | 7268 | -532 | 64 |
| H(53B) | 2818 | 7076 | -337 | 64 |
| H(53C) | 3769 | 6707 | -86 | 64 |
| H(54A) | 3434 | 7118 | 949 | 67 |
| H(54B) | 2467 | 7506 | 747 | 67 |
| H(54C) | 3467 | 7952 | 1189 | 67 |
| H(13A) | 5835(14) | 6425(14) | 5696(12) | 28(7) |
| H(13B) | 5080(20) | 5828(11) | 5811(12) | 33(8) |
| H(62A) | 5231 | 6304 | 6820 | 54 |
| H(62B) | 4832 | 7049 | 7026 | 54 |
| H(62C) | 5944 | 7041 | 6716 | 54 |
| H(63A) | 5403 | 7669 | 5921 | 61 |
| H(63B) | 4291 | 7758 | 6212 | 61 |
| H(63C) | 4265 | 7396 | 5533 | 61 |
| H(64A) | 3053 | 6253 | 5729 | 57 |
| H(64B) | 3043 | 6624 | 6403 | 57 |
| H(64C) | 3434 | 5865 | 6256 | 57 |
| H(66A) | 6805 | 7931 | 5108 | 58 |
| H(66B) | 7233 | 8266 | 4548 | 58 |
| H(66C) | 7600 | 7544 | 4697 | 58 |
| H(67A) | 4455 | 7502 | 4059 | 62 |
| H(67B) | 5319 | 8227 | 4104 | 62 |
| H(67C) | 4908 | 7960 | 4694 | 62 |
| H(68A) | 6927 | 6877 | 3699 | 56 |
| H(68B) | 6571 | 7583 | 3510 | 56 |
| H(68C) | 5703 | 6857 | 3444 | 56 |
| H(70A) | 2796 | 6626 | 3618 | 69 |
| H(70B) | 1565 | 6220 | 3582 | 69 |

| | | | | |
|---|---|---|---|---|
| H(70C) | 2537 | 5770 | 3552 | 69 |
| H(71A) | 1705 | 5217 | 4411 | 78 |
| H(71B) | 828 | 5742 | 4449 | 78 |
| H(71C) | 1617 | 5728 | 5021 | 78 |
| H(72A) | 2257 | 7056 | 5122 | 67 |
| H(72B) | 1463 | 7079 | 4554 | 67 |
| H(72C) | 2734 | 7389 | 4571 | 67 |
| H(1S1) | 8170 | 5616 | 4310 | 62 |
| H(1S2) | 7504 | 5605 | 3689 | 62 |
| H(1T1) | 7775 | 5771 | 3209 | 80 |
| H(1T2) | 7569 | 5582 | 3856 | 80 |
| H(2S1) | 9522 | 7864 | 9313 | 54 |
| H(2S2) | 8897 | 7715 | 9885 | 54 |
| H(2T1) | 9126 | 7788 | 9353 | 57 |
| H(2T2) | 8941 | 7895 | 10045 | 57 |
| H(3S1) | 8238 | 248 | 3554 | 59 |
| H(3S2) | 8950 | 552 | 4171 | 59 |
| H(4S1) | 5681 | 3848 | 7250 | 52 |
| H(4S2) | 4981 | 3597 | 7768 | 52 |
| H(5S1) | 3315 | 1630 | 1539 | 55 |
| H(5S2) | 3761 | 1927 | 2215 | 55 |

Table S6. Hydrogen bonds for **X8_12060** [Å and °].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| N(1)-H(1A)...Cl(2) | 0.910(17) | 2.574(19) | 3.446(2) | 161(3) |
| N(1)-H(1A)...Cl(3) | 0.910(17) | 2.62(3) | 3.066(2) | 111(2) |
| N(1)-H(1B)...Cl(9S) | 0.900(17) | 2.88(2) | 3.725(2) | 157(3) |
| N(4)-H(4A)...Cl(1) | 0.907(17) | 2.448(18) | 3.340(2) | 168(3) |
| N(4)-H(4B)...Cl(5S)#2 | 0.891(17) | 2.94(2) | 3.765(2) | 154(2) |
| N(7)-H(7A)...Cl(6) | 0.904(17) | 2.465(18) | 3.361(2) | 171(3) |
| N(7)-H(7B)...Cl(4T)#3 | 0.913(17) | 2.98(3) | 3.806(14) | 151(2) |
| N(10)-H(10A)...Cl(5) | 0.890(17) | 2.517(19) | 3.377(2) | 163(3) |
| N(13)-H(13B)...Cl(9)#1 | 0.905(17) | 2.513(18) | 3.404(2) | 168(3) |
| N(13)-H(13B)...Cl(10)#1 | 0.905(17) | 2.76(3) | 3.207(2) | 112(2) |

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1  #2 x-1,y,z  #3 x,y,z-1

**Table S7**. Crystal data and structure refinement for $[W(NAd)_2Cl(\mu\text{-}Cl)(AdNH_2)]_2$ (**1b**).

| | | |
|---|---|---|
| Identification code | X8_12067 | |
| Empirical formula | $C_{65}\ H_{104}\ Cl_{14}\ N_6\ W_2$ | |
| Formula weight | 1833.54 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | P1 | |
| Unit cell dimensions | $a$ = 16.100(2) Å | $\alpha$= 95.280(3)°. |
| | $b$ = 19.006(3) Å | $\beta$= 110.896(3)°. |
| | $c$ = 19.600(3) Å | $\gamma$ = 94.619(4)°. |
| Volume | 5537.7(13) Å$^3$ | |
| $Z$ | 3 | |
| Density (calculated) | 1.649 Mg/m$^3$ | |
| Absorption coefficient | 3.663 mm$^{-1}$ | |
| $F$(000) | 2766 | |
| Crystal size | 0.25 x 0.20 x 0.15 mm$^3$ | |
| Theta range for data collection | 1.08 to 31.00°. | |
| Index ranges | -23<=$h$<=21, -27<=$k$<=27, 0<=$l$<=28 | |
| Reflections collected | 35319 | |
| Independent reflections | 35319 [$R_{int}$ = 0.0000] | |
| Completeness to theta = 31.00° | 99.9 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.6095 and 0.4611 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 35319 / 229 / 1263 | |
| Goodness-of-fit on $F^2$ | 1.037 | |
| Final $R$ indices [$I$>2$\sigma$($I$)] | $R$1 = 0.0326, $wR$2 = 0.0816 | |
| $R$ indices (all data) | $R$1 = 0.0399, $wR$2 = 0.0851 | |
| Largest diff. peak and hole | 3.249 and -2.347 e.Å$^{-3}$ | |

Table S8. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for **X8_12067**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Cl(1) | 261(1) | 7086(1) | 1992(1) | 17(1) |
| Cl(3) | 2186(1) | 7504(1) | 3463(1) | 14(1) |
| W(1) | 529(1) | 7101(1) | 3281(1) | 13(1) |
| N(1) | 1241(2) | 6812(1) | 4388(1) | 16(1) |
| C(10) | 1257(2) | 7144(1) | 5120(1) | 16(1) |
| C(11) | 1847(2) | 6739(2) | 5721(1) | 20(1) |
| C(12) | 1865(2) | 7057(2) | 6476(1) | 21(1) |
| C(13) | 2262(2) | 7839(2) | 6630(2) | 24(1) |
| C(14) | 1682(2) | 8246(2) | 6027(2) | 24(1) |
| C(15) | 1661(2) | 7927(1) | 5273(2) | 21(1) |
| C(16) | 312(2) | 7076(2) | 5120(1) | 19(1) |
| C(17) | 336(2) | 7403(2) | 5875(2) | 26(1) |
| C(18) | 913(2) | 6997(2) | 6473(2) | 26(1) |
| C(19) | 727(2) | 8187(2) | 6025(2) | 30(1) |
| N(2) | -449(2) | 6558(1) | 3140(1) | 17(1) |
| C(20) | -1274(2) | 6086(1) | 2923(1) | 15(1) |
| C(21) | -1696(2) | 6139(2) | 3514(2) | 28(1) |
| C(22) | -2576(2) | 5632(2) | 3250(2) | 27(1) |
| C(23) | -3218(2) | 5832(2) | 2543(2) | 33(1) |
| C(24) | -2812(2) | 5773(2) | 1952(2) | 36(1) |
| C(25) | -1937(2) | 6286(2) | 2207(2) | 31(1) |
| C(26) | -1085(2) | 5318(2) | 2798(2) | 33(1) |
| C(27) | -1963(2) | 4805(2) | 2542(2) | 36(1) |
| C(28) | -2374(2) | 4875(2) | 3137(2) | 31(1) |
| C(29) | -2614(3) | 5018(2) | 1824(2) | 46(1) |
| N(3) | 320(1) | 7983(1) | 3450(1) | 15(1) |
| C(30) | -263(2) | 8529(1) | 3423(1) | 14(1) |
| C(31) | 297(2) | 9246(1) | 3804(1) | 17(1) |
| C(32) | -312(2) | 9836(1) | 3745(1) | 19(1) |
| C(33) | -826(2) | 9898(1) | 2934(2) | 21(1) |
| C(34) | -1393(2) | 9187(2) | 2550(1) | 19(1) |
| C(35) | -787(2) | 8597(1) | 2607(1) | 17(1) |
| C(36) | -938(2) | 8348(1) | 3793(2) | 18(1) |
| C(37) | -1548(2) | 8938(2) | 3731(2) | 19(1) |
| C(38) | -985(2) | 9647(2) | 4111(2) | 22(1) |
| C(39) | -2066(2) | 9001(2) | 2917(2) | 22(1) |
| Cl(2) | 3184(1) | 6262(1) | 4536(1) | 16(1) |
| Cl(4) | 1270(1) | 5847(1) | 3062(1) | 14(1) |
| W(2) | 2928(1) | 6247(1) | 3251(1) | 13(1) |
| N(4) | 2239(2) | 6537(1) | 2138(1) | 16(1) |
| C(40) | 2251(2) | 6181(1) | 1423(1) | 17(1) |
| C(41) | 1727(2) | 6588(2) | 794(2) | 24(1) |
| C(42) | 1743(3) | 6234(2) | 60(2) | 30(1) |
| C(43) | 2713(3) | 6245(2) | 107(2) | 33(1) |
| C(44) | 3229(2) | 5842(2) | 731(2) | 26(1) |
| C(45) | 3216(2) | 6203(1) | 1464(2) | 20(1) |
| C(46) | 1806(2) | 5412(1) | 1276(1) | 20(1) |
| C(47) | 1815(2) | 5058(2) | 540(2) | 25(1) |
| C(48) | 1300(2) | 5461(2) | -86(2) | 31(1) |

| | | | | |
|---|---|---|---|---|
| C(49) | 2784(2) | 5069(2) | 589(2) | 29(1) |
| N(5) | 3928(2) | 6778(1) | 3414(1) | 17(1) |
| C(50) | 4769(2) | 7231(1) | 3667(1) | 16(1) |
| C(51) | 5387(2) | 7011(2) | 4394(2) | 21(1) |
| C(52) | 6278(2) | 7507(2) | 4689(2) | 25(1) |
| C(53) | 6727(2) | 7441(2) | 4119(2) | 24(1) |
| C(54) | 6119(2) | 7668(2) | 3398(2) | 21(1) |
| C(55) | 5228(2) | 7174(2) | 3101(2) | 20(1) |
| C(56) | 4596(2) | 8007(2) | 3805(2) | 24(1) |
| C(57) | 5486(2) | 8496(2) | 4094(2) | 27(1) |
| C(58) | 6100(2) | 8276(2) | 4818(2) | 30(1) |
| C(59) | 5934(2) | 8439(2) | 3525(2) | 25(1) |
| N(6) | 3132(1) | 5361(1) | 3091(1) | 15(1) |
| C(60) | 3720(2) | 4812(1) | 3161(1) | 14(1) |
| C(61) | 4423(2) | 4965(1) | 2813(2) | 18(1) |
| C(62) | 5043(2) | 4379(2) | 2930(2) | 19(1) |
| C(63) | 5523(2) | 4353(2) | 3757(2) | 24(1) |
| C(64) | 4823(2) | 4191(2) | 4102(1) | 20(1) |
| C(65) | 4211(2) | 4782(1) | 3992(1) | 18(1) |
| C(66) | 3167(2) | 4089(1) | 2801(1) | 17(1) |
| C(67) | 3786(2) | 3500(1) | 2911(1) | 18(1) |
| C(68) | 4487(2) | 3657(2) | 2568(2) | 20(1) |
| C(69) | 4265(2) | 3474(1) | 3737(2) | 20(1) |
| Cl(5) | 6498(1) | 9624(1) | 11271(1) | 17(1) |
| Cl(6) | 4565(1) | 9168(1) | 9790(1) | 15(1) |
| W(3) | 6230(1) | 9637(1) | 9986(1) | 14(1) |
| N(7) | 5510(2) | 9927(1) | 8879(1) | 17(1) |
| C(70) | 5465(2) | 9570(1) | 8148(1) | 16(1) |
| C(71) | 6408(2) | 9560(2) | 8144(1) | 19(1) |
| C(72) | 6354(2) | 9200(2) | 7390(2) | 24(1) |
| C(73) | 5873(2) | 8442(2) | 7249(2) | 27(1) |
| C(74) | 4924(2) | 8460(2) | 7250(2) | 23(1) |
| C(75) | 4982(2) | 8814(1) | 8005(2) | 20(1) |
| C(76) | 4938(2) | 10000(2) | 7546(2) | 22(1) |
| C(77) | 4878(2) | 9650(2) | 6789(2) | 25(1) |
| C(78) | 5830(2) | 9629(2) | 6786(2) | 28(1) |
| C(79) | 4400(2) | 8894(2) | 6645(2) | 27(1) |
| N(8) | 7210(2) | 10196(1) | 10138(1) | 18(1) |
| C(80) | 8059(2) | 10630(1) | 10353(1) | 16(1) |
| C(81) | 7905(2) | 11415(2) | 10439(2) | 24(1) |
| C(82) | 8802(2) | 11889(2) | 10691(2) | 26(1) |
| C(83) | 9420(2) | 11705(2) | 11428(2) | 30(1) |
| C(84) | 9586(2) | 10927(2) | 11352(2) | 25(1) |
| C(85) | 8688(2) | 10445(2) | 11095(2) | 22(1) |
| C(86) | 8500(2) | 10512(2) | 9777(2) | 23(1) |
| C(87) | 9403(2) | 10992(2) | 10034(2) | 23(1) |
| C(88) | 9236(2) | 11772(2) | 10116(2) | 24(1) |
| C(89) | 10015(2) | 10804(2) | 10772(2) | 26(1) |
| N(9) | 6456(2) | 8764(1) | 9816(1) | 17(1) |
| C(90) | 6993(2) | 8187(1) | 9844(1) | 16(1) |
| C(91) | 7646(2) | 8299(1) | 9444(1) | 17(1) |
| C(92) | 8200(2) | 7672(1) | 9504(1) | 18(1) |
| C(93) | 8738(2) | 7623(2) | 10318(2) | 19(1) |
| C(94) | 8084(2) | 7504(1) | 10718(1) | 18(1) |

| | | | | |
|---|---|---|---|---|
| C(95) | 7532(2) | 8130(1) | 10660(1) | 17(1) |
| C(96) | 6367(2) | 7485(1) | 9493(1) | 17(1) |
| C(97) | 6922(2) | 6860(1) | 9554(1) | 19(1) |
| C(98) | 7575(2) | 6979(1) | 9155(1) | 20(1) |
| C(99) | 7457(2) | 6810(1) | 10367(2) | 20(1) |
| C(1S) | 1507(2) | 8693(2) | 2109(2) | 30(1) |
| Cl(11) | 1461(1) | 9614(1) | 2239(1) | 42(1) |
| Cl(12) | 2531(1) | 8500(1) | 2030(1) | 28(1) |
| C(2S) | 9444(3) | 5801(2) | 8029(2) | 41(1) |
| Cl(21) | 9788(1) | 6230(1) | 7412(1) | 80(1) |
| Cl(22) | 9397(1) | 6399(1) | 8738(1) | 42(1) |
| C(3S) | 5250(2) | 8037(2) | 1237(2) | 34(1) |
| Cl(31) | 5427(1) | 7141(1) | 1188(1) | 54(1) |
| Cl(32) | 4178(1) | 8150(1) | 1246(1) | 29(1) |
| C(4S) | 1815(3) | 4672(2) | 4424(3) | 48(1) |
| Cl(41) | 2147(1) | 3841(1) | 4653(1) | 43(1) |
| Cl(42) | 847(1) | 4841(1) | 4601(1) | 33(1) |
| C(5S) | 7154(3) | 542(2) | 5582(2) | 43(1) |
| Cl(51) | 7473(1) | 126(1) | 4882(1) | 46(1) |
| Cl(52) | 5995(1) | 541(1) | 5274(1) | 42(1) |
| C(6S) | 6398(3) | 2729(2) | 1155(2) | 44(1) |
| Cl(61) | 5943(1) | 3094(1) | 1779(1) | 48(1) |
| Cl(62) | 7578(1) | 2902(1) | 1516(1) | 35(1) |
| C(7S) | 8689(8) | 7955(8) | 6731(8) | 55(2) |
| Cl(71) | 8538(4) | 8618(6) | 6215(6) | 94(3) |
| Cl(72) | 8035(5) | 7922(6) | 7251(6) | 124(3) |
| C(7T) | 8498(15) | 7925(9) | 6742(10) | 86(4) |
| Cl(73) | 8579(6) | 8727(6) | 6380(6) | 85(2) |
| Cl(74) | 8113(3) | 7987(4) | 7451(4) | 62(1) |
| C(8S) | 4651(9) | 4777(6) | -225(5) | 43(2) |
| Cl(81) | 5163(6) | 5625(4) | -182(4) | 56(1) |
| Cl(82) | 5130(3) | 4402(3) | 589(3) | 66(2) |
| C(8T) | 4600(40) | 4650(20) | 2(11) | 70(7) |
| Cl(83) | 5036(19) | 5384(15) | -299(12) | 83(6) |
| Cl(84) | 4917(7) | 4789(8) | 959(7) | 81(4) |

Table S9. Bond lengths [Å] and angles [°] for **X8_12067**.

| | |
|---|---|
| Cl(1)-W(1) | 2.4048(7) |
| Cl(3)-W(1) | 2.6023(7) |
| Cl(3)-W(2) | 2.8172(6) |
| W(1)-N(2) | 1.732(2) |
| W(1)-N(3) | 1.762(2) |
| W(1)-N(1) | 2.206(2) |
| W(1)-Cl(4) | 2.8155(7) |
| N(1)-C(10) | 1.503(3) |
| N(1)-H(1A) | 0.920(17) |
| N(1)-H(1B) | 0.899(17) |
| C(10)-C(16) | 1.516(4) |
| C(10)-C(15) | 1.532(4) |
| C(10)-C(11) | 1.539(4) |
| C(11)-C(12) | 1.536(4) |
| C(11)-H(11A) | 0.9900 |
| C(11)-H(11B) | 0.9900 |
| C(12)-C(18) | 1.526(4) |
| C(12)-C(13) | 1.529(4) |
| C(12)-H(12) | 1.0000 |
| C(13)-C(14) | 1.537(4) |
| C(13)-H(13A) | 0.9900 |
| C(13)-H(13B) | 0.9900 |
| C(14)-C(19) | 1.531(5) |
| C(14)-C(15) | 1.534(4) |
| C(14)-H(14) | 1.0000 |
| C(15)-H(15A) | 0.9900 |
| C(15)-H(15B) | 0.9900 |
| C(16)-C(17) | 1.539(4) |
| C(16)-H(16A) | 0.9900 |
| C(16)-H(16B) | 0.9900 |
| C(17)-C(18) | 1.529(5) |
| C(17)-C(19) | 1.529(5) |
| C(17)-H(17) | 1.0000 |
| C(18)-H(18A) | 0.9900 |
| C(18)-H(18B) | 0.9900 |
| C(19)-H(19A) | 0.9900 |
| C(19)-H(19B) | 0.9900 |
| N(2)-C(20) | 1.444(3) |
| C(20)-C(26) | 1.531(4) |
| C(20)-C(25) | 1.532(4) |
| C(20)-C(21) | 1.536(4) |
| C(21)-C(22) | 1.540(4) |
| C(21)-H(21A) | 0.9900 |
| C(21)-H(21B) | 0.9900 |
| C(22)-C(23) | 1.507(5) |
| C(22)-C(28) | 1.514(4) |
| C(22)-H(22) | 1.0000 |
| C(23)-C(24) | 1.520(5) |
| C(23)-H(23A) | 0.9900 |
| C(23)-H(23B) | 0.9900 |
| C(24)-C(29) | 1.513(6) |
| C(24)-C(25) | 1.539(4) |

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| C(24)-H(24) | 1.0000 |
| C(25)-H(25A) | 0.9900 |
| C(25)-H(25B) | 0.9900 |
| C(26)-C(27) | 1.544(4) |
| C(26)-H(26A) | 0.9900 |
| C(26)-H(26B) | 0.9900 |
| C(27)-C(28) | 1.535(5) |
| C(27)-C(29) | 1.537(6) |
| C(27)-H(27) | 1.0000 |
| C(28)-H(28A) | 0.9900 |
| C(28)-H(28B) | 0.9900 |
| C(29)-H(29A) | 0.9900 |
| C(29)-H(29B) | 0.9900 |
| N(3)-C(30) | 1.445(3) |
| C(30)-C(31) | 1.537(4) |
| C(30)-C(36) | 1.540(3) |
| C(30)-C(35) | 1.543(3) |
| C(31)-C(32) | 1.535(4) |
| C(31)-H(31A) | 0.9900 |
| C(31)-H(31B) | 0.9900 |
| C(32)-C(33) | 1.528(4) |
| C(32)-C(38) | 1.534(4) |
| C(32)-H(32) | 1.0000 |
| C(33)-C(34) | 1.532(4) |
| C(33)-H(33A) | 0.9900 |
| C(33)-H(33B) | 0.9900 |
| C(34)-C(35) | 1.531(4) |
| C(34)-C(39) | 1.537(4) |
| C(34)-H(34) | 1.0000 |
| C(35)-H(35A) | 0.9900 |
| C(35)-H(35B) | 0.9900 |
| C(36)-C(37) | 1.533(4) |
| C(36)-H(36A) | 0.9900 |
| C(36)-H(36B) | 0.9900 |
| C(37)-C(38) | 1.527(4) |
| C(37)-C(39) | 1.535(4) |
| C(37)-H(37) | 1.0000 |
| C(38)-H(38A) | 0.9900 |
| C(38)-H(38B) | 0.9900 |
| C(39)-H(39A) | 0.9900 |
| C(39)-H(39B) | 0.9900 |
| Cl(2)-W(2) | 2.4001(7) |
| Cl(4)-W(2) | 2.5997(7) |
| W(2)-N(5) | 1.739(2) |
| W(2)-N(6) | 1.764(2) |
| W(2)-N(4) | 2.212(2) |
| N(4)-C(40) | 1.506(3) |
| N(4)-H(4A) | 0.903(17) |
| N(4)-H(4B) | 0.900(17) |
| C(40)-C(45) | 1.523(4) |
| C(40)-C(46) | 1.531(4) |
| C(40)-C(41) | 1.539(4) |
| C(41)-C(42) | 1.540(4) |
| C(41)-H(41A) | 0.9900 |

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| C(41)-H(41B) | 0.9900 |
| C(42)-C(43) | 1.530(5) |
| C(42)-C(48) | 1.535(4) |
| C(42)-H(42) | 1.0000 |
| C(43)-C(44) | 1.524(5) |
| C(43)-H(43A) | 0.9900 |
| C(43)-H(43B) | 0.9900 |
| C(44)-C(49) | 1.537(4) |
| C(44)-C(45) | 1.542(4) |
| C(44)-H(44) | 1.0000 |
| C(45)-H(45A) | 0.9900 |
| C(45)-H(45B) | 0.9900 |
| C(46)-C(47) | 1.539(4) |
| C(46)-H(46A) | 0.9900 |
| C(46)-H(46B) | 0.9900 |
| C(47)-C(48) | 1.527(4) |
| C(47)-C(49) | 1.527(5) |
| C(47)-H(47) | 1.0000 |
| C(48)-H(48A) | 0.9900 |
| C(48)-H(48B) | 0.9900 |
| C(49)-H(49A) | 0.9900 |
| C(49)-H(49B) | 0.9900 |
| N(5)-C(50) | 1.441(3) |
| C(50)-C(51) | 1.537(4) |
| C(50)-C(55) | 1.538(4) |
| C(50)-C(56) | 1.540(4) |
| C(51)-C(52) | 1.539(4) |
| C(51)-H(51A) | 0.9900 |
| C(51)-H(51B) | 0.9900 |
| C(52)-C(58) | 1.528(5) |
| C(52)-C(53) | 1.534(4) |
| C(52)-H(52) | 1.0000 |
| C(53)-C(54) | 1.527(4) |
| C(53)-H(53A) | 0.9900 |
| C(53)-H(53B) | 0.9900 |
| C(54)-C(59) | 1.534(4) |
| C(54)-C(55) | 1.539(4) |
| C(54)-H(54) | 1.0000 |
| C(55)-H(55A) | 0.9900 |
| C(55)-H(55B) | 0.9900 |
| C(56)-C(57) | 1.531(4) |
| C(56)-H(56A) | 0.9900 |
| C(56)-H(56B) | 0.9900 |
| C(57)-C(58) | 1.530(5) |
| C(57)-C(59) | 1.532(4) |
| C(57)-H(57) | 1.0000 |
| C(58)-H(58A) | 0.9900 |
| C(58)-H(58B) | 0.9900 |
| C(59)-H(59A) | 0.9900 |
| C(59)-H(59B) | 0.9900 |
| N(6)-C(60) | 1.448(3) |
| C(60)-C(66) | 1.535(4) |
| C(60)-C(61) | 1.538(3) |
| C(60)-C(65) | 1.544(3) |

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| C(61)-C(62) | 1.533(4) |
| C(61)-H(61A) | 0.9900 |
| C(61)-H(61B) | 0.9900 |
| C(62)-C(63) | 1.534(4) |
| C(62)-C(68) | 1.536(4) |
| C(62)-H(62) | 1.0000 |
| C(63)-C(64) | 1.533(4) |
| C(63)-H(63A) | 0.9900 |
| C(63)-H(63B) | 0.9900 |
| C(64)-C(69) | 1.530(4) |
| C(64)-C(65) | 1.532(4) |
| C(64)-H(64) | 1.0000 |
| C(65)-H(65A) | 0.9900 |
| C(65)-H(65B) | 0.9900 |
| C(66)-C(67) | 1.536(4) |
| C(66)-H(66A) | 0.9900 |
| C(66)-H(66B) | 0.9900 |
| C(67)-C(68) | 1.530(4) |
| C(67)-C(69) | 1.533(4) |
| C(67)-H(67) | 1.0000 |
| C(68)-H(68A) | 0.9900 |
| C(68)-H(68B) | 0.9900 |
| C(69)-H(69A) | 0.9900 |
| C(69)-H(69B) | 0.9900 |
| Cl(5)-W(3) | 2.4021(7) |
| Cl(6)-W(3) | 2.6359(7) |
| Cl(6)-W(3)#1 | 2.7708(7) |
| W(3)-N(8) | 1.744(2) |
| W(3)-N(9) | 1.755(2) |
| W(3)-N(7) | 2.210(2) |
| W(3)-Cl(6)#1 | 2.7708(7) |
| N(7)-C(70) | 1.503(3) |
| N(7)-H(7A) | 0.912(17) |
| N(7)-H(7B) | 0.902(17) |
| C(70)-C(71) | 1.523(4) |
| C(70)-C(75) | 1.530(4) |
| C(70)-C(76) | 1.534(4) |
| C(71)-C(72) | 1.540(4) |
| C(71)-H(71A) | 0.9900 |
| C(71)-H(71B) | 0.9900 |
| C(72)-C(73) | 1.532(4) |
| C(72)-C(78) | 1.534(4) |
| C(72)-H(72) | 1.0000 |
| C(73)-C(74) | 1.531(4) |
| C(73)-H(73A) | 0.9900 |
| C(73)-H(73B) | 0.9900 |
| C(74)-C(75) | 1.536(4) |
| C(74)-C(79) | 1.541(4) |
| C(74)-H(74) | 1.0000 |
| C(75)-H(75A) | 0.9900 |
| C(75)-H(75B) | 0.9900 |
| C(76)-C(77) | 1.535(4) |
| C(76)-H(76A) | 0.9900 |
| C(76)-H(76B) | 0.9900 |

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| C(77)-C(79) | 1.526(4) |
| C(77)-C(78) | 1.538(5) |
| C(77)-H(77) | 1.0000 |
| C(78)-H(78A) | 0.9900 |
| C(78)-H(78B) | 0.9900 |
| C(79)-H(79A) | 0.9900 |
| C(79)-H(79B) | 0.9900 |
| N(8)-C(80) | 1.439(3) |
| C(80)-C(81) | 1.537(4) |
| C(80)-C(85) | 1.537(4) |
| C(80)-C(86) | 1.542(4) |
| C(81)-C(82) | 1.530(4) |
| C(81)-H(81A) | 0.9900 |
| C(81)-H(81B) | 0.9900 |
| C(82)-C(83) | 1.525(5) |
| C(82)-C(88) | 1.532(4) |
| C(82)-H(82) | 1.0000 |
| C(83)-C(84) | 1.526(5) |
| C(83)-H(83A) | 0.9900 |
| C(83)-H(83B) | 0.9900 |
| C(84)-C(89) | 1.537(4) |
| C(84)-C(85) | 1.538(4) |
| C(84)-H(84) | 1.0000 |
| C(85)-H(85A) | 0.9900 |
| C(85)-H(85B) | 0.9900 |
| C(86)-C(87) | 1.544(4) |
| C(86)-H(86A) | 0.9900 |
| C(86)-H(86B) | 0.9900 |
| C(87)-C(89) | 1.525(4) |
| C(87)-C(88) | 1.531(4) |
| C(87)-H(87) | 1.0000 |
| C(88)-H(88A) | 0.9900 |
| C(88)-H(88B) | 0.9900 |
| C(89)-H(89A) | 0.9900 |
| C(89)-H(89B) | 0.9900 |
| N(9)-C(90) | 1.443(3) |
| C(90)-C(91) | 1.534(4) |
| C(90)-C(95) | 1.542(3) |
| C(90)-C(96) | 1.545(4) |
| C(91)-C(92) | 1.532(4) |
| C(91)-H(91A) | 0.9900 |
| C(91)-H(91B) | 0.9900 |
| C(92)-C(98) | 1.532(4) |
| C(92)-C(93) | 1.535(4) |
| C(92)-H(92) | 1.0000 |
| C(93)-C(94) | 1.536(4) |
| C(93)-H(93A) | 0.9900 |
| C(93)-H(93B) | 0.9900 |
| C(94)-C(95) | 1.531(4) |
| C(94)-C(99) | 1.534(4) |
| C(94)-H(94) | 1.0000 |
| C(95)-H(95A) | 0.9900 |
| C(95)-H(95B) | 0.9900 |
| C(96)-C(97) | 1.532(4) |

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| C(96)-H(96A) | 0.9900 |
| C(96)-H(96B) | 0.9900 |
| C(97)-C(98) | 1.533(4) |
| C(97)-C(99) | 1.534(4) |
| C(97)-H(97) | 1.0000 |
| C(98)-H(98A) | 0.9900 |
| C(98)-H(98B) | 0.9900 |
| C(99)-H(99A) | 0.9900 |
| C(99)-H(99B) | 0.9900 |
| C(1S)-Cl(11) | 1.757(3) |
| C(1S)-Cl(12) | 1.773(3) |
| C(1S)-H(1S1) | 0.9900 |
| C(1S)-H(1S2) | 0.9900 |
| C(2S)-Cl(21) | 1.737(4) |
| C(2S)-Cl(22) | 1.739(4) |
| C(2S)-H(2S1) | 0.9900 |
| C(2S)-H(2S2) | 0.9900 |
| C(3S)-Cl(31) | 1.748(3) |
| C(3S)-Cl(32) | 1.763(3) |
| C(3S)-H(3S1) | 0.9900 |
| C(3S)-H(3S2) | 0.9900 |
| C(4S)-Cl(41) | 1.754(4) |
| C(4S)-Cl(42) | 1.760(4) |
| C(4S)-H(4S1) | 0.9900 |
| C(4S)-H(4S2) | 0.9900 |
| C(5S)-Cl(52) | 1.744(4) |
| C(5S)-Cl(51) | 1.772(4) |
| C(5S)-H(5S1) | 0.9900 |
| C(5S)-H(5S2) | 0.9900 |
| C(6S)-Cl(61) | 1.755(4) |
| C(6S)-Cl(62) | 1.766(4) |
| C(6S)-H(6S1) | 0.9900 |
| C(6S)-H(6S2) | 0.9900 |
| C(7S)-Cl(71) | 1.667(15) |
| C(7S)-Cl(72) | 1.710(9) |
| C(7S)-H(7S1) | 0.9900 |
| C(7S)-H(7S2) | 0.9900 |
| C(7T)-Cl(74) | 1.710(11) |
| C(7T)-Cl(73) | 1.755(13) |
| C(7T)-H(7T1) | 0.9900 |
| C(7T)-H(7T2) | 0.9900 |
| C(8S)-Cl(81) | 1.732(9) |
| C(8S)-Cl(82) | 1.753(10) |
| C(8S)-H(8S1) | 0.9900 |
| C(8S)-H(8S2) | 0.9900 |
| C(8T)-Cl(83) | 1.747(15) |
| C(8T)-Cl(84) | 1.748(15) |
| C(8T)-H(8T1) | 0.9900 |
| C(8T)-H(8T2) | 0.9900 |

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| W(1)-Cl(3)-W(2) | 105.81(2) |
| N(2)-W(1)-N(3) | 106.79(10) |
| N(2)-W(1)-N(1) | 94.31(9) |
| N(3)-W(1)-N(1) | 104.15(9) |

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|---|---|
| N(2)-W(1)-Cl(1) | 94.58(7) |
| N(3)-W(1)-Cl(1) | 97.38(7) |
| N(1)-W(1)-Cl(1) | 153.19(6) |
| N(2)-W(1)-Cl(3) | 160.78(8) |
| N(3)-W(1)-Cl(3) | 92.35(7) |
| N(1)-W(1)-Cl(3) | 78.86(6) |
| Cl(1)-W(1)-Cl(3) | 84.53(2) |
| N(2)-W(1)-Cl(4) | 86.74(8) |
| N(3)-W(1)-Cl(4) | 166.47(7) |
| N(1)-W(1)-Cl(4) | 73.92(6) |
| Cl(1)-W(1)-Cl(4) | 81.399(19) |
| Cl(3)-W(1)-Cl(4) | 74.122(19) |
| C(10)-N(1)-W(1) | 128.80(16) |
| C(10)-N(1)-H(1A) | 108(2) |
| W(1)-N(1)-H(1A) | 104(2) |
| C(10)-N(1)-H(1B) | 108(2) |
| W(1)-N(1)-H(1B) | 105(2) |
| H(1A)-N(1)-H(1B) | 99(3) |
| N(1)-C(10)-C(16) | 109.2(2) |
| N(1)-C(10)-C(15) | 110.3(2) |
| C(16)-C(10)-C(15) | 110.9(2) |
| N(1)-C(10)-C(11) | 108.1(2) |
| C(16)-C(10)-C(11) | 109.5(2) |
| C(15)-C(10)-C(11) | 108.8(2) |
| C(12)-C(11)-C(10) | 109.4(2) |
| C(12)-C(11)-H(11A) | 109.8 |
| C(10)-C(11)-H(11A) | 109.8 |
| C(12)-C(11)-H(11B) | 109.8 |
| C(10)-C(11)-H(11B) | 109.8 |
| H(11A)-C(11)-H(11B) | 108.2 |
| C(18)-C(12)-C(13) | 109.8(2) |
| C(18)-C(12)-C(11) | 109.4(2) |
| C(13)-C(12)-C(11) | 109.1(2) |
| C(18)-C(12)-H(12) | 109.5 |
| C(13)-C(12)-H(12) | 109.5 |
| C(11)-C(12)-H(12) | 109.5 |
| C(12)-C(13)-C(14) | 109.3(2) |
| C(12)-C(13)-H(13A) | 109.8 |
| C(14)-C(13)-H(13A) | 109.8 |
| C(12)-C(13)-H(13B) | 109.8 |
| C(14)-C(13)-H(13B) | 109.8 |
| H(13A)-C(13)-H(13B) | 108.3 |
| C(19)-C(14)-C(15) | 109.3(2) |
| C(19)-C(14)-C(13) | 109.4(3) |
| C(15)-C(14)-C(13) | 109.8(2) |
| C(19)-C(14)-H(14) | 109.4 |
| C(15)-C(14)-H(14) | 109.4 |
| C(13)-C(14)-H(14) | 109.4 |
| C(10)-C(15)-C(14) | 109.0(2) |
| C(10)-C(15)-H(15A) | 109.9 |
| C(14)-C(15)-H(15A) | 109.9 |
| C(10)-C(15)-H(15B) | 109.9 |
| C(14)-C(15)-H(15B) | 109.9 |
| H(15A)-C(15)-H(15B) | 108.3 |

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|---|---|
| C(10)-C(16)-C(17) | 108.9(2) |
| C(10)-C(16)-H(16A) | 109.9 |
| C(17)-C(16)-H(16A) | 109.9 |
| C(10)-C(16)-H(16B) | 109.9 |
| C(17)-C(16)-H(16B) | 109.9 |
| H(16A)-C(16)-H(16B) | 108.3 |
| C(18)-C(17)-C(19) | 109.9(3) |
| C(18)-C(17)-C(16) | 109.3(2) |
| C(19)-C(17)-C(16) | 109.7(2) |
| C(18)-C(17)-H(17) | 109.3 |
| C(19)-C(17)-H(17) | 109.3 |
| C(16)-C(17)-H(17) | 109.3 |
| C(12)-C(18)-C(17) | 109.3(2) |
| C(12)-C(18)-H(18A) | 109.8 |
| C(17)-C(18)-H(18A) | 109.8 |
| C(12)-C(18)-H(18B) | 109.8 |
| C(17)-C(18)-H(18B) | 109.8 |
| H(18A)-C(18)-H(18B) | 108.3 |
| C(17)-C(19)-C(14) | 109.4(2) |
| C(17)-C(19)-H(19A) | 109.8 |
| C(14)-C(19)-H(19A) | 109.8 |
| C(17)-C(19)-H(19B) | 109.8 |
| C(14)-C(19)-H(19B) | 109.8 |
| H(19A)-C(19)-H(19B) | 108.2 |
| C(20)-N(2)-W(1) | 172.53(18) |
| N(2)-C(20)-C(26) | 109.1(2) |
| N(2)-C(20)-C(25) | 108.7(2) |
| C(26)-C(20)-C(25) | 109.7(3) |
| N(2)-C(20)-C(21) | 111.9(2) |
| C(26)-C(20)-C(21) | 108.6(2) |
| C(25)-C(20)-C(21) | 108.9(2) |
| C(20)-C(21)-C(22) | 109.6(2) |
| C(20)-C(21)-H(21A) | 109.8 |
| C(22)-C(21)-H(21A) | 109.8 |
| C(20)-C(21)-H(21B) | 109.8 |
| C(22)-C(21)-H(21B) | 109.8 |
| H(21A)-C(21)-H(21B) | 108.2 |
| C(23)-C(22)-C(28) | 110.6(3) |
| C(23)-C(22)-C(21) | 109.7(3) |
| C(28)-C(22)-C(21) | 109.0(3) |
| C(23)-C(22)-H(22) | 109.1 |
| C(28)-C(22)-H(22) | 109.1 |
| C(21)-C(22)-H(22) | 109.1 |
| C(22)-C(23)-C(24) | 109.9(3) |
| C(22)-C(23)-H(23A) | 109.7 |
| C(24)-C(23)-H(23A) | 109.7 |
| C(22)-C(23)-H(23B) | 109.7 |
| C(24)-C(23)-H(23B) | 109.7 |
| H(23A)-C(23)-H(23B) | 108.2 |
| C(29)-C(24)-C(23) | 109.6(3) |
| C(29)-C(24)-C(25) | 109.5(3) |
| C(23)-C(24)-C(25) | 109.2(3) |
| C(29)-C(24)-H(24) | 109.5 |
| C(23)-C(24)-H(24) | 109.5 |

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|---|---|
| C(25)-C(24)-H(24) | 109.5 |
| C(20)-C(25)-C(24) | 109.5(2) |
| C(20)-C(25)-H(25A) | 109.8 |
| C(24)-C(25)-H(25A) | 109.8 |
| C(20)-C(25)-H(25B) | 109.8 |
| C(24)-C(25)-H(25B) | 109.8 |
| H(25A)-C(25)-H(25B) | 108.2 |
| C(20)-C(26)-C(27) | 110.2(2) |
| C(20)-C(26)-H(26A) | 109.6 |
| C(27)-C(26)-H(26A) | 109.6 |
| C(20)-C(26)-H(26B) | 109.6 |
| C(27)-C(26)-H(26B) | 109.6 |
| H(26A)-C(26)-H(26B) | 108.1 |
| C(28)-C(27)-C(29) | 109.4(3) |
| C(28)-C(27)-C(26) | 108.8(3) |
| C(29)-C(27)-C(26) | 108.4(3) |
| C(28)-C(27)-H(27) | 110.0 |
| C(29)-C(27)-H(27) | 110.0 |
| C(26)-C(27)-H(27) | 110.0 |
| C(22)-C(28)-C(27) | 109.5(3) |
| C(22)-C(28)-H(28A) | 109.8 |
| C(27)-C(28)-H(28A) | 109.8 |
| C(22)-C(28)-H(28B) | 109.8 |
| C(27)-C(28)-H(28B) | 109.8 |
| H(28A)-C(28)-H(28B) | 108.2 |
| C(24)-C(29)-C(27) | 110.3(3) |
| C(24)-C(29)-H(29A) | 109.6 |
| C(27)-C(29)-H(29A) | 109.6 |
| C(24)-C(29)-H(29B) | 109.6 |
| C(27)-C(29)-H(29B) | 109.6 |
| H(29A)-C(29)-H(29B) | 108.1 |
| C(30)-N(3)-W(1) | 153.22(18) |
| N(3)-C(30)-C(31) | 109.9(2) |
| N(3)-C(30)-C(36) | 112.2(2) |
| C(31)-C(30)-C(36) | 109.1(2) |
| N(3)-C(30)-C(35) | 108.14(19) |
| C(31)-C(30)-C(35) | 108.8(2) |
| C(36)-C(30)-C(35) | 108.6(2) |
| C(32)-C(31)-C(30) | 110.3(2) |
| C(32)-C(31)-H(31A) | 109.6 |
| C(30)-C(31)-H(31A) | 109.6 |
| C(32)-C(31)-H(31B) | 109.6 |
| C(30)-C(31)-H(31B) | 109.6 |
| H(31A)-C(31)-H(31B) | 108.1 |
| C(33)-C(32)-C(38) | 109.0(2) |
| C(33)-C(32)-C(31) | 109.5(2) |
| C(38)-C(32)-C(31) | 109.2(2) |
| C(33)-C(32)-H(32) | 109.7 |
| C(38)-C(32)-H(32) | 109.7 |
| C(31)-C(32)-H(32) | 109.7 |
| C(32)-C(33)-C(34) | 109.5(2) |
| C(32)-C(33)-H(33A) | 109.8 |
| C(34)-C(33)-H(33A) | 109.8 |
| C(32)-C(33)-H(33B) | 109.8 |

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| C(34)-C(33)-H(33B) | 109.8 |
| H(33A)-C(33)-H(33B) | 108.2 |
| C(35)-C(34)-C(33) | 109.9(2) |
| C(35)-C(34)-C(39) | 109.3(2) |
| C(33)-C(34)-C(39) | 109.6(2) |
| C(35)-C(34)-H(34) | 109.3 |
| C(33)-C(34)-H(34) | 109.3 |
| C(39)-C(34)-H(34) | 109.3 |
| C(34)-C(35)-C(30) | 110.1(2) |
| C(34)-C(35)-H(35A) | 109.6 |
| C(30)-C(35)-H(35A) | 109.6 |
| C(34)-C(35)-H(35B) | 109.6 |
| C(30)-C(35)-H(35B) | 109.6 |
| H(35A)-C(35)-H(35B) | 108.2 |
| C(37)-C(36)-C(30) | 109.7(2) |
| C(37)-C(36)-H(36A) | 109.7 |
| C(30)-C(36)-H(36A) | 109.7 |
| C(37)-C(36)-H(36B) | 109.7 |
| C(30)-C(36)-H(36B) | 109.7 |
| H(36A)-C(36)-H(36B) | 108.2 |
| C(38)-C(37)-C(36) | 109.8(2) |
| C(38)-C(37)-C(39) | 109.3(2) |
| C(36)-C(37)-C(39) | 110.0(2) |
| C(38)-C(37)-H(37) | 109.3 |
| C(36)-C(37)-H(37) | 109.3 |
| C(39)-C(37)-H(37) | 109.3 |
| C(37)-C(38)-C(32) | 109.9(2) |
| C(37)-C(38)-H(38A) | 109.7 |
| C(32)-C(38)-H(38A) | 109.7 |
| C(37)-C(38)-H(38B) | 109.7 |
| C(32)-C(38)-H(38B) | 109.7 |
| H(38A)-C(38)-H(38B) | 108.2 |
| C(37)-C(39)-C(34) | 108.8(2) |
| C(37)-C(39)-H(39A) | 109.9 |
| C(34)-C(39)-H(39A) | 109.9 |
| C(37)-C(39)-H(39B) | 109.9 |
| C(34)-C(39)-H(39B) | 109.9 |
| H(39A)-C(39)-H(39B) | 108.3 |
| W(2)-Cl(4)-W(1) | 105.93(2) |
| N(5)-W(2)-N(6) | 106.23(10) |
| N(5)-W(2)-N(4) | 95.08(9) |
| N(6)-W(2)-N(4) | 104.29(9) |
| N(5)-W(2)-Cl(2) | 93.75(7) |
| N(6)-W(2)-Cl(2) | 96.87(7) |
| N(4)-W(2)-Cl(2) | 153.74(6) |
| N(5)-W(2)-Cl(4) | 161.82(7) |
| N(6)-W(2)-Cl(4) | 91.94(7) |
| N(4)-W(2)-Cl(4) | 79.53(6) |
| Cl(2)-W(2)-Cl(4) | 84.43(2) |
| N(5)-W(2)-Cl(3) | 87.70(7) |
| N(6)-W(2)-Cl(3) | 166.06(7) |
| N(4)-W(2)-Cl(3) | 74.22(6) |
| Cl(2)-W(2)-Cl(3) | 81.489(19) |
| Cl(4)-W(2)-Cl(3) | 74.133(19) |

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| C(40)-N(4)-W(2) | 126.86(16) |
| C(40)-N(4)-H(4A) | 107(2) |
| W(2)-N(4)-H(4A) | 106(2) |
| C(40)-N(4)-H(4B) | 104(2) |
| W(2)-N(4)-H(4B) | 109(2) |
| H(4A)-N(4)-H(4B) | 99(3) |
| N(4)-C(40)-C(45) | 109.4(2) |
| N(4)-C(40)-C(46) | 109.8(2) |
| C(45)-C(40)-C(46) | 110.6(2) |
| N(4)-C(40)-C(41) | 108.9(2) |
| C(45)-C(40)-C(41) | 109.1(2) |
| C(46)-C(40)-C(41) | 109.1(2) |
| C(40)-C(41)-C(42) | 109.4(2) |
| C(40)-C(41)-H(41A) | 109.8 |
| C(42)-C(41)-H(41A) | 109.8 |
| C(40)-C(41)-H(41B) | 109.8 |
| C(42)-C(41)-H(41B) | 109.8 |
| H(41A)-C(41)-H(41B) | 108.2 |
| C(43)-C(42)-C(48) | 109.6(3) |
| C(43)-C(42)-C(41) | 109.6(3) |
| C(48)-C(42)-C(41) | 109.0(2) |
| C(43)-C(42)-H(42) | 109.6 |
| C(48)-C(42)-H(42) | 109.6 |
| C(41)-C(42)-H(42) | 109.6 |
| C(44)-C(43)-C(42) | 109.7(2) |
| C(44)-C(43)-H(43A) | 109.7 |
| C(42)-C(43)-H(43A) | 109.7 |
| C(44)-C(43)-H(43B) | 109.7 |
| C(42)-C(43)-H(43B) | 109.7 |
| H(43A)-C(43)-H(43B) | 108.2 |
| C(43)-C(44)-C(49) | 109.6(3) |
| C(43)-C(44)-C(45) | 109.2(2) |
| C(49)-C(44)-C(45) | 109.2(2) |
| C(43)-C(44)-H(44) | 109.6 |
| C(49)-C(44)-H(44) | 109.6 |
| C(45)-C(44)-H(44) | 109.6 |
| C(40)-C(45)-C(44) | 109.4(2) |
| C(40)-C(45)-H(45A) | 109.8 |
| C(44)-C(45)-H(45A) | 109.8 |
| C(40)-C(45)-H(45B) | 109.8 |
| C(44)-C(45)-H(45B) | 109.8 |
| H(45A)-C(45)-H(45B) | 108.2 |
| C(40)-C(46)-C(47) | 109.1(2) |
| C(40)-C(46)-H(46A) | 109.9 |
| C(47)-C(46)-H(46A) | 109.9 |
| C(40)-C(46)-H(46B) | 109.9 |
| C(47)-C(46)-H(46B) | 109.9 |
| H(46A)-C(46)-H(46B) | 108.3 |
| C(48)-C(47)-C(49) | 109.6(3) |
| C(48)-C(47)-C(46) | 109.9(2) |
| C(49)-C(47)-C(46) | 109.0(2) |
| C(48)-C(47)-H(47) | 109.4 |
| C(49)-C(47)-H(47) | 109.4 |
| C(46)-C(47)-H(47) | 109.4 |

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| C(47)-C(48)-C(42) | 109.5(3) |
| C(47)-C(48)-H(48A) | 109.8 |
| C(42)-C(48)-H(48A) | 109.8 |
| C(47)-C(48)-H(48B) | 109.8 |
| C(42)-C(48)-H(48B) | 109.8 |
| H(48A)-C(48)-H(48B) | 108.2 |
| C(47)-C(49)-C(44) | 109.9(3) |
| C(47)-C(49)-H(49A) | 109.7 |
| C(44)-C(49)-H(49A) | 109.7 |
| C(47)-C(49)-H(49B) | 109.7 |
| C(44)-C(49)-H(49B) | 109.7 |
| H(49A)-C(49)-H(49B) | 108.2 |
| C(50)-N(5)-W(2) | 171.01(19) |
| N(5)-C(50)-C(51) | 108.8(2) |
| N(5)-C(50)-C(55) | 111.5(2) |
| C(51)-C(50)-C(55) | 109.2(2) |
| N(5)-C(50)-C(56) | 108.8(2) |
| C(51)-C(50)-C(56) | 109.1(2) |
| C(55)-C(50)-C(56) | 109.3(2) |
| C(50)-C(51)-C(52) | 109.5(2) |
| C(50)-C(51)-H(51A) | 109.8 |
| C(52)-C(51)-H(51A) | 109.8 |
| C(50)-C(51)-H(51B) | 109.8 |
| C(52)-C(51)-H(51B) | 109.8 |
| H(51A)-C(51)-H(51B) | 108.2 |
| C(58)-C(52)-C(53) | 109.7(2) |
| C(58)-C(52)-C(51) | 109.8(3) |
| C(53)-C(52)-C(51) | 108.7(2) |
| C(58)-C(52)-H(52) | 109.5 |
| C(53)-C(52)-H(52) | 109.5 |
| C(51)-C(52)-H(52) | 109.5 |
| C(54)-C(53)-C(52) | 109.5(2) |
| C(54)-C(53)-H(53A) | 109.8 |
| C(52)-C(53)-H(53A) | 109.8 |
| C(54)-C(53)-H(53B) | 109.8 |
| C(52)-C(53)-H(53B) | 109.8 |
| H(53A)-C(53)-H(53B) | 108.2 |
| C(53)-C(54)-C(59) | 110.4(2) |
| C(53)-C(54)-C(55) | 109.2(2) |
| C(59)-C(54)-C(55) | 109.3(2) |
| C(53)-C(54)-H(54) | 109.3 |
| C(59)-C(54)-H(54) | 109.3 |
| C(55)-C(54)-H(54) | 109.3 |
| C(50)-C(55)-C(54) | 109.3(2) |
| C(50)-C(55)-H(55A) | 109.8 |
| C(54)-C(55)-H(55A) | 109.8 |
| C(50)-C(55)-H(55B) | 109.8 |
| C(54)-C(55)-H(55B) | 109.8 |
| H(55A)-C(55)-H(55B) | 108.3 |
| C(57)-C(56)-C(50) | 109.7(2) |
| C(57)-C(56)-H(56A) | 109.7 |
| C(50)-C(56)-H(56A) | 109.7 |
| C(57)-C(56)-H(56B) | 109.7 |
| C(50)-C(56)-H(56B) | 109.7 |

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| H(56A)-C(56)-H(56B) | 108.2 |
| C(58)-C(57)-C(56) | 109.5(3) |
| C(58)-C(57)-C(59) | 109.7(3) |
| C(56)-C(57)-C(59) | 109.5(3) |
| C(58)-C(57)-H(57) | 109.4 |
| C(56)-C(57)-H(57) | 109.4 |
| C(59)-C(57)-H(57) | 109.4 |
| C(52)-C(58)-C(57) | 109.7(2) |
| C(52)-C(58)-H(58A) | 109.7 |
| C(57)-C(58)-H(58A) | 109.7 |
| C(52)-C(58)-H(58B) | 109.7 |
| C(57)-C(58)-H(58B) | 109.7 |
| H(58A)-C(58)-H(58B) | 108.2 |
| C(57)-C(59)-C(54) | 109.1(2) |
| C(57)-C(59)-H(59A) | 109.9 |
| C(54)-C(59)-H(59A) | 109.9 |
| C(57)-C(59)-H(59B) | 109.9 |
| C(54)-C(59)-H(59B) | 109.9 |
| H(59A)-C(59)-H(59B) | 108.3 |
| C(60)-N(6)-W(2) | 152.40(19) |
| N(6)-C(60)-C(66) | 109.9(2) |
| N(6)-C(60)-C(61) | 112.5(2) |
| C(66)-C(60)-C(61) | 109.2(2) |
| N(6)-C(60)-C(65) | 107.51(19) |
| C(66)-C(60)-C(65) | 109.1(2) |
| C(61)-C(60)-C(65) | 108.6(2) |
| C(62)-C(61)-C(60) | 109.9(2) |
| C(62)-C(61)-H(61A) | 109.7 |
| C(60)-C(61)-H(61A) | 109.7 |
| C(62)-C(61)-H(61B) | 109.7 |
| C(60)-C(61)-H(61B) | 109.7 |
| H(61A)-C(61)-H(61B) | 108.2 |
| C(61)-C(62)-C(63) | 109.9(2) |
| C(61)-C(62)-C(68) | 109.4(2) |
| C(63)-C(62)-C(68) | 109.2(2) |
| C(61)-C(62)-H(62) | 109.4 |
| C(63)-C(62)-H(62) | 109.4 |
| C(68)-C(62)-H(62) | 109.4 |
| C(64)-C(63)-C(62) | 109.1(2) |
| C(64)-C(63)-H(63A) | 109.9 |
| C(62)-C(63)-H(63A) | 109.9 |
| C(64)-C(63)-H(63B) | 109.9 |
| C(62)-C(63)-H(63B) | 109.9 |
| H(63A)-C(63)-H(63B) | 108.3 |
| C(69)-C(64)-C(65) | 109.8(2) |
| C(69)-C(64)-C(63) | 109.8(2) |
| C(65)-C(64)-C(63) | 109.2(2) |
| C(69)-C(64)-H(64) | 109.4 |
| C(65)-C(64)-H(64) | 109.4 |
| C(63)-C(64)-H(64) | 109.4 |
| C(64)-C(65)-C(60) | 110.0(2) |
| C(64)-C(65)-H(65A) | 109.7 |
| C(60)-C(65)-H(65A) | 109.7 |
| C(64)-C(65)-H(65B) | 109.7 |

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| C(60)-C(65)-H(65B) | 109.7 |
| H(65A)-C(65)-H(65B) | 108.2 |
| C(60)-C(66)-C(67) | 109.9(2) |
| C(60)-C(66)-H(66A) | 109.7 |
| C(67)-C(66)-H(66A) | 109.7 |
| C(60)-C(66)-H(66B) | 109.7 |
| C(67)-C(66)-H(66B) | 109.7 |
| H(66A)-C(66)-H(66B) | 108.2 |
| C(68)-C(67)-C(69) | 108.9(2) |
| C(68)-C(67)-C(66) | 109.9(2) |
| C(69)-C(67)-C(66) | 109.4(2) |
| C(68)-C(67)-H(67) | 109.5 |
| C(69)-C(67)-H(67) | 109.5 |
| C(66)-C(67)-H(67) | 109.5 |
| C(67)-C(68)-C(62) | 109.7(2) |
| C(67)-C(68)-H(68A) | 109.7 |
| C(62)-C(68)-H(68A) | 109.7 |
| C(67)-C(68)-H(68B) | 109.7 |
| C(62)-C(68)-H(68B) | 109.7 |
| H(68A)-C(68)-H(68B) | 108.2 |
| C(64)-C(69)-C(67) | 109.6(2) |
| C(64)-C(69)-H(69A) | 109.8 |
| C(67)-C(69)-H(69A) | 109.8 |
| C(64)-C(69)-H(69B) | 109.8 |
| C(67)-C(69)-H(69B) | 109.8 |
| H(69A)-C(69)-H(69B) | 108.2 |
| W(3)-Cl(6)-W(3)#1 | 105.86(2) |
| N(8)-W(3)-N(9) | 106.74(11) |
| N(8)-W(3)-N(7) | 94.78(10) |
| N(9)-W(3)-N(7) | 104.27(9) |
| N(8)-W(3)-Cl(5) | 94.59(7) |
| N(9)-W(3)-Cl(5) | 96.43(7) |
| N(7)-W(3)-Cl(5) | 153.70(6) |
| N(8)-W(3)-Cl(6) | 162.53(8) |
| N(9)-W(3)-Cl(6) | 90.68(8) |
| N(7)-W(3)-Cl(6) | 79.19(6) |
| Cl(5)-W(3)-Cl(6) | 84.59(2) |
| N(8)-W(3)-Cl(6)#1 | 88.45(8) |
| N(9)-W(3)-Cl(6)#1 | 164.80(8) |
| N(7)-W(3)-Cl(6)#1 | 74.15(6) |
| Cl(5)-W(3)-Cl(6)#1 | 81.61(2) |
| Cl(6)-W(3)-Cl(6)#1 | 74.15(2) |
| C(70)-N(7)-W(3) | 128.15(16) |
| C(70)-N(7)-H(7A) | 109(2) |
| W(3)-N(7)-H(7A) | 105(2) |
| C(70)-N(7)-H(7B) | 108(2) |
| W(3)-N(7)-H(7B) | 104(2) |
| H(7A)-N(7)-H(7B) | 98(3) |
| N(7)-C(70)-C(71) | 109.6(2) |
| N(7)-C(70)-C(75) | 109.6(2) |
| C(71)-C(70)-C(75) | 110.8(2) |
| N(7)-C(70)-C(76) | 108.4(2) |
| C(71)-C(70)-C(76) | 109.0(2) |
| C(75)-C(70)-C(76) | 109.4(2) |

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| C(70)-C(71)-C(72) | 109.2(2) |
| C(70)-C(71)-H(71A) | 109.8 |
| C(72)-C(71)-H(71A) | 109.8 |
| C(70)-C(71)-H(71B) | 109.8 |
| C(72)-C(71)-H(71B) | 109.8 |
| H(71A)-C(71)-H(71B) | 108.3 |
| C(73)-C(72)-C(78) | 109.5(3) |
| C(73)-C(72)-C(71) | 109.3(2) |
| C(78)-C(72)-C(71) | 109.2(2) |
| C(73)-C(72)-H(72) | 109.6 |
| C(78)-C(72)-H(72) | 109.6 |
| C(71)-C(72)-H(72) | 109.6 |
| C(74)-C(73)-C(72) | 110.2(2) |
| C(74)-C(73)-H(73A) | 109.6 |
| C(72)-C(73)-H(73A) | 109.6 |
| C(74)-C(73)-H(73B) | 109.6 |
| C(72)-C(73)-H(73B) | 109.6 |
| H(73A)-C(73)-H(73B) | 108.1 |
| C(73)-C(74)-C(75) | 109.0(2) |
| C(73)-C(74)-C(79) | 109.2(2) |
| C(75)-C(74)-C(79) | 109.6(2) |
| C(73)-C(74)-H(74) | 109.7 |
| C(75)-C(74)-H(74) | 109.7 |
| C(79)-C(74)-H(74) | 109.7 |
| C(70)-C(75)-C(74) | 109.1(2) |
| C(70)-C(75)-H(75A) | 109.9 |
| C(74)-C(75)-H(75A) | 109.9 |
| C(70)-C(75)-H(75B) | 109.9 |
| C(74)-C(75)-H(75B) | 109.9 |
| H(75A)-C(75)-H(75B) | 108.3 |
| C(70)-C(76)-C(77) | 109.8(2) |
| C(70)-C(76)-H(76A) | 109.7 |
| C(77)-C(76)-H(76A) | 109.7 |
| C(70)-C(76)-H(76B) | 109.7 |
| C(77)-C(76)-H(76B) | 109.7 |
| H(76A)-C(76)-H(76B) | 108.2 |
| C(79)-C(77)-C(76) | 109.1(2) |
| C(79)-C(77)-C(78) | 109.8(3) |
| C(76)-C(77)-C(78) | 109.1(2) |
| C(79)-C(77)-H(77) | 109.6 |
| C(76)-C(77)-H(77) | 109.6 |
| C(78)-C(77)-H(77) | 109.6 |
| C(72)-C(78)-C(77) | 109.3(2) |
| C(72)-C(78)-H(78A) | 109.8 |
| C(77)-C(78)-H(78A) | 109.8 |
| C(72)-C(78)-H(78B) | 109.8 |
| C(77)-C(78)-H(78B) | 109.8 |
| H(78A)-C(78)-H(78B) | 108.3 |
| C(77)-C(79)-C(74) | 109.7(2) |
| C(77)-C(79)-H(79A) | 109.7 |
| C(74)-C(79)-H(79A) | 109.7 |
| C(77)-C(79)-H(79B) | 109.7 |
| C(74)-C(79)-H(79B) | 109.7 |
| H(79A)-C(79)-H(79B) | 108.2 |

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| C(80)-N(8)-W(3) | 172.94(19) |
| N(8)-C(80)-C(81) | 108.4(2) |
| N(8)-C(80)-C(85) | 109.0(2) |
| C(81)-C(80)-C(85) | 109.4(2) |
| N(8)-C(80)-C(86) | 111.9(2) |
| C(81)-C(80)-C(86) | 109.1(2) |
| C(85)-C(80)-C(86) | 109.1(2) |
| C(82)-C(81)-C(80) | 109.6(2) |
| C(82)-C(81)-H(81A) | 109.7 |
| C(80)-C(81)-H(81A) | 109.7 |
| C(82)-C(81)-H(81B) | 109.7 |
| C(80)-C(81)-H(81B) | 109.7 |
| H(81A)-C(81)-H(81B) | 108.2 |
| C(83)-C(82)-C(81) | 109.5(3) |
| C(83)-C(82)-C(88) | 109.6(2) |
| C(81)-C(82)-C(88) | 109.6(3) |
| C(83)-C(82)-H(82) | 109.4 |
| C(81)-C(82)-H(82) | 109.4 |
| C(88)-C(82)-H(82) | 109.4 |
| C(82)-C(83)-C(84) | 110.1(2) |
| C(82)-C(83)-H(83A) | 109.6 |
| C(84)-C(83)-H(83A) | 109.6 |
| C(82)-C(83)-H(83B) | 109.6 |
| C(84)-C(83)-H(83B) | 109.6 |
| H(83A)-C(83)-H(83B) | 108.1 |
| C(83)-C(84)-C(89) | 109.2(2) |
| C(83)-C(84)-C(85) | 109.4(3) |
| C(89)-C(84)-C(85) | 108.7(2) |
| C(83)-C(84)-H(84) | 109.8 |
| C(89)-C(84)-H(84) | 109.8 |
| C(85)-C(84)-H(84) | 109.8 |
| C(80)-C(85)-C(84) | 109.8(2) |
| C(80)-C(85)-H(85A) | 109.7 |
| C(84)-C(85)-H(85A) | 109.7 |
| C(80)-C(85)-H(85B) | 109.7 |
| C(84)-C(85)-H(85B) | 109.7 |
| H(85A)-C(85)-H(85B) | 108.2 |
| C(80)-C(86)-C(87) | 109.5(2) |
| C(80)-C(86)-H(86A) | 109.8 |
| C(87)-C(86)-H(86A) | 109.8 |
| C(80)-C(86)-H(86B) | 109.8 |
| C(87)-C(86)-H(86B) | 109.8 |
| H(86A)-C(86)-H(86B) | 108.2 |
| C(89)-C(87)-C(88) | 109.9(2) |
| C(89)-C(87)-C(86) | 109.1(2) |
| C(88)-C(87)-C(86) | 109.0(2) |
| C(89)-C(87)-H(87) | 109.6 |
| C(88)-C(87)-H(87) | 109.6 |
| C(86)-C(87)-H(87) | 109.6 |
| C(87)-C(88)-C(82) | 109.4(2) |
| C(87)-C(88)-H(88A) | 109.8 |
| C(82)-C(88)-H(88A) | 109.8 |
| C(87)-C(88)-H(88B) | 109.8 |
| C(82)-C(88)-H(88B) | 109.8 |

| | |
|---|---|
| H(88A)-C(88)-H(88B) | 108.2 |
| C(87)-C(89)-C(84) | 110.1(2) |
| C(87)-C(89)-H(89A) | 109.6 |
| C(84)-C(89)-H(89A) | 109.6 |
| C(87)-C(89)-H(89B) | 109.6 |
| C(84)-C(89)-H(89B) | 109.6 |
| H(89A)-C(89)-H(89B) | 108.2 |
| C(90)-N(9)-W(3) | 157.23(19) |
| N(9)-C(90)-C(91) | 112.6(2) |
| N(9)-C(90)-C(95) | 108.1(2) |
| C(91)-C(90)-C(95) | 108.9(2) |
| N(9)-C(90)-C(96) | 109.0(2) |
| C(91)-C(90)-C(96) | 109.3(2) |
| C(95)-C(90)-C(96) | 108.9(2) |
| C(92)-C(91)-C(90) | 109.7(2) |
| C(92)-C(91)-H(91A) | 109.7 |
| C(90)-C(91)-H(91A) | 109.7 |
| C(92)-C(91)-H(91B) | 109.7 |
| C(90)-C(91)-H(91B) | 109.7 |
| H(91A)-C(91)-H(91B) | 108.2 |
| C(98)-C(92)-C(91) | 109.7(2) |
| C(98)-C(92)-C(93) | 109.5(2) |
| C(91)-C(92)-C(93) | 109.8(2) |
| C(98)-C(92)-H(92) | 109.3 |
| C(91)-C(92)-H(92) | 109.3 |
| C(93)-C(92)-H(92) | 109.3 |
| C(92)-C(93)-C(94) | 108.9(2) |
| C(92)-C(93)-H(93A) | 109.9 |
| C(94)-C(93)-H(93A) | 109.9 |
| C(92)-C(93)-H(93B) | 109.9 |
| C(94)-C(93)-H(93B) | 109.9 |
| H(93A)-C(93)-H(93B) | 108.3 |
| C(95)-C(94)-C(99) | 109.6(2) |
| C(95)-C(94)-C(93) | 109.4(2) |
| C(99)-C(94)-C(93) | 109.8(2) |
| C(95)-C(94)-H(94) | 109.3 |
| C(99)-C(94)-H(94) | 109.3 |
| C(93)-C(94)-H(94) | 109.3 |
| C(94)-C(95)-C(90) | 109.9(2) |
| C(94)-C(95)-H(95A) | 109.7 |
| C(90)-C(95)-H(95A) | 109.7 |
| C(94)-C(95)-H(95B) | 109.7 |
| C(90)-C(95)-H(95B) | 109.7 |
| H(95A)-C(95)-H(95B) | 108.2 |
| C(97)-C(96)-C(90) | 109.8(2) |
| C(97)-C(96)-H(96A) | 109.7 |
| C(90)-C(96)-H(96A) | 109.7 |
| C(97)-C(96)-H(96B) | 109.7 |
| C(90)-C(96)-H(96B) | 109.7 |
| H(96A)-C(96)-H(96B) | 108.2 |
| C(96)-C(97)-C(98) | 109.4(2) |
| C(96)-C(97)-C(99) | 109.7(2) |
| C(98)-C(97)-C(99) | 109.0(2) |
| C(96)-C(97)-H(97) | 109.6 |

| | |
|---|---|
| C(98)-C(97)-H(97) | 109.6 |
| C(99)-C(97)-H(97) | 109.6 |
| C(92)-C(98)-C(97) | 109.8(2) |
| C(92)-C(98)-H(98A) | 109.7 |
| C(97)-C(98)-H(98A) | 109.7 |
| C(92)-C(98)-H(98B) | 109.7 |
| C(97)-C(98)-H(98B) | 109.7 |
| H(98A)-C(98)-H(98B) | 108.2 |
| C(97)-C(99)-C(94) | 109.5(2) |
| C(97)-C(99)-H(99A) | 109.8 |
| C(94)-C(99)-H(99A) | 109.8 |
| C(97)-C(99)-H(99B) | 109.8 |
| C(94)-C(99)-H(99B) | 109.8 |
| H(99A)-C(99)-H(99B) | 108.2 |
| Cl(11)-C(1S)-Cl(12) | 111.86(17) |
| Cl(11)-C(1S)-H(1S1) | 109.2 |
| Cl(12)-C(1S)-H(1S1) | 109.2 |
| Cl(11)-C(1S)-H(1S2) | 109.2 |
| Cl(12)-C(1S)-H(1S2) | 109.2 |
| H(1S1)-C(1S)-H(1S2) | 107.9 |
| Cl(21)-C(2S)-Cl(22) | 111.9(2) |
| Cl(21)-C(2S)-H(2S1) | 109.2 |
| Cl(22)-C(2S)-H(2S1) | 109.2 |
| Cl(21)-C(2S)-H(2S2) | 109.2 |
| Cl(22)-C(2S)-H(2S2) | 109.2 |
| H(2S1)-C(2S)-H(2S2) | 107.9 |
| Cl(31)-C(3S)-Cl(32) | 112.04(18) |
| Cl(31)-C(3S)-H(3S1) | 109.2 |
| Cl(32)-C(3S)-H(3S1) | 109.2 |
| Cl(31)-C(3S)-H(3S2) | 109.2 |
| Cl(32)-C(3S)-H(3S2) | 109.2 |
| H(3S1)-C(3S)-H(3S2) | 107.9 |
| Cl(41)-C(4S)-Cl(42) | 112.4(2) |
| Cl(41)-C(4S)-H(4S1) | 109.1 |
| Cl(42)-C(4S)-H(4S1) | 109.1 |
| Cl(41)-C(4S)-H(4S2) | 109.1 |
| Cl(42)-C(4S)-H(4S2) | 109.1 |
| H(4S1)-C(4S)-H(4S2) | 107.9 |
| Cl(52)-C(5S)-Cl(51) | 110.7(2) |
| Cl(52)-C(5S)-H(5S1) | 109.5 |
| Cl(51)-C(5S)-H(5S1) | 109.5 |
| Cl(52)-C(5S)-H(5S2) | 109.5 |
| Cl(51)-C(5S)-H(5S2) | 109.5 |
| H(5S1)-C(5S)-H(5S2) | 108.1 |
| Cl(61)-C(6S)-Cl(62) | 111.0(2) |
| Cl(61)-C(6S)-H(6S1) | 109.4 |
| Cl(62)-C(6S)-H(6S1) | 109.4 |
| Cl(61)-C(6S)-H(6S2) | 109.4 |
| Cl(62)-C(6S)-H(6S2) | 109.4 |
| H(6S1)-C(6S)-H(6S2) | 108.0 |
| Cl(71)-C(7S)-Cl(72) | 114.1(7) |
| Cl(71)-C(7S)-H(7S1) | 108.7 |
| Cl(72)-C(7S)-H(7S1) | 108.7 |
| Cl(71)-C(7S)-H(7S2) | 108.7 |

| | |
|---|---|
| Cl(72)-C(7S)-H(7S2) | 108.7 |
| H(7S1)-C(7S)-H(7S2) | 107.6 |
| Cl(74)-C(7T)-Cl(73) | 114.0(9) |
| Cl(74)-C(7T)-H(7T1) | 108.7 |
| Cl(73)-C(7T)-H(7T1) | 108.7 |
| Cl(74)-C(7T)-H(7T2) | 108.7 |
| Cl(73)-C(7T)-H(7T2) | 108.7 |
| H(7T1)-C(7T)-H(7T2) | 107.6 |
| Cl(81)-C(8S)-Cl(82) | 112.4(6) |
| Cl(81)-C(8S)-H(8S1) | 109.1 |
| Cl(82)-C(8S)-H(8S1) | 109.1 |
| Cl(81)-C(8S)-H(8S2) | 109.1 |
| Cl(82)-C(8S)-H(8S2) | 109.1 |
| H(8S1)-C(8S)-H(8S2) | 107.9 |
| Cl(83)-C(8T)-Cl(84) | 110.1(16) |
| Cl(83)-C(8T)-H(8T1) | 109.6 |
| Cl(84)-C(8T)-H(8T1) | 109.6 |
| Cl(83)-C(8T)-H(8T2) | 109.6 |
| Cl(84)-C(8T)-H(8T2) | 109.6 |
| H(8T1)-C(8T)-H(8T2) | 108.1 |

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+2,-z+2

Table S10. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **X8_12067**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Cl(1) | 16(1) | 20(1) | 14(1) | 4(1) | 4(1) | 6(1) |
| Cl(3) | 13(1) | 13(1) | 16(1) | 3(1) | 5(1) | 3(1) |
| W(1) | 12(1) | 15(1) | 13(1) | 3(1) | 5(1) | 5(1) |
| N(1) | 17(1) | 18(1) | 15(1) | 3(1) | 6(1) | 7(1) |
| C(10) | 19(1) | 15(1) | 13(1) | 3(1) | 6(1) | 3(1) |
| C(11) | 24(1) | 19(1) | 16(1) | 6(1) | 6(1) | 7(1) |
| C(12) | 29(1) | 20(1) | 14(1) | 4(1) | 6(1) | 2(1) |
| C(13) | 26(1) | 21(1) | 19(1) | 2(1) | 3(1) | -2(1) |
| C(14) | 34(2) | 14(1) | 19(1) | -1(1) | 4(1) | -1(1) |
| C(15) | 24(1) | 16(1) | 19(1) | 6(1) | 4(1) | 0(1) |
| C(16) | 17(1) | 22(1) | 17(1) | -1(1) | 6(1) | 0(1) |
| C(17) | 24(1) | 35(2) | 21(1) | -5(1) | 12(1) | 3(1) |
| C(18) | 31(2) | 30(2) | 18(1) | -1(1) | 13(1) | -5(1) |
| C(19) | 36(2) | 29(2) | 21(1) | -5(1) | 6(1) | 11(1) |
| N(2) | 16(1) | 21(1) | 13(1) | 4(1) | 5(1) | 5(1) |
| C(20) | 12(1) | 15(1) | 17(1) | 2(1) | 5(1) | 2(1) |
| C(21) | 29(2) | 31(2) | 24(1) | -5(1) | 15(1) | -8(1) |
| C(22) | 28(2) | 27(2) | 29(1) | -3(1) | 16(1) | -8(1) |
| C(23) | 18(1) | 30(2) | 52(2) | 14(2) | 12(1) | 4(1) |
| C(24) | 21(1) | 52(2) | 26(2) | 18(1) | -3(1) | -8(1) |
| C(25) | 19(1) | 42(2) | 26(1) | 18(1) | 1(1) | -4(1) |
| C(26) | 20(1) | 22(2) | 59(2) | 0(1) | 16(2) | 5(1) |
| C(27) | 27(2) | 16(1) | 65(2) | -6(1) | 19(2) | 1(1) |
| C(28) | 24(1) | 24(2) | 39(2) | 14(1) | 3(1) | 1(1) |
| C(29) | 40(2) | 62(3) | 30(2) | -22(2) | 16(2) | -22(2) |
| N(3) | 14(1) | 18(1) | 14(1) | 4(1) | 4(1) | 8(1) |
| C(30) | 12(1) | 14(1) | 14(1) | 1(1) | 3(1) | 5(1) |
| C(31) | 17(1) | 16(1) | 17(1) | 1(1) | 4(1) | 2(1) |
| C(32) | 24(1) | 14(1) | 16(1) | 0(1) | 4(1) | 4(1) |
| C(33) | 28(1) | 16(1) | 19(1) | 5(1) | 7(1) | 7(1) |
| C(34) | 20(1) | 21(1) | 13(1) | 3(1) | 1(1) | 8(1) |
| C(35) | 19(1) | 18(1) | 13(1) | 1(1) | 5(1) | 6(1) |
| C(36) | 19(1) | 17(1) | 20(1) | 5(1) | 10(1) | 4(1) |
| C(37) | 17(1) | 23(1) | 21(1) | 6(1) | 9(1) | 6(1) |
| C(38) | 29(1) | 21(1) | 18(1) | 1(1) | 10(1) | 9(1) |
| C(39) | 15(1) | 27(1) | 23(1) | 4(1) | 4(1) | 7(1) |
| Cl(2) | 16(1) | 20(1) | 13(1) | 4(1) | 5(1) | 6(1) |
| Cl(4) | 14(1) | 13(1) | 16(1) | 2(1) | 6(1) | 3(1) |
| W(2) | 13(1) | 14(1) | 13(1) | 3(1) | 5(1) | 5(1) |
| N(4) | 18(1) | 15(1) | 14(1) | 3(1) | 6(1) | 6(1) |
| C(40) | 23(1) | 16(1) | 12(1) | 3(1) | 6(1) | 3(1) |
| C(41) | 36(2) | 18(1) | 16(1) | 7(1) | 5(1) | 8(1) |
| C(42) | 55(2) | 18(1) | 14(1) | 4(1) | 9(1) | 1(1) |
| C(43) | 57(2) | 25(2) | 20(1) | 0(1) | 21(1) | -5(1) |
| C(44) | 34(2) | 26(2) | 25(1) | -2(1) | 19(1) | -1(1) |
| C(45) | 26(1) | 17(1) | 20(1) | 0(1) | 13(1) | 1(1) |
| C(46) | 29(1) | 15(1) | 16(1) | 3(1) | 8(1) | 0(1) |
| C(47) | 39(2) | 16(1) | 18(1) | 1(1) | 10(1) | -1(1) |
| C(48) | 46(2) | 25(2) | 16(1) | 2(1) | 6(1) | -3(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(49) | 45(2) | 22(1) | 23(1) | -2(1) | 17(1) | 6(1) |
| N(5) | 20(1) | 17(1) | 16(1) | 3(1) | 7(1) | 5(1) |
| C(50) | 17(1) | 14(1) | 18(1) | 4(1) | 7(1) | 4(1) |
| C(51) | 18(1) | 25(1) | 20(1) | 8(1) | 5(1) | 2(1) |
| C(52) | 18(1) | 30(2) | 22(1) | 8(1) | 1(1) | -1(1) |
| C(53) | 15(1) | 23(1) | 34(2) | 10(1) | 7(1) | 4(1) |
| C(54) | 20(1) | 19(1) | 28(1) | 6(1) | 12(1) | 3(1) |
| C(55) | 22(1) | 21(1) | 21(1) | 2(1) | 11(1) | 1(1) |
| C(56) | 19(1) | 18(1) | 35(2) | 2(1) | 11(1) | 4(1) |
| C(57) | 24(1) | 17(1) | 41(2) | 1(1) | 13(1) | 3(1) |
| C(58) | 28(2) | 30(2) | 29(2) | -4(1) | 10(1) | -4(1) |
| C(59) | 22(1) | 20(1) | 35(2) | 13(1) | 9(1) | 3(1) |
| N(6) | 16(1) | 18(1) | 13(1) | 4(1) | 5(1) | 6(1) |
| C(60) | 12(1) | 17(1) | 15(1) | 2(1) | 5(1) | 8(1) |
| C(61) | 17(1) | 17(1) | 21(1) | 4(1) | 9(1) | 3(1) |
| C(62) | 16(1) | 22(1) | 23(1) | 5(1) | 10(1) | 7(1) |
| C(63) | 16(1) | 26(1) | 25(1) | 0(1) | 2(1) | 8(1) |
| C(64) | 22(1) | 20(1) | 14(1) | 1(1) | 1(1) | 10(1) |
| C(65) | 22(1) | 17(1) | 13(1) | 2(1) | 4(1) | 9(1) |
| C(66) | 16(1) | 18(1) | 16(1) | 1(1) | 4(1) | 4(1) |
| C(67) | 22(1) | 13(1) | 18(1) | 0(1) | 5(1) | 3(1) |
| C(68) | 24(1) | 20(1) | 18(1) | 0(1) | 10(1) | 11(1) |
| C(69) | 27(1) | 16(1) | 19(1) | 6(1) | 8(1) | 7(1) |
| Cl(5) | 16(1) | 19(1) | 15(1) | 4(1) | 3(1) | 6(1) |
| Cl(6) | 14(1) | 12(1) | 17(1) | 3(1) | 4(1) | 3(1) |
| W(3) | 13(1) | 14(1) | 14(1) | 3(1) | 4(1) | 4(1) |
| N(7) | 19(1) | 16(1) | 16(1) | 5(1) | 6(1) | 6(1) |
| C(70) | 19(1) | 14(1) | 14(1) | 3(1) | 4(1) | 3(1) |
| C(71) | 19(1) | 19(1) | 18(1) | 3(1) | 7(1) | 1(1) |
| C(72) | 28(1) | 25(1) | 21(1) | 0(1) | 11(1) | 1(1) |
| C(73) | 35(2) | 21(1) | 23(1) | -1(1) | 10(1) | 5(1) |
| C(74) | 30(2) | 14(1) | 19(1) | 1(1) | 4(1) | -2(1) |
| C(75) | 21(1) | 15(1) | 20(1) | 6(1) | 5(1) | 1(1) |
| C(76) | 28(1) | 18(1) | 18(1) | 6(1) | 4(1) | 5(1) |
| C(77) | 34(2) | 20(1) | 16(1) | 5(1) | 4(1) | 0(1) |
| C(78) | 41(2) | 25(2) | 18(1) | 0(1) | 11(1) | -4(1) |
| C(79) | 33(2) | 22(1) | 19(1) | 4(1) | 2(1) | -2(1) |
| N(8) | 17(1) | 20(1) | 17(1) | 5(1) | 5(1) | 4(1) |
| C(80) | 15(1) | 14(1) | 20(1) | 3(1) | 6(1) | 2(1) |
| C(81) | 20(1) | 18(1) | 34(2) | 4(1) | 10(1) | 3(1) |
| C(82) | 26(1) | 14(1) | 41(2) | 3(1) | 15(1) | 5(1) |
| C(83) | 27(2) | 30(2) | 29(2) | -4(1) | 11(1) | -6(1) |
| C(84) | 20(1) | 28(2) | 23(1) | 8(1) | 3(1) | -1(1) |
| C(85) | 19(1) | 25(1) | 21(1) | 8(1) | 4(1) | 0(1) |
| C(86) | 22(1) | 23(1) | 23(1) | 1(1) | 10(1) | -2(1) |
| C(87) | 23(1) | 22(1) | 28(1) | 3(1) | 14(1) | 2(1) |
| C(88) | 23(1) | 19(1) | 32(2) | 8(1) | 10(1) | 3(1) |
| C(89) | 20(1) | 22(1) | 36(2) | 7(1) | 10(1) | 2(1) |
| N(9) | 17(1) | 18(1) | 16(1) | 4(1) | 5(1) | 7(1) |
| C(90) | 14(1) | 18(1) | 15(1) | 4(1) | 4(1) | 8(1) |
| C(91) | 19(1) | 14(1) | 17(1) | 3(1) | 5(1) | 2(1) |
| C(92) | 18(1) | 18(1) | 18(1) | 4(1) | 7(1) | 4(1) |
| C(93) | 14(1) | 23(1) | 20(1) | 4(1) | 3(1) | 6(1) |
| C(94) | 21(1) | 18(1) | 13(1) | 3(1) | 3(1) | 8(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(95) | 20(1) | 18(1) | 12(1) | 0(1) | 4(1) | 6(1) |
| C(96) | 15(1) | 17(1) | 18(1) | 3(1) | 4(1) | 2(1) |
| C(97) | 22(1) | 14(1) | 16(1) | 0(1) | 4(1) | 2(1) |
| C(98) | 26(1) | 18(1) | 16(1) | 0(1) | 8(1) | 7(1) |
| C(99) | 26(1) | 17(1) | 19(1) | 6(1) | 9(1) | 7(1) |
| C(1S) | 31(2) | 24(1) | 39(2) | 11(1) | 16(1) | 5(1) |
| Cl(11) | 52(1) | 27(1) | 63(1) | 15(1) | 37(1) | 13(1) |
| Cl(12) | 31(1) | 24(1) | 32(1) | 9(1) | 14(1) | 6(1) |
| C(2S) | 59(2) | 32(2) | 45(2) | 7(1) | 34(2) | 10(2) |
| Cl(21) | 146(1) | 42(1) | 101(1) | 15(1) | 104(1) | 7(1) |
| Cl(22) | 50(1) | 31(1) | 53(1) | -4(1) | 33(1) | 1(1) |
| C(3S) | 30(1) | 26(1) | 50(2) | 16(1) | 15(2) | 6(1) |
| Cl(31) | 78(1) | 31(1) | 88(1) | 24(1) | 64(1) | 24(1) |
| Cl(32) | 30(1) | 23(1) | 36(1) | 9(1) | 12(1) | 4(1) |
| C(4S) | 49(2) | 34(2) | 79(3) | 32(2) | 37(2) | 16(2) |
| Cl(41) | 62(1) | 32(1) | 43(1) | 17(1) | 20(1) | 19(1) |
| Cl(42) | 36(1) | 29(1) | 34(1) | 6(1) | 13(1) | 3(1) |
| C(5S) | 40(2) | 50(2) | 33(2) | -11(2) | 12(1) | 4(2) |
| Cl(51) | 32(1) | 51(1) | 54(1) | -21(1) | 23(1) | -8(1) |
| Cl(52) | 48(1) | 52(1) | 39(1) | 9(1) | 25(1) | 20(1) |
| C(6S) | 47(2) | 46(2) | 37(2) | -13(2) | 20(2) | -7(2) |
| Cl(61) | 32(1) | 63(1) | 47(1) | -13(1) | 21(1) | -5(1) |
| Cl(62) | 42(1) | 37(1) | 33(1) | 3(1) | 21(1) | 12(1) |
| C(7S) | 30(4) | 62(5) | 73(6) | -18(3) | 21(4) | 15(4) |
| Cl(71) | 42(2) | 106(5) | 133(6) | 35(4) | 23(3) | 20(3) |
| Cl(72) | 88(4) | 145(5) | 181(7) | 21(5) | 101(5) | 15(4) |
| C(7T) | 131(13) | 64(7) | 60(7) | 4(6) | 36(7) | -7(9) |
| Cl(73) | 88(4) | 79(3) | 83(3) | 26(3) | 27(2) | -11(2) |
| Cl(74) | 24(1) | 78(2) | 90(3) | 29(2) | 21(2) | 7(1) |
| C(8S) | 32(5) | 54(5) | 37(4) | -2(4) | 10(4) | -4(4) |
| Cl(81) | 46(3) | 59(3) | 65(3) | 14(2) | 22(3) | -3(2) |
| Cl(82) | 42(2) | 70(3) | 67(3) | 24(3) | -3(2) | -7(2) |
| C(8T) | 49(15) | 65(14) | 61(7) | -15(12) | -13(14) | 6(13) |
| Cl(83) | 55(10) | 117(16) | 67(9) | 17(10) | 8(7) | 15(12) |
| Cl(84) | 51(6) | 119(11) | 67(6) | 5(6) | 19(5) | 1(6) |

Table S11. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for **X8_12067**.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1A) | 1060(20) | 6332(10) | 4339(18) | 19 |
| H(1B) | 1809(13) | 6793(17) | 4420(18) | 19 |
| H(11A) | 1604 | 6229 | 5621 | 24 |
| H(11B) | 2463 | 6777 | 5719 | 24 |
| H(12) | 2243 | 6791 | 6866 | 25 |
| H(13A) | 2882 | 7878 | 6637 | 29 |
| H(13B) | 2281 | 8049 | 7118 | 29 |
| H(14) | 1939 | 8758 | 6128 | 29 |
| H(15A) | 1295 | 8193 | 4885 | 25 |
| H(15B) | 2276 | 7962 | 5269 | 25 |
| H(16A) | 61 | 6568 | 5022 | 23 |
| H(16B) | -75 | 7326 | 4727 | 23 |
| H(17) | -286 | 7366 | 5876 | 32 |
| H(18A) | 921 | 7198 | 6960 | 31 |
| H(18B) | 658 | 6490 | 6377 | 31 |
| H(19A) | 733 | 8401 | 6507 | 36 |
| H(19B) | 350 | 8450 | 5639 | 36 |
| H(21A) | -1816 | 6634 | 3607 | 33 |
| H(21B) | -1275 | 6010 | 3980 | 33 |
| H(22) | -2850 | 5673 | 3634 | 33 |
| H(23A) | -3349 | 6326 | 2627 | 39 |
| H(23B) | -3788 | 5512 | 2378 | 39 |
| H(24) | -3243 | 5903 | 1484 | 43 |
| H(25A) | -1673 | 6257 | 1822 | 37 |
| H(25B) | -2064 | 6781 | 2289 | 37 |
| H(26A) | -657 | 5189 | 3261 | 40 |
| H(26B) | -810 | 5275 | 2420 | 40 |
| H(27) | -1839 | 4304 | 2456 | 43 |
| H(28A) | -2933 | 4542 | 2985 | 37 |
| H(28B) | -1951 | 4751 | 3605 | 37 |
| H(29A) | -2346 | 4981 | 1441 | 56 |
| H(29B) | -3178 | 4690 | 1647 | 56 |
| H(31A) | 635 | 9210 | 4329 | 21 |
| H(31B) | 734 | 9366 | 3569 | 21 |
| H(32) | 58 | 10299 | 3997 | 23 |
| H(33A) | -399 | 10023 | 2692 | 25 |
| H(33B) | -1218 | 10279 | 2894 | 25 |
| H(34) | -1725 | 9229 | 2019 | 23 |
| H(35A) | -363 | 8708 | 2359 | 20 |
| H(35B) | -1156 | 8139 | 2356 | 20 |
| H(36A) | -1304 | 7888 | 3550 | 22 |
| H(36B) | -612 | 8304 | 4318 | 22 |
| H(37) | -1982 | 8818 | 3974 | 23 |
| H(38A) | -659 | 9613 | 4639 | 26 |
| H(38B) | -1380 | 10026 | 4076 | 26 |
| H(39A) | -2466 | 9377 | 2878 | 27 |
| H(39B) | -2440 | 8545 | 2667 | 27 |
| H(4A) | 2400(20) | 7008(10) | 2163(18) | 19 |

| | | | | |
|---|---|---|---|---|
| H(4B) | 1654(12) | 6546(17) | 2058(18) | 19 |
| H(41A) | 2001 | 7090 | 890 | 29 |
| H(41B) | 1100 | 6582 | 766 | 29 |
| H(42) | 1406 | 6500 | -349 | 36 |
| H(43A) | 2726 | 6021 | -365 | 39 |
| H(43B) | 2999 | 6743 | 197 | 39 |
| H(44) | 3862 | 5847 | 760 | 32 |
| H(45A) | 3563 | 5952 | 1875 | 24 |
| H(45B) | 3495 | 6703 | 1558 | 24 |
| H(46A) | 1181 | 5404 | 1253 | 24 |
| H(46B) | 2133 | 5146 | 1680 | 24 |
| H(47) | 1528 | 4554 | 444 | 30 |
| H(48A) | 671 | 5453 | -120 | 37 |
| H(48B) | 1301 | 5229 | -559 | 37 |
| H(49A) | 2799 | 4831 | 124 | 35 |
| H(49B) | 3119 | 4807 | 994 | 35 |
| H(51A) | 5503 | 6512 | 4312 | 25 |
| H(51B) | 5094 | 7040 | 4761 | 25 |
| H(52) | 6679 | 7364 | 5162 | 30 |
| H(53A) | 7310 | 7746 | 4306 | 29 |
| H(53B) | 6839 | 6942 | 4032 | 29 |
| H(54) | 6418 | 7630 | 3030 | 25 |
| H(55A) | 4833 | 7312 | 2629 | 24 |
| H(55B) | 5341 | 6676 | 3009 | 24 |
| H(56A) | 4194 | 8153 | 3340 | 28 |
| H(56B) | 4301 | 8048 | 4169 | 28 |
| H(57) | 5370 | 8999 | 4182 | 32 |
| H(58A) | 6673 | 8595 | 5010 | 36 |
| H(58B) | 5814 | 8321 | 5189 | 36 |
| H(59A) | 6503 | 8762 | 3704 | 30 |
| H(59B) | 5537 | 8580 | 3056 | 30 |
| H(61A) | 4119 | 4984 | 2279 | 21 |
| H(61B) | 4780 | 5432 | 3041 | 21 |
| H(62) | 5498 | 4482 | 2702 | 23 |
| H(63A) | 5928 | 3978 | 3833 | 28 |
| H(63B) | 5887 | 4815 | 3995 | 28 |
| H(64) | 5133 | 4173 | 4641 | 23 |
| H(65A) | 4573 | 5245 | 4229 | 21 |
| H(65B) | 3768 | 4688 | 4226 | 21 |
| H(66A) | 2849 | 4103 | 2268 | 21 |
| H(66B) | 2714 | 3986 | 3024 | 21 |
| H(67) | 3422 | 3031 | 2673 | 22 |
| H(68A) | 4186 | 3666 | 2032 | 24 |
| H(68B) | 4885 | 3277 | 2640 | 24 |
| H(69A) | 3819 | 3366 | 3966 | 24 |
| H(69B) | 4660 | 3092 | 3812 | 24 |
| H(7A) | 4944(13) | 9974(17) | 8861(18) | 20 |
| H(7B) | 5710(20) | 10392(10) | 8915(18) | 20 |
| H(71A) | 6761 | 9295 | 8539 | 22 |
| H(71B) | 6711 | 10053 | 8236 | 22 |
| H(72) | 6972 | 9183 | 7388 | 29 |
| H(73A) | 5842 | 8206 | 6767 | 32 |
| H(73B) | 6213 | 8163 | 7636 | 32 |
| H(74) | 4613 | 7964 | 7153 | 27 |

| | | | | |
|---|---|---|---|---|
| H(75A) | 4372 | 8829 | 8013 | 23 |
| H(75B) | 5314 | 8535 | 8395 | 23 |
| H(76A) | 5241 | 10493 | 7641 | 27 |
| H(76B) | 4328 | 10021 | 7551 | 27 |
| H(77) | 4535 | 9931 | 6398 | 30 |
| H(78A) | 5800 | 9405 | 6300 | 34 |
| H(78B) | 6139 | 10120 | 6876 | 34 |
| H(79A) | 4355 | 8664 | 6157 | 32 |
| H(79B) | 3785 | 8908 | 6642 | 32 |
| H(81A) | 7500 | 11537 | 9963 | 29 |
| H(81B) | 7619 | 11496 | 10806 | 29 |
| H(82) | 8699 | 12400 | 10749 | 31 |
| H(83A) | 9144 | 11787 | 11802 | 36 |
| H(83B) | 9997 | 12016 | 11596 | 36 |
| H(84) | 9993 | 10809 | 11836 | 30 |
| H(85A) | 8792 | 9940 | 11042 | 27 |
| H(85B) | 8407 | 10512 | 11467 | 27 |
| H(86A) | 8099 | 10627 | 9296 | 27 |
| H(86B) | 8599 | 10006 | 9715 | 27 |
| H(87) | 9690 | 10915 | 9661 | 28 |
| H(88A) | 8836 | 11892 | 9637 | 29 |
| H(88B) | 9810 | 12086 | 10272 | 29 |
| H(89A) | 10601 | 11103 | 10935 | 31 |
| H(89B) | 10119 | 10299 | 10716 | 31 |
| H(91A) | 7309 | 8336 | 8919 | 20 |
| H(91B) | 8050 | 8748 | 9666 | 20 |
| H(92) | 8622 | 7748 | 9240 | 21 |
| H(93A) | 9147 | 8068 | 10546 | 23 |
| H(93B) | 9103 | 7223 | 10358 | 23 |
| H(94) | 8430 | 7471 | 11248 | 22 |
| H(95A) | 7935 | 8577 | 10892 | 21 |
| H(95B) | 7117 | 8060 | 10925 | 21 |
| H(96A) | 5942 | 7410 | 9749 | 21 |
| H(96B) | 6016 | 7514 | 8969 | 21 |
| H(97) | 6515 | 6408 | 9324 | 22 |
| H(98A) | 7933 | 6575 | 9189 | 24 |
| H(98B) | 7236 | 7005 | 8627 | 24 |
| H(99A) | 7812 | 6404 | 10407 | 24 |
| H(99B) | 7041 | 6730 | 10630 | 24 |
| H(1S1) | 1003 | 8476 | 1657 | 36 |
| H(1S2) | 1439 | 8478 | 2530 | 36 |
| H(2S1) | 9865 | 5458 | 8241 | 49 |
| H(2S2) | 8844 | 5531 | 7763 | 49 |
| H(3S1) | 5318 | 8237 | 809 | 41 |
| H(3S2) | 5711 | 8304 | 1689 | 41 |
| H(4S1) | 1698 | 4689 | 3895 | 57 |
| H(4S2) | 2310 | 5050 | 4710 | 57 |
| H(5S1) | 7354 | 286 | 6019 | 51 |
| H(5S2) | 7451 | 1039 | 5729 | 51 |
| H(6S1) | 6158 | 2936 | 688 | 53 |
| H(6S2) | 6217 | 2208 | 1046 | 53 |
| H(7S1) | 9326 | 8004 | 7062 | 66 |
| H(7S2) | 8561 | 7498 | 6404 | 66 |
| H(7T1) | 8091 | 7562 | 6343 | 103 |

| | | | | |
|---|---|---|---|---|
| H(7T2) | 9096 | 7758 | 6919 | 103 |
| H(8S1) | 4699 | 4468 | -641 | 51 |
| H(8S2) | 4007 | 4797 | -323 | 51 |
| H(8T1) | 4831 | 4218 | -143 | 84 |
| H(8T2) | 3942 | 4585 | -233 | 84 |

Table S12. Hydrogen bonds for **X8_12067** [Å and °].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| N(1)-H(1A)...Cl(42) | 0.920(17) | 2.941(19) | 3.835(2) | 164(3) |
| N(1)-H(1B)...Cl(2) | 0.899(17) | 2.45(2) | 3.301(2) | 158(3) |
| N(1)-H(1B)...Cl(3) | 0.899(17) | 2.62(3) | 3.069(2) | 112(2) |
| N(4)-H(4A)...Cl(12) | 0.903(17) | 2.869(19) | 3.757(2) | 168(3) |
| N(4)-H(4B)...Cl(1) | 0.900(17) | 2.51(2) | 3.354(2) | 157(3) |
| N(7)-H(7A)...Cl(5)#1 | 0.912(17) | 2.437(19) | 3.330(2) | 166(3) |
| N(7)-H(7B)...Cl(32)#2 | 0.902(17) | 2.818(19) | 3.693(2) | 164(3) |

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+2,-z+2 #2 -x+1,-y+2,-z+1

**Table S13**. Crystal data and structure refinement for $W(NAd)_2(CH_2CMe_2Ph)_2$ (**2b**).

| | | |
|---|---|---|
| Identification code | 12033 | |
| Empirical formula | $C_{40}\ H_{56}\ N_2\ W$ | |
| Formula weight | 748.72 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | P1 | |
| Unit cell dimensions | $a$ = 12.451(2) Å | $\alpha$= 89.600(2)°. |
| | $b$ = 12.881(2) Å | $\beta$= 66.785(2)°. |
| | $c$ = 12.923(2) Å | $\gamma$ = 65.290(2)°. |
| Volume | 1699.2(5) Å$^3$ | |
| $Z$ | 2 | |
| Density (calculated) | 1.463 Mg/m$^3$ | |
| Absorption coefficient | 3.429 mm$^{-1}$ | |
| $F$(000) | 768 | |
| Crystal size | 0.20 x 0.20 x 0.10 mm$^3$ | |
| Theta range for data collection | 1.77 to 30.03°. | |
| Index ranges | -17<=$h$<=15, -18<=$k$<=18, -18<=$l$<=0 | |
| Reflections collected | 9892 | |
| Independent reflections | 9892 [$R_{int}$ = 0.0474] | |
| Completeness to theta = 30.03° | 99.5 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.7255 and 0.5471 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 9892 / 4 / 404 | |
| Goodness-of-fit on $F^2$ | 1.044 | |
| Final $R$ indices [$I$>2$\sigma$($I$)] | $R$1 = 0.0195, $wR$2 = 0.0434 | |
| $R$ indices (all data) | $R$1 = 0.0227, $wR$2 = 0.0444 | |
| Largest diff. peak and hole | 0.813 and -0.864 e.Å$^{-3}$ | |

Table S14. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for **12033**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| W(1) | 3318(1) | 3398(1) | 1072(1) | 12(1) |
| C(1) | 5056(2) | 2652(2) | 1352(2) | 15(1) |
| C(2) | 4987(2) | 2238(2) | 2493(2) | 15(1) |
| C(3) | 6167(2) | 2162(2) | 2678(2) | 21(1) |
| C(4) | 5094(2) | 1011(2) | 2407(2) | 20(1) |
| C(5) | 3708(2) | 3099(2) | 3489(2) | 15(1) |
| C(6) | 2708(2) | 2808(2) | 4132(2) | 19(1) |
| C(7) | 1543(2) | 3621(2) | 5014(2) | 22(1) |
| C(8) | 1352(2) | 4736(2) | 5283(2) | 23(1) |
| C(9) | 2329(2) | 5047(2) | 4659(2) | 22(1) |
| C(10) | 3491(2) | 4236(2) | 3774(2) | 19(1) |
| C(11) | 2055(2) | 5147(2) | 1963(2) | 17(1) |
| C(12) | 1290(2) | 6192(2) | 1523(2) | 15(1) |
| C(13) | 2254(2) | 6480(2) | 531(2) | 20(1) |
| C(14) | 463(2) | 5867(2) | 1096(2) | 22(1) |
| C(15) | 426(2) | 7264(2) | 2501(2) | 16(1) |
| C(16) | -858(2) | 8032(2) | 2722(2) | 21(1) |
| C(17) | -1619(2) | 8979(2) | 3632(2) | 25(1) |
| C(18) | -1118(2) | 9180(2) | 4347(2) | 24(1) |
| C(19) | 168(2) | 8437(2) | 4132(2) | 22(1) |
| C(20) | 926(2) | 7501(2) | 3221(2) | 19(1) |
| N(1) | 3920(2) | 3416(1) | -400(1) | 15(1) |
| C(21) | 4260(2) | 3123(2) | -1604(1) | 13(1) |
| C(22) | 3027(2) | 3511(2) | -1812(2) | 22(1) |
| C(23) | 3426(2) | 3195(2) | -3098(2) | 29(1) |
| C(24) | 4220(3) | 3810(2) | -3769(2) | 37(1) |
| C(25) | 5454(3) | 3424(2) | -3571(2) | 31(1) |
| C(26) | 5064(2) | 3739(2) | -2289(2) | 24(1) |
| C(27) | 5092(2) | 1803(2) | -2024(2) | 17(1) |
| C(28) | 5493(2) | 1486(2) | -3308(2) | 17(1) |
| C(29) | 4258(2) | 1878(2) | -3507(2) | 23(1) |
| C(30) | 6289(2) | 2105(2) | -3974(2) | 24(1) |
| N(2) | 2424(2) | 2597(1) | 1520(1) | 16(1) |
| C(31) | 1659(2) | 1991(2) | 1569(2) | 14(1) |
| C(32) | 2347(2) | 1036(2) | 500(2) | 17(1) |
| C(33) | 1502(2) | 415(2) | 586(2) | 18(1) |
| C(34) | 1299(2) | -138(2) | 1655(2) | 21(1) |
| C(35) | 614(2) | 807(2) | 2723(2) | 21(1) |
| C(36) | 1456(2) | 1428(2) | 2642(2) | 20(1) |
| C(37) | 315(2) | 2871(2) | 1652(2) | 18(1) |
| C(38) | -529(2) | 2250(2) | 1736(2) | 20(1) |
| C(39) | 169(2) | 1297(2) | 666(2) | 19(1) |
| C(40) | -722(2) | 1695(2) | 2807(2) | 23(1) |

Table S15. Bond lengths [Å] and angles [°] for **12033**.

| | |
|---|---|
| W(1)-N(1) | 1.7520(15) |
| W(1)-N(2) | 1.7564(16) |
| W(1)-C(11) | 2.1256(19) |
| W(1)-C(1) | 2.1467(18) |
| C(1)-C(2) | 1.548(2) |
| C(1)-H(1A) | 0.988(15) |
| C(1)-H(1B) | 0.985(15) |
| C(2)-C(4) | 1.531(3) |
| C(2)-C(5) | 1.532(3) |
| C(2)-C(3) | 1.543(3) |
| C(3)-H(3A) | 0.9800 |
| C(3)-H(3B) | 0.9800 |
| C(3)-H(3C) | 0.9800 |
| C(4)-H(4A) | 0.9800 |
| C(4)-H(4B) | 0.9800 |
| C(4)-H(4C) | 0.9800 |
| C(5)-C(10) | 1.397(3) |
| C(5)-C(6) | 1.398(3) |
| C(6)-C(7) | 1.394(3) |
| C(6)-H(6) | 0.9500 |
| C(7)-C(8) | 1.377(3) |
| C(7)-H(7) | 0.9500 |
| C(8)-C(9) | 1.386(3) |
| C(8)-H(8) | 0.9500 |
| C(9)-C(10) | 1.394(3) |
| C(9)-H(9) | 0.9500 |
| C(10)-H(10) | 0.9500 |
| C(11)-C(12) | 1.545(3) |
| C(11)-H(11A) | 0.989(15) |
| C(11)-H(11B) | 0.983(15) |
| C(12)-C(14) | 1.534(3) |
| C(12)-C(15) | 1.539(3) |
| C(12)-C(13) | 1.541(2) |
| C(13)-H(13A) | 0.9800 |
| C(13)-H(13B) | 0.9800 |
| C(13)-H(13C) | 0.9800 |
| C(14)-H(14A) | 0.9800 |
| C(14)-H(14B) | 0.9800 |
| C(14)-H(14C) | 0.9800 |
| C(15)-C(16) | 1.393(3) |
| C(15)-C(20) | 1.401(3) |
| C(16)-C(17) | 1.395(3) |
| C(16)-H(16) | 0.9500 |
| C(17)-C(18) | 1.379(3) |
| C(17)-H(17) | 0.9500 |
| C(18)-C(19) | 1.389(3) |
| C(18)-H(18) | 0.9500 |
| C(19)-C(20) | 1.387(3) |
| C(19)-H(19) | 0.9500 |
| C(20)-H(20) | 0.9500 |
| N(1)-C(21) | 1.448(2) |
| C(21)-C(27) | 1.535(3) |

| | |
|---|---|
| C(21)-C(22) | 1.537(3) |
| C(21)-C(26) | 1.540(3) |
| C(22)-C(23) | 1.538(3) |
| C(22)-H(22A) | 0.9900 |
| C(22)-H(22B) | 0.9900 |
| C(23)-C(24) | 1.526(4) |
| C(23)-C(29) | 1.530(3) |
| C(23)-H(23) | 1.0000 |
| C(24)-C(25) | 1.530(4) |
| C(24)-H(24A) | 0.9900 |
| C(24)-H(24B) | 0.9900 |
| C(25)-C(30) | 1.532(3) |
| C(25)-C(26) | 1.535(3) |
| C(25)-H(25) | 1.0000 |
| C(26)-H(26A) | 0.9900 |
| C(26)-H(26B) | 0.9900 |
| C(27)-C(28) | 1.534(2) |
| C(27)-H(27A) | 0.9900 |
| C(27)-H(27B) | 0.9900 |
| C(28)-C(30) | 1.529(3) |
| C(28)-C(29) | 1.533(3) |
| C(28)-H(28) | 1.0000 |
| C(29)-H(29A) | 0.9900 |
| C(29)-H(29B) | 0.9900 |
| C(30)-H(30A) | 0.9900 |
| C(30)-H(30B) | 0.9900 |
| N(2)-C(31) | 1.447(2) |
| C(31)-C(32) | 1.537(3) |
| C(31)-C(37) | 1.539(3) |
| C(31)-C(36) | 1.541(2) |
| C(32)-C(33) | 1.539(3) |
| C(32)-H(32A) | 0.9900 |
| C(32)-H(32B) | 0.9900 |
| C(33)-C(34) | 1.529(3) |
| C(33)-C(39) | 1.532(3) |
| C(33)-H(33) | 1.0000 |
| C(34)-C(35) | 1.531(3) |
| C(34)-H(34A) | 0.9900 |
| C(34)-H(34B) | 0.9900 |
| C(35)-C(40) | 1.535(3) |
| C(35)-C(36) | 1.537(3) |
| C(35)-H(35) | 1.0000 |
| C(36)-H(36A) | 0.9900 |
| C(36)-H(36B) | 0.9900 |
| C(37)-C(38) | 1.540(3) |
| C(37)-H(37A) | 0.9900 |
| C(37)-H(37B) | 0.9900 |
| C(38)-C(40) | 1.533(3) |
| C(38)-C(39) | 1.536(3) |
| C(38)-H(38) | 1.0000 |
| C(39)-H(39A) | 0.9900 |
| C(39)-H(39B) | 0.9900 |
| C(40)-H(40A) | 0.9900 |
| C(40)-H(40B) | 0.9900 |

| | |
|---|---|
| N(1)-W(1)-N(2) | 114.42(7) |
| N(1)-W(1)-C(11) | 107.76(7) |
| N(2)-W(1)-C(11) | 107.79(7) |
| N(1)-W(1)-C(1) | 103.41(7) |
| N(2)-W(1)-C(1) | 111.24(7) |
| C(11)-W(1)-C(1) | 112.22(7) |
| C(2)-C(1)-W(1) | 119.70(12) |
| C(2)-C(1)-H(1A) | 108.5(13) |
| W(1)-C(1)-H(1A) | 100.3(13) |
| C(2)-C(1)-H(1B) | 109.0(13) |
| W(1)-C(1)-H(1B) | 112.6(13) |
| H(1A)-C(1)-H(1B) | 105.4(18) |
| C(4)-C(2)-C(5) | 111.83(15) |
| C(4)-C(2)-C(3) | 107.44(15) |
| C(5)-C(2)-C(3) | 109.72(15) |
| C(4)-C(2)-C(1) | 108.71(15) |
| C(5)-C(2)-C(1) | 109.58(14) |
| C(3)-C(2)-C(1) | 109.51(15) |
| C(2)-C(3)-H(3A) | 109.5 |
| C(2)-C(3)-H(3B) | 109.5 |
| H(3A)-C(3)-H(3B) | 109.5 |
| C(2)-C(3)-H(3C) | 109.5 |
| H(3A)-C(3)-H(3C) | 109.5 |
| H(3B)-C(3)-H(3C) | 109.5 |
| C(2)-C(4)-H(4A) | 109.5 |
| C(2)-C(4)-H(4B) | 109.5 |
| H(4A)-C(4)-H(4B) | 109.5 |
| C(2)-C(4)-H(4C) | 109.5 |
| H(4A)-C(4)-H(4C) | 109.5 |
| H(4B)-C(4)-H(4C) | 109.5 |
| C(10)-C(5)-C(6) | 117.05(17) |
| C(10)-C(5)-C(2) | 120.19(16) |
| C(6)-C(5)-C(2) | 122.75(17) |
| C(7)-C(6)-C(5) | 121.31(19) |
| C(7)-C(6)-H(6) | 119.3 |
| C(5)-C(6)-H(6) | 119.3 |
| C(8)-C(7)-C(6) | 120.64(19) |
| C(8)-C(7)-H(7) | 119.7 |
| C(6)-C(7)-H(7) | 119.7 |
| C(7)-C(8)-C(9) | 119.25(19) |
| C(7)-C(8)-H(8) | 120.4 |
| C(9)-C(8)-H(8) | 120.4 |
| C(8)-C(9)-C(10) | 120.10(19) |
| C(8)-C(9)-H(9) | 120.0 |
| C(10)-C(9)-H(9) | 120.0 |
| C(9)-C(10)-C(5) | 121.65(18) |
| C(9)-C(10)-H(10) | 119.2 |
| C(5)-C(10)-H(10) | 119.2 |
| C(12)-C(11)-W(1) | 127.92(12) |
| C(12)-C(11)-H(11A) | 109.6(13) |
| W(1)-C(11)-H(11A) | 106.9(13) |
| C(12)-C(11)-H(11B) | 110.3(13) |
| W(1)-C(11)-H(11B) | 95.7(13) |

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|---|---|
| H(11A)-C(11)-H(11B) | 103.3(18) |
| C(14)-C(12)-C(15) | 111.41(15) |
| C(14)-C(12)-C(13) | 109.51(15) |
| C(15)-C(12)-C(13) | 108.24(15) |
| C(14)-C(12)-C(11) | 108.49(15) |
| C(15)-C(12)-C(11) | 109.24(14) |
| C(13)-C(12)-C(11) | 109.94(15) |
| C(12)-C(13)-H(13A) | 109.5 |
| C(12)-C(13)-H(13B) | 109.5 |
| H(13A)-C(13)-H(13B) | 109.5 |
| C(12)-C(13)-H(13C) | 109.5 |
| H(13A)-C(13)-H(13C) | 109.5 |
| H(13B)-C(13)-H(13C) | 109.5 |
| C(12)-C(14)-H(14A) | 109.5 |
| C(12)-C(14)-H(14B) | 109.5 |
| H(14A)-C(14)-H(14B) | 109.5 |
| C(12)-C(14)-H(14C) | 109.5 |
| H(14A)-C(14)-H(14C) | 109.5 |
| H(14B)-C(14)-H(14C) | 109.5 |
| C(16)-C(15)-C(20) | 116.94(18) |
| C(16)-C(15)-C(12) | 123.12(17) |
| C(20)-C(15)-C(12) | 119.94(16) |
| C(15)-C(16)-C(17) | 121.39(19) |
| C(15)-C(16)-H(16) | 119.3 |
| C(17)-C(16)-H(16) | 119.3 |
| C(18)-C(17)-C(16) | 120.7(2) |
| C(18)-C(17)-H(17) | 119.7 |
| C(16)-C(17)-H(17) | 119.7 |
| C(17)-C(18)-C(19) | 118.98(19) |
| C(17)-C(18)-H(18) | 120.5 |
| C(19)-C(18)-H(18) | 120.5 |
| C(20)-C(19)-C(18) | 120.23(19) |
| C(20)-C(19)-H(19) | 119.9 |
| C(18)-C(19)-H(19) | 119.9 |
| C(19)-C(20)-C(15) | 121.77(18) |
| C(19)-C(20)-H(20) | 119.1 |
| C(15)-C(20)-H(20) | 119.1 |
| C(21)-N(1)-W(1) | 159.84(13) |
| N(1)-C(21)-C(27) | 109.86(14) |
| N(1)-C(21)-C(22) | 111.13(15) |
| C(27)-C(21)-C(22) | 108.93(15) |
| N(1)-C(21)-C(26) | 108.76(15) |
| C(27)-C(21)-C(26) | 108.97(15) |
| C(22)-C(21)-C(26) | 109.16(16) |
| C(21)-C(22)-C(23) | 109.67(16) |
| C(21)-C(22)-H(22A) | 109.7 |
| C(23)-C(22)-H(22A) | 109.7 |
| C(21)-C(22)-H(22B) | 109.7 |
| C(23)-C(22)-H(22B) | 109.7 |
| H(22A)-C(22)-H(22B) | 108.2 |
| C(24)-C(23)-C(29) | 109.31(19) |
| C(24)-C(23)-C(22) | 109.43(19) |
| C(29)-C(23)-C(22) | 109.73(17) |
| C(24)-C(23)-H(23) | 109.5 |

| | |
|---|---|
| C(29)-C(23)-H(23) | 109.5 |
| C(22)-C(23)-H(23) | 109.5 |
| C(23)-C(24)-C(25) | 109.67(17) |
| C(23)-C(24)-H(24A) | 109.7 |
| C(25)-C(24)-H(24A) | 109.7 |
| C(23)-C(24)-H(24B) | 109.7 |
| C(25)-C(24)-H(24B) | 109.7 |
| H(24A)-C(24)-H(24B) | 108.2 |
| C(24)-C(25)-C(30) | 109.71(18) |
| C(24)-C(25)-C(26) | 109.61(19) |
| C(30)-C(25)-C(26) | 109.33(18) |
| C(24)-C(25)-H(25) | 109.4 |
| C(30)-C(25)-H(25) | 109.4 |
| C(26)-C(25)-H(25) | 109.4 |
| C(25)-C(26)-C(21) | 109.56(16) |
| C(25)-C(26)-H(26A) | 109.8 |
| C(21)-C(26)-H(26A) | 109.8 |
| C(25)-C(26)-H(26B) | 109.8 |
| C(21)-C(26)-H(26B) | 109.8 |
| H(26A)-C(26)-H(26B) | 108.2 |
| C(28)-C(27)-C(21) | 110.32(15) |
| C(28)-C(27)-H(27A) | 109.6 |
| C(21)-C(27)-H(27A) | 109.6 |
| C(28)-C(27)-H(27B) | 109.6 |
| C(21)-C(27)-H(27B) | 109.6 |
| H(27A)-C(27)-H(27B) | 108.1 |
| C(30)-C(28)-C(29) | 109.63(17) |
| C(30)-C(28)-C(27) | 109.18(16) |
| C(29)-C(28)-C(27) | 109.14(15) |
| C(30)-C(28)-H(28) | 109.6 |
| C(29)-C(28)-H(28) | 109.6 |
| C(27)-C(28)-H(28) | 109.6 |
| C(23)-C(29)-C(28) | 109.64(17) |
| C(23)-C(29)-H(29A) | 109.7 |
| C(28)-C(29)-H(29A) | 109.7 |
| C(23)-C(29)-H(29B) | 109.7 |
| C(28)-C(29)-H(29B) | 109.7 |
| H(29A)-C(29)-H(29B) | 108.2 |
| C(28)-C(30)-C(25) | 109.48(16) |
| C(28)-C(30)-H(30A) | 109.8 |
| C(25)-C(30)-H(30A) | 109.8 |
| C(28)-C(30)-H(30B) | 109.8 |
| C(25)-C(30)-H(30B) | 109.8 |
| H(30A)-C(30)-H(30B) | 108.2 |
| C(31)-N(2)-W(1) | 162.84(13) |
| N(2)-C(31)-C(32) | 111.44(15) |
| N(2)-C(31)-C(37) | 109.07(15) |
| C(32)-C(31)-C(37) | 109.12(15) |
| N(2)-C(31)-C(36) | 109.13(14) |
| C(32)-C(31)-C(36) | 108.91(15) |
| C(37)-C(31)-C(36) | 109.15(15) |
| C(31)-C(32)-C(33) | 109.78(15) |
| C(31)-C(32)-H(32A) | 109.7 |
| C(33)-C(32)-H(32A) | 109.7 |

| | |
|---|---|
| C(31)-C(32)-H(32B) | 109.7 |
| C(33)-C(32)-H(32B) | 109.7 |
| H(32A)-C(32)-H(32B) | 108.2 |
| C(34)-C(33)-C(39) | 109.34(16) |
| C(34)-C(33)-C(32) | 109.74(15) |
| C(39)-C(33)-C(32) | 109.53(16) |
| C(34)-C(33)-H(33) | 109.4 |
| C(39)-C(33)-H(33) | 109.4 |
| C(32)-C(33)-H(33) | 109.4 |
| C(33)-C(34)-C(35) | 109.60(16) |
| C(33)-C(34)-H(34A) | 109.8 |
| C(35)-C(34)-H(34A) | 109.8 |
| C(33)-C(34)-H(34B) | 109.8 |
| C(35)-C(34)-H(34B) | 109.8 |
| H(34A)-C(34)-H(34B) | 108.2 |
| C(34)-C(35)-C(40) | 109.29(16) |
| C(34)-C(35)-C(36) | 109.73(16) |
| C(40)-C(35)-C(36) | 109.34(17) |
| C(34)-C(35)-H(35) | 109.5 |
| C(40)-C(35)-H(35) | 109.5 |
| C(36)-C(35)-H(35) | 109.5 |
| C(35)-C(36)-C(31) | 109.78(15) |
| C(35)-C(36)-H(36A) | 109.7 |
| C(31)-C(36)-H(36A) | 109.7 |
| C(35)-C(36)-H(36B) | 109.7 |
| C(31)-C(36)-H(36B) | 109.7 |
| H(36A)-C(36)-H(36B) | 108.2 |
| C(31)-C(37)-C(38) | 109.94(15) |
| C(31)-C(37)-H(37A) | 109.7 |
| C(38)-C(37)-H(37A) | 109.7 |
| C(31)-C(37)-H(37B) | 109.7 |
| C(38)-C(37)-H(37B) | 109.7 |
| H(37A)-C(37)-H(37B) | 108.2 |
| C(40)-C(38)-C(39) | 109.40(16) |
| C(40)-C(38)-C(37) | 109.20(16) |
| C(39)-C(38)-C(37) | 109.34(16) |
| C(40)-C(38)-H(38) | 109.6 |
| C(39)-C(38)-H(38) | 109.6 |
| C(37)-C(38)-H(38) | 109.6 |
| C(33)-C(39)-C(38) | 109.57(15) |
| C(33)-C(39)-H(39A) | 109.8 |
| C(38)-C(39)-H(39A) | 109.8 |
| C(33)-C(39)-H(39B) | 109.8 |
| C(38)-C(39)-H(39B) | 109.8 |
| H(39A)-C(39)-H(39B) | 108.2 |
| C(38)-C(40)-C(35) | 109.72(16) |
| C(38)-C(40)-H(40A) | 109.7 |
| C(35)-C(40)-H(40A) | 109.7 |
| C(38)-C(40)-H(40B) | 109.7 |
| C(35)-C(40)-H(40B) | 109.7 |
| H(40A)-C(40)-H(40B) | 108.2 |

Symmetry transformations used to generate equivalent atoms:

Table S16. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **12033**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| W(1) | 12(1) | 12(1) | 11(1) | 2(1) | -4(1) | -6(1) |
| C(1) | 14(1) | 16(1) | 14(1) | 3(1) | -4(1) | -7(1) |
| C(2) | 14(1) | 15(1) | 14(1) | 2(1) | -6(1) | -6(1) |
| C(3) | 15(1) | 25(1) | 21(1) | 2(1) | -9(1) | -7(1) |
| C(4) | 22(1) | 14(1) | 22(1) | 4(1) | -8(1) | -7(1) |
| C(5) | 14(1) | 17(1) | 13(1) | 3(1) | -6(1) | -6(1) |
| C(6) | 20(1) | 21(1) | 18(1) | 5(1) | -8(1) | -11(1) |
| C(7) | 16(1) | 32(1) | 17(1) | 6(1) | -4(1) | -12(1) |
| C(8) | 16(1) | 29(1) | 15(1) | 0(1) | -5(1) | -4(1) |
| C(9) | 23(1) | 16(1) | 22(1) | -2(1) | -9(1) | -5(1) |
| C(10) | 18(1) | 19(1) | 20(1) | 3(1) | -6(1) | -10(1) |
| C(11) | 18(1) | 18(1) | 14(1) | 3(1) | -7(1) | -8(1) |
| C(12) | 12(1) | 14(1) | 15(1) | 2(1) | -4(1) | -6(1) |
| C(13) | 18(1) | 20(1) | 16(1) | 6(1) | -3(1) | -8(1) |
| C(14) | 18(1) | 22(1) | 24(1) | 0(1) | -11(1) | -7(1) |
| C(15) | 15(1) | 14(1) | 16(1) | 4(1) | -4(1) | -8(1) |
| C(16) | 16(1) | 20(1) | 25(1) | 5(1) | -8(1) | -8(1) |
| C(17) | 16(1) | 17(1) | 33(1) | 2(1) | -5(1) | -4(1) |
| C(18) | 20(1) | 17(1) | 26(1) | -1(1) | 0(1) | -7(1) |
| C(19) | 23(1) | 21(1) | 20(1) | 2(1) | -5(1) | -13(1) |
| C(20) | 15(1) | 19(1) | 21(1) | 2(1) | -6(1) | -7(1) |
| N(1) | 14(1) | 15(1) | 16(1) | 3(1) | -5(1) | -6(1) |
| C(21) | 13(1) | 15(1) | 12(1) | 3(1) | -4(1) | -6(1) |
| C(22) | 18(1) | 23(1) | 20(1) | 0(1) | -10(1) | -3(1) |
| C(23) | 28(1) | 29(1) | 23(1) | -3(1) | -17(1) | 0(1) |
| C(24) | 59(2) | 20(1) | 17(1) | 4(1) | -16(1) | -5(1) |
| C(25) | 49(1) | 25(1) | 14(1) | 2(1) | 0(1) | -26(1) |
| C(26) | 31(1) | 24(1) | 16(1) | 0(1) | -1(1) | -20(1) |
| C(27) | 17(1) | 16(1) | 16(1) | 3(1) | -6(1) | -7(1) |
| C(28) | 17(1) | 16(1) | 17(1) | 1(1) | -5(1) | -7(1) |
| C(29) | 23(1) | 28(1) | 20(1) | -2(1) | -10(1) | -11(1) |
| C(30) | 24(1) | 28(1) | 16(1) | -2(1) | 0(1) | -17(1) |
| N(2) | 16(1) | 18(1) | 16(1) | 5(1) | -8(1) | -9(1) |
| C(31) | 16(1) | 16(1) | 15(1) | 4(1) | -6(1) | -10(1) |
| C(32) | 15(1) | 17(1) | 17(1) | 0(1) | -4(1) | -8(1) |
| C(33) | 17(1) | 18(1) | 19(1) | 0(1) | -6(1) | -9(1) |
| C(34) | 22(1) | 18(1) | 30(1) | 8(1) | -13(1) | -12(1) |
| C(35) | 27(1) | 28(1) | 20(1) | 10(1) | -12(1) | -20(1) |
| C(36) | 25(1) | 26(1) | 19(1) | 10(1) | -12(1) | -18(1) |
| C(37) | 16(1) | 16(1) | 22(1) | 2(1) | -8(1) | -8(1) |
| C(38) | 14(1) | 19(1) | 26(1) | 1(1) | -8(1) | -7(1) |
| C(39) | 20(1) | 21(1) | 21(1) | 4(1) | -11(1) | -11(1) |
| C(40) | 21(1) | 29(1) | 19(1) | 0(1) | -3(1) | -17(1) |

Table S17. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for **12033**.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1A) | 5260(20) | 3318(16) | 1311(19) | 18 |
| H(1B) | 5804(18) | 2036(17) | 708(16) | 18 |
| H(3A) | 6125 | 2937 | 2740 | 31 |
| H(3B) | 6982 | 1632 | 2026 | 31 |
| H(3C) | 6142 | 1869 | 3384 | 31 |
| H(4A) | 5006 | 754 | 3139 | 31 |
| H(4B) | 5948 | 475 | 1798 | 31 |
| H(4C) | 4396 | 1017 | 2228 | 31 |
| H(6) | 2824 | 2041 | 3964 | 23 |
| H(7) | 875 | 3403 | 5435 | 27 |
| H(8) | 560 | 5285 | 5889 | 28 |
| H(9) | 2206 | 5815 | 4835 | 26 |
| H(10) | 4152 | 4462 | 3354 | 23 |
| H(11A) | 1460(20) | 5120(20) | 2731(14) | 20 |
| H(11B) | 2717(19) | 5270(20) | 2105(19) | 20 |
| H(13A) | 1761 | 7144 | 257 | 30 |
| H(13B) | 2821 | 5804 | -98 | 30 |
| H(13C) | 2791 | 6675 | 801 | 30 |
| H(14A) | -1 | 6511 | 785 | 32 |
| H(14B) | -174 | 5716 | 1735 | 32 |
| H(14C) | 1036 | 5167 | 495 | 32 |
| H(16) | -1224 | 7908 | 2242 | 25 |
| H(17) | -2492 | 9491 | 3762 | 31 |
| H(18) | -1644 | 9816 | 4976 | 29 |
| H(19) | 530 | 8570 | 4611 | 26 |
| H(20) | 1807 | 7007 | 3081 | 23 |
| H(22A) | 2483 | 4362 | -1546 | 27 |
| H(22B) | 2502 | 3121 | -1372 | 27 |
| H(23) | 2621 | 3448 | -3231 | 35 |
| H(24A) | 3684 | 4663 | -3515 | 45 |
| H(24B) | 4469 | 3617 | -4597 | 45 |
| H(25) | 5972 | 3828 | -4013 | 37 |
| H(26A) | 4537 | 4592 | -2026 | 29 |
| H(26B) | 5860 | 3496 | -2159 | 29 |
| H(27A) | 5886 | 1543 | -1888 | 20 |
| H(27B) | 4583 | 1399 | -1588 | 20 |
| H(28) | 6035 | 625 | -3572 | 21 |
| H(29A) | 4507 | 1673 | -4333 | 28 |
| H(29B) | 3745 | 1474 | -3081 | 28 |
| H(30A) | 6563 | 1898 | -4805 | 29 |
| H(30B) | 7087 | 1855 | -3845 | 29 |
| H(32A) | 3213 | 466 | 439 | 21 |
| H(32B) | 2486 | 1386 | -196 | 21 |
| H(33) | 1955 | -205 | -111 | 22 |
| H(34A) | 2156 | -720 | 1601 | 26 |
| H(34B) | 759 | -540 | 1708 | 26 |
| H(35) | 484 | 444 | 3421 | 26 |
| H(36A) | 2315 | 861 | 2596 | 24 |

| | | | | |
|---|---|---|---|---|
| H(36B) | 1016 | 2034 | 3336 | 24 |
| H(37A) | 437 | 3238 | 966 | 21 |
| H(37B) | -134 | 3491 | 2337 | 21 |
| H(38) | -1401 | 2825 | 1790 | 24 |
| H(39A) | -372 | 898 | 711 | 23 |
| H(39B) | 293 | 1650 | -28 | 23 |
| H(40A) | -1275 | 1303 | 2873 | 27 |
| H(40B) | -1173 | 2306 | 3499 | 27 |

**Table S18**. Crystal data and structure refinement for $[W(N\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)Cl_2(py)]_2$ (**3a**).

| | | |
|---|---|---|
| Identification code | X8_12031 | |
| Empirical formula | $C_{28}\ H_{48}\ Cl_4\ N_4\ W_2$ | |
| Formula weight | 950.20 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | $P2_1/c$ | |
| Unit cell dimensions | $a$ = 13.9455(13) Å | $\alpha$= 90°. |
| | $b$ = 9.6269(9) Å | $\beta$= 107.163(2)°. |
| | $c$ = 14.1894(13) Å | $\gamma$ = 90°. |
| Volume | 1820.1(3) Å$^3$ | |
| $Z$ | 2 | |
| Density (calculated) | 1.734 Mg/m$^3$ | |
| Absorption coefficient | 6.631 mm$^{-1}$ | |
| $F$(000) | 920 | |
| Crystal size | 0.28 x 0.25 x 0.06 mm$^3$ | |
| Theta range for data collection | 1.53 to 30.51°. | |
| Index ranges | -19<=$h$<=19, -13<=$k$<=13, -20<=$l$<=20 | |
| Reflections collected | 115442 | |
| Independent reflections | 5555 [$R_{int}$ = 0.0496] | |
| Completeness to theta = 30.51° | 100.0 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.6918 and 0.2582 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 5555 / 194 / 218 | |
| Goodness-of-fit on $F^2$ | 1.130 | |
| Final $R$ indices [$I$>2$\sigma$($I$)] | $R$1 = 0.0443, $wR$2 = 0.1040 | |
| $R$ indices (all data) | $R$1 = 0.0458, $wR$2 = 0.1048 | |
| Largest diff. peak and hole | 4.900 and -4.241 e.Å$^{-3}$ | |

Table S19. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for **X8_12031**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Cl(1) | 1350(1) | 4331(1) | 7030(1) | 36(1) |
| Cl(2) | 220(1) | 6626(1) | 5198(1) | 30(1) |
| W(1) | 1558(1) | 4663(1) | 5421(1) | 32(1) |
| C(1) | 2557(6) | 6098(9) | 5845(8) | 43(2) |
| C(2) | 3627(7) | 6386(10) | 6257(8) | 63(3) |
| C(3) | 4286(9) | 5088(13) | 6326(14) | 92(5) |
| C(4) | 3827(11) | 6990(20) | 7296(11) | 115(5) |
| C(5) | 3952(10) | 7432(15) | 5586(14) | 102(5) |
| C(1A) | 2738(16) | 5780(30) | 5890(30) | 73(6) |
| C(2A) | 3778(13) | 6110(20) | 6010(20) | 75(5) |
| C(3A) | 4090(20) | 7550(30) | 6470(40) | 102(9) |
| C(4A) | 4460(30) | 5020(40) | 6670(30) | 107(12) |
| C(5A) | 3960(30) | 6120(50) | 4990(30) | 101(9) |
| N(1) | 2237(4) | 3225(6) | 5386(4) | 44(1) |
| C(11) | 2667(5) | 1822(8) | 5336(6) | 52(2) |
| C(12) | 3385(8) | 1933(12) | 4716(10) | 98(4) |
| C(13) | 1811(6) | 854(8) | 4890(6) | 51(2) |
| C(14) | 3199(7) | 1399(9) | 6410(8) | 82(3) |
| N(2) | 1256(4) | 5095(5) | 3833(3) | 34(1) |
| C(15) | 1333(5) | 6385(7) | 3503(4) | 38(1) |
| C(16) | 1133(5) | 6700(6) | 2517(5) | 42(1) |
| C(17) | 836(6) | 5641(6) | 1832(5) | 42(1) |
| C(18) | 768(5) | 4309(6) | 2157(4) | 40(1) |
| C(19) | 979(5) | 4077(6) | 3159(4) | 36(1) |

Table S20. Bond lengths [Å] and angles [°] for **X8_12031**.

| | |
|---|---|
| Cl(1)-W(1) | 2.4056(13) |
| Cl(2)-W(1) | 2.6085(13) |
| Cl(2)-W(1)#1 | 2.6781(13) |
| W(1)-N(1) | 1.687(6) |
| W(1)-C(1A) | 1.915(11) |
| W(1)-C(1) | 1.928(8) |
| W(1)-N(2) | 2.207(5) |
| W(1)-Cl(2)#1 | 2.6781(13) |
| C(1)-C(2) | 1.459(11) |
| C(1)-H(1) | 0.9500 |
| C(2)-C(4) | 1.532(11) |
| C(2)-C(3) | 1.537(11) |
| C(2)-C(5) | 1.543(11) |
| C(3)-H(3A) | 0.9800 |
| C(3)-H(3B) | 0.9800 |
| C(3)-H(3C) | 0.9800 |
| C(4)-H(4A) | 0.9800 |
| C(4)-H(4B) | 0.9800 |
| C(4)-H(4C) | 0.9800 |
| C(5)-H(5A) | 0.9800 |
| C(5)-H(5B) | 0.9800 |
| C(5)-H(5C) | 0.9800 |
| C(1A)-C(2A) | 1.448(13) |
| C(1A)-H(1A) | 0.9500 |
| C(2A)-C(4A) | 1.536(12) |
| C(2A)-C(3A) | 1.537(12) |
| C(2A)-C(5A) | 1.543(12) |
| C(3A)-H(3A1) | 0.9800 |
| C(3A)-H(3A2) | 0.9800 |
| C(3A)-H(3A3) | 0.9800 |
| C(4A)-H(4A1) | 0.9800 |
| C(4A)-H(4A2) | 0.9800 |
| C(4A)-H(4A3) | 0.9800 |
| C(5A)-H(5A1) | 0.9800 |
| C(5A)-H(5A2) | 0.9800 |
| C(5A)-H(5A3) | 0.9800 |
| N(1)-C(11) | 1.488(9) |
| C(11)-C(13) | 1.499(11) |
| C(11)-C(12) | 1.519(12) |
| C(11)-C(14) | 1.539(12) |
| C(12)-H(12A) | 0.9800 |
| C(12)-H(12B) | 0.9800 |
| C(12)-H(12C) | 0.9800 |
| C(13)-H(13A) | 0.9800 |
| C(13)-H(13B) | 0.9800 |
| C(13)-H(13C) | 0.9800 |
| C(14)-H(14A) | 0.9800 |
| C(14)-H(14B) | 0.9800 |
| C(14)-H(14C) | 0.9800 |
| N(2)-C(15) | 1.342(8) |
| N(2)-C(19) | 1.344(8) |
| C(15)-C(16) | 1.378(8) |

| | |
|---|---|
| C(15)-H(15) | 0.9500 |
| C(16)-C(17) | 1.385(9) |
| C(16)-H(16) | 0.9500 |
| C(17)-C(18) | 1.375(8) |
| C(17)-H(17) | 0.9500 |
| C(18)-C(19) | 1.382(8) |
| C(18)-H(18) | 0.9500 |
| C(19)-H(19) | 0.9500 |

| | |
|---|---|
| W(1)-Cl(2)-W(1)#1 | 105.28(4) |
| N(1)-W(1)-C(1A) | 92.3(11) |
| N(1)-W(1)-C(1) | 103.7(3) |
| C(1A)-W(1)-C(1) | 11.6(11) |
| N(1)-W(1)-N(2) | 93.6(2) |
| C(1A)-W(1)-N(2) | 97.9(12) |
| C(1)-W(1)-N(2) | 94.9(4) |
| N(1)-W(1)-Cl(1) | 98.35(19) |
| C(1A)-W(1)-Cl(1) | 94.2(12) |
| C(1)-W(1)-Cl(1) | 94.4(3) |
| N(2)-W(1)-Cl(1) | 162.60(13) |
| N(1)-W(1)-Cl(2) | 168.3(2) |
| C(1A)-W(1)-Cl(2) | 98.3(11) |
| C(1)-W(1)-Cl(2) | 86.8(3) |
| N(2)-W(1)-Cl(2) | 79.98(13) |
| Cl(1)-W(1)-Cl(2) | 85.95(4) |
| N(1)-W(1)-Cl(2)#1 | 94.8(2) |
| C(1A)-W(1)-Cl(2)#1 | 172.9(11) |
| C(1)-W(1)-Cl(2)#1 | 161.5(3) |
| N(2)-W(1)-Cl(2)#1 | 82.71(14) |
| Cl(1)-W(1)-Cl(2)#1 | 83.75(4) |
| Cl(2)-W(1)-Cl(2)#1 | 74.72(4) |
| C(2)-C(1)-W(1) | 145.1(7) |
| C(2)-C(1)-H(1) | 107.4 |
| W(1)-C(1)-H(1) | 107.4 |
| C(1)-C(2)-C(4) | 109.4(8) |
| C(1)-C(2)-C(3) | 113.1(8) |
| C(4)-C(2)-C(3) | 108.3(10) |
| C(1)-C(2)-C(5) | 109.2(8) |
| C(4)-C(2)-C(5) | 110.0(10) |
| C(3)-C(2)-C(5) | 106.8(9) |
| C(2)-C(3)-H(3A) | 109.5 |
| C(2)-C(3)-H(3B) | 109.5 |
| H(3A)-C(3)-H(3B) | 109.5 |
| C(2)-C(3)-H(3C) | 109.5 |
| H(3A)-C(3)-H(3C) | 109.5 |
| H(3B)-C(3)-H(3C) | 109.5 |
| C(2)-C(4)-H(4A) | 109.5 |
| C(2)-C(4)-H(4B) | 109.5 |
| H(4A)-C(4)-H(4B) | 109.5 |
| C(2)-C(4)-H(4C) | 109.5 |
| H(4A)-C(4)-H(4C) | 109.5 |
| H(4B)-C(4)-H(4C) | 109.5 |
| C(2)-C(5)-H(5A) | 109.5 |
| C(2)-C(5)-H(5B) | 109.5 |

| | |
|---|---|
| H(5A)-C(5)-H(5B) | 109.5 |
| C(2)-C(5)-H(5C) | 109.5 |
| H(5A)-C(5)-H(5C) | 109.5 |
| H(5B)-C(5)-H(5C) | 109.5 |
| C(2A)-C(1A)-W(1) | 153.1(19) |
| C(2A)-C(1A)-H(1A) | 103.4 |
| W(1)-C(1A)-H(1A) | 103.4 |
| C(1A)-C(2A)-C(4A) | 109.7(12) |
| C(1A)-C(2A)-C(3A) | 113.3(12) |
| C(4A)-C(2A)-C(3A) | 107.8(12) |
| C(1A)-C(2A)-C(5A) | 109.6(12) |
| C(4A)-C(2A)-C(5A) | 109.3(13) |
| C(3A)-C(2A)-C(5A) | 107.1(12) |
| C(2A)-C(3A)-H(3A1) | 109.5 |
| C(2A)-C(3A)-H(3A2) | 109.5 |
| H(3A1)-C(3A)-H(3A2) | 109.5 |
| C(2A)-C(3A)-H(3A3) | 109.5 |
| H(3A1)-C(3A)-H(3A3) | 109.5 |
| H(3A2)-C(3A)-H(3A3) | 109.5 |
| C(2A)-C(4A)-H(4A1) | 109.5 |
| C(2A)-C(4A)-H(4A2) | 109.5 |
| H(4A1)-C(4A)-H(4A2) | 109.5 |
| C(2A)-C(4A)-H(4A3) | 109.5 |
| H(4A1)-C(4A)-H(4A3) | 109.5 |
| H(4A2)-C(4A)-H(4A3) | 109.5 |
| C(2A)-C(5A)-H(5A1) | 109.5 |
| C(2A)-C(5A)-H(5A2) | 109.5 |
| H(5A1)-C(5A)-H(5A2) | 109.5 |
| C(2A)-C(5A)-H(5A3) | 109.5 |
| H(5A1)-C(5A)-H(5A3) | 109.5 |
| H(5A2)-C(5A)-H(5A3) | 109.5 |
| C(11)-N(1)-W(1) | 169.8(5) |
| N(1)-C(11)-C(13) | 107.6(6) |
| N(1)-C(11)-C(12) | 107.9(7) |
| C(13)-C(11)-C(12) | 112.2(8) |
| N(1)-C(11)-C(14) | 106.1(7) |
| C(13)-C(11)-C(14) | 110.2(7) |
| C(12)-C(11)-C(14) | 112.6(8) |
| C(11)-C(12)-H(12A) | 109.5 |
| C(11)-C(12)-H(12B) | 109.5 |
| H(12A)-C(12)-H(12B) | 109.5 |
| C(11)-C(12)-H(12C) | 109.5 |
| H(12A)-C(12)-H(12C) | 109.5 |
| H(12B)-C(12)-H(12C) | 109.5 |
| C(11)-C(13)-H(13A) | 109.5 |
| C(11)-C(13)-H(13B) | 109.5 |
| H(13A)-C(13)-H(13B) | 109.5 |
| C(11)-C(13)-H(13C) | 109.5 |
| H(13A)-C(13)-H(13C) | 109.5 |
| H(13B)-C(13)-H(13C) | 109.5 |
| C(11)-C(14)-H(14A) | 109.5 |
| C(11)-C(14)-H(14B) | 109.5 |
| H(14A)-C(14)-H(14B) | 109.5 |
| C(11)-C(14)-H(14C) | 109.5 |

| | |
|---|---|
| H(14A)-C(14)-H(14C) | 109.5 |
| H(14B)-C(14)-H(14C) | 109.5 |
| C(15)-N(2)-C(19) | 117.6(5) |
| C(15)-N(2)-W(1) | 121.3(4) |
| C(19)-N(2)-W(1) | 121.1(4) |
| N(2)-C(15)-C(16) | 123.0(6) |
| N(2)-C(15)-H(15) | 118.5 |
| C(16)-C(15)-H(15) | 118.5 |
| C(15)-C(16)-C(17) | 118.7(6) |
| C(15)-C(16)-H(16) | 120.7 |
| C(17)-C(16)-H(16) | 120.7 |
| C(18)-C(17)-C(16) | 119.1(6) |
| C(18)-C(17)-H(17) | 120.4 |
| C(16)-C(17)-H(17) | 120.4 |
| C(17)-C(18)-C(19) | 118.8(6) |
| C(17)-C(18)-H(18) | 120.6 |
| C(19)-C(18)-H(18) | 120.6 |
| N(2)-C(19)-C(18) | 122.9(6) |
| N(2)-C(19)-H(19) | 118.6 |
| C(18)-C(19)-H(19) | 118.6 |

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+1,-z+1

Table S21. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **X8_12031**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Cl(1) | 49(1) | 33(1) | 23(1) | 2(1) | 6(1) | -2(1) |
| Cl(2) | 40(1) | 25(1) | 26(1) | -2(1) | 11(1) | -3(1) |
| W(1) | 30(1) | 39(1) | 26(1) | 5(1) | 7(1) | 1(1) |
| C(1) | 30(3) | 36(4) | 59(5) | 4(4) | 6(3) | 3(3) |
| C(2) | 30(3) | 52(5) | 104(6) | -8(4) | 15(4) | -1(3) |
| C(3) | 28(4) | 51(5) | 170(14) | -9(6) | -14(7) | 2(4) |
| C(4) | 64(8) | 139(14) | 119(8) | -53(9) | -8(7) | -20(8) |
| C(5) | 55(6) | 75(8) | 192(13) | 25(9) | 60(9) | 0(6) |
| C(1A) | 45(8) | 78(12) | 89(11) | 19(11) | 9(9) | 0(9) |
| C(2A) | 41(8) | 67(9) | 110(10) | 3(9) | 11(8) | 7(8) |
| C(3A) | 64(15) | 78(11) | 146(18) | -9(14) | 2(17) | -5(11) |
| C(4A) | 56(15) | 81(14) | 140(20) | 6(17) | -37(19) | -2(15) |
| C(5A) | 67(17) | 110(20) | 133(15) | 3(15) | 42(15) | -7(19) |
| N(1) | 42(3) | 47(3) | 45(3) | 10(2) | 14(2) | 8(2) |
| C(11) | 42(3) | 42(4) | 68(5) | 14(3) | 11(3) | 5(3) |
| C(12) | 71(6) | 77(7) | 174(13) | -31(7) | 81(8) | -1(5) |
| C(13) | 60(4) | 44(4) | 50(4) | 6(3) | 15(3) | 7(3) |
| C(14) | 70(6) | 49(4) | 90(7) | 11(4) | -32(5) | 9(4) |
| N(2) | 38(2) | 36(2) | 31(2) | 6(2) | 16(2) | 7(2) |
| C(15) | 47(3) | 36(3) | 35(3) | 2(2) | 18(2) | 4(2) |
| C(16) | 62(4) | 31(3) | 40(3) | 7(2) | 26(3) | 7(3) |
| C(17) | 65(4) | 34(3) | 32(3) | 5(2) | 23(3) | 10(3) |
| C(18) | 59(4) | 34(3) | 33(3) | 3(2) | 22(3) | 8(3) |
| C(19) | 46(3) | 32(3) | 33(3) | 5(2) | 18(2) | 7(2) |

Table S22. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for **X8_12031**.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 2217 | 6965 | 5746 | 52 |
| H(3A) | 4994 | 5347 | 6595 | 138 |
| H(3B) | 4172 | 4688 | 5667 | 138 |
| H(3C) | 4113 | 4403 | 6759 | 138 |
| H(4A) | 4544 | 7196 | 7571 | 172 |
| H(4B) | 3624 | 6320 | 7719 | 172 |
| H(4C) | 3440 | 7851 | 7262 | 172 |
| H(5A) | 4671 | 7625 | 5858 | 154 |
| H(5B) | 3572 | 8296 | 5550 | 154 |
| H(5C) | 3819 | 7037 | 4923 | 154 |
| H(1A) | 2528 | 6510 | 6241 | 88 |
| H(3A1) | 4765 | 7774 | 6432 | 153 |
| H(3A2) | 4104 | 7527 | 7167 | 153 |
| H(3A3) | 3614 | 8248 | 6119 | 153 |
| H(4A1) | 5164 | 5260 | 6756 | 161 |
| H(4A2) | 4316 | 4104 | 6354 | 161 |
| H(4A3) | 4333 | 4998 | 7310 | 161 |
| H(5A1) | 4628 | 6505 | 5049 | 152 |
| H(5A2) | 3449 | 6688 | 4530 | 152 |
| H(5A3) | 3926 | 5165 | 4736 | 152 |
| H(12A) | 3945 | 2544 | 5047 | 147 |
| H(12B) | 3030 | 2317 | 4068 | 147 |
| H(12C) | 3644 | 1008 | 4634 | 147 |
| H(13A) | 1487 | 1120 | 4203 | 77 |
| H(13B) | 1322 | 907 | 5263 | 77 |
| H(13C) | 2065 | -99 | 4912 | 77 |
| H(14A) | 3763 | 2029 | 6691 | 123 |
| H(14B) | 3449 | 446 | 6425 | 123 |
| H(14C) | 2724 | 1454 | 6798 | 123 |
| H(15) | 1535 | 7114 | 3972 | 46 |
| H(16) | 1197 | 7625 | 2311 | 50 |
| H(17) | 682 | 5831 | 1146 | 50 |
| H(18) | 578 | 3563 | 1702 | 48 |
| H(19) | 926 | 3157 | 3381 | 43 |

**Table S23**. Crystal data and structure refinement for W(N-t-Bu)(CH-t-Bu)(pyr)(OHMT) (**8a**).

| | | |
|---|---|---|
| Identification code | X8_12105 | |
| Empirical formula | $C_{37}$ $H_{48}$ $N_2$ O W | |
| Formula weight | 720.62 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | $P2_1/n$ | |
| Unit cell dimensions | $a$ = 11.8827(14) Å | $\alpha$= 90°. |
| | $b$ = 16.2588(19) Å | $\beta$= 92.693(2)°. |
| | $c$ = 18.144(2) Å | $\gamma$ = 90°. |
| Volume | 3501.4(7) Å$^3$ | |
| $Z$ | 4 | |
| Density (calculated) | 1.367 Mg/m$^3$ | |
| Absorption coefficient | 3.327 mm$^{-1}$ | |
| $F$(000) | 1464 | |
| Crystal size | 0.18 x 0.12 x 0.08 mm$^3$ | |
| Theta range for data collection | 1.68 to 31.30°. | |
| Index ranges | -17<=$h$<=16, -23<=$k$<=23, -26<=$l$<=26 | |
| Reflections collected | 274022 | |
| Independent reflections | 11466 [$Rint$ = 0.0335] | |
| Completeness to theta = 31.30° | 100.0 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.7767 and 0.5857 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 11466 / 370 / 473 | |
| Goodness-of-fit on $F^2$ | 1.083 | |
| Final $R$ indices [$I$>2$\sigma$($I$)] | $R$1 = 0.0201, $wR$2 = 0.0456 | |
| $R$ indices (all data) | $R$1 = 0.0232, $wR$2 = 0.0470 | |
| Largest diff. peak and hole | 1.705 and -1.335 e.Å$^{-3}$ | |

Table S24. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for **X8_12105**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| W(1) | 4242(1) | 6942(1) | 3246(1) | 20(1) |
| C(1) | 4794(3) | 5918(2) | 2884(2) | 21(1) |
| C(2) | 4409(6) | 5064(7) | 2655(6) | 26(1) |
| C(3) | 5430(4) | 4555(3) | 2422(3) | 42(1) |
| C(4) | 3555(7) | 5094(8) | 1988(6) | 33(1) |
| C(5) | 3866(10) | 4637(7) | 3325(7) | 34(2) |
| C(1A) | 2714(3) | 7179(3) | 3557(3) | 26(1) |
| C(2A) | 1511(10) | 6900(7) | 3492(6) | 29(2) |
| C(3A) | 1237(10) | 6183(5) | 2932(5) | 40(2) |
| C(4A) | 809(6) | 7631(5) | 3208(6) | 73(3) |
| C(5A) | 1125(7) | 6628(6) | 4256(4) | 59(2) |
| N(1) | 2854(2) | 6814(2) | 3306(2) | 21(1) |
| C(6) | 1653(9) | 6810(6) | 3472(5) | 29(1) |
| C(7) | 1216(5) | 7652(4) | 3429(5) | 62(2) |
| C(8) | 1534(5) | 6406(5) | 4199(4) | 59(2) |
| C(9) | 1095(10) | 6270(8) | 2906(7) | 91(3) |
| N(1A) | 4095(3) | 5955(2) | 2912(2) | 26(1) |
| C(6A) | 4180(8) | 5105(9) | 2639(7) | 29(2) |
| C(7A) | 3888(16) | 4522(10) | 3243(9) | 44(3) |
| C(8A) | 3348(11) | 5041(11) | 2000(8) | 56(3) |
| C(9A) | 5366(5) | 4940(5) | 2443(5) | 61(2) |
| O(1) | 5227(1) | 7296(1) | 4014(1) | 26(1) |
| C(21) | 5960(1) | 7468(1) | 4592(1) | 23(1) |
| C(22) | 5582(2) | 7936(1) | 5174(1) | 24(1) |
| C(23) | 6345(2) | 8116(1) | 5759(1) | 35(1) |
| C(24) | 7448(2) | 7834(2) | 5765(1) | 40(1) |
| C(25) | 7806(2) | 7376(2) | 5177(1) | 35(1) |
| C(26) | 7072(2) | 7184(1) | 4578(1) | 26(1) |
| C(27) | 4396(1) | 8238(1) | 5164(1) | 23(1) |
| C(28) | 3604(2) | 7828(1) | 5582(1) | 26(1) |
| C(29) | 2508(2) | 8138(1) | 5590(1) | 33(1) |
| C(30) | 2187(2) | 8833(2) | 5190(1) | 37(1) |
| C(31) | 2974(2) | 9217(1) | 4769(1) | 34(1) |
| C(32) | 4072(2) | 8925(1) | 4741(1) | 26(1) |
| C(33) | 3914(2) | 7057(1) | 6005(1) | 39(1) |
| C(34) | 998(2) | 9166(2) | 5215(2) | 60(1) |
| C(35) | 4886(2) | 9344(1) | 4250(1) | 35(1) |
| C(36) | 7446(1) | 6698(1) | 3936(1) | 26(1) |
| C(37) | 7614(2) | 5849(1) | 4003(1) | 32(1) |
| C(38) | 7967(2) | 5408(1) | 3396(1) | 34(1) |
| C(39) | 8137(2) | 5782(1) | 2724(1) | 30(1) |
| C(40) | 7960(1) | 6625(1) | 2668(1) | 27(1) |
| C(41) | 7623(1) | 7091(1) | 3264(1) | 25(1) |
| C(42) | 7387(3) | 5406(2) | 4711(1) | 51(1) |
| C(43) | 8506(2) | 5288(2) | 2074(1) | 39(1) |
| C(44) | 7470(2) | 8007(1) | 3180(1) | 32(1) |
| N(2) | 4420(1) | 7669(1) | 2356(1) | 26(1) |
| C(10) | 3972(2) | 8450(1) | 2257(1) | 33(1) |
| C(11) | 4452(2) | 8825(1) | 1674(1) | 37(1) |

| | | | | |
|---|---|---|---|---|
| C(12) | 5219(2) | 8261(1) | 1390(1) | 34(1) |
| C(13) | 5179(2) | 7566(1) | 1811(1) | 32(1) |

Table S25. Bond lengths [Å] and angles [°] for **X8_12105**.

| | |
|---|---|
| W(1)-N(1) | 1.670(3) |
| W(1)-N(1A) | 1.720(3) |
| W(1)-O(1) | 1.8691(12) |
| W(1)-C(1) | 1.916(3) |
| W(1)-C(1A) | 1.964(5) |
| W(1)-N(2) | 2.0214(16) |
| C(1)-C(2) | 1.514(12) |
| C(1)-H(1) | 0.955(18) |
| C(2)-C(4) | 1.543(8) |
| C(2)-C(3) | 1.545(8) |
| C(2)-C(5) | 1.566(9) |
| C(3)-H(3A) | 0.9800 |
| C(3)-H(3B) | 0.9800 |
| C(3)-H(3C) | 0.9800 |
| C(4)-H(4A) | 0.9800 |
| C(4)-H(4B) | 0.9800 |
| C(4)-H(4C) | 0.9800 |
| C(5)-H(5A) | 0.9800 |
| C(5)-H(5B) | 0.9800 |
| C(5)-H(5C) | 0.9800 |
| C(1A)-C(2A) | 1.499(13) |
| C(1A)-H(1A) | 0.946(19) |
| C(2A)-C(4A) | 1.526(10) |
| C(2A)-C(5A) | 1.546(11) |
| C(2A)-C(3A) | 1.570(10) |
| C(3A)-H(3A1) | 0.9800 |
| C(3A)-H(3A2) | 0.9800 |
| C(3A)-H(3A3) | 0.9800 |
| C(4A)-H(4A1) | 0.9800 |
| C(4A)-H(4A2) | 0.9800 |
| C(4A)-H(4A3) | 0.9800 |
| C(5A)-H(5A1) | 0.9800 |
| C(5A)-H(5A2) | 0.9800 |
| C(5A)-H(5A3) | 0.9800 |
| N(1)-C(6) | 1.473(11) |
| C(6)-C(7) | 1.465(8) |
| C(6)-C(9) | 1.483(10) |
| C(6)-C(8) | 1.487(9) |
| C(7)-H(7A) | 0.9800 |
| C(7)-H(7B) | 0.9800 |
| C(7)-H(7C) | 0.9800 |
| C(8)-H(8A) | 0.9800 |
| C(8)-H(8B) | 0.9800 |
| C(8)-H(8C) | 0.9800 |
| C(9)-H(9A) | 0.9800 |
| C(9)-H(9B) | 0.9800 |
| C(9)-H(9C) | 0.9800 |
| N(1A)-C(6A) | 1.473(14) |
| C(6A)-C(8A) | 1.491(11) |
| C(6A)-C(9A) | 1.494(9) |
| C(6A)-C(7A) | 1.501(12) |
| C(7A)-H(7A1) | 0.9800 |

| | |
|---|---|
| C(7A)-H(7A2) | 0.9800 |
| C(7A)-H(7A3) | 0.9800 |
| C(8A)-H(8A1) | 0.9800 |
| C(8A)-H(8A2) | 0.9800 |
| C(8A)-H(8A3) | 0.9800 |
| C(9A)-H(9A1) | 0.9800 |
| C(9A)-H(9A2) | 0.9800 |
| C(9A)-H(9A3) | 0.9800 |
| O(1)-C(21) | 1.3600(19) |
| C(21)-C(22) | 1.394(2) |
| C(21)-C(26) | 1.400(2) |
| C(22)-C(23) | 1.394(2) |
| C(22)-C(27) | 1.491(2) |
| C(23)-C(24) | 1.387(3) |
| C(23)-H(23A) | 0.9500 |
| C(24)-C(25) | 1.385(3) |
| C(24)-H(24A) | 0.9500 |
| C(25)-C(26) | 1.397(2) |
| C(25)-H(25A) | 0.9500 |
| C(26)-C(36) | 1.493(2) |
| C(27)-C(32) | 1.400(2) |
| C(27)-C(28) | 1.403(3) |
| C(28)-C(29) | 1.397(3) |
| C(28)-C(33) | 1.508(3) |
| C(29)-C(30) | 1.388(3) |
| C(29)-H(29A) | 0.9500 |
| C(30)-C(31) | 1.383(3) |
| C(30)-C(34) | 1.515(3) |
| C(31)-C(32) | 1.392(3) |
| C(31)-H(31A) | 0.9500 |
| C(32)-C(35) | 1.508(3) |
| C(33)-H(33A) | 0.9800 |
| C(33)-H(33B) | 0.9800 |
| C(33)-H(33C) | 0.9800 |
| C(34)-H(34A) | 0.9800 |
| C(34)-H(34B) | 0.9800 |
| C(34)-H(34C) | 0.9800 |
| C(35)-H(35A) | 0.9800 |
| C(35)-H(35B) | 0.9800 |
| C(35)-H(35C) | 0.9800 |
| C(36)-C(37) | 1.398(3) |
| C(36)-C(41) | 1.401(3) |
| C(37)-C(38) | 1.396(3) |
| C(37)-C(42) | 1.508(3) |
| C(38)-C(39) | 1.384(3) |
| C(38)-H(38A) | 0.9500 |
| C(39)-C(40) | 1.390(3) |
| C(39)-C(43) | 1.509(3) |
| C(40)-C(41) | 1.394(2) |
| C(40)-H(40A) | 0.9500 |
| C(41)-C(44) | 1.507(3) |
| C(42)-H(42A) | 0.9800 |
| C(42)-H(42B) | 0.9800 |
| C(42)-H(42C) | 0.9800 |

| | |
|---|---|
| C(43)-H(43A) | 0.9800 |
| C(43)-H(43B) | 0.9800 |
| C(43)-H(43C) | 0.9800 |
| C(44)-H(44A) | 0.9800 |
| C(44)-H(44B) | 0.9800 |
| C(44)-H(44C) | 0.9800 |
| N(2)-C(13) | 1.379(3) |
| N(2)-C(10) | 1.385(2) |
| C(10)-C(11) | 1.369(3) |
| C(10)-H(10A) | 0.9500 |
| C(11)-C(12) | 1.408(3) |
| C(11)-H(11A) | 0.9500 |
| C(12)-C(13) | 1.366(3) |
| C(12)-H(12A) | 0.9500 |
| C(13)-H(13A) | 0.9500 |

| | |
|---|---|
| N(1)-W(1)-N(1A) | 79.81(16) |
| N(1)-W(1)-O(1) | 125.10(12) |
| N(1A)-W(1)-O(1) | 126.88(13) |
| N(1)-W(1)-C(1) | 105.63(14) |
| N(1A)-W(1)-C(1) | 25.90(14) |
| O(1)-W(1)-C(1) | 108.10(10) |
| N(1)-W(1)-C(1A) | 22.69(15) |
| N(1A)-W(1)-C(1A) | 101.8(2) |
| O(1)-W(1)-C(1A) | 106.25(15) |
| C(1)-W(1)-C(1A) | 127.23(18) |
| N(1)-W(1)-N(2) | 105.42(10) |
| N(1A)-W(1)-N(2) | 106.04(12) |
| O(1)-W(1)-N(2) | 109.29(6) |
| C(1)-W(1)-N(2) | 100.62(10) |
| C(1A)-W(1)-N(2) | 104.33(13) |
| C(2)-C(1)-W(1) | 141.9(3) |
| C(2)-C(1)-H(1) | 116(2) |
| W(1)-C(1)-H(1) | 102(2) |
| C(1)-C(2)-C(4) | 111.5(8) |
| C(1)-C(2)-C(3) | 109.6(6) |
| C(4)-C(2)-C(3) | 107.3(7) |
| C(1)-C(2)-C(5) | 108.9(8) |
| C(4)-C(2)-C(5) | 110.0(8) |
| C(3)-C(2)-C(5) | 109.4(8) |
| C(2)-C(3)-H(3A) | 109.5 |
| C(2)-C(3)-H(3B) | 109.5 |
| H(3A)-C(3)-H(3B) | 109.5 |
| C(2)-C(3)-H(3C) | 109.5 |
| H(3A)-C(3)-H(3C) | 109.5 |
| H(3B)-C(3)-H(3C) | 109.5 |
| C(2)-C(4)-H(4A) | 109.5 |
| C(2)-C(4)-H(4B) | 109.5 |
| H(4A)-C(4)-H(4B) | 109.5 |
| C(2)-C(4)-H(4C) | 109.5 |
| H(4A)-C(4)-H(4C) | 109.5 |
| H(4B)-C(4)-H(4C) | 109.5 |
| C(2)-C(5)-H(5A) | 109.5 |
| C(2)-C(5)-H(5B) | 109.5 |

| | |
|---|---|
| H(5A)-C(5)-H(5B) | 109.5 |
| C(2)-C(5)-H(5C) | 109.5 |
| H(5A)-C(5)-H(5C) | 109.5 |
| H(5B)-C(5)-H(5C) | 109.5 |
| C(2A)-C(1A)-W(1) | 144.0(6) |
| C(2A)-C(1A)-H(1A) | 116(3) |
| W(1)-C(1A)-H(1A) | 100(3) |
| C(1A)-C(2A)-C(4A) | 107.2(7) |
| C(1A)-C(2A)-C(5A) | 109.7(8) |
| C(4A)-C(2A)-C(5A) | 110.2(9) |
| C(1A)-C(2A)-C(3A) | 116.3(9) |
| C(4A)-C(2A)-C(3A) | 105.4(8) |
| C(5A)-C(2A)-C(3A) | 107.8(8) |
| C(2A)-C(3A)-H(3A1) | 109.5 |
| C(2A)-C(3A)-H(3A2) | 109.5 |
| H(3A1)-C(3A)-H(3A2) | 109.5 |
| C(2A)-C(3A)-H(3A3) | 109.5 |
| H(3A1)-C(3A)-H(3A3) | 109.5 |
| H(3A2)-C(3A)-H(3A3) | 109.5 |
| C(2A)-C(4A)-H(4A1) | 109.5 |
| C(2A)-C(4A)-H(4A2) | 109.5 |
| H(4A1)-C(4A)-H(4A2) | 109.5 |
| C(2A)-C(4A)-H(4A3) | 109.5 |
| H(4A1)-C(4A)-H(4A3) | 109.5 |
| H(4A2)-C(4A)-H(4A3) | 109.5 |
| C(2A)-C(5A)-H(5A1) | 109.5 |
| C(2A)-C(5A)-H(5A2) | 109.5 |
| H(5A1)-C(5A)-H(5A2) | 109.5 |
| C(2A)-C(5A)-H(5A3) | 109.5 |
| H(5A1)-C(5A)-H(5A3) | 109.5 |
| H(5A2)-C(5A)-H(5A3) | 109.5 |
| C(6)-N(1)-W(1) | 169.5(5) |
| C(7)-C(6)-N(1) | 109.3(7) |
| C(7)-C(6)-C(9) | 111.7(8) |
| N(1)-C(6)-C(9) | 105.5(7) |
| C(7)-C(6)-C(8) | 114.3(7) |
| N(1)-C(6)-C(8) | 108.5(6) |
| C(9)-C(6)-C(8) | 107.2(8) |
| C(6)-C(7)-H(7A) | 109.5 |
| C(6)-C(7)-H(7B) | 109.5 |
| H(7A)-C(7)-H(7B) | 109.5 |
| C(6)-C(7)-H(7C) | 109.5 |
| H(7A)-C(7)-H(7C) | 109.5 |
| H(7B)-C(7)-H(7C) | 109.5 |
| C(6)-C(8)-H(8A) | 109.5 |
| C(6)-C(8)-H(8B) | 109.5 |
| H(8A)-C(8)-H(8B) | 109.5 |
| C(6)-C(8)-H(8C) | 109.5 |
| H(8A)-C(8)-H(8C) | 109.5 |
| H(8B)-C(8)-H(8C) | 109.5 |
| C(6)-C(9)-H(9A) | 109.5 |
| C(6)-C(9)-H(9B) | 109.5 |
| H(9A)-C(9)-H(9B) | 109.5 |
| C(6)-C(9)-H(9C) | 109.5 |

| | |
|---|---|
| H(9A)-C(9)-H(9C) | 109.5 |
| H(9B)-C(9)-H(9C) | 109.5 |
| C(6A)-N(1A)-W(1) | 170.3(5) |
| N(1A)-C(6A)-C(8A) | 105.9(10) |
| N(1A)-C(6A)-C(9A) | 109.2(9) |
| C(8A)-C(6A)-C(9A) | 113.6(10) |
| N(1A)-C(6A)-C(7A) | 109.0(10) |
| C(8A)-C(6A)-C(7A) | 110.8(12) |
| C(9A)-C(6A)-C(7A) | 108.2(10) |
| C(6A)-C(7A)-H(7A1) | 109.5 |
| C(6A)-C(7A)-H(7A2) | 109.5 |
| H(7A1)-C(7A)-H(7A2) | 109.5 |
| C(6A)-C(7A)-H(7A3) | 109.5 |
| H(7A1)-C(7A)-H(7A3) | 109.5 |
| H(7A2)-C(7A)-H(7A3) | 109.5 |
| C(6A)-C(8A)-H(8A1) | 109.5 |
| C(6A)-C(8A)-H(8A2) | 109.5 |
| H(8A1)-C(8A)-H(8A2) | 109.5 |
| C(6A)-C(8A)-H(8A3) | 109.5 |
| H(8A1)-C(8A)-H(8A3) | 109.5 |
| H(8A2)-C(8A)-H(8A3) | 109.5 |
| C(6A)-C(9A)-H(9A1) | 109.5 |
| C(6A)-C(9A)-H(9A2) | 109.5 |
| H(9A1)-C(9A)-H(9A2) | 109.5 |
| C(6A)-C(9A)-H(9A3) | 109.5 |
| H(9A1)-C(9A)-H(9A3) | 109.5 |
| H(9A2)-C(9A)-H(9A3) | 109.5 |
| C(21)-O(1)-W(1) | 173.81(13) |
| O(1)-C(21)-C(22) | 118.51(15) |
| O(1)-C(21)-C(26) | 119.33(15) |
| C(22)-C(21)-C(26) | 122.14(15) |
| C(21)-C(22)-C(23) | 117.97(16) |
| C(21)-C(22)-C(27) | 120.61(15) |
| C(23)-C(22)-C(27) | 121.42(16) |
| C(24)-C(23)-C(22) | 121.21(18) |
| C(24)-C(23)-H(23A) | 119.4 |
| C(22)-C(23)-H(23A) | 119.4 |
| C(25)-C(24)-C(23) | 119.68(18) |
| C(25)-C(24)-H(24A) | 120.2 |
| C(23)-C(24)-H(24A) | 120.2 |
| C(24)-C(25)-C(26) | 121.11(18) |
| C(24)-C(25)-H(25A) | 119.4 |
| C(26)-C(25)-H(25A) | 119.4 |
| C(25)-C(26)-C(21) | 117.89(16) |
| C(25)-C(26)-C(36) | 121.82(16) |
| C(21)-C(26)-C(36) | 120.29(15) |
| C(32)-C(27)-C(28) | 120.07(16) |
| C(32)-C(27)-C(22) | 120.27(16) |
| C(28)-C(27)-C(22) | 119.66(16) |
| C(29)-C(28)-C(27) | 118.96(17) |
| C(29)-C(28)-C(33) | 119.98(18) |
| C(27)-C(28)-C(33) | 121.05(17) |
| C(30)-C(29)-C(28) | 121.43(19) |
| C(30)-C(29)-H(29A) | 119.3 |

| | |
|---|---|
| C(28)-C(29)-H(29A) | 119.3 |
| C(31)-C(30)-C(29) | 118.66(18) |
| C(31)-C(30)-C(34) | 120.8(2) |
| C(29)-C(30)-C(34) | 120.6(2) |
| C(30)-C(31)-C(32) | 121.74(18) |
| C(30)-C(31)-H(31A) | 119.1 |
| C(32)-C(31)-H(31A) | 119.1 |
| C(31)-C(32)-C(27) | 119.08(17) |
| C(31)-C(32)-C(35) | 119.72(18) |
| C(27)-C(32)-C(35) | 121.19(17) |
| C(28)-C(33)-H(33A) | 109.5 |
| C(28)-C(33)-H(33B) | 109.5 |
| H(33A)-C(33)-H(33B) | 109.5 |
| C(28)-C(33)-H(33C) | 109.5 |
| H(33A)-C(33)-H(33C) | 109.5 |
| H(33B)-C(33)-H(33C) | 109.5 |
| C(30)-C(34)-H(34A) | 109.5 |
| C(30)-C(34)-H(34B) | 109.5 |
| H(34A)-C(34)-H(34B) | 109.5 |
| C(30)-C(34)-H(34C) | 109.5 |
| H(34A)-C(34)-H(34C) | 109.5 |
| H(34B)-C(34)-H(34C) | 109.5 |
| C(32)-C(35)-H(35A) | 109.5 |
| C(32)-C(35)-H(35B) | 109.5 |
| H(35A)-C(35)-H(35B) | 109.5 |
| C(32)-C(35)-H(35C) | 109.5 |
| H(35A)-C(35)-H(35C) | 109.5 |
| H(35B)-C(35)-H(35C) | 109.5 |
| C(37)-C(36)-C(41) | 119.99(17) |
| C(37)-C(36)-C(26) | 120.04(18) |
| C(41)-C(36)-C(26) | 119.97(17) |
| C(38)-C(37)-C(36) | 118.98(19) |
| C(38)-C(37)-C(42) | 120.0(2) |
| C(36)-C(37)-C(42) | 121.04(19) |
| C(39)-C(38)-C(37) | 122.07(19) |
| C(39)-C(38)-H(38A) | 119.0 |
| C(37)-C(38)-H(38A) | 119.0 |
| C(38)-C(39)-C(40) | 118.02(17) |
| C(38)-C(39)-C(43) | 120.91(19) |
| C(40)-C(39)-C(43) | 121.07(19) |
| C(39)-C(40)-C(41) | 121.81(18) |
| C(39)-C(40)-H(40A) | 119.1 |
| C(41)-C(40)-H(40A) | 119.1 |
| C(40)-C(41)-C(36) | 119.11(17) |
| C(40)-C(41)-C(44) | 119.74(17) |
| C(36)-C(41)-C(44) | 121.14(16) |
| C(37)-C(42)-H(42A) | 109.5 |
| C(37)-C(42)-H(42B) | 109.5 |
| H(42A)-C(42)-H(42B) | 109.5 |
| C(37)-C(42)-H(42C) | 109.5 |
| H(42A)-C(42)-H(42C) | 109.5 |
| H(42B)-C(42)-H(42C) | 109.5 |
| C(39)-C(43)-H(43A) | 109.5 |
| C(39)-C(43)-H(43B) | 109.5 |

| | |
|---|---|
| H(43A)-C(43)-H(43B) | 109.5 |
| C(39)-C(43)-H(43C) | 109.5 |
| H(43A)-C(43)-H(43C) | 109.5 |
| H(43B)-C(43)-H(43C) | 109.5 |
| C(41)-C(44)-H(44A) | 109.5 |
| C(41)-C(44)-H(44B) | 109.5 |
| H(44A)-C(44)-H(44B) | 109.5 |
| C(41)-C(44)-H(44C) | 109.5 |
| H(44A)-C(44)-H(44C) | 109.5 |
| H(44B)-C(44)-H(44C) | 109.5 |
| C(13)-N(2)-C(10) | 106.18(16) |
| C(13)-N(2)-W(1) | 126.76(13) |
| C(10)-N(2)-W(1) | 125.86(13) |
| C(11)-C(10)-N(2) | 109.70(18) |
| C(11)-C(10)-H(10A) | 125.2 |
| N(2)-C(10)-H(10A) | 125.2 |
| C(10)-C(11)-C(12) | 107.02(19) |
| C(10)-C(11)-H(11A) | 126.5 |
| C(12)-C(11)-H(11A) | 126.5 |
| C(13)-C(12)-C(11) | 107.13(19) |
| C(13)-C(12)-H(12A) | 126.4 |
| C(11)-C(12)-H(12A) | 126.4 |
| C(12)-C(13)-N(2) | 109.96(18) |
| C(12)-C(13)-H(13A) | 125.0 |
| N(2)-C(13)-H(13A) | 125.0 |

Symmetry transformations used to generate equivalent atoms:

Table S26. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **X8_12105**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| W(1) | 18(1) | 21(1) | 22(1) | -3(1) | -5(1) | 0(1) |
| C(1) | 17(2) | 23(1) | 23(1) | -1(1) | 0(1) | 0(1) |
| C(2) | 27(3) | 20(2) | 31(2) | -4(2) | -2(2) | -2(2) |
| C(3) | 30(2) | 30(2) | 65(3) | -17(2) | 7(2) | 3(2) |
| C(4) | 33(2) | 31(3) | 36(3) | -5(2) | 0(2) | 0(2) |
| C(5) | 38(3) | 24(3) | 41(4) | 5(3) | 7(3) | 0(2) |
| C(1A) | 23(2) | 31(2) | 25(2) | 4(2) | -2(1) | 0(2) |
| C(2A) | 17(3) | 39(3) | 30(3) | 7(2) | -6(2) | -8(2) |
| C(3A) | 48(4) | 32(2) | 42(3) | 3(2) | 13(3) | -10(2) |
| C(4A) | 36(3) | 32(3) | 148(8) | 26(3) | -25(4) | -3(3) |
| C(5A) | 61(5) | 82(6) | 35(3) | -1(3) | 12(3) | -33(4) |
| N(1) | 17(1) | 21(1) | 24(1) | 1(1) | 1(1) | -1(1) |
| C(6) | 21(3) | 36(3) | 29(2) | 8(2) | 1(2) | -3(2) |
| C(7) | 32(3) | 46(3) | 110(6) | 24(3) | 20(3) | 12(2) |
| C(8) | 43(3) | 71(4) | 66(3) | 32(3) | 28(2) | 12(3) |
| C(9) | 41(4) | 133(7) | 99(5) | -66(6) | 6(4) | -15(4) |
| N(1A) | 28(2) | 24(2) | 26(2) | -3(1) | -2(1) | -3(1) |
| C(6A) | 32(4) | 23(2) | 33(3) | -7(2) | -1(3) | -3(3) |
| C(7A) | 69(6) | 29(4) | 32(3) | -2(3) | -9(3) | 4(4) |
| C(8A) | 73(6) | 42(5) | 50(5) | 6(4) | -30(5) | -3(6) |
| C(9A) | 42(3) | 49(4) | 92(5) | -32(4) | 13(3) | 3(3) |
| O(1) | 20(1) | 37(1) | 20(1) | -6(1) | -2(1) | -3(1) |
| C(21) | 20(1) | 30(1) | 19(1) | -3(1) | -3(1) | 0(1) |
| C(22) | 23(1) | 31(1) | 19(1) | -2(1) | -2(1) | 3(1) |
| C(23) | 32(1) | 49(1) | 23(1) | -12(1) | -6(1) | 7(1) |
| C(24) | 32(1) | 59(1) | 30(1) | -15(1) | -13(1) | 8(1) |
| C(25) | 24(1) | 51(1) | 30(1) | -9(1) | -8(1) | 7(1) |
| C(26) | 21(1) | 34(1) | 23(1) | -5(1) | -2(1) | 2(1) |
| C(27) | 24(1) | 27(1) | 18(1) | -2(1) | 0(1) | 3(1) |
| C(28) | 29(1) | 28(1) | 23(1) | 2(1) | 4(1) | 5(1) |
| C(29) | 31(1) | 39(1) | 29(1) | 2(1) | 10(1) | 5(1) |
| C(30) | 30(1) | 47(1) | 34(1) | 0(1) | 1(1) | 15(1) |
| C(31) | 39(1) | 33(1) | 29(1) | 5(1) | -1(1) | 13(1) |
| C(32) | 31(1) | 26(1) | 22(1) | 1(1) | 0(1) | 1(1) |
| C(33) | 46(1) | 34(1) | 37(1) | 11(1) | 12(1) | 10(1) |
| C(34) | 39(1) | 83(2) | 58(2) | 11(2) | 9(1) | 33(1) |
| C(35) | 45(1) | 32(1) | 29(1) | 4(1) | 6(1) | -6(1) |
| C(36) | 19(1) | 32(1) | 27(1) | -6(1) | -1(1) | 1(1) |
| C(37) | 31(1) | 34(1) | 30(1) | -1(1) | -1(1) | 4(1) |
| C(38) | 32(1) | 28(1) | 40(1) | -5(1) | 0(1) | 6(1) |
| C(39) | 20(1) | 35(1) | 34(1) | -11(1) | 2(1) | 2(1) |
| C(40) | 20(1) | 31(1) | 29(1) | -6(1) | 5(1) | -4(1) |
| C(41) | 17(1) | 28(1) | 29(1) | -6(1) | 2(1) | -3(1) |
| C(42) | 74(2) | 42(1) | 38(1) | 9(1) | 5(1) | 8(1) |
| C(43) | 35(1) | 40(1) | 42(1) | -17(1) | 7(1) | 4(1) |
| C(44) | 33(1) | 27(1) | 35(1) | -5(1) | 7(1) | -5(1) |
| N(2) | 25(1) | 25(1) | 29(1) | 1(1) | -7(1) | -1(1) |
| C(10) | 43(1) | 26(1) | 30(1) | 0(1) | 2(1) | 5(1) |
| C(11) | 46(1) | 30(1) | 36(1) | 4(1) | 0(1) | 2(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(12) | 28(1) | 36(1) | 37(1) | 2(1) | 2(1) | -3(1) |
| C(13) | 21(1) | 31(1) | 43(1) | 3(1) | 0(1) | 1(1) |

Table S27. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for **X8_12105**.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 5590(16) | 6000(20) | 2930(20) | 25 |
| H(3A) | 5175 | 4008 | 2259 | 63 |
| H(3B) | 5974 | 4499 | 2842 | 63 |
| H(3C) | 5789 | 4833 | 2015 | 63 |
| H(4A) | 3335 | 4532 | 1847 | 50 |
| H(4B) | 3900 | 5365 | 1573 | 50 |
| H(4C) | 2886 | 5403 | 2122 | 50 |
| H(5A) | 3608 | 4085 | 3180 | 51 |
| H(5B) | 3223 | 4963 | 3477 | 51 |
| H(5C) | 4426 | 4595 | 3737 | 51 |
| H(1A) | 2860(40) | 7650(20) | 3850(20) | 31 |
| H(3A1) | 433 | 6050 | 2935 | 60 |
| H(3A2) | 1681 | 5697 | 3077 | 60 |
| H(3A3) | 1426 | 6356 | 2435 | 60 |
| H(4A1) | 12 | 7474 | 3170 | 110 |
| H(4A2) | 1054 | 7793 | 2721 | 110 |
| H(4A3) | 911 | 8093 | 3551 | 110 |
| H(5A1) | 334 | 6457 | 4213 | 88 |
| H(5A2) | 1207 | 7089 | 4603 | 88 |
| H(5A3) | 1590 | 6166 | 4437 | 88 |
| H(7A) | 1307 | 7871 | 2932 | 93 |
| H(7B) | 1632 | 7997 | 3791 | 93 |
| H(7C) | 415 | 7651 | 3536 | 93 |
| H(8A) | 1838 | 5846 | 4184 | 89 |
| H(8B) | 735 | 6383 | 4311 | 89 |
| H(8C) | 1949 | 6722 | 4583 | 89 |
| H(9A) | 1407 | 5714 | 2951 | 137 |
| H(9B) | 1225 | 6488 | 2414 | 137 |
| H(9C) | 283 | 6253 | 2980 | 137 |
| H(7A1) | 3115 | 4625 | 3383 | 66 |
| H(7A2) | 4408 | 4606 | 3672 | 66 |
| H(7A3) | 3952 | 3955 | 3067 | 66 |
| H(8A1) | 2589 | 5145 | 2167 | 84 |
| H(8A2) | 3380 | 4487 | 1788 | 84 |
| H(8A3) | 3530 | 5447 | 1625 | 84 |
| H(9A1) | 5866 | 4991 | 2886 | 91 |
| H(9A2) | 5589 | 5338 | 2072 | 91 |
| H(9A3) | 5419 | 4382 | 2244 | 91 |
| H(23A) | 6106 | 8436 | 6160 | 42 |
| H(24A) | 7955 | 7955 | 6171 | 48 |
| H(25A) | 8564 | 7190 | 5181 | 42 |
| H(29A) | 1971 | 7866 | 5875 | 40 |
| H(31A) | 2759 | 9692 | 4492 | 41 |
| H(33A) | 3239 | 6825 | 6215 | 58 |
| H(33B) | 4469 | 7190 | 6404 | 58 |
| H(33C) | 4237 | 6655 | 5672 | 58 |
| H(34A) | 982 | 9613 | 5576 | 90 |
| H(34B) | 491 | 8725 | 5359 | 90 |

| | | | | |
|---|---|---|---|---|
| H(34C) | 754 | 9374 | 4727 | 90 |
| H(35A) | 4992 | 9003 | 3813 | 53 |
| H(35B) | 5611 | 9420 | 4521 | 53 |
| H(35C) | 4582 | 9880 | 4096 | 53 |
| H(38A) | 8095 | 4834 | 3444 | 40 |
| H(40A) | 8071 | 6891 | 2211 | 32 |
| H(42A) | 7435 | 4811 | 4632 | 77 |
| H(42B) | 6631 | 5547 | 4864 | 77 |
| H(42C) | 7947 | 5571 | 5096 | 77 |
| H(43A) | 9077 | 4887 | 2243 | 59 |
| H(43B) | 8826 | 5658 | 1712 | 59 |
| H(43C) | 7856 | 4999 | 1846 | 59 |
| H(44A) | 7780 | 8187 | 2715 | 47 |
| H(44B) | 7866 | 8289 | 3594 | 47 |
| H(44C) | 6666 | 8141 | 3177 | 47 |
| H(10A) | 3415 | 8689 | 2549 | 40 |
| H(11A) | 4298 | 9365 | 1495 | 44 |
| H(12A) | 5678 | 8347 | 982 | 41 |
| H(13A) | 5610 | 7083 | 1739 | 38 |

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